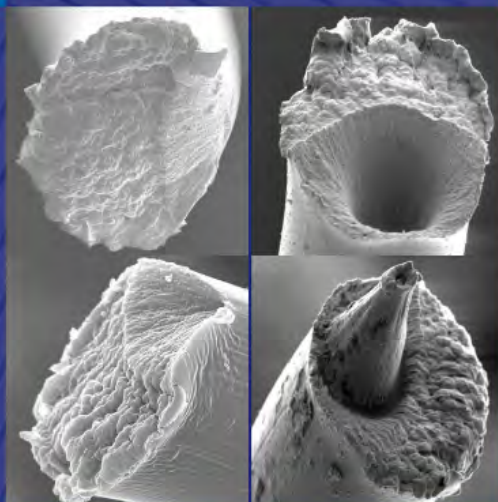


WOODHEAD PUBLISHING IN TEXTILES



Handbook of tensile properties of textile and technical fibres

Edited by A. R. Bunsell



The Textile Institute

WP

Handbook of tensile properties of textile and technical fibres

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Edited by

A. R. Bunsell



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Anthony R. Bunsell
Paris

Introduction to fibre tensile properties and failure

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Abstract: Fibres are an extraordinary form of matter, that find many applications both in traditional textile and highly technical applications. Such structures owe their characteristics to the behaviour of the fibres from which they are made but the fibres are so fine that their contribution is only vaguely appreciated. In this chapter the special features of fibres which must be considered are explained. The units of measure used for fibres due to their fineness are discussed as is the reason why even very stiff materials can be made so as to be supple enough to be woven. The chapter allows comparisons to be made between different types of fibres and with some reference to bulk materials. The fineness of fibres means that any structure based on them will contain thousands and most probably millions of them. Such large populations require a statistical approach to their analysis and this is treated in detail. Finally some aspects of the economics of fibres and their markets are discussed.

Key words: fibre units, flexibility, properties, statistics of fibre failure, economics and markets.

1.1 Introduction

This book intends to provide a convenient handbook on a wide range of fibres used both in traditional textiles and other technical applications. It covers a large number of fibre types, although inevitably there are others that could have been included but for various reasons it has not been possible to do so. The book covers both natural and synthetic fibres and all the contributors have been encouraged to adopt a common approach. They have been asked to explain how the fibres are produced, how the fibre structure determines their properties and to give typical values of useful properties, as well as discussing their tensile failure.

Fibres can be natural, both vegetable and animal in origin and also synthetic. They are long, fine forms of matter with diameters generally of the order of 10 μm (microns) and lengths ranging from a few millimetres to virtually being continuous. As their diameters are usually only a fraction of the diameter of a human hair, fibres go almost unremarked, as it is the

finished product which is seen, whether it is a shirt made of cotton or part of a plane made of carbon fibres. They are remarkable forms of matter and often possess properties far superior to those which have the same materials in bulk form. Their fineness conveys to them great flexibility. This characteristic means that they are used principally to support tensile loads. This handbook treats the subject of the tensile behaviour of fibres, how their tensile properties depend on their microstructures and how they fail. It will be shown how they are tested and how their microstructures are studied. It is hoped that the handbook will provide a useful reference source.

Although natural fibres have been used by people throughout their history, synthetic fibres are much more recent newcomers. Even so, since their initial development, synthetic fibres have grown to rival and in some markets replace natural fibres. Polyester is now the most widely used fibre both for textile fabrics and for technical applications. These fibres were first produced in 1947. The first truly synthetic fibre was polyamide, or nylon, which began to be commercially produced in 1938. The last 40 years have seen advanced synthetic fibres develop into technical filaments with properties which have been created by the control of their molecular structures. The most advanced fibres possess properties, particularly stiffness allied with low density, which are close to the highest that nature and physics will allow. This allows technical structures based on the fibres to be made with extraordinary properties and which are often the basis of new technical innovations. Natural fibres, though, have qualities which synthetic fibres cannot challenge, especially for comfort, but they are also renewable and a cheap source of structural reinforcements, which are finding new applications outside of traditional textiles. Some are being examined anew with the possibility of developing completely new markets. Both natural and synthetic fibres are finding increasing uses as functional materials, so whether it is clothes which can react to the environment, used to recharge your phone or biomaterials such as synthetic skin or prostheses, fibres are often the most essential component.

1.2 Units of measure for fibres and their structures

The small diameters of fibres has presented particular challenges to the fibre industry which have led to ways of defining fibres and their properties that are different from those used in traditional engineering materials. The concerns are the same. How is it possible to normalise characteristics, such as strength and stiffness, so that fibres can be compared? With most engineering materials it is Hooke's law which shows the way of comparing materials. Specimens can be compared through normalising the applied force by dividing by the cross-section of the specimen to obtain the stress and relating it to the strain, which is the increase in length divided by its original length. This cannot

easily be done with fibres as they are very fine and, particularly in the case of many natural fibres, of irregular cross-section, so their cross-sections cannot easily be measured. Even the best optical microscopes are of little help because their resolving powers are limited by the wavelength of light, about half a micron. Today, the scanning electron microscope, which was developed in the second half of the twentieth century, allows the fibres to be observed in great detail owing to the very short wavelengths of electrons when they act as waves. However, observation by scanning electron microscopy is not always possible and because the specimens have to be prepared for observation, it is not a very rapid technique.

The traditional unit of definition for fibres has been the ‘**denier**’, which is the weight of the fibre or fibre assembly as a function of length. One denier is one gram per nine kilometres. The denier is still in wide use but has been replaced as an international unit by the ‘**tex**’ which is one gram per kilometre. This means that the tex is a less fine unit than the earlier denier and for this reason the unit which is often used is the **decitex (dtx)**, one gram per ten kilometres, not so different from the denier.

Strength is given as the force to produce failure (gram for example) per textile unit (denier or tex). This can be seen to be related to traditional engineering units of strength as it is equal to the force multiplied by the length and divided by the weight:

$$\begin{aligned} \text{Force} \times \frac{\text{length}}{\text{weight}} &= \text{Force} \times \frac{\text{length}}{\text{volume} \times \text{density}} \\ &= \text{Force} \times \frac{\text{length}}{\text{length} \times \text{cross-section} \times \text{density}} \\ &= \frac{\text{Force}}{\text{cross-section} \times \text{density}} \end{aligned}$$

As force/cross-section is the engineering definition of stress, it can be seen that strengths given in textile units are related to engineering units through the density of the fibres.

1.3 Fineness and flexibility

An obvious characteristic of fibres is their flexibility. Their ability to bend is the basis of the drapability of cloth and this is important not only in textile applications but also in manufacturing processes for advanced fibre reinforced materials. Some of the fibres which are used are extremely stiff in tension; some are several times stiffer than steel, yet they can still be flexible. That means that they can be woven, knitted or transformed in any number of the ways that the textile industry has developed. In order to understand this characteristic, consider the factors which govern stiffness in bending. For

that we shall consider a simple elastic beam, fixed horizontally at one end, as shown in Fig. 1.1. If it is thin enough we will be able to see it bending under its own weight. Alternatively we could apply a load to make it deflect from the horizontal. The question is, how does the flexibility of the beam vary when we alter its thickness?

As the beam bends, its lower, concave, side is being put into compression whereas the upper, convex, side is being stretched and experiences tension. There is a neutral axis where the stresses are zero. If the beam is made of an elastic material this neutral axis will be at the midsection, CC. If we consider a small deflection, we can write:

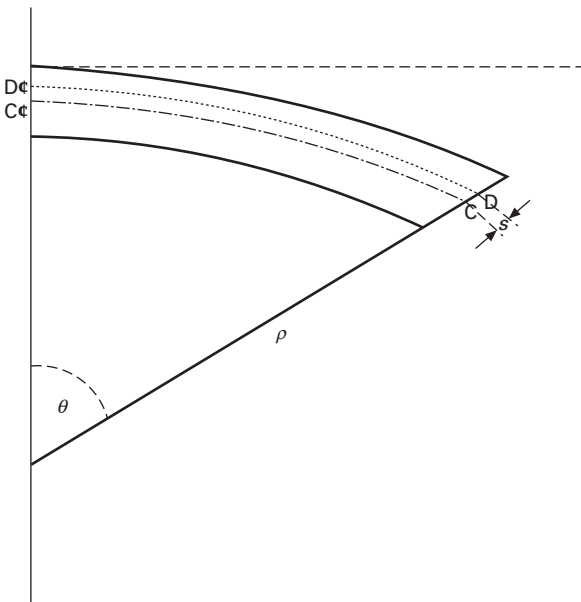
$$CC = \rho \theta$$

Consider a section DD some way from the neutral axis. As we have depicted this section in Fig. 1.1, the material is being stretched and its length is:

$$DD = (\rho + S) \theta$$

From the above two equations we can see that the imposed strain in section DD is then the increase in length divided by the original, unstrained, length of the beam;

$$\text{Induced strain in } DD = \frac{DD - CC}{CC} = \frac{(\rho + S)\theta - \rho\theta}{\rho\theta} = \frac{S}{\rho} = \frac{S}{r} \quad 1.1$$



1.1 A horizontal beam, fixed at one end, bends under its own weight.

The beam has a cross-section and stress along the line, DD . If we assume it has a very small thickness, the stress is given by the force, δF , on this elementary part of the beam divided by its cross-section δA . From Hooke's law, which relates stress, σ , strain, ϵ , and stiffness, E , the latter being called Young's modulus. For an elastic body, we can write $\sigma = E\epsilon$. So:

$$\frac{dF}{dA} = E \cdot \frac{S}{r} \quad 1.2$$

As DD is a distance S from the neutral line CC , the force δF produces turning moment δFS in the beam so that, from equation 1.2 we obtain:

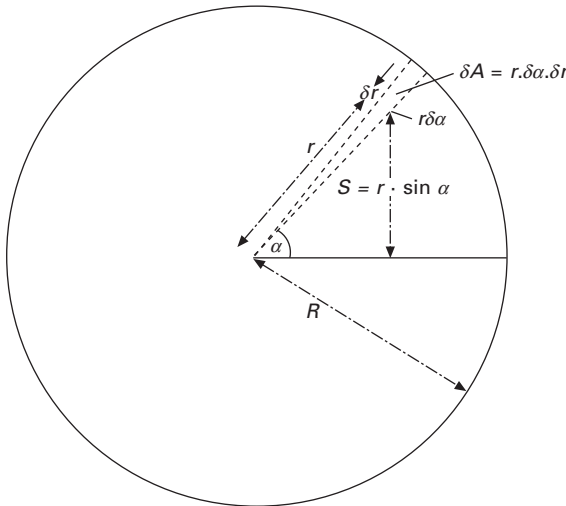
$$dFS = E \frac{S^2}{r} dA$$

which means that the total bending moment M_s is given by

$$M_s = \int E \cdot \frac{S^2}{r} dA = \frac{E}{r} \left(\int S^2 dA \right) \equiv \frac{E}{r} I_A \quad 1.3$$

where I_A is known as the second moment of inertia. It should be noted that this is to do with bending and nothing to do with movement, as in the inertia defined by Newton's first law.

If we consider that our fibre is circular in cross-section we can work out the second moment of inertia for a circular beam. Figure 1.2 shows the cross-section of the circular beam. We must write a relationship for the cross-section of the elementary section at a distance S from the neutral axis, which runs through the centre of the fibre. We see, from Fig. 1.2,



1.2 Cross-section of a circular fibre.

that, in polar coordinates, δA can be written as $r \cdot \delta r \cdot \delta \alpha$ and also that $S = r \sin \alpha$.

From equation 1.3 we can now write:

$$I_A = \int_0^{2\pi} \int_0^R r^2 \sin^2 \alpha (r \cdot dr \cdot d\alpha)$$

So that

$$I_A = \int_0^{2\pi} \sin^2 \alpha d\alpha \int_0^R r^3 dr$$

Now

$$\sin^2 \alpha = \frac{1 - \cos 2\alpha}{2}$$

So that:

$$I_A = \int_0^{2\pi} \frac{1 - \cos 2\alpha}{2} d\alpha \int_0^R r^3 dr$$

$$I_A = \left[\frac{\alpha}{2} - \frac{\sin 2\alpha}{4} \right]_0^{2\pi} \left[\frac{r^4}{4} \right]_0^R$$

As $\sin 2\pi = 0$

$$I_A = \left[\frac{2\pi}{2} - 0 \right] \frac{R^4}{4} = \frac{\pi R^4}{4}$$

Or, if D is the fibre diameter

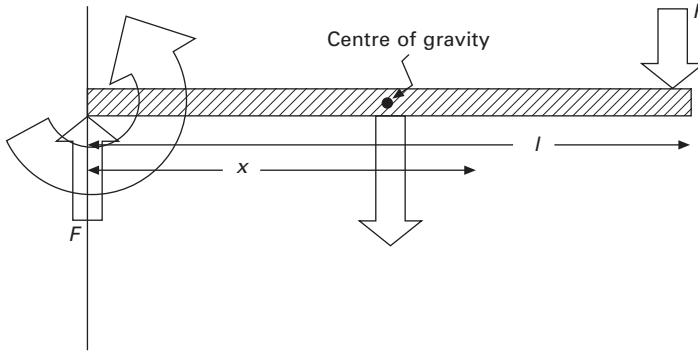
$$I_A = \frac{\pi D^4}{64} \quad 1.4$$

The stiffness of the cylinder or fibre is related to the fourth power of the diameter.

To quantify the flexibility of a fibre further we can calculate the total bending of a circular horizontal beam held at one end and loaded by a force F , as shown schematically in Fig. 1.3. The bending moment Fl produced by the applied force at the free end will induce by reaction a turning moment at the fixed end and in the opposite sense.

The bending moment at any point along the beam at a distance x from the fixed end is given from equation 1.3 as:

$$M(x) = \frac{E}{r} I_A$$



1.3 A horizontal beam held at one end and subjected to a downwards force at the other end will have a tendency to bend.

Now let's look at Fig. 1.4. The equation of the curve that describes the bending of the beam is given by:

$$\frac{1}{r} = \frac{y'''}{[1 + (y')^2]^{3/2}} \quad 1.5$$

For small deflections $dy/dx \ll 1$ so that we can write, from equation 1.5, that $1/\rho = y''$. We can now write:

$$\frac{d^2y}{dx^2} = y'' = -\frac{M(x)}{EI_A} \quad 1.6$$

The bending moment at a point x along the beam is given by the balance of the moment generated by the force F at the end of the beam, of value Fl , and the opposing moment due to the reaction at the fixed end which has a value of $-Fx$. So:

$$M(x) = -Fx + Fl$$

Then we can write from equation 1.6:

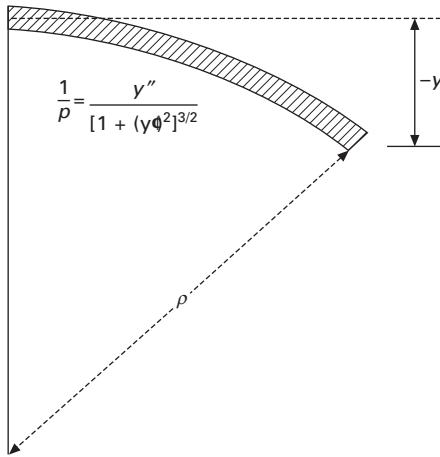
$$-\frac{d^2y}{dx^2} EI_A = M(x) = -Fx + Fl$$

Integrating;

$$-\frac{dy}{dx} EI_A = -\frac{Fx^2}{2} + Flx$$

plus a constant but as at $x = 0$, $dy/dx = 0$ so the constant is zero. Integrating again:

$$-y(x) EI_A = \left[-\frac{Fx^3}{6} + \frac{Flx^2}{2} \right]_0^l$$



1.4 The bending of a beam fixed at one end.

plus a constant but as at $x = 0$, $y = 0$ the constant is zero.

$$-y(l) EI_A = -\frac{Fl^3}{6} + \frac{El^3}{2} = Fl^3 \left[-\frac{1}{6} + \frac{3}{2} \right]$$

$$-y(l) EI_A = \frac{Fl^3}{3}$$

The minus sign reflects the downward deflection which is a distance of:

$$|y| = \frac{Fl^3}{3EI_A}$$

From equation 1.4 the total deflection is;

$$|y| = \frac{64Fl^3}{3E\pi D^4} \quad 1.7$$

We see then that the flexibility of a circular beam and hence a fibre is a function of the reciprocal of the diameter to the fourth power.

Clearly, reducing the diameter of a fibre by one half increases its flexibility 16 times. This shows why a very stiff material in the form of a fine fibre can still be extremely flexible.

1.4 Typical fibre properties

Some typical fibre properties are shown in the following tables. The figures represent typical values as there is considerable scatter in the literature, particularly for natural and regenerated fibres. One reason for this is the irregular cross-sections of these fibres. For greater detail see the relevant

chapters. Table 1.1 compares some properties of synthetic technical fibres with traditional engineering materials. Tables 1.2 to 1.4 give typical values for the fibres considered in this book.

1.5. Statistical nature of fibre properties

In any fibre structure there will be thousands and often millions of fibres and the characteristics of the structure depend on the sum of the fibres of which it is composed. Such large populations of fibres require a statistical approach to understanding their behaviour not least because fibres usually show a wide scatter in their mechanical properties. Chapter 2 describes how fibres are tested in tension. The results of tensile tests need Weibull statistics for their analysis.

Materials break from their weakest point or from regions of stress concentration. Testing a fibre in tension involves applying a load to it and determining the load at which it breaks. If such a tensile test is conducted on many fibres, usually a large scatter in breaking loads is observed within the population tested. This behaviour can be treated by Weibull statistics.

Table 1.1 Comparison of some fibres with traditional engineering metals

Material	Specific gravity	Young's modulus (GPa)	Specific modulus (GPa)
Steel	7.9	200	25.3
Aluminium	2.7	76	28
Titanium	4.5	116	25.7
Polyester (PET)	1.38	15	10.8
Spider silk	1.4	12	8.5
Wool	1.3	2	1.5
Flax	1.53	65	43
Kevlar	1.45	135	93
Zylon	1.56	280	180
Glass	2.5	72	27.6
Carbon (high strength)	1.8	295	164
Carbon (ultra high modulus)	2.16	830	384
Hi-Nicalon	2.74	265	97
Nextel 610	3.75	370	99

Table 1.2 Typical properties of some organic synthetic fibres

Fibre	Diameter (μm)	Specific gravity	Strength σ (GPa)	Strain to failure ϵ (%)	Young's modulus E (GPa)
Polyamide 66	20	1.2	1	20	< 5
Polyester (PET)	15	1.38	0.8	15	15
Nomex	15	1.38	0.64	22	17
Technora	12	1.39	3	4.4	70
Kevlar 49	12	1.45	3	4.5	135
Zylon	12	1.56	5.8	2.5	280
Polyethylene	38	0.96	3	3.5	117

Table 1.3 Typical properties of glass, carbon and ceramic fibres

Type of fibre	Diam. (μm)	Density (g/cm^3)	Tensile failure strength (GPa)	Tensile failure strain (%)	Young's modulus (GPa)
E type glass	14	2.54	3.5	4.5	73
S type glass	14	2.49	4.65	5.3	86
Carbon (Ex-PAN)					
High strength (1st generation)	7	1.80	4.4	1.8	250
High strength (2nd generation)	5	1.82	7.1	2.4	294
High modulus (1st generation)	7	1.84	4.2	1.0	436
High modulus (2nd generation)	5	1.94	3.92	0.7	588
Carbon (Ex-pitch)					
Petroleum pitch	11	2.10	3.7	0.9	390
High modulus derived from petroleum pitch	11	2.16	3.5	0.5	780
Derived from coal-based pitch	10	2.12	3.6	0.58	620
High modulus derived from coal-based pitch	10	2.16	3.9	0.48	830
Hi-Nicalon	12	2.74	2.8	1	270
Tyranno SA	10	3	2.9	0.78	375
Nextel 610	10	3.75	1.9	0.5	370
Nextel 720	12	3.4	2.1	0.81	260

Table 1.4 Typical properties of natural fibres

Fibre	Diameter (μm)	Length	Specific gravity	Strength σ (GPa)	Strain to failure ϵ (%)	Young's modulus E (GPa)
Cotton	10–27	10–50 mm	1.54	0.6	7	8
Wool	15–40	25–355 mm	1.3	0.17	35	2
Flax	15–20	25 mm	1.4	0.65	1–3	65
Silk (silk worm)	12	>10 m	1.4	0.40	25	8
Silk (spider)	2	>10 m	1.4	0.6	25	12
Hemp	45	25 m	1.5	0.50	1–2	50
Jute	69	2 m	1.4	0.35	2.5	35
Regenerated cellulose Rayon	4–60	Continuous	1.52	0.50	~25	3–11

Let us consider a chain consisting of n links as shown in Fig. 1.5. It will fail when the weakest link breaks. The probability of failure for a link under an applied load σ is P_0 . The probability of the chain surviving under the same stress is $1 - P_0$. As there are n links the survival probability of the entire chain under an applied stress σ is given by $(1 - P_0)^n$.

Now, if we consider the chain as a whole, without considering its structure made of links we can write that the probability of the chain's failure can be written as P_n , so that.

$$1 - P_n = (1 - P_0)^n.$$



1.5 A chain consisting of n links

By taking the natural logarithm and then the exponential of the expression the probability of the chain's failure, under an applied stress of, becomes:

$$P_n = 1 - \exp n \ln (1 - P_0) \quad 1.8$$

Weibull defined $-n \ln (1 - P_0)$ as the risk of failure 'R'. A material has a volume, however, so if Weibull statistics are to be applied to real materials, such as fibres, we have to define what is analogous to a link. For a specimen of volume V , consider it divided up into small volumes V_0 which each contain a defect which is considered an intrinsic characteristic of the material. The assumption here is that there is only one type of defect population in the material. In this way we can write $V/V_0 \approx n$. In this way

$$R = -\frac{V}{V_0} \ln (1 - P_0)$$

The risk of failure of an elementary small volume dV is

$$dR = -\frac{1}{V_0} \ln (1 - P_0) dV$$

So that

$$dR = -f\left(\frac{\sigma}{\sigma_0}, \frac{1}{V_0}\right) dV \Rightarrow R = -\int_V f\left(\frac{\sigma}{\sigma_0}, \frac{1}{V_0}\right) dV$$

From equation 1.8 we now write:

$$P_V = 1 - \exp \left[-\int_V f\left(\frac{\sigma}{\sigma_0}, \frac{1}{V_0}\right) dV \right]$$

Weibull put

$$f\left(\frac{\sigma}{\sigma_0}, \frac{1}{V_0}\right) = \left[\frac{\sigma - \sigma_u}{\sigma_0} \right]^m$$

in which σ is the applied stress, σ_u is a stress threshold below which there is no possibility of failure, σ_0 and m are material parameters. The scatter of the strengths is quantified by m which is known as the Weibull modulus.

We can now write:

$$P_V = 1 - \exp \left[-\int_V \left[\frac{\sigma - \sigma_u}{\sigma_0} \right]^m dV \right]$$

For an evenly distributed stress throughout the body

$$P_V = 1 - \exp \left[- \left(\frac{s - s_u}{s_0} \right)^m \right] V \quad 1.9$$

The Weibull modulus, m , allows the scatter in fibre strengths to be quantified. For example the average strength of two materials could be the same but the two materials could have very different scatter in their strengths and that could be important in assessing the risk of failure of a structure as shown in Fig. 1.6.

Now let us consider two populations of the same material, for example a type of fibre, but with different volumes because they are of different lengths. If the volumes are V_1 and V_2 we could test a number of the specimens and determine at which stresses half of each group was broken. That is to say, when the probabilities of each group are both equal to a half. These are known as the median strengths of each population, $\bar{s}_1$ and $\bar{s}_2$.

If we consider that $\sigma_u = 0$ we can now write, from equation 1.9:

$$1/2 = 1 - \exp \left[- \left(\frac{\bar{s}_1}{s_0} \right)^m \right] V_1 = 1 - \exp \left[- \left(\frac{\bar{s}_2}{s_0} \right)^m \right] V_2$$

So

$$\left(\frac{\bar{s}_1}{s_0} \right)^m V_1 = \left(\frac{\bar{s}_2}{s_0} \right)^m V_2$$

so that

$$\left(\frac{\bar{s}_1}{s_0} \right)^m \left(\frac{s_0}{\bar{s}_2} \right)^m = \frac{V_2}{V_1}$$

This gives

$$\left(\frac{\bar{s}_1}{\bar{s}_2} \right)^m = \frac{V_2}{V_1} \quad 1.10$$

Equation 1.10 illustrates the dependence of strength on volume. Going back to the chain analogy, it means that the bigger the volume, the longer the chain and the greater the number of links. This increases the probability of there being an extra weak link in the chain. In fibres it means that the longer the fibre, the greater the chance of there being a major defect which weakens it.

Now, from equation 1.9, we obtain:

$$P_V - 1 = -P_S = - \exp \left[- \left(\frac{s - s_u}{s_0} \right)^m \right] V$$

Taking the natural logarithm:

$$-\ln P_s = \left[\frac{(\mathbf{s} - \mathbf{s}_u)}{\mathbf{s}_0} \right]^m V$$

Taking the natural logarithm again:

$$\ln \ln \frac{1}{P_s} = \ln V + m \ln \mathbf{s} - m \ln \mathbf{s}_0 \quad 1.11$$

As m and σ_0 are intrinsic material parameters, $m \ln \sigma_0$ is constant. For a population of fibres of variable diameters D but all of the same length, equation 1.11 becomes:

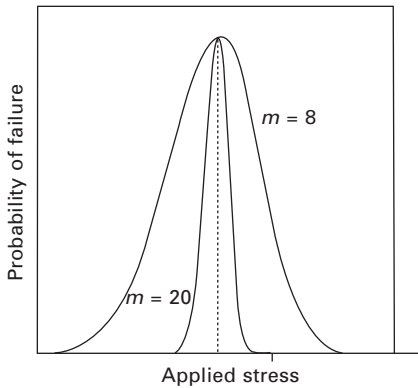
$$\ln \ln \frac{1}{P_s} = m \ln \mathbf{s} + 2 \ln D + \text{constant} \quad 1.12$$

If D can be considered constant, then equation 1.12 becomes:

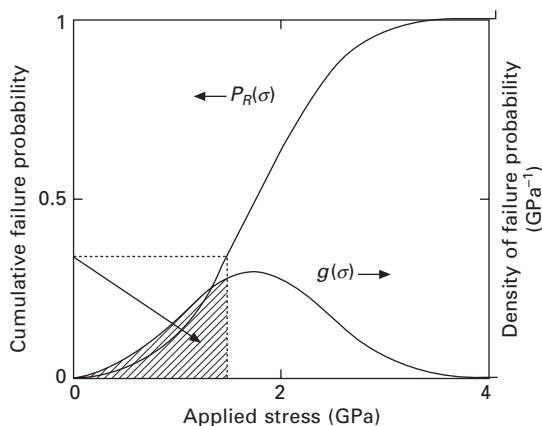
$$\ln \ln \frac{1}{P_s} = m \ln \mathbf{s} + \text{constant} \quad 1.13$$

Plotting $\ln \ln 1/P_s$ as a function of $\ln \sigma$ allows the Weibull modulus, m , to be determined.

The probability of failure for a population of specimens, such as fibres, can be presented, as in Fig. 1.6 which shows the density of the failure probability, or as a cumulative failure probability going from zero, when no specimens are broken, to one, when all specimens are broken. Both types of curve are shown in Fig. 1.7. The S-shaped cumulative failure curve is characteristic of a single defect population. Although to draw the whole cumulative curve it is necessary, theoretically, to test an infinite number of fibres, the shape of



1.6 Two materials could have the same mean strength but different scatter in strength. The higher the Weibull modulus, m , the smaller the scatter.



1.7 Two ways of depicting failure probability.

the curve can be obtained as the results from, say, 30 tests, fall on the curve, as can be seen from Fig. 1.8, which plots the results from 30 tensile tests on carbon fibres. All the fibres had the same dimensions. In order to draw such a curve the results of the tensile tests are ranked in increasing order of failure stress. The probability of failure of a fibre within the 30 fibres tested is calculated by dividing the rank of the fibre by the total number of fibres tested plus one. In this way the limitation of testing a finite number of specimens is countered. This limitation is due to there being a finite probability of stronger or weaker fibres existing than those tested.

Using equation 1.13 the data shown in Fig. 1.8 can be converted so as to plot the straight line curve shown in Fig. 1.9 and its gradient gives the value of the Weibull modulus.

An alternative method for obtaining the Weibull modulus is to plot the median strength of the fibres as a function of gauge length. With an increasing length of fibre the volume increases and the median strength decreases.

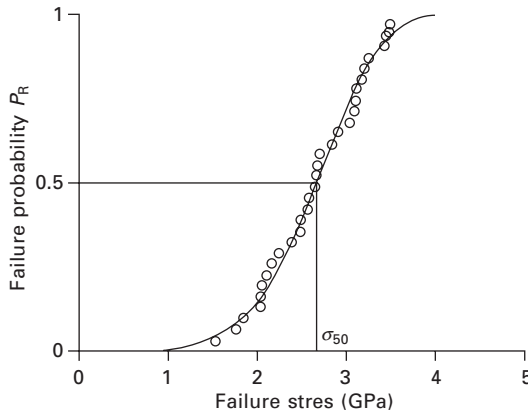
From equation 1.11 we can write:

$$\ln [-\ln (0.5)] = m \ln (\bar{\sigma}) + \ln (l) + 2 \ln (\pi D/4) - m \ln (\sigma_0)$$

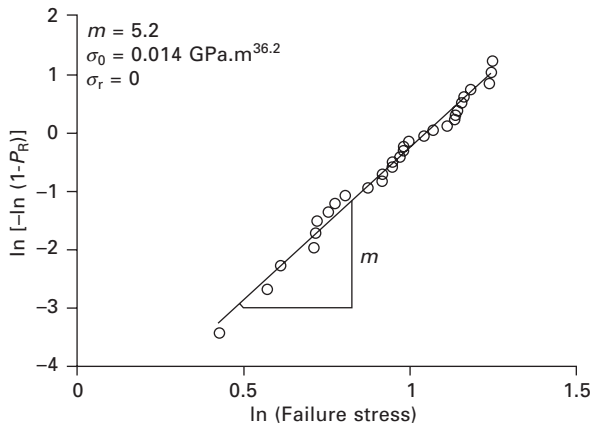
If we take the diameter of the fibres to be constant we obtain:

$$\ln (\bar{\mathbf{s}}) = -\frac{1}{m} \ln (l) + \text{constant} \quad 1.14$$

A plot of $\ln (\bar{\sigma})$ as a function of $\ln(l)$ for several gauge lengths gives a straight line curve with a gradient of $-1/m$, as can be seen from Fig. 1.10. With this technique, care has to be taken. The difficulty is that with weak or brittle fibres the selection of fibre specimens with the longer gauge lengths may inadvertently remove the weaker fibres, so altering the probability distribution.



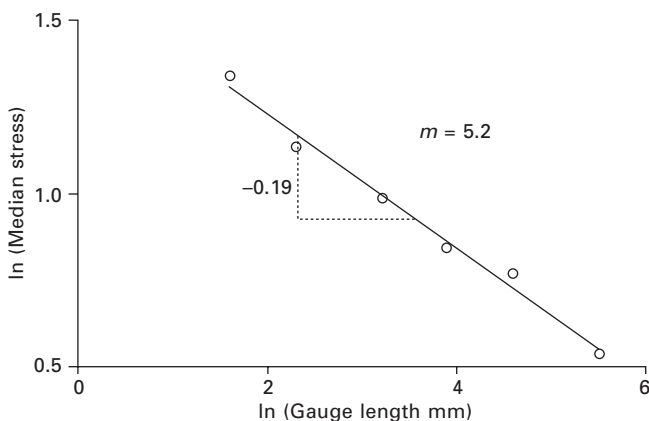
1.8 The cumulative failure curve obtained from 30 tensile tests on carbon fibres.



1.9 The data used to draw Fig. 1.7 can be replotted according to equation 1.13 so as to obtain a straight line curve the gradient of which gives the Weibull modulus.

1.6 Markets

The fibre industry produces, globally, around 70 million metric tonnes of fibre, both synthetic and natural. At the end of the first decade of the twenty-first century, the production of synthetic fibres is estimated to be around 45 million tonnes. This includes polyester, polypropylene, nylon and acrylic fibres and others but around 70% is accounted for by polyester fibres, 13% by polyolefins (polypropylene and polyethylene), 12% nylon and 5% acrylic. Around 25 million tonnes of natural fibres, such as cotton, jute, wool and silk, are produced, of which cotton largely dominates, accounting for 90%



1.10 The plot of the logarithm of the median strengths of the carbon fibres for different gauge lengths allows the Weibull modulus to be determin

of production. The figures for production and markets are very volatile with considerable variations from one year to the next but the trend for fibre production is up, for both natural and synthetic fibres, with a growth rate of around 5% per year. For traditional textile uses, the trend of where the fibres are being made is also clear: for both synthetic and natural fibres, overall, it is in developing countries, particularly countries which are also seeing their internal markets growing. China and, more generally, Asian countries are the region in which greatest growth in production and sales are seen. The exceptions are for technical fibres, such as carbon, aramid or other high performance fibres used in advanced composite materials. These are produced in advanced industrial countries, such as Japan, the USA and Europe. This is also true for advanced technical organic fibres including polyester for tyre cords and high performance ropes as well as fibres. However, China is also expected to become a major player in these areas.

Cost is the driving force determining where fibres are made, with advanced industrial nations losing out to less well-developed countries where labour costs are lower. This has meant, for example, that although the USA has been a traditional cotton producer, it is losing ground to India, Pakistan and particularly China. The overtaking of natural fibres by synthetic fibres is also largely driven by cost. Natural fibres are produced in countries which have the right climate. Labour costs are important and production is not concentrated in one small area. In addition other issues should be considered, as fibres such as cotton require very large quantities of water and fertilisers, which are demanding on the environment. Synthetic fibres require an initial investment but once the production plant is built running costs are low.

Wool production can be seen as a special case as the industry is dominated by New Zealand and Australia.

Advanced fibres for reinforcement are made in much smaller quantities, although they show much greater added value than the fibres for traditional textile end-uses. The world production of carbon fibres is around 45 000 tonnes, although demand outstrips supply so that new production lines are continually coming on stream. Around five million tonnes of glass fibre are produced as reinforcement but if insulation is considered, production is much higher.

1.7 Conclusions

Fibres represent both traditional industry and the most recent and innovative. They have been used throughout history and the textile industry was the first to experience the industrial revolution. Traditional sectors have moved to developing countries, in the main, but improvements are being made in industrial nations and new fibres have been produced which have allowed some of the most advanced industries to be developed. Fibres are remarkable forms of matter which require special techniques to be converted into structure as well as to be characterised. Their fineness means that a section of any one fibre structure can contain millions of fibres, which for the most part go unnoticed since it is the overall structure which is seen. Fibres represent both the past and the future.

Tensile testing of textile fibres

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Abstract: The fineness of fibres requires special testing techniques in order to determine their mechanical characteristics. Traditionally the properties of fibres have been normalised to their linear weight because of the difficulties of measuring fibre cross-sections exactly; however, precise measuring techniques are now available which allow their properties to be expressed in engineering terms familiar to all engineers working on structural materials. Traditional and conventional engineering units will be found in this book. The properties of the fibres are determined by their molecular or atomic structures which can be investigated by means such as Raman spectroscopy, X-ray diffraction and electron microscopy.

Key words: dimension measurement, mechanical characterisation, microstructure.

2.1 Introduction

As we have seen in Chapter 1, fibres owe their flexibility to their fineness as it is related to the reciprocal of the fibre diameter to the fourth power. This means that if the diameter of a fibre is reduced by a half it becomes 16 times more flexible. This characteristic is obviously very important in determining their use; after all sheet metal, or even chain mail, never became a fashion item except for medieval knights and they had to be careful not to fall over in case they could not get up. Drapability, coupled with lightness, therefore explains, to a great extent, the success of fibres for clothing and these are often the reasons why fibres find use in technical applications. However, this means that the nature of structures made from fibres is different from other structural materials. Cloth is a two-dimensional structure, which can easily take complex forms, bending in more than one plane to take the shape of a person or of a complex mould. Most other structural materials are three dimensional and have to be worked to achieve the final desired form. Even as fibre reinforced composite materials, composites are usually in the form of thin sheets. It also means that fibres are mostly used in tension as they buckle usually under compression and makes characterising fibres particularly challenging (Bunsell and Schwartz, 2000).

The development of the scanning electron microscope in the 1960s made

it possible, for the first time, to examine fibres up close and to accurately determine their cross-sections. As we have already seen, the fineness of fibres had led the fibre industry to develop its own units of measure, based on weight per unit length. The accurate measurement of the cross-sectional areas of fibres, however, remains difficult. The limit of resolution of an optical microscope is determined by physical limitation due to the wavelength of light, which is around half a micron. The test methods, which have been developed for conventional engineering materials, are often therefore poorly adapted to the characterisation of fibres. This chapter attempts to explain how these properties are measured, mainly in tension but also a few other techniques will be described.

2.2 Determination of fibre dimensions

2.2.1 Weighing methods

The linear density, a measure of the mass per unit length of a fibre, is used by fibre manufacturers as a measure of fineness. The most common units are known as the denier, which is the traditional unit for which the weight of the fibre, in grams, is normalised to a length of 9000 m; the tex, the internationally recognised unit normalised to a length of 1000 m and the decitex, normalised to 10000 m. The denier and the decitex are close in value and for this reason both are often used in the clothing industry. Often the linear density of individual fibres is not provided by the manufacturer. Rather the linear density of the entire yarn or tow and the number of fibres are provided; simple division provides the average linear density of a filament and this number is often used.

When evaluating fibres it is often necessary to work with the linear density of the individual fibres. This can be done by weighing. If d_l is the linear density and w the weight of a fibre of known length l , then

$$d_l = \frac{wS}{l} \quad 2.1$$

S is the normalising factor given above for each type of unit; denier, decitex and tex.

$$\text{As } d_l = A\rho S \quad 2.2$$

The fibre cross-sectional area, A , may therefore be determined and hence, for a fibre with a circular cross-section, the diameter, φ , from the linear density if the density, ρ , is known using

$$A = \frac{d_l}{\rho S} = \frac{\pi \varphi^2}{4} \quad 2.3$$

Weighing methods give an average value of the fibre or fibres and so if the characteristics of individual tested fibres are required, they are of limited use; however, linear density is insensitive to the cross-sectional shape of the fibre. As seen in eq. (2.3), the area is directly obtained from mass and density; fibre dimensions are not necessary. This makes this technique especially attractive for irregular cross-sections.

2.2.2 Vibrational methods

Vibrational techniques are widely used in the textile industry to measure the linear density of extremely fine fibres. All vibrosopes (Gonsalvas, 1947) use the principle of a string vibrating at its fundamental, natural frequency, f , to determine the linear density of a fibre. For a perfectly flexible string under tension, T , fixed at two nodes, and undergoing vibration in a viscous medium with no damping effects, the linear density, d_l , is related to the fundamental natural frequency

$$f = \sqrt{\frac{T}{4d_l l^2}} \quad 2.4$$

where l is the nodal length.

Vibrosopic methods are most applicable to fibres with linear densities less than 1 mg/m (9 denier, 10 decitex, 1 tex), and the main types of excitation methods are mechanical, electrostatic and acoustic. Because the fibre elongates, the fibre tension should be chosen so as not to unduly affect the fibre cross-sectional area. ASTM D 1557 (ASTM, 1989) recommends that the applied load produce no more than 0.5% extension.

Because the linear density and, using eq. (2.3), cross-sectional area are directly determined, irregular fibre cross-sections do not cause concern. Robinson *et al.* (1987), using Au and W fibres, have shown that the values of linear density obtained using either vibroscope or direct weighing are essentially the same.

2.2.3 Light microscopy

Engineers working with materials usually normalise characteristics by the cross-sectional area of the material. In this way force to failure is converted into stress. Light microscopy is not sufficiently accurate for the cross-sectional area to be measured. This cannot be solved by using more and more sophisticated light microscopes, as the limitation comes from the nature of light itself. The wavelength of visible light is around half a micron and it is difficult to resolve objects in this size range.

Resolving power is the ability to distinguish between two closely spaced objects. Under ideal conditions, an unaided human eye can resolve two objects

approximately 60 μm apart but more generally the spatial resolution ranges between 120 and 300 μm (McCrone *et al.*, 1984). Using a light microscope, the resolving power can be as high as 100 nm. Generally, the resolving power, RP , of a lens is given by

$$RP = \frac{0.61 \lambda}{NA} \quad 2.5$$

where λ is the wavelength of the illuminating electromagnetic radiation (about 450 nm for visible light) and NA is the numerical aperture of the objective lens.

There are two simple ways to measure the linear dimensions of a fibre. The first technique is to either photograph or project the image from the microscope onto a surface. The final linear magnification, M_{tot} , is

$$M_{\text{tot}} = \frac{D_p \cdot M_{\text{obj}} \cdot M_{\text{occ}}}{25} \quad 2.6$$

in which D_p is the distance, in centimetres, to the projection surface or film plane, M_{obj} is the magnification of the objective lens, and M_{occ} is the magnification of the ocular lens (McCrone *et al.*, 1984). The dimensions of the fibre can be measured on the photograph or projection surface and the actual dimensions found by dividing the results by M_{tot} . This technique is accurate to within 2–5%.

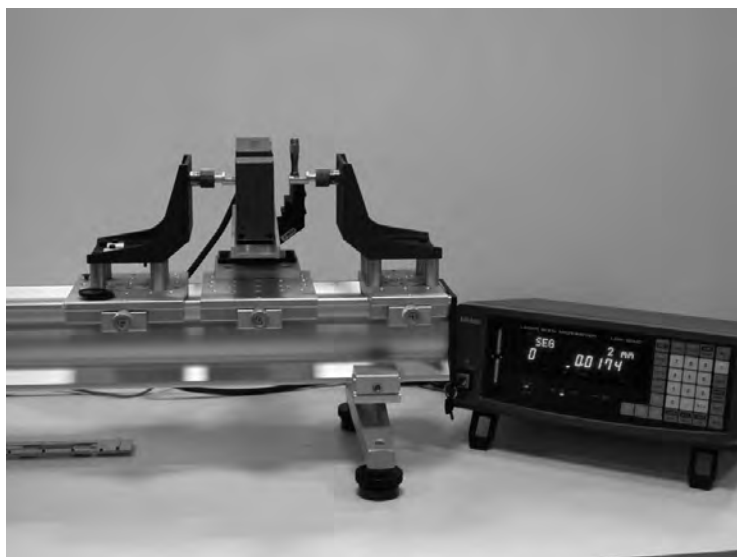
A more straightforward and accurate technique is to use a micrometer ocular to directly measure the size from the viewed image. The degree of accuracy using this technique is related to the ability to determine the edge of the specimen which may be slightly out of focus owing to the lack of sufficient depth of field. The depth of field is the maximum vertical separation that can exist between two objects that are in focus, and is approximately $0.5 (NA)^{-2} \mu\text{m}$. Also affecting the measurement are the kind and quality of the illumination, errors in the lens system, and the refractive indices of the fibre and the mounting medium.

2.2.4 Diameter distribution along the length of a fibre

There is often a considerable scatter in fibre diameters between fibres taken from a bundle. However, with many fibres their diameters can also vary along their length, which makes conversion of the breaking load into failure stress more difficult and increases the dispersion of the results. A technique described by Morimoto *et al.* (1998) allows the diameter of a fine fibre to be measured at each point along its length. Two rectangular flat glass slides are separated from each other by two short lengths of glass fibre, between the

slides, at one end and one short length of glass fibre placed between them at the other end. The glass fibres are placed parallel to the longest side of the slides and positioned to form an isosceles triangle. The fibre to be tested is then placed at right angles over the single short length of glass fibre so that its thickness at the point of contact lifts one slide. The angle between the glass slides is measured precisely using the optical interference technique with a He–Ne laser and the diameter of the fibre simply calculated knowing the distance between the spacing glass fibres. A maximum error of 0.1 μm is claimed for this technique.

A particularly interesting technique for measuring fibre diameter, both at a given point on the fibre and for scanning along the length of the fibre is provided by the Japanese company, Mitutoyo. Their apparatus is shown in Fig. 2.1 and is suitable for fibres with diameters from a few microns up. A laser beam scans across the fibre, which, in the figure, is held horizontally between two grips. The time of occlusion of the light is measured by a light cell and the diameter calculated. The measurements should be verified initially, for each fibre type, by comparison with results from a scanning electron microscope but after this is done, measurements of fibre diameter can be made rapidly and with great accuracy. Verification with results from a scanning electron microscope is advisable as the light from the laser may



2.1 The Mitutoyo apparatus for determining fibre diameter. It is suitable for fibres with circular cross-sections with diameters from a few microns up. A laser beam scans across the fibre, which, in the figure, is held horizontally between two grips. The time of occlusion of the light is measured by a light cell and the diameter calculated.

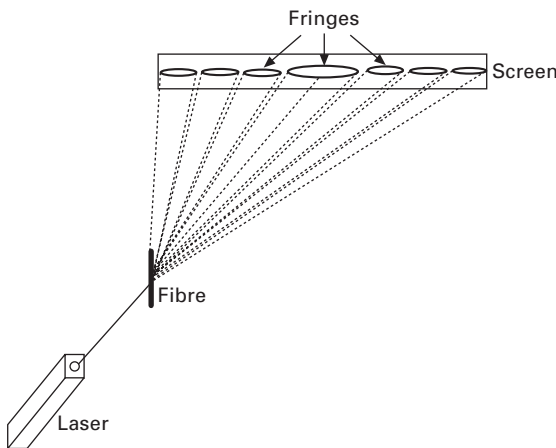
interact differently with different fibres, so that refraction at the surface of transparent fibres can occur and differences in surface roughness between different types of fibres can also modify the results. As can be seen, the equipment can be arranged so that the length of the fibre can be scanned and variations of diameter easily determined. The equipment can also be easily mounted on a testing machine.

2.2.5 Laser interferometry

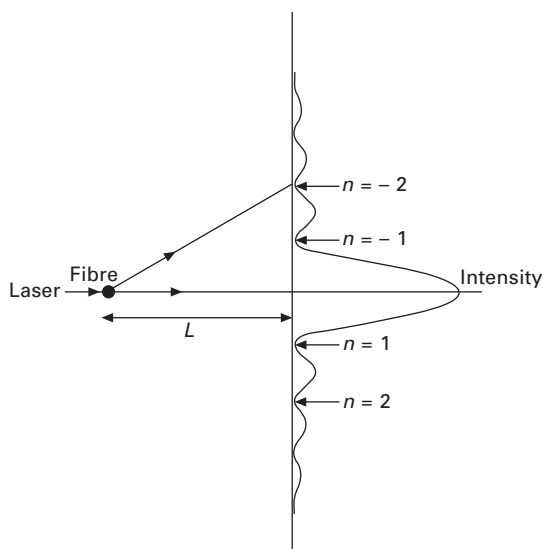
Laser interferometry has been seen by many as a means of measuring fibre diameters with greater accuracy than is possible with ordinary optical microscopy. This technique employs a low power laser beam (<0.5 mW), for instance of the He-Ne type. The technique is illustrated in Fig. 2.2. A screen is placed normal to the beam, and the fibre, which has been glued across a rectangular aperture in a piece of Bristol card is put in the beam. The interference pattern varies in intensity as is shown in Fig. 2.3. The diameter of the fibre (d) is given by:

$$d = n\lambda \left[1 + \frac{2L}{\lambda Z_n} \right]^{-\frac{1}{2}} \quad 2.7$$

where L is the distance from fibre to screen, n is the number of fringe nodes chosen for the measurement, Z_n is the distance between these two n th nodes and λ is the wavelength of the laser beam. The distance L must be adjusted according to the diameter to be measured. This technique is



2.2 Laser interferometry can be used to determine the diameter of fibres with a circular cross-section. The fibre is placed in the beam and the interference fringes projected onto a screen.

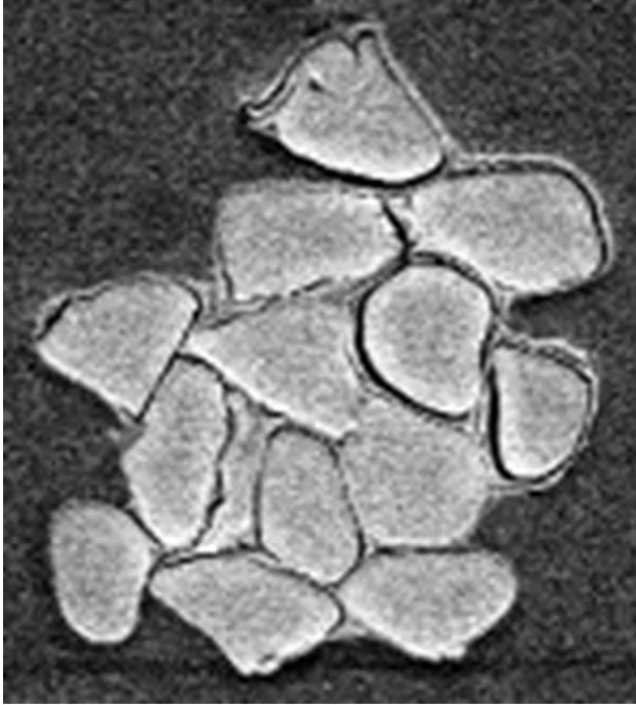


2.3 The interference pattern varies in intensity.

particularly suitable for opaque fibres (carbon fibres, SiC fibres, etc.). In the case of transparent and translucent fibres (thermoplastic, glass fibres, etc.) it is advisable to coat them by metal deposition, prior to measurement, with an opaque layer of negligible thickness, which is the technique employed for preparing insulating specimens for the scanning electron microscope.

2.2.6 Direct measurement of cross-sectional area

When the fibre cross-section is irregular, it is advisable to obtain a direct measurement of the cross-sectional area. A bundle of the fibres can be embedded in a suitable resin such as epoxy resin, then sectioned and polished in order to examine the cross-sections of the fibres with an optical microscope in the reflection mode. The cross-sectional area can then be measured, either from a photographic print, after suitable magnification and photographic enlargement, by planimetry, or directly, if available, with an image analyser. Using the contrast between features and background, the image analyser allows a quantitative evaluation of the fibres seen in a field of view. In the case of fibre cross-sections the main difficulties arise from fibres in contact, but mathematical morphology software is available to overcome this problem (Hagege and Bunsell, 1988). Figure 2.4 shows a cross-section of an industrial silk filament. The mean cross-section of each filament, or bave, determined by image analysis, is 200 μm^2 , from which an effective diameter can be calculated, if necessary. Silk baves are each made up of two silk fibres surrounded by a layer of sericine, as described in Chapter 6.



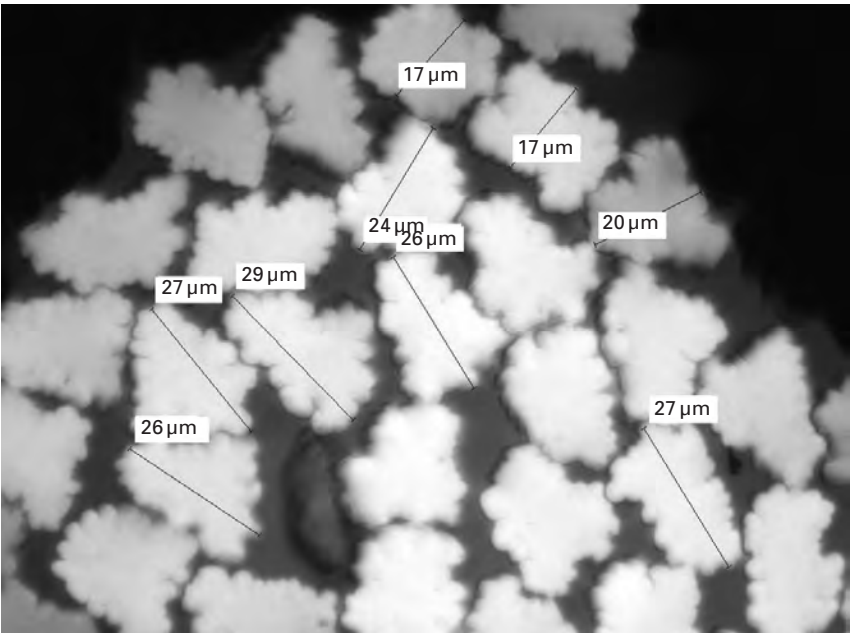
2.4 A cross-section of an industrial silk filament containing several silk fibres or baves. The mean cross-section of each filament, or bave, determined by image analysis, is $200\text{ }\mu\text{m}$.

Figure 2.5 shows the cross-sections of rayon fibres made from regenerated cellulose by the ENKA Company in Germany and taken from one of their products of 330 dtex containing 60 rayon filaments. These fibres show that synthetic fibres can also vary in dimensions and cross-sections.

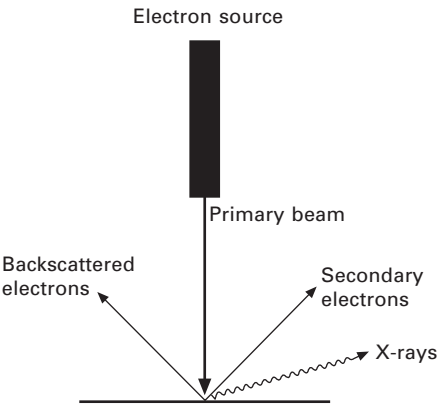
2.2.7 Scanning electron microscopy

Almost all the photographs of fibres which appear in this book have been taken using a scanning electron microscope (SEM). Before development of these microscopes in the 1960s there was no way of examining closely individual fibres or their fracture morphologies. An analogy with optical microscopes can be made, but instead of a beam of light, a beam of electrons is used in the SEM. The electron beam acts as waves analogous to photons but at a much shorter wavelength, which results not only in much greater magnification but also much greater depth of field.

When a beam of free electrons impinges upon a fibre there are two likely outcomes, as shown in Fig. 2.6. Some electrons are scattered back (Rutherford



2.5 Rayon fibres made from regenerated cellulose. (Courtesy of Enka Co.)



2.6 Interactions of the incident electron beam with the specimen and the resulting emissions in a scanning electron microscope.

backscattering) because of the interaction with the positively charged nuclei. Other electrons may interact directly with the electron shells of the atoms, knocking them free as secondary electrons. These secondary electrons are used to produce images. If the secondary electron is from an inner shell, a less tightly bound electron will fall to fill the vacancy, releasing energy in

the form of a photon, often in the X-ray range which possesses a wavelength characteristic of the interaction, so enabling the identification of the excited atom.

The resolving power of SEMs follows Eq. (2.5). Following Halliday and Resnick (1986), the de Broglie wavelength of an electron in the primary beam of an electron microscope is

$$\lambda = \frac{h}{\sqrt{2meV}} \quad 2.8$$

where h is Planck's constant (6.63×10^{-34} Js), m is the electron mass (9.11×10^{-31} kg), e is the electron charge (1.60×10^{-19} C), and V is the accelerating voltage. Using eq. (2.8), an accelerating voltage of 100 kV produces electrons having wavelengths of 0.4 nm. The resolving power of such instruments, because of the short wavelengths and sharp focus of the electron beam ($NA \approx 0.002$), is in the 1 nm range. Because of the low numerical aperture, the depth of field in an SEM is extremely high.

Measuring distances using the SEM can be accomplished by several techniques. Similar to the photographic/projection technique used in light microscopy, the fibre dimensions can be measured on a photographic image and converted, using the known magnification, to the actual dimension. Most SEMs print a scale bar on the image to facilitate this sort of measurement. However, it is important to calibrate the scale bar. SEMs can give the distance between any two selected points on the image, greatly simplifying the measurement.

The collection of electrons on the surface of a specimen, which is known as charging, will cause perturbations in the electromagnetic field within the SEM and prevent usable photographs being made. This is a particular problem with non-conducting specimens, such as most fibres. It is usually necessary, therefore, to sputter on a conductive coating (e.g., Au-Pd) to prevent charging from the electron beam. As the thickness of the coating is normally one or two atomic layers and the fibre diameter is in the micrometre range, negligible error is introduced. In some instances, non-conducting fibres can be imaged in a non-coated state if very low accelerating voltages are used. Equations (2.5) and (2.8) show that the resolving power is proportional to $V^{-0.5}$. The major limitation when using low accelerating voltages, however, is the low signal to noise ratio, resulting in a poor image. The SEMs with a field effect gun results in a greater brightness which allows much lower accelerating voltages to be used. With this type of SEM, voltages down to a few hundred volts are possible but usually one or two kilovolts are used. Lower accelerating voltages allow greater surface detail to be obtained as the electrons do not have the energy to penetrate into the surface of the specimen.

2.3 Surface analysis

2.3.1 Scanning electron microscopy

Scanning electron microscopes provide several different opportunities to study the surface of fibres. Imaging of the fibre surface may be accomplished in the SEM using any of the three different by-products of the incident beam – primary and secondary electrons and characteristic X-rays.

Elemental contrast

The yields of both backscattered and secondary electrons depend on the atomic number, Z , of the atoms on the fibre surface (Campbell and White, 1989). For backscattered electrons the yield varies roughly as Z^2 . The relative yield may be used to provide a map of the distribution of different elements on the surface of a fibre. The signals from secondary electrons, which are of lower energy, are removed by using multiple detectors and adding or subtracting the signals recorded by each.

X-ray maps

X-rays are emitted when an outer shell electron falls into the gap created by the production of a secondary electron; the energy of the X-ray is determined by the difference in binding energy between the two shells. The binding energy is a function of the nuclear charge, and hence the atomic number Z . By measuring the energy of the emitted X-rays, the identity of elements on the fibre surface may be determined. The technique is capable of detecting boron and heavier elements.

Surface topography

The secondary electron yield is very sensitive to the surface contours and defocused secondary electrons will be reabsorbed by the material and not be available for collection by the detection device. Secondary electrons formed on a high point will be collectable. In the former case the secondary electron yield will be low and in the latter, high, providing surface contrast. Identical to the case of elemental contrast, the signals from backscattered electrons are filtered out through the use of multiple detectors.

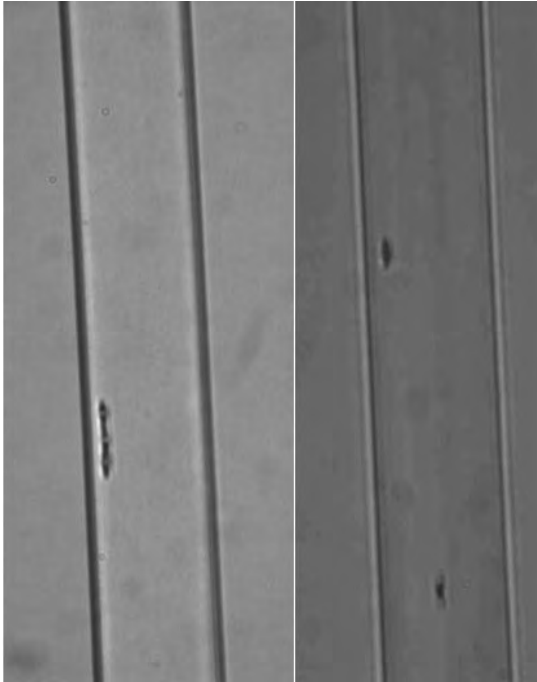
The creation of artefacts by the electron beam has the potential to cause problems when studying surface topography. Chain-scission and polymer decomposition can result in the creation of volatile species that can produce surface craters and roughness. For fibres that are poor thermal conductors, the differential thermal expansion between the polymer and the metallic coating can create surface cracks and blistering.

2.4 Internal structure

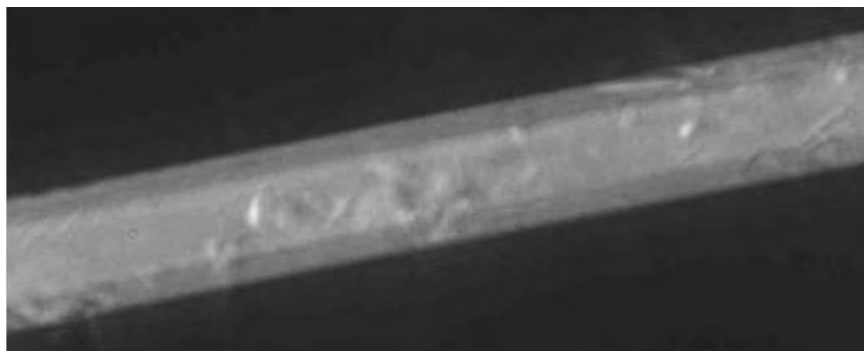
2.4.1 Optical microscopy

The optical microscope is the obvious instrument to examine the internal structure of transparent fibres. The fibre is immersed in a liquid possessing approximately the same refractive index, typically 1.515, so as to facilitate observation and optical microscopy is unsurpassed in revealing internal details. Figure 2.7 shows two images of different lengths of a poly(ethylene terephthalate) (PET) fibre revealing the presence of particles of sizes less than one micron. These particles are of antimony used as a catalyst in the manufacture of the fibre. Another part of the same fibre, viewed in polarised light is shown in Fig. 2.8. This technique makes use of the anisotropy of the refractive index of the fibre so that the effect of birefringence occurs and can be used to reveal variations in the internal structure of the fibre, such as the existence of a skin or variations in molecular orientation.

Optical microscopy combined with ultramicrotomy allows closer inspection of the internal structure of fibres. Microtomy is a technique developed first for histology, the study of biological materials. By the use of a fine knife or blade the material is cut into thin slices with thicknesses less than 5 μm thick



2.7 Transmission optical micrograph of PET fibres, of $18\mu\text{m}$ diameter, revealing inclusions.



2.8 Birefringence of PET of 18 μm diameter showing variations in the internal structure.

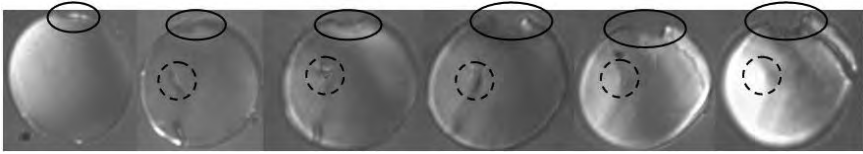
and an ultramicrotome is used to obtain thickness of around one micron for optical microscopy and down to 50 nm for transmission electron microscopy. For the examination of fibres the specimens are usually embedded in a resin which is then presented to the glass or diamond knife and successive slices cut. The knife advances at a controlled rate with respect to the specimen so that successive sections of the fibre are cut. These sections fall onto water from which they are recovered for examination. Figure 2.9 shows an example of successive slices of a PET fibre after fatigue at a temperature above its glass transition temperature. The fibre has been cut normal to the fibre axis direction and the successive slices reveal an initial fracture initiated at the surface and then the appearance of an internal crack which does not exit at the surface. Finally a large part of the surface can be seen to have been separated from the fibre (Le Clerc *et al.*, 2007).

2.4.2 Infrared spectroscopy

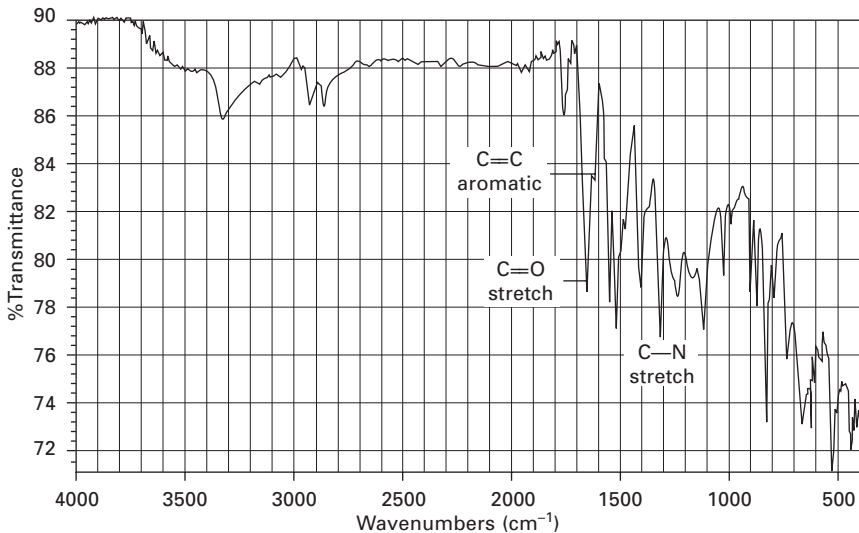
Electromagnetic radiation in the infrared region (2500–15 000 nm) can excite the molecules on the fibre surface to a higher energy state. The absorption is quantised; the molecule absorbs selected frequencies determined by its chemical structure and the existence of bonds that provide an electrical dipole (Pavia *et al.*, 1979).

Figure 2.10 shows an infrared spectrum for an aramid fibre, Kevlar[®]. The major peaks of the spectrum are identified. The location of these peaks is associated with the different modes of bond deformations – stretch, bend, twist, rock, scissor (shear), wag. It is customary in infrared spectroscopy to use wavenumbers $\bar{\nu}$, instead of wavelengths, λ . The relationship between wavenumber (cm^{-1}) and wavelength (cm) is

$$\bar{\nu} = \lambda^{-1} \quad 2.9$$



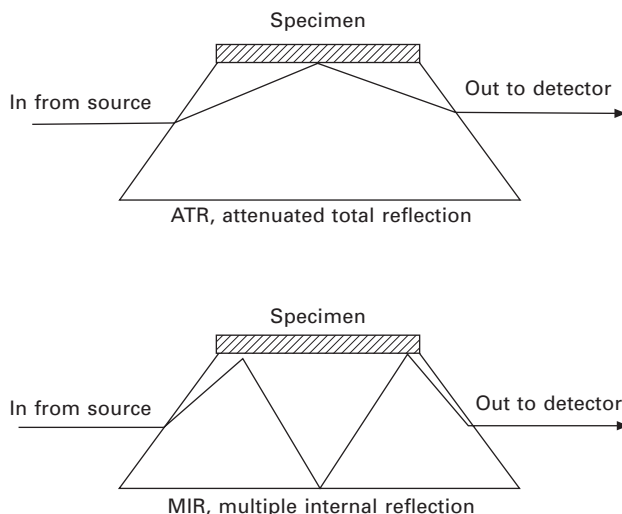
2.9 A sequence of sections obtained by ultramicrotoming of a PET which has been subjected to fatigue loading at a temperature above its glass transition temperature (T_g). Damage can be seen to have been initiated at the surface but also an internal crack which has not broken through to the surface can be seen.



2.10 Infrared spectrum of an aramid fibre.

For example, in the spectrum in Fig. 2.10 there is a peak at 1641 cm^{-1} due to the stretch of the carbonyl ($\text{C}=\text{O}$) group, a peak at 1305 cm^{-1} due to the amine ($\text{C}-\text{N}$) stretch, and a peak at 1612 cm^{-1} due to the ‘breathing’ of the aromatic ring (Pavia *et al.*, 1979). As the location of each of the peaks is a function of the molecular environment, the exact locations are impossible to predict but fall within narrowly defined regions.

Most fibres are too thick to allow for the transmission of infrared radiation so different techniques are generally used to collect spectra. The two major techniques used are attenuated total reflection (ATR) and multiple internal reflection (MIR), illustrated in Fig. 2.11. In each case the fibres are mounted on the surface of a crystal, usually KBr, and the infrared beam glances off the surface of the fibre, where it is then collected and analysed. The glancing limits the depth of analysis to a few micrometres.



2.11 Internal reflection in infrared spectroscopy.

2.4.3 Raman spectroscopy

The interaction of light with matter is usually elastic Rayleigh scattering. This means that it is scattered possessing the same energy and frequency. However, a very small proportion, less than one-thousandth of the incident light, interacts with the matter. This is the Raman effect. With this type of interaction the incident light, having a certain energy proportional to its frequency, interacts with the electric dipole of a molecule, or part of a molecule. The effect is to raise the electronic energy level of the molecule to a virtual state which then immediately, in less than 10^{-4} seconds, relaxes into a vibrational excited state. In doing so light is emitted with an energy and frequency which are characteristic of the molecular species as the vibrational energy of the molecular species depends on its structure and environment. Raman spectroscopy uses monochromatic laser light so that the exciting frequency and wavelength of the light are known exactly. The Raman shift $\bar{\nu}$ in wavenumbers (cm^{-1}) is given by the difference between the initial and final vibrational states:

$$\bar{\nu} = \frac{1}{I_{\text{incident}}} - \frac{1}{I_{\text{scattered}}} \quad 2.10$$

In equation 2.10, $\bar{\nu}$ is the wavenumber shift and λ is the wavelength of the light.

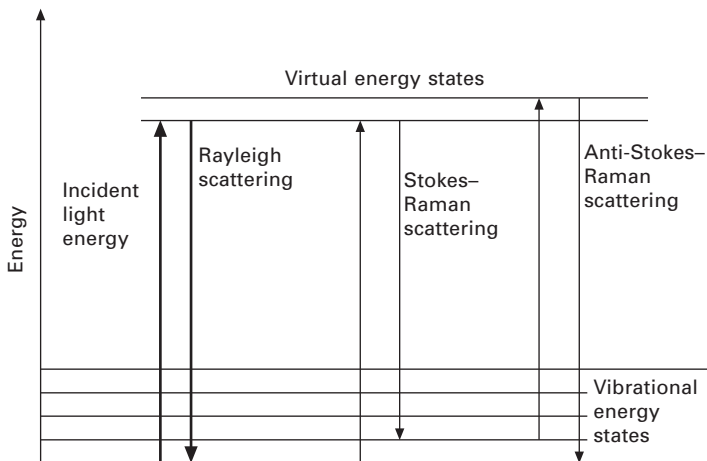
Most of this interaction raises the electronic level from the ground level and when the excited state relaxes it does so to one of the vibrational energy states which exists for the molecule. This is Stokes–Raman scattering, as

shown in Fig. 2.12. In some cases, however, the incident light encounters the molecular species which is already in a raised energy state so that it is raised to a higher virtual state only to relax to the ground state at the temperature of the material, as illustrated in Fig. 2.12. This is known as anti-Stokes–Raman scattering and it is weaker than Stokes–Raman scattering. Both types of scattering give the same frequency information and the ratio of the two types of scattering depends on the temperature of the material. The spectra for both Stokes and anti-Stokes scattering using laser light polarised parallel and perpendicular to the fibre axis are shown in Fig. 2.13 for a polyamide 66 specimen.

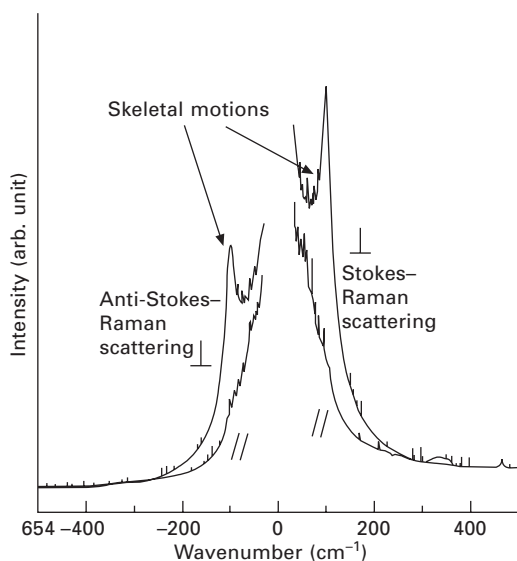
For the study of fibres the exciting incident light is concentrated using a light microscope to a spot size of around $1.5\text{ }\mu\text{m}$ for the micro-Raman measurements in backscattering configuration. The excitation power is kept to a few milliwatts/ mm^2 measured on the sample, in order to avoid inducing any thermal effects in the fibre structure.

Depending on the frequencies investigated in the Raman spectrum, different parts of a macromolecular structure can be investigated. Low wavenumbers ($\sim 100\text{ cm}^{-1}$) reveal information on macromolecular skeletal movements and the amorphous and crystalline domains in the fibre whereas higher wavenumbers ($\sim 1600\text{ cm}^{-1}$) can be used to investigate particular molecular species or bonds.

A comparison of Raman scattering obtained from fibres drawn to different extents shows clearly the rise of peaks at certain frequencies which can therefore be associated with crystalline or amorphous regions and in



2.12 A small fraction of incident light interacts with the specimen and molecular species are raised to higher energy states before falling back to characteristic energy levels. This is exploited in Raman spectroscopy.



2.13 Raman scattering from a polyamide 66 fibre.

some cases, such as PET, the transformation of *gauche* to *trans*-molecular conformations, aiding crystallinity (Colomban *et al.*, 2006).

A shift in a peak can be interpreted as showing a varying stress state in the fibre. As the various molecular entities react very much like mechanical resonators, an applied tensile stress will stretch the bond and result in a shift towards lower frequencies. A compressive stress produces a shift in the opposite direction. Figure 2.14 shows how scanning across a 24 mm diameter polyamide 66 fibre reveals an decrease in wavenumber and therefore a fall in frequency towards the centre of the fibre. This directly demonstrates that the surface of the fibre was in compression, with respect to its core, owing to the effects of cooling during manufacture.

By adding a tensile testing device Raman spectroscopy can be used *in situ* to examine changes in the molecular morphology of fibres during loading and in this way can act as a strain measurement device at the molecular level.

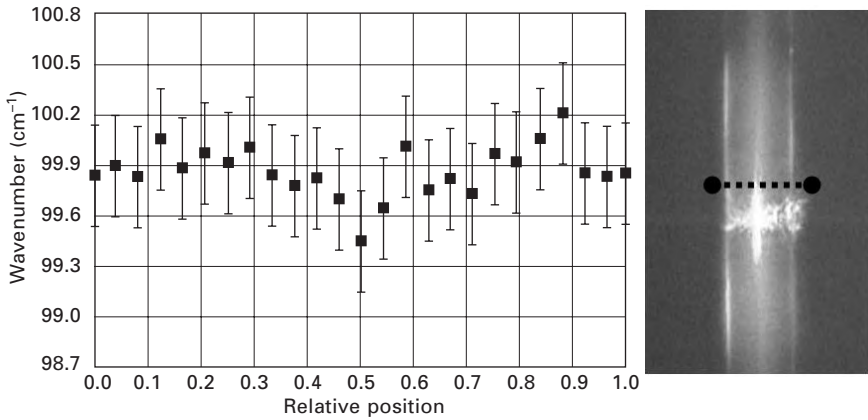
The strain-induced Raman wavenumber shift ($\Delta\nu$) is linearly related to the tensile strain ($\Delta\epsilon$) so that we can write the empirical relationship (Colomban, 2002):

$$\Delta\nu = S^\epsilon \Delta\epsilon \quad 2.11$$

and the above equation is microscopically analogous to Hooke's law

$$\Delta\sigma = E \Delta\epsilon \quad 2.12$$

Young's modulus, E , is indeed the result, at the macroscopic scale, of the force constant of the various chemical bonds. Consequently we can write:



2.14 Variation of wavenumber across a polyamide 66 fibre of 24 μm diameter, revealing that the surface is in compression compared with the core.

$$\mathbf{D}\nu = \mathbf{S}^e \mathbf{\epsilon} \mathbf{D}\epsilon = \mathbf{S}^e \mathbf{\epsilon} \mathbf{D}\sigma \quad 2.13$$

In this way it can be seen from eq. (2.13) that a wavenumber shift due to an imposed macroscopic strain can be used to calculate internal stress states of molecular species. This also means that a wavenumber shift can be used to calculate internal stress states, as has been shown for Fig. 2.11.

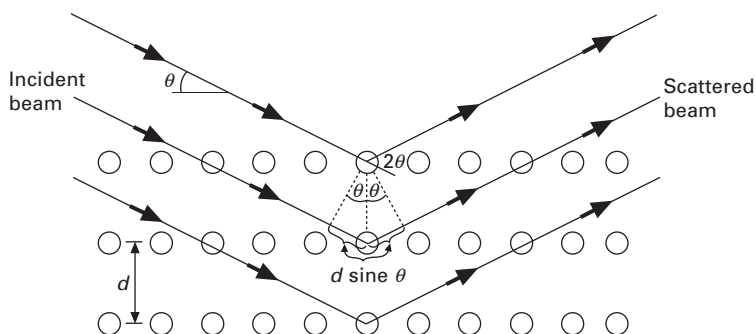
2.4.4 X-ray diffraction

Diffraction is the scattering of waves from a regular array with distances between layers in the structure similar to the lengths of the incident waveform. At particular angles the waves scattered from different rows or planes in the material are in phase and interfere constructively. At other angles the interference leads to a reduction in intensity so that peaks in intensity are observed at angles for which the scattered waves are in phase. Figure 2.15 shows this concept, which is known as Bragg diffraction and leads to the relationship:

$$2d \sin \theta = n\lambda \quad 2.14$$

This relationship can be understood by considering the geometry of the layers shown in Fig. 2.15, noting that the incident angle is θ , the regular distance between the structural layers is d , and the wavelength of the incident rays is λ .

Wide angle X-ray scattering (WAXS) is the most commonly used technique in which the specimen is impinged by a monochromatic X-ray beam at angles usually in the range 3–45° as shown in Fig. 2.15. The diffraction pattern generated allows the chemical or phase composition of materials to



2.15 Bragg diffraction showing how, at certain angles, constructive interference occurs from crystalline phases and this can be used to determine their dimension.

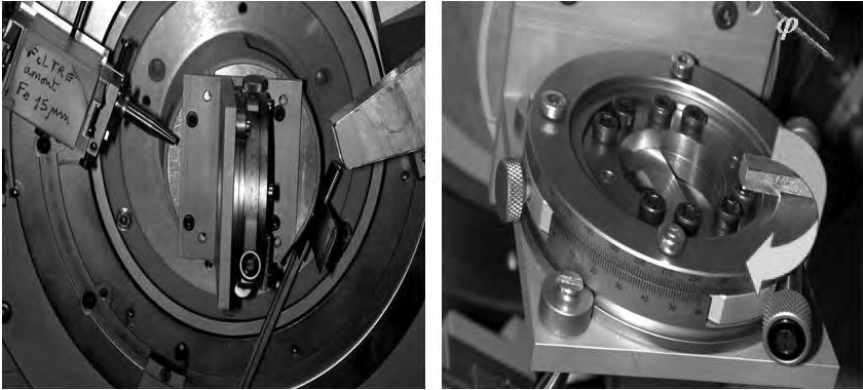
be determined and dimensions of the atomic structure to be obtained. Small angle X-ray scattering (SAXS), with scattering angles less than 1° allows larger structural units to be measured such as the long periods in polymers. The SAXS technique requires particular equipment because of the small angular separation of the direct beam, which is very intense and the scattered beam. This means large specimens to detect distances in the range of 0.5 to 10 m and high quality optical systems are necessary.

In order to obtain sufficiently intense patterns it is usual to irradiate a bundle of fibres although the intense radiation from a synchrotron source allows single fibres to be analysed. The specimens are placed in a goniometer, as shown in Fig. 2.16, which allows the specimen to be rotated through an angle ϕ . This is shown schematically in Fig. 2.17. The anisotropy of the fibres is revealed by variation of peak intensities as the specimen is rotated, as shown in Fig. 2.18 obtained with polyamide 66 fibres. The spectra obtained can then be analysed and deconvoluted by various techniques so as to reveal the presence of crystalline and amorphous phases, as illustrated in Fig. 2.19, taken from a study on polyamide 66 fibres (Marcellan *et al.*, 2006).

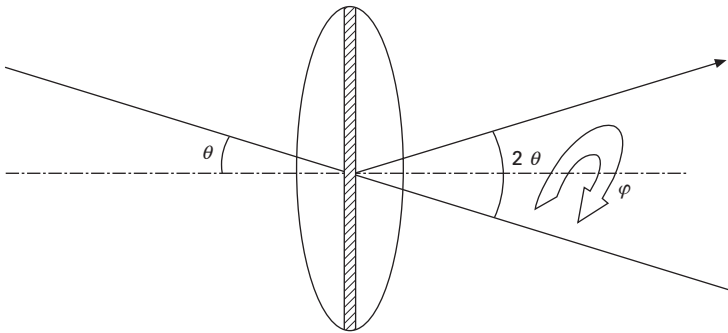
2.4.5 Transmission electron microscopy

The structure of fibres down to atomic dimensions can be investigated using transmission electron microscopy. Particular difficulties with the technique are electron beam damage to organic fibres and thin foil specimen preparation of brittle fibres.

In the case of polyamide, polyester and acrylic fibres, it is possible to obtain good quality ultrathin sections by the use of an ultra-microtome equipped with a diamond knife. The fibres are embedded in a suitable resin before sectioning, and thicknesses of around 80 nm can be obtained. Better results are obtained if the fibre is coated with a layer of gold (by a sputtering technique



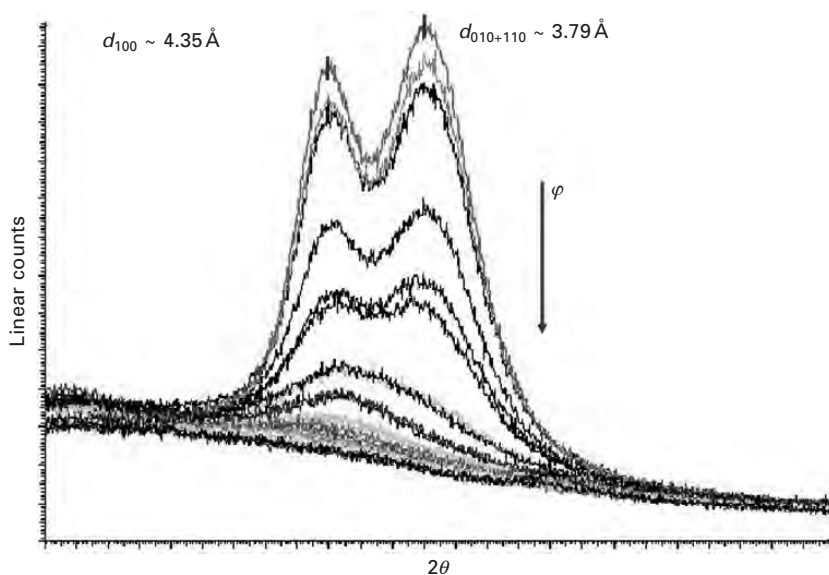
2.16 The goniometer allows the fibre to be rotated in position with respect to the incident X-rays.



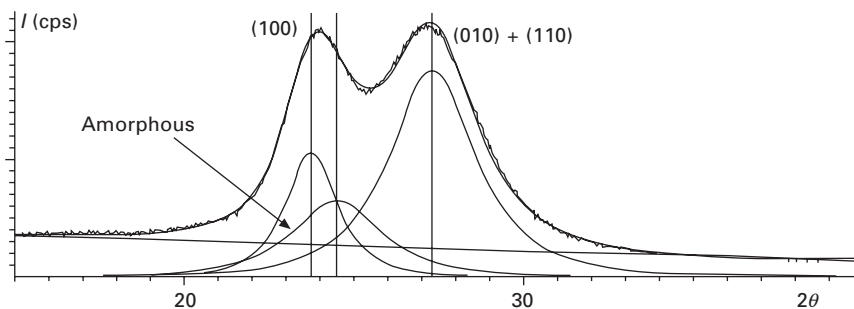
2.17 The fibre is held in the X-ray beam and can be rotated to reveal differences due to orientation of the molecular morphology.

analogous to the one used for SEM investigation) prior to embedding; in such circumstances good adhesion is achieved between fibre and resin, and sectioning is easier.

Ultramicrotomy is also easy in the case of preoxidised poly(acrylonitrile) (PAN) fibres or cellulosic fibres (previously treated by a chemical 'fixative' mixture). At temperatures below the glass transition temperature (T_g) polyolefin fibres and even amorphous fibres can be sectioned. This can involve cooling the specimens with liquid nitrogen. In the case of carbon fibres, longitudinal sections are obtained without too much difficulty. For glass or SiC fibres and sectioning normal to the longitudinal axis of carbon fibres, ultrathin sectioning is not feasible. In these cases another thinning technique such as the one developed by Berger and Bunsell (1993) must be used. In this technique the fibres are stuck with an adhesive onto a small rigid sheet of metal hollowed at its centre as shown in Fig. 2.20a,b. The fibres must be



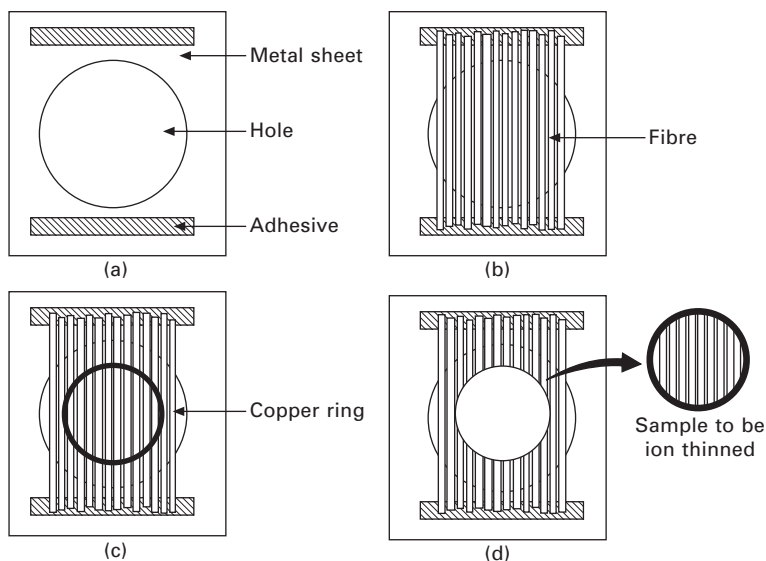
2.18 The X-ray peaks vary as the fibre is rotated due to the anisotropy of the molecular structure.



2.19 The X-ray spectrum can be analysed so as to obtain information about the different crystalline and amorphous phases making up its structure.

carefully aligned and in contact with each other to avoid the thinning of the fibres' edges. A 3 mm external diameter copper or molybdenum ring held with tweezers is put on a drop of epoxy glue and stuck on the fibres, as shown in Fig. 2.20c. The ring is then separated from the mount by cutting the outside fibres; see Fig. 2.20d.

In the case of fibres with diameters of less than 50 μm the prepared sample can be directly thinned by argon ion milling. However, for fibres of larger diameters, the thinning would take too long, would induce thinning artefacts and the copper ring would be thinned before the fibres. Prior to this ionic



2.20 Preparation of thin specimens of brittle fibres for examination by transmission electron microscopy.

thinning, the thickness of the sample must be reduced down to 50 μm by mechanical grinding. To ensure the cohesion of the material only the centre of the sample is ground down to 20 μm by concave grinding. The sample is then put in the ion thinning chamber of a 'Gatan dual ion mill 600'. Two guns ionise an argon gas and deliver two focused beams of Ar^+ accelerated by 6 kW with a 1 mA gun current. The beams sputter the centre of the sample with an incident angle of 15° on each side of the disc. This attack angle of 15° corresponds to a better sputtering rate without ion implantation or surface structuring. After around 20 hours the attack angle is then reduced to 7° for a final period of one hour to obtain larger thin regions for observation. To obtain finer results, particularly with multiphase structures, finer angles of attack can be used; however, the time to achieve the required thickness increases. In this way tapered sections of the fibres can be obtained and the microstructure studied in the thinnest parts.

Selected area electron diffraction (SAED) is possible on ultrathin sections of single fibres, if necessary by the use of low dose techniques (in the case of electron sensitive polymeric organic fibres). This technique can be used to determine crystallinity and crystal orientation. For the study of polymeric fibres dark field imaging is an even more useful technique than SAED. Dark field microscopy is an imaging technique using some particular spots of the diffraction patterns; in such circumstances, crystalline domains (crystallites) appear as bright spots on a black or dark background. The amorphous zones as well as the crystallites which are oriented out of the Bragg position are not

seen. By such a method, the sizes and shapes of crystallites and the mode of segregation between crystalline and amorphous zones can be determined.

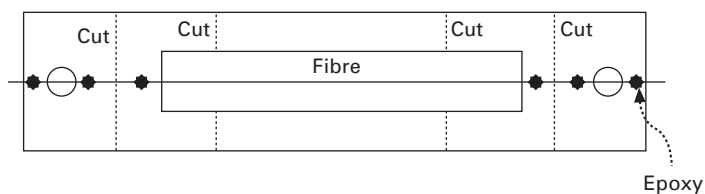
2.5 Mechanical characterisation

2.5.1 Mounting specimens for testing

The mounting of single fibres in a testing machine should be done with great care. The fibre should be secured without crushing it; misalignment of the fibre in the grips of the testing machine can lead to bending stresses in the fibre at the grips and premature failure. In both cases errors in measurement of the fibre properties are the result.

Some types of fibre specimens can be mounted directly in the testing machine, with a minimum of care, such as protecting them in the grips with tabs of adhesive paper or tape. However, for brittle fibres it is the common practice to mount the individual fibres on stiff paper or cardboard tabs in preparation for testing, as illustrated in Fig. 2.21. The tab has a central cut-out that matches the desired gauge length for the test. A gauge length of 25 mm is commonly used. A drop of quick drying epoxy or similar adhesive anchors the fibre in place. The ends of the frame can be cut away, along the dotted line, before the test and the part of the fibre passing over the two holes can be kept for subsequent examination. The tab is gripped in the jaws of the testing machine and, just prior to testing, cuts are made from each side to the central cut-out, ensuring that only the fibre is loaded during the test.

In the case of brittle fibres, such as carbon or ceramic fibres, failure results in the fragmentation of the specimen and this can be a problem if the initial fracture surface needs to be observed. In this case, tests specifically designed to identify the initial fracture surface are carried out. The whole specimen is immersed in liquid paraffin so that the energy released at break is dampened by the surrounding medium. Alternatively, carefully coating the fibre with grease can also give more controlled fractures. In the latter cases, it is advisable to use these techniques only to obtain the initial fracture



2.21 The fibre is glued onto a card frame which is then placed in the grips before being cut away in the centre to allow the fibre to be tested.

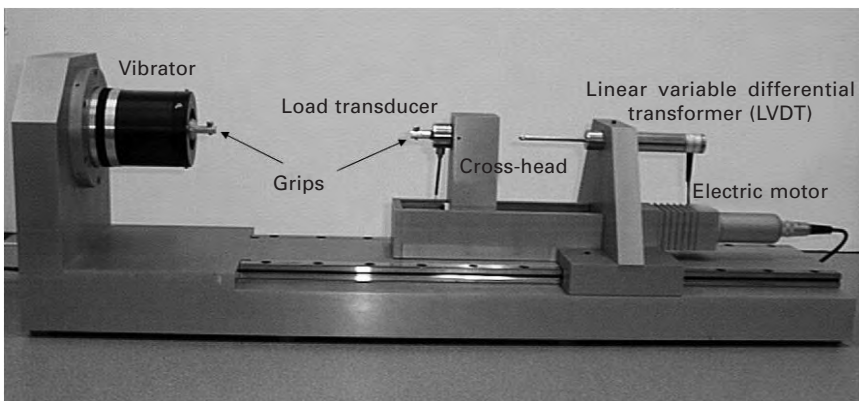
morphologies as the loads recorded at failure may be altered by the medium around the fibre.

2.5.2 Mechanical testing procedure

The testing of single fine fibres in tension, relaxation, creep and fatigue has been extensively studied by Bunsell *et al.* (1971) using a 'Universal Fibre Testing Machine'. These tests have revealed a distinctive tensile fatigue process in thermoplastic fibres (Oudet and Bunsell, 1987; Marcellan *et al.*, 2003; Herrera Ramirez *et al.*, 2006; Le Clerc *et al.*, 2007) and have also been used to characterise aramid (Lafitte and Bunsell, 1985) and carbon fibres (Bunsell and Somer, 1992) in fatigue. The mechanical part of the machine is shown in Fig. 2.22 It is controlled electronically and permits high loading precision. It can be used for:

- Tensile tests: by setting a constant deformation rate.
- Relaxation or creep tests: by either setting a constant deformation or a constant load. The addition of a furnace has allowed evaluation of the creep of ceramic fibres at high temperatures.
- Fatigue tests: setting the required mean load and amplitude of vibrations controls hence the lower and upper limits of imposed load. The limiting loads are therefore symmetrical about the mean load.

The fibre is held horizontally between two clamps. One clamp is connected to a movable cross-head which also contains the load cells. A displacement transducer records the total movement of the cross-head during a test. The steady load is measured by one load cell and the cyclic loads, during a fatigue experiment, are monitored by a piezoelectric transducer. The loading conditions of interest are pre-selected and an electronic servo system controls



2.22 The mechanical part of a universal fibre testing machine.

the distance between the jaws and so regulates the load conditions on the fibre.

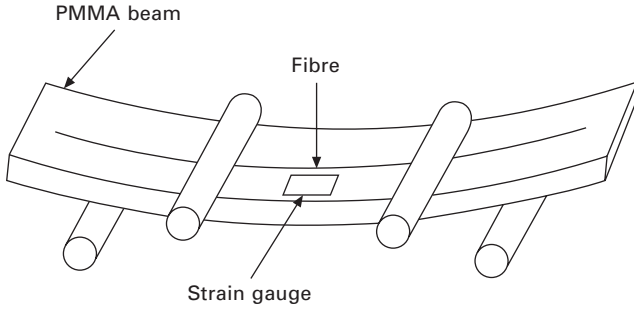
Tensile tests

The tensile strength and modulus of a fibre are determined by straining the fibre in tension until failure. The strain rate used is often adjusted to result in fibre failure after approximately 20 seconds. The load–elongation curve for the fibre is recorded by a computer or on a curve plotter. The fibre's failure stress and strain, yield strength and strain, initial modulus, secant modulus, and work of rupture may be determined from this experiment.

In the absence of sufficiently sensitive equipment pultruded specimens of unidirectional composite composed of strands of the fibres embedded in a matrix can be tested to failure in tension. The failure load of the specimen is divided by the number of fibres in the strand. This technique is often used and can give slightly different results from those found with single fibres. This is because the strength of fibres varies, on average, with gauge length and often an average fibre diameter is used which in practice is rounded down to the nearest micron. This leads to an overestimation of fibre properties as the calculation of strength and elastic modulus requires dividing breaking load by the square of the diameter and even a reduction of a fraction of a micron on the real diameter can result in a significant increase in the calculated values.

2.5.3 Raman spectroscopy and four-point bending technique to determine compressive properties

A four-point bending beam method has been used to determine the compressive properties of several different types of fibres. Raman spectroscopy has been used to follow the molecular deformation of aramid, carbon and alumina–zirconia fibres (Young *et al.*, 1996). Certain Raman bands have been found to be sensitive to the applied stress and shift to lower frequencies under tension and to higher frequencies on compression (Vlattsos and Galiotis, 1994; Andrews *et al.*, 1996). This behaviour reflects the deformation of the polymer backbones or other atomic bonds in response to the applied stress. It is necessary to know the Raman band shift as a function of stress of the fibre so that a stress–strain curve can be determined (Colomban, 2002). The fibre to be studied is placed on the surface of a rectangular poly(methyl methacrylate) (PMMA) beam, as shown in Fig. 2.23, and covered with a solution of PMMA/chloroform to seal it into the surface. The beam is loaded in four-point bending and the strain gauges measure the strain of the concave surface. The shift in frequency of the Raman peak then gives a direct measurement of the strain of the fibre at the molecular level.



2.23 Compression behaviour of a fibre can be obtained by embedding the fibre in the surface of a PMMA beam which is then bent so as to put the surface in compression.

2.5.4 Elastica loop test

The loop test was originally described for obtaining the tensile properties of fibres (Sinclair, 1950; Jones and Johnson, 1971). However, in this type of test, most organic fibres will yield in compression by developing shear bands known as kink bands. The fibre is twisted into a loop and the size of the loop reduced until the first kink band is observed at the bottom of the loop where the radius of curvature is smallest. Figure 2.24 shows the experimental arrangement as described by Fidan *et al.* (1993). The test is usually conducted under a microscope with the fibre specimen positioned in an oil film, to aid observation, between two glass slides or in a scanning electron microscope. When the first kink band is observed the loop size is recorded and the radius of curvature measured or calculated so as to obtain the critical compressive strain ϵ_{cr} which is given by

$$\epsilon_{cr} = d/2R_m \quad 2.15$$

where d is the fibre diameter and R_m is the minimum radius of curvature at the location where the first kink band is seen. R_m can be obtained either graphically from the minimum radius of the circle drawn into the loop or from equations of elastica:

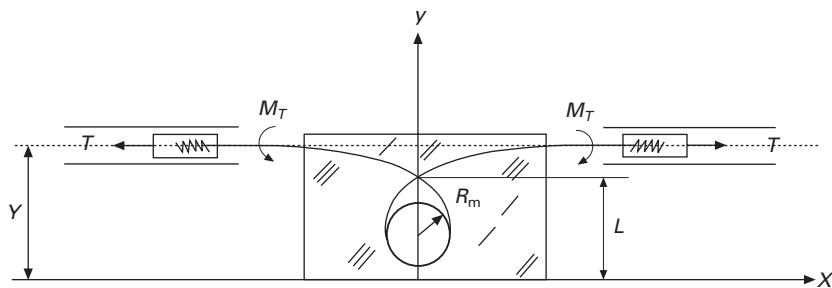
$$R_m = Y/4, \quad Y^2 = 4EI/T \quad 2.16$$

where Y is the distance from the arm to the bottom of the loop, E the elastic modulus, I the moment of inertia and T the tension in the fibre.

2.6 High temperature characterisation

2.6.1 Loop test for high temperature evaluation

A variation of the above loop test has been developed and used, above all, for evaluating the time-dependent properties of ceramic fibres at very high



2.24 Elastica loop test. The fibre is twisted into a loop which is reduced in diameter until the plastic deformation or failure occurs.

temperatures. Although such fibres are elastic and brittle at temperatures, usually up to 1000 °C, they are candidates as reinforcements in composite structures which will experience much higher temperatures and creep has been shown to be a major factor to be considered (DiCarlo, 1977; Morscher and DiCarlo, 1992). An evaluation of the resistance to creep is given by the bend stress relaxation observed when the fibres are bent into a loop and then heated to high temperatures. If the fibre remains elastic it returns to its original straight form after such a test whereas if relaxation occurs a residual curvature is seen. The curvature allows the creep resistance of different fibres to be classed.

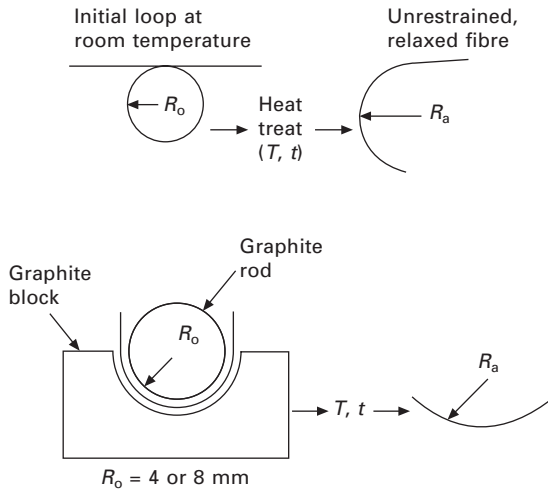
An initial elastic bend strain is imposed on the fibre by forming it into a loop, or by placing it between cylindrical male and female ceramic forms, as shown in Fig. 2.25. The initial stress, σ_0 and strain ϵ_0 vary within the fibre by the relations $\sigma_0 = E\epsilon_0$ and $\epsilon_0 = z/R_0$, where E is the Young's modulus of the fibre, z is the distance from the fibre axis in the plane of the loop ($0 \leq z \leq d/2$) and R_0 is the loop radius. The fibre is then heated, usually in an inert atmosphere and if relaxation occurs, on cooling back to room temperature a residual curvature, R_a , will be observed that will decrease with time. If no relaxation has occurred and the fibre has behaved in a purely elastic fashion, R_a will be infinity. A relaxation factor, m , has been defined as:

$$m(t, T) = 1 - R_0/R_a \quad 2.17$$

where $m = 0$ if the fibre is completely relaxed and $m = 1$ if no relaxation occurs and the fibre has remained perfectly elastic during the test. This technique has proved to be a valuable method for classifying the creep resistance of many ceramic fibres from whiskers of only 1 mm diameter to large diameter ceramic fibres.

2.6.2 High temperature tensile and creep tests

The universal fibre tester, with a furnace is positioned between the jaws, described above for tensile and fatigue tests, can also be used for evaluating



2.25 The loop test imposes an initial elastic bending strain on the fibre or the specimen can be constrained in a bent configuration. After heating the residual curvature is a measure of creep at high temperature.

high performance fibres at very high temperatures. The fibres are mounted on a card frame, as in Fig. 2.21, but with a specimen length of around 30 cm as the tubular furnace is placed between the jaws which remain outside. The jaws remain at room temperature. Placing the jaws inside the furnace is an attractive concept but is rarely feasible as the fibre has to be cemented to the jaws, which increases the test time enormously, and all too often there is a reaction at high temperatures between the cement and the fibre which causes failure in the grips. Hot jaws have, however, been used in the evaluation of carbon fibres (Tanabe *et al.*, 1991). Fibres which need to be protected from oxidation are tested in flowing argon which excludes oxygen from the hot zone. For a creep test the machine is instructed to maintain a constant applied load on the fibre. Relaxation of the fibre will cause the load to fall but the servo system continually increases the distance between the jaws so as to maintain the load constant. This technique is preferable to simply applying a weight to the fibre as the difficulty of avoiding applying an overload or a shock on mounting the fibre is considerable and can easily break the filament. In addition a simple weight applied to the specimen is very sensitive to vibrations.

The creep rate of the fibre can vary as a function of temperature, above a certain threshold temperature, so that it is necessary to determine the temperature profile within the furnace and to conduct tests at different temperatures so as to identify the threshold point. The part of the fibre which is above the threshold temperature contributes to the overall creep

but by varying amounts owing to the variation of the temperature. The creep behaviour observed at different temperatures above the threshold can be used simply to determine the overall creep rate by a step model in which the fibre is considered to be at constant temperature over the summation of short lengths, each at a constant temperature, within the hot zone. The overall creep observed is the sum of all the contributions. The technique has been used to determine the creep behaviour of many different types of ceramic fibres (Simon and Bunsell, 1984; Lavaste *et al.*, 1995).

A particularly efficient way of testing electrically conducting fibres, such as carbon fibres, at high temperature involves passing an electric current through the fibre under vacuum. The temperature of the fibre can be raised to above 2000 °C whilst the grips holding the fibre remain at room temperature. This is because of the small mass of the fibre compared with that of the grips. Tensile and creep data can be obtained in this way without the complication of a varying temperature profile within a furnace (Sauder *et al.*, 2004).

2.7 Conclusions

Fibres are very fine forms of matter and require special techniques for their characterisation. Although used since time immemorial, it is only in the past few decades that controlled tests and observations of fibres have become possible. However, special mechanical testing machines, coupled with techniques such as scanning electron microscopy and Raman spectroscopy, now allow extremely detailed knowledge to be obtained about the relationships between structure and properties enabling fibres to be optimised and their full potential to be better understood.

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Tensile properties of cotton fibers

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Abstract: This chapter deals with the tensile behavior of cotton fiber with the main objective being to point out some of the key challenges facing understanding the tensile failure of cotton fiber and characterization techniques. Specific subjects discussed include: fiber tensile behaviour during cotton handling (e.g. harvesting through weaving), the effect of fiber tensile strength on yarn strength, effects of fiber structure on tensile strength, tensile testing techniques, and external factors influencing the characterization of cotton tensile behavior. These subjects are discussed using examples of medium-staple and extra-long staple (ELS) cottons.

Key words: cotton, harvesting, stripper, spindle, roller ginning, saw ginning, opening, cleaning, carding, drawing, spinning, weaving, knitting, sizing, tenacity, elongation, elastic limit, toughness, flexibility, sonic modulus, viscosity.

3.1 Introduction

The merits of using cotton fibers to make textile products are realized by billions of users of cotton textile products representing all cultures, ages, genders, and religions. They are also realized by the numerous products in which cotton fibers are used from garments to sheets, towels to surgical drapes, and disposable to biodegradable products. This realization is a historical one. Indeed, the popularity of cotton in everyday life cannot be separated from the historical evolution of cotton discovery and cotton utilization. Although it is difficult for historians to trace cotton to its true origin, there is a general agreement that the use of cotton goes back beyond recorded history. As early as 3000 BC cotton was grown and used in the Indus Valley of India. Ancient Egypt and China also spun and wove it. In the Middle Ages, the Arabs brought the cotton plant from India and Spain. They called it '*qutun*', from which comes the name cotton. The most established historical fact about cotton is that the popular status that cotton enjoys today is fully credited to the USA. It is in the USA that Eli Whitney invented the cotton gin in 1793, which forever revolutionized the whole concept of cotton production. By 1800 cotton production had increased from about 3000 bales a year to 73000. History also tells us that cotton was the main reason behind the American

Civil War initiated by the slavery in the South needed for cotton picking. Shortly after Eli Whitney invented the cotton gin, planters turned from tobacco and rice to cotton. To supply the growing demands of mill owners in England and New England, they imported more slaves to work the cotton fields. The number soared from about 700 000 in 1793 to nearly 4 000 000 by 1860. Plantations sprang up in Alabama, Mississippi, Missouri, Louisiana, Tennessee, and Arkansas. By spreading slavery in the South, cotton helped bring on the American Civil War.

Today, millions of cotton bales are produced around the world and over 25 million tonnes of cotton fibers are expected to be used by spinning mills in 2009, providing a solid evidence of the robustness of this important fiber in the face of the dynamic changes in the global market and the introduction of numerous new fibers. One of the main reasons for the everlasting use of cotton fiber is the diversity of products that can be made from it. Indeed, a single bale of cotton weighing about 230 kg can produce over 700 men's dress shirts, over 1200 men's T-shirts, over 400 men's sport shirts, over 6000 women's knitted briefs (pants), about 22 000 women's handkerchiefs, over 4000 mid-calf socks, over 200 jeans, approximately 240 bed sheets, over 600 terry bath towels, over 1200 pillowcases, over 2000 boxer shorts, or over 3000 diapers (nappies).

The diversity of cotton products is primarily a result of the unique combination of physical properties that this fiber enjoys. The intimacy associated with apparels makes cotton fiber an excellent candidate for most apparel products, particularly underwear, men's shirts, and pants (trousers). Cotton fibers respond to this intimacy with an uncontested feel driven by unique surface characteristics. Cotton is a natural product which is made up, at all levels, of oriented fibrils. In a blind test, one can easily identify the surface of the fiber by touching or handling the fibrous assembly. More interestingly, touching and feeling of cotton fibers result in an instantaneous acquaintance and comfortable bonding, much like touching a soft human skin. When moisture management is required, the porous structure of cotton fibers makes it an excellent candidate for applications involving a combination of moisture absorption and wicking. Finally, when durability is a primary concern, cotton fibers will stand to prove excellent durability against both chemical and mechanical effects.

The main focus of this chapter is on the tensile failure of cotton fiber, or the reaction of the fiber to an axial force that can ultimately cause fiber breakage. The tensile behavior of a cotton fiber is manifested in all aspects of cotton handling such as cotton ginning, spinning, weaving, and knitting. Indeed, from the field to end use, cotton fibers are subjected to numerous external axial stresses. This is primarily due to the fact that a cotton fiber is essentially a seed coated hair with an aspect ratio (length–diameter ratio) in the order of thousands. This pronounced length gives the fiber its linear

nature and results in a length-bias handling of the fiber. Indeed, one can describe the conversion of cotton fiber into a textile end product by a series of mechanical actions that are primarily applied along the fiber axis.

3.2 Fiber tensile behavior during cotton handling

Supplying cotton fibers of high strength and elongation is one of the major concerns of all cotton producers. Even more important is to produce cotton with consistent and uniform levels of fiber strength and elongation. These goals require careful handling of cotton throughout the different stages of processing from fiber to yarn.

During harvesting, fibers are either pulled manually from the cotton boll, which involves a straightforward manual tensile force, or mechanically using stripper harvesting or spindle harvesting. In the context of cotton quality, the main difference between the two types of mechanical harvesting is the yield and the amount of trash and dust produced by each method. Typically, stripper harvesting gathers much more trash with the seed cotton than spindle picking. As a worst-case scenario, approximately 1000 kg of seed cotton are harvested using a brush stripper to obtain a 230 kg of cotton lint (the typical weight of a cotton bale). In spindle harvesting, only 650 kg of seed cotton is typically harvested to obtain a 230 kg bale of lint. This substantial difference between the two types of harvesting is reflected in the amount of trash picked with the seed cotton with each method. In the context of fiber tensile strength, the two methods involve pulling the fibers from the cotton boll that has to be achieved very carefully and at appropriate rates to minimize fiber damage. Indeed, it is at the harvesting stage that the onset of fiber damage is observed as a result of pulling fibers beyond their elastic limits.

During ginning, cotton fibers must be separated from the seed. This process must protect both the seed and the fiber from damage as each represents an important commodity. Typically, the production of a 230 kg bale is associated with the production of about 340 kg of cotton seed. This separation process is achieved via shearing and pulling the fibers from the seed. The central fear of damaging fibers during this process is fiber breakage or shortening the fiber by breaking it into fiber fragments. This typically occurs to a small extent during pulling fibers from the seeds and to a larger extent during the additional lint cleaning applied on the fibers to upgrade their quality for classing purposes. Two type of mechanical ginning are commonly used: (1) saw ginning used for medium and short-staple cottons (e.g. Upland-like cotton) and (2) roller ginning used for long and extra-long staple (ELS) cottons (e.g. American Pima cotton). In general, saw ginning is a harsher approach to ginning but it yields larger quantities of ginned cotton.¹ Upon ginning, fibers undergo a lint-cleaning process to remove trash particles and

seedcoat fragments. This mechanical process is often responsible for a great deal of fiber tensile failure as indicated by the excessive short fiber content of lint-cleaned cotton fibers.

In the spinning mill, cotton fibers are subjected to a variety of external stresses.² During processing they are typically stretched, pulled, compressed, twisted, bent, and rubbed against each other and against metallic surfaces. These stresses are a result of the need to manipulate fibers in many different ways so that a yarn of desirable characteristics can be produced. During opening and cleaning, cotton fibers are subjected to tensile forces imposed by the effects of metallic wires and needles of the rotating opening and cleaning rolls. In the carding zone, fibers are being pulled in the carding zone to provide straightening and removal of neps, which are small knots or clusters of entangled fibers, often including seed-coat fragments. During drafting, the fiber strand is reduced to the desired thickness. This is achieved using drafting rollers to reduce the mass of fiber flow by sliding fibers against each other in an accelerated fashion so that only the desired number of fibers per strand cross-section is delivered. A snap shot at the drafting zone (between two pairs of rolls) during fiber flow can easily reveal three possible fiber positions: some fiber ends may be caught at the nip of the front roller, other ends may be caught at the nip of the back roller, and some may be caught by the nips of both the front and the back rolls. These three positions are associated with different degrees of pulling along the fiber axis. The third position is the most serious one as it can result in significant stretching and breaking of the fibers. Finally, the consolidation of fibers into a yarn in the spinning process requires some degree of tension to allow uniform twist insertion. The highest tension is witnessed in ring spinning, particularly in the zone between the nip of the front roll and the twist insertion point (the spinning triangle). Almost all end breakage in ring spinning occurs in this zone as a result of fiber tensile failure or some fibers failing to withstand the spinning tension applied along the fiber axis.

During weaving, cotton yarns must withstand the axial stresses applied on them during weaving preparation (winding, warping, and sizing) and during the weaving process itself. Of particular interest is the sizing process in which yarns are coated by a size material to improve their abrasion resistance and reduce hairiness. This process must be optimized to avoid loss of yarn elasticity as it often comes at the expense of yarn elongation, which can deteriorate significantly as a result of the application of size material. This loss of elasticity can be compensated for by using cotton fibers of high elongation. In the knitting process, yarn tensile strength is not as important as that in the weaving process. However, yarn elasticity is a key aspect in providing sufficient pliability and easy bending of the yarn around the different knitting components.

3.3 The contribution of cotton fiber tensile behavior to yarn strength

One of the main reasons for testing fiber tensile strength is to evaluate its impact on yarn strength. In a yarn structure, fibers contribute to strength through two factors: inter-fiber friction, and fiber tensile strength.³ These two effects were demonstrated in the classic analysis by Hearle *et al.*⁴ in which theoretical interpretation of the strength–twist relationship was presented. This analysis yielded the equation of yarn to fiber modulus ratio:

$$\frac{\text{Yarn modulus}}{\text{Fiber modulus}} = \frac{E_y}{E_f} = \cos^2 \alpha [1 - k \operatorname{cosec} \alpha]$$

where E_y is yarn modulus, E_f is fiber modulus, α is the twist angle, and k is expressed by the following equation:

$$k = \frac{\sqrt{2}}{3L_f} \frac{E_f a Q}{\mu}$$

where L is the fiber length, a is the fiber radius, Q is the migration period, and μ is the coefficient of friction.

The above equation indicates that there are two basic components determining yarn strength–twist relationship for a given fiber strength: the $\cos^2 \alpha$ (which is the only component needed in case of continuous filament yarn) and the $(1 - k \operatorname{cosec} \alpha)$ required to adjust for spun yarn structure. The former component yields a decreasing strength with the increase in twist angle and the latter yields an increasing strength with twist, which is largely dependent on the k value (higher k values will result in lower strength ratios). Fiber properties reflected in this equation are fiber length and fiber fineness (or fiber diameter). As fiber length increases, k decreases, leading to higher yarn strength; as the fiber diameter increases, k increases, leading to lower yarn strength. The equation also indicates that the increase in friction results in a decrease in k value, or an increase in yarn strength. This point is highly questionable as friction is typically associated with a trade-off between too slippery and too tight contact from preparation to fiber consolidation.

3.4 Cotton fiber structure

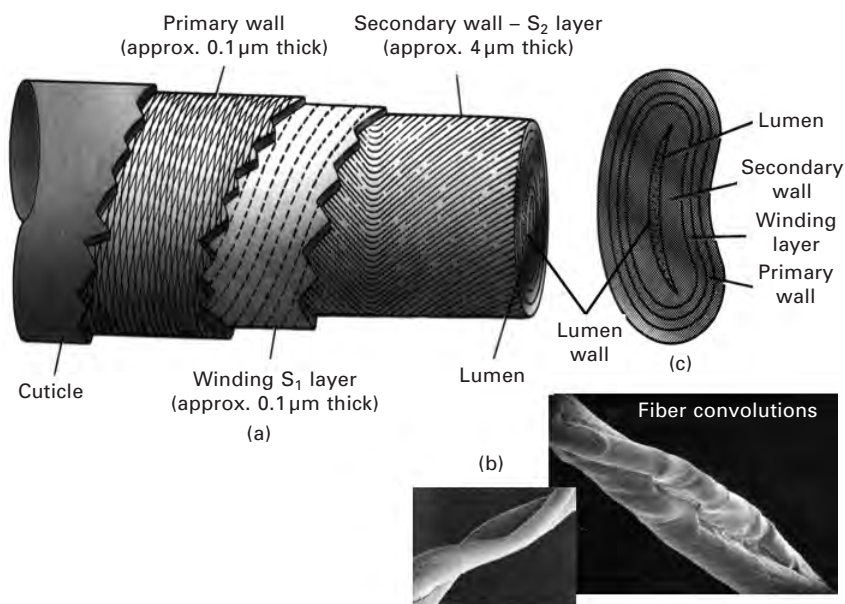
Any study of the tensile behavior of cotton fibers should be based on an understanding fiber structure. This subject has been covered in many previous publications. In this section, it will be revisited in the context of the tensile behavior of the fibers.

In general, the cotton fiber is described as being composed mostly of the long-chain carbohydrate molecule cellulose (the sugar of cell walls).

After ginning, the fiber typically contains 95% cellulose.^{5–9} This, in all cell walls, is in small, crystalline microfibrils that are arranged in multilayer structures.⁹ However, cotton is not entirely crystalline as a certain fraction of cellulose molecules do not necessarily associate into crystallites but rather into disordered or amorphous regions. A combination of crystalline and amorphous regions typically provides a combination of good durability and good absorption characteristics, respectively. Most cotton fiber long cellulose molecules run parallel to the fiber axis.

The structure of a mature cotton fiber may be viewed as consisting of six main parts.^{5–7, 10} As shown in Fig. 3.1, the first is the cuticle, or the ‘skin’ of the fiber. This waxy and smooth layer contains pectin and proteinaceous materials. The presence of this layer has a significant impact on the smoothness and the handling of cotton during processing. It also influences the inter-fiber friction in a bundle-strength test or in the yarn. However, the fact that it is a very thin layer, only a few molecules thick, makes it vulnerable to environmental effects, such as those due to heavy rain and high temperature. Upon scouring, this layer is removed, which explains the increase in fiber/fiber friction and the increase in the strength of a scoured fiber bundle.¹⁰

The second part is the primary wall. This is the original thin cell wall and is mainly cellulose made up of a network of fine fibrils. The primary wall may be visualized as a sheath of spiraling fibrils where each layer spirals 20–30° to the fiber axis. The thickness of this wall correlates with the extent of maturity of cotton fiber, the thicker the wall the higher the maturity. In



3.1 Structural features of cotton fiber.

general, highly mature cotton fibers exhibit higher tensile strengths than immature fibers, everything else being equal. The primary wall makes for a well-organized system of continuous very fine capillaries. These fine capillaries 'rob' liquids from coarse capillaries; an action that contributes greatly to a cotton material's wipe-dry performance.

The third part is called the winding layer or S1 layer. This is the first layer of secondary thickening and it differs in structure from either the primary wall or the remainder of the secondary wall. It is an open 'netting' pattern of fibrils that are aligned at 40–70° angles to the fiber axis.⁵ The fourth part is the secondary wall, which consists of concentric layers of pure cellulose constituting the main portion of the cotton fiber (also called the S2 layer). Secondary wall fibrils close to the primary wall lie at an approximate 45° angle to the fiber axis, while this orientation becomes aligned more closely with the fibrillar axis as the fiber core, or lumen, is approached.⁹ The thickness of the secondary wall, from primary wall to lumen, determines fineness, and defines the fiber's maturity. Fibers with no secondary wall development exhibit no individual fiber integrity and can exist only in clumps. Development of the secondary wall provides the fiber with rigidity and body.⁹

The fifth part is the lumen wall. This wall separates the secondary wall from the lumen, which represents the sixth part. It appears to be more resistant to certain reagents than the secondary wall layers. The lumen is a hollow canal that runs the length of the fiber. It is filled with living protoplasts during the growth period. After the fiber matures and the boll opens, the protoplast dries up and the lumen will naturally collapse.

Geometrically, the cotton fiber has a twisted-ribbon shape along the length of the fiber and a kidney-shaped cross-section. These features are shown in Fig. 3.1(b) and (c), respectively. This convoluted surface of the cotton fiber is largely attributed to the lumen collapse. Typically, there are about 20–40 twists/cm. Scanning electron microscopy (SEM) analysis^{5,6,9} reveals additional distinct features: ribbon-like shape, with nearly elliptical transverse surface, folds on the surface of fibers, and reversals of fibrillar texture prominent on the fiber surface. The latter is a result of the fact that the direction of the spiral around the axis of the fiber reverses at random intervals along the length of the fiber.

The convoluted arrangement of the fibrils has a great impact on the tensile behavior of cotton fibers, particularly fiber elongation. It is those fibrils that sense the axial stretch of a fiber and before the fiber reaches its breaking elongation, they have to be aligned and elongated along the fiber axis, overcoming their angle of inclination. In addition, the reversals indicated above represent zones of variations in breaking strength;⁹ the areas immediately adjacent to either side of a reversal are more likely to break under stress than other areas in the fiber.

Another important structural feature of cotton fiber is that it is tapered on one end and fibrillated on the other end where it is joined to the seed. In a fiber bundle strength test, this tapered end could have a significant effect as it could result in a differential friction along its length. Friction at the root was found to be higher than that at the tip of the fiber.⁷ The difference was found to be significant, particularly at low levels of normal loads. The presence of differential friction was supported by two experimental observations:⁷ (i) a lower convolution angle at the tip than at the root of the fiber (the difference in this angle was as high as 175% within a fiber) and (ii) a lower surface area at the tip than at the root.

Cotton fiber molecular orientation is commonly examined using the birefringence index, $\Delta n = n_p - n_\lambda$, in which n_p is the refractive index with the polarized light oscillating in a plane parallel to the fiber axis, and n_λ is the refractive index with the light oscillating in a plane perpendicular to the fiber axis. Some studies⁸ have revealed that a typical birefringence index of cotton may range from 0.04 to 0.09. Within a given fiber, this index increases from the tip (0–0.008) to the root of the fiber (above 0.04). This change in molecular orientation from the tip to the fiber root suggests that when a fiber is broken during processing at some points along its length, we could have two fiber fragments with substantially different tensile behaviors, with the fragment closer to the fiber root being stronger than the one near the fiber tip.

3.5 The tensile behavior of cotton fiber

As indicated earlier, the tensile behavior of a cotton fiber can be determined by testing the reaction of a cotton fiber to an axial force. However, this reaction is affected by many factors that should be taken into consideration in order to obtain reliable values of fiber strength. These factors are as follows:

- the testing technique;
- sampling method and sample size;
- strength characterization;
- the condition of the fiber prior to testing.

3.5.1 The testing technique

Over the years, developing reliable testing techniques of cotton fiber strength has been a challenging task. This has been a result of the many parameters involved in tensile testing including: sample type (single or bundle), the type of clamps to be used, the mechanism of fiber loading, the rate of loading to be applied, the gauge length to be used, and the presence of fiber impurities. Earlier systems of testing include:¹¹ the Pressley and the Stelometer tester.

These two systems are still used in some countries and they are considered as references to some of the more recent instruments. The Pressley tests a flat bundle of parallel fibers clamped between a set of jaws at a zero gauge length or a 3.175 mm length. The mass of the broken bundle is measured to determine fiber tenacity. The Stelometer uses the Pressley jaws and a pendulum principle to apply a constant rate of loading on the cotton fiber being held at a 3.175 mm gauge length (ASTM D-1445).

In the early 1980s, a rapid fiber testing system called the high volume instrument (HVI) was developed. This system is now produced by Uster® Technologies to test a number of key fiber properties including: fiber length, Micronaire, color, trash area, and fiber strength (ASTM D-4605). A bundle consisting of thousands of fibers is picked randomly from a larger specimen using a special picking comb. It is then combed and brushed to form a fiber beard of parallel and straight fibers. The beard is then held between two clamps at a gauge length of 3.175 mm. The movement of the clamp results in stretching the fiber beard progressively until breakage occurs at such a point the breaking force and the breaking elongation can be recorded. It is important to note that the HVI is designed to test cotton fibers in their raw form.

Another strength tester, which was used mainly in research environments is the Mantis® single fiber tensile tester.^{12,13} This tester is capable of testing single fiber strength using a pair of clamps that grip the fiber ends. An electro-optical system is used for measuring the projected ribbon width of each fiber prior to breaking. Some studies^{13,14} showed that the bundle strength of cotton, measured by the HVI or the Stelometer, can be accurately predicted by knowledge of the force to break individual fibers and their electro-optically measured ribbon width as measured by Mantis. Single fiber strength testing can also be performed using the familiar Instron tester at different gauge length and elongation rates.

One of the key issues regarding the testing technique of cotton fiber strength is the differences in merits and utilizations between bundle and single fiber strength. In practice, cotton fibers flow in groups or bundles during processing. This results in mutual fiber assistance with the longer fibers carrying the shorter ones by virtue of inter-fiber contact. When fibers are converted into a yarn, the role of fiber assistance becomes even greater, particularly when the yarn is subjected to tensile stresses. These points make the evaluation of bundle strength more beneficial to most practical applications. As a result, today's cotton strength data are entirely reported for fiber bundles. The merits of using single-fiber strength testing primarily stem from the need to understand the fundamental nature of cotton fiber strength and the relationship between fiber strength and various fiber structural parameters. As indicated earlier, some studies revealed that there are good correlations between single-fiber strength and bundle strength of cotton fibers.¹⁴ The

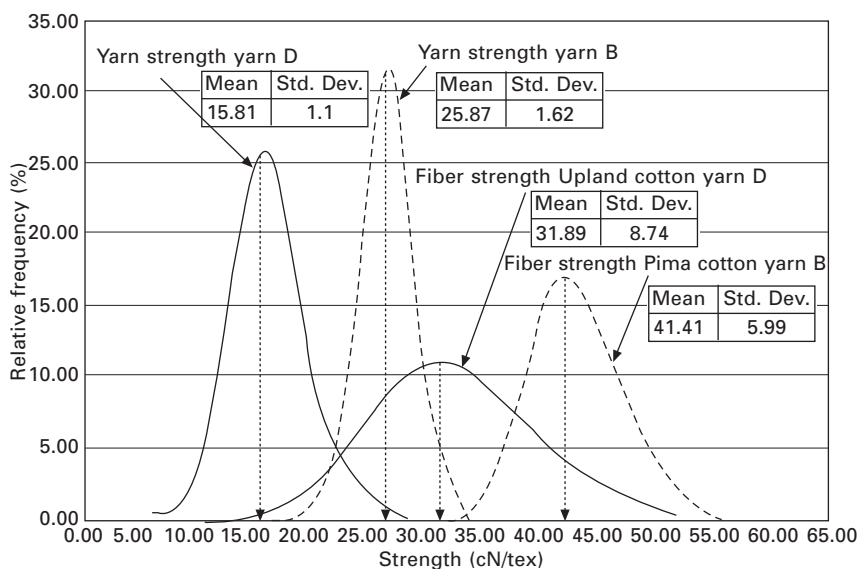
point that was not clear in these studies was the extent of variability in fiber strength. This means that correlations between strength values obtained by these two methods were based on the average values of fiber strength. This point will be illustrated further later in this chapter.

Another critical issue related to the testing techniques of cotton fiber strength is sample preparation. In practice, cotton fibers are not typically straight; they exhibit natural crimp and they are often bent at one or both ends, forming fiber hooks. In addition, raw cotton may contain a great deal of impurities and fiber neps. As a result, the fiber specimen should be combed and brushed carefully prior to testing. The question of how much combing and brushing should be applied on a fiber specimen can be critical since different levels of combing and brushing could result in different values of fiber strength and elongation. Another effect of the combing and brushing process is that it may create a systematic length and fineness bias in the fiber specimen. In the HVI system, this effect is minimized through picking a random specimen at random points along the length of different fibers and maintaining a consistent application of combing and brushing on each specimen to ensure equal preparatory conditions.

3.5.2 Sampling method and sample size for cotton tensile testing

Unlike synthetic fibers, cotton fibers exhibit a great deal of variability in all properties. Indeed, no two fibers are alike even if they are obtained from the same boll of cotton. They will be different in diameter, length, maturity, and strength. To make matters additionally complex, a single cotton fiber often exhibits variation in dimensional and strength characteristics along its length. The fiber is thicker at the bottom end and tapered toward the other end; the convolution pattern also tends to change along the fiber; and as indicated earlier, the molecular orientation of a fiber varies from the bottom end to the tapered end of the fiber. These different sources of variability are often reflected in the values of fiber strength for both medium-staple and extra-long staple cottons, particularly in single-fiber tensile testing. This point is illustrated in Fig. 3.2 in which the frequency distributions of yarn strength for two yarns, one made from Upland cotton and the other made from Pima cotton, and the corresponding distributions of single fiber strength of fibers extracted from the yarns are shown.

The selection of an appropriate sample of cotton fibers faces many challenges. Typically, the fiber population will be a cotton bale that may weigh about 220 kg if produced in the USA, or 170–233 kg, depending on the country in which it is produced. The volumetric density of a cotton bale may range from 360 to 450 kg/m³. This means that the number of fibers in a single bale is in the order of many millions, depending on fiber fineness and



3.2 Frequency distributions of fiber and yarn strength.

fiber length. Since testing the tensile behavior of cotton fibers may be made using a single fiber or a small bundle of fibers, one can imagine the critical need for a fiber sample that can truly reflect this huge population of fibers. This point represents a true challenge to obtaining a reliable characterization of cotton fiber properties that may never be completely overcome. Instead, attempts are made to select samples as representative as possible. In the USA, cotton fiber samples are normally taken immediately after ginning for the purpose of cotton classing. Spinning mills may take cotton samples from the different sides of a cotton bale and from different bales of the bale laydown (prior to opening and cleaning).

Another aspect of sampling is sample size, or how many fibers or fiber bundles to be tested in order to obtain reliable results. This is largely a statistical issue. Theoretically, the minimum sample size, n , is obtained from the following general equation:

$$n = \frac{\hat{\sigma}^2 z^2}{\hat{d}^2}$$

where σ is the standard deviation, z is a statistic indicating the degree of confidence or significance of results, and d is the magnitude of the anticipated or desired difference between the sample average and the population average.

The above equation indicates that the minimum sample size required will primarily vary in accordance to the variability of the population from which the sample is withdrawn. Based on our experience in the field, the

variability in fiber strength within a single bale fiber population can indeed be very large depending on the cotton variety being tested, the harvesting method, the ginning method, and the storage and retrieval environment of cotton. Owing to these multiple effects, values of coefficient of variation (CV%) cotton fiber tenacity within a single bale can be as low as 12% and as high as 40%. For bundle strength tests, lower CV% values are expected. This explains why most commercial cotton fiber strength testers use bundles instead of single fibers. Figure 3.2 clearly demonstrates the effect of high population variability on the standard deviation of single fiber strength for both Upland and Pima cottons.

3.5.3 Strength characterization

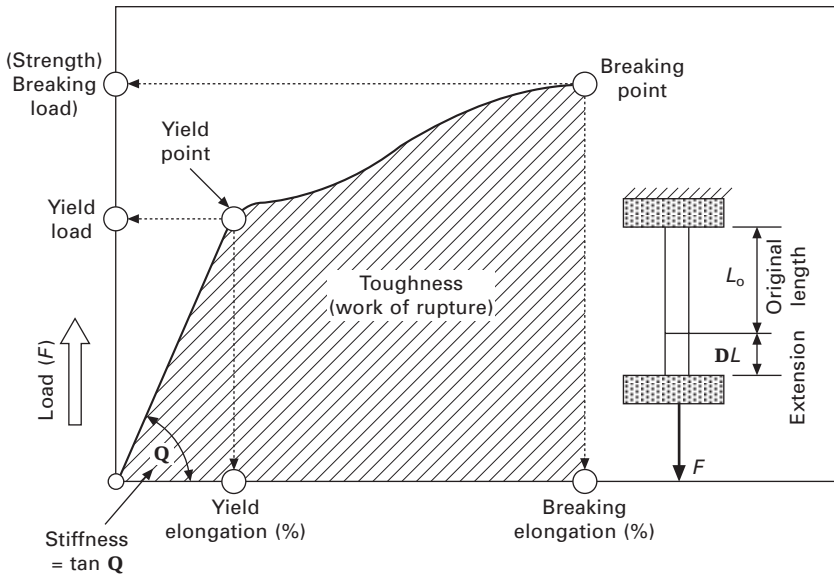
Fiber strength and extensibility are measured during a tensile test in which an elongation is applied to a specimen of a single fiber or a bundle of fibers in its axial direction. This elongation causes a tension to be developed as the specimen is extended in length. The tension continues to build up until the specimen breaks. The load at which the specimen breaks provides a measure of fiber strength, and the corresponding increase in specimen length provides a measure of the breaking elongation. This process can be described by the load–elongation curve, which is a plot that describes the process of stretching a specimen of a length L_0 by a force F to a length DL in excess of its original length until breakage finally occurs. An example of this curve is shown in Fig. 3.3. With the aid of this curve, we can determine many useful strength parameters. Typical single-fiber tenacity–strain curves of different types of cotton fibers are illustrated in Fig. 3.4. Some of the parameters described by the tenacity–strain curve are described below.

Tenacity or specific stress of cotton fibers

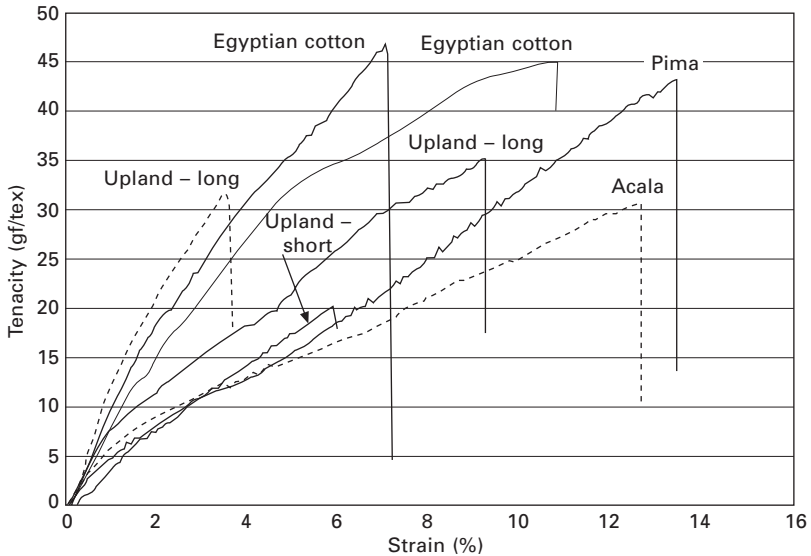
This is the breaking load divided by the linear density of fiber expressed in cN/tex:

$$\text{Tenacity} = \frac{F_{\text{at break}}}{\text{linear density (tex)}} \text{ cN/tex}$$

Table 3.1 provides some useful conversion constants of fiber tenacity. Criteria associated with typical values of Upland cotton fiber strength are reported for beard strength in Table 3.2. Values of tenacity of single cotton fibers can be as low as 12 gf/tex (117.7 mN/tex) and as high as 45 gf/tex (441 mN/tex). This wide range is attributed to the differences in structural parameters of different cotton types. One of the key parameters that has a significant effect on fiber strength is the degree of molecular orientation as measured by X-ray diffraction.¹⁵ In the case of cotton, this parameter largely reflects the angle



3.3 The load–elongation curve.



3.4 Typical tenacity–strain curves of different cotton types.

of the fibrils spiraling around the fiber axis; the smaller this angle, the higher the degree of orientation. Typical values of this angle for ELS cotton fibers (e.g. American Supima and Egyptian Giza) may range from 20° to 30° , and for Upland-like medium staple cotton fibers may range from 40° to 45° .

Table 3.1 Important conversion formula of strength (for cotton)

Tenacity	Conversion
g _t /tex	= 0.981 cN/tex = breaking length in kilometers = 9 $\frac{1}{\text{N}}$ tenacity in g/denier = 0.671 $\frac{1}{\text{N}}$ breaking stress in 10 ⁸ dyn/cm ² = 0.658 $\frac{1}{\text{N}}$ breaking stress in kg/mm ² = 0.457 $\frac{1}{\text{N}}$ breaking stress in 10 ³ lb/in ²

Table 3.2 Strength-related parameters of Upland cotton fibers

Criteria	Breaking strength (cN/tex)	Breaking elongation (%)
Very low	< 21	< 5.0
Low	22–24	5.1–5.8
Medium	25–27	5.9–6.7
High	28–30	6.8–7.6
Very high	>30	>7.6

Another parameter that influences fiber strength is the molecular weight. The authors of this chapter performed viscosity analyses (TAPPI T230 om-89) as a measure of this parameter. Table 3.3 and Fig. 3.5 show typical dynamic viscosity values (centipoises) and corresponding fiber strength values for different cotton types. Note that the ELS cottons have higher viscosity values than the medium or short-staple cottons. Comparison of different cotton types reveals that fiber strength is positively correlated to fiber maturity and fiber length, and negatively correlated to Micronaire and fiber elongation. Some of these correlations are listed in Table 3.4.

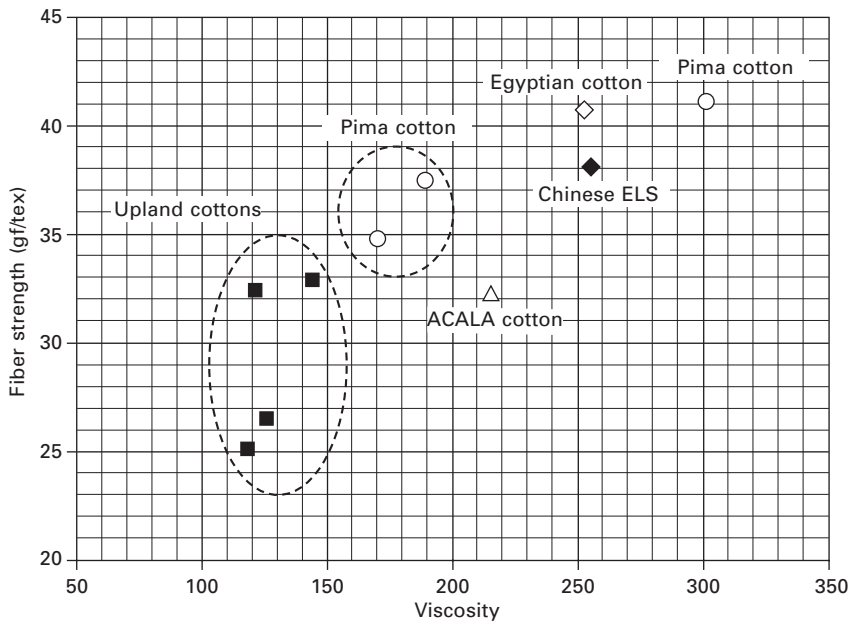
Breaking elongation, stiffness, and elasticity of cotton fibers

Breaking elongation is the percent elongation at break, $100(\mathbf{DL}_{\text{break}}/L_o)$. Criteria associated with typical values of cotton fiber bundle elongation are reported in Table 3.2. The benefits of considering the breaking elongation of fibers are well known. In general, fiber elongation partially reflects the extent of ease of stretching a fiber; a fiber of high breaking elongation with respect to breaking strength is known to be easily stretchable under small loads. In practice, fibers exhibiting this behavior are generally known to be highly flexible.

The elongation behavior of a single cotton fiber can be quite complex owing to the multiplicity of factors influencing it. A cotton fiber typically exhibits natural crimp, which is important for fibers to be adhered together during processing.^{1,2,10,16} As a result, the initial loading of the fiber in single-fiber strength tests can be fully consumed in removing this crimp, leading to initial over-estimation of the inherent fiber elongation. In bundle strength

Table 3.3 Strength and viscosity values of different fiber types

Fiber	Viscosity (centipoise)	HVI strength (gf/tex)
Upland cotton-S1	118.3	25.1
Upland cotton-S2	121.5	32.4
Upland cotton-S3	125.5	26.5
Upland cotton-S4	144.0	32.9
Pima-S5	170.0	34.8
Pima-S6	189.0	37.5
ACALA-S7	215.3	32.3
GIZA70-S8	252.7	40.7
CHINESE-S9	255.3	38.1
PIMA-S10	301.0	41.1



3.5 The load–elongation curve.

Table 3.4 Correlation coefficients between strength parameters and other fiber properties

	Strength	Elongation
Strength	1.000	
Elongation	−0.712	1.000
Micronaire	−0.399	0.275
Maturity ratio	0.694	−0.371
HVI length	0.924	−0.524
Viscosity	0.850	−0.400

tests, cotton fibers are combed prior to testing, which assists in removing a great deal of crimp but can also elongate the fibers unnecessarily. Again, this can lead to an error in testing the actual elongation value of the fiber bundle. These factors can be multiplied by the high sensitivity of the fiber to testing parameters such as the degree of tightness of fiber clamps and the initial momentum imposed by the movement of the clamp to apply the load during testing.

A key point related to breaking elongation is that it directly influences the breaking extension of yarn. In other words, fibers of high breaking elongation will result in yarns of high breaking extension. This point is critical on the ground that cotton yarns must be sized (coated by a surface film to reduce hairiness and improve abrasion resistance) before it can be woven. As pointed out earlier, size treatment will inevitably reduce yarn elongation, particularly when size add-on is increased. This leads to undesirable stiffness in the yarn during weaving. It is important, therefore, to use fibers of high elongation so that yarns made from these fibers will likely to survive the reduction in elongation upon sizing.

Fiber stiffness is commonly determined by the initial slope of the tenacity–strain curve ($\tan \theta$ in Fig. 3.3). This is commonly known as the initial modulus; the higher the initial modulus, the stiffer the fiber and the lower the initial modulus, the more flexible the fiber. With cotton fibers, this initial slope is typically difficult to determine as it is highly sensitive to the initial crimp in the fiber and the extent of bundle fiber preparation. Typical values of cotton fiber initial modulus may range from 350 to 800 gf/tex (3431–7843 mN/tex).

Fiber elasticity is commonly determined by the extent of recovery of a fiber after being subjected to loading and unloading action; an elastic fiber is one that exhibits full dimensional recovery upon removal of loading. A cotton fiber exhibits only partial elasticity, meaning it will likely suffer some permanent elongation upon loading and then unloading. In a tenacity–strain curve of elastic material, the curve zone between the origin and the yield point is largely straight (see Fig. 3.3). For cotton fibers this linear behavior does not fully exist because of the reasons mentioned earlier. Given the fact that cotton fibers are subjected to repeated loading and unloading during processing and in end use applications, the recovery of the fiber from small loading is often of great concern. This leads us to another related parameter, which is the elastic recovery of fiber; or the percentage of recovery in fiber length upon removal of a certain loading level. Flax, which is a long vegetable fiber, typically recovers up to 80% of its length upon loading and unloading of stress reaching about 1 g/denier (88 mN/tex). By comparison, cotton fiber will only recover 50% of its length upon loading and unloading of the same stress. In progressive processing, this may result in stiffening of the cotton fiber as it flows from one stage of processing to another.

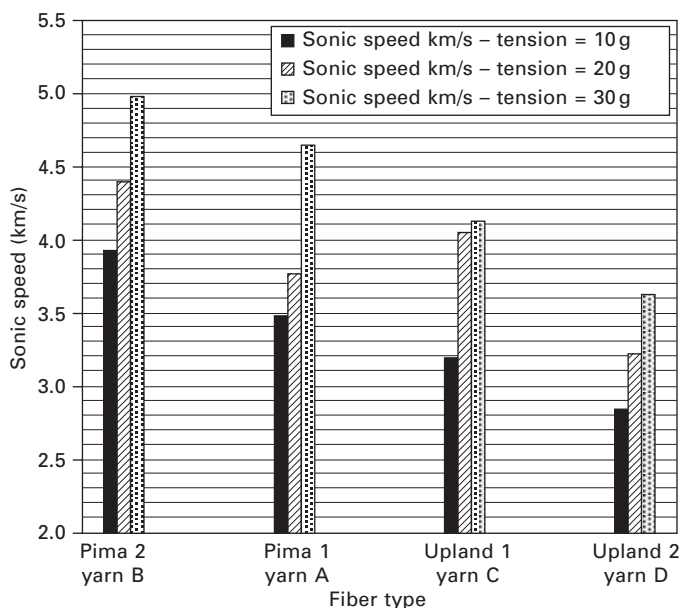
Dynamic strength behavior of cotton fibers

Cotton fibers are subject to dynamic stresses during processing in which repeated cyclic loading and unloading are applied to the fiber by the different mechanical actions. Indeed, one would expect fibers to be subjected to thousands of stretch–release cycles in the fiber-to-yarn conversion system by virtue of the different mechanical manipulations applied. Therefore, it is important to evaluate the resistance of fiber to dynamic stresses. The common parameter used for this evaluation is the ratio of the energy absorbed to the energy recovered when a fiber is stretched and then released.¹⁶ An indirect measure of this energy is the so-called fiber toughness estimated by the work done in stretching a fiber to the breaking point. This is obtained from the area under the load–elongation curve expressed in g_fcm . Specific work of rupture is an index of fiber toughness determined by the area under the specific stress–strain curve and expressed in g_f/tex . Typical values of cotton fiber toughness may range from 5 to 15 mN/tex . In general, cotton fiber toughness increases with water treatments that result in fiber swelling. Upon drying of fibers, the toughness decreases significantly.

The authors of this chapter conducted experiments using sonic modulus techniques to measure the speed of sound through cotton fibers, which is directly related to the dynamic modulus of fibers. This is not a common method for cotton fibers but it has been used for many synthetic fibers. In principle, the method is based on measuring the speed of sound as it goes through a fiber or yarn sample mounted under initial tension; the higher the speed of sound, the more oriented the structure. In these experiments, four yarns were produced; yarns A and B from Pima cotton, and yarns C and D from Upland cotton. All yarns were made on ring spinning of a 35s count and a twist level of 23 turns per 25 mm. This is to ensure approximately identical structures. Properties of these four yarns are listed in Table 3.5. Figure 3.6 shows the differences of sonic speed of the four yarns. As can be seen in this figure, yarns made from Pima cotton have higher sonic speeds than those made from Upland cottons, despite the similarity in yarn structure. These differences are reflected in yarn strength and elongation values as shown in Table 3.5.

Table 3.5 Yarn properties of four yarns made from Pima and Upland cottons

	Cone A	Cone B	Cone C	Cone D
Count (Ne)	35	35	35	35
Twist (TPI)	22.395	22.14	23	23.425
B-Force (kgf)	0.45	0.45	0.28	0.27
Elongation (%)	6.62	6.76	5.71	5.37
Tenacity (cN/tex)	26.06	25.87	16.49	15.81
B-Work (kgfcm)	0.69	0.69	0.41	0.38



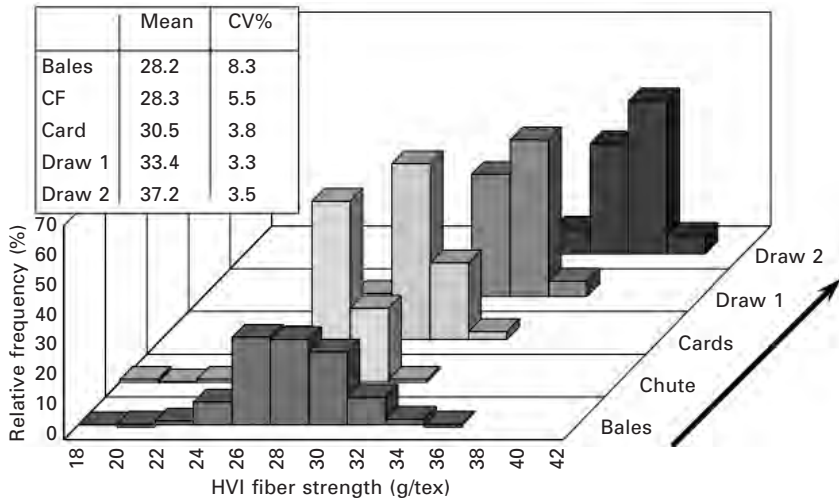
3.6 Sonic speed values for four yarn samples made from Pima and Upland cottons.

3.5.4 The condition of the fiber prior to testing

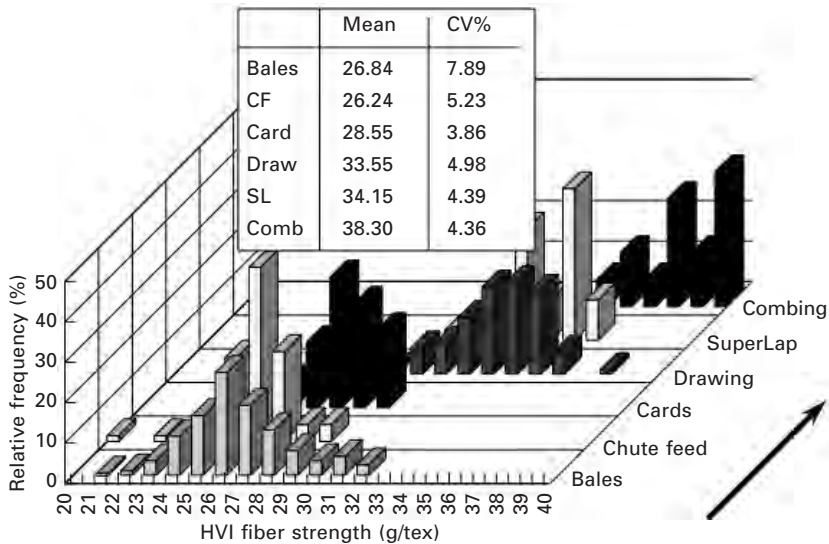
One of the critical aspects of tensile strength measurements is the condition of the sample prior to testing. In this regard, a number of factors should be considered including: mechanical history, sample preparation, relative humidity and temperature of the surrounding air, gauge length, rate of loading, and degree of impurities. The importance of these factors stems from the fact that each can have a significant effect on the value of cotton fiber strength.

Cotton fiber strength is commonly measured in the raw fiber form (prior to spinning). Measurements at this stage assist cotton growers and ginner in determining ways to improve fiber strength. They also assist spinners in selecting fibers suitable for the desired yarn and fabric characteristics, particularly when durability is of primary concern. From a characterization viewpoint, measuring fiber strength during processing (e.g. after opening and cleaning or upon combing) has not been a common practice. It is the opinion of the authors that such measurements can indeed be useful to evaluate the changes in the mechanical behavior of fiber as a result of mechanical stresses and other modifications that occur during processing. In an earlier study by Elmogahzy and Chewning,² fiber strength and elongation were measured after each stage of processing in the fiber-to-yarn conversion system. Measurements were made using the HVI system by following a bale laydown throughout the different stages of processing and taking corresponding consecutive

samples. Results of the levels of bundle fiber strength at different stages of processing for an open-end carded and ring-spun combed yarn processes are shown in Figs 3.7 and 3.8, respectively. As can be seen in these figures, bundle strength of fibers increases significantly particularly after drawing and



3.7 Distributions of HVI fiber strength in different processing stages (open-end carded-yarn process).



3.8 Distributions of fiber strength in different processing stages (ring-spun combed-yarn process).

combing. These increases are primarily due to the systematic bias introduced by the drawing and combing processes.

The drawing process produces a sample that consists of straight and parallel fibers at a much higher degree of orientation and alignment that can be made possible by the combing and brushing actions applied to a sample of raw cotton during HVI testing. The combing process removes short fibers, and results in a highly combed sliver that is virtually impurity free. In both processes, a great deal of the natural crimp of fibers is removed. As a result, the tendency for fiber strength increase should be highly expected. This type of analysis reveals two important points, one is technological and the other is testing-related. From a technological viewpoint, such measurements can be helpful to detect any abnormality occurring during processing including fiber damage or fiber brittleness. From a testing viewpoint, such measures raise an important question regarding the true value of bundle strength and how much combing and brushing should be applied to produce an inherently reliable value.

Another critical factor influencing fiber strength is humidity and moisture content. In general, moisture content can influence many fiber attributes. These include fiber dimensions, fiber strength, flexibility, and electrical resistance. In general, bone-dry cotton is likely to be harsh and brittle. Excessively wet cotton is likely to be 'clingly' and 'swelly'. The moisture regain of cotton under standard conditions should be in the range from 6.75 to 8.25%. The effect of moisture on cotton fiber strength is well recognized.^{17–20} A cotton fiber when wet is stronger than when it is dry. Some studies suggest that a 4% increase in fiber moisture may cause cotton strength to increase by more than 6 g/tex, other studies showed that a change in laboratory relative humidity of 3–5% would cause a change of 1 g/tex in measured fiber strength. It is important, therefore, to condition the cotton samples prior to strength testing (65% RH, 70° F, i.e. 21°C). The conditioning period may range from 24–72 hours to ensure that the sample has reached its equilibrium condition. In practice, a period of 24–72 hours is considered to be too long for many industrial processes and alternative drying conditions have been developed.

In many situations, production pressure and demand for quick information force violation of these standard periods. Some find it ironic that with instrumentation systems that can provide data within seconds, one must wait many hours to get the data. In order to minimize conditioning time, the rapid conditioning concept was introduced into US Department of Agriculture (USDA) cotton classification facilities in 1993 as an improved means of conditioning cotton samples.^{21–23} The underlying concept of rapid conditioning is to draw conditioned air down through cotton samples to enable them to reach the proper moisture content level for HVI testing. A typical rapid conditioning unit is composed of a wire mesh conveyor equipped with

a sheet metal plenum that is connected to the facility's mechanical system. While plastic trays filled with cotton samples move along the mesh conveyor for approximately 10 minutes, conditioned air from the surrounding room is drawn down through the samples and into the plenum. The air is then returned through the mechanical system where it is reconditioned before being delivered back into the room as conditioned air. Moisture readings are taken regularly during shift operation to verify that cotton samples leaving the rapid conditioning unit are within the allowable moisture range. Samples not achieving this moisture level are returned back to the loading end of the unit to be processed again.

3.6 Conclusions

The task of evaluating the tensile behavior of cotton fiber introduces a number of challenges that should be overcome in order to determine the true tensile strength of fiber and the tensile failure behavior. In this chapter, key issues related to the tensile behavior of cotton fibers were addressed. These included: testing techniques, sampling methods, sample size, strength characterization, and the condition of the fiber prior to testing. Although a great deal of progress has been made in dealing with these issues, more research is needed to truly reveal the tensile behavior and the nature of failure of cotton fibers. In an earlier work by Hearle *et al.*,²⁴ descriptive evaluation of cotton fiber tensile failure was made using SEM analysis. This evaluation revealed the complexity of the nature of this failure as the behavior of dry cotton fiber was different from that of wet cotton fiber and a fiber that has undergone chemical treatments exhibited different tensile failure than that of raw cotton. It is important therefore to combine efforts to conduct a more in-depth study in which all relevant factors are examined.

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Tensile properties of hemp and *Agave americana* fibres

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Abstract: Natural fibres are becoming increasingly important owing to their desirable environmental properties. The tensile behaviour of these fibres is affected by plant growth and processing conditions and their microstructure. These properties can be improved by chemically modifying the fibres for a variety of uses. In this chapter, tensile properties of hemp and *Agave americana* fibres are investigated. The effect of processing conditions such as retting duration, mercerization in sodium hydroxide and hydrothermal treatment on the tensile properties of these fibres is reported. Also, the tensile behaviour of the fibres is linked to their microstructure. It is found that duration of retting has no effect on the tensile properties of hemp fibres. Hydrothermal treatment and mercerization affect the surface morphology of hemp fibre surface. These properties may have significance for use of hemp fibres in composites.

Agave americana fibres get initial improvement in tensile strengths during mercerization at room temperature but properties remain almost constant over longer times. The unusually high breaking strains of *Agave americana* fibres can be better understood by modelling the tensile behaviour of its single fibres. These single fibres have a zigzag structure that unravels upon stress application. In general, natural fibres have a great potential as a shift towards the use of more renewable and environmentally friendly materials takes hold. This is despite their major weaknesses such as high moisture intake.

Key words: hemp fibre, *Agave americana* fibre, tensile strength, tensile strain.

4.1 Introduction

In the last two decades renewed interest in the use of plant fibres has been growing rapidly. This is due to an increasing environmental awareness and knowledge of health hazards associated with the manufacture and use of some synthetic fibres. Plant fibres such as hemp, *Agave americana*, wheat, corn, cotton, wood and others are cheap, renewable, recyclable, abundant and biodegradable. They are polysaccharide materials obtained from the stems, leaves and seeds of plants [1]. Plant fibres are used in textiles, ropes,

reinforcement in polymer composites, and in many other applications. During their use, these fibres are subjected to a variety of stresses depending on applications. Therefore their tensile properties and fracture mechanisms must be clearly understood in order to utilize them effectively and to maximize their mechanical properties. We have selected two fibres, hemp and *Agave americana* (also known as century plant), to study in detail and present in this chapter.

Hemp is a plant cultivated worldwide and in different climatic conditions. Its fibre is one of the most valuable parts of the hemp plant. It has been used in textiles, ropes, paper, clothing and as composites reinforcement. It grows on the outer portion of the hemp stalk and forms part of the fibres referred to as ‘bast fibres’. This fibre provides strength to the plant and runs the entire length of the plant. Preference for its use in different applications arises from its excellent physical properties such as strength and modulus, cost effectiveness and increasing availability [2, 3]. In this chapter, some factors affecting tensile behaviour of hemp fibre are investigated. The hemp fibre bundles are also subjected to various surface treatment processes that influence their morphology and properties such as moisture resistance.

Agave americana is a slow-growing plant found in arid and semi-arid regions of the world [4]. The structure of its leaves include strong fibres that have been used for different purposes in different parts of the world. These include uses such as traditional hats and baskets in Southern Africa, ropes and cordage in North Africa and other uses [5–7]. *Agave americana* fibre properties have become a focus of research attention recently. This is in part due to a renewed interest in natural fibres especially with potential applications in natural fibre composites (NFCs) [8, 9]. In our past studies, we reported that mercerization (soaking natural fibres in a solution of sodium hydroxide (NaOH)) improved the tensile strengths of the fibres [8]. However, the treatment was only done for 24 hours and only at 25 °C and was meant to improve the fibre surface properties. As the NaOH attacks the lignin binding the fibres, both the duration and temperature of the treatment can influence the final fibre properties. In this study we look at how the duration and temperature of mercerization may affect the tensile strength of *Agave americana* fibre bundles.

Further, Chaabouni [7] observed that *Agave americana* fibre bundles have high breaking strains which could be related to the nature of their single fibres. This study also focuses on explaining the microstructural impact of the fibres on their breaking strains. This is done by modelling the behaviour of single fibres during deformation under tension and relating this to apparent deformation of the fibre bundle. To our knowledge, the unique properties of *Agave americana* fibres have not been previously explained with such models.

4.2 The experiment

4.2.1 Materials

Hemp fibres used in this study were obtained from hemp stems harvested from a trial plot in Belleville, Ontario, Canada. The harvested hemp stems were left on the field to allow biological degradation (known as dew retting) of the stems. Bundles of hemp stems were collected from the field after one, two and three weeks' duration. In order to extract fibres from the retted hemp stems, a constructed wooden device modelled on equipment used in old farming technology (shown in Fig. 4.1) was used to crush the stems in a process referred to as 'scutching.' This process separates the wooden core from the outer epidermis layer which has fibre bundles (bundle of single fibres joined together by pectin and lignin). The decorticated fibre bundles were further subjected to combing and brushing to clean them.

The hemp fibre bundles were then subjected to hydrothermal treatment. The purpose of this stage is to depolymerize the hemicelluloses and pectin in the cell walls of the fibres into lower molecular aldehyde and phenolic functionalities such as glucose, arabinose, mannose, etc. Then, after drying the fibres, these products are polymerized under high temperature in ovens resulting in thermosetting resins on the surface. The process changes surface morphology and is thought to improve moisture resistance of the fibres. To achieve this, the fibres were treated in an autoclave (Autoclave Engineers Inc.) containing steam at 165 °C and a pressure of between 552 and 586 kPa for 10 minutes. The fibres were then rinsed and dried under ambient conditions. In



4.1 Scutching of retted hemp stems.

the second heating step, the dried fibres were placed in an oven and exposed to a temperature of 160 °C for 30 minutes.

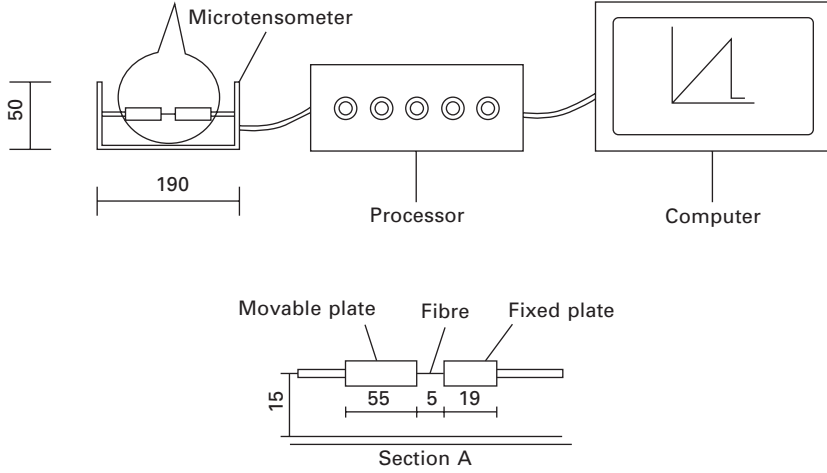
These fibres were also subjected to mercerization using NaOH. Dew-retted fibres were immersed in a solution of 1N NaOH for 4 hours. The fibres were then rinsed and dried in oven at 60 °C for 24 hours.

The *Agave americana* fibres came from Lesotho (southern Africa). The extraction of these fibres followed a traditional method used there. The leaves were first heated in boiling water for 2 hours, at which point they were soft enough to be removed by threshing the leaves between shaped rocks and washing away the soft matrix with water [8]. The fibres were then dried for 24 hours in the wind and sun by putting them along the fence. Mercerization was done in two ways. First the fibres were soaked in 1N NaOH solution for varying periods of 0, 50, 100, 150 and 200 hours to determine the influence of duration at 25 °C on the properties. To determine the influence of temperature, the soaked fibres were subjected to a 130 °C temperature in an autoclave for periods of 0, 0.5, 1, 25 and 300 hours.

4.2.2 Mechanical testing and scanning electron microscopy (SEM)

Hemp single fibres were carefully extracted by hand from the already processed fibre bundles in order to reduce the amount of damage inflicted on the fibres. They were then mounted on a rectangular cardboard frame (with an opening cut in the middle portion equal to the gauge length) with two-part epoxy glue. The samples were stored under ambient conditions for at least 24 hours before testing. The mounted fibre was placed on a microtensometer connected to a computer (Fig. 4.2). The rectangular card was carefully cut using a pair of scissors and a blade to prevent fibre breakage. The single fibre tensile tests were performed at two different gauge lengths (3 and 5 mm) and strain rates (0.3 and 0.5 mm/min) until fracture of the fibre occurred. The fibre diameters were measured using a Clemex vision PE 4.0 image analysis software (Clemex Technologies Inc.) connected to Leica DM LB2 optical microscope. The fibres were assumed to be circular in cross-section [8], the cross-sectional areas were calculated and thus the fracture load of the fibres could be converted to stress. Thirty fibre bundles per variable were tested for both the unretted and for the retted hemp fibres. The fractured samples from the tensile test were kept in a desiccator under ambient conditions prior to SEM analysis of the fractured surfaces. In the SEM analysis, the fibre fractured surfaces were covered with 50 nm gold layer using a gold coating machine to increase the conductivity of the surfaces. The fibre specimens were then observed on a JEOL JSM 840 scanning electron microscope with an operating voltage of 10 kV.

The tensile testing and SEM analysis of *Agave americana* fibres followed



4.2 Schematic representation of the single fibre testing devices. Drawing is not to scale. All dimensions in millimetres.

the same procedure used for hemp fibres except for a few differences. *Agave americana* fibre bundles rather than single fibres were tested for strength. The single fibres were too small to be handled for testing with the available equipment (around 3 mm in diameter). The gauge length used was 7 mm with the strain rate of 0.2 cm/min. The angles of single fibres were measured using Clemex vision image analysis software. Twenty samples were used per variable.

In our previous work the tensile strength results of *Agave americana* fibres were analysed using a two-parameter Weibull model (equation 4.1), the details of which can be found in Thamae and Baillie [8] and Zafeiropoulos and Baillie [10], where P is the probability of failure of fibre of length L , σ is failure strength, σ_0 is the characteristic strength and m is Weibull modulus. In this chapter, both the hemp and *Agave americana* fibres were also analysed using this model. The theory is based on the supposition that a failure of the entire fibre under stress results from failure of the weakest part on the fibre (weakest link theory).

$$P = 1 - \exp \left[-L \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad 4.1$$

By taking natural logarithms on both sides of equation 4.1 and rearranging, we get equation 4.2:

$$\ln \left[\ln \left(\frac{1}{1-P} \right) \right] - \ln(L) = m \ln(\sigma) - m \ln(\sigma_0) \quad 4.2$$

This is followed by plotting the values of $\ln[\ln(1/(1-P))]$ against $\ln(\sigma)$ at

which m is a slope and σ_0 is deduced from the intercept. If the plot follows a straight line, the tensile behaviour of the materials follows a Weibull distribution (Fig. 4.3). To determine P , failure strengths per variable were ranked from the weakest to the strongest and the P could be found using several estimators. One of the largely used estimators is $P_i = [(i - 0.5)/n]$ where i is the rank of the i th data point and n is the number of specimens tested per variable [10]. The average Weibull strengths $\bar{\sigma}$ and standard deviations σ were determined using Equation 4.3 and 4.4 [11,12] where Γ is gamma function

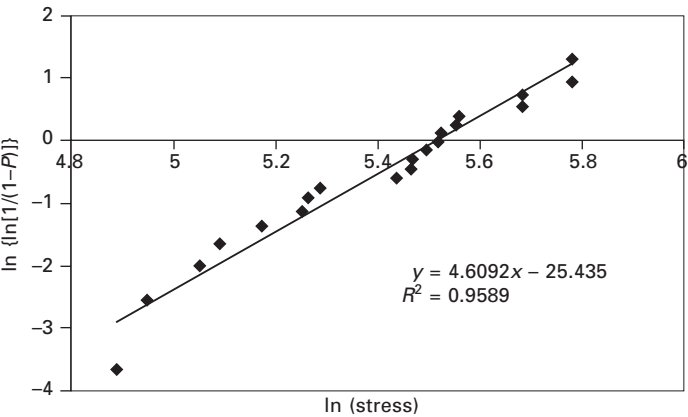
$$\bar{s} = s_0 \left[L^{\frac{1}{m}} \Gamma\left(\frac{1}{m}\right) + \frac{1}{m} \right] \tag{4.3}$$

$$s = s_0 \left[L^{\frac{1}{m}} \Gamma\left(\frac{1}{m}\right) + \frac{2}{m} - \Gamma^2\left(\frac{1}{m}\right) + \frac{1}{m} \right]^{\frac{m}{2}} \tag{4.4}$$

4.3 Results and discussion

4.3.1 Tensile strengths of hemp fibres

The tensile strength values for plant fibres are based on either single fibre or fibre bundle strength [13,14]. The fibre bundle is the smallest fibre easily extracted and is often itself made up of a bundle of smaller single fibres. As well as their inherent structure, the strength of fibres depends on several parameters such as the growth stage, preparation and testing methods, etc. [15,16]. These factors translate into flaws on the fibre surfaces. The flaws



4.3 Weibull analysis plot of *Agave americana* fibres treated at 25°C for 50 hours.

are viewed as critical factors affecting the strength of fibres [11,12]. Average tensile strength of hemp fibres measured at gauge lengths of 3 and 5 mm are shown in Table 4.1. The tensile strength of the single hemp fibre is in the range of 340–527 MPa, within the range of values reported in the literature for single hemp fibre [17]. The fibres exhibit very high standard deviations owing to the high number of flaws and other variables related to their growth and processing. There is no significant difference between the data at 3 or 5 mm or the 0.3 or 0.5 mm/min strain rates. The Weibull strength data is also displayed in Table 4.1 and shows much higher values.

The values of the tensile strength of hemp fibres (both single and bundles) reported in some common literature are shown in Table 4.2. The differences in the values of the tensile properties of the hemp fibres could result from the different varieties of hemp fibre tested, the growth, processing, and testing conditions of the fibre.

4.3.2 Influence of retting duration on tensile strengths of hemp fibres

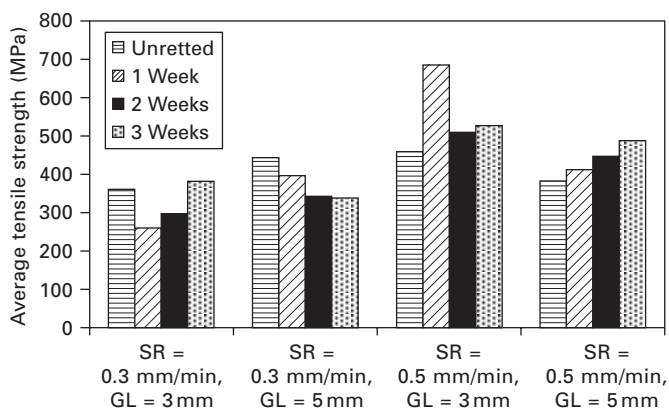
The variation of the average tensile strength of the hemp fibre as a result of different retting duration is shown in Fig. 4.4. The hemp fibre strength differences were not statistically significant (assessed by analysis of variance F -test) from the unretted to three weeks retted hemp fibre (observed value of $F_{\text{crit}} = 2.68$, $p < 0.05$). Similar observations have been reported with other fibres [22,23] which are closely related to hemp fibres.

Table 4.1 Tensile strength of hemp fibre

Strain rate (mm/min)	Gauge length (mm)	Average fibre strength (MPa)	Average diameter (mm)	Weibull modulus	Characteristic strength (σ_0) (MPa)
0.3	3	383 $\pm$ 183	49.9 $\pm$ 9.90	2.06	761
	5	340 $\pm$ 175	44.6 $\pm$ 10.2	2.10	826
0.5	3	527 $\pm$ 330	47.2 $\pm$ 19.3	1.38	1073
	5	490 $\pm$ 314	43.7 $\pm$ 10.8	1.74	1386

Table 4.2 Tensile strength of hemp fibre reported in the literature

Hemp fibre	Tensile strength (MPa)	Tensile modulus (GPa)	Fibre level	Reference
1	550–1400	–	Bundle	3
2	530–650	50–65	Bundle	2
3	161–1178	15–68	Single	18
4	690	90	Single	19
5	490–620	–	Single	20
6	450–800	25–30	Single	21

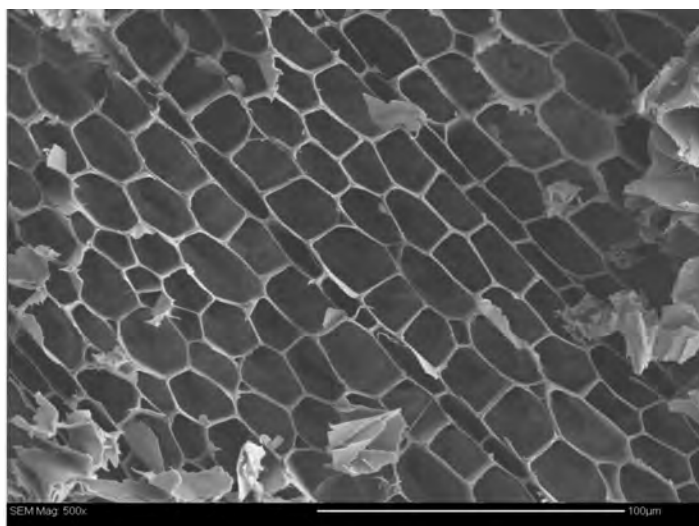


4.4 Average tensile strength of unretted and retted hemp fibres at different testing conditions of gauge length (GL) and strain rate (SR).

4.3.3 The structure of hemp fibres

Microstructure

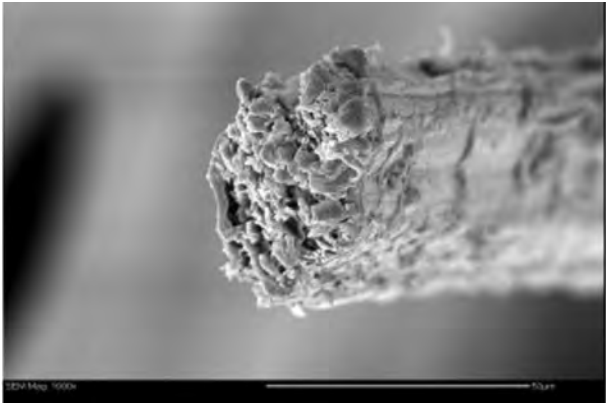
Hemp fibres are multicellular, like other bast fibres. They are situated in the cortex tissue of the stem, and encircle the core cambium and xylem layer. In the cortex, single fibres made up of phloem or parenchyma cells of 20–50 mm in length are held together through their middle lamella to form fibre bundles situated parallel to the longitudinal axis of the stem [3,24]. The fibres are reported to be made up of primary and secondary single fibres and usually take a pericyclic form as shown in Fig. 4.5. The primary fibres are formed during the early growth stage and are reported to be large; about 20 mm long and have cell wall thickness of 7–13 μm . The secondary fibres are smaller in dimension; about 2 mm long and have cell wall thickness of 3–6 μm [3,25]. A single hemp fibre consists of cell walls which gradually build-up during plant development. At maturation of the single fibre, the cell walls surround a small lumen and consist of a middle lamella on the outside, a primary wall and a secondary wall [3,26]. The middle lamella cements together the primary wall of adjacent single fibre and is rich in resins such as pectin and lignin [20,27]. The primary cell wall consists of cellulose microfibril joined together with hemicellulose to form a cellulose–hemicellulose network, which is embedded in a pectin and lignin matrix. The thickness of the primary cell wall has been estimated to be around 70–110 nm [3]. The secondary wall is formed after the completion of the primary wall and is periodically deposited inside the primary wall [12]. The thickness of the secondary wall is observed to be greater than the thickness of the primary cell [3] and is spread over three layers referred to as the S1, S2 and S3 [26].



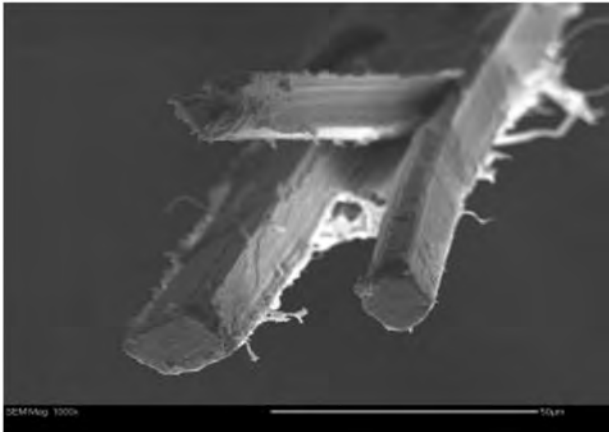
4.5 Section of a hemp stem showing the pericyclic shape of single fibres joined together through their middle lamella.

SEM analysis of fractured surfaces of hemp fibre

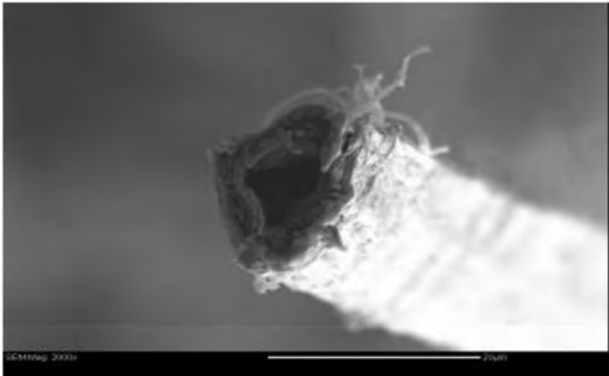
The fractured surfaces of hemp single fibres were examined by SEM in order to understand the fracture behaviour of the fibre. Figure 4.6 shows the fractured surfaces of typical hemp fibres. The pattern of the fractured surface in Fig. 4.6(a) shows that there is a ductile failure in the hemp fibre which is common for cellulose materials. The crack propagation results in irregular tearing of the cell wall of the fibre. The fracture surface in Fig. 4.6(b) reflects a single cleavage plane perpendicular to the axis of the fibre. This form of failure is characteristic of classical brittle failure which obeys linear elastic fracture. In the fractured surface in Fig. 4.6(c), this kind of failure is not entirely the case. It is observed here that brittle failure is evident, as well as microfibrils pulling-out of the fibre cell wall, especially the secondary wall. The microfibrils pull-out can be attributed to decohesion of the cell walls (which are composite of cellulose fibrils embedded in hemicellulose and lignin matrix) under strain resulting in the slippage of the microfibrils [18,27]. It is observed in Fig. 4.6 that the propagation of crack occurs at an angle perpendicular to the fibre axis which is commonly observed in many cellulosic fibres. Dijon [11], in a study of flax fibre which has similar characteristics to hemp fibre, observed that crack propagation through the cell walls could also occur at other angles which were not perpendicular to the direction of the fibre axis. The initiation of crack on the fibre during stress application frequently commences from pre-existing flaws (nodes, kink, etc.) on the surface of the fibres which must have arisen from growth



(a)



(b)



(c)

4.6 Typical fracture surfaces of hemp fibres after tensile test: (a) ductile failure; (b) brittle fracture; (c) brittle and fibre pull-out.

and processing conditions. As the stress continues to increase, the crack propagates between cell walls or within the cell walls of the fibres until a complete rupture of the fibre occurs. The propagation of crack between cell walls can result in microfibril pull-out [22,27] as shown in Fig. 4.6(c).

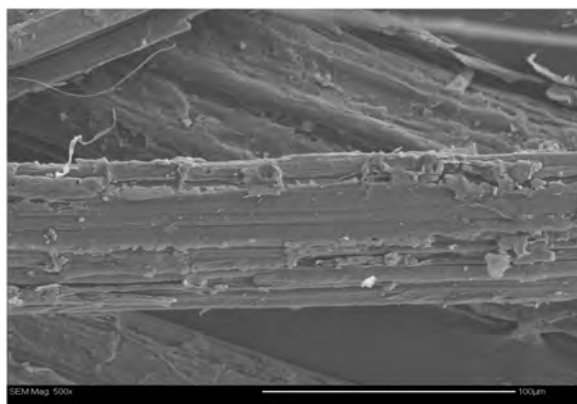
SEM analysis of surface morphology of hemp fibre

When used in composites, hemp fibres are commonly treated to improve the final properties of these materials [14,28]. Typical treatments to improve moisture resistance include NaOH and hydrothermal treatment. The surfaces of untreated, NaOH and hydrothermal treated fibres were observed using a scanning electron microscope. An untreated hemp fibre can be seen in Fig. 4.7(a), while NaOH and hydrothermal treated fibres are seen in Fig. 4.7(b) and 4.7(c) respectively. From the SEM micrographs, it appears that the polysaccharides of lignin, pectin and hemicellulose are highly localized on the surfaces of the untreated hemp fibres. The surface of the NaOH-treated fibres is characterized by a rough morphology with less lignin, pectin and hemicellulose. In contrast, the hydrothermal treated fibres have much cleaner and smoother surfaces. Similar observations have been reported for hemp fibres after alkali treatment [29,30]. The rough surface is reported by some workers to be advantageous for mechanical interlocking when fibres are used in polymer composites [29].

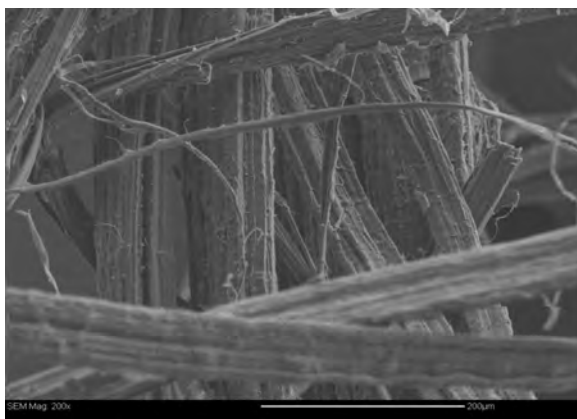
4.3.4 Influence of mercerization on the tensile properties of *Agave americana* fibres

The alkali treatment is thought to improve the overall strength of the natural fibres by removing weaker binding materials such as lignin and hemicelluloses while leaving a load-bearing cellulose [8]. These weaker materials can be viewed as impurities which could initiate stress concentrations under applied tension. However, it can be assumed that after much longer exposure, the alkali would begin to degrade the load-bearing cellulose structure, thus reducing fibre properties [31].

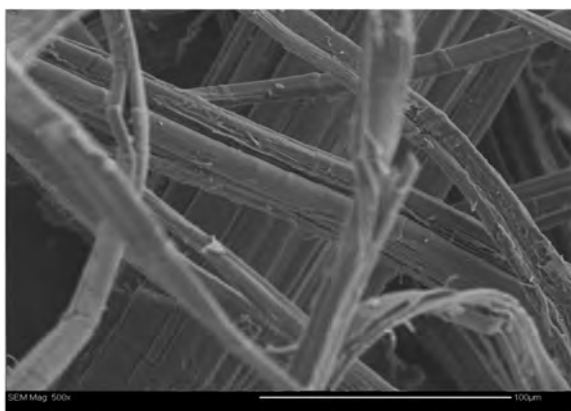
The inherent variability of natural fibres makes it difficult to make conclusive observations. Many kinds of defects and irregularities during natural growth are characteristic in natural fibres and result in high coefficients of variation of typically 15–30% [32]. However, the results in Table 4.3 indicate that the fibre strength improves during the mercerization period of 0–200 hours. The average strength values suggest improvement from 160 to 228 MPa at 0–50 hours of treatment. Beside the result at 100 hours, there is almost constant strength between 50 and 200 hours of soaking. The Weibull average strengths show the fibres, which have reached a plateau between 50 hours and 150 hours, reaching the highest strength of 332 MPa at 200 hours. The average



(a)



(b)



(c)

4.7 SEM micrograph of (a) the surface of untreated dew-retted hemp fibre; (b) sodium hydroxide treated dew-retted hemp fibre; (c) hydrothermally treated dew-retted hemp fibre.

Table 4.3 Influence of mercerization duration on the tensile properties of *Agave americana* fibre bundle at 25 °C

Duration (hours)	Average strength (MPa)	Characteristic strength (MPa)	Weibull modulus	Weibull average strength (MPa)	Average breaking strain (mm/mm)
0	160 ± 73	367	2.8	162 ± 63	0.38 ± 0.16
50	228 ± 57	380	4.6	228 ± 56	0.45 ± 0.15
100	204 ± 68	395	3.5	237 ± 65	0.39 ± 0.13
150	221 ± 80	478	3.0	222 ± 81	0.45 ± 0.11
200	227 ± 58	538	4.9	332 ± 77	0.45 ± 0.07

strains are generally large and range from 0.38 to 0.45 mm/mm for the 200 hour duration.

From the surveyed literature, the highest temperature to which *Agave americana* fibres have been subjected to an alkali solution is 130 °C at 3.8% NaOH [7]. The authors assumed that the structure of cellulose was not destroyed at these conditions. In this study, the fibres were subjected to these conditions to determine the behaviour of the breaking strains, the implications of which are analysed in Section 4.3.6. In Table 4.4, it can be seen that in the first hour, there was almost no difference in tensile strength of the fibre. However, the strength had declined significantly after 25 hours and, as expected, had dropped considerably after 300 hours of treatment. The Weibull average values at 300 hours are not included as it was evident the fibre no longer followed Weibull distributions at this point (i.e. its Weibull plots did not follow a straight line, see Fig. 4.3). The next section investigates the microstructure implications of these observations and the reasons behind the large breaking strains of *Agave americana* fibre bundles in general.

4.3.5 The nature of *Agave americana* single fibres

The single fibres of *Agave americana* have a very small diameter of around 3 μm [8]. If we assume a circular cross-section¹ of both the fibre bundle of a diameter D and the single fibre of a diameter d , and assume the single fibres are so close to each other so as to ignore spaces left between them (Fig. 4.8a), the number of single fibres m which each fibre bundle would hold is

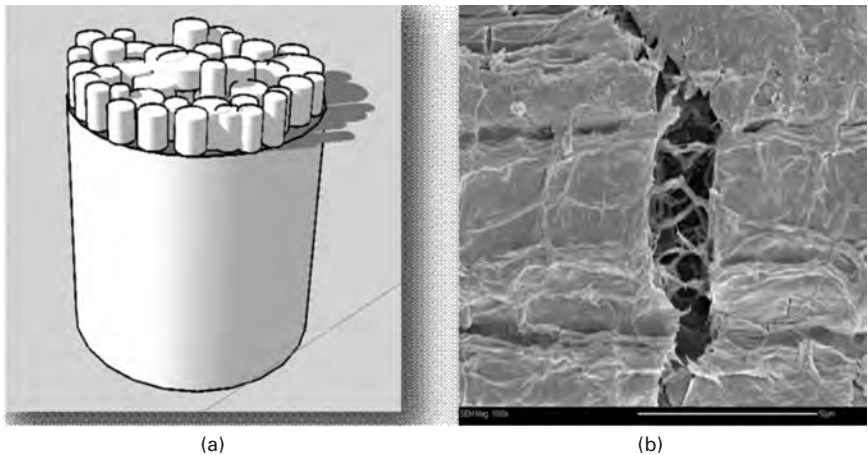
$$m = \frac{D^2}{d^2} \quad 4.5$$

¹The fibres are considered circular for simplicity. SEM pictures reveal a more complex shape.

Table 4.4 Influence of mercerization duration on the tensile properties of *Agave americana* fibre bundle at 130°C

Duration (hours)	Average strength (MPa)	Characteristic strength (MPa)	Weibull modulus	Weibull average strength (MPa)	Average breaking strain (mm/mm)
0	160 ± 73	367	2.8	162 ± 63	0.38 ± 0.16
0.5	159 ± 52	292	3.8	159 ± 46	0.30 ± 0.07
1	160 ± 68	346	2.9	160 ± 59	0.33 ± 0.28
25	136 ± 61	334	2.5	136 ± 58	0.38 ± 0.15
300	28 ± 15	N/A	N/A	N/A	0.11 ± 0.11

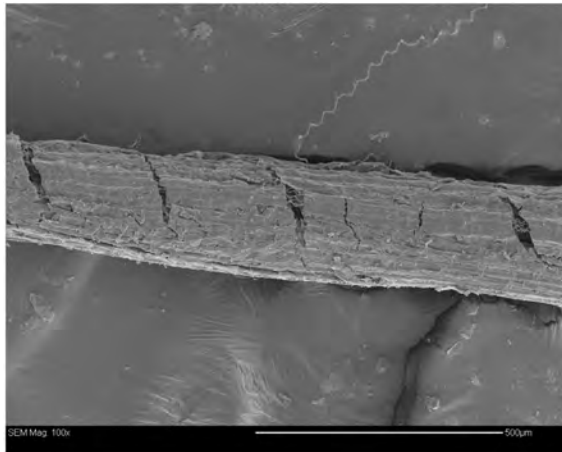
N/A: None applicable.



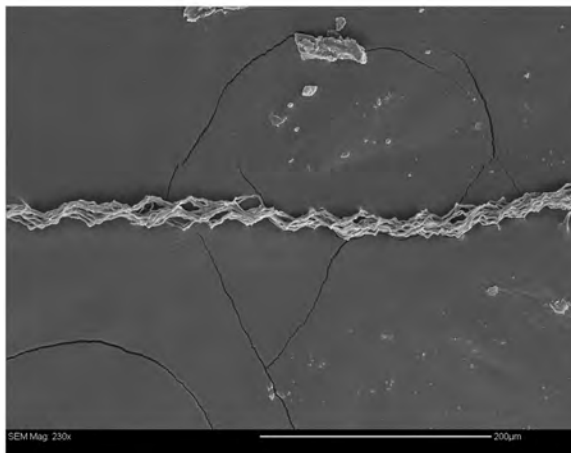
4.8 (a) *Agave americana* single fibres assumed to be fitting side by side in a bundle. (b) An SEM picture of *Agave americana* single fibres in bundle (1000×).

From equation 4.5, an *Agave americana* fibre bundle with a diameter of 200 mm would hold around 4500 single fibres. In reality, a smaller figure can be expected if significant spaces between single fibres are taken into account (Fig. 4.8b). From the SEM pictures (Fig. 4.9), if we observe these single fibres at rest, they are not long straight cylinders. Rather, they show a form of a zigzag structure. Figure 4.9(a) shows one of the single fibres sticking out of a fibre bundle and Fig. 4.9(b) has a portion of a group of these single fibres in their intertwined state. This geometry of the single fibres has an influence on the tensile behaviour of the *Agave americana* fibre bundles.

Fibre bundles of *Agave americana* have relatively high strains of up to over 60% (Fig. 4.10 and Table 4.3). This is in contrast to other natural fibres which normally extend to 10% of their length before breaking. Looking at both pictures in Fig. 4.9, it can be suggested that an applied force on these



(a)



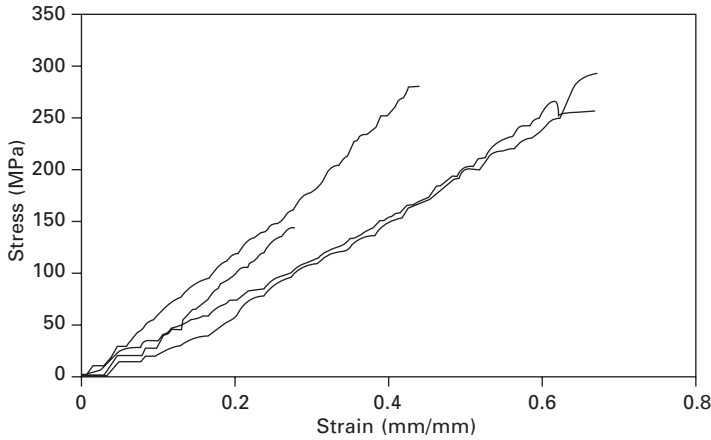
(b)

4.9 SEM pictures of (a) a zigzagged *Agave americana* single fibre sticking out of a fibre bundle (100 $\times$) and (b) a group of *Agave americana* single fibres (200 $\times$).

fibres will first straighten ('unravel') them before pulling them apart to a breaking point. This factor is assumed to contribute to the high strains of the fibre bundles and forms the basis of our modelling.

4.3.6 Modelling the influence of *Agave americana* single fibre angles

It is difficult to model the behaviour of naturally occurring materials such as natural fibres without the risk of being overly simplistic. The structure of



4.10 A typical stress-strain curve of *Agave americana* fibre bundle.

natural fibres is complex, highly variable and poorly understood. However, we attempt to model the structure in the following section in order to understand as much of the behaviour as possible.

An *Agave americana* single fibre can be considered as a long cylinder having a zigzag structure at rest, before a tensile force F is applied to it (Figs 4.9 and 4.11). Straight lines may be drawn as shown on Fig. 4.10 to simulate a zigzag structure. This structure can then be reduced to a series of isosceles triangles, each triangle having two equal sides of length a and the base of length x , representing the apparent length of one structure element. The angle ϕ , opposite to x relates true length $2a$ to the apparent length x :

$$x = 2a \sin\left(\frac{1}{2} \phi\right) \quad 4.6$$

The length l_0 can be any length that covers a number n of sides x such that

$$l_0 = nx \quad 4.7$$

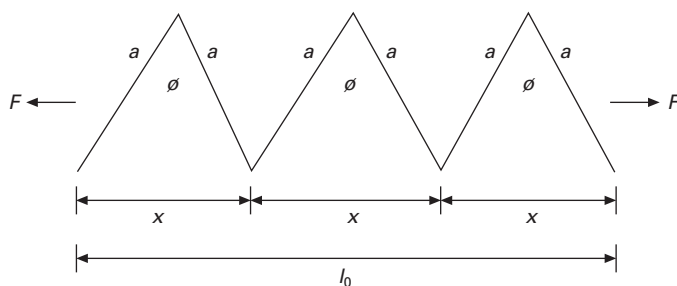
If the force F is applied on the single fibre, the single fibre will increase from l_0 until the fibre is fully extended at length Z such that all the angles ϕ are equal to 180° (Fig. 4.11). Therefore from Fig. 4.11:

$$Z = 2an \quad 4.8$$

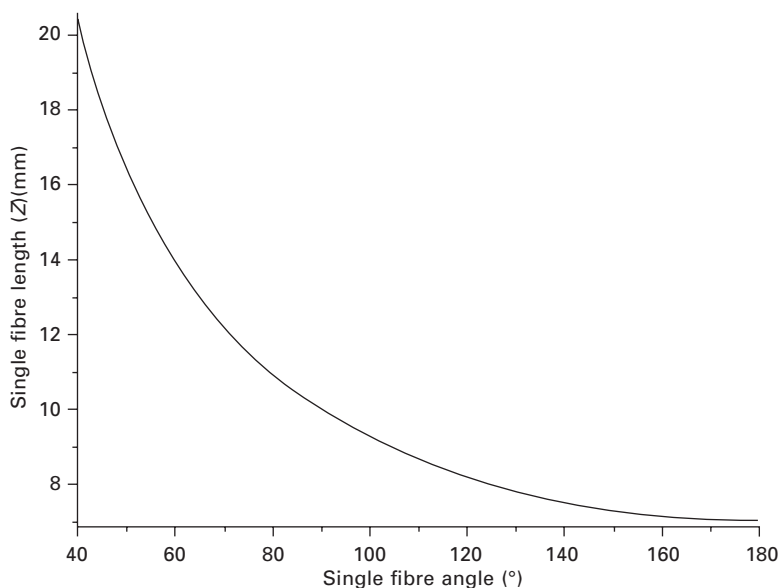
From 4.6, 4.7 and 4.8, it can be shown that

$$Z = \frac{l_0}{\sin\left(\frac{1}{2} \phi\right)} \quad 4.9$$

Equation 4.9 implies that starting with the fibre of length l_0 where the fibre is at rest, the length to which the single fibre will extend to the full, Z , is a function of the fibre angle ϕ . The smaller the fibre angle ϕ , the larger the



4.11 The simplified geometry of *Agave americana* single fibres.



4.12 The theoretical influence of *Agave americana* single fibre angle on single fibre length extension Z assuming a gauge length of 7 mm.

length Z will be and vice versa (Fig. 4.12, plotted from equation 4.9). Since the length l_0 is the length of the fibre before any application of force, it can also be viewed as a gauge length. In Fig. 4.12, a gauge length of 7 mm was assumed.

As a first approximation, it can be assumed that a fibre bundle is made up of any number of single fibres which have similar properties² and do not interact with one another during deformation³. Then the length Z will be the same for both the bundle and any one of the single fibres if the same stress

²Same shape, length and angles.

³Section 4.3.9 discusses why this assumption presents a problem.

σ is applied to them until they are fully extended. Therefore, what appears as an extension of a fibre bundle to a length Z is, in fact, the unravelling of the single fibres within the bundle until they are fully stretched.

From the above discussions, when a single fibre of length l_0 is extended by force F until it breaks at length L , the apparent single fibre strain ϵ_b measured on this fibre is a function of two extensions (Fig. 4.13). The *unravelling extension* is the extension $Z - l_0$ which is a result of unravelling of the single fibres of angle ϕ in its structure. When the angle ϕ reaches 180° , Z stops increasing, and the secondary extension begins. This secondary extension $\mathbf{Dl}$ is the *structural extension* of the single fibres; that is, the extension of its molecular chains. Given the gauge length l_0 , the total fibre extension δ_b will be the sum of unravelling and structural extensions:

$$\delta_b = (Z - l_0) + \mathbf{Dl} \quad 4.10$$

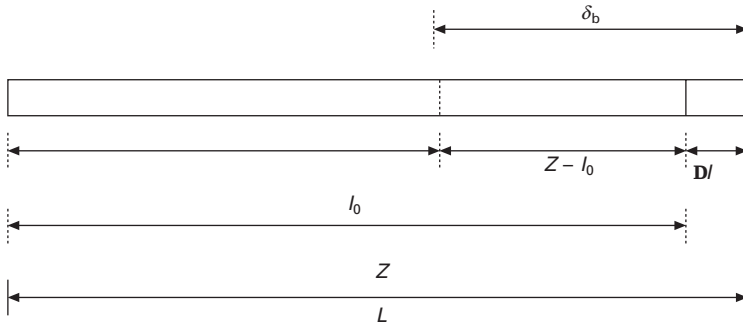
The *total single fibre strain* ϵ_b resulting from both the unravelling and structural extensions follows:

$$\epsilon_b = \frac{\mathbf{d}_b}{l_0} = \frac{(Z + \mathbf{Dl} - l_0)}{l_0} \quad 4.11$$

From strain definition, Fig. 4.13 and equation 4.9, the structural extension $\mathbf{Dl}$ can be expressed as

$$\mathbf{Dl} = Z\epsilon_f = L - Z = l_0 + \mathbf{d}_b - Z = L - \left[\frac{\dot{\mathbf{E}}}{\mathbf{f}} \frac{l_0}{\sin(\frac{1}{2}\mathbf{f})} \right] \quad 4.12$$

where the strain ϵ_f is the *structural strain* or *single fibre structural strain* (due to structural extension $\mathbf{Dl}$). From 4.9, 4.11 and 4.12, the total single fibre strain ϵ_b can be expressed as a function of the structural strain, ϵ_f and the angle ϕ :



4.13 A model of *Agave americana* single fibre extension at different stages of deformation.

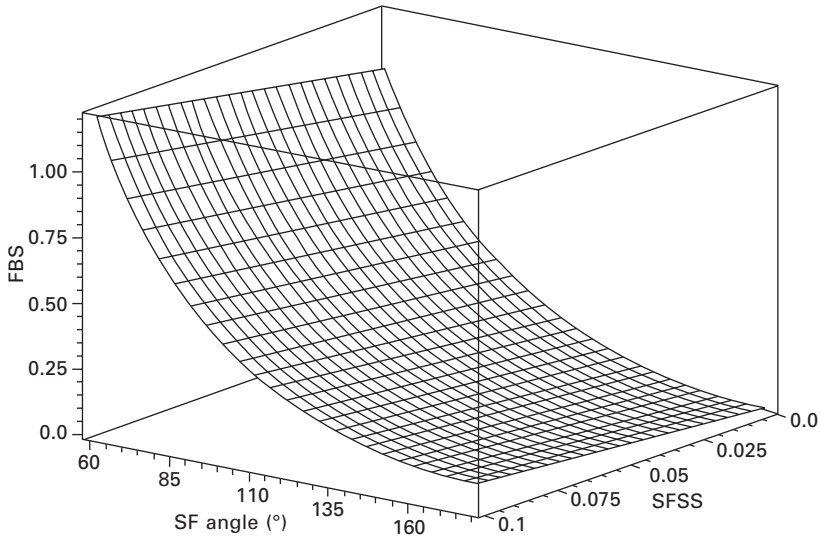
$$\epsilon_b = \frac{1 + \epsilon_f}{\sin(\frac{1}{2}\phi)} - 1 \quad 4.13$$

Rearranging 4.13, the structural strain, ϵ_f , can be written as

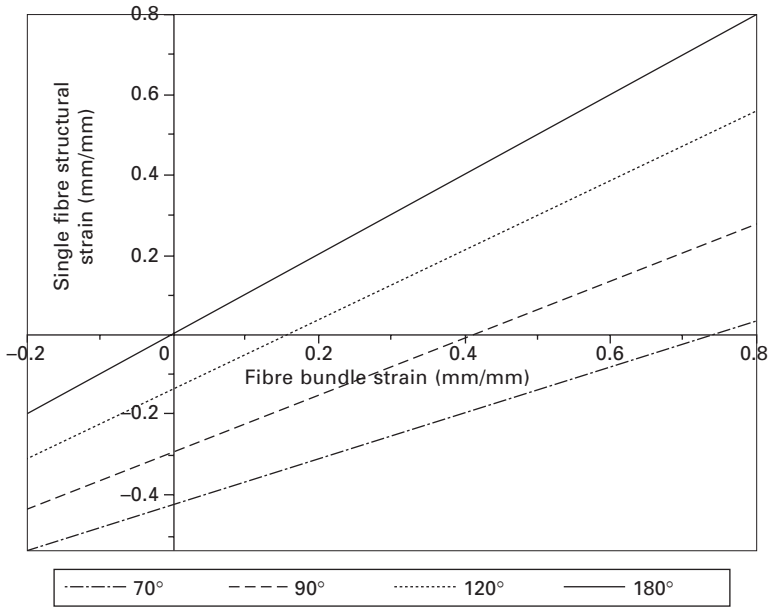
$$\epsilon_f = \sin(\frac{1}{2}\phi)(\epsilon_b + 1) - 1 \quad 4.14$$

From the assumption of non-interacting similar single fibres under the same stress, *total single fibre strain* (resulting from unravelling and structural extensions) is the same thing as the *fibre bundle strain*. This is because the extension of each single fibre in a bundle is the same as the extension of all other single fibres in a bundle, and hence it is the same as extension of the bundle itself. Therefore equation 4.14 implies that if we know the angle ϕ and the fibre bundle strain ϵ_b , both of which can be measured, we can find the structural strain of the single fibre ϵ_f without measuring it directly. Note that ϵ_f is independent of the values of a , x and l_0 in Fig. 4.11. Figure 4.14 shows the fibre bundle strain, ϵ_b (FBS), as a function of single fibre structural strain, ϵ_f (SFSS), and single fibre angles (SF angles) plotted from Equation 4.13. Low values of ϕ and high values of ϵ_f lead to high fibre bundle strains ϵ_b and vice versa.

It can be expected that for any single fibre angle, there are ϵ_b values below which ϵ_f is negative (does not exist). These points are at the extension point Z at which the single fibre becomes fully extended and extension **D** begins to occur. As can be seen on Fig. 4.15 (plotted from equation 4.13), these



4.14 A theoretical relationship between *Agave americana* fibre total fibre bundle strain ϵ_b (FBS) and its single fibre structural strain ϵ_f (SFSS) at different single fibre angles.



4.15 The theoretical relationships between *Agave americana* fibre bundle strain ϵ_b and single fibre structural strain ϵ_f at different single fibre angles.

points are 0.74, 0.41, 0.15 and 0 when single fibre angles are 70°, 90°, 120° and 180° respectively.

As can be seen on Fig. 4.15, when the single fibre angle is 180° from the start, ϵ_b equals ϵ_f at any point of fibre bundle deformation. This would happen when the zigzag structure of the single fibres have been destroyed so that the unravelling extension $Z-l_0$ equals zero. The single fibres are already straight before deformation.

4.3.7 Influence of single fibre angle on the toughness of *Agave americana* fibre bundles

Assuming that *Agave americana* fibre bundles follow Hooke's law from the beginning of deformation to the point of fracture (Fig. 4.10), the stress ϵ_b versus the fibre bundle strain ϵ_b curve for the fibre bundle would follow

$$\sigma_f = E_b \epsilon_b \quad 4.15$$

where E_b is the modulus of the fibre bundle. Taking the integral to find the toughness of the fibre bundle U_b leads to

$$U_b = \frac{1}{2} E_b \epsilon_b^2 \quad 4.16$$

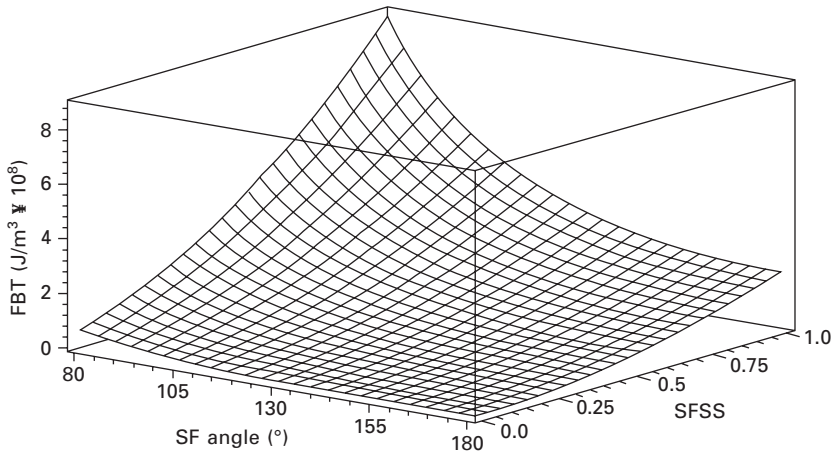
From 4.13 and 4.16

$$U_b = \frac{1}{2} E_b \left[\frac{1 + \epsilon_f}{\sin(\frac{1}{2}\phi)} - 1 \right]^2 \quad 4.17$$

According to Fig. 4.16 (plotted using equation 4.17), a combination of low single fibre angles ϕ (SF angles) and high single fibre structural strains ϵ_f (SFSS) leads to very high fibre bundle toughness (FBT in J/m³) assuming a constant modulus of 400 MPa (a typical modulus). If *Agave americana* fibre has any of these combinations, it would resist fracture better.

4.3.8 Model verification

Theories that relate synthetic fibre bundles to their single fibre properties are normally easy to verify. This is because both the properties of single fibres and fibre bundles can be tested independently. This situation does not apply in the case of *Agave americana* fibres. The single fibres modelled are so small that handling them with the present equipment is impractical. Fibres of up to 10 mm in diameter have been tested using conventional approaches [33]. As fibres used in reinforcement get smaller; scientists are developing new suitable approaches [34]. Tan and Lim [35] developed a method to test tensile properties of micro and nanofibres using a nano-indentation system based on atomic force microscope (AFM). In future work, this method and other similar methods could be tried for testing single fibres of *Agave americana*. If ϵ_f could be independently measured, one way to verify this



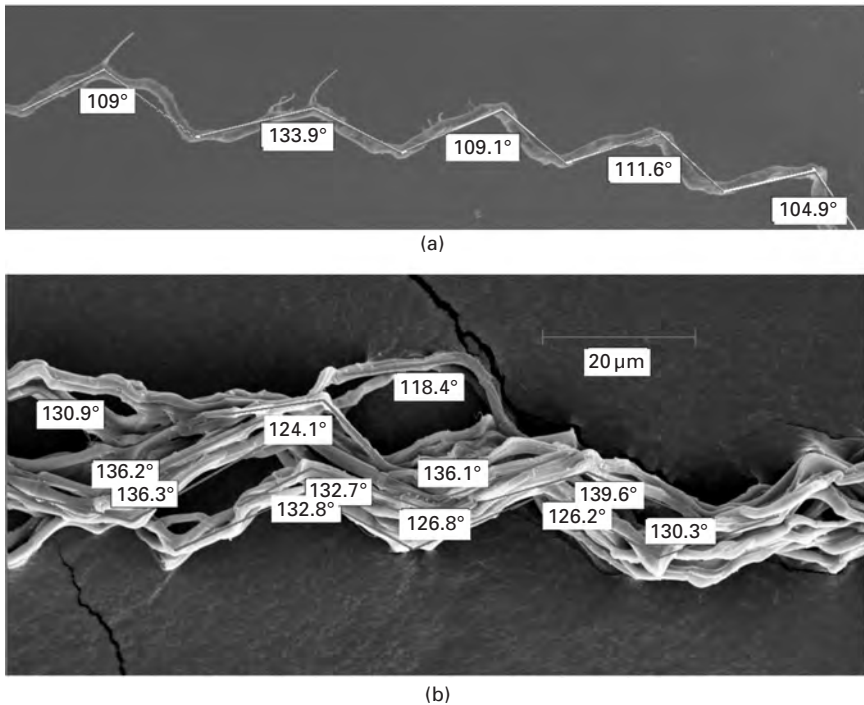
4.16 The theoretical *Agave americana* fibre bundle toughness U_b (FBT in J/m³) against single fibre structural strains ϵ_f (SFSS) at a randomly selected modulus of 400 MPa and different single fibre angles ϕ .

model would be to estimate it using equation 4.14 where ϵ_b and average ϕ are known. Then the ϵ_f measured directly could be compared with the ϵ_f calculated from equation 4.14.

From the above discussions, it is possible that the higher angles of single fibres in Fig. 4.17(b) compared with (a) may have contributed to the comparatively short strains after 300 hour mercerization at 130 °C, perhaps by weakening the joints at which the fibres form angles.

4.3.9 The limitations of the model

The model assumes the single fibres are lying side by side without any meaningful interaction in a bundle and it ignores the influence of lignin matrix. In reality, single fibres of *Agave americana* fibre bundles have a complex interwoven structure as shown in Figs 4.9(b) and 4.17(a). If viewed as if the fibres do not interact and are not embedded in a matrix, the fibre bundles would register a minimal force from l_0 to Z (Fig. 4.12). The resistance would only be due to the single fibres resisting transition from



4.17 (a) The *Agave americana* single fibre angles of a fibre bundle mercerized for 24 hours at 25 °C (500 $\times$). (b) The single fibre angles of a fibre bundle mercerized for a duration of 300 hours under at 130 °C (1000 $\times$).

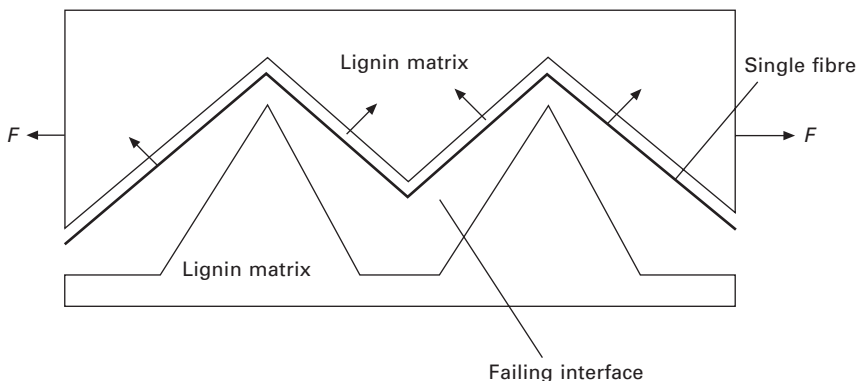
their preferred conformations. The significant force would register only from Z to L as the individual fibres would now be structurally deforming (not just unravelling).

The fact that the bundles seem to register a significant force in this region, l_0 to Z, shows that they encounter some significant resistance during deformation as shown in Fig. 4.9, making it difficult to identify where the transition at extension Z is. There are several possibilities. The one side of a sides (Fig. 4.11) of the single fibres are likely pushing against the walls of the matrix as they straighten (Fig. 4.18). The opposite side of side a could be pulling away from the matrix. Keeping in mind the fact that the fibres are intermingled, there will be frictional forces among them and between themselves and the matrices as they unravel and extend. Hence each single fibre may experience tensile, compressive and shear forces to contend with during extension. All these possibilities give rise to the resistance force F in the region of l_0 to Z. It is possible that some of the single fibres (or even all of them) do not survive to see the extension Z.

Lastly, the model ignores the size dependence of fibre tensile strengths. It is well known that fibre tensile strengths improve as the fibres get smaller. This is due to the fact that large fibres have more flaws than small fibres, hence more probability of failure. Consequently a fibre bundle with more flaws may break 'before its time', that is before the fibre could be fully extended.

4.3.10 Challenges and opportunities with natural fibres

Plant-based natural fibres such as hemp and *Agave americana* may not meet certain strength requirements in particular applications as well as synthetic



4.18 The likely picture of deformation during *Agave americana* single fibre extension.

fibres. Nevertheless, these fibres have some desirable features absent in synthetic fibres. They have good health and environmental qualities. When used in clothing, they can be more comfortable (better feel) and healthier to wear. They are less associated with certain health problems, unlike glass fibres. Also, these fibres are derived from renewable resources as opposed to many synthetic fibres. So their supply may be more sustainable. When used in composites for automotive applications, they lead to less fuel consumption due to their lightweight (densities of hemp and *Agave americana* fibres are 1.48 g/cm^3 [36] and 1.36 g/cm^3 [7] respectively). This factor leads to a more positive automotive environmental impact in the long run [37].

Other benefits of plant-based natural fibres are related to their processing and costs. Natural fibres are less abrasive to composite processing equipment than some synthetic fibres. In addition, these fibres are abundant and come in various forms, available in almost all regions of the world. This makes them cheaper than synthetic fibres.

Nevertheless, natural fibres have some undesirable properties especially in their use in plastic and other composites. Their structure is mainly cellulose, hemicelluloses and lignin. These substances (especially cellulose) are rich in hydroxyl groups which make natural fibres much hydrophilic. So their affinity to moisture invites use of chemicals in composites to reduce their moisture absorption which would otherwise weaken the fibre–matrix interface and general properties of the composites. Also, as is true for most biological materials, natural fibres have high scatter in properties, making it more difficult to predict their behavior in use.

4.4 Conclusions

As mentioned, hemp and *Agave americana* fibres have both traditional and modern significance. Whereas these fibres have had more traditional uses such as in ropes, textiles and cordage, the renewed interest in these fibres (like other natural fibres) is now in conjunction with their use in reinforcing plastics to make plastic composites.

Hemp fibre is one of the most important plant fibres and shows promising properties with wide varieties of applications. If its properties are clearly understood, its use in many applications could be maximized. The tensile strength properties of hemp fibre measured in this work ranges between 340 and 527 MPa. These values are within the range of values reported in other works and are known to depend on several parameters related to the growth and processing of the fibres. It was observed that retting of the hemp plants for up to three weeks after harvesting would not affect the strength. When stress is applied to the fibre, it is observed that the fibre can exhibit both brittle and ductile mode of failure which is closely related to the microstructure arrangement of the fibre.

Also, the study has found that at 25 °C mercerization improves the tensile strength of the *Agave americana* fibre bundles between 0 and 50 hours of exposure. The strength seems to be less affected by the duration of mercerization during the period from 50 to 200 hours. The fibre bundles of *Agave americana* are also shown to have high tensile strains. The high breaking strains of *Agave americana* fibres can be understood by modelling the geometry of their single fibres which show a zigzag structure at rest, making it easier for them to straighten before deformation. It is possible that mercerizing the fibres at 130 °C weakens the joints that form the angles of single fibres, increasing the sizes of these angles and reducing the breaking strains of the fibre bundles.

4.5 References

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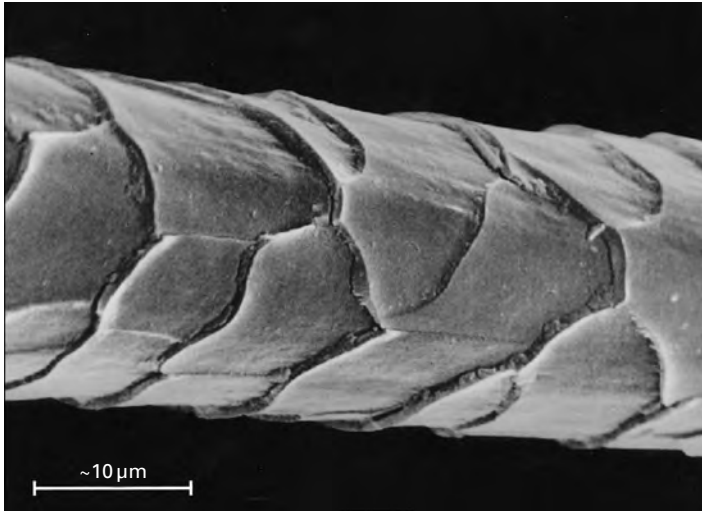
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Abstract: The chapter begins by describing the complex chemical and physical structure of wool. It then reviews the different structure–property models of strength which attempt to explain the shape of the stress–strain curve in terms of wool’s known structure. The alternative methods of measuring fibre strength are discussed as well as the difficulties associated with measuring strength in non-uniform fibers. Finally the chapter looks at the way in which a range of environmental, processing and service conditions affect the tensile failure properties of wool.

Key words: wool tensile properties, structure of wool, non-uniform fibers, environment, effect of processing, effect of service conditions.

5.1 Introduction

Wool is a complex biocomposite, typically 16–30 μm in diameter with an outer covering of overlapping cuticle cells which form a protective sheath and also confer on wool its ability to felt. A scanning electron micrograph of a clean Merino wool fibre is shown in Fig. 5.1. Wool has been used as a textile fibre since before the beginning of recorded history, the earliest type of fabric made from wool probably being a felt. It has been the subject of serious research for the last 80 years, with researchers from around the world meeting every five years at an International Wool Textile Research Conference. Early work focused on trying to understand the basic chemistry and physics of the fibre with structure–property relationships and the chemical nature of the surface becoming more important with time. There has always been strong interest in the tensile properties of wool, with a recognition that weak fibers break during processing, decreasing fibre length in the top and increasing losses during processing. A lot of effort has gone into trying to understand the stress–strain properties of α -keratin fibers, including wool, with the major focus being non-failure properties such as modulus, yield stress and post-yield slope. This work has been well documented by Feughelman (1982, 1997, 2002), Hearle (2000, 2002, 2003, 2007) and Chapman (1969a,b). Less effort has gone into failure properties, although Reis (1992) has reviewed the variations in the strength (breaking stress) of wool fibers.



5.1 Scanning electron micrograph of a Merino fibre, showing overlapping cuticle cells (Christoe *et al.*, 2003).

The first part of this chapter elucidates the complex chemical and physical structure of wool that was the focus of much of this early work. The next section summarizes the models and theories of the strength of wool that were developed during the 1960s and are still being refined today. This is followed by a section on methods of measurement, focusing particularly on the specific challenges that wool brings, viz. its non-uniformity and moisture dependence. The heart of the chapter deals with the effect of processing and environmental conditions on the tensile failure properties of wool, in particular the effects of torsion, abrasion, moisture, rate of testing, dyeing and setting. Finally there are sections dealing with applications, sources of further information and advice and a comprehensive list of references.

5.2 Structure of wool

5.2.1 Chemical

Wool is a semi-crystalline, proteinaceous polymer, part of the family of proteins called α -keratins, which also include materials such as hooves, horns, claws and beaks (Rippon, 1992). The basic building blocks of proteins are amino acids and extensive research has shown that wool is made up of 18 α -amino acids with typical percentages as shown in Table 5.1. Amino acids have the general structure $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COOH}$ where R represents the side group of the amino acid. Multiple amino acids condense by reaction of adjacent amino and carboxyl groups to form proteins or polypeptides with a general

Table 5.1 Amino acid composition of Merino wool

Amino acid	Amino acid content ^a	Side group	Nature of side group
Glycine	8.4	-H	Aliphatic hydrocarbon
Alanine	5.4	-CH ₃	Aliphatic hydrocarbon
Valine	5.6	-CH(CH ₃) ₂	Aliphatic hydrocarbon
Leucine	7.7	-CH ₂ ·CH(CH ₃) ₂	Aliphatic hydrocarbon
Isoleucine	3.1	-CH(CH ₃)·CH ₂ ·CH ₃	Aliphatic hydrocarbon
Phenylalanine	2.9	-CH ₂ ·C ₆ H ₅	Aromatic hydrocarbon
Serine	10.4	-CH ₂ ·OH	Hydroxyl
Threonine	6.4	-CH ₂ (OH)·CH ₃	Hydroxyl
Tyrosine	3.8	-CH ₂ ·C ₆ H ₄ OH	Hydroxyl
Aspartic acid ^b	6.5	-CH ₂ ·COOH	Acidic
Glutamic acid ^c	11.9	-CH ₂ ·CH ₂ ·COOH	Acidic
Lysine	0.9	-CH ₂ ·CH ₂ ·CH ₂ ·CH ₂ ·NH ₂	Basic
Arginine	6.9	-(CH ₂) ₃ ·NH·C(NH)NH ₂	Basic
Histidine	2.9	$\begin{array}{c} \text{N}=\text{CH} \\ \\ -\text{CH}_2-\text{C}=\text{CH} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{NH}$	Basic
Methionine	0.5	-CH ₂ ·CH ₂ ·S·CH ₃	Sulphur containing
Cystine	10.3 ^d	-CH ₂ ·S·S·CH ₂ -	Sulphur containing
Tryptophan ^e	0.5	$\begin{array}{c} -\text{CH}_2-\text{C} \\ \\ \text{CH} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{NH} \\ \text{C}_6\text{H}_4 \end{array}$	Heterocyclic
Proline	6.6	$\begin{array}{c} -\text{CH}_2- \\ \diagup \quad \diagdown \\ -\text{CH}_2- \end{array} \text{CH}_2$	Heterolytic

^aResidues/100 residues (Bradbury *et al.*, 1968; Leeder and Marshall, 1982).

^bIncludes asparagine.

^cIncludes glutamine.

^dThe value shown is for the reduction product, cysteine (also termed 'half-cystine').

^eTryptophan is destroyed under the conditions used for these analyses; values of about 0.5 residues % have been obtained by alternative techniques (Christoe *et al.*, 2003).

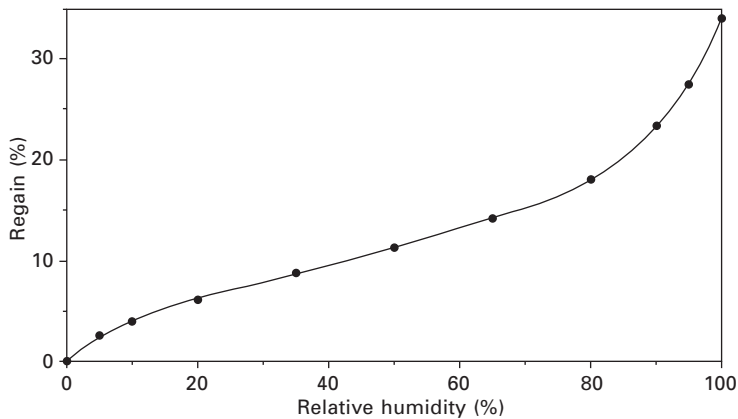
structure $-(\text{NHCHRCO})_n-$. In wool the 18 amino acids combine in many different ways leading to about 170 different types of polypeptides varying in relative molecular mass from below 10 000 to greater than 50 000 Da (Zahn and Kusch, 1981; Gillespie, 1990).

The side groups of the amino acids vary markedly in size and chemical nature and play an important role in the physical and chemical properties of the wool fibre. The low-sulphur proteins, containing a high proportion of amino acids that contribute to α -helix formation (glutamic acid, aspartic acid, leucine, lysine, arginine), assemble into rod-like intermediate filaments (microfibrils). These crystalline microfibrils make up approximately 25–30% of the dry fibre (Feughelman, 1989) and play a dominant role in the tensile properties of the fibre, particularly when wet. The microfibrils are embedded

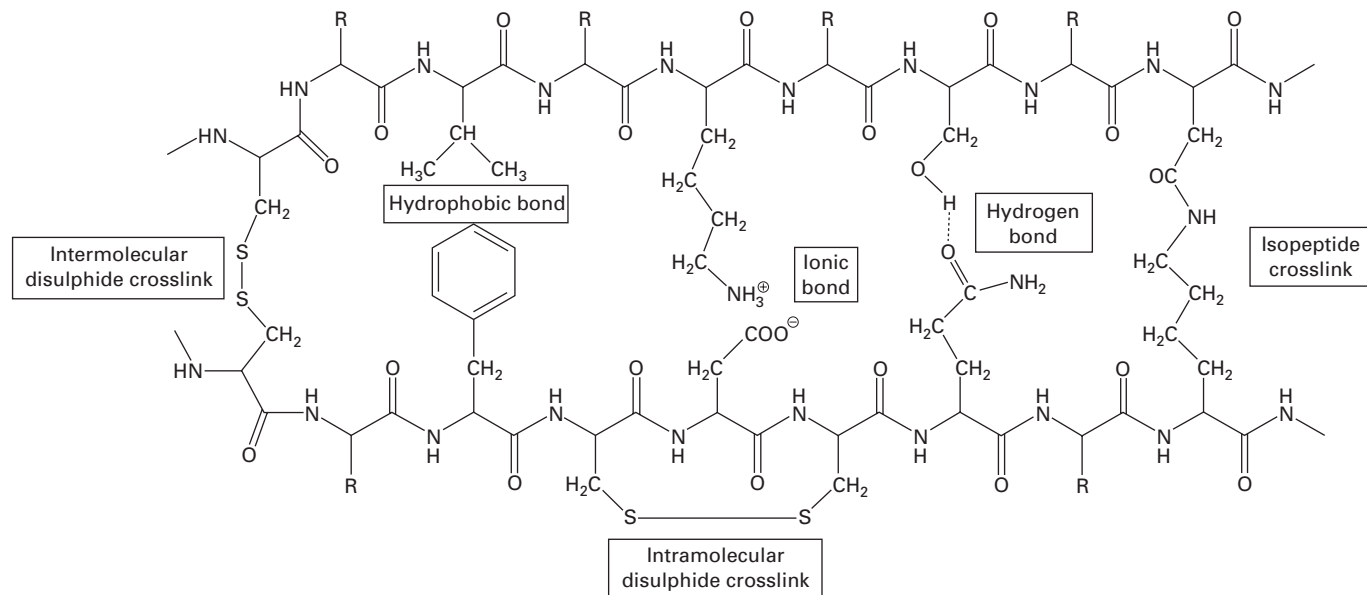
in a matrix which consists largely of high-sulphur proteins, rich in cysteine, proline, serine and threonine, and high-glycine, high-tyrosine proteins which are also rich in serine.

The large number of polar groups present in wool means that it has a strong affinity for water, taking up 34–37% (Speakman and Cooper, 1936; Warburton, 1947; Watt and D'Arcy, 1979) by mass of water on going from completely dry to wet (Fig. 5.2). The water is believed to go mainly into the amorphous matrix, the tightly packed crystalline microfibrils preventing water from entering, although some X-ray evidence has been presented to suggest that a small amount of water is absorbed in the interior of the microfibrils (Watt, 1980).

Of the matrix amino acids, cysteine is particularly important. The thiol side groups in adjacent protein molecules react to form disulphide crosslinks, thus stabilizing the matrix structure. Note that coupling of two cysteine amino acids results in the amino acid cystine. Since chemical analysis of wool is generally done by acid hydrolysis, the concentration of the reduction product, cysteine (also termed 'half-cystine') is generally reported. Besides disulphide crosslinks, lysine and either aspartic or glutamic acid can form covalent isopeptide crosslinks and a number of amino acids can form non-covalent bonds, all of which have a significant influence on the physical properties of the fibre (Feughelman, 1973). All the polar amino acids can form hydrogen bonds, forming both inter- and intramolecular linkages. Carboxyl and amino groups in some of the side chains can form strong electrostatic interactions (ionic bonds, or 'salt linkages') when ionized. Finally amino acids such as leucine and phenylalanine, with hydrophobic side chains, can form hydrophobic bonds between protein molecules. The different types of crosslinks are shown in Fig. 5.3.



5.2 Moisture regain of a wool fibre as a function of relative humidity (adapted from Watt and D'Arcy, 1979).

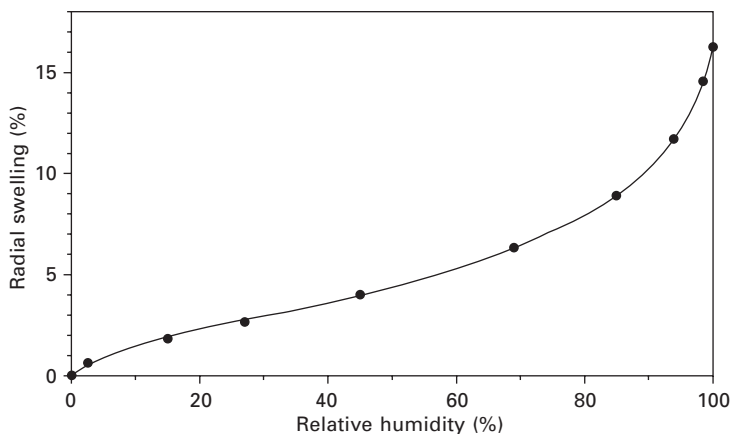


5.3 Types of covalent and non-covalent bonds in wool (Christoe *et al.*, 2003).

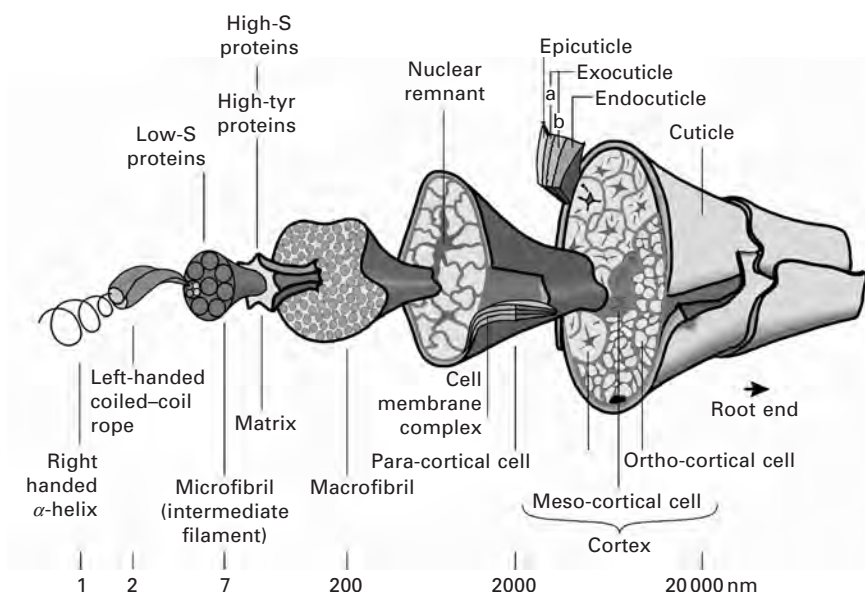
Whilst the hydrophobic bonds play a significant role in the mechanical properties of wet keratin fibers, all the other secondary bonds are disrupted by water. Consequently wool is a material whose properties are highly susceptible to changes in humidity. For instance on going from completely dry to wet, wool swells 16% in the radial direction (Warburton, 1947) (Figure 5.4), shows a decrease of 180 °C in glass transition temperature (Wortmann *et al.*, 1984; Kure *et al.*, 1997), a decrease of 70 °C in melting point temperature (Haly and Snaith, 1967), a decrease of 60% in the initial modulus (Feughelman and Robinson, 1967, 1971; Postle *et al.*, 1988; Huson, 1998) and an increase of 80% in elongation at break (Postle *et al.*, 1988).

5.2.2 Physical

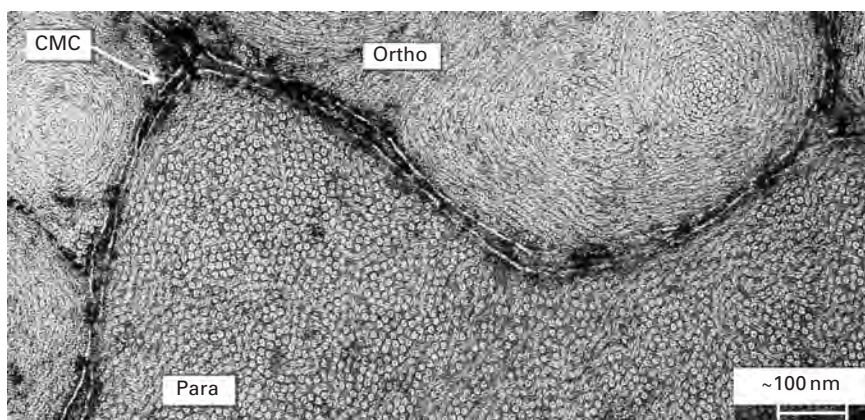
The wool fibre has a complex hierarchical structure which is shown schematically in Fig. 5.5. As already mentioned the low-sulphur proteins can form α -helical structures which assemble into rod-like intermediate filaments (microfibrils). Two right handed α -helices twist together to form a left-handed coiled-coil structure. Four of these double helix structures in turn self assemble to form a protofilament of about 2 nm in diameter and finally eight protofilaments form a ring-type arrangement to generate a microfibril (Wortmann and Zahn, 1994) with a diameter of about 7 nm and a length of at least 1 μm (Rippon, 1992). The crystalline microfibrils are embedded in an amorphous crosslinked matrix (Fig. 5.6), with many microfibrils grouped together to form a macrofibril. Several macrofibrils make up each cortical cell. Cortical cells account for almost 90% of the fibre bulk and are largely responsible for the mechanical properties. The overlapping cells are spindle shaped and approximately 100 μm long and 3–6 μm wide. They are separated



5.4 Radial swelling of a wool fibre as a function of relative humidity (adapted from Huson, 1998, data from Warburton, 1947).



5.5 Schematic diagram of the structure of a fine Merino wool fibre.



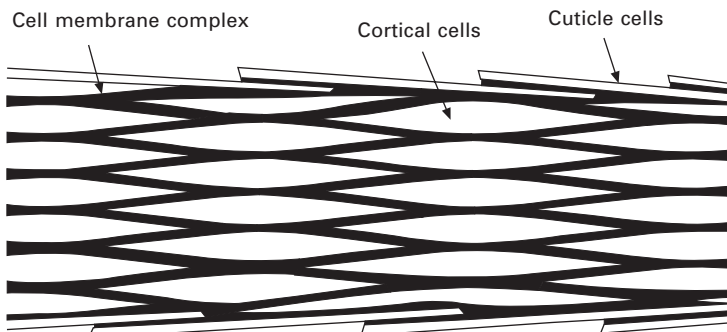
5.6 Transmission electron microscopy (TEM) image of a fine Merino wool fibre cross-section showing the hexagonal packing of aligned intermediate filaments in the paracortex and the whorl-like arrangement in the orthocortex. Separating the cells is the cell membrane complex (CMC). Image courtesy of L.N. Jones, CSIRO.

by the cell membrane complex (CMC) which is approximately 25 nm wide (Leeder, 1986) and shows a central darkly stained region sandwiched between two thin lightly stained regions (Fig. 5.6). Despite being a relatively minor fraction of the total fibre (6% of the mass of the cortex; Leeder, 1986), the CMC is nevertheless of increasing interest (see Bryson *et al.*, 1992, for review)

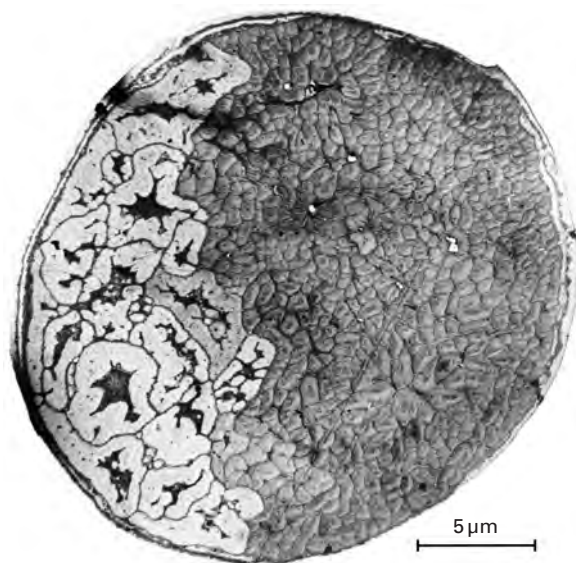
because it is the only continuous phase extending throughout the fibre (Fig. 5.7) and is believed to play an important role in the penetration of water and chemical reagents into wool fibers. Figure 5.7 would suggest that the CMC should play a significant role in the tensile properties of wool fibers; however, failure does not generally follow the CMC boundary, suggesting that the CMC or CMC/cortical cell interface is not the weak link in the biocomposite. The exception to this is when the fibre has been subjected to chemical treatments that damage the CMC (Anderson *et al.*, 1971) or repeated cyclic stress such as in abrasion testing and torsional fatigue deformation (Anderson and Robinson, 1971; Orwin and Thomson, 1975; Allen *et al.*, 1980; Allen and Leeder, 1982; Feldtman *et al.*, 1983; Tester, 1984) or even repeated freeze/thawing (Ito *et al.*, 1984). In these cases failure appears to be at the CMC, resulting in a fibrillated fibre end.

Two types of cortical cell can be distinguished in fine wool; ortho- and paracortical cells. They differ slightly in composition and properties. In cross-section, paracortical cells are more clearly defined, with each cell clearly outlined by the CMC and containing a central region of non-keratineous nuclear remnant material (Fig. 5.8). By contrast, in the orthocortex the non-keratineous material is not concentrated in the centre of the cells, but is distributed as an intermacrofibrillar network, making the macrofibrils more easily distinguished but the cortical cells themselves less clearly delineated. In many coarser fibers a third type, viz. mesocortical cells, can be distinguished, with properties intermediate between paracortical and orthocortical cells. Some coarser fibers also exhibit a medulla, a central core of hollow, air-filled cells whose function appears to be to confer maximum thermal insulation. Somewhat surprisingly the presence of a medulla does not result in any decrease in tensile strength (Mason, 1964).

The paracortex has been shown to have a lower microfibrillar content (Dobb, 1970) and higher levels of cystine (Rippon, 1992) and hence crosslinking. The microfibrils are also more aligned than those in the orthocortex which



5.7 Schematic diagram of a wool fibre longitudinal section showing the outer cuticle cells, spindle-shaped cortical cells and the continuous CMC phase.



5.8 TEM image of an embedded and sectioned Merino wool fibre stained with phosphotungstic acid. Reprinted from Fraser *et al.* (1972), courtesy of Charles C. Thomas Publisher, Ltd, Springfield, Illinois.

tend to form whorls (Fig. 5.6). As a consequence of these differences the orthocortex is generally more readily swollen and more chemically reactive. Differential staining with dyes is the most common method of discriminating ortho/para cells. Paracortical cells have also been shown to have a higher melting point (Wortmann and Deutz, 1998; Huson *et al.*, 2002), increased modulus (Feughelman and Haly, 1960b) and increased wet torsional modulus (Andrews *et al.*, 1962). The increased stiffness of the paracortex was determined experimentally by abrading away the outer paracortical layers of Lincoln wool fibers and is surprising in light of the lower crystallinity of the paracortex. The better alignment of the microfibrils and the increased crosslink density have been suggested to explain the result (Feughelman and Haly, 1960b); however, Collins and Chaikin (1969) questioned the interpretation of the results, proposing that rather than being due to differences between the ortho- and paracortex, the results came about because of damage to the fibers during abrasion. In single fibre studies on the effect of cortical cell type on fibre strength, Thorsen (1958) reported increased resistance to extension (stress at 30% strain) of wet fibers when the proportion of paracortex increased. However, Thompson (1998) found no correlation between paracortical content and intrinsic fibre strength. The picture is equally unclear when staple strength is used as a measure of strength. Orwin *et al.* (1985) reported an increase in strength for Romney wool with a higher proportion of orthocortex, whereas Hansford and Kennedy (1990) found no relationship between the proportions

of ortho-, meso- and paracortex and staple strength of Merino wool from sheep that were on different diets or pregnant/lactating.

In most fine Merino wool the arrangement of orthocortex and paracortex is bilateral, leading to crimp in the fibre with the orthocortex on the outside of the crimp curve. In coarser Merino wool the distribution of cell types is less well defined and in breeds such as Lincoln the arrangement is core/sheath with the core of the fibre being orthocortex.

Surrounding and protecting the assembly of cortical cells are the overlapping cuticle cells. They have a higher level of cystine and hence are more heavily crosslinked but do not contain any microfibrils or other crystalline material (Rippon, 1992). Cuticle cells have a laminar substructure (Fig. 5.5) with different layers containing different levels of cysteine; epicutical (12%), exocuticle-A (35%), exocuticle-B (15%) and endocuticle (3%). On the very outer surface of the fibre there is a unique covalently bound lipid, 18-methyleicosanoic acid (18MEA), which forms a hydrophobic barrier (Christoe *et al.*, 2003). In fine Merino wool, the cuticle is normally one cell thick (approximately $20 \times 30 \times 0.5 \mu\text{m}^3$) (Christoe *et al.*, 2003) and is partially wrapped around the fibre. In contrast, in human hair the cuticle is from five to ten scales thick (Robbins, 1994).

The cuticle cells are believed to be weakly attached to the cortex by the CMC and therefore not to contribute to the tensile properties (Feughelman, 1982); however, there is no definitive proof. Swift (2000) has suggested that in hair fibers, with multiple layers of cuticle, that the cuticle could play a significant role in bending stiffness. Fine Merino fibers have a higher proportion of cuticle, therefore if it was not contributing to the strength of the fibre one might expect these fibers to appear weaker by virtue of a greater overestimation of their effective cross-sectional area. The reality is that the intrinsic strength has been shown to increase as fibers become finer (Thompson, 1998; Huson and Turner, 2001).

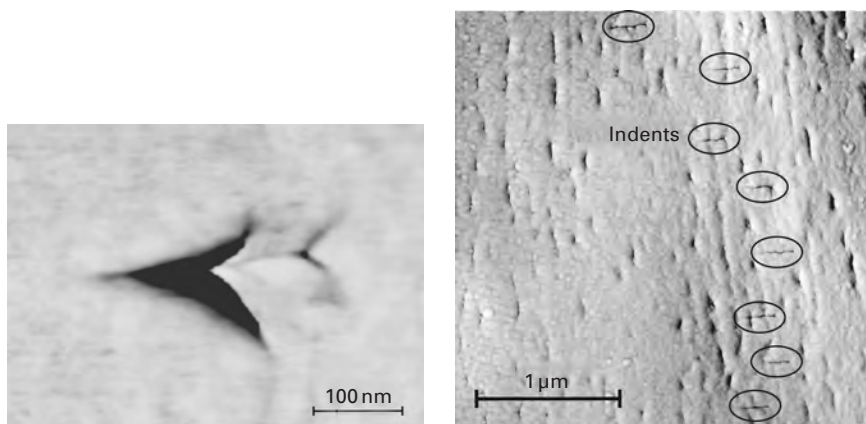
Feughelman and Haly (1960b) showed decreased stress at 15% strain on abrading the outer layers of Lincoln wool fibers. They attributed the result to the removal of the stiffer paracortical cells compared with orthocortical cells but in their experiment they also removed the cuticle and the results could equally be explained by the removal of the stiffer cuticle. Further work is needed in this area.

Scanning probe microscopy (SPM) studies investigating scale height changes proposed increased swelling of the cuticle relative to the fibre as a whole (Phillips *et al.*, 1995), in agreement with torsional measurements on human hair which also suggest that the cuticle takes up more moisture than the whole fibre and has a lower wet torsional modulus (Wolfram and Albrecht, 1985; Feughelman, 1997). More recent studies using SPM suggest that the exocuticle may be as much as five times as stiff as the cortex in air (Parbhu *et al.*, 1999). Another SPM study (Maxwell and Huson, 2005) estimated the

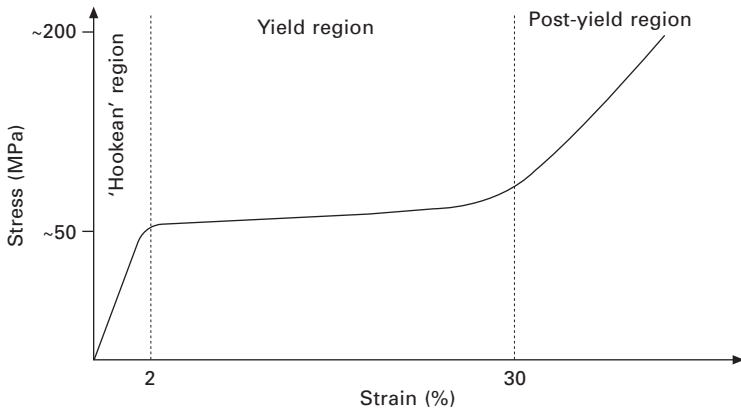
exocuticular stiffness to be about 2 GPa, similar to values for the whole fibre determined via tensile and transverse compression tests (Kawabata *et al.*, 1995). This study also showed the viscoelastic nature of the cuticle. Force curves, in which the silicon probe is pushed into the sample, left indents in the fibre cuticle which closed slowly over a few minutes, leaving narrow slits (Fig. 5.9).

5.3 Models and theories of strength

A stylised stress–strain curve for wool, showing the three regions of mechanical behaviour, is shown in Fig. 5.10. Attempts to model the stress–strain curves of wool go back to 1924 when Shorter (1924) used a model consisting of two springs in series, one of them working in a viscous medium. Later Speakman (1927) interpreted his data on the influence of temperature and moisture on the stress–strain curves of wool by invoking a two-phase model, the forerunner of the crystalline rod embedded in an amorphous matrix model proposed by Feughelman (1959). Feughelman later refined this model to include two regions of thermal and mechanical stability in the crystalline phase, the so-called series-zone model which accounted for the change in slope of the curve in the post-yield region (Feughelman and Haly, 1959, 1960a). The less stable X-zones were deemed to open freely and be responsible for extension in the yield region, whereas the more highly crosslinked Y-zones were more difficult to extend, giving rise to the increased slope in the post-yield region. On the basis of studies on porcupine quills the matrix was deemed to show thixotropic behaviour in water, consistent



5.9 SPM phase images showing an indent left by a silicon tip immediately after a force curve measurement was taken (left) and the indents after about 10 min (right). These images were captured under ambient conditions. Reprinted from Maxwell and Huson (2005), Scanning probe microscopy examination of the surface properties of keratin fibres, with permission from Elsevier.



5.10 A stylised stress-strain curve for wool, showing the Hookean, yield and post-yield regions (x axis has been distorted to show the Hookean region more clearly).

with a gel-sol transition (Feughelman and Druhala, 1975). In more recent times Wortmann and Zahn (1994) offered a structural explanation for the X and Y zones, viz. two distinctly different and well-defined portions of the monomer of the intermediate filament, with disulphide bonds influencing one of the portions and resulting in increased resistance to extension.

In the same year Feughelman proposed a new model, based on the matrix consisting of water together with globular high sulphur protein (Feughelman, 1994). The post-yield region was explained in terms of the intermediate filaments coming together upon extension of the fibre and jamming the globular protein once the more mobile water had moved out of the space between the intermediate filaments. This seems the least likely of the proposed models.

Concurrent with these developments Chapman (1969a) proposed a model, later refined and developed by Chapman, Hearle and others (Hearle and Chapman, 1968a,b; Chapman and Hearle, 1970, 1971; Hearle *et al.*, 1971; Hearle and Susutoglu, 1985), in which the intermediate filaments show a slight yielding at 2% strain but then a constant stress as the α -helix unfolds to form the extended beta structure. The matrix is modelled as a highly crosslinked rubber and accounts for the increased stiffness in the post-yield region.

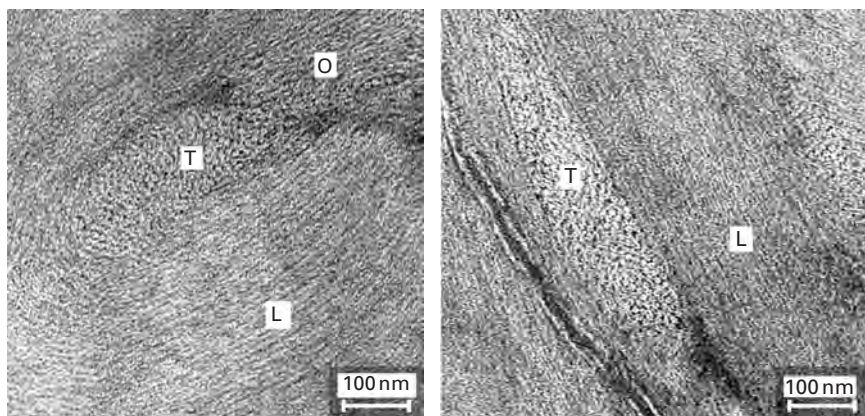
All the models propose that the Hookean region results primarily from stretching of the α -helix in the intermediate filaments and the yield region from the unfolding of the α -helix. Where they differ is in the explanation of the response of the fibre in the post-yield region and the properties of the matrix. It is worth noting that the matrix properties used in Feughelman's series zone model are based on stress-strain curves for porcupine quill, measured in a direction at right angles to the direction of growth. The assumption is that, like wool fibers, the intermediate filaments are parallel to the growth direction and therefore would not be expected to contribute to the

lateral tensile properties. More recent studies (Maxwell, 2002) confirmed the lateral tensile properties of porcupine quill; however, transmission electron microscope (TEM) images of the cross-section of a quill (Fig. 5.11) showed that the intermediate filaments are oriented in all directions, not just parallel to the direction of growth. Consequently, lateral tensile tests will not be a measure of the matrix properties alone. Furthermore TEM and SPM studies revealed that the structure of the quill is complex, showing features quite different from those observed in wool fibre cross-sections. Hence, the validity of using porcupine quill to explain the deformation of wool fibers during mechanical stretching needs to be questioned.

More detail on this topic can be obtained from the book by Feughelman (1997), the review article by Chapman (1969b) and the chapter (Hearle, 2002) and recent reviews (Hearle, 2000, 2007) by Hearle. In light of the emergence of new science technologies that provide in-depth data on fibre hierarchical structure and morphology, subcellular properties, protein composition and structure, scientists are starting to think about more comprehensive computational modelling to understand and then to predict quantitatively the relation between the fibre structure and fibre properties (Hearle, 2003; Bryson *et al.*, 2005).

5.4 Methods of measurement

When measuring the tensile properties of wool fibers two major issues need to be addressed: in what form (single fibre, bundle, staple, yarn or fabric) should we test the wool and how do we deal with the non-uniform diameter of the fibre? Wool fibers start life on a sheep, nicely aligned and clumped



5.11 TEM images of a porcupine quill cross-section showing that the intermediate filaments have been sectioned transversely (T), longitudinally (L) and obliquely (O), indicating they do not run exclusively parallel to the direction of quill growth (Maxwell, 2002).

together into staples. During scouring to remove the wool grease, they become entangled. They are subsequently disentangled and aligned during carding and combing before spinning into yarn. Finally the yarn is woven or knitted into fabric. All stages along this pipeline are open to testing; however, in this section we have concentrated on single fibre testing as the only true measure of the fibre properties. Briefer mention is made of the testing of staple, yarn and aligned bundles.

5.4.1 Staple

For wool, strength is often measured by testing whole staples. This is generally done with a gauge length of 50–60 mm at a speed of 300 mm/s using either a standard tensile tester or a dedicated ATLAS instrument (Australian Wool Testing Authority). The peak force is normalized by the linear density of the staple to give a result in N/ktex. Typical values are between 15 and 55 N/ktex with wool below 30 N/ktex referred to as ‘tender’ and discounted at auction. Staple strength does not correlate well with the average strength of individual fibers (Thompson *et al.*, 1995; Peterson *et al.*, 1998; Thompson, 1998); rather it is a measure of the reduced number and diameter of fibers at a distinct point in the staple and the degree of alignment of individual fibers in the staple (Schlink *et al.*, 2000). It nevertheless remains commercially very important because it is used (along with measures of staple length, the proportion of mid-breaks and mean diameter) in prediction equations such as TEAM (1988) which enable exporters and topmakers to objectively estimate the average length of fibre in the wool top and the amount of short fibers that are removed during processing.

5.4.2 Yarn

Yarn strength can readily be measured on a standard tensile tester, but because of the commercial importance it is routinely tested using an automated dedicated tester such as the Tensorapid (Uster Technologies AG) or Statimat (Textechno Herbert Stein GmbH & Co. KG). Most of these tests involve long gauge lengths where the gauge length is much greater than the fibre length. The consequence of this is that the yarn strength is heavily dependent on the structure and integrity of the yarn. Twist in the yarn is critical to developing transverse pressure and hence axial friction which allows the fibers to be gripped. At low twist levels (low helix angle) fibers mostly pull out of the assembly leading to low strength. As the helix angle increases, strength increases to a maximum before dropping again at high levels of twist. Whilst extremely important commercially, yarn strength is more about the yarn structure than the material properties of the wool and hence is largely outside of the scope of this chapter.

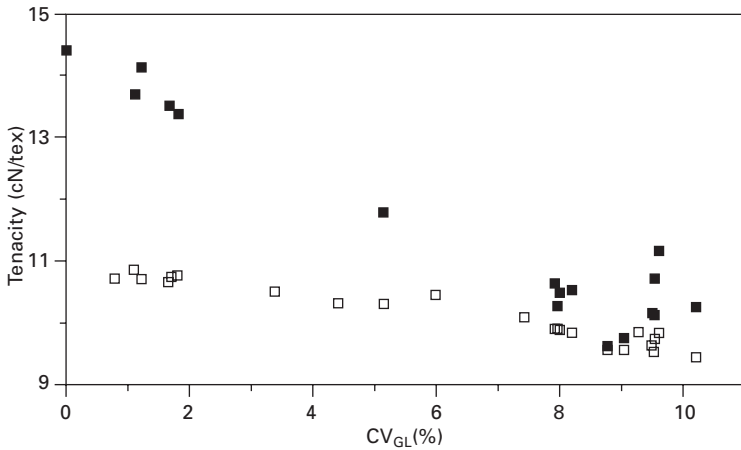
5.4.3 Fibre bundles

Although single fibre tests are readily done on a standard tensile tester, many fibers must be tested in order to get a meaningful average. An alternative method is to test bundles of fibers. Whilst much quicker, the method introduces additional complications in bundle preparation, particularly in crimped fibers such as wool (Yang *et al.*, 1996). Bundles can be prepared and tested on a standard tensile tester or a dedicated bundle tester such as the Sirolan-Tensor developed by CSIRO. Gauge lengths are always short, typically 0–5 mm. The shorter the gauge length the less accurate the strain data, with the data becoming completely meaningless at a nominal zero gauge length.

The mean strength of a fibre bundle is expected to be less than the sum of the strengths of individual fibers constituting the bundle. This is because individual fibers in the bundle have slightly different lengths and also break at different strains (Yang *et al.*, 1996). Thus when the peak load in the bundle curve occurs, some fibers may have already broken and some will not yet have reached their maximum load. The different fibre lengths generally arise because of different levels of crimp in the fibre (Yang *et al.*, 1996), even though the bundle test has been designed to straighten all the fibers prior to clamping. In spite of these shortcomings bundle strength measurements are nevertheless still very useful for comparative studies, e.g. the effect of dyeing time and temperature on the strength of wool.

The relationship between average single fibre strength and bundle strength has been studied by a number of workers and models have been developed in an attempt to predict tensile properties of bundles from single fibre properties and vice versa (Platt *et al.*, 1952; Nachane and Iyer, 1980; Sasser *et al.*, 1991; Frydrych, 1995; Huson and Turner, 2001; Yu *et al.*, 2003). Huson and Maxwell (2004) used experimental single fibre stress–strain curves to simulate a bundle test and showed that bundle tenacity is highly dependent on the variations in strain at break (as measured by the coefficient of variation, CV_{SB}) of the individual fibers in the bundle as well as the variation in gauge lengths (CV_{GL}) within the fibre bundle (Fig. 5.12). The CV_{GL} is a measure of how well the bundle has been prepared. For the particular wool fibers studied, with a variation in strain at break of 16.7%, this resulted in a decrease in tenacity relative to average fibre tenacity of about 25% for perfectly prepared bundles ($CV_{GL} = 0$). The effect of a less than perfectly prepared bundle with a broad distribution of fibre lengths (increased CV_{GL}) was a further small drop in tenacity. Results from a range of individual sheep show that CV_{SB} is quite varied, typically varying from 15 to 30% for sheep on a live weight maintenance diet. If this variability is also present in samples of top then it is not expected that bundle tenacity would be a good measure of average intrinsic fibre strength.

As expected, the initial slope of the bundle stress–strain curve was insensitive



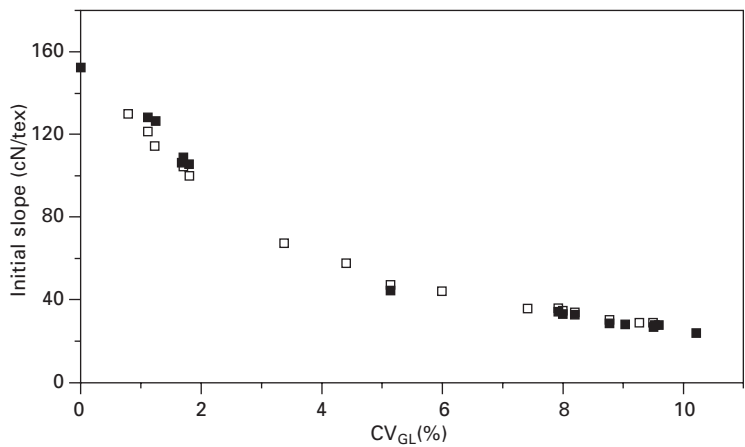
5.12 Effect of gauge length distribution (CV_{GL}) on the tenacity of simulated bundle tensile curves using experimental force–extension data from single fibres. Results are shown for a typical distribution of strain at break values, $CV_{SB} = 16.7\%$ (□) and for $CV_{SB} = 0\%$ (■) (Huson and Maxwell, 2004).

to variation in individual fibre breaking strain but highly dependent on gauge length distribution (Fig. 5.13). The important point to note is that preparing a bundle of fibers consistently is not easy, thus CV_{GL} will vary making the initial slope a very poor measure of fibre modulus. It is much more likely to be a measure of how well the bundle has been prepared.

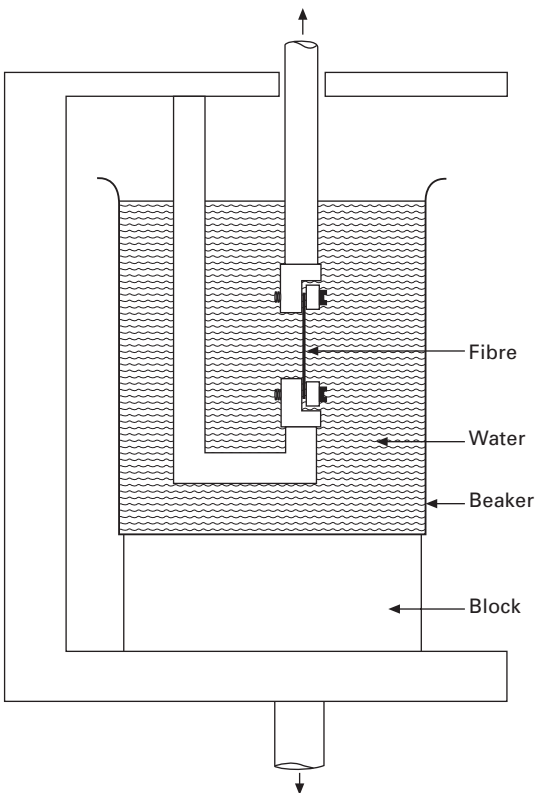
5.4.4 Single fibers

It is a relatively simple matter to measure the force–extension characteristics of a single wool fibre provided the tensile tester has a sensitive enough load cell (1–5 N). If measurements are required in water, a jig can be built (Fig. 5.14) that allows the clamped fibre to be immersed. Any part of the assembly that is withdrawn from the water will result in a reduction in buoyancy forces on the load cell. Thus either the water level needs to be continually adjusted to keep the buoyancy force constant, or care needs to be taken that the part being withdrawn is small and uniform. In the latter case a correction can easily be made if the change in buoyancy force is significant compared with the strength of the fibre. Typical force–extension curves for a wool fibre in air and water are shown in Fig. 5.15.

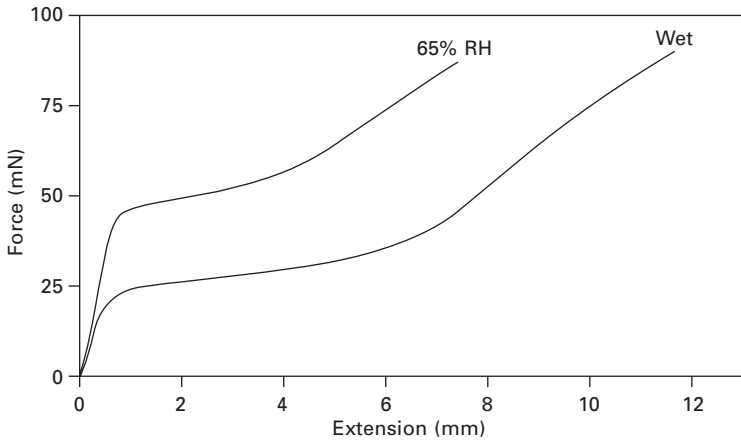
In order to convert the curves to stress–strain curves we need to divide the force by either cross-sectional area or linear density and the extension by the gauge length. The latter is easy, but wool fibers are not uniform along their length in either diameter or cross-sectional shape so normalizing the force is problematic. Figure 5.16 shows that the diameter can easily vary



5.13 Effect of gauge length distribution (CV_{GL}) on the initial slope of simulated bundle tensile curves using experimental force–extension data from single fibres. Results are shown for a typical distribution of strain at break values, $CV_{SB} = 16.7\%$ ($\square$) and for $CV_{SB} = 0\%$ ($\blacksquare$) (Huson and Maxwell, 2004).



5.14 Jig to allow tensile tests to be carried out in water using a standard upright tensile tester.



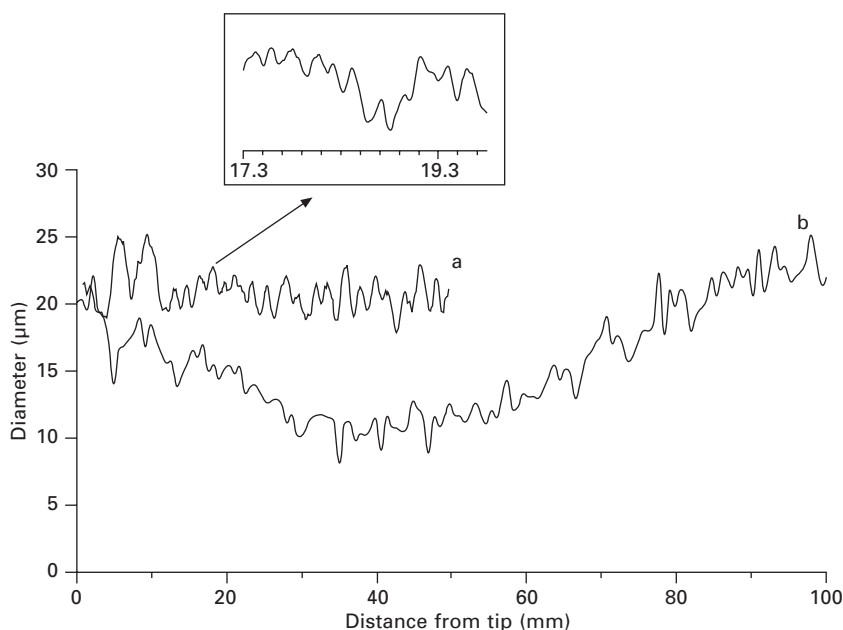
5.15 Typical force–extension curves for Merino wool fibres of 21 μm diameter and 20 mm gauge length, tested in air and water.

by several micrometres over a 20 mm gauge length. Even when wool is grown under controlled conditions by keeping the sheep indoors in a pen and maintaining it on a constant diet, there are variations in diameter of a few micrometres along the length. Interestingly if we zoom in on the diameter profile (Fig. 5.16, inset) then fine scale waviness is evident with a periodicity of about 300 μm . This is roughly equal to a single day's growth and has been attributed to the animal's individual and daily biological cycle (circadian rhythm) (Wortmann *et al.*, 2000). Because of this non-uniformity, workers (Gourdie *et al.*, 1992; Thompson, 1998; Huson and Turner, 2001; Huson and Maxwell, 2004) often measure the diameter of the fibre after failure, generally after allowing the deformed fibre to recovery in water.

As an alternative to measuring the diameter, the linear density can be measured on an instrument such as the Vibroskop (Lenzing Instruments), allowing force data to be converted to specific stress. The vibroscope technique involves allowing a string or fibre, of linear density, m , to vibrate at its natural frequency, F , by varying the load, T , and/or length, L , of the fibre. Under these circumstances,

$$F = \frac{1}{2L} \sqrt{\frac{T}{m}} (1 + a) \quad 5.1$$

where a is a correction factor involving the load as well as the shape, length and elastic modulus (Montgomery, 1953; Voong and Montgomery, 1953; Morton and Hearle, 1993; Titz and Hunter, 2004) of the material. For many fibers a is less than 3% (Morton and Hearle, 1993) and can be neglected. However, the vibrating string theory was developed for uniform round fibers and as we know wool fibers are neither round nor uniform along their length.



5.16 Diameter profiles of Merino wool fibres, (a) grown under controlled conditions (pen-grown) and (b) field grown showing the effects of nutrition and the environment. Measurements acquired using a SIFAN (BSC Electronics Pty. Ltd).

In a study looking at the effect of shape on the vibrational characteristics of vocal ligaments, Titze and Hunter (2004) showed that the non-uniform cross-sectional area of the vibrating element resulted in an increase in the normal mode frequencies of the order of 30%, thus non-uniformity in a wool fibre will lead to an underestimation of the linear density.

There are no clear guidelines on how to treat single fibre tensile data; however, the most sensible seems to be to use the cross-sectional area at the position of break to normalize the data (Viney, 2002). This position is likely to, but not required to, coincide with the minimum initial cross-sectional area of the fibre. Whatever method is used, however, needs to be used consistently for all samples that are to be compared and thought needs to go into the consequences of the non-uniformity of the fibre.

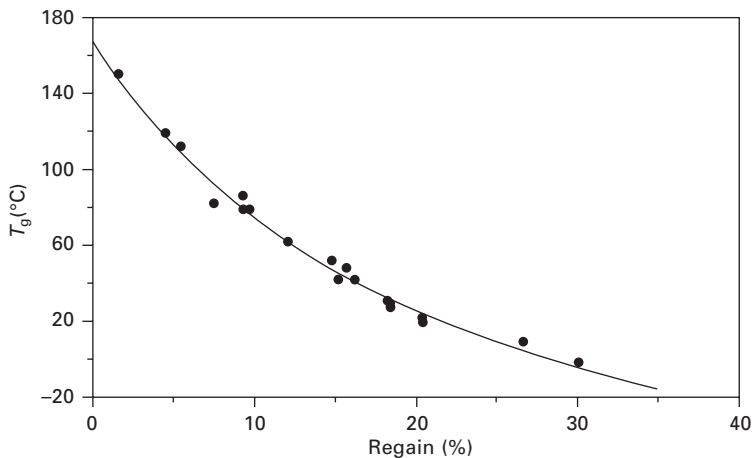
5.5 Tensile failure

There are a number of parameters such as specimen shape and size, rate and temperature of test and degradation in service that affect the tensile failure properties of all polymeric materials. For a natural material such as wool, which has the ability to absorb large quantities of water, the relative humidity

of the environment is also of utmost importance. During its lifetime wool needs to perform under a range of different conditions. During scouring it is wet and deforms slowly, whereas during early stage processing (carding and combing) deformation is rapid and the fibre is dry. During wear, fibers undergo torsional/abrasive deformation, mostly in a dry state but occasionally wet during laundering. During formation of the fibre and for many applications it is exposed to sunlight.

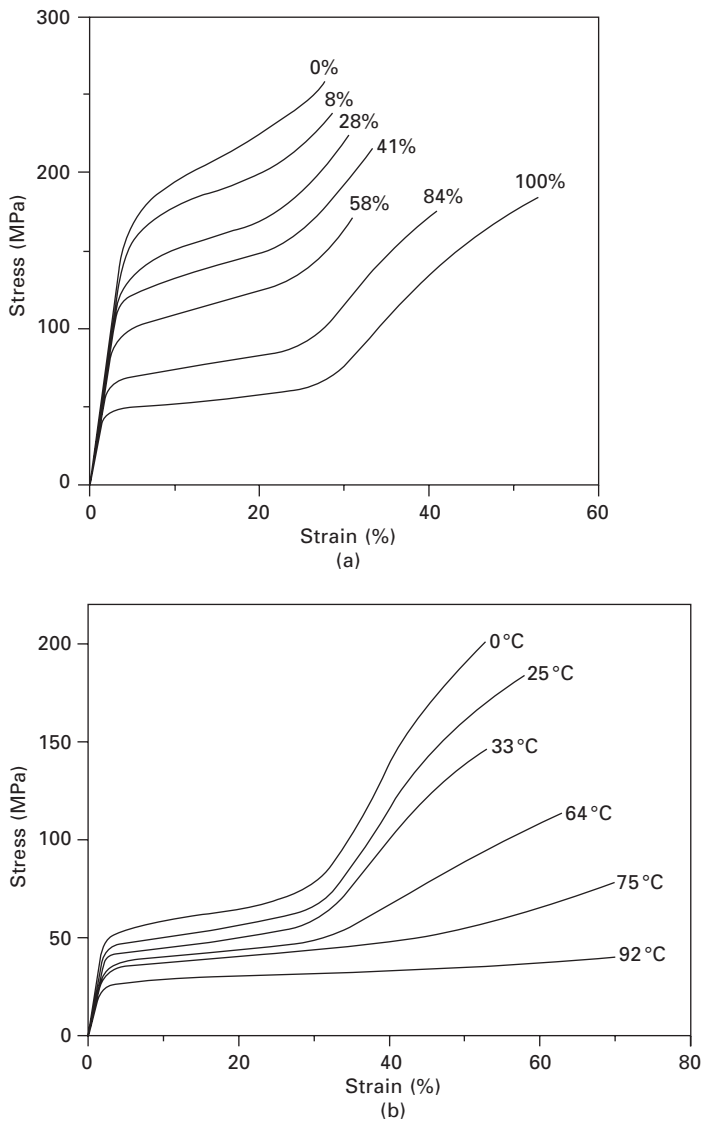
5.5.1 Effect of moisture, temperature and rate of test

The ease with which molecules can rotate about their backbone, and through this allow effective cooperative segmental motion, has a dramatic affect on the tensile properties of the material. The more mobility the molecules possess and the more time they have for cooperative segmental motion, the less stiff the material will be. Some polymers, such as rubber, are naturally very mobile at room temperature. Others, such as PVC, are stiff at room temperature but can be made flexible by the addition of a plasticizer which acts as an internal lubricant. For wool, water is an excellent plasticizer, dramatically altering the physical properties of the fibre. The best indicator of molecular mobility is the glass transition temperature, T_g . If the T_g is below room temperature then the material exhibits rubbery behaviour and if the T_g is above room temperature then the material is more glass-like and brittle. For wool fibers the T_g is about 60°C under standard conditions but changes dramatically as the fibre dries out or takes up more moisture in response to changes in the environment (Fig. 5.17). This results in a decrease in strain at break and

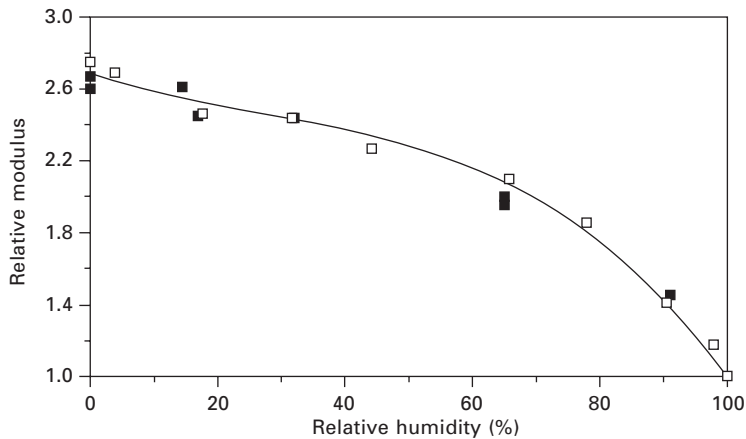


5.17 Glass transition temperature of wool as a function of moisture regain. The curve is a fit of the Fox equation (adapted from Kure *et al.*, 1997).

an increase in stress at break as the fibre goes from wet to completely dry (Fig. 5.18a). The modulus also increases by about three times as the fibre dries (Huson, 1998) (Fig. 5.19). The mobility can similarly be increased or decreased by altering the temperature (Fig. 5.18b).



5.18 Stress–strain curves of typical wool fibres tested (a) at different relative humidities and (b) in water at different temperatures (adapted from Speakman, 1927).

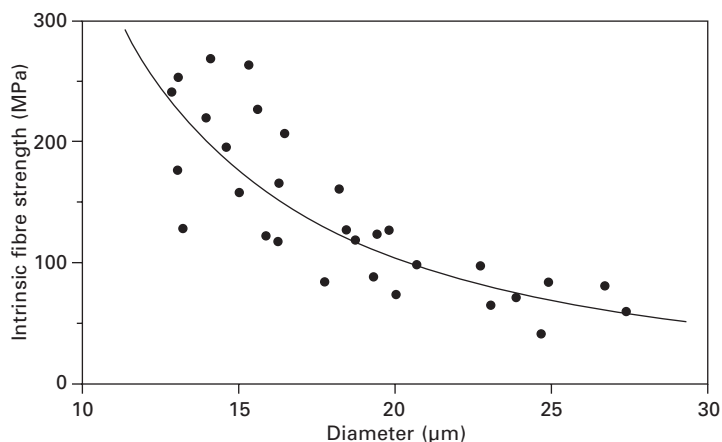


5.19 Variation of the relative modulus of a wool fibre as a function of relative humidity (figure adapted from Huson, 1998, data from Feughelman and Robinson, 1971 (■) and Feughelman and Robinson, 1967 (□)).

5.5.2 Effect of diameter and gauge length

Wool fibers vary naturally in diameter, both between fibers and along the length of individual fibers (Fig. 5.16). It has been shown (Collins and Chaikin, 1965, 1968, 1969, 1971; Shah and Whiteley, 1966), both experimentally and theoretically, that along-fibre variability results in an increase in the yield slope and a decrease in elongation at break. A decrease in breaking stress is also reported but this is based on mean cross-sectional area. It is difficult to see how changes in fibre dimensions along the fibre can lead to a change in strength, provided that the force to break is normalized by the cross-sectional area at the point of break (Thompson, 1998). Using this method Gourdie *et al.* (1992) found no evidence to suggest that intrinsic strength was influenced by along-fibre variability.

When strength is plotted against diameter, an unailing result for all wools tested has been the decrease in intrinsic strength for larger diameter fibers (Fig. 5.20) (Huson and Turner, 2001). This occurs both within sheep and also across sheep when sheep averages are considered. It is a result that is consistent with other workers (Gourdie *et al.*, 1992; Thompson, 1998) who have used the diameter at break to normalize the force data, but in contrast to workers (Burgmann, 1959; Shah and Whiteley, 1966; Collins and Chaikin, 1968) who have used some average measure of diameter or linear density. The structural features responsible for this phenomenon of decreased intrinsic strength with increased diameter are still unclear, but the possibility of errors in the measurement of diameter being responsible have been considered and discounted (Huson and Turner, 2001). This result holds for fibers tested under



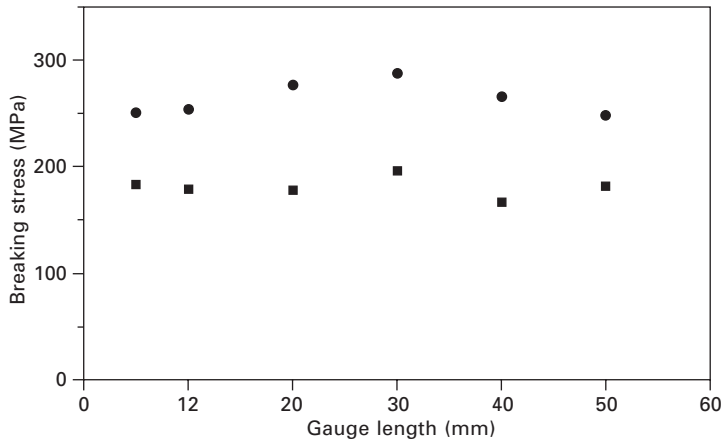
5.20 Intrinsic strength of single wool fibres in water, as a function of the diameter at the break.

ambient conditions and in water. An obvious explanation is that failure is occurring by a flaw mechanism; however, this is not believed to be the case as discussed below.

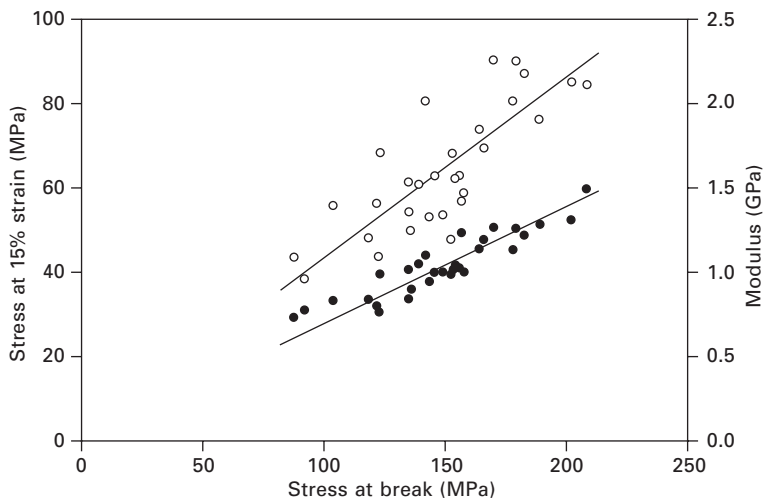
For many materials decreasing the size of the test piece results in an increase in strength (Chawla, 2002). This size effect is generally ascribed to a reduction in the probability of finding a flaw or critical defect and is commonly analysed by applying Weibull statistics to the strength data (Chawla, 2002). A good example of this behaviour is seen in brittle glass fibers; however, the use of the Weibull analysis for partially ductile fibers such as silk has also been shown to be appropriate (Viney, 2002).

For wool fibers it has been suggested that failure is due to the presence of surface flaws or defects within the fibre (Andrews, 1964; Mason, 1964) and non-uniformities in diameter along the fibre length (Shah and Whiteley, 1966; Collins and Chaikin, 1968). Although this may explain the diameter effect seen in Fig. 5.20, it is at odds with the lack of sensitivity of breaking stress to gauge length (Fig. 5.21) or the good correlation of breaking stress with non-failure properties such as modulus and stress at 15% strain (Thompson, 1998) (Fig. 5.22). Furthermore the strain at break does not decrease as the diameter increases, nor does it correlate with breaking stress. Fibers which failed prematurely at flaws would be expected to show lower breaking strain; however, this is not the case and in fact comparison of a weak fibre with a fibre more than three times stronger (Fig. 5.23) shows a remarkable similarity in the shapes of the two stress–strain curves.

It has also been shown that introducing notches into wool fibers with a razor blade had surprisingly little effect on the force–extension behaviour, right up to the breaking point (Mason, 1964). When referred to the proportion of cross-sectional area remaining after the notch was cut in the side of the

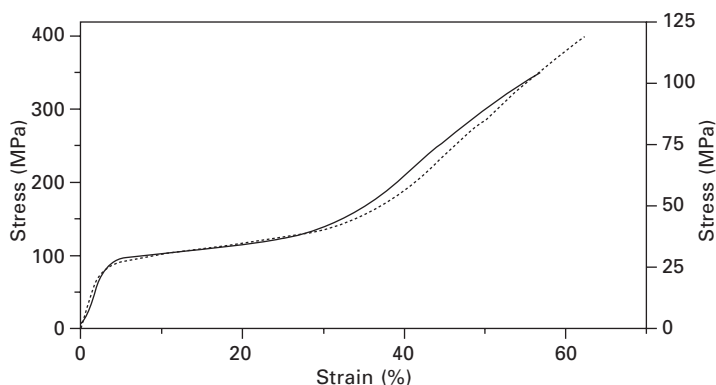


5.21 Effect of gauge length on breaking stress of Lincoln wool fibres tested in air (●) and water (■).



5.22 Data showing the good correlation between intrinsic fibre strength and non-failure properties such as modulus (○) and stress at 15% strain (●).

fibre, the tensile strength actually showed an increase with increasing depth of cut. Although the authors argue that this can be explained if it is assumed that a normal, unmodified wool fibre fractures by crack-propagation from relatively few naturally occurring flaws, it could equally be explained on the basis of wool being a tough biocomposite that is not readily affected by flaws or defects. All of this taken together strongly suggests that a flaw mechanism is not operating but rather that the variation in strength is due to changes in the structure (amino acid content, cortical cell size, crystallinity, density or

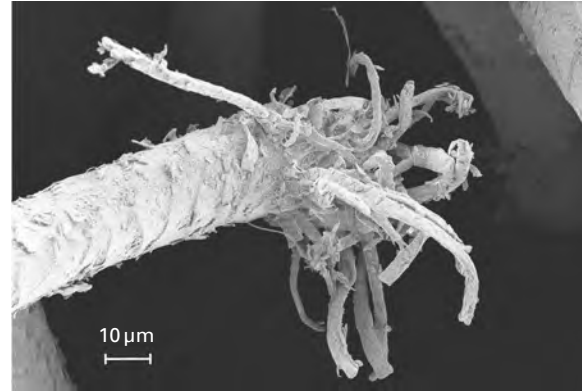
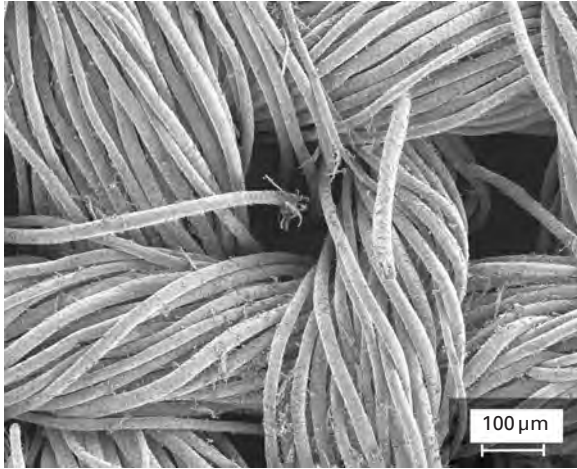


5.23 Stress-strain curves showing the remarkable similarity in the shapes of the curves for a strong (broken curve, left axis) and a weak (solid curve, right axis) fibre tested in water.

distribution of crosslinks, etc.) of the fibre. Attempts to elucidate the structure property relationship have so far been unsuccessful (Thompson, 1998), owing in part to the variability both between and along fibers, necessitating the measurement of structure at the fibre or parts of fibre level.

5.5.3 Effect of torsion and abrasion

During wear, fibers in a fabric are subjected to the repetitive application of a range of different forces, generally resulting in low levels of strain, but eventually resulting in fatigue failure of the fibers. Many attempts have been made to simulate wear in the laboratory, using a variety of abrasion and flex fatigue tests (Morton and Hearle, 1993). Whilst agreement with wear trials is only tenuous, abrasion tests remain popular and the belief is that torsional fatigue plays an important role in the failure mechanism. These repetitive low level strains have been shown to result in failure at the CMC (Orwin and Thomson, 1975; Tester, 1984), resulting in fibrillation of fibre ends (Anderson and Robinson, 1971) (Fig. 5.24). Others have shown that subjecting wool to chemical treatments (such as sodium dodecyl benzene sulphonate or the proteolytic enzyme trypsin) that damage the CMC results in a dramatic decrease in abrasion resistance (Anderson *et al.*, 1971). Attempts to modify the CMC showed that treatment with *o*-chlorophenol (Anderson *et al.*, 1971) and swelling solvents such as ethanol (Körner, 1990), formic acid (Feldtman and Leeder, 1984) and *n*-propanol (Feldtman and Leeder, 1984) led to significant improvements in abrasion resistance. The mechanism by which this improvement is gained is not yet known but the extraction of lipids and proteins from the cell membrane is believed to play a role (Feldtman and Leeder, 1984; Körner, 1990). The treatment did not, however, lead to



5.24 Scanning electron micrograph of a piece of wool fabric (left) after failure by abrasion and a close up of the fibrillated fibre end (right).

any change in tensile properties as measured by wet bundle strength tests (Körner, 1990) or dry fabric tensile tests (Feldtman and Leeder, 1984).

5.5.4 Effect of crimp

Several workers (Barach and Rainard, 1950; Evans, 1954; Dusenbury and Wakelin, 1958; Gullbrandson, 1958; Collins and Chaikin, 1968; Ross, 1971; Bendit, 1980) have investigated the effects of both natural and artificial crimp on the tensile properties of wool. A number of these (Evans, 1954; Dusenbury and Wakelin, 1958; Collins and Chaikin, 1968; Bendit, 1980) showed that the modulus or Hookean slope decreases with increasing levels of crimp. Evans (1954) interpreted the results by suggesting that the inside of the crimp is under greater tension than the outside. Barach and Rainard (1950), as well as Ross (1971), crimped wool artificially and obtained large reductions in tensile strength, modulus and elongation at break. They ascribed the weaknesses to stress concentration effects at bends in the fibers. However, Huson and Turner (2001) showed no significant correlation between fibre strength and crimp or curvature in a study involving wool from 11 different bloodlines and also separated out the effects of curvature and setting (Huson, 1992).

5.5.5 Effect of chemical processing

The most common chemical treatment of wool is to dye it. This usually involves holding the wool at the boil for prolonged periods (up to two hours). These conditions almost always result in a reduction in strength of the wool, particularly if the pH of the dyebath is outside the isoelectric region of the wool (ca. pH 4–5; Harrigan and Rippon, 1988; Lewis, 1990; Huson, 1992). The loss of strength has been ascribed to extraction of soluble proteins from the cell membrane complex (Baumann, 1979), a breakdown of cystine linkages to form thiol groups (Peryman, 1954; Römer, 1979; Römer *et al.*, 1980; Maclaren and Milligan, 1981b; Cook and Fleischfresser, 1990) and, under severe conditions, hydrolysis of peptides to form amino groups (Römer, 1979; Römer *et al.*, 1980; Maclaren and Milligan, 1981b). By contrast, heating wool dry yielded no apparent change in tensile properties of fabrics after treatment for four hours at 160 °C in air or nitrogen (Schmidt *et al.*, 2002) or any evidence of peptide bond breakdown after 20 days at 110 °C in air (Dhingra *et al.*, 1989).

Several authors (Feughelman, 1963, 1997; Cook and Fleischfresser, 1990) have shown that treatments which cause a decrease in the disulphide content, result in fibers and yarns with reduced modulus, stress at 15% strain and stress at break along with an increase in breaking strain. This is in contrast to fibers with a natural variation in sulphur where the picture is less clear. Whitely and McMahon (1965) showed that within flock, a

decrease in sulphur content brought about a decrease in intrinsic strength of wool fibers; however, no such relationship was found between breeds. Wool that has a reduced tensile strength due to an inadequate supply of copper (Purser, 1979; Gillespie, 1983), as well as 'tender' wools (Orwin *et al.*, 1980; Huson and Turner, 2001) have been shown to have less ultra-high-sulphur proteins or half-cystine. In contrast, Feughelman and Reis (1967) found no significant differences in the tensile properties of wool fibers where the sulphur content was increased from 3.1% to 4.2% by the abomasal infusion of methionine.

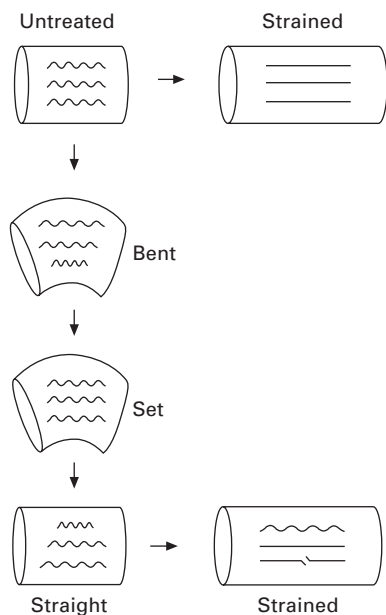
Setting is also thought to be implicated in strength losses associated with dyeing. During dyeing, at temperatures above 70 °C, chemical stress relaxation via the thiol–disulphide interchange reaction results in strained wool fibers being set in a new configuration. Thus fibers in a curved configuration as a result of twisting in a yarn, or weave crimp become permanently set in this curved state during dyeing.

Gullbrandson (1958) has suggested that all of the reduction in fibre tenacity resulting from dyeing is due to setting of bends (i.e. curvature) in the fibers. However, in a more detailed study, Huson (1992) showed a 10% decrease in strength for straight fibers and a 20% decrease in strength for curved fibers (Table 5.2). A mechanism was proposed to explain this additional strength loss in terms of the distribution of covalent bonds in the wool and the homogeneous transferral of stresses onto the molecular chains (Fig. 5.25).

Scanning electron microscopy lent support to this theory, showing the fracture initiating at the inside edge of a permanently set helix (Fig. 5.26a). The fracture lines propagate radially out from the point of origin, converge slightly and then terminate in a rougher region in the opposite half of the fibre. This rougher region shows the distinctive V- or U-shaped ramps characteristic of tear fracture (Engel *et al.*, 1981). The open end of the V-shaped ramps point in the direction of the fracture propagation. A close-up of the origin of the fracture (Fig. 5.26b) shows that the fracture initiates at the edge of the cortex rather than in the cuticle. The absence of any fibrils greater than 1 μm in length indicates an essentially brittle failure. The change in mode of

Table 5.2 Tensile properties of fibres set at the boil for 10 min (permanent set) or set in room temperature water for 5 min (temporary set). Fibres tested at 65% relative humidity (Huson, 1992)

Specimen treatment		Breaking stress (MPa)	Breaking strain (%)	Breaking energy (MPa)	Modulus (MPa)
Set	Shape				
Permanent	Straight	175	40.5	48.8	4120
Permanent	Helix	158	37.4	41.8	2280
Temporary	Straight	191	43.7	56.1	4270
Temporary	Helix	193	43.5	55.9	2370



5.25 Schematic diagram showing the effect of setting and curvature on the transferral of stresses onto the molecular chains and the subsequent effect on the tensile failure properties of wool fibres (adapted from Huson, 1992).

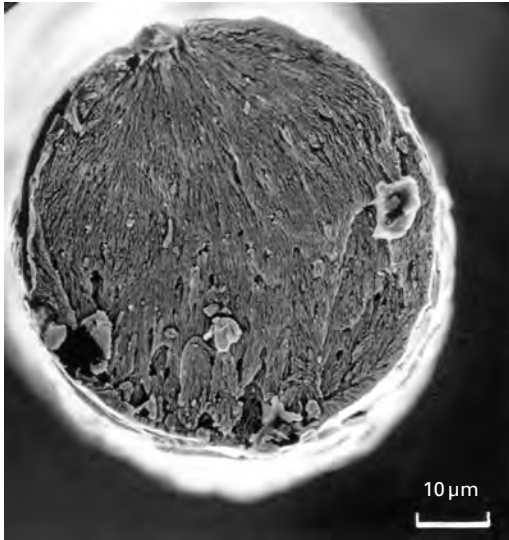
fracture probably occurs as a result of the decrease in the rate of propagation of the fracture as stresses are relieved.

Modulus values were shown to be relatively unaffected by setting operations but highly sensitive to the degree of curvature in the fibre (Table 5.2). The decreased stiffness of the curved fibers is attributed to the disruption of a stable network of secondary bonds between the polypeptide chains and suggests that secondary bonds play a dominant role at low strain levels (<1.5%).

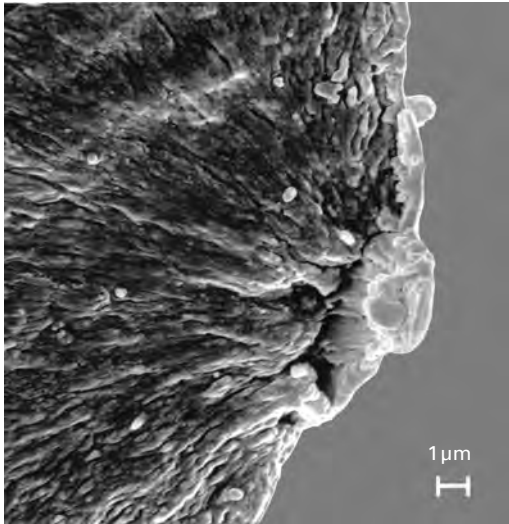
5.5.6 Effect of UV light

When wool is exposed to sunlight for extended periods it is prone to yellowing and eventually loss of strength or tendering. The yellowing of wool in particular is a serious commercial shortcoming compared with cotton and synthetic fibers, particularly when photostable brilliant whites and bright pastel shades are required. For this reason considerable effort has gone into understanding the factors that affect photoyellowing, including oxidative bleaching, fluorescent whitening and the presence of moisture (Maclaren and Milligan, 1981a; Simpson, 1999; Millington, 2006).

On the sheep's back the tip is more prone to weathering than the root end of the fibre, leading to effects such as increased swelling and tippy dyeing



(a)



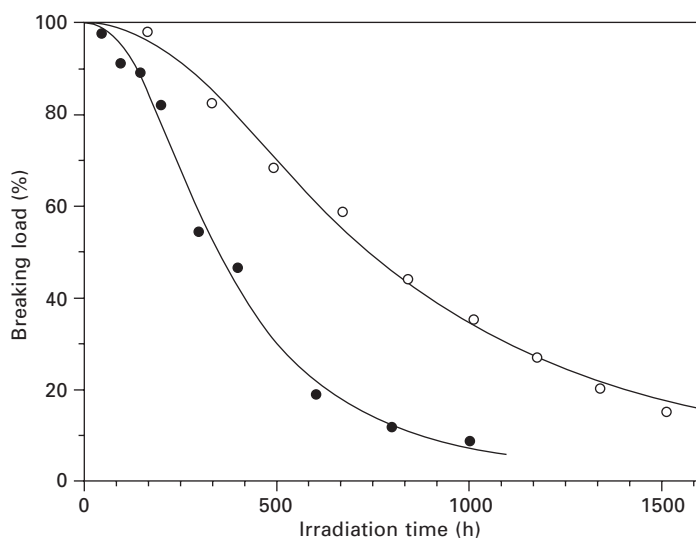
(b)

5.26 Scanning electron micrograph of the fracture surface of a wool fibre permanently set into a helical configuration: (a) part of the helix showing the point of origin of the fracture occurring at the inside edge of the helix; (b) close-up of the fracture origin (adapted from Huson, 1992).

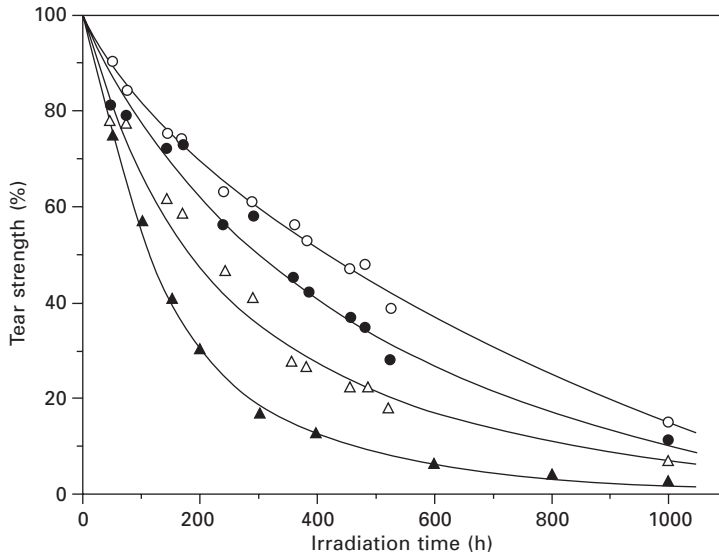
(Maclaren and Milligan, 1981a). Dunn and Weatherall (1992) compared the tensile properties of the tip and root halves of fibers taken from the midback region of sheep reared outdoors. The tip halves were shown to have lower modulus but no difference in failure properties was detected. Haly *et al.* (1957)

showed that exposing wool to irradiation for two hours by wavelengths above 290 nm resulted in the loss of approximately 25% of the cystine content; however, no change could be detected in the load–extension curves of single fibers in water. Smith *et al.* (2005) tested fabric strips and reported an initial increase in breaking strength of almost 20% after 500 hours of exposure to simulated sunlight. The strength then declined with further exposure, eventually reaching a value 10% lower than the initial strength after 2500 hours. In contrast, many researchers (Lee and Finkner, 1967; Waters and Evans, 1983; Holt and Milligan, 1984; Evans *et al.*, 1986a,b; Dhingra *et al.*, 1989; Schmidt and Wortmann, 1994; Riedel and Hocker, 1996; Zimmermann and Hocker, 1996; Jones *et al.*, 1998) have used fibre bundle tests and fabric tensile, tear and abrasion tests to show that exposure of wool to a range of wavelengths results in considerable loss of mechanical integrity. Increased temperature during the UV exposure significantly accelerated the degradation (Lee and Finkner, 1967; Holt and Milligan, 1984); however, temperature on its own appeared to have very little effect (Dhingra *et al.*, 1989).

The influence of temperature is of particular importance in automotive upholstery where temperatures of 95 °C are not uncommon in hot climates (Dhingra *et al.*, 1989). In the case of vehicles and also for curtains and carpets the radiation is often filtered through glass. This can have a significant protective effect on the wool (Evans *et al.*, 1986a) by filtering out wavelengths below about 300 nm but can be offset by higher service temperatures as in vehicles. Figures 5.27 and 5.28 are typical examples (Holt and Milligan,



5.27 The effect of time and temperature (○ 45 °C; ●, 75 °C) of exposure on the strength of wool fabric exposed to simulated sunlight. Breaking load expressed as a percentage of initial load (adapted from Holt and Milligan, 1984).



5.28 The effect of time and temperature (○ 35°C; ● 45°C; ■ 55°C; ▲ 75°C) of exposure on the tear strength of wool fabric exposed to simulated sunlight. Tear strength expressed as a percentage of initial strength (adapted from Holt and Milligan, 1984).

1984) of the damage caused by photodegradation. They show the effect of time and temperature of exposure for fabric exposed 215 mm from a 500 W Phillips ML G/74 mercury vapour tungsten phosphor lamp B. Wool can be protected to some extent against photodegradation by the application of UV absorbers (Waters and Evans, 1983; Evans *et al.*, 1986a,b; Riedel and Hocker, 1996; Jones *et al.*, 1998; Smith *et al.*, 2005); however, degradation is only slowed down, not stopped.

5.6 Applications and examples

In service, wool is subjected to a range of deformations and mostly fails through wear by abrasion or fatigue. This is particularly true of apparel and carpets and the lack of failure by straight tensile failure suggests that wool's strength is more than adequate. Fibers do fail during early stage processing (carding, combing, spinning and weaving or knitting), however, leading to a reduction in processing efficiency at significant cost to the industry. Furthermore, many of the later stage processes (dyeing, finishing, shrinkproofing, etc.) required to turn wool fibre into an acceptable end product result in a reduction in strength. Several strategies employed to try to minimize this damage are reported here. Wool garments can also be deemed to have failed on aesthetic grounds. So, for instance, curtains or garments that have faded or yellowed may no longer be acceptable to the consumer. Also, particularly in knitwear,

pilling is an undesirable property which results in a product that is no longer acceptable. Fading and yellowing involve chemical changes and are outside of the scope of this chapter; however, pilling is known to be related to fibre strength and hence will be discussed briefly.

5.6.1 Shrinkproofing

The presence of cuticle cells on the surface of wool fibers means that the friction in the direction of the scales is lower than in the direction against the scales. This differential friction causes fibers to migrate preferentially in one direction and, with sufficient movement, results in felting of the wool fabric. Felting is exacerbated at elevated temperatures and relative humidities; hence the need for dry cleaning of many wool garments. Whilst felting is desirable in the manufacture of hats and billiard cloths, it is a major source of angst for the consumer of apparel. Early treatments to shrinkproof wool involved treatment with a variety of oxidizing agents, which had the effect of damaging or even stripping off the scales. In the process considerable damage was also done to the fibre as a whole. The use of oxidizing agents in organic solvents (Freney and Lipson, 1940) or saturated salt solutions (McPhee, 1959, 1960a,b) restricted damage to the fibre, presumably by restricting swelling of the fibre and thereby confining the oxidation to the surface of the fibre. The salt/KMnO₄ process is used commercially on a small scale in India; however, environmental concerns have prevented its widespread use. None of the other processes became commercial and nowadays the most common method is to pre-treat the fibre with chlorine followed by the deposition of a thin layer of polymer, Hercosett (a polyamide–epichlorohydrin resin). Strength loss due to the chlorination is still possible but in recent years the concentration of chlorine has been reduced and loss of strength is typically limited to 5–10%.

5.6.2 Anti-pilling treatments

Pilling has been the subject of extensive research and it is now understood that the life of a pill comprises four stages: fuzz formation, entanglement, growth and pill wear-off (Ukponmwan *et al.*, 1998). Attempts to eliminate pilling have focused on increasing fibre security to prevent fuzz formation or weakening the fibre so that, once formed, the pill readily wears off. The former strategy is indistinguishable from the approach to prevent wool from felting and so typical shrinkproofing treatments generally have the added benefit of improving the pilling performance of wool fabrics. The second approach involves degradation of the wool using chemical oxidants such as chlorine or sodium dichloroisocyanuric acid. These treatments have been shown (Naylor and Williams, 1988) to result in a small decrease in fibre

tenacity and a significant decrease in torsional fatigue lifetime; the maximum pilling decreasing exponentially with a decrease in torsional fatigue lifetime. Other approaches have involved degradative treatments using UV light (Millington, 1998) and enzymes (Ukponmwan *et al.*, 1998; Prabhu and Kanoongo, 2005).

5.6.3 Dyeing

The negative impact of dyeing on tensile properties has already been discussed in Section 5.5.5 on the effect of chemical processing. Both general degradation and the setting of curvature into fibers have been shown to result in a decrease in tensile properties. Two strategies are employed to minimize these strength losses.

It has been shown that reactive dyes (Lewis, 1989) and a range of oxidants (Hird and Yates, 1961a,b; Cookson *et al.*, 1991; Huson, 1992) minimize the fibre degradation during dyeing via their ability to inhibit the thiol–disulphide interchange reaction. The addition of these so-called anti-setting agents to the dyebath also has added benefits in reducing hygral expansion of the fabric (Cookson *et al.*, 1991), a trait that can sometimes cause shape retention problems such as seam pucker or flagging of garment fronts, lapels or vents.

The degradation of the fibre is directly linked to the time spent at elevated temperature and the pH of the dye liquor. The damage is minimized if dyeing is carried out at pH 4–5 for as short a time and at as low a temperature as possible. The balance of course is to minimize damage whilst still achieving good dye exhaustion, penetration and levelness (Brady, 1985). This has led to a large number of methods for increasing dye penetration at low temperature (Brady, 1985; Harrigan and Rippon, 1988; Rippon and Harrigan, 1994; Rippon, 1998).

5.7 Future trends

Wool is a medium strength fibre and, for the most part, performs more than adequately. In recent years, however, with the advent of synthetic microfibers, there has been a push to soft, next to skin, lightweight fabrics and the easiest way to achieve this goal is to reduce the diameter of fibers. The Australian clip, for instance, has changed significantly in the last decade. In 1993/1994 only 8.5% of the total clip was 19 μm or finer and 12 years later 31% was 19 μm or finer (AWI, 2007). As wool fibers get finer, strength becomes more of an issue. A 25 μm fibre with an intrinsic strength of 200 MPa requires a force of 100 mN to break whereas an 18 μm fibre only needs half that force for failure to occur. There have been programmes to increase strength by transgenic means (Rogers, 1990; Bawden *et al.*, 2000; Rogers, 2000a,b) and

by breeding but neither of these approaches is easy or quick. In the short term it is thus likely to become even more important to process wool in such a way that strength is maintained. Treatments such as those listed in the previous section need to be improved and/or new ones developed. This work needs to be underpinned by further basic research in this area.

5.8 Sources of further information and advice

The book *Physical Properties of Textile Fibers* by Morton and Hearle (1993) is an excellent starting point for readers wanting to understand the tensile properties of fibers: whilst covering all textiles there are significant sections dealing with wool. Max Feughelman's book (1997) on the mechanical properties and structure of alpha-keratin fibers deals more specifically with alpha keratins and covers much of his own extensive work on wool. Maclaren and Milligan's book (1981a), although only occasionally dealing with physical properties, is an excellent source for understanding the chemical reactivity of the wool fibre. For a good summary of the chemical and physical structure of the wool fibre see Rippon's (1992) chapter in *Wool Dyeing* and for detailed information on the cell membrane complex see the review by Leeder (1986). More specifically on the topic of this chapter there are several good review articles and chapters on wool properties by Feughelman (1982, 2002), Hearle (2000, 2002, 2003) and Reis (1992) and a good general encyclopaedia article (Christoe *et al.*, 2003) that includes a section on wool properties. Finally, since 1955 there has been an international conference on wool every 5 years. The proceedings of the conferences listed below are a superb record of wool research over the last 55 years:

- Proc. 1st Int. Wool Text. Res. Conf., Melbourne, Australia, 1955.
- Proc. 2nd Int. Wool Text. Res. Conf., Harrogate, UK, 1960.
- Proc. 3rd Int. Wool Text. Res. Conf., Paris, France, 1965.
- Proc. 4th Int. Wool Text. Res. Conf., San Francisco, USA, 1970; published in *Appl. Polym. Symp.*, No. 18, Interscience Publishers, a Division of John Wiley & Sons, Inc., New York, 1971.
- Proc. 5th Int. Wool Text. Res. Conf., Aachen, Germany, 1975.
- Proc. 6th Int. Wool Text. Res. Conf., Pretoria, South Africa, 1980.
- Proc. 7th Int. Wool Text. Res. Conf., Tokyo, Japan, 1985.
- Proc. 8th Int. Wool Text. Res. Conf., Christchurch, NZ, 1990.
- Proc. 9th Int. Wool Text. Res. Conf., Biella, Italy, 1995.
- Proc. 10th Int. Wool Text. Res. Conf., Aachen, Germany, 2000.
- Proc. 11th Int. Wool Text. Res. Conf., Leeds, UK, 2005.

There are several industry groups and research organisations active in this area and they all have useful information on their websites, dealing with research and current issues in the wool industry.

Australian Wool Innovation Ltd (AWI) (www.wool.com.au) is a key player in funding wool research, creating new products, marketing the benefits of wool, building existing markets and opening new ones. In a recent initiative they funded a collaborative project between CSIRO, DWI (Deutschen Wollforschungsinstitut) and Canesis (now part of AgResearch NZ) to compile a CD-based database (Harland *et al.*, 2006) with dimensional data on all the key structural components of a Merino wool fibre. Although primarily aimed at mathematical modellers, the articles, images and data in this database are likely to be useful to anyone with a scientific interest in the internal structure of wool.

The Australian Government operates a Cooperative Research Centre (CRC) Program which aims to create centres of excellence in a range of different areas. The CRC for Sheep Industry Innovation (www.sheepcrc.org.au) is a collaboration between Australia's leading sheep industry organizations and will support industry to transform wool, meat and the sheep that produce them in a comprehensive seven-year programme of research, development, extension and education, running from 2007 to 2014. Program 2 deals with next generation wool quality, tackling issues such as comfortable, prickle free knits for next to skin wear and options for genetic selection and sheep management in order to produce white wool that does not require bleaching and is photostable.

CSIRO Materials Science and Engineering (formerly the Division of Textile and Fibre Technology and before that the Division of Wool Technology) has, in recent years, diversified into a wide range of textile areas but remains the premier wool research organization in the world. Their website (www.csiro.au/science/textiles) offers a sample of their work and also links to key players in the field. Other research organizations that are substantial contributors in the world of wool research are:

- the German Wool Research Institute, DWI (Deutschen Wollforschungsinstitut) (www.dwi.rwth-aachen.de) which is linked to the Aachen University via the Chair of Textile Chemistry and Macromolecular Chemistry;
- agResearch, New Zealand's largest Crown Research Institute, an independent, Government-owned, R&D company (www.agresearch.co.nz);
- the Department of Textiles and Paper, School of Materials, University of Manchester (www.materials.manchester.ac.uk);
- the Textile Research Institute (TRI) in Princeton (www.triprinceton.org).

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Types, structure and mechanical properties of silk

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Abstract: Silk fibres are produced by a variety of animals but the most widely used silk is made from the cocoon of the *Bombyx mori* larvae. Silk from spiders has been found to possess greater strength and elongation to failure and this has prompted research into improving the properties of traditional silk for textile applications and also for more technical uses. The fibre is protein based and the possibility of creating regenerated fibres or films for technical applications is appealing but requires a detailed knowledge of the fibre structure. Techniques such as Fourier transform infrared spectroscopy, X-ray diffraction and Raman spectroscopy are amongst the techniques used for such analyses.

Key words: *Bombyx mori* silk, spider silk, regenerated silk, microstructure, mechanical properties.

6.1 Introduction

6.1.1 History

Throughout history, silk fibres have been the fibre of choice for the most luxurious of cloths, originally reserved exclusively for the Chinese emperor, his close family and court dignitaries. The desire to produce a cheaper, artificial type of silk was the inspiration for the earliest efforts to produce synthetic fibres for textile uses. Silk has been such a valuable commodity that, in its long history, silk has even been used as currency and has been the subject of bartering between countries and dynasties. Sericulture, the cultivation of silk moths and the production of silk yarns and fabrics, is believed to have begun in China five or six thousand years BC and for centuries its details were a jealously guarded secret. It was introduced into Korea around 200 BC and five hundred years later to India and Byzantium and the Middle East through the Silk Road. European production began first in Italy, in the thirteenth century AD, when many craftsmen escape from Byzantium after the sack of the imperial city by the Crusaders.

Although there are many types of wild silk moths, silk production is based on one major species, the domestic *Bombyx mori*. This is a blind, flightless

moth which has been bred over the centuries, most probably from the wild *Bombyx mandarina* moth, which is found only in China and which lives on the white mulberry tree. It is clear that, very early on, the silk from this moth was found to be better than that of other species. The *Bombyx mori* moth is a creature, bred by people, that is only capable of reproducing and laying eggs for the next generation of silkworms.

Recently interest has turned also to silks produced by spiders as they possess different, and in some respects superior, properties to those of the silk of the *Bombyx mori*.

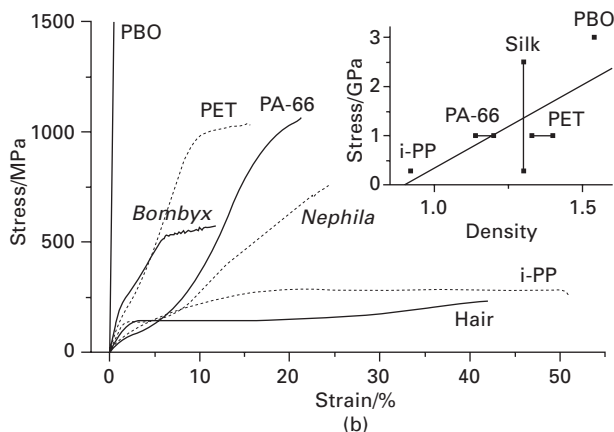
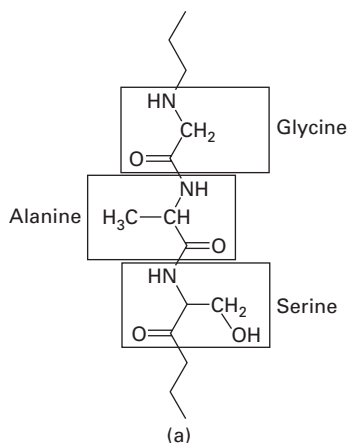
6.1.2 Uses

Today silk retains its position as the finest fibre for apparel and its worldwide production is increasing despite competition from synthetic fibres. Silk is produced in countries such as China, Brazil and India, where silk yarns and textiles are produced, and is also exported to Europe where companies manufacture high quality silk cloth products. Japanese and Korean companies are also important producers but silkworm farms are often located in other countries (Brazil, Vietnam, etc.). Most of the silk is produced by the *Bombyx mori* domesticated moth. Other commercial silks come from other moths such as *Antheraea* (Tussah) and a small production from wild *Gonometa* harvested by South African indigenous peoples.

There is a renewal in interest in this type of natural fibre with attempts to promote sustainable production, not only for traditional textile products but also for a variety of technical and biomedical applications as potential support for tissue engineering. Technical uses have included parachute cords and canopies, ropes and suture materials (Altman *et al.*, 2003). In the near future, silk is expected to be a major biopolymer in biomedical applications. Regenerated, silk can be used in different shape: electrospun fibres, foams, or sheets improved by encapsulation or coating. Furthermore, silk can be modified by biotechnology (Grenier *et al.*, 2004; Royer *et al.*, 2005). Its potential is large: intra-articular ligament (Bartow, 1916; Liu *et al.*, 2007), cartilage and bone scaffold (Meinel *et al.*, 2004, 2005, 2006; Luan *et al.*, 2006; Kirker-Head *et al.*, 2007; Meechaisue *et al.*, 2007), skin (Min *et al.*, 2004), artificial blood vessel (Lovett *et al.*, 2007; Priestley, 2007; Yang *et al.*, 2007) and nerves (Wang *et al.*, 2007) are proposed applications.

6.1.3 Creatures producing silk

Technically, silks are fibrous protein polymers containing highly repetitive sequences of amino acids: As sketched in Fig. 6.1(a), the macromolecular polypeptide chain consists of a polyamide backbone $[-R_{n1}CH-(N-H)-(C=O)-R_{n2}CH-(N-H)-(C=O)-R_{n3}CH-\dots]$, the side chains R_{ni} consist



6.1 (a) Schematic representation of a portion of the silk chain indicating the polyamide backbone and the amino acid residues as side chains. (b) Comparison of the *Nephila madagascarensis* spider silk tensile behaviour with those of different synthetic fibres: PBO (paraphenylenbenzonnitrozy), breaking point not shown at 3 GPa), polyamide 66 (PA66), poly(ethylene terephthalate) (PET), isotactic polypropylene (i-PP) and keratine fibre (hair). Inserted graph; stress at break vs. density. Reproduced from Colomban *et al.*, 2008 J. Raman Spectroscopy, © Wiley & Sons.

of 20 differing amino acid residues (Table 6.1). Glycine, alanine and serine represent more than 75% of these residues.

Silk fibre production is not confined to butterflies, moths and spiders, but produced by creatures of a variety of different classes: arachnids, insects but also molluscs. Bees and wasps (Hymenoptera) embed simple silk fibres into wax of their combs, fleas (Siphonaptera) use silk in their nests and cocoons, lacewings (Neuroptera) employ it to cement eggs onto stalks, caddisfly

Table 6.1 Major amino acids of silk

Amino acid	One letter code	Three letter code
Glycine	G	Gly
Alanine	A	Ala
Serine	S	Ser
Tyrosine	Y	Tyr
Phenylalanine	F	Phe
Proline	P	Pro
Asparagine	N	Asn
Glutamic acid	E	Glu
Tryptophan	W	Trp
Aspartic acid	D	Asp
Threonine	T	Thr

larvae (Trichoptera) use it to bind debris into nests or make underwater webs. Amongst the arachnids, silk is used for nest building in the pseudo scorpions and mites and for many uses by true spiders (Araneids). The precursor of the silk is produced and stored in the creature's complex gland as a liquid and converted into fibre(s) through the narrow ducts and then the spinneret(s). The production of silk fibres, either as regenerated silk or by genetic modification of silk worms with spider DNA, potentially opens up new engineering applications for these fibres. In the last decade, spider silk has received considerable attention because the variety of silk types produced by the specialized glands of *Araneids* result in outstanding properties, from being very strong to highly extensible (Vollrath and Knight, 2001). However, farming Arachnids is very difficult and alternative production routes are being investigated so as to benefit from this type of silk and to overcome the problems involved. Production routes such as regenerated silk spinning and gene modifications of the *Bombyx mori* (Grenier *et al.*, 2004; Royer *et al.*, 2005) is being actively pursued. Attempts have even been made to produce a silk precursor from the milk of genetically modified goats.

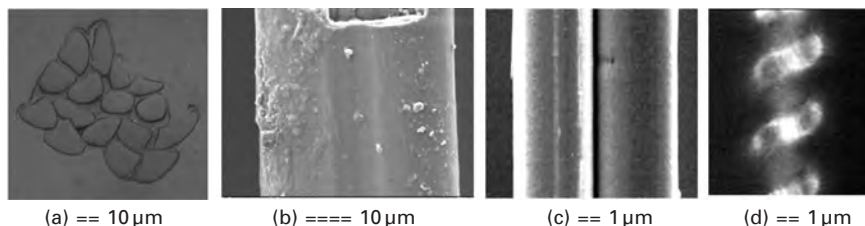
6.1.4 Silk variability

Silk is light as well as strong but a review of the literature shows that it is difficult to extract characteristic properties because of the variability of the material. Figure 6.1(b) compares representative stress–strain plots of synthetic advanced fibres with those of a spider silk, *Nephila madagascariensis* and of *Bombyx mori* Type II, see below. Compared on a weight basis, the specific gravity of silk (1.3) is close to that of polyamide and polyethylene terephthalate – the properties of silk fibres compete well with those of many advanced fibres and often show greater strain to failure. However, as a biomaterial, the first characteristic to be underlined for silk fibres is their variability; variability from the sources (species, individual), variability in their compositions (amino

acid variety and sequences), variability in geometry (section dimension and shape, see Fig. 6.2) and variability due to processing (degumming, weaving, dyeing). The calculation of failure stress, in engineering terms, requires the knowledge of the fibre section at the failure point; a difficult problem that is discussed elsewhere. The scope of variation appears much larger for this natural product than for synthetic fibres; however, although this variability has been occasionally pointed out in the literature, the effect on the fibre properties has not often been considered in detail.

Traditional empirical silk conditioning techniques have evolved over the centuries and these chemical treatments, namely degumming and dyeing, result in a fall in mechanical properties. However, the removal of the soluble sericine is mandatory so as to achieve controllable dyeing of silk cloth. For that reason wild and un-degummed silk fibres remain primarily used for woven textile applications, the dyeing being performed as one of the final processes employed. As is the case for fine wine and wool production, the details of the silk producers and the origin of the silk are important criteria for quality. In this chapter we will try to review the state of the art of the knowledge concerning production, processing, mechanical properties and nanostructure of representative silk fibres. Many questions remain unanswered: what is the relationship between the different silk 'structures' and their mechanical properties, what is the reason for the better properties obtained in high strain rate tests; in brief what determines the behaviour of silk fibres?

The variability of mechanical properties and the need of a statistical approach are well established (Marcelan *et al.*, 2003; Colomban *et al.*, 2006). This is true for many materials but particularly true for silk; however, the data to be found in the literature are incomplete and in many case the variations in properties are not quantified. Figure 6.2 compares the photomicrographs of some silk fibres and reveals the difficulty in determining cross-sectional areas. The fibres shown are, from left to right: a set of *Bombyx mori* fibres



6.2 Scanning electron (b, c) and optical (a, d) microphotographs of silk fibres: (a) section of a *Bombyx mori* silk yarn made of 8 $\times$ 2 fibres (note the two fibres from a same bave on the top left); (b) as-spun bave consisting of two fibres in the same sericine envelope; (c) two *Nephila madagascarensis* fibres, free of any sericin coating; (d) drag line of a araneid consisting of a straight fibre with a second one wrapped around it.

associated to form a yarn. Note that the silkworm spin a double fibre, the 'bave' which are both coated by sericine, a wax compound which protects the fibre. The section of the yarn shows clearly the pair of fibres (see top left) and the variety of their forms; section variability is much larger for wild moth silk (Colomban *et al.*, 2008). In contrast the shape of spider silk appears more regular and is free of any sericine coating. However different diameters are observed in silk fibres produced by the same spider. Spider silk is finer than traditional silk, often being in the range 2–5 μm , whereas from the *Bombyx mori* 'equivalent diameters' of the fibres range from ~ 10 to 15 μm .

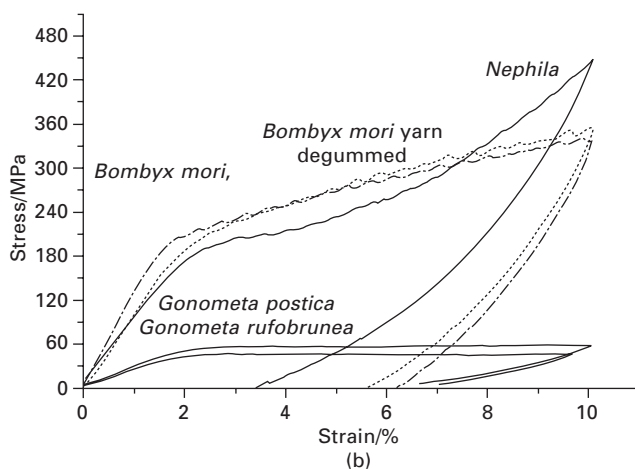
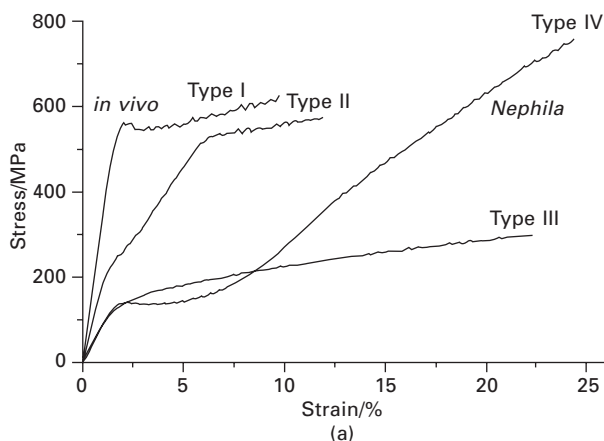
Variability of spider silk arises from the number of specialized glands and associated spinnerets and the different amino acid compositions found in them (Gosline *et al.*, 2002) (Ko, 2004). Figure 6.2(d) shows the optical photomicrograph of a spider drag line consisting of a main fibre with a helicoidal smaller fibre wrapped around it (Colomban and Gouadec, 2007).

Figure 6.3 compares the different stress–strain curves obtained with a variety of *Bombyx mori* silk measured as raw materials (fresh and aged cocoons, flote, degummed fibres, dyed yarns, etc.). Similar results have been obtained for *Antheraea* (Tussah) and for some extent for *Gonometa* silk fibres (Colomban *et al.*, 2008). The flote is the processed yarn used by the silk industry to produce cloth and consists of several silk filaments collected together in one yarn so as to minimize variability. Comparison is made with a *Nephila madagascarensis* spider fibre, however one of indeterminate age.

Four different types of stress/strain curves are shown:

- *Type I*: elastic behaviour up to $\sim 2\%$ of strain and then a more-or-less flat, quasi-plateau; this behaviour is very rare for processed fibres/yarns but frequent for fibres extracted from fresh cocoons and dominant for just hand-spun fibres from a silk moth extracted from its cocoon (Dinh *et al.*, 2008).
- *Type II*: elastic behaviour up to $\sim 2\%$, then linear up to 5–6% and a third, rather flat plateau up to the breaking point; this behaviour is common for dry, processed fibres/yarns.
- *Type III*: after elastic behaviour up to 1.5% a continuous variation is observed in the section above the linear behaviour. This signature is observed for fibres saturated with water and for many de-gummed or dyed fibres.
- *Type IV*: after the viscoelastic or plateau behaviour, a hardening is observed up to the breaking point. This behaviour is rather common for spider silk but not very rare for dried silk obtained from the *Bombyx mori*.
- *Type V (not shown)*: the breaking point occurs in the elastic domain; dyed fibres or fibres chemically treated with acid show this behaviour.

Vollrath and Knight (2001) report rather similar behaviour for spider



6.3 (a) Representation of the three types of mechanical behaviours of *Bombyx mori* silk (I to III), Type IV is observed for some spider silk, here *Nephila madagascariensis*. (b) Comparison of the different stress-strain curves obtained with different silks, partial reversibility is shown for fibres strained up to 10%. After Dinh *et al.* (2008).

draglines but assign each one to a different family (Pisauridae, Araneidae, Theridiidae, Araneidae, Tetragnathidae). These authors may have overlooked some variability and it is expected that an approach taking into account the history of each tested fibre would give rather similar results to those recorded for *Bombyx mori* fibres (Dinh *et al.*, 2008). Moreover they note ‘there seems to be significant variability in silk properties even for the same silk produced the same spider on different days or even on the same day under different environmental conditions, spinning conditions, variability in the amino acid composition..., some of which might be affected by diet’. It is well known by

silk producers and users that the art of silk farming (nursing, diet, selection) determines the quality of the silk. Table 6.2 gives a representative view for the main properties of different varieties of silk.

6.2 Silks

6.2.1 Silk from *Bombyx mori* and other moths

Composition

Silk is described using its amino acid sequences (Table 6.1) because much of the studies have been performed on dissolved/cut polymer, i.e. by destruction of the solid materials and the loss of its specificity. As sketched in Fig. 6.1(a), the stacking of the different bricks, namely the various amino acids, form a polyamide chain, a backbone common to keratin and synthetic polyamides. This backbone is grafted by functional chain called residue – specific for each amino acid – leading to a specific microstructure explaining the mechanical. Furthermore, the amino acid grafts play important role on chemical properties. Various sequences have been proposed (Hayashi *et al.*, 1999; Nirmala *et al.*, 2001; Fedič *et al.*, 2003; Sehnal and Žurovec, 2004) and their modification will change the detail of the shape of the macromolecule and its chemical properties/reactivity. As for many peptide polymers, the local conformations of the chains are categorized as regular α -helix, irregular helicoidal fragments/turns and untwisted ribbons remain β -sheet. Furthermore intermediate conformations between the three above categories also exist. The large size of some ‘rigid’ or ‘long’ amino acid residues of the silk macromolecule (arginine and phenylalanine amino acids, etc.) hinders regular configuration of the helix and hence can explain the formation of kinks as sketched in Fig. 6.3. In the case of silk from *Bombyx mori*, the presence of tyrosine impedes crystallization and prevents the formation of a regular spacing between adjacent macromolecules, hence promoting orientation disorder at the short scale (0.1–0.5 nm). This limits the crystallinity of the material. Possible motifs and their likely secondary structures have been discussed by Hayashi *et al.* (1999).

The silk polymer is composed of three proteins: (i) a fibroin heavy chain (molecular weight ~350 kDa (Inoue, 2000)), (ii) a fibroin light chain (~26kDa), both linked together by a covalent bond, a di-sulfure bridge (two amino acids ‘cysteine’ – from each protein – are linked by their sulfure) as observed for keratin fibres (Paquin and Colomban, 2007), and (iii) a protein called P25 factor which combines three heavy chain/light chain fibroins complexes together. Only the heavy chain is considered as being fibrous, as its spatial conformation permits intra- and intermolecular interactions. Light fibroin and P25 factor have only intramolecular interactions, leading to a more viscous component.

Table 6.2 Mechanical parameters of various fibres: diameter, modulus, ultimate strength and strain (gauge length 30 mm)

	<i>Bombyx mori</i> domestic (Pérez-Rigueiro <i>et al.</i> , 2000; Zhao <i>et al.</i> , 2007)	<i>Bombyx mori</i> yarn domestic (Pérez-Rigueiro <i>et al.</i> , 2000)	<i>Gonometa rufobrunea</i> wild (Colomban <i>et al.</i> , 2008)	<i>Gonometa postica</i> wild (Colomban <i>et al.</i> , 2008)	<i>Nephila magadas-gariensis</i> spider (Colomban <i>et al.</i> , 2008)	<i>Nephila clavipes</i> spider (Cunniff <i>et al.</i> , 1994)
Diameter (µm)	10–15	64		15–25	2–6	~3
Modulus (GPa)	12–16					
Final stress (MPa)	180–1400	400–500	300	175	750	875–975
Final strain (%)	4–27	15–19	25	34	25	18

The heavy chain in fibroin is made up of 12 domains, excluding the beginning and the end (Zhou *et al.*, 2000). Statistically, each group is built in the same way: (a) a repetition of the main motif GAGAGS (see Table 6.1 for amino acid name correspondence), then (b) a repetition of two other motifs GAGAGY and GAGAGSGAAS. This can be repeated several times depending on the 'domain'. Between each 'domain', a common sequence (c) GTGSSGFGPYVANGGYS GYEYAWSSSEDFGT which is expected to have a twisted structure (Mita *et al.*, 1994; Ha *et al.*, 2005). Fractionation with an enzymatic attack gives two parts. First, the precipitate fraction (Cp) is only composed of glycine, alanine and serine with a few tyrosine, hence, the main motif is GAGAGS and this is representative of the parts (a). Then, the soluble fraction (Cs) is more complex with the same amino acid composition added as valine, this is representative of the parts (b) and the separators (c). The relative importance of each part is a ratio of 55:45 in terms of amino acid residues (Shimura, 1983). It is reasonable to assume that the composition in amino acid could be specific for each animal or even individual; this difference is observable for the major amino acids ratio, depending on the authors and/or analysed materials (Table 6.3).

Bombyx mori fibres are coated with a protecting material. In contrast, no coating is present on spider draglines. Sericine is composed of different proteins with a molecular weight between 65 to 400 kDa (Garel *et al.*, 1997). Sericine proteins are rich in serine; they have some long repetitive sequences but not very well conserved (Takasu *et al.*, 2007) (Dash *et al.*, 2007). Amino acid composition changes with the molecular weight and with the samples/authors (Table 6.4).

Technology and silk production

The elements which go into the making of silk, by whatever animal, need to be stored in a gland. They then need to be secreted before being spun into filaments. This method of production of silks is common to all types of animal producing silk; nevertheless, some differences can be highlighted,

Table 6.3 Main amino acid composition for different silk fibres (fibroin)

Amino acids (%mol.)	<i>Bombyx mori</i> domestic (Shimura, 1983)	<i>Gonometa mellonella</i> wild (Žurovec and Sehnal, 2002)	<i>Gonometa postica</i> wild (Colomban <i>et al.</i> , 2008)	<i>Antheraea pernyi</i> wild (Žurovec and Sehnal, 2002)
Glycine	49.4	31.6	18.7	27.3
Alanine	29.8	23.8	14.8	43.1
Serine	11.3	18.1	11.5	11.3
Tyrosine	4.6	0.2	7.1	5.3
Valine	2.0	16.0	1.6	

Table 6.4 Main amino acid composition for different silk coating (sericine)

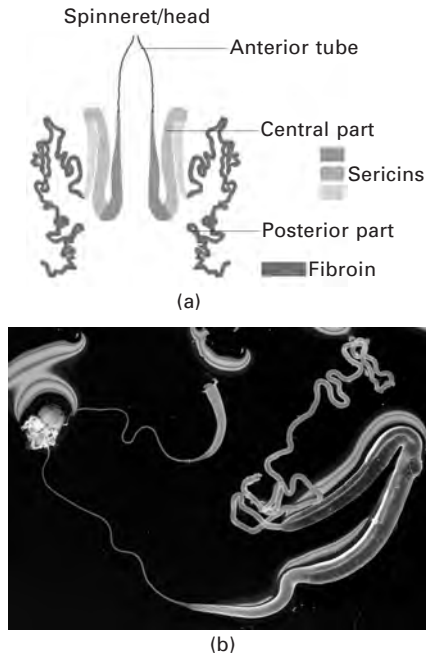
	<i>Bombyx mori</i> (Shimura, 1983)	<i>Bombyx mori</i> (Dash <i>et al.</i> , 2007)	<i>Bombyx mori</i> (Pérez- Rigueiro <i>et al.</i> , 2007)	<i>Antheraea mylitta</i> , wild	<i>Cricula trifenestrata</i> wild (Dash <i>et al.</i> , 2007)
Glycine	13.5	14.1	8–14	19.20	20.8
Alanine	6.0	8.1	3–5	2.95	4.9
Serine	33.4	33.2	21–37	19.40	39.8
Threonine	0.53	12.2	6.5–10	12.32	13.1
Histidine	1.3			13.51	
Aspartic acid	16.7			14–17.5	

such as the number and characteristics of glands producing the polymers and the way these polymers are spun. Furthermore, the period of life when the organism is able to produce silk differs depending on the organism.

The life cycle of the *Bombyx mori* involves two phases. First, the larval phase starts when caterpillars hatch from eggs laid by the months. Their growth goes through five larval steps separated by metamorphosis. The caterpillar produces its silk in order to build a cocoon as protection for its metamorphosis into a pupa. Finally, the butterfly phase is necessary for reproduction permitting the production of eggs and completion of the cycle. The *Bombyx mori* is therefore able to produce silk only during a short part of its life, which is the fifth period in the larval stage. The silkworms feed until they have stored up enough energy to enter the cocoon stage. While they are growing they have to be protected from such things as loud noises, draughts and strong smells.

The pair of *Bombyx mori* glands grows very quickly, with the increase of the size being due to the growth of each cell and not an increase of the number of cells. As represented in Fig. 6.4, the glands have three parts: the main central part with a Z shape, diameter ~3–4 mm in the middle and length ~60 mm, two very fine tubes, the excretor (diameter ~0.05–0.3 mm, length 35 mm) which terminates in a spinneret located in the head of the larva and a broader one (~0.4–0.8 mm, ~100 mm) where fibroin is produced by the rear gland cells. The sericine coating, a type of wax is made in the anterior region of the central Z part. Recent Raman and IR *in vivo* analysis confirms that the silk precursor contains a lot of water (Dinh *et al.*, 2008).

When it is time to build their cocoons, the worms extract the stocked substance, which hardens when it comes into contact with air. Silkworms spend one to three days spinning a cocoon around themselves until they look like puffy, white balls. After eight or nine days in a warm, dry place the cocoons are ready to be unwound. First they are steamed or baked to kill the worms, or pupae. The cocoons are then dipped into hot water to loosen the tightly woven filaments. These filaments are unwound onto a spool. Each cocoon is made up of a filament between 500 and 1500 metres length! Between five and

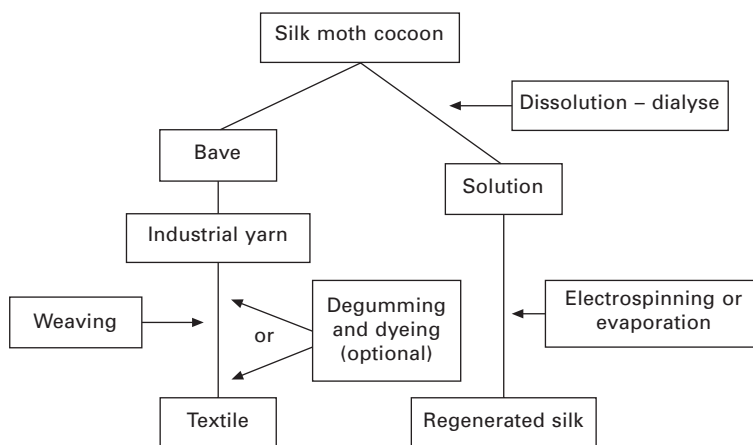


6.4 Schematic of the pair of *Bombyx mori* silk glands. Each gland is composed of posterior, middle and anterior regions, the middle region itself being composed of three parts. A microphotograph of a gland (dried) is given in (b); the animal head is on the top left side.

eight of these super-fine filaments are twisted together to make one thread (flotte). Finally this thread is used by silk makers and woven into yarn, and then into textiles or used for embroidery work. Degumming – removal of sericine coating – and dyeing can take place before or after weaving – see Fig. 6.5.

Hence, the fibroin starts from an aqueous solution to become a fibre after losing water which increases its viscosity. The sericine absorbs some of the water, allowing the fibroin to be dried. It also has a use in the protection of the fibroin and acts like a glue for the building of the cocoon (Iizuka, 1983). Ion transfer, notably copper (Zhou *et al.*, 2003), calcium and magnesium, is important in stabilizing the polymer in solution and certainly controls its solidification (Pérez-Rigueiro *et al.*, 2007). These are incorporated in fibroin in the medium gland, leading to the formation of ‘salt bridges’ between the carboxyl groups of the macromolecules.

The silkworm extrudes the silk through its mouth and it is the sideways movement of the head after initially sticking the fibre end tip at one spot that permits the silk to be spun or extruded and that may induce orientation in the fibre structure through shearing of the polymer. If the silkworm wants to stop the production, it has to cut its fibre. Production speed is around 10 mm/s.



6.5 Flow chart of the different steps leading to silk product.

(Kiyosawa *et al.*, 1999). The cocoon is made up of one continuous fibre, the diameter of which reduces throughout the cocoon, with the innermost part, the last part to be produced by the creature, being made of the finest fibres. This results in a variation of diameter, with a factor $R = 1.5 \pm 0.3$ between the outside to the fibre on the inside of the cocoon. However, measurement of diameter is difficult because of the shape of the cross-section (Fig. 6.2). This is easily observable and already pointed out in literature (Pérez-Rigueiro *et al.*, 1998).

6.2.2 Silk from spiders

Composition

The diversity of spiders results in a wide variety of silks. Indeed, depending on the species, the spider can possess from two to nine glands, producing different polymers and fibres. The gland can act like a spinneret, leading to a fibre with good orientation and mechanical characteristics, or used as an extruder, producing silk more used as a glue than a fibre but still composed of macromolecular polymers. These silks can have different uses such as: protection, feeding and, eggs. Spiders can produce their polymer, named spidroin, throughout their life, and, in contrast to silkworms, spiders have innervated spinnerets, permitting a closer control of the spinning (Craig, 1997).

In the production of spider silk, the amino acid composition can change depending on the gland used. Thus, for *Araneus diadematus*, the minor ampullate gland produces a silk rich in Gly and Ala (80%) which is translated by medium values of extensibility and low values of strength and toughness. The major ampullate gland produces a silk (the dragline and the web frame)

with almost the same quantity of Ala but much less of Gly with a global ratio of these amino acids of 0.5. This results in higher strength but lower extensibility.

Finally, aciniform gland silk has much less Ala and Gly (25%) and shows low strength but high extensibility and toughness. Stiffness is very similar for all of these silks (Hayashi *et al.*, 2004). We will focus our discussion on dragline silk produced by the major ampullate gland because the silk produced by this gland has better mechanical properties and can be compared to the silk moth single fibre.

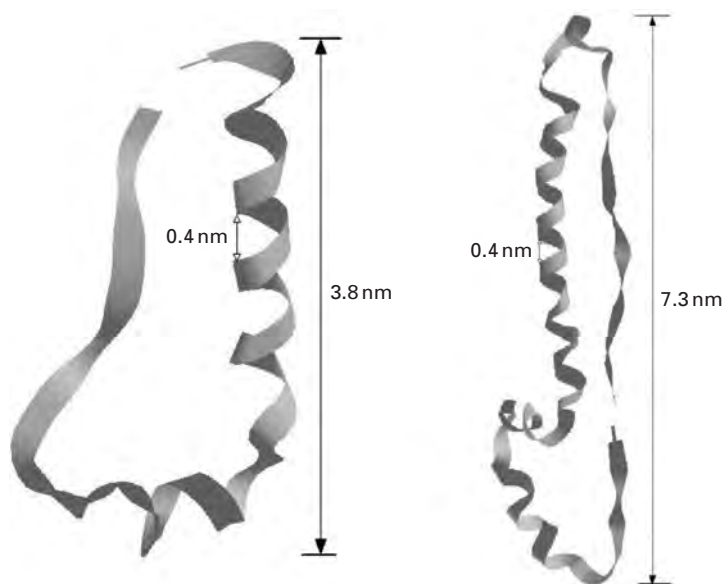
The polymers found in spider silks are called spidroins. There are two kinds of spidroin, Spidroin I and II, both fibrous, in contrast with those produced by the *Bombyx mori*. The apparent molecular weight has been determined (by dissolution and electrophoresis) as 275–320 kDa. It is reported that intermolecular disulphide bonds permit these two chains to be linked together as in keratine to form an oligomer with a molecular weight of ~725 kDa. First of all, spidroins are characterized by repetitions of alanines (A)_n. Then, another motif is present in all species: GPGG(Xaa) or simply GG(Xaa), where Xaa is an unspecific amino acid (Bittencourt *et al.*, 2007).

However, the sequence can be much more complex for species such as *Araneus diadematus*, the only commonality being the richness of glycine and alanine. It has been shown that silks produced by different glands, major and minor ampullate gland, aciniform, flagelliform or tubuliform gland are different. The function and the mechanical properties also change, as has been shown for different kinds of fibre produced by *Argiope trifasciata* (Hayashi *et al.*, 2004).

In order to give a view of the possible conformations, sketches were made by Colomban *et al.* 2008 using the Chem3D software with the sequence reported for spidroin 2 (Kaplan *et al.*, 1994) with 38 and also 72 amino acids (labels are given in Table 6.1):

```
GPGGYGPGQQGPGGYGPGQQGPSGGPGSAAAAAAAAAAGPGGY
GPGQQGPGGYGPGQQGPSGGPGSAAAAAAAAAAGPGGYGPGQQG
PGG YG PGQQGPS GGPGSAAAAAAAAA
```

The amino acid composition of this sequence is: 36.8% glycine, 26.3% alanine, 15.8% proline, 10.5% tyrosine, 5.3% serine and 5.3% tyrosine with ten hydrophobic and six hydrophilic residues for the 38 amino acids. A helical conformation has been obtained from 27 to 36 positions (26%) whereas the 1 to 26 region (74%) is a random coil part in the involved chain (Fig. 6.6). The same result is obtained for the double sequence, an alpha helix from 27 to 36 positions and also from 65 to 74 corresponding to the GSAAAAAAAAA part. NH₂ addition to end the chain decreases or even suppresses the flat ribbon part. It is reasonable to think that chemical treatments such as degumming can modify or interact with some grafts that



6.6 Schematic of the local conformation of spider silk macromolecule.

will modify the structure and associated phase transition. Nevertheless, the model goes some way to explain the low crystallinity of silk fibres made by spiders. Rigid (composed of aromatic rings) or long amino acid side grafts can impose specific bond angles in the polyamide chain and hence may destroy the regular structure.

Technology and silk production

Spiders are not amenable to being cultivated on an industrial scale as they are quite aggressive to one another and are cannibalistic. Hence the use of spider silk is still mainly limited to laboratory studies. An experimental farm was managed in the 1970s in Madagascar and this *Nephila madagascarensis* silk production has been studied by Colomban *et al.* 2008. The most extensively studied spider silk is that produced by *Nephila clavipes*.

The set of spider glands (usually seven for *Araneid*) is much more complex. The major and minor ampullate glands produce the dragline and the frame threads of the web whilst the minor ones provide fibres that can be added to the web. The aciniform glands make the silk for wrapping prey, the cylindrical glands make the wrapping silk for the egg sac and the pyriform glands make the silk for attachments and for joining threads (Vollrath and Knight, 2001). The flagelliform glands provide the core of the threads used in the web to capture prey, whilst the coating for the thread is made by the aggregate glands.

6.2.3 Regenerated silk

Silks can be spun naturally as described above, but can also be artificially produced by dissolving natural silk, forming a solution or a gel as a function of the water content. In order to dissolve silks, different techniques are used. A (fresh) ionic solution of LiBr is often used (Colomban *et al.*, 2008), but a mix of calcium chloride, ethanol and water is also possible (Ki *et al.*, 2007a); finally, the use of calcium nitrate has also been studied (Ha *et al.*, 2003). Dialysis is necessary in order to remove the large amount of ions introduced for dissolution, and then fibres are spun or film cast. The method of dissolution more or less degrades, the polymer chains. Studies are in progress in order to better understand the impact of this step on the regenerated silk (Yamada *et al.*, 2001).

The stress–strain curves of such regenerated silk exhibit non-linear behaviour similar to natural silk but the ultimate strength and strain to failure is far from those of the natural fibres (Jelinski *et al.*, 1999; Dinh *et al.*, 2008). Nevertheless, biotechnology permitting modified regenerated spider or *Bombyx mori* silk to be obtained could provide fibres with controlled properties close to those of natural spider silk (Lazaris *et al.*, 2002).

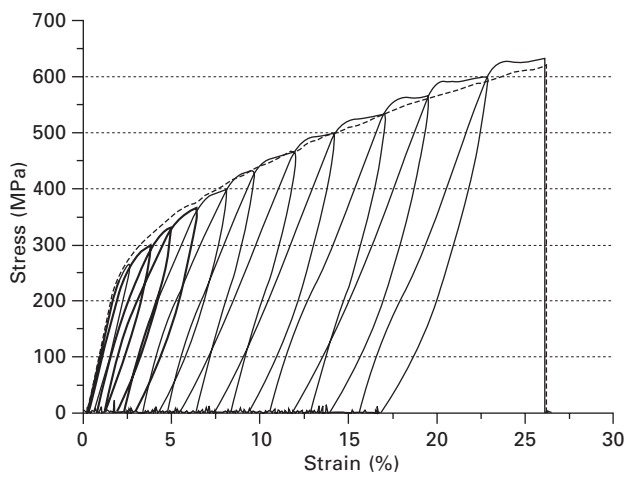
6.3 Mechanical properties and microstructure

6.3.1 Mechanical properties of traditional silk

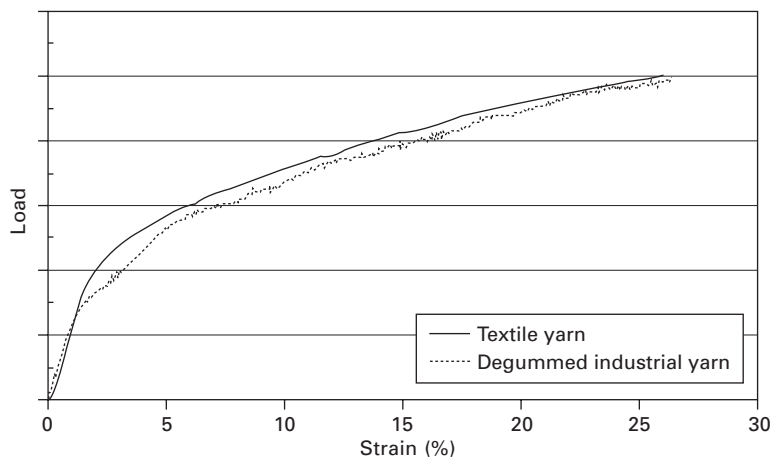
Silk fibres possess useful mechanical properties but the variability is huge and problematic, in particular, the fibre cross-section, which ensures the fibre can support the stresses, is not circular and varies along the fibre length, making it difficult to measure. Nevertheless, silk shows competitive moduli and failure stress compared with synthetic fibres. However, silk presents interesting deformability with a superior strain at break (see Table 6.2).

Silk is a viscoelasto-plastic material; its properties have been studied with relaxation tests by Parthasarathy *et al.* (1996), and also cyclic loads (Fig. 6.7). The influence of the different compounds – fibroin and sericine – on the mechanical behaviour is difficult to over-emphasize. Figure 6.8 shows a comparison between the stress–strain curve of an industrial yarn and of a single fibre, the fracture morphology of which is presented in Fig. 6.9. It can be observed that sericine and the yarn structure associated hardly modify the curve. Nevertheless, if the mechanical tests of an industrial yarn degummed and not degummed are compared, a reduction in failure stress can be found. Hence, sericine is not completely passive during loading even if its modulus seems to be very low. Studies about sericine behaviour and fibroin–sericine interaction and adhesion are still to be undertaken.

Treatments can induce modification in the mechanical behaviour, notably degumming. Hence sericine is removed from the fibroin by different techniques,

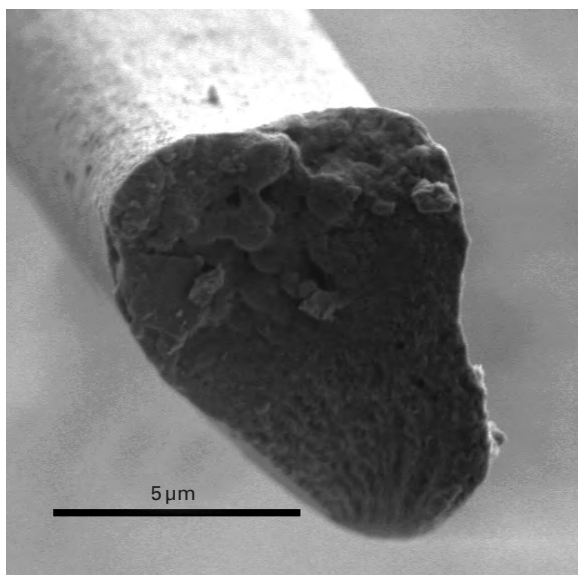


6.7 Effect of cycling loads on *Bombyx mori* silk.



6.8 Comparison between textile yarn and degummed industrial fibre, curves normalized.

mainly in water heated to close to 100 °C. Proteases (Freddi *et al.*, 2003) such as minerals (sodium carbonate and borate buffer) or organic (succinic acid and urea) solutions can be used (Jiang *et al.*, 2006). These processes seem to lower the properties of the silk and increase the variability. Notably, boiling water reduces the modulus and yield stress, and failure strain and stress (Pérez-Rigueiro *et al.*, 2002). Pre-treatment by methacrylamide can completely change the mechanical behaviour of silk. Hence, failure stress and strain reduce, but rigidity greatly increases and the stress–strain curve changes a lot with a more drawn-out plasticization (Kawahara *et al.*, 1996).



6.9 Tensile test fracture morphology of *Bombyx mori* silk fibre.

Another way to control the mechanical properties of spun fibres is a physical method: the forced silking. It consists of controlling the spinning rate of the fibre by stretching the fibres directly after spinning. Increasing rate increases the value of failure stress but decreases those of strain to failure (Shao and Vollrath, 2002; Du *et al.*, 2006).

Mechanical tests can be carried out under different conditions or atmospheres. Notably, some tests have been conducted in air, as well as immersed in water, ethanol, acetone or isopropanol. We can see that the different organic solvents have the same effects on the fibres: they increase the stiffness and reduce the elongation at break. Water has the opposite effect. Normally, water affects weak hydrogen bond interactions, and solvents the van der Waals bonds. However, they act in opposing ways. The explanation could be that silk fibres are mainly structured by weak hydrogen bonds and water is able to disrupt them, leading to plasticization. Organic solvents have only a role in desiccation of fibres (Pérez-Rigueiro *et al.*, 2000).

Finally, regeneration has to be improved in order to achieve fibre characteristics closer to those of natural silk fibres. Indeed, failure stress decreases three times during silk regeneration, independent of the solvents used (Holland *et al.*, 2007). It has also been shown that reducing the diameter of the fibre allows properties to be obtained closer to those of the natural properties of silk. Notably, reducing the aperture of the spinneret and increasing the draw ratio permit the beta sheet fraction to be increased and lead to an increase in properties. Residual sericine – from 0 to 18.9%

of initial sericine – seems to increase mechanical properties by increasing crystallization (Ki *et al.*, 2007b).

6.3.2 Mechanical properties of spider silk

The diversity of spiders and of the polymers they produce, depending on the gland employed, lead to a large range of mechanical properties (Table 6.5) (Blackledge and Hayashi, 2006). A typical stress–strain curve of major ampullate gland silk fibre of *Nephila madagascariensis* can be seen in Fig. 6.3(b) (Colomban *et al.*, 2008).

The mechanical properties of silk fibres are directly linked to their microstructures. Hence, the smaller the crystallites and the better they are oriented, the stronger will be the fibre. Ultimate mechanical properties, such as stiffness, can then be improved artificially. Indeed, even if the orientation of natural fibres is already almost maximized, the reduction in crystallite size can still be improved by forced silking at higher reeled rate than that which occurs naturally. Inter-plane distances increase with elongation, showing that crystals are involved in the mechanical behaviour from the beginning of the tensile test. Their role has been shown also through simulation which can explain the elastic phase of the stress–strain curves (Termonia, 1994; Vehoff *et al.*, 2007).

Mechanical properties can also be modified by the environment. For example, immersion of spider silk in water or methanol induces super-contraction, which is a specific state when fibres shrink by approximately 40–50%. The initial stiffness drops by three orders of magnitude, and the material becomes rubber-like in its behaviour (Gosline *et al.*, 1999). The nature of the solvent has great importance in determining behaviour, indeed, for example, ethanol does not induce any super contraction. Silk is also more or less sensitive to super-contraction, depending on its composition, hence minor and major ampullate silks do not react in the same way. It has been shown by nuclear magnetic resonance (NMR) that plasticizing by water occurs with glycine, tyrosine and leucine but not with alanine, explaining the different reaction depending on amino acid composition (Jelinski *et al.*, 1999; Vollrath and Porter, 2006).

6.3.3 Structures of silks

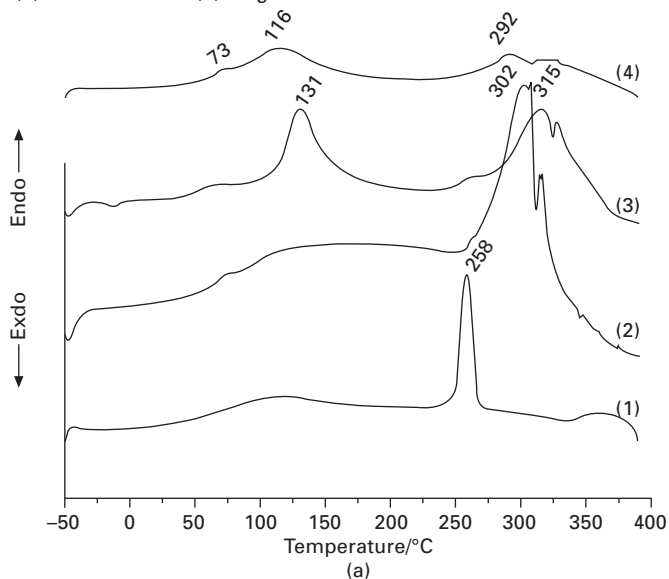
Microstructure identification

As for many complex polymers, the structure of silk remains a source of debate. Figure 6.10 compares differential scanning calorimetry (DSC) traces recorded for a semicrystalline polymer, the polyamide PA66 fibre, with those of silks – different silkworms (*Bombyx mori*, *Gonometa rufobrunea*, *Samia cynthia*) – or *Bombyx mori* silk of different history – flotte, not degummed

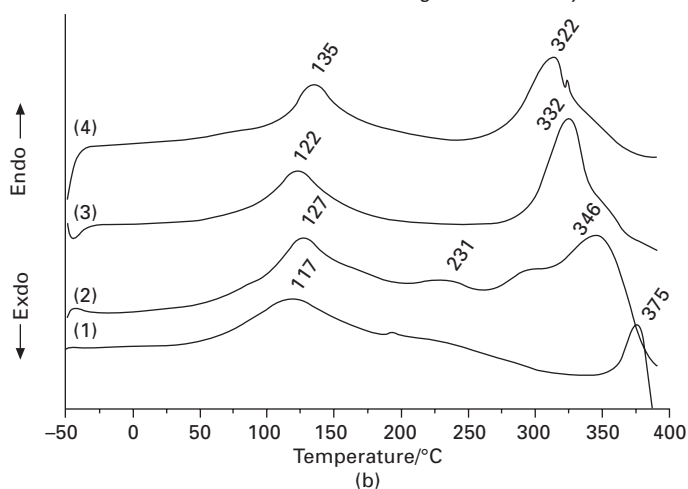
Table 6.5 Mechanical parameters of various spider silks diameter, modulus, stress, strain and toughness

	<i>Nephila clavipes</i> (Vehoff <i>et al.</i> , 2007)	<i>Nephila senegalensis</i> (Vehoff <i>et al.</i> , 2007)	<i>Araneus sericatus</i> (Denny, 1976)	<i>Araneus sericatus</i> High strain rate (Denny, 1976)	<i>Argiope trifasciata</i> (Guinea <i>et al.</i> , 2005)	<i>Deinopsis spinosa</i> (Blackledge and Hayashi, 2006)	<i>Hyptiotes cavatus</i>	<i>Uloborus diversus</i>
Diameter (μm)					3.2–4	0.4–0.6	0.9	0.6
E (GPa)	13–14.7	7.4–11.1	8.6–9.8	20.5	10.5–11.9	12.7–14.5	10.2–11.2	6.2–9.4
Stress (MPa)			810–880	1420	1123–1261	1101–1427	1834–1840	163–165
Strain (%)	21.4–26.1	16.9–27	24	27	17–23	22	20	22
Toughness ($\mu\text{J m}^{-3}$)	29.7–41.7	34.9–54.9	91–105	158		131–145	163–166	131–185

- (1) Polyamide 66 (3) *Bombyx mori* flotte
(2) Gland (4) Regenerated film



- (1) *Samia cynthia* (cocoon) (3) Raw silk AAA
(2) *Gonometa rufobrunnea* (4) Degummed *Bombyx mori*



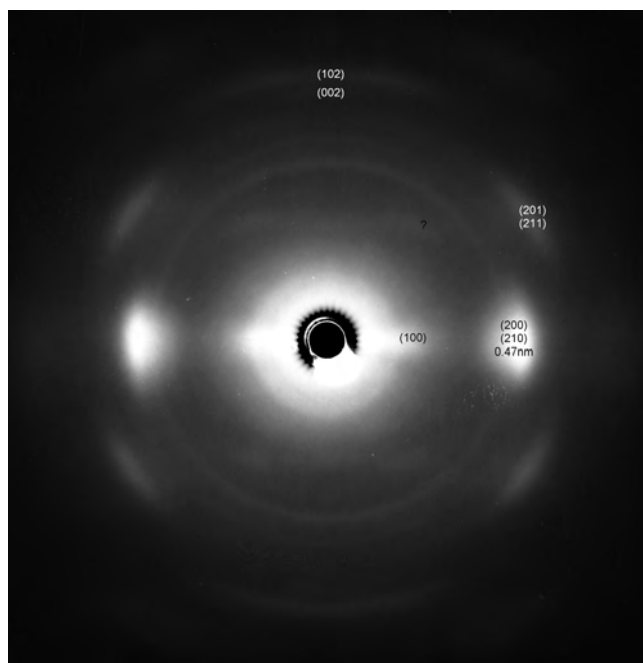
6.10 Comparison of the DSC traces (a) for *Bombyx mori* silk precursor (dried gland central part), silk fibre and regenerated film and (b) for different silks: degummed *Bombyx mori*, *Gonometa rufobrunnea*, Tussah, *Samia cynthia* and *Nephila madascarensis*, a comparison is made with PA 66 polyamide.

‘grège’ or degummed fibres, textile yarn and regenerated films. DSC gives a global view of the polymer properties and structure. The trace of PA66 fibre, a semicrystalline material – ~50% of crystallinity (Marcellan *et al.*, 2004) – shows a rather broad endothermic (onset ~250 °C), owing to the melting of a semicrystalline material and a weak event related to the presence of water, at ~120 °C (<2–3%wt). In contrast, the melting peak of silk is three or four times broader, suggesting a less crystalline structure. A large mid-height width of the peak is a maximum for regenerated amorphous silk. The shift of the onset of melting temperature from ~275 °C (*Bombyx mori*) to ~360 °C (*Samia cynthia*) reveals the composition, length and structural differences between the fibroin chains. Very small events are superimposed and can be associated to the crystallization (if exothermic) or melting (endothermic) of minor phases. Desiccated glands appear almost free of water although a strong water endothermic event is observed at 120–140 °C for the fibre. Within *Bombyx mori* silks, the highest melting temperature is measured for the best quality of not degummed Chinese silk. A much broader melting peak is measured for the regenerated film peaks owing to its more amorphous character. The crystallinity of regenerated films can, however, be preserved with optimized procedures. Different types of water are observed for regenerated films and for the silk precursor according to their specific microstructures.

Although still open for discussion, *Bombyx mori* silk is generally described as being composed of mixture of a ‘disordered’ Silk I and a ‘crystallized’ Silk II. The repetitive amino acid sequences GAGAGS are assumed to promote an intra or extra-molecular interaction, leading to a crystal creation called a β -sheet. Repetitive GAGAGY and separators lead to an amorphous or α -helix structure. Nevertheless, the polymer is not crystallized before spinning and is considered to be like Silk I in structure. Furthermore, models of transition of the crystalline part from un-spun Silk I to spun Silk II have been proposed from β -turns to β -sheets on the basis of NMR techniques (Asakura *et al.*, 1997, 2001, 2005; Demura *et al.*, 1998; Kameda *et al.*, 2002), X-ray (Marsh *et al.*, 1955; Lotz and Cesari, 1979; Rössle *et al.*, 2004), infrared (Chen *et al.*, 2001; Taddei and Monti, 2005; Hu *et al.*, 2006), circular dichroism (Wilson *et al.*, 2000; Li *et al.*, 2001; Dicko *et al.*, 2004; Termonia, 2004) and Raman scattering (Colomban *et al.*, 2008) analysis. Similiar observations have been made for wild silkworms (Nakazawa *et al.*, 1999; Magoshi *et al.*, 2000; Asakura and Nakazawa, 2004; Asakura *et al.*, 2007) and spiders (Parkhe *et al.*, 1997; Lefèvre *et al.*, 2007a). There is considerable discussion in the literature as to the degree of crystallinity in different silks. Some researchers have concluded that crystallinity is low (Colomban *et al.*, 2008) whilst others find much higher values, up to 50% (Lefèvre *et al.*, 2007b) for *Bombyx mori* and from ~10% (Gosline *et al.*, 1999) for spider silk in water to ~30% for dry spider silk (Lefèvre *et al.*, 2007b) (Table 6.6). Figure 6.11 shows typical X-ray diffraction pattern: broad rings

Table 6.6 Relative microstructure composition of *Bombyx mori*, a wild silkworm and spiders, from Lefevre *et al.* 2007b

Microstructure type	Coil (%)	α -helices (%)	β -sheets (%)	β -turns (%)
<i>Bombyx mori</i>	8	14	50	28
<i>Samia cynthia ricini</i>	10	14	45	31
<i>Nephila clavipes</i>	12	18	37	33
<i>Nephila edulis</i>	11	22	36	31



6.11 2D X-ray diffraction image of *Bombyx mori* silk ($\lambda_{\text{Co}} K_{\alpha} = 1.789 \text{ \AA}$).

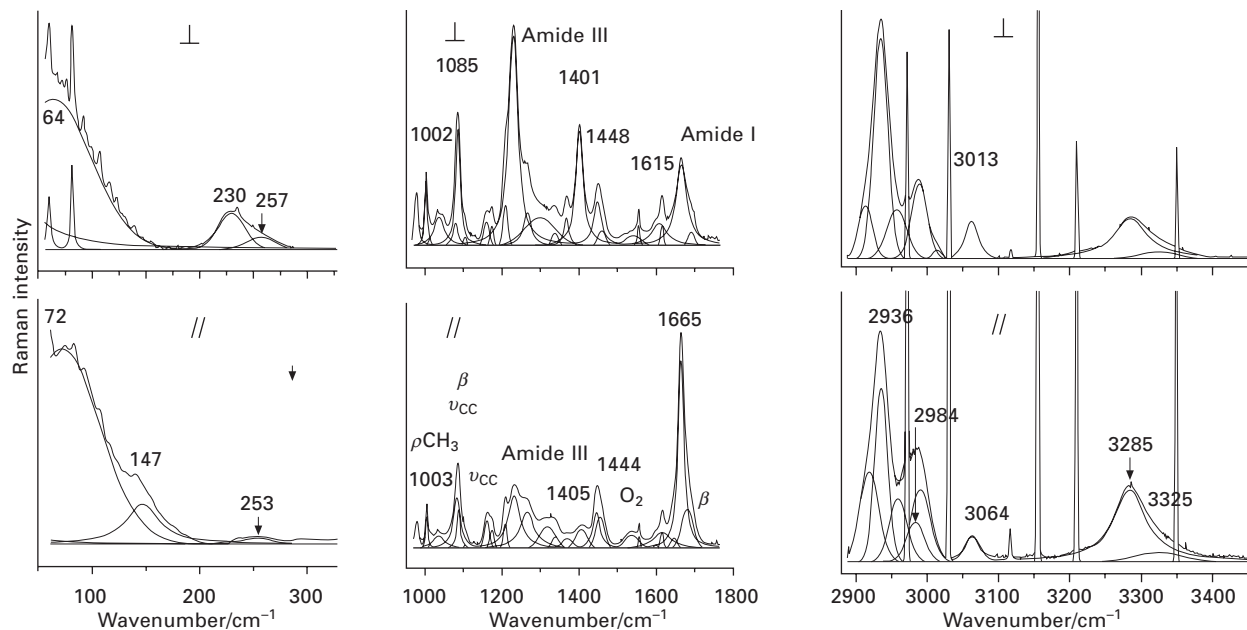
and rare Bragg peaks (indicating the partial fibre texture) are observed; the notation of crystallographic plans comes from Drummy *et al.* (2005).

The crystallinity of macromolecular compounds is hindered by the great length of the macromolecules, the same chain going through regions of different degrees of organization. Orientational disorder occurs readily for polymer backbones and hinders accurate structure determination. This point deserves further study and data must be read with caution, as most authors ignore the intrinsic variability of the silk fibres: it is not possible to know the age of the fibre and the corresponding Type, I, II, III or IV.

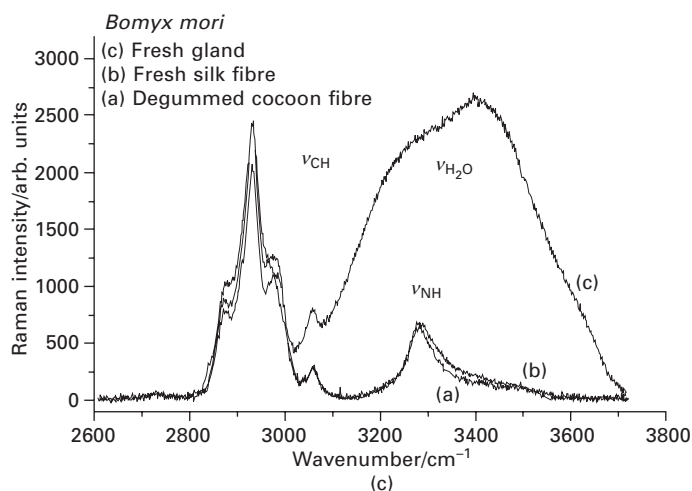
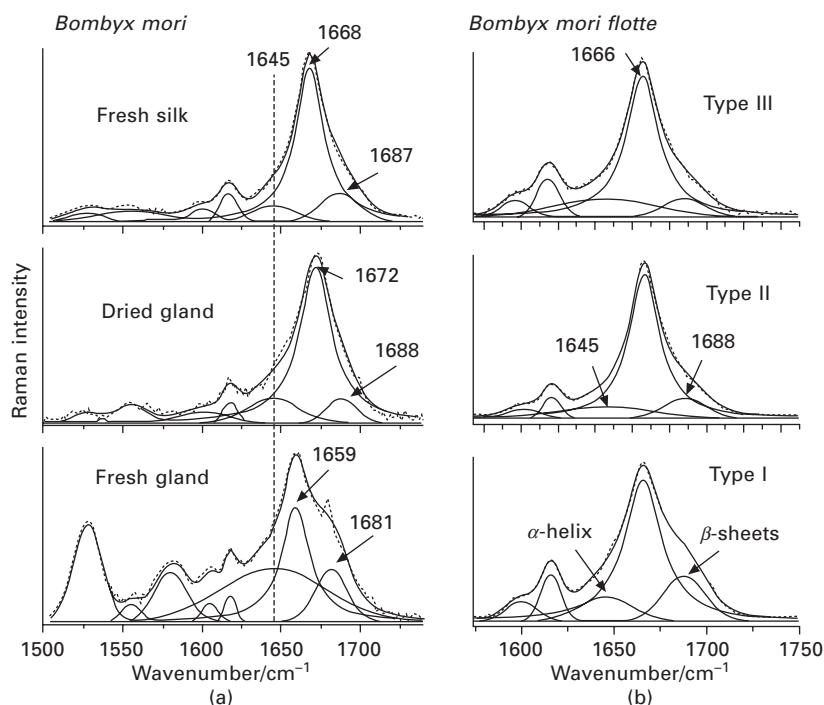
Vibrational spectroscopy offers an alternative route to understanding the structure of amorphous or low crystalline materials (Gouadec and Colombari, 2007). However, the vibrational probe is the chemical bond itself, a

subnanometric probe: stretching and bending modes probe the chemical bonds and their environment, the information also obtained from, for example, NMR technique, but librational and lattice modes probe long-distance correlations in the same manner as X-ray diffraction. For silk, the most pertinent probes are those related to the chain backbone (amide group signature) and to the interaction between the N—H group and neighbouring O or N atoms of the grafted amino acids of the same or adjacent chains. Amide groups have very characteristic vibrational signatures: (a) the amide I mode, originating from the stretching of the nC=O bond coupled with the C—N bond, shows a well-defined peak, both in IR and Raman spectroscopy at $\sim 1630\text{--}1670\text{ cm}^{-1}$; and (b) the amide III mode originating from the nC-N bond which is also both IR and Raman active and results in peaks between 1200 and 1300 cm^{-1} . The isolated nN-H vibration mode at $\sim 3285\text{ cm}^{-1}$ offers a very sensitive tool to probe the short-range environment of the N—H bond and associated hydrogen bonds. Finally the low wavenumber range ($< 200\text{ cm}^{-1}$, librational and lattice modes) is the most pertinent region to obtain structural information at medium to long range, including giving information on the degree of crystallinity (Colomban *et al.*, 2006; Gouadec and Colomban, 2007). Such studies require high-resolution instruments and require a solid state physics approach, only recently developed for polymers (Herrera Ramirez, 2004, 2006; Colomban *et al.*, 2006). Although information on the orientation of molecular bonds is difficult to obtain from internal modes, the polarization of the low wavenumber region reflects the fibre anisotropy very well, as shown in Fig. 6.12. In contrast to other semicrystalline polymers, such as polyamides or polyethylene terephthalate (Colomban *et al.*, 2006) for which a separation between ‘narrow’ low wavenumber lattice modes of the crystalline domains merge with the broad contribution of the amorphous matrix, the analogous signature for silk remains broad. This has been interpreted by Colomban *et al.* (2006) due to indicate a much lower, quasi-amorphous, character of the silk.

Figure 6.13 compares the Raman signature in the N—H and amide I regions recorded on the liquid present in the gland and on fresh silk, freshly spun from the animal, as well as those of fibres with Type I, II and III signatures as well as silk in the gland (dried). The structural differences are obvious, especially with the shift of the component wavenumber and the change of the relative intensity. The huge intensity of the ca. 3450 cm^{-1} band indicates that the liquid in the gland is mainly water and that most of the water is eliminated before the formation of the silk fibre at the spinneret. Amide I mode, in other words the stretching mode of the C=O bond coupled with adjacent C—N and C—C bonds (see Fig. 6.1a), is used to discriminate between the different chain conformations: the Raman signature of α -helix peaks at ca. 1650 cm^{-1} and for the β -sheet at ca. 1690 cm^{-1} whatever the protein chain (keratin, fibroin spidroin, etc.). The assignment of the main peak is much



6.12 Peak fitting of the Raman signature of *Bombyx mori* degummed single fibre at 0% strain for parallel and perpendicular polarizations. Note the narrow peaks due to neon lamp used as very accurate internal reference wavenumber. Reprinted from *Journal of Raman Spectroscopy* (2008), 39, © Wiley, with permission.



6.13 Comparison of the Raman signatures in the $\nu N-H$ (c) and amide I (a,b) regions for the (a) central part of a fresh gland ($\sim in vivo$), for a fibre as spun by a living silkworm and for a dried gland (central part). Amide I signature of Type I, II and III fibre are given (after Dinh *et al.* 2008).

debated and may correspond to intermediate structures with some helical characteristic (Monti *et al.*, 2001; Rousseau *et al.*, 2004, 2006; Colomban *et al.*, 2008). The decreasing intensity of the α -helix and β -sheet components as well as the broadening of the bands indicates that the crystallinity of the fibre decreases with time and that the adsorbed water also decreases the crystallinity.

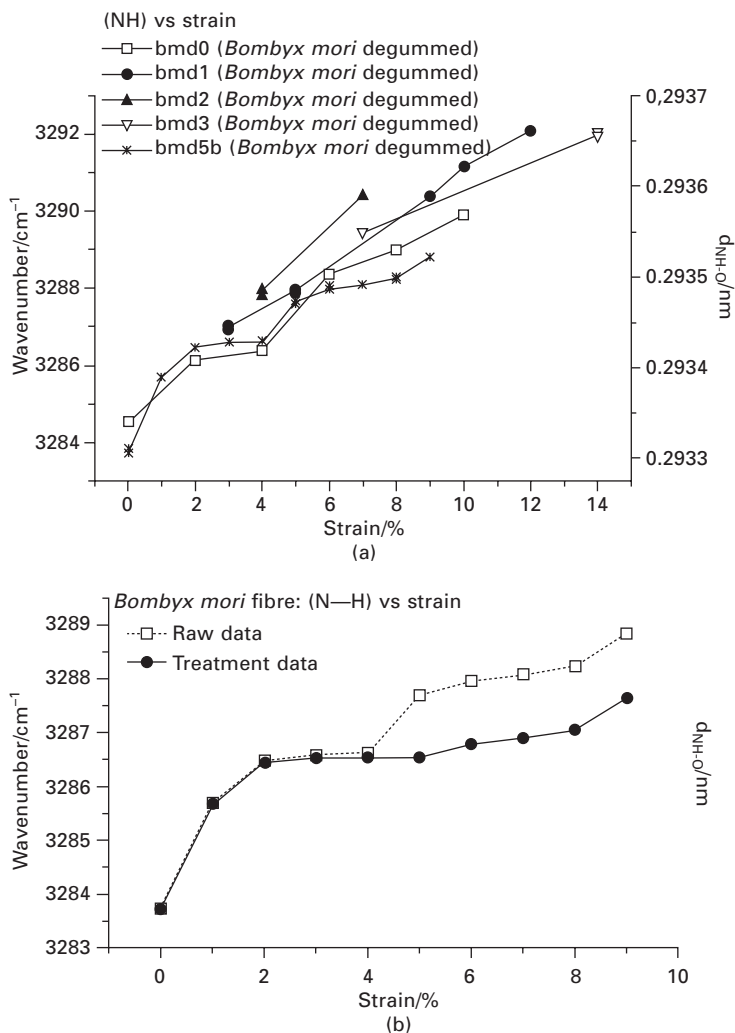
Relationship between chain structure and stress–strain behaviour thanks to Raman analysis under controlled strain

It has long been understood that a relationship exists between the molecular chain arrangements in organic polymer fibres and their stress–strain curves. A review on the subject has been written by Gosline *et al.* (1999) on mechanical link with microstructure of spider silk. Experimental confirmation has been provided by nanomechanics, i.e. the quantitative study of the bond change under controlled tensile/compressive stress–strain, measured by Raman scattering (Marcellan *et al.*, 2003; Colomban, 2002; Colomban *et al.*, 2006; Gouadec and Colomban, 2007). These studies confirm that mechanical properties are driven by the main phase, the amorphous one, and in most of the cases, even in polymers with a high crystalline content, the crystalline phase does not play a significant role in determining the form of the tensile curve.

Obviously the instant lengthening of a helix is consistent with an obvious plateau in the tensile curve. On the other hand, no phase transition plateau is expected for flat ribbon conformations. However, it is difficult to predict the effects of twists and distorted helices on the tensile curve. Knot formation is possible and in this case a flat plateau can be ruled out. This can be consistent with the hardening observed for Type IV curves (Fig. 6.3a). Sliding and opening between **b**-like ribbons can explain a straight stress–strain curve.

The low wavenumber modes assigned to chain translation are strain-dependent (Colomban *et al.*, 2008). This is similar to amide III modes and some other modes of the 1200–1600 cm^{-1} region obtained by experiment at the bond level with macroscopic strains applied to the single fibre (Sirichasit *et al.*, 2000, 2003; Colomban *et al.*, 2008). These data reflect rather well the macroscopic mechanical behaviour with a first elastic behaviour up to 2% of strain and then a more or less defined plateau.

We report here the analysis of the nN-H modes (see Dinh *et al.*, 2008, for details). The N-H modes are very sensitive because the elasticity of the N-H bond when the $\text{H}\cdots\text{X}$ hydrogen bond is modified. Measurement as a function of time for a fibre under a controlled stress level shows a slow viscoelastic behaviour which is significant for the time of recording (2 to 5 hours). For this reason this effect has been subtracted. The difference observed on stress–strain plots is confirmed by the Raman measurements and shown in Fig. 6.14.



6.14 Plots of the $\nu\text{N—H}$ wavenumber for five fibres strained up to the fracture in dry environment: (a) raw data, measurement at 6% was made during the night with a much longer recording time, and (b) after the step due to the evolution during the night (at 5%) has been corrected.

It has long been established that a reliable relationship exists between X—H (X = O or N) stretching wavenumbers and the distance with the nearest acceptor (O or H) to an hydrogen bond. Using the correlation established by Gruger *et al.* (1995) the corresponding distance of hydrogen bonding has been reported as shown in Fig. 6.14. It is obvious that the geometrical distortion is weak and can be assigned to mainly intra-chain bonding. However, this

demonstrates that a lengthening of the chain bond takes place in the elastic regime and then the bonds are not so affected by the stress applied at the macro-scale.

6.4 Conclusions

Silk fibres are made up of proteins which form naturally occurring polymers consisting of chains of amino acids. Many creatures produce silk fibres, which can be of a wide variety of dimensions and cross-sections, so complicating their study. The most widely used silk fibre comes from the larvae of the *Bombyx mori* moth. The traditional textile use of these fibres can be extended to new applications in technical textiles and biomedical applications. There is great potential for these new uses owing to the biological nature of the fibres, which permits genetic modifications to the standard silk, as well as the possibility of regeneration of silk from solution. Comparison with the properties of spider silk suggests that the mechanical properties of traditional silk could be improved by genetic modification, and regeneration of silk could produce fibres with exceptional properties. Much still needs to be investigated, however, so as to obtain a better understanding of the microstructure of silk and the links between microstructure and mechanical characteristics.

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6.6 References

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Structure and behavior of collagen fibers

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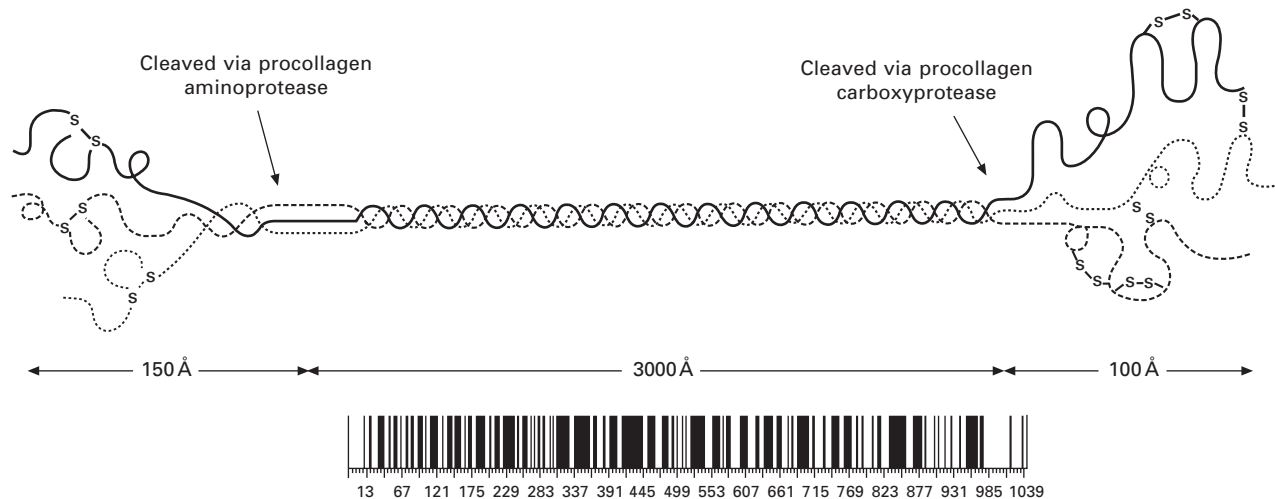
Abstract: Collagen fibers form the structural scaffolds of vertebrate tissues that store elastic energy, facilitate joint movement, and dissipate excess energy upon completion of joint movement. The purpose of this chapter is to discuss the molecular, microfibrillar and fibrillar structures of collagen fibers and the mechanism by which energy is stored, transmitted, and dissipated. The ability of collagen fibers to prevent premature mechanical failure of vertebrate tissues is also examined as well as the failure mechanisms of collagen fibers.

Key words: collagen fibers, energy storage, fiber failure, defibrillation, collagen structure.

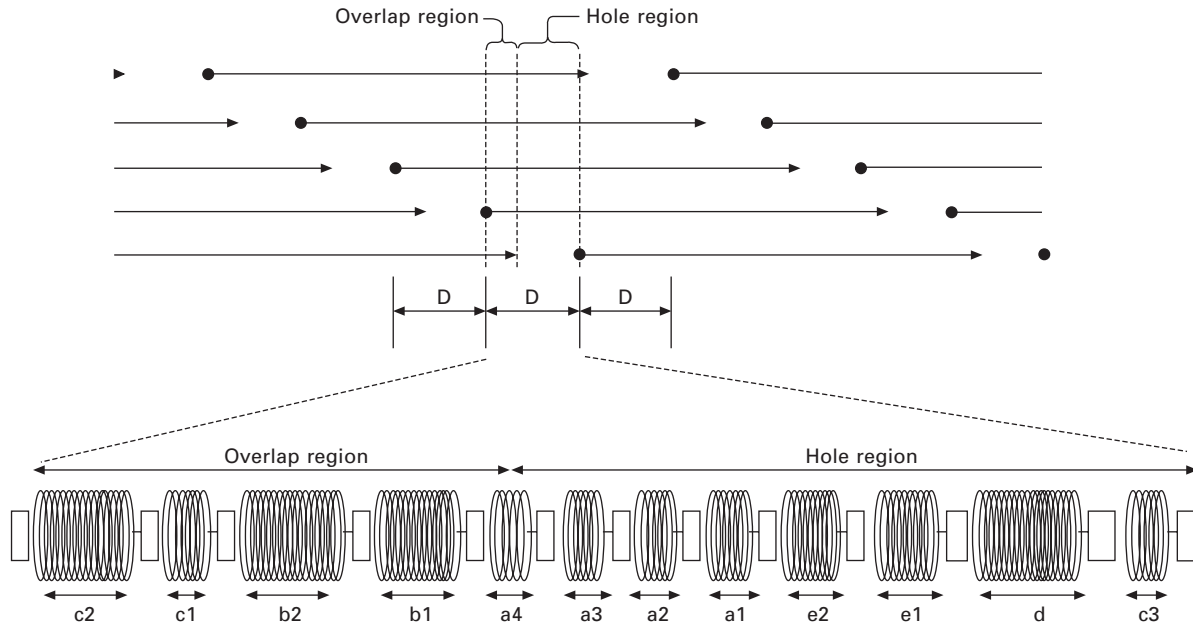
7.1 Introduction

Collagen fibers form the basic structural components of the extracellular matrix (ECM) of vertebrates that serve to: store elastic energy during muscular deformation, transmit stored energy into joint movement, and transfer excess energy from the joint back to the attached muscles for dissipation (Silver and Landis, 2008). They also act as mechanotransducers by transferring stress borne by the musculoskeleton to the attached cells in order to regulate tissue metabolism, either up or down, as a result of changes in mechanical loading (Silver, 2006). Finally, they prevent premature mechanical failure of tissues and limit deformation of most ECMs and organs (Dunn and Silver, 1983). Therefore, the ECM structure is intimately related to the failure properties of tissues.

The basic structural unit of collagen fibers is the collagen molecule that is in the form of a triple helix (Fig. 7.1). Collagen triple helices are packed into a ‘quarter-staggered’ packing pattern that results in nearest neighboring molecules being staggered longitudinally by about 22% of their molecular lengths with a space or hole between the head of one molecule and the tail of the next (Fig. 7.2) (Silver *et al.*, 2003). Five collagen molecules are packed laterally into a quarter-staggered unit that is in turn longitudinally packed into microfibrils that are believed to be continuous and run the length of a



7.1 The structure of procollagen, the biosynthetic precursor of the collagen molecule. Procollagen molecules are formed within the cell and the large propeptides are extracellularly cleaved during self-assembly into crosslinked collagen fibers. Collagen molecules are triple helical rods about 300 nm in length as shown by the arrows. The flexibility profile is shown below the diagram of the collagen triple helix and the 300 nm (3000 Å) line that represents the triple helical portion. The dark vertical lines represent rigid regions and the light areas depict the flexible domains of the collagen triple helix at the bottom of the figure. The amino acid residue numbers along the axis of the triple helical collagen molecule are shown at the bottom of the flexibility profile.



7.2 The top portion illustrates the structure of a five membered microfibrillar unit that is believed to be the repeat unit found in collagen fibrils and fibers. In this packing pattern five collagen molecules are staggered by about 22% of the molecular length of 300 nm with respect to their nearest neighbors. A space or hole 0.6 D in length ($D \pm 67$ nm) is left between neighboring molecules. The collagen molecule is 4.4 D long, where D is the stagger between neighboring collagen molecules and consists of a overlap zone of 0.4 D and a hole region of 0.6 D (shown by the vertical dotted lines that are superimposed on the microfibril). The overlap and hole regions that make up the D repeat consist of 13 rigid and 12 flexible domains and are depicted by the rectangles and springs shown, respectively. The 12 flexible regions are identical to the 12 bands denoted c2 through c3 that are seen as dark vertical lines across the collagen fibril when collagen is stained with heavy metals and viewed in the electron microscope. The 12 flexible regions are believed to be stretched when collagen fibrils are mechanically deformed. Collagen molecules in tendon are held together in the microfibril with crosslinks that are at the ends of each molecule.

tissue. Collagen microfibrils are laterally packed into fibrils and fibers in most tissues (Silver *et al.*, 2003).

Collagen fibers are viscoelastic and exhibit time-dependent mechanical behavior. Viscoelasticity may be important in resisting impact loads especially in the musculoskeleton; however, it complicates the understanding of ECM behavior since most real-time measurements made on these tissues contain both elastic and viscous contributions (Dunn and Silver, 1983). The elastic behavior varies from as high as about 90% of the total stress for tendon to as low as about 50% for skin depending on the collagen fiber orientation, rate of loading and the quantity of other tissue constituents (Dunn and Silver, 1983).

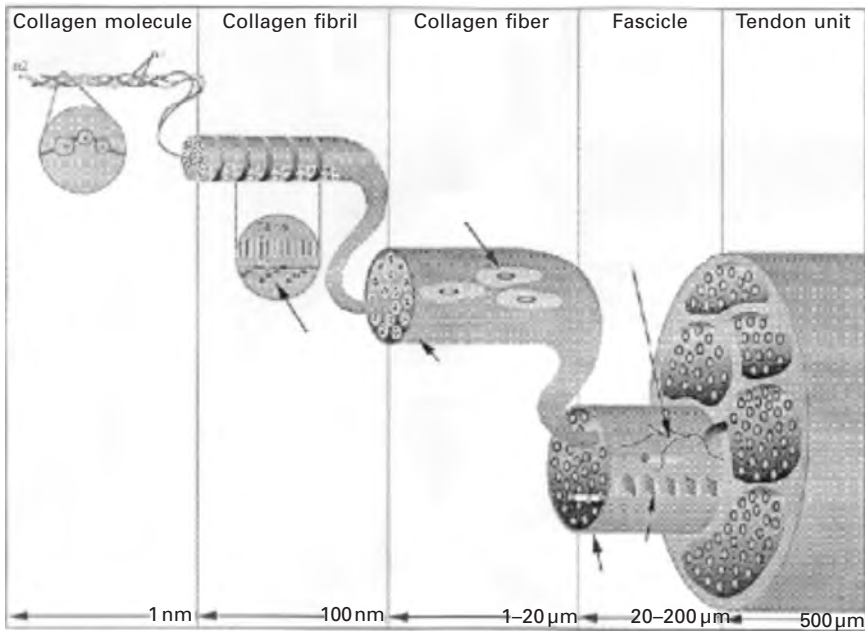
The purpose of this chapter is to examine the relationships between structure, orientation and mechanisms of collagen fiber failure. Information presented below suggests that collagen fiber structure and orientation play important roles in dictating the mechanical properties of ECMs and fiber failure mechanisms.

7.2 Collagen fiber structure

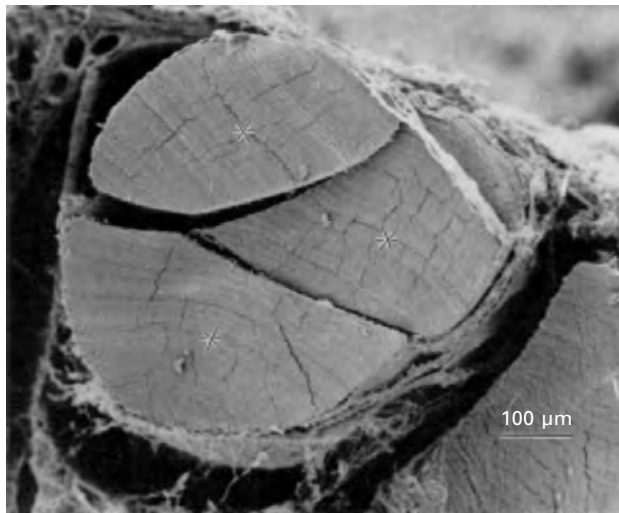
Collagen fibers limit deformation of most ECMs and organs (Dunn and Silver, 1983). In addition, by virtue of mechanochemical transduction and the repair process, collagen fibrils and fibers are synthesized and catabolized as a result of changes in the local mechanical demands (Silver and Landis, 2008). In oriented collagenous networks such as those found in tendons, the fibers have hierarchical structures that include the collagen molecule, microfibril, fibrils, fibril bundles, and crimped fascicles in tendon (Fig. 7.3). In other tissues, groups of collagen fibrils and fibers are packed into three-dimensional arrangements along with other components such as proteoglycans, smooth muscle cells, and elastic fibers. Thus collagen fibers can be found in uniaxially oriented, biaxially oriented, circumferentially oriented, and multiaxially oriented structures with varying mechanical properties (Silver and Landis, 2008). In this chapter we will limit the discussion to the structure and failure of uniaxially oriented collagen fibers in tendon.

7.3 Chemical structure of collagen fibers

Collagen is the major structural protein found in vertebrate tissues that is a family of over 50 collagens and collagen-like proteins (Hulmes, 2008). The chemical description of collagen is a protein containing three polypeptide chains, each of which is composed of one or more regions containing the sequence Gly-X-Y, where X and Y can be any other amino acid residue. This three-chain molecule forms a right-handed triple helical structure containing glycine residues buried at the center of the cylindrical molecule. In humans,



(a)



(b)

7.3 Structural hierarchy in the tendon. (a) The relationship between collagen molecules, fibrils, fibers, fascicles, and tendon units. Although the diagram does not show fibril subunits, collagen fibrils appear to be self-assembled from intermediates integrated within the fibril termed microfibrils. The arrows point to the locations of interactions between collagen fibers and fibroblasts found in tendon. (b) Scanning electron micrograph of a rat-tail tendon fiber showing the fascicles (see asterisks) that make up the tendon unit.

there are currently 28 different proteins known as collagens that are grouped into a number of subfamilies. The most abundant subfamily is the fibrillar collagens of which type I collagen is found in tendons, skin, cornea, bone, lung, and vessel walls (Hulmes, 2008). This collagen is thought to give rise to the high tensile strengths of collagen fibers in tendon. However, collagen fibrils are composed of mixtures of different collagen types as described below.

7.4 Collagen fibrillar structure

Collagen fibrils are actually heterogeneous assemblies of more than one collagen type (Hulmes, 2008). Collagen microfibrils appear to be made up of a single collagen type, while collagen fibrils are mixtures of other collagen types, including I, II, III, V, XI, XXIV and XXVII. For the purposes of this chapter, tendons will be considered to be made up of exclusively type I collagen. In tendon, collagen fibril diameters are between 20 and 280 nm and collagen fibers have diameters are between 1 and 300 μm (Silver *et al.*, 2003). While collagen fibrils form from lateral addition of smaller fibrils they form bundles of fibrils and larger bundles termed fascicles as shown in Fig. 7.3. Groups of fibril bundles form fascicles that in turn make up the cross-section of a tendon bundle (Fig. 7.3). These structural elements acting in concert give rise to the mechanical properties of tendon.

The ultrastructure of tendon has been studied extensively as a function of maturation (Torp *et al.*, 1974; Parry *et al.*, 1978). Early studies recognized that five collagen molecules were packed in staggered fashion to form a microfibril (Smith, 1968; Hodge and Petruska, 1963) that was identified by electron microscopy (Pease and Bouteille, 1971). Collagen microfibrils appeared to be held together by an interfibrillar matrix containing proteoglycans (Scott, 1996). These collagen fibrils were observed to have a planar waveform, termed crimp, and be the load-bearing units (Diamant *et al.*, 1972). Upon deformation, the crimp straightens and explains the low modulus region at the beginning of the stress–strain curve of tendon (Diamant *et al.*, 1972). After birth, the distribution of fibril diameters from rat tail tendons is fairly flat, supporting the concept that fibril diameter and length increase occur by the lateral fusion of fibril bundles (Torp *et al.*, 1974; McBride *et al.*, 1985, 1988; Birk *et al.*, 1989). The volume fraction of collagen fibrils increases during maturation until it reaches about 0.5; in fibril cross-sections of tendon, small collagen fibrils fill the space between larger ones (Torp *et al.*, 1974).

The ability of collagen molecules to self-assemble into fibrils occurs not only in tissues but also *in vitro*. The self-assembly of collagen molecules from solutions of type I collagen is a model that has been used to understand the structure and mechanical behavior of collagen fibers in tissues.

7.5 Collagen self-assembly

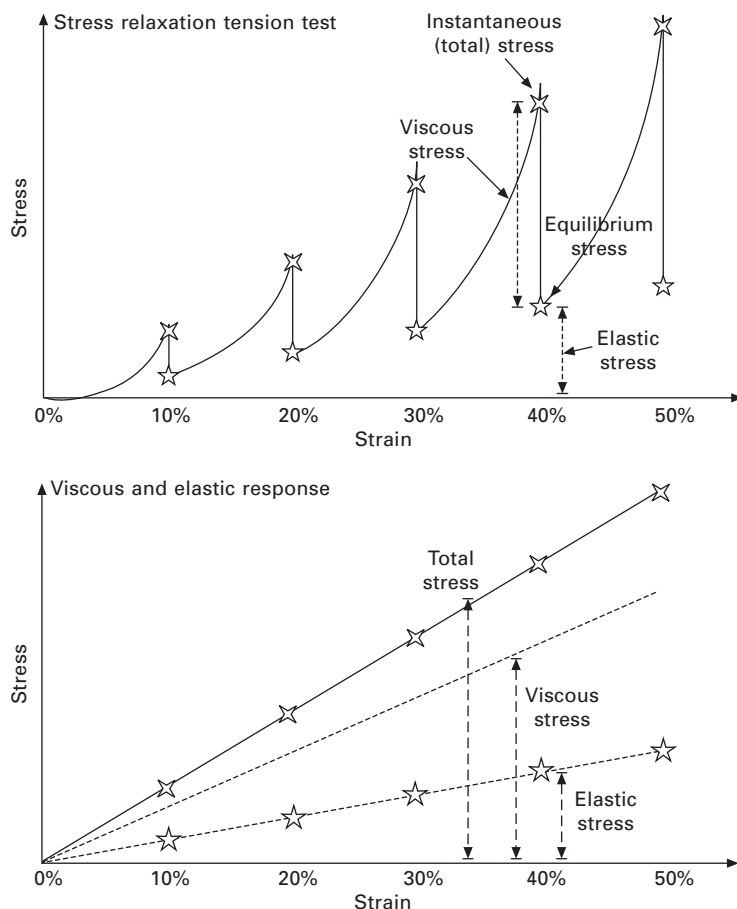
Collagen molecules self-assemble under physiological conditions into a quarter-staggered structure, termed the microfibril, that in turn grows linearly and laterally into collagen fibrils (Silver *et al.*, 2003). Collagen triple helices and microfibrils are very long and thin and are therefore quite flexible. Solution studies suggest that the collagen molecule can be modeled as a semi-flexible rod with bend angles up to about 120° with respect to the molecular axis (Silver *et al.*, 2001a, 2003). This flexibility allows collagen molecules to undergo conformational changes required for self-assembly into long thin fibrils via end-overlap of several molecules followed by lateral assembly into microfibrils with diameters that are multiples of 4 nm. The flexibility of collagen molecules and fibrils allows both load transmission and energy storage (Silver, 2006).

7.6 Viscoelastic behavior of tendon

A number of excellent studies have been published that have helped in the interpretation of the stress–strain behavior of tendon (McBride *et al.*, 1985, 1988; Knorzer *et al.*, 1986; Folkhard *et al.*, 1987; Fratzl *et al.*, 1998; Misof *et al.*, 1997; Sasaki *et al.*, 1999). Much of current understanding of the relationship between hierarchical structure and viscoelastic behavior of ECMs is based on studies of the mechanical properties of developing and mature tendons (Torp *et al.*, 1974; McBride, 1984; McBride *et al.*, 1985, 1988). The properties of developing tendon rapidly change just prior to the onset of locomotion. The maximum total stress that can be borne by a 14-day-old embryonic chick leg extensor tendon is about 2 MPa and increases to 60 MPa, 2 days after birth (McBride *et al.*, 1985, 1988). This rapid increase in tensile stress by tendon occurs without large changes in its hierarchical structure (McBride *et al.*, 1985, 1988). In this case, the collagen fibril length appears to be more important for energy storage and for increased ultimate tensile strength than fibril diameter; but the two parameters are linked together since fibrils have been shown to grow in length by lateral fusion of fibril bundles (Torp *et al.*, 1974; McBride *et al.*, 1988; Silver *et al.*, 2003). During mechanical loading, a tensional increase in the D period is observed with increasing strain that is associated with (1) molecular elongation, (2) increases in the gap distance and (3) molecular slippage (Sasaki *et al.*, 1999). Molecular stretching occurs at lower stresses compared to increases in the gap spacing and molecular sliding.

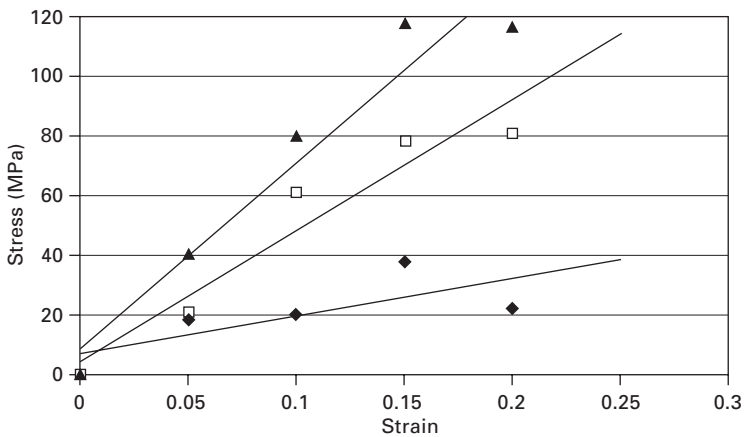
The time-dependent behavior of tendon makes it difficult to interpret stress–strain relationships for these tissues. However, using incremental stress–strain curves, the elastic and viscous behaviors can be separated and analyzed in terms of tissue structure (Dunn and Silver, 1983). The viscoelastic properties of ECMs have been obtained by constructing incremental stress–

strain curves for a variety of tissues including tendon (Dunn and Silver, 1983; Silver, 2006). Such incremental stress–strain curves are derived for tendon and other ECMs by stretching the tissue in a series of strain increments and then allowing the stress to relax to an equilibrium value at each strain increment before another strain increment is added (Fig. 7.4) (Dunn and Silver, 1983).



7.4 Incremental stress–strain curves for ECMs tested in tension. Top: a strain increment is applied to the ECM and the initial stress is measured. The strain increment varies from about 2% for tendon to about 10% for skin. The stress is allowed to relax at room temperature until an equilibrium value is reached. The process is repeated until the sample fails. Bottom: plots of all the initial (total) and equilibrium stresses are made versus strain as well as plot of the total minus equilibrium stress–strain. The equilibrium stress–strain curve is equivalent to the elastic stress–strain curve while the difference between the total and equilibrium stress is the viscous stress (Seehra and Silver, 2006).

By subtracting the elastic stress (equilibrium stress value) from the initial or total stress value, the viscous stress is obtained. By plotting the equilibrium stress versus strain and the total stress minus equilibrium stress versus strain (Fig. 7.5) we get elastic and viscous stress–strain curves for tendon (Silver *et al.* 2008). From these curves and the literature, important information can be obtained concerning the mechanism of stretching and sliding of the collagen molecules and fibrils that make up the structure of tendon (Silver, 2006). It turns out that the slope of the elastic stress–strain curve is proportional to the elastic modulus of the collagen molecule (Silver *et al.*, 2001b), while the viscous stress at a particular strain is a measure of the fibril length (Silver *et al.*, 2001b). An estimate of the elastic modulus of the collagen molecule is obtained by dividing the slope of the elastic stress–strain curve by the collagen content and by the ratio of the molecular strain (change in h spacing axial rise per amino acid residue) divided by the macroscopic strain (0.1 for tendon) (Silver, 2006). Using this approach a value of between 7 to 9 GPa for the elastic modulus of the collagen molecule is found for rat tail tendon collagen (Table 7.1) (Silver, 2006). Collagen fibril lengths calculated from the viscous stress and hydrodynamic theory (Silver, 2006) range from about 20 μm for developing tendon to in excess of 1 μm for adult tendons (Table 7.2) (Silver, 2006).



7.5 Total ◆, elastic □ and viscous ▲ stress–strain curves for tendon. The elastic stress–strain curve is approximately linear with strain and is above the viscous curve, illustrating that more energy is stored during tensile deformation of tendon than is dissipated as heat during stretching.

Table 7.1 Estimated elastic moduli for collagen based on elastic stress measurements for various ECMs (Silver, 2006)

Molecule	Tissue	Elastic modulus (GPa)
Type I	Self-assembled	6.51
	Rat tail tendon	7.69
	Turkey tendon	4.20 (no mineral)
	Turkey tendon	7.22 (mineral 0.245)
Types I and III	Skin	4.4
Type II	Articular cartilage	7.0 (surface parallel)
	Articular cartilage	2.21 (surface perpendicular)
	Articular cartilage	4.91(whole parallel)
	Articular cartilage	1.52 (whole perpendicular)
	Osteoarthritic cartilage	0.092 (whole perpendicular)
Elastin	Skin	0.040
	Vessel wall	0.01

Table 7.2 Estimated collagen fibril lengths based on mechanical measurements of viscous loss in different ECMs (Silver, 2006)

Tissue		Fibril length (mm)
Rat tail tendon		0.860
Self-assembled collagen fibers		0.0373
Turkey tendon (no mineral)		0.108
Turkey tendon (0.245 mineral content)		0.575
Human skin		0.0548
Articular cartilage	(surface parallel)	1.265
	(surface perpendicular)	0.688
	(whole parallel)	0.932
	(whole perpendicular)	0.696
Osteoarthritic	(whole perpendicular)	0.164

7.7 Viscoelasticity of self-assembled type I collagen fibers

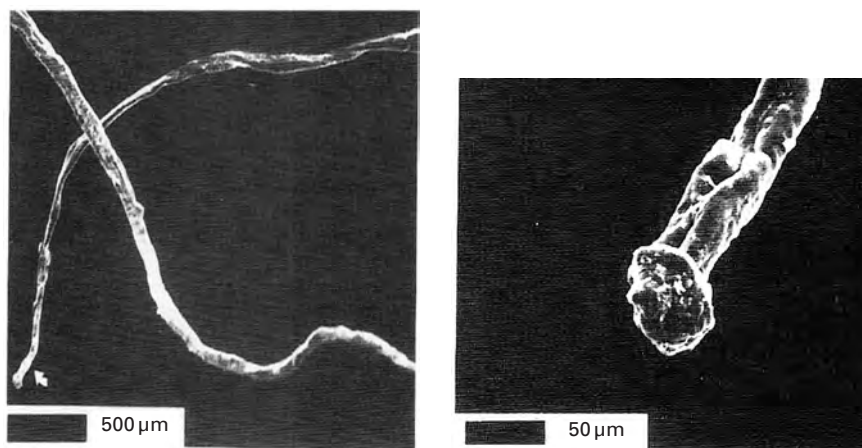
Additional information concerning the deformation mechanisms of tendon can be derived from understanding the behavior of model systems such as self-assembled type I collagen fibers derived from solubilized rat tail tendon collagen (Silver *et al.*, 2001a). The fibers are self-assembled under conditions that produce D-banded collagen fibrils similar to those seen in rat tail tendons (Silver *et al.*, 2000). The purified type I collagen fibrils produced by self-assembly are much narrower than those observed in tendon, i.e. between about 20 and 40 nm in diameter, as compared with those in tendon which are as large as several 1 μm . Incremental stress–strain curves for self-assembled purified type I collagen are linear for uncrosslinked collagen fibers (Silver *et al.*, 2000, 2001a). However, unlike the incremental stress–strain curves for rat tail tendon, the viscous stress–strain curve for uncrosslinked self-assembled

collagen fibers is above the elastic stress–strain curve (Silver *et al.*, 2001a). This result suggests that in the absence of crosslinks the ability of collagen fibers to transmit tensile forces is impaired; transmission of tensile forces appears increased by the formation of crosslinks (Silver, 2006). When the self-assembled collagen fibers are subsequently crosslinked by aging at room temperature, the elastic stress–strain curve is then above the viscous one (Silver *et al.*, 2001a). On comparison of the slopes of the elastic stress–strain curves for tendon and self-assembled collagen fibrils, the slope of the elastic stress–strain curve for crosslinked self-assembled collagen fibrils is much closer to that of tendon than is the slope for uncrosslinked collagen fibers (Silver, 2006). This result underscores the need for end-to-end crosslinking between collagen molecules in order to facilitate tensile force transmission during stretching (Silver, 2006). The tensile properties of tendon and self-assembled collagen fibers are very similar. The transmission of tensile forces by tendon is attributable to direct stretching of the triple helix; energy loss occurs through the sliding of fibrils and bundles of fibrils during tensile deformation. The behavior of other ECMs is a bit more complicated because of the presence of additional components including elastic and smooth muscle fibers and differences in collagen fiber orientation (Silver, 2006).

Morphologic studies on collagen fibers suggest that mechanical deformation leads to collagen fibril alignment as well as development of fibril substructure that affect the failure mechanisms of collagen fibers (Pins *et al.*, 1997). Stretching results in collagen fibers with the outer fibrils containing additional axial orientation and a more prominent fibrillar substructure compared to fibrils found in the center of the fiber (Pins *et al.*, 1997). Stretching also leads to increased ultimate tensile strengths and axial alignment of the collagen subfibrils (Pins *et al.*, 1997). Stretched uncrosslinked collagen fibers require more energy to pull to failure and the failed fiber surface shows more plastic deformation than do the fracture surfaces of unstretched collagen fibers (Fig. 7.6) (Pins *et al.*, 1997).

7.8 Collagen fiber failure

The effects of cycling on the structure of collagen fibrils in tendon have been reported in the literature (Torp *et al.*, 1974). Repeated mechanical cycling leads to the formation of voids within collagen fibrils (Torp *et al.*, 1974). Dissociation of fibrils starts in spots where voids are seen and results in the observation of 15 nm in diameter subunits that lack the collagen D-period (Torp *et al.*, 1974). Fissures become apparent under repeated tensile loading at sites where fibroblasts are in contact with the collagen fibrils. Collagen fibril failure is reported to occur primarily by progressive dissociation into subfibrils, 15 nm in diameter with some loss of the axial alignment of the fibrils. In addition, a secondary mechanism of failure is observed in rats 7.5



7.6 SEMs of failure surfaces of rat tail tendon fibers stretched in tension at low (left) and high (right) magnifications. Note arrow in left figure site of enlargement of figure in right SEM. Rat tail tendon fibers show extensive plastic deformation at site of failure with flow and retraction around fiber end. Figure modified from Pins *et al.* (1997).

months and older. Fibroblasts in tendons from this age group appear to develop fissures that eventually extend to other fibroblasts leading to tendon failure (Torp *et al.*, 1974). The improved failure stress observed with increased age appears to be a result of increased crosslinking that leads to reduced slippage between the subfibrils and microfibrils (Torp *et al.*, 1974).

While macroscopic fiber failure is quite apparent since visible fiber breakage can be observed (Fig. 7.6), subfiber failure has been observed and attempts have been made to quantitatively analyze these changes based on observed behavioral differences. Subfiber failure can be used to examine a number of altered mechanical phenomena in tendons and ligaments including increased laxity (Panjabi *et al.*, 1996; Provenzano *et al.*, 2002a,b) and decreased stiffness (Panjabi *et al.*, 1999; Provenzano *et al.*, 2002a,b). Subfiber failure leads to collagen disorganization (Torp *et al.*, 1974; McBride *et al.*, 1985, 1988), fibroblast necrosis (Provenzano *et al.*, 2002a,b), and altered collagen fiber orientation (Quinn and Winkelstein, 2008). At the macroscopic level collagen fiber failure in tendon has a distinct morphological character.

Statistical analyses indicate that the onset of subfailure occurs at a strain of about 5% in a ligament which is below the threshold for structural damage (Provenzano *et al.*, 2002a,b). Cellular damage induced by ligament sprains occurs at strains significantly below failure strains (Provenzano *et al.*, 2002a,b). Subfiber failure appears to be associated with altered collagen fiber rotation during tissue extension (Quinn and Winkelstein, 2008). While tissue remodeling and synthesis of collagen Types I and III can occur at

subfailure strains through fibroblast mediated processes, the pre-subfailure strengths of ligaments are never regained and permanent joint laxity occurs (Provenzano *et al.*, 2002a,b, 2005). Subfiber failure is first observed in thin diameter collagen fibrils followed by failure of the larger diameter collagen fibrils (Yahia *et al.*, 1990).

Ker (2008) has recently reviewed the macroscopic fracture mechanics of tendon. When a tendon is notched laterally and loaded in tension longitudinally, the crack opens up and the tip becomes curved. Since the ratio of the shear modulus to that of the tensile modulus of tendon is about 10^{-3} , the crack propagates longitudinally and leads to a mode of failure called 'interdigitation'. This failure surface is characterized by the presence of numerous collagen fibrils that one by one tear at different lengths and morphologically look like series of fingers projecting across the failed tendon ends. Ker *et al.* (2000) reported a correlation between stress-in-life (physiological operating stress levels) and resistance to fatigue damage leading to the conclusion that all tendons are equally likely to experience damage independent of their normal operating stresses. Ker and coworkers (Ker *et al.*, 2000; Ker, 2008) further hypothesized that damage of tendon during normal loading acts to trigger tendon repair processes and that tendon damage and failure are limited by the weakness of the attached muscle.

7.9 Conclusions

Collagen fibers are the structural elements found in vertebrate tissues that transmit forces, and store and dissipate elastic energy. Collagen fibers limit the deformation of tendon and other load-bearing tissues and have a hierarchical structure that includes collagen molecules, microfibrils, fibrils, fibers, and fascicles. They are packed into a quarter-stagger arrangement with neighboring molecules staggered by multiples of D, which is about 22% of the molecular length. During mechanical deformation collagen molecules are stretched as well as the gap region of the D period. At larger strains, molecules and fibrils slide by each other, which leads to energy losses. Finally, collagen fiber failure occurs by disintegration of some of the hierarchical structure yielding collagen subfibrils that lose much of their mechanical strengths.

In tissues, collagen subfiber stretching leads to laxity; the repair process directed by fibroblasts can result in collagen deposition and improvement in the mechanical properties of tendons and ligaments. However, collagen subfiber failure does not lead to regeneration and the mechanical properties of a sprained ligament only approach those of the original tendon.

Future studies are needed to identify the failure mechanisms of collagen fibers in tissues containing more complex ECMs. These ECMs contain collagen fibers that are oriented in more than one direction and form multilayered sheets such as is observed in cartilage and bone.

7.10 References and further reading

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Manufacturing, properties and tensile failure of nylon fibres

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Abstract: Production, properties and tensile failure behaviour of various nylons, in particular nylon 6 and nylon 6.6, are discussed. The chapter starts with a brief discussion on raw materials and mechanisms of polymerisation for nylon 6 and nylon 6.6. Fibre manufacturing sequences, including melt spinning, drawing and other processes, are discussed at length and fibre structure and properties of nylon 6 and nylon 6.6 are critically reviewed. A section in the chapter is dedicated to describing the preparation and properties of commercially available nylons other than nylon 6 and nylon 6.6. In a separate section, tensile fracture and fatigue failure of nylon 6 and nylon 6.6 fibres are analysed. The chapter also deals with market trends and various applications of nylon 6 and nylon 6.6 fibres.

Key words: polyamide, fibres, nylon 6, nylon 6.6, nylon 4.6, nylon 6.10, nylon 6.12, nylon 11, nylon 4, manufacturing, melt, spinning, drawing, structure, morphology, properties, tensile, fracture, fatigue, failure, performance, market, trends, applications.

8.1 Introduction¹⁻³

The name ‘nylons’ refers to the group of thermoplastics known as aliphatic polyamides. Nylons are typified by amide group ($-\text{CONH}-$) and encompass a range of material types (e.g. nylon 6.6, nylon 6.12, nylon 4.6, nylon 6, nylon 12), providing an extremely broad range of properties suitable for a wide range of applications from heavy-duty aircraft tyre reinforcement to a finer parachute cloth. Today nylon polymers are not only used in the production of industrial fibres but also in making performance clothing and sophisticated apparel manufacturing. Also nylon polymers are used for making films and base compound fibre-reinforced engineering plastics.

Nylons are formed by two methods. The first method involves a polycondensation reaction between a diamine and a dibasic acid producing a nylon salt. The nylons produced by this method carry dual numbers (e.g. nylon 6.6, nylon 4.6). The first number of the nylon type refers to the number of carbon atoms in the diamine and the second number is the quantity in the acid. The second method involves a polycondensation reaction of an amino acid or opening up a monomer containing both amine and acid groups known

as a lactam ring. The nylon identity is based on the number of carbon atoms in the amino acid or lactam monomer (e.g. nylon 6, nylon 12).

Only a few of a large number of aliphatic polyamides or 'nylons' have been truly successful in large-scale commercial production. Amongst those successful polyamides, nylon 6 and nylon 6.6 account for 90% of global aliphatic polyamide production. Both nylon 6 and nylon 6.6 polymers are widely used in fibres, films and engineering plastics. The general characteristics of both polymers are somewhat similar; however, the main differences are being that nylon 6 has a lower melting point, greater moisture absorption and slightly greater affinity for the dyeing process compared with its counterpart nylon 6.6. To keep the task manageable for this chapter, the major emphasis on discussion will hence be limited to nylon 6 and nylon 6.6 polymers.

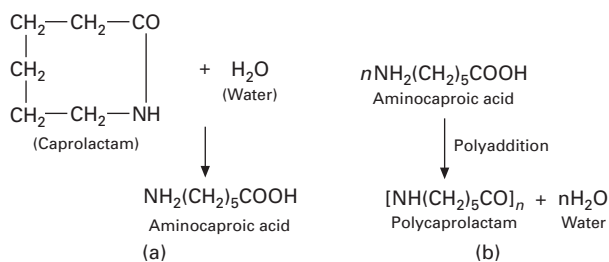
8.2 Raw materials and mechanisms of polymerisation¹⁻⁷

8.2.1 Nylon 6

In 1939 Paul Schlack became the inventor of nylon 6 fibre yielded from a compound called caprolactam. Today caprolactam is generally used as monomer in the manufacturing of nylon 6 polymer. Caprolactam is normally synthesised from cyclohexanol. Caprolactam is a white crystalline compound with a melting point of 69°C. In the production of high quality nylon 6 polymer suitable for good quality fibrous materials, the purity of caprolactam is critically important.

Caprolactam is a cyclic compound. In the presence of water, scission of the caprolactam ring takes place giving rise to aminocaproic acid as shown in Fig. 8.1(a). Subsequently polymerisation can proceed with the polyaddition (or even polycondensation) of aminocaproic acid to form polycaprolactam as shown in Fig. 8.1(b). It is widely believed that polyaddition is the most probable mechanism in the formation of polycaprolactam.

The industrial polymerisation process of caprolactam into polycaprolactam (otherwise known as nylon 6) is carried out either in a batch process in autoclaves or in a continuous process in a long tube. At the beginning of the polymerisation process, a heated vessel melts caprolactam approximately at 80°C. The required amount of additives, stabiliser and water is added to the molten caprolactam. When all the components are well mixed, the molten compound is sent to the autoclaves for polymerisation. It is important to remember that an appropriate amount of water is essential to form a linear chain of aminocaproic acid and subsequently to produce the linear polymer of nylon 6. The conversion of caprolactam into polycaprolactam and the corresponding degree of polymerisation are largely dependent upon water content of the mixture along with reaction temperature and time.



8.1 Formation of (a) aminocaproic acid from caprolactam and (b) polycaprolactam from aminocaproic acid.

When the polymerisation process is complete, the molten polymer is released from the bottom of the autoclave and extruded through spinnerets to form one or more threads. Molten threads are cooled down in water bath and cut into 3–4 mm chips for inspection and storage.

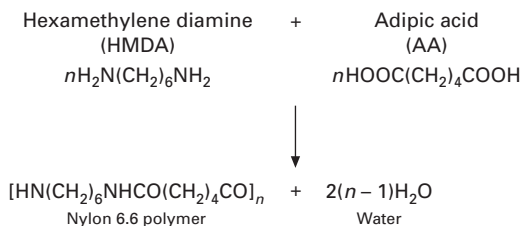
8.2.2 Nylon 6.6

In early 1934 Dupont scientist Wallace Carothers initiated his work on polyamide. On 25, February 1935, his laboratory produced poly(hexamethylene adipamide). Patents for the world's first synthetic fibre were granted on 20 September 1938 and the official announcement of commercialisation of this fibre by the Dupont de Nemours Company came in October 1938. Commercial production of nylon 6.6 fibres started in 1939.

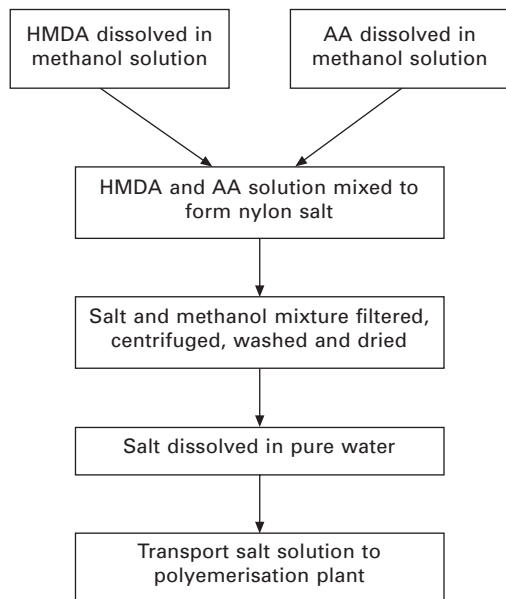
Nylon 6.6 is produced from the reaction of a dibasic acid (adipic acid) and a dibasic amine (hexamethylene diamine). The basic chemistry and the reaction mechanisms of the formation of nylon 6.6 polymer molecules are outlined in Fig. 8.2. Commercial production of nylon 6.6 polymer is composed of four steps: (1) nylon 6.6 salt preparation, (2) polycondensation, (3) extrusion and milling, and (4) spinning into polymer chips.

High molecular weight nylon 6.6 chain can be obtained only if equimolecular amounts of the two components are used, since an excess of one of the components would terminate the chain by formation of an acid or amino end group. For this reason the salt, called the AH salt of equimolar adipic acid (AA) and hexamethylene diamine (HMDA), is initially formed and is used as an intermediate. Figure 8.3 schematically outlines the process of nylon 6.6 salt production.

The formation of nylon 6.6 polymer from the nylon 6.6 salt is carried out either in a batch process in autoclaves or in a continuous process involving a long tube. The physical process is very similar to the nylon 6 process although the primary reaction parameters such as reaction temperature and time are somewhat different.



8.2 Reaction mechanisms to the formation of nylon 6.6 polymer molecules.



8.3 Schematic flow diagram of nylon 6.6 salt production.

8.3 Manufacturing of nylon 6 and nylon 6.6 fibres^{1,2,3,7,8}

Both nylon 6 and nylon 6.6 polymers are widely used in the formation of fibres. Two processes are used in converting polymer chips into a good quality fibre. These processes are called: (1) melt spinning and (2) drawing. Both the processes are very similar for nylon 6 and nylon 6.6 although primary process variables (such as melt temperature) are different. Both processes are described in the following paragraphs.

8.3.1 Melt spinning

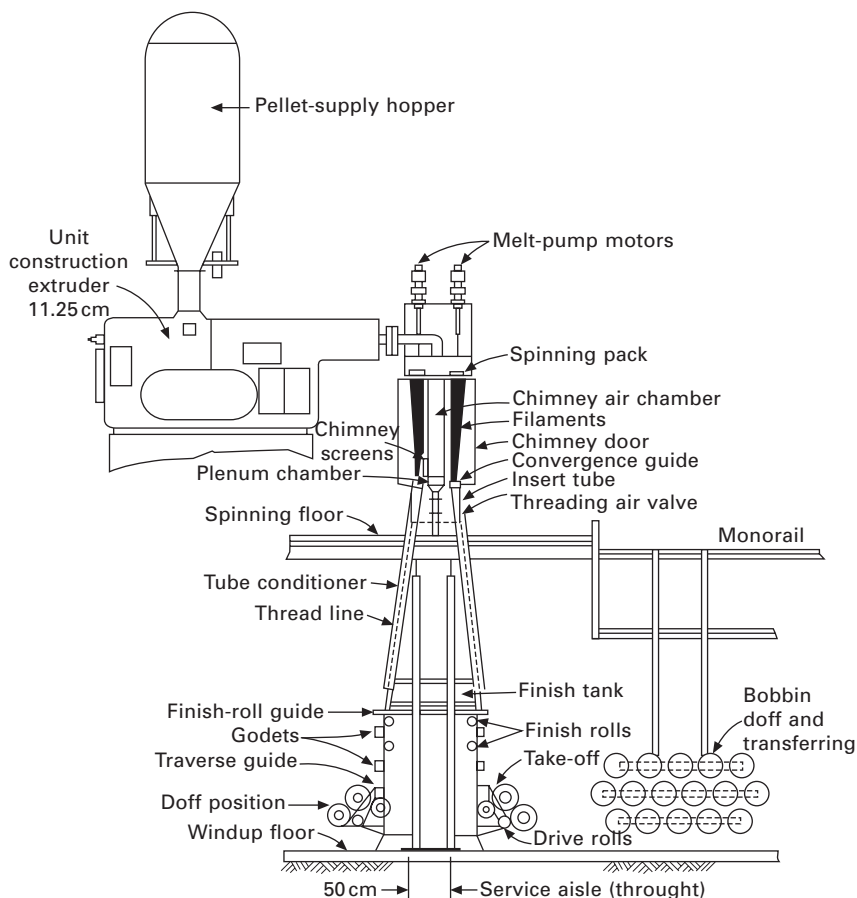
All aliphatic polyamides are thermoplastic polymers. By and large these polymers are sufficiently stable in the molten state and their melt viscosities

are relatively low. Most aliphatic polyamides can thus be spun well in the molten state. For nylon 6 and nylon 6.6 polymers, melt spinning is the preferred and technologically suitable route of production of fibres. Melt spinning process is economical and, in addition, environmentally friendly.

The melt spinning process for the production of nylon 6 fibre is very similar to that for nylon 6.6 fibre. The basic process of melt spinning consists of preparation of the polymer melt to possess the required melt viscosity, extrusion of the polymer melt through spinneret orifices, extension of polymer jets leaving the orifices, solidification of molten threadlines and winding up of the solidified filaments to an appropriate package. The spinning assembly consists of a melt grid or extruder for melting the polymer, a small pool to collect the molten polymer for the metering pump, a filter pack to remove large particles, foreign matters and gel, etc., from the molten polymer and a spinneret to extrude filament. Also, following spinning, molten filaments pass through a quench zone for solidification, a steam zone for conditioning and winding-up zone for building suitable packages. All the above three zones are part of the spinning assembly.

A schematic layout of the extruder-based melt spinning process is shown in Fig. 8.4. Polymer pellets or chips are melted involving a heated grid or extruder system. The melt temperature at the grid or extruder should be 250–265 °C for nylon 6 and 285–300 °C for nylon 6.6. The retention time or residence time of the molten polymer must be long enough at the temperature mentioned above to obtain clear homogeneous melt. The molten polymer is then taken through a spinning metering pump to control flow through the spinneret. The metering pump accurately meters molten polymer to a pack consisting of a filter system and spinneret. Before the polymer is extruded through the spinneret, it is passed through the filter system to remove impurities. Normally sand packs, metal screens and nonwoven structures are used as filters. Molten polymer from the filter passes through a metal plate (called a spinneret) containing a large number of holes to extrude filaments. In spinnerets, the holes are usually round but can have other cross-sections (trilobal, pentalobal, etc.) if necessary. In designing the spinneret, the length of the capillary in relation to the diameter of the holes must be appropriate to the melt viscosity of the polymer at the extrusion temperature and to the extrusion rate.

Once the molten filament is extruded, it passes through a 1–1.5 metre length of quench zone. Solidification of the filaments occurs in this zone where enough heat transfer takes place from the molten threadline to the surroundings. From the spinneret tip to the tip of the winder, the stretch is technically called the spinning axis. A progressive velocity gradient along the spinning axis has a much greater effect upon good fibre formation than an average ratio between the winding speed and the extrusion speed. A good



8.4 Schematic layout of extruder-based melt spinning process (adapted from Saunders⁷).

velocity gradient allows the polymer molecules to align in more favourable positions within the structure for better drawing. Once the filaments pass through the quench zone, it enters into a conditioning tube heated with saturated steam. The steam conditioning offers a first level of heat setting for structural stability. After steam conditioning, an emulsion called spin finish is applied to the threadline to reduce friction and enhance cohesion between the filaments. The filaments are then wound to suitable packages for the subsequent process called drawing.

8.3.2 Drawing

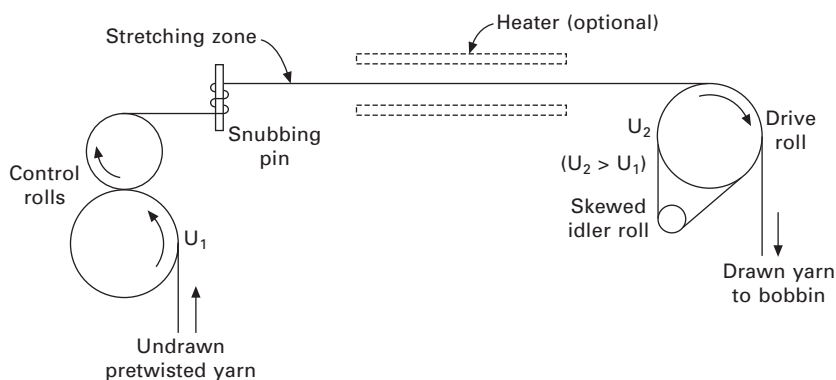
Spun polyamide yarns are largely amorphous, which means that such yarns are neither adequately crystallised nor are their molecules sufficiently

oriented. Spun polyamide yarns do not offer properties suitable for any applications. Thus spun yarns are required to be drawn as needed to develop useful properties for various applications.

The drawing of spun fibre is accomplished by stretching the filament between 200 and 500% of its original length. In principle, the spun yarn is passed through a set of feed rollers at a given surface speed and then drawn through another set of rollers (normally called draw rolls) at a surface speed between two and five times higher than the feed rolls speed. The ratio of surface speed between draw rolls and feed rolls is technically called the draw ratio. The drawing process facilitates orientation of chain molecules and enhances the process of crystallisation within the fibre morphology. A schematic diagram of drawing process used for spun polyamide yarns is given in Fig. 8.5. In this figure v_1 and v_2 are the surface speed of feed and draw rolls respectively. Drawing of polyamide yarn is normally accomplished at a temperature above the glass transition point of the spun material.

Normally polyamide yarns used for industrial applications require high mechanical performance. Such yarns need a high degree of crystallinity and high level of molecular orientation. Yarns for industrial applications are therefore drawn with a 4–5 times draw ratio; however, yarns for apparel applications are drawn between 2 and 2.5 times for moderate mechanical performance coupled with high uniformity in dye diffusion.

In the early 1970s, a single stage spinning and drawing process was commercialised. The successful combination of spinning and drawing process offered certain technical advantages along with reduction of manufacturing costs associated in making polyamide yarns. In the early 1960s, the introduction of high-speed winders helped to initiate a single stage process of spinning followed by drawing in a single unit. Table 8.1 summarises process speeds for both single and two stage yarn production.



8.5 Line diagram of drawing process used for polyamide fibres (adapted from Mukhopadhyay⁹).

Table 8.1 Summary of process speeds in making nylon 6 and nylon 6.6 yarns

Process of yarn formation	Linear speed (m/min)
Two stage process	
(a) Spinning	400–1000
(b) Drawing	600–1500
Single stage process	3000–4000

8.3.3 Other processes

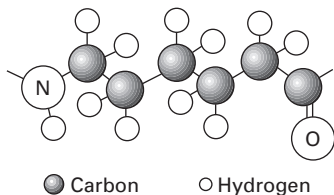
Nylon multifilament yarns often go through some other processes following drawing. The most commonly used processes are: twisting, texturing and heat-setting. The draw winding process is sometimes substituted by a draw twisting process whereby immediately after drawing, a small amount of twist is inserted in the yarns to enhance coherence of the filament bundle so as to better withstand stresses and strains in the further downstream processing. In some applications of nylon 6 and nylon 6.6 yarns, drawn materials are required to texture using false twist texturing or air-jet texturing methods. Heat-setting is an important process for the nylon yarns and performance of the finished products made of such yarns. Heat-setting provides a better thermodynamic definition to the morphology and thereby enhances dimensional stability of the finished products. During the yarn formation, following spinning and solidification, yarns are processed through saturated steam in a conditioner tube. This is the first level of heat-setting in the yarn manufacturing process. Depending on the finished product performance requirements, heat-setting is accomplished in more than one step in downstream processes before finished products are released for use. Details of twisting, texturing and heat-setting processes are widely available in the published literature.

8.4 Fibre structure and properties of nylon 6 and nylon 6.6^{9–19}

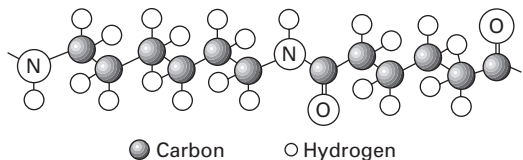
8.4.1 Molecular structure and fibre morphology

The formation of nylon 6 and nylon 6.6 polymers is shown in Figs 8.1(b) and 8.2 respectively. The characteristic feature of both the polyamides is the presence of polyamide ($-\text{NHCO}-$) linkage. The building blocks and the arrangements of atoms of both the polymers within the building blocks are shown in Fig. 8.6 for nylon 6 and Fig. 8.7 for nylon 6.6 polymers.

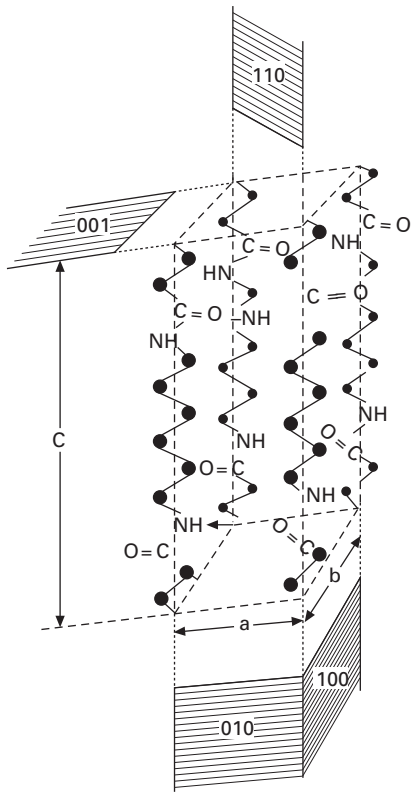
The stable structure of nylon 6 and nylon 6.6 is generated in the alpha form within the morphology. This is achieved by aggregation of molecules in monoclinic unit cell for nylon 6 and triclinic unit cell for nylon 6.6. The unit cell structures of nylon 6.6 and nylon 6 are shown in Figs 8.8 and 8.9 respectively. The unit cells normally combine to stacks of sheets of planar



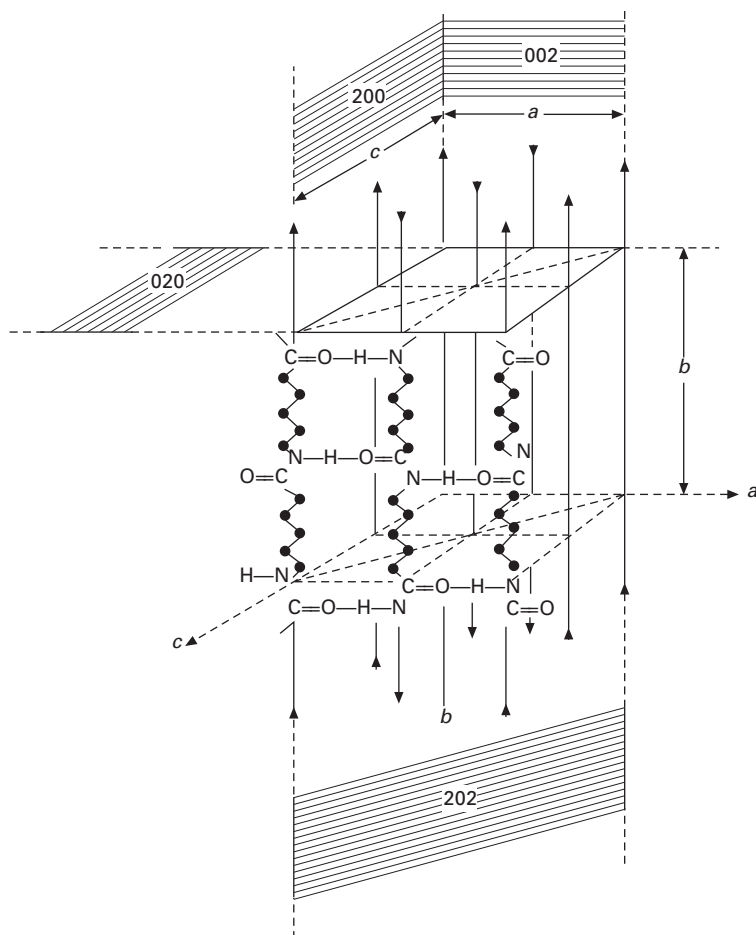
8.6 The atomic arrangement in the building block for nylon 6 (adapted from Gupta¹⁰).



8.7 The atomic arrangement in the building block for nylon 6.6 (adapted from Gupta¹⁰).



8.8 Unit cell of nylon 6.6 (adapted from Reimschuessel¹¹).



8.9 Unit cell of monoclinic alpha-form of nylon 6 (adapted from Reimschuessel¹¹).

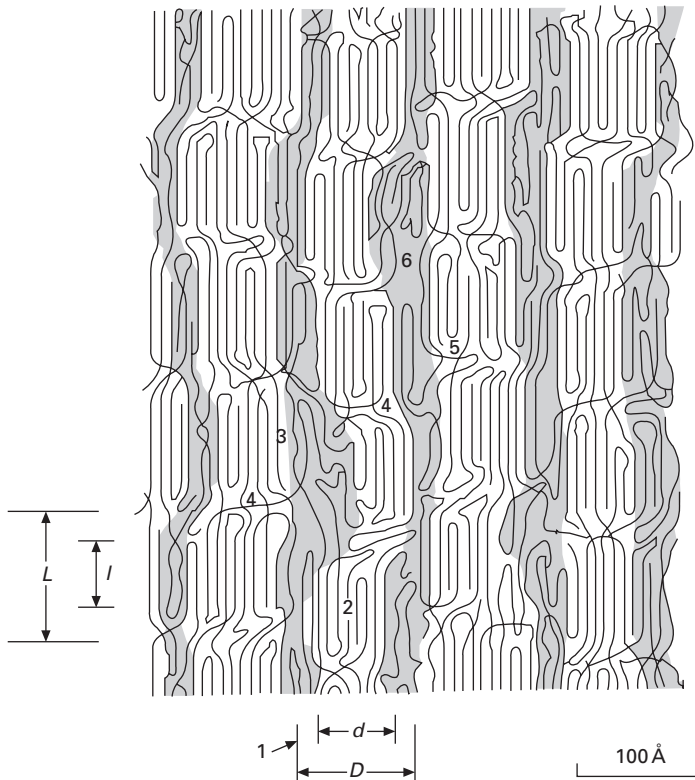
hydrogen-bonded extended chain segments. Owing to relatively high hydrogen bonding, the chain-to-chain distance does not change easily. However, the sheet-to-sheet distance represented by van der Waals force is more easily affected and susceptible to change in response to crystallisation conditions and applied external forces.

In nylons, as the methylene group and amide linkage ratio ($-\text{CH}_2/-\text{CONH}-$) increases, the physical characteristics of the material increasingly resemble those of polyolefins because of the decreasing concentration of H-bonds. The magnitude of the influence of H-bonding can be appreciated by comparing the melting point of nylon 12 (179°C) with that of nylon 4.6 (295°C). The most commercially successful of the nylons – nylon 6 and nylon 6.6 – have identical $-\text{CH}_2/-\text{CONH}-$ ratios but the ability of nylon

6.6 chain to crystallise in both parallel and anti-parallel configurations can result in a higher H-bond concentration and hence a higher melting point.

The formation of the crystalline structure for nylon 6 and nylon 6.6 requires good lateral packing consistent with the appropriate distance for intermolecular forces between the chain segments so that the potential energy of the structure is minimal. Hence in the polyamide crystal morphology, the extended chains are bound together into sheets by hydrogen bonds.

Both nylon 6 and nylon 6.6 fibres are produced by melt spinning and drawing operations as described in Section 8.2. Extensional flow arising from spinning and plastic deformation arising from drawing, produces a microfibrillar morphology for nylon 6 and nylon 6.6 fibres. The microfibrillar structure is a regular stacking of alternate crystalline and amorphous regions. Many attempts were made using analytical measurements to define various structural and morphological features of these two fibres. A proposed model of nylon 6 with various morphological details is shown in Fig. 8.10



8.10 A proposed model of nylon 6 with morphological details: 1 fibril, 2 crystallites, 3 partially extended molecules in the inter-fibrillar regions, 4 tie molecules in the interlamellar region, 5 free chain ends, 6 voids (adapted from Murthy *et al.*¹²)

The crystalline structure of nylon 6 and nylon 6.6 can be analysed by various methods such as X-ray diffraction and infrared absorption. Also electron microscopy can be used to characterise the rearrangement of the structure during drawing. The above techniques can be successfully used to analyse the proportions of alpha, beta and gamma fractions of the crystalline structure in the fibres. For example, analytical measurements have shown that nylon 6.6 initially crystallises in the gamma form and gradually transforms into alpha form as the sample is heated during drawing. Also nylon 6 fibres spun at conventional speed normally contain an equal amount of alpha and gamma fractions. However, increasing drawing temperature and high draw ratio coupled with heat-setting at elevated temperature can result in transformation of gamma fraction into alpha form.

Cold drawn nylon 6 under the electron microscope exhibits an intermediate state between fibrillar and lamellar morphology. However, such a structure can be transformed into typical fibrillar morphology by annealing treatments in different media. Also various measurements have shown that virtually equilibrium structure of nylon 6.6 entails a perpendicular sheet-sheet distance of 0.36 nm in the chain direction. Amongst other analytical observations, it was found that orientation in the crystalline and amorphous phases of nylon 6.6 could increase with take-up speed in high speed spinning. However, crystalline orientation could increase rapidly in drawing with increased draw ratio. The birefringence and density of as-spun nylon 6.6 filaments can increase with increasing take-up speed in spinning. The above-mentioned structural characteristics seem to be very similar to the behaviour of nylon 6 fibres.

Fibre properties

Aliphatic polyamides or nylons are largely semicrystalline. These fibres are also oriented. Nylons, as polymers, are mechanically tough materials. Both nylon 6 and nylon 6.6 have good thermal and chemical resistance. Density, melting point and moisture content of nylon polymers tend to reduce as the nylon number increases. Both mechanical and thermal responses of nylon 6 and nylon 6.6 fibres are well documented in the published literature. Table 8.2 provides values of various mechanical and thermal parameters of nylon 6 and nylon 6.6 fibres.

Mechanical properties of both fibres are primarily dependent on molecular weight and weight distribution of polymeric chains along with structural morphologies of the fibres, orientation of the chain molecules and the degree of order. It is appropriate to mention here that the conditions of spinning, drawing and subsequent heat treatments largely dictate the structural morphologies of the fibres. However, the presence of functional additives

Table 8.2 Mechanical and thermal properties of nylon 6 and nylon 6.6 fibres

Properties	Nylon 6	Nylon 6.6
Tenacity (cN/tex)	45–90 (540–1080 in MPa)	55–90 (660–1080 in MPa)
Breaking extension (%)	15–40	15–30
Initial moduli (cN/tex)	150–500 (1800–6000 in MPa)	250–450 (3000–5400 in MPa)
Glass transition temp. (°C)	25	47
Melting temp (°C)	215	260
Sp. heat capacity (J/g °C)	430	620
Limiting oxygen index	20	22

Source: various.

and any other polymeric components can strongly influence both structural morphologies and ultimate fibre properties.

Both nylon 6 and nylon 6.6 are high tenacity fibres. Depending on the crystallinity and molecular orientation, tenacity can vary between 50 and 90 cN/tex or between 550 and 1100 MPa. Nylons also offer high extensibility. Nylons are partly hydrophilic in nature. The effect of humidity on breaking extension is greater than on tenacity. With increasing temperature, tenacity goes down and extensibility goes up. The effect of temperature on tenacity and extension is greater at high humidity than at low.

The thermal behaviour of nylon 6 and nylon 6.6 fibres is linked to crystalline and amorphous structures of the fibres. Using various catalysts into the polymer recipe before spinning, different structural morphologies can be developed which in turn can offer somewhat different thermal responses of these two polymers. Nylon 6 has lower melting and glass transition temperatures than nylon 6.6. Also its specific heat capacity is lower than both nylon 6.6 and nylon 4.6. Because of its relatively inferior thermal responses of nylon 6 fibre over nylon 6.6, nylon 6 has never been recognised as a suitable fibre for reinforcing aircraft tyres, in automotive airbags and timing-belt applications. Also very often nylon 6.6 is made as fibres adding 2–3% of nylon 6 in the polymeric components. This is done to enhance processability of the polymer both at spinning and drawing stages. Such copolymeric yarns offer excellent mechanical performance and can be comparable to the overall performance with 100% nylon 6.6 (called nylon 6.6 homopolymer) polymer-based yarns. However, copolymeric nylon 6.6 yarns are somewhat inferior in thermomechanical responses and long-term ageing behaviour. Normally copolymeric nylon 6.6 yarns are not used for automotive safety components such as in timing belts reinforcement, for airbag and airbag sewing threads. These yarns are also not recommended for aeronautical applications such as in parachutes, para-gliders and hot-air balloons.

Both nylon 6 and nylon 6.6 can provide good resistance to most chemicals but can be attacked by strong acids, alcohols and alkalis. Mineral acids even at room temperature can cause slow hydrolysis; however, strong oxidising agents such as nitric acid or potassium permanganate can disintegrate the structure. Nylons have very good resistance to oils, fats and hydrocarbons. Nylon 6 and nylon 6.6 cannot retain their original strengths if exposed to high temperatures over a long period of time; however, with the incorporation of heat stabilisers and suitable fillers in the structures, loss of strength on exposure to heat over a long period of time can be minimised.

Being thermoplastic in nature, nylon fibres shrink at high temperatures. There are two elements of thermal shrinkage in nylons – reversible and irreversible. If nylon fibres are adequately heat-set at a certain temperature for a length of time, then they do not undergo further irreversible shrinkage on subsequent heat treatment unless the treatment temperature exceeded the previous heat-set temperature. Nylon structure swells in the presence of water. In fact, in the presence of water, molecular mobility increases significantly with increased temperature compared with the mobility behaviour of molecules in dry heat at a similar temperature. Apart from swelling, water has no major effect on nylons at room temperature over a long period of time but water under high pressure above 150°C can cause hydrolysis.

Nylon 6 and nylon 6.6 fibres have excellent abrasion resistance. Both the fibres also offer outstanding flex fatigue behaviour under a high degree of bending strain. In abrasion resistance both nylon 6 and nylon 6.6 fibres surpass virtually all other fibres except high molecular weight gel-spun polyethylene. Apart from unique abrasion and flex fatigue resistance, nylon 6 and nylon 6.6 offer outstanding elasticity and degree of resilience. The excellent balance of elasticity and resilience provides a high level of dimensional and structural stability. The unique balance of elasticity, resilience, abrasion resistance and flex fatigue behaviour enables fabrication of numerous products capable of maintaining their original shapes over a long period of time under the exposure of frequent high degree of stresses and strains. Women's hosiery, sports garments, tyre reinforcement, automotive timing-belts are some good examples of the characteristics mentioned above.

On exposure to UV radiation over a long period of time, both nylon 6 and nylon 6.6 undergo photo-oxidative degradation manifested by loss of strength. High temperature exposure and presence of delustrant additive such as titanium dioxide in the polymer recipe can enhance the photo-oxidative degradation process. Suitable UV stabilisers are often used to minimise the photo-oxidative degradation process.

8.5 Preparation and properties of other nylons^{7, 20–22}

Since the inception of nylon 6 and nylon 6.6 polymers into fibres, scientists looked into other aliphatic polyamides and introduced the following commercially viable polyamide polymers suitable in fibre application.

8.5.1 Nylon 4.6



Nylon 4.6 is produced by the polycondensation of 1,4 diaminobutane and adipic acid. Although this polymer has a similar structure to that of nylon 6.6, the higher number of amide links per given length of chain and the more symmetrical structure result in a higher melting temperature of 295 °C, a higher crystallinity and faster crystallisation.

Nylon 4.6 is widely used as an engineering polymer where its toughness, wear resistance and high melting point give it advantages over other polymers. It is often filled with materials such as glass and is easily processed by injection moulding.

For fibre end uses nylon 4.6 can be processed using equipment similar to that used for nylon 6.6 and polyester, at typical low oriented yarn (LOY) spinning speeds. The polymer has to be dried before spinning and requires a high melt temperature in the order of 310 °C, with a short melt residence time to minimise degradation. The spun yarn can be drawn on a normal drawtwister. See Table 8.3 for typical properties of nylon 4.6 polymer.

Table 8.3 Various properties of other nylons (excluding nylon 6 and nylon 6.6)

Properties	Nylon 4.6	Nylon 6.10	Nylon 6.12	Nylon 11	Nylon 4
Density (g/cc)	1.2	1.32	1.08	1.03	–
Moisture regain (%) (@65% RH and 21°C)	3.3	1.0	1.5	1.3	8.0
Tenacity (cN/tex)	40–45 (465–525 in MPa)	40–50 (420–525 in MPa)	40–50 (515–650 in MPa)	35–45 (470–600 in MPa)	45–55
Elongation at break (%)	40	30	72	115	60
Glass transition temp (°C)	75	72	–	46	–
Melting temp (°C)	295	216	206	183	260
Specific heat capacity (J/g/°C)	771	–	174	–	–
Limiting oxygen index	26.3	21	20	24	–

Source: various.

8.5.2 Nylon 6.10



Nylon 610 is produced by the reaction of hexamethylenediamine with sebacic acid, initially to form a 1:1 nylon 610 salt, which is then polymerised at about 240 °C. The polymer has a melting point of around 216 °C and a low water absorption of around 1–1.2% at 21 °C and 65% RH, which gives it better dimensional stability and electrical properties than nylon 6 and nylon 6.6. It is a commercially important polymer and is often used in place of nylon 6 and nylon 6.6 in engineering plastics applications. Mechanical properties of the dry polymer are lower than those for nylon 6 and nylon 6.6 (tensile modulus is typically 70% of that for the other two polymers). It is frequently used as extruded monofilament. See Table 8.3 for typical properties of nylon 6.10 polymer.

8.5.3 Nylon 6.12



Nylon 612 is produced by reacting hexamethylenediamine with 1,10-decanedicarboxylic acid. The polymer is used as an engineering plastic, often glass filled. It is sometimes used to replace nylon 610, having a melting point of around 205–215 °C and an even lower water absorption of around 0.5% at 50% RH. See Table 8.3 for typical properties of nylon 6.12 polymer.

8.5.4 Nylon 11



Nylon 11 is produced by polymerisation of 11-aminoundecanoic acid at ~ 215 °C and has commercial application in both fibre and engineering plastic end uses. Its properties are similar to those of nylon 6, but with a lower melting point of around 182–185 °C, a T_g of 46 °C and a low water absorption of 1.2–1.4% at 21 °C and 65% RH. As a textile material it is said to have a richer, drier feel than nylon 6 and nylon 6.6. See Table 8.3 for typical properties.

8.5.5 Nylon 4



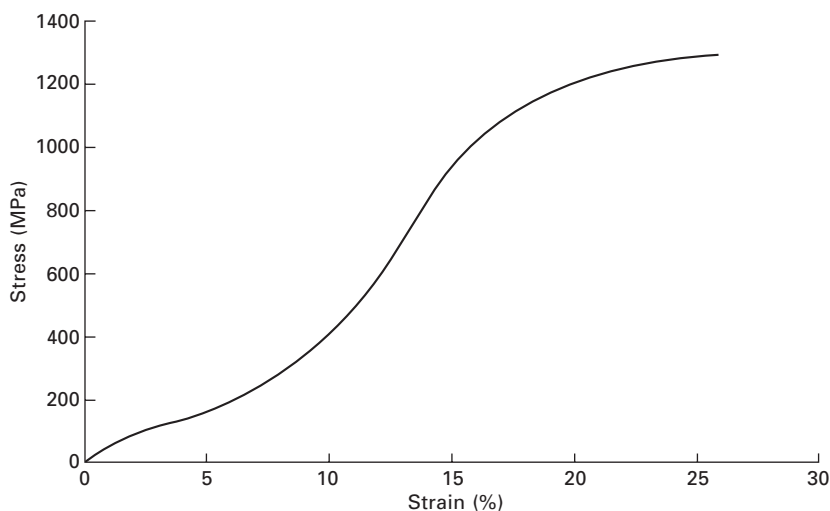
Nylon 4 is synthesised by ring-opening polymerisation of pyrrolidone by anionic polymerisation. It cannot be prepared by heating its parent amino acid since it cyclises to the lactam. It has a melting temperature between

260 and 265 °C and a relatively high water absorption (~8–10% at 21 °C and 65% RH), considered to be suitable for textile end uses. See Table 8.3 for typical properties of nylon 4 polymer.

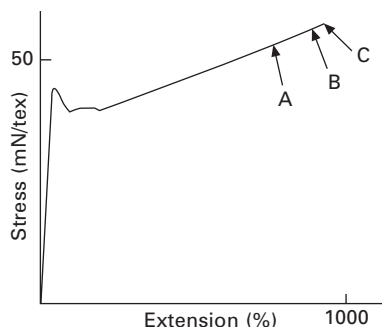
8.6 Tensile fracture and fatigue failure of nylon fibres^{9,10, 23–25}

8.6.1 Tensile fracture

On tensile loading, the rupture of melt-spun fibres, such as nylon, is partly dominated by the yield stress as shown in Fig. 8.11 which illustrates the stress–strain behaviour of nylon 6.6 yarn used for tyre applications. Well-oriented high tenacity nylon filaments used for tyre cord and other industrial filament yarns illustrate an initial straight line in its stress–strain behaviour. This represents a pure elastic nature of the material within approximately 1% of the initial strain. This is followed by a yielding of the fibre structure which is indicated by a S-shaped profile of the stress–strain curve as shown in Fig. 8.11. Ductile fracture is the common mode of nylon fibre's failure. The study of a thick undrawn nylon monofilament clearly shows the mechanism of ductile crack propagation leading to break. In Fig. 8.12, three main regions can be identified in the ductile break: initiation at A, stable crack propagation at B and final catastrophic failure at C. Very often initiation is due to development of voids below the fibre surface. On tensile loading, a void can open up and transform into a crack. According to Hearle and co-workers²³ 'Cavitation is presumably a detailed way in which a crack forms.



8.11 Stress–strain profile of a high performance tyre yarn made of nylon 6.6 fibres (Courtesy: Professor A R Bunsell).

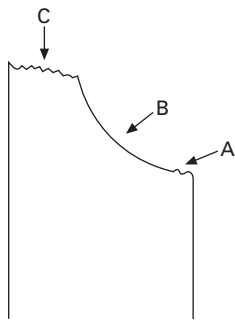


8.12 Stress-strain (% extension) curve of an undrawn nylon monofilament: A crack observed, B crack propagation, C final break (Adapted from Hearle *et al.*²³).

The transition from the crack zone B to the final failure zone C is possibly due to an alteration of break and stick'. The schematic diagram of the broken end of a nylon monofilament (originally undrawn) as outlined in Fig. 8.13 shows three main regions corresponding to three regions of the stress-strain curve of the nylon monofilament shown in Fig. 8.12.

Figure 8.14 is a scanning electron micrograph of a highly drawn nylon 6.6 fibre broken in tension. The micrograph illustrates one side of the break and is a representation of ductile failure. The mechanisms of ductile break for drawn nylon fibres are shown in Fig. 8.15. They are similar to those for undrawn fibres except some possible differences in the initiation and transition regions. It is fairly well established that on tensile loading to a drawn nylon fibre, initially it extends uniformly. When the load reaches to a certain point, a crack initiates from a surface flaw. In other words, a crack initiates at a point of physical or chemical damage or stress concentration due to inclusions. Although there is evidence of failure in nylon fibres being initiated internally in the fibre as shown in Fig. 8.16, the great bulk of the evidence is that it is primarily a surface phenomenon. In Fig. 8.15(a), the filament is under load and is being stretched. Fig. 8.15(b) shows that the crack is initiated and immediately opens up due to the increased stress in the unbroken part as in Fig. 8.15(c). In Fig. 8.15(d) the rate of stress increase exceeds the ability of the material to relax and failure occurs. On high speed tensile failure another factor becomes dominant. The stretching process essentially becomes adiabatic. On high speed straining, frictional forces between the macromolecules significantly increase, leading to the filament temperature increase towards the melting point of the material. When the rupture finally occurs, the snap-back of the very soft broken end gives rise to a distinctive mushroom appearance.

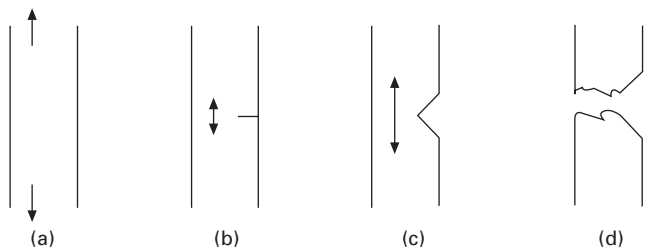
Based on the discussions above, it is appropriate to surmise that in individual filaments, tensile rupture is initiated when a crack opens up at



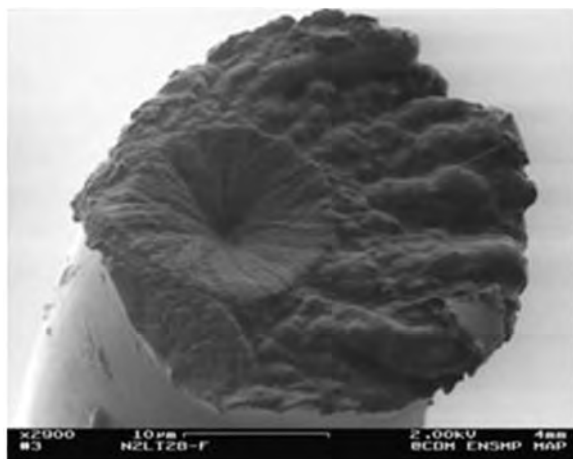
8.13 Schematic diagram of ductile break of an undrawn nylon monofilament: A crack initiation, B crack growth across fibre, C final failure region (adapted from Hearle *et al.*²³).



8.14 Scanning electron micrograph of one side of a highly drawn nylon 6.6 filament broken in tension (courtesy: Professor A R Bunsell).



8.15 The process of ductile failure of a drawn nylon fibre: (a) The filament is under tension; (b) the crack is initiated; (c) stress increases and crack propagates; (d) failure occurs (adapted from Hearle *et al.*²³).



8.16 Scanning electron micrograph of failure of a highly drawn nylon 6.6 filament initiated internally (Courtesy: Professor A R Bunsell).

the site of physical or chemical damage. As straining is continued, the crack widens and penetrates across the filament diameter until final break occurs. Other factors that can influence the failure mode include the evenness of load-sharing in the filament bundle (for multifilament yarn) and the degree of cohesion. A ductile break is distinctive of the tensile failure mode in pull-to-rupture tests; however, failure of yarns operating below their ultimate tensile properties often show different kinds of failure modes which could be due to abrasion and/or fatigue.

8.6.2 Fatigue failure

Nylon fibres can fail when subjected to cyclical tensile loading of a reasonable magnitude. The change in performance over a period of time is called fatigue. It is postulated that fatigue is a function of the rate at which the bonds of the polyamide chains are broken. Repeated tensile deformation cycles result in more bond breakages. Broken bonds can lead to the initiation of heterogeneities or micro-cracks. These micro-cracks can in turn give rise to classical fatigue failure. Also cyclic loading initiates the generation of heat within the molecular structure. Polyamid, which exhibits low thermal conduction, can thus have localised heat build-up in the structure. As a result the applied stress may exceed the yield stress due to possible decay in thermomechanical response of the structure leading to localised crack initiation and ultimate failure of the material.

Also under cyclic loading, below the yield stress or fracture stress but with reasonably large load amplitude frequency, microscopic cracks initiate. A possible fatigue crack involves the interaction of two different slip systems

with different directions and planes of slip, both produced during the tensile half cycle but at different stresses. This crack-like entity can propagate through a sample cross-section and lead to failure.

In tensile fatigue, nylon 6 and nylon 6.6 fibres have shorter lifetime than polyester (mainly PET) fibres. In both the nylons, tensile fatigue generates axial cracks and on failure they produce short tails on the broken fibre ends, unlike the long tail ends produced by the polyester fibres. In flex fatigue, both nylon 6 and nylon 6.6 fibres provide much greater fatigue life than polyester fibres. In flex fatigue with nylons, bending of fibres with yield in compression causes appearance of kink bands. Repeated flexing causes the kink bands to break up and end up with a craze formation, where the fibres ultimately fail.

It is appropriate to mention here that the fatigue performance of polyamide and polyester (in particular PET) fibres is dealt with in detail in Chapter 9 and could be referred to if required.

8.7 Market trends of nylon 6 and nylon 6.6 fibres^{26–29}

Over the past 15 years both the production capacity and the consumption pattern of nylon 6 and nylon 6.6 polymers have steadily increased and the trend is going to continue for nylon 6 polymer both for production and consumption at least until 2015. For nylon 6.6 fibres, the overall consumption is going to continue closer to the current level in the coming years. It is unlikely that significant new nylon 6.6 polymer capacity will be available over the next five to seven years. This situation is expected to put a strain on the supply–demand balance in nylon 6.6 markets. Table 8.4 outlines global capacity and consumption patterns of nylon 6 and nylon 6.6 polymers between 1995 and 2015.

Table 8.4 World capacity and consumption in kilotonnes of nylon 6 and nylon 6.6 polymers

Year	1995	2007	2015*
Nylon 6			
Capacity	3911	5895	6374
Consumption	3024	4577	5808
Surplus/(deficit)	887	1318	566
Nylon 6.6			
Capacity	2210	3343	3372
Consumption	2081	3185	3895
Surplus/(deficit)	129	158	(523)

*Estimated.

Source: Scheidl.²⁸

Both nylon 6 and nylon 6.6 polymers are used exclusively in two major application areas: (i) textile fibres and (ii) engineering plastics/films. A snapshot of consumption pattern of these two polymers between 1995 and 2015 (estimated consumption) in the above two application areas has shown that there has been a steady decrease (in percentage terms) of the polymers in fibre application and a steady increase in engineering plastic/film application. Table 8.5 summarises the consumption pattern of the two polymers in the two major application areas.

For nylon fibres in textile applications, both nylon 6 and nylon 6.6 are used for staple fibre yarn and filament yarn manufacturing. Current consumption of the two polymers for the fibre industry is just over 4.3 million tonnes of which filament yarn accounts for 90% of the consumption and the remaining portion goes to staple fibre yarn manufacturing. Table 8.6 outlines capacity and consumption of nylon 6 and nylon 6.6 polymers for the fibre industry.

China is currently the world's largest manufacturer of nylon 6 industrial filament yarn and a significant manufacturer of nylon 6.6 industrial filament yarn. It is expected that by the year 2010, China will have 60% of global production in nylon 6 and 28–30% of global output of nylon 6.6 industrial filament yarn.

Steadily increasing raw materials prices for both nylon 6 and nylon 6.6 polymers coupled with global inflationary pressure and the sub-prime crisis in the USA have put a strain on the polyamide fibre industry. This is because nylon 6 and nylon 6.6, filament yarns mainly go to textile, carpet and industrial applications. A growing demand for nylon yarn is noticeable for industrial end uses whilst yarns in textile and carpet applications have steadily declined over the last few years. In nylon industrial yarn manufacturing,

Table 8.5 World consumption of nylon 6 and nylon 6.6 polymers in fibres and engineering plastic/films

Year	1995	2007	2015*
Fibre (%)	73	56	44
Engineering plastic/film (%)	27	44	56
Total consumption (kilotonne)	5105	7762	9703

*Estimated.

Source: Scheidl.²⁸

Table 8.6 World capacity and consumption in kilotonnes of nylon 6 and nylon 6.6 polymers in fibres

Year	1995	2007	2015*
Capacity	4407	5531	
Consumption	3740	4344	4285

*Estimated.

Source: Scheidl.²⁸

global markets have steadily grown in the past few years. While Europe has managed to increase its output slightly to defend its position, the USA has seen its market share decline in volume for industrial polyamide yarns and the trend is expected to continue in the coming years.

From the statistics of recent years, it is clearly evident that there has been a reduction in the polyamide yarn manufacturing (particularly nylon 6) in the USA and Western Europe. This has been offset by higher production in Asia, particularly in China, Thailand and India.

8.8 Application of nylon 6 and nylon 6.6 fibres^{7,9,11,17,30}

For many years, nylon 6 and nylon 6.6 fibres were mainly used in carpets, apparel and tyre reinforcement for the excellent wear resistance, retention of appearance, good affinity of range of colours, high tenacity, high toughness, excellent fatigue behaviour and good resilience. However, in the past 15–20 years nylon has lost its market share in apparel to polyester because of polyester's excellent market economics coupled with its outstanding easy care and wrinkle resistance characteristics. Also, consumption of nylon fibres in carpets has significantly reduced owing to consumers' preference for acrylic and polypropylene fibres in carpets for economic reasons and choice of wooden floors for aesthetic and hygiene reasons. However, both nylon 6 and nylon 6.6 continue to be used extensively in heavy-duty truck, bus, earth-mover, etc., tyres for their excellent strength to weight ratio, resilience, adhesion to rubber and flex fatigue characteristics. For aircraft tyres, nylon 6.6 is the globally accepted reinforcing material for its superior thermomechanical performance over nylon 6.

Both nylon 6 and nylon 6.6 fibres are successfully used in a wide range of industrial and military applications because of the unique characteristics of these two fibres for strength, toughness, abrasion and fatigue resistance. Along with these unique combinations of physical performance coupled with the superior thermomechanical performance of nylon 6.6 over nylon 6, nylon 6.6 fibre has established its position as an ideal fibre for automotive airbag and timing belt applications. Figure 8.17 illustrates how successfully nylon 6.6 is used in airbag as a critical safety component not only for motor cars but also for motor cycles, trucks, buses, etc.

Other applications of nylon 6 and nylon 6.6 fibres include industrial and marine ropes, fishing lines and nets, substrates for various coated fabrics including high performance tents, performance fabrics in sportswear (as shown in Fig. 8.18), etc. For superior thermomechanical performance and relatively better resistance to ageing over nylon 6, nylon 6.6 fibre is also used exclusively in parachute fabric, and in para-glider and hot air balloon applications. Both the fibres are also used in a range of industrial and military



8.17 Use of nylon 6.6 fibre for an airbag as a passive safety system in a motorcycle (Source: Honda Motorcycle Business Literature, 2006).



8.18 Polyamide fibres such as nylon 6.6 are widely used in sportswear to enhance performance.

applications for their strength, toughness, abrasion resistance and good adhesion to rubber characteristics. Amongst those applications, mechanical rubber goods, coated fabrics for protective gear, tents, ruck-sacks, climbing ropes, etc. are notable.

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The chemistry, manufacture and tensile behaviour of polyester fibers

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Abstract: Polyester fibers take a leading position among all chemical fibers. The unique properties of these fibers are due to the presence of aliphatic and aromatic parts in macromolecular chains and the regular molecular structure. Poly(ethylene terephthalate) (PET) is the predominant polyester used for fiber production, not only because of its good end-use properties and economy of production but in particular because of the ease of physical and chemical modification, suppressing negative and enhancing positive properties of PET. Despite the fact that PET and modified PET fibers were widely investigated, there are still no fully described phenomena of predicting the mechanical behavior and tensile failure based on the structure or manufacturing parameters. One of the main reasons is the complex character of changes during fiber manufacturing and modifications of structure during influence of stress field, temperature, time and environmental factors.

This chapter provides basic information about chemistry, fabrication technology and structure of PET and modified PET fibers. The structure evolution during fiber processing (spinning, drawing and heat treatment) is discussed. The main approaches to the modeling of tensile behavior of polymeric fibers focused on PET are presented. The first part (Sections 9.2 and 9.3) reviews manufacturing techniques of standard polyester fibres and their modifications. The basic routes for synthesizing and treatment of polyesters are discussed. In the second part (Sections 9.4–9.8), the technologies of spinning, drawing, heat setting and corresponding complex changes in fibres are presented. The third part (Sections 9.9–9.11) describes the mechanical behavior and tensile failure of polyester fibres. At the same time the influence of internal structure on the mechanical characteristics of polyester fibres is discussed. The influence of degradation processes due to the environmental effects on strength and the fracture processes in PET fibers is described.

Key words: polyester fibers, preparation of polymers, processing of fibers, structure and properties, modified polyester fibers, mechanical models, environmental effects, tensile behavior, failure.

9.1 Introduction

Polyester is the most used synthetic fiber in the world and can be found in several areas of application, ranging from classical textiles to technical and special textile structures [1]. ‘Polyester fiber is currently defined as a manufactured

fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to terephthalate units and para substituted hydroxybenzoate units' [2]. Nevertheless, poly(ethylene terephthalate) (PET) is the predominant polyester used for fiber production, not only because of its good end-use properties and economy of production but in particular because of easy physical and chemical modification, suppressing negative and enhancing positive properties of PET [3].

Polyester fibers have low moisture absorbency, good resiliency and dimensional stability, excellent wear resistance, good weather and light resistance, good abrasion resistance and good blending ability with cotton. They are relatively flame resistant, resistant to micro-organisms and insects, physiologically inert and thermoplastic. Depending on molecular mass and structure they soften at 230–245 °C and melt at 256–280 °C. By proper drawing and heat setting, the fibers' shrinkage can be changed over a wide range. Breaking strength can vary in broad bounds, depending upon manufacturing conditions. This range of properties is determined by the chemical and physical structure. The melting point of the polyesters is sufficiently high for fiber creation and end use. A high glass transition temperature of around 70 °C, high degree of order and good resistance to heat and chemical degradation also qualify this polymer for most of technical textile applications. Many manufacturers across the world produce polyester under different commercial names with almost tailor-made properties.

Other generic types of polyester fiber (with higher numbers of methylene units between aromatic rings) have been able to compensate for some of the difficulties associated with PET. Well-known polytrimethyleneterephthalate (PTT) and polybutyleneterephthalate (PBT) fibers were discovered at almost the same time as PET. The main advantages of PBT or PTT in comparison with PET are [1]:

- PTT has better recovery properties than PBT and PET;
- PBT and PTT are softer and more elastic than PET;
- PBT and PTT impart more comfort than PET;
- PTT has the best soft hand of all, PBT is close to PET;
- PTT and PBT can be easily dyed at 100 °C; PET requires higher temperatures (130 °C).

Polyester fibers can be readily modified and easily textured. It is possible to modify their elasticity, pilling tendency and propensity for dyeing as well as shrinkage properties [3].

The first part of this chapter (Sections 9.2 and 9.3) reviews manufacturing techniques of standard polyester fibres and their modifications. The basic routes for synthesizing and treatment of polyesters are discussed. In the second part (Sections 9.4–9.8), the technologies of spinning, drawing, heat

setting and corresponding structural changes are presented. The third part (Sections 9.9–9.11) is devoted to the description of mechanical behaviour and tensile failure of polyester fibres. At the same time influence of internal structure on the mechanical characteristics of polyester fibres is discussed.

9.2 Chemistry and production of polyester fibers

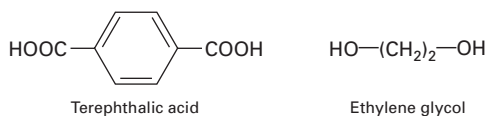
Polyesters are the polycondensation products of dicarboxylic acids with dihydroxy alcohols (diols) i.e. polymers that contain ester groups attached to the main chain. The formation of ester link is schematically shown in Fig. 9.1.

The first polyester was synthesized in 1833 by the famous French chemist and physicist Joseph-Louis Gay-Lussac by polymerization of lactic acid [4]. The synthetic polyester, glycerine phthalate, was used in the First World War for waterproofing. Systematic research in preparation of polyesters for fiber creation was started by Carothers and his research group in 1928. They synthesized many types of polyester, mainly aliphatic. The majority of these polyesters had melting points too low for practical use, and there were also problems with low hydrolytic stability. PET was made in the Carothers laboratory by E. W. Spanagel in 1934, but only because he was trying to make small cyclic molecules [1]. In 1939 research into polyesters was resumed in England by Whinfield. His approach was based on the assumption that the melting point and the other fiber-forming properties of polymers would be dependent on the molecular symmetry of the monomers used. He studied the properties of polyesters made from phthalic acids and ethylene glycol respectively. He found that the terephthalic acid gave a polymer with a melting point of about 260 °C, capable of crystallization and which could be spun into fibers. In 1940, Whinfield and Dickson at the laboratories of the Calico Printers Association (CPA) in the UK prepared fiber-forming polyester from ethylene glycol and terephthalic acid (see Fig. 9.2).

The first patent application was filed on 29 July, 1941 [5]. The patent was sold to ICI and subsequently licensed to DuPont [1]. In 1944 ICI produced the first PET fibers on a laboratory scale. The first information about the fiber was released in October 1946, when ICI launched a pilot plant for the



9.1 Schematic creation of ester link.



9.2 Structure of PET basic components.

production of the fiber. The basic patents expired in 1966. Use of terephthalic acid and 1,4-butanediol for the development of polyester fibers was investigated almost at the same time by Schlack (see [6]). In 1944, Izard from DuPont independently developed ET [1].

Based on an ICI license, the commercial production of PET fibers under the trade name 'Dacron' was started by DuPont in Kinston, NC, USA in 1953. In Europe commercial production of PET fibers (ICI 'Terylene') began in 1955. In 1960 the share of polyester fibers in the world production of synthetic fibers attained the level of 17%. In 1974 it was 41% and in 1980 the level of 50% was attained. In 2006, the 22 largest companies in the world, including Sinopec (China), Reliance (India), NanYA (Taiwan), Huvis (South Korea), Invista (USA), Teijin (Japan), etc., produced more than 11 million tonnes of PET fibers and yarn, including 5.5 million tonnes of staple fiber, 5.4 million tonnes of textile, and 0.5 million tonnes of industrial fibers [7]. In this volume, approximately 7.0 million tonnes was produced by 10 Chinese companies.

Many other types of polyester and modified PET were investigated after the invention of PET. In general the intermediates were more expensive and the polymers were not commercialized at that time. The first patents covering the preparation of a modified PET fiber using isophthalic acid were filed to circumvent the patent protection of Terylene. ICI filed a patent covering improved dyeability and water-absorbing capacity of PET fibers through modification with alkylene oxides [8]. Filed nearly at the same time were a number of other patent applications which proposed replacing part of the terephthalic acid with another dicarboxylic acid or part of the ethylene glycol with other diols.

There are numerous patents and processes covering chemical, physical and combined modifications of PET [3]. One of the first purely physical modifications was based on a shortening of the PET polymer chains to reduce the pilling tendency in the fiber [9]. Furthermore, physical modification methods were used to prepare shrinkable fibers. But to obtain selective shrinking in boiled water or at higher temperature in air, physical and chemical modification methods had to be combined.

In 1959 Eastman Kodak described fiber in which ethylene glycol was replaced by 1,4-bis(hydroxymethyl) cyclohexane [10]. By substituting butylene glycol for ethylene glycol, PBT was obtained and by substituting propylene glycol for ethylene glycol, PTT fibers were produced. Fibers made of PBT and PTT were rapidly accepted, especially in the carpet industry [3].

From other types of polyester used in the production of fibers, mentioned should be those made of the polyethylene oxybenzoate [11], produced by polymerizing 4-hydroxybenzoic acid; and polylactic acid [12], produced from lactic acid. Some other fiber-forming polyester developments are mentioned, for instance, in the books [1, 3, 13].

The traditional way of synthesizing polyesters is polycondensation using diols and a diacid (or an acid derivative), or from a hydroxy acid. Very high conversion is desirable to obtain polymer chains of sufficiently high molecular masses to provide useful mechanical properties in the fibers. In spite of all precautions, a high degree of polymerization is very difficult to achieve by this method because of side reactions and the volatilization of monomers, which leads to a stoichiometric imbalance of reactants. Ring-opening polymerization of lactones, cyclic diesters (lactides and glycolides) and cyclic ketene acetals is an alternative method, which has been successfully employed to yield high molecular mass polymers under relatively mild conditions. This polyaddition reaction can be carried out with no or very limited side reactions, making it possible to control properties such as molecular weight and molecular weight distribution [14].

9.2.1 PET fibers

PET is produced commercially by the dimethyl terephthalate (DMT) and terephthalic acid (TPA) processes [15]. The first commercially successful route to prepare TPA was oxidation of *p*-xylene under pressure using dilute nitric acid. The final TA contained colored and color-forming impurities that could not have been removed, so it was necessary to react it with methanol to form DMT. By recrystallization and distillation of DMT it was possible to remove these impurities. The standard route to DMT preparation (Katzschmann) is based on two air oxidations (starting *p*-xylene to *p*-toluic acid and methyl *p*-toluate to monomethyl terephthalate) and two esterifications (*p*-toluic acid esterified by methanol to form methyl *p*-toluate and monomethyl terephthalate esterified by methanol to make DMT) [1, 13].

Direct oxygen oxidation of *p*-xylene to TPA uses acetic acid as a solvent at temperature of about 200 °C and a combination of cobalt, manganese acetates with bromide ions as catalysts. The process adopted by Amoco also incorporated a purification of TPA and simultaneous catalytic hydrogenation of impurities from super-heated water under pressure at about 250 °C [1, 16]. This process allowed preparation of PET by direct esterification of TPA by the ethylene glycol (EG). Direct esterification (TPA process) has become more widely used than the process using DMT. Industrially, PET is prepared in high molecular weight, generally using two successive stages:

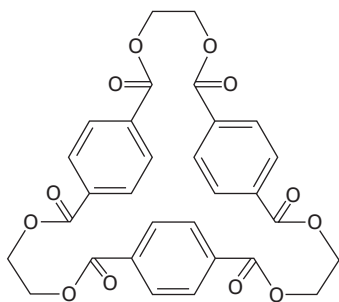
1. In the first stage, a mixture of EG esters of TPA as oligoesters and bis(hydroxyethyl)terephthalate (molecular weight M_n 100–2000 g/mol, depending on the molar ratio of the starting compounds) is produced at 180–240 °C either by ester interchange (transesterification) or by direct esterification with excess of EG under pressure. During the reaction water should be eliminated. The Mn, Cd, Zn or Co acetate are used as catalysts of ester interchange. During direct esterification the acid-catalyzed side

reaction can be prevented by adding small amounts of sodium hydroxide or a quaternary organic hydroxide.

2. The EG esters of TPA mixture is subjected to a polycondensation at 285 °C and reduced pressure 1 mbar that produces fiber-forming PET ($M_n > 10\,000$ g/mol). The condensation reaction is virtually reversible and glycol as a by-product should be removed. Effective methods for expelling glycol have been reported by Stevenson [17]. The antimony trioxide (Sb_2O_3) is obviously used as a catalyst. The trioxide reacts with the glycol to form various glycoloxides which are probably the true catalysts. Antimony trioxide functions very well but owing to the formation of a very fine colloidal metallic antimony suspension in the PET, grey discoloration occurs. This is especially true if the stabilizer is a trivalent phosphorus compound [18]. There are 200–300 ppm of antimony and 20–100 ppm of phosphorus in most commercial PET [18]. Either TiO_2 or a mixture with SiO_2 or TiO_2/ZrO_2 compositions can be used as polymerization catalysts (AKZO patent) as well [19]. The discoloration, occurring when titanium alkoxides are employed, is usually attributed to organic contaminants formed during the polymerization process [20]. It was found that the C-94 catalyst (TiO_2 and SiO_2 with a ratio of 9:1 w/w) [20] is six to eight times as active as antimony oxide catalyst [21]. Germanium oxide is also very effective. Other common catalyst systems are listed in the review by Pang *et al.* [22]. Antimony catalyst typically leads to production 1–2 mol% of diethyleneglycol (DEG) but for other catalysts the amount of DEG can be higher [23].

Since melt spinning can take place at temperatures above the melting point, degradation processes occur. It is then necessary to develop technologies under controlled degradation or using side reactions. One of the most important side reactions is forming a DEG unit $HO(CH_2)_2O(CH_2)_2OH$ in the chain. The polymer chain length is not changed but modifying DEG components are included in backbone. The presence of DEG reduces crystallinity and lowers both thermal and hydrolytic stability. PET produced by the direct esterification of TPA generally contains more DEG than PET produced by the transesterification of DMT [24]. During the heat treatment of PET fibers, crystallization occurs by squeezing the DEG rich portion out to the amorphous region [25]. The kinetic and mechanism of DEG formation is described in the work [26]. It is impossible to completely eliminate DEG formation and around 1.5 mole% is always present [19]. In PET chips, stable cyclic trimer (see Fig. 9.3) in concentration of about 2% w/w is present. Cyclic trimer can be extracted from PET chip with hot xylene but if the extracted polymer is re-melted, the same level of trimer reforms.

A major disadvantage of both DMT and TPA processes is a long polymerization time. It takes around 5 h for the first stage and 5 h for the second (polycondensation) stage. The final step of PET polymer preparation



9.3 Structure of cyclic trimmer.

in the **batch process** is extrusion under inert gas (usually nitrogen), cooling and creation of polymer chips. In the **continuous polymerization process** the molten polymer may be delivered directly to a spinning unit.

The PET obtained by the DMT or TPA process is different in the amount and in the type of catalyst remnants. In particular, PET obtained by the DMT process is less stable because it contains generally larger amounts of antimony catalyst remnants together with catalyst remnants of the transesterification step (generally Mn, Zn and Co) as well as phosphorus derivatives, which are added in the polycondensation step to complex the transesterification catalysts. Polymer from the TPA process can be generally spun at higher speeds [27]. For the same take-up speed, commercial fibers from TPA always show higher tenacity (lower molecular orientation in the amorphous phase) and lower ductility than fibers from DMT. For the fibers from the DMT process, an earlier crystallization (related to their slightly higher melting temperatures and melt viscosities) occurs, which constrains the amorphous phase orientation. Earlier crystallization of the fibers from DMT could be due to the lower amount of diethylene glycol content [28].

Several other novel processes for manufacturing TA have been patented, and some of them have been used commercially, but TPA or DMT (for special cases) remains the most important. The limitations of polycondensation for molecular weight increase are due to the reversibility of polymerization reaction and also to the degradation reactions at higher reaction temperatures (necessary for reduction the increasing melt viscosity). Tomita [29] showed that with increasing polymerization temperature, the optimum reaction time and the maximum molecular weight are both reduced. Thus polymerization at low temperature is desirable to obtain higher molecular weight PET. However, the polymerization rate at low temperature is usually very slow.

Solid phase polymerization (SPP) is potentially an attractive means of overcoming these difficulties [1, 13, 19, 27]. The first step is pre-crystallization of initially amorphous chips carried out by heating (around 160–170 °C). The crystallization process is quite exothermic. This crystallization permits

temperatures to be used above the normal melting point of PET and to prevent stickiness of chips during SPP [13]. The pre-crystallized chips are then heated in a stream of hot inert gas or else agitated in a vacuum drier to remove small traces of glycol and other volatiles until the desirable molecular weight is obtained. The best results are obtained if the SSP reaction is carried out in vacuum [30]. Since the reaction temperature is below the melting point (SPP), the chips do not fully sinter together and the lower reaction temperature constrains degradation reactions. The polymerization rates are here higher due to the shorter diffusion path in smaller particles [31, 32]. It was found that the rate of SSP increases with increase of catalyst concentration within the range 0–100 ppm Sb in starting chips [18].

The kinetic rate equation describing empirical relation between solid state polymerization time t [hours], temperature T [°C] and molecular weight M_t [g/mol] is given by [30]:

$$M_t = M_0 + 9.3 \cdot 10^{12} \exp \left(\frac{-10693}{T + 273.15} \right) \sqrt{t} \quad 9.1$$

where M_0 [g/mol] is initial number average molecular weight of precursor (starting chips).

It has been shown that the rate of polycondensation in the solid state depends on the relative rates of two types of diffusion. The diffusion of reaction by-products (physical diffusion) controls the rate of the forward reactions. On the other hand the diffusion of end groups (chemical diffusion) allows the reaction to proceed [21].

SSP works because it allows chain growth and minimizes chain scission, owing to the diverse kinetics and activation energies of these two different processes. This process was developed for the production of fibers for high performance technical textiles and tire cord filaments or for soft drink bottles.

Increasing the molecular weight of normal as-spun PET fibers the SSP can be used as well. A simple method of SPP for as-spun PET fibers consists of three stages [33]:

1. The as-spun PET fibers are dried at 100 °C for 3 hours under vacuum.
2. Dry fibers are crystallized at 220 °C for 2 hours to overcome the problem with stickiness.
3. The SSP is realized at 240 °C for constant time in the range of 1–3 hours under an argon gas flow.

The solid state polymerized fibers have a high crystallinity (about 60 wt%) and the lowest temperature for drawing is around 130 °C. The highest draw ratio increases with the increase of drawing temperature. Under an appropriate heat treatment condition, the tensile modulus and strength can be quite high (modulus 23 GPa and tenacity 1.1 GPa, respectively [33]).

PET with ultra-high molecular weight can be obtained by swollen-state polymerization in specific solvents (hydrogenated terphenyl) under bubbling nitrogen gas at atmospheric pressure. The rate of swollen-state polymerization is strongly related to the degree of swelling [34].

Relatively new ring-opening polymerization (ROP) of cyclic oligoesters offers advantages over the conventional polymerization method. A higher polymer molecular weight results in shorter reaction times under atmospheric pressure and no by-product generation. Additionally the low melt viscosity of the cyclic oligomers allows easier processing [22].

9.3 Modified poly(ethylene terephthalate) (PET) fibers

The term ‘modification’ is used to mean a deliberate change in composition or structure leading to an improvement in some fiber properties. The main aims of PET fiber modification are:

- obtaining new properties such as affinity for cationic dyes or elastomeric response;
- enhancing some positive properties such as tenacity or resistance to ultraviolet radiation;
- suppressing some negative properties such as hydrophobicity or pilling tendency.

In spite of the great number of existing modification methods no consistent classification is available as yet [35]. From the general viewpoint, however, it is possible to classify the modification methods by the production steps at which they are applied. The following classification scheme results [3]:

1. *Modification in course of polymer preparation*
 - Preparation of copolymers,
 - preparation of polymer blends,
 - using additives and fillers,
 - reducing the molecular mass.
2. *Modification in course of fiber preparation*
 - Drawing and setting conditions readjusting,
 - changing of spinning rate,
 - texturing,
 - cross-section or longitudinal geometry changing,
 - fineness changing (microfibers between 1.0 and 0.3 dtex)
 - bi-component and multi-component fiber production.
3. *Modification applied to commercial fibers*
 - Grafting,
 - plasma etching,
 - laser treatment,
 - controlled removal of surface layers.

4. *Combined modification*

(E.g. hollow microporous copolyester fibers containing additives.)

Details about these modifications are summarized in Militký *et al.* [3].

Basic negative properties of polyester (PET) fibers are low water absorption, high pilling, static electrification and difficult dyeability. To suppress these properties chemical modification is generally needed. This is achieved by the replacement of part of TPA or EG by other substances (comonomers). For PET fibers the main types of potential commoners are:

- **adipic acid** – concentration range 6–8 mol%
- **isophthalic acid** – concentration range 10–15 mol%
- **5-sulfoisophthalic acid** – concentration range 1–3 mol%
- **butyleneglycol** – concentration range 8–10 mol%
- **polyethyleneglycol (80–150 units)** – concentration range 5–8 weight%
- **pentaerythritol** – concentration range less than 1 mol%

Modification generally affects other technologically important characteristics such as the technology of fiber preparation, molecular mass of melt, degree of melt degradation and rate of crystallization. It is therefore difficult to separate effect of chemical modification from modification of technological parameters.

A very interesting example of how the properties of fibers made from one original copolymer can be varied by varying the draw-setting conditions is given in by Militký *et al.* [3]. PET fiber modified with isophthalic acid and a sodium salt of dimethyl sulfoisophthalic acid was used. The draw-setting conditions were varied so as to obtain fibers with different properties, i.e.

- a fiber shrinking in boiling water (sample S);
- a fiber with low shrinkage in boiling water and high shrinkage in hot air at temperatures above 170 °C (sample D);
- a non-shrink fiber dyeable without carrier at temperatures up to 100 °C (sample B);

The selected properties of these fibers are given in Table 9.1. The characteristics in Table 9.1 have the following meaning: DR is draw ratio, T_S (°C) is setting temperature, S_B (%) is contraction at boiling point, S_A (%) is contraction in hot air at 175 °C, K_D (min⁻¹) is dyeing-rate constant for the disperse dye Palanilblau 3 RE (a concentration of 2 mass% of material) at 100 °C and C_F (mg g⁻¹) is amount of dye in the fiber after 80 minutes of non-isothermal dyeing (50 minutes of boiling). More detailed information on fiber preparation and methods of these quantities determination is given by Militký *et al.* [3]). The results summarized in Table 9.1 show that fiber S shrinks in boiling water, fiber D exhibits low shrinkage in boiling water

Table 9.1 Effect of physical modification on the properties of modified PET fibers

Sample	DR	$T_S(^{\circ}\text{C})$	$S_B(\%)$	$S_A(\%)$	$K_D(\text{min}^{-1})$	$C_F(\text{mg g}^{-1})$
S	4.6	35	30	38.3	0.0216	11.48
D	4.5	120	3.2	22.9	0.0123	8.72
B	3.7	150	1.3	3.2	0.0131	14.72

but shrinks significantly in hot air and fiber B can be dyed relatively well without a carrier in boiling water. It should be added that the absolute strength of these fibers was in the narrow range of 130–150 mN, elongation varied between 28% and 68%, and flexing resistance (expressed in terms of the number of flex to break) was in the range 1220–2200 [3]. In comparison with other modification methods used to obtain similar effects, the changing of draw-setting conditions does not involve deterioration of the mechanical and physical properties of the fibers.

9.3.1 Chemical modification

The simplest chemical modification is the ‘unwanted’ modification with DEG which is produced by the effect of side reactions during the production of PET fibers. This modification just increases the length and mobility of aliphatic chains. This leads to the formation of different configurations composed of *trans*- and *gauche*-conformations of individual groups in PET chains. In some patents it has been suggested, however, that it is possible to enhance dyeability by adding DEG intentionally during polycondensation. The effect of DEG content on the dyeability of PET fibers has been studied [36].

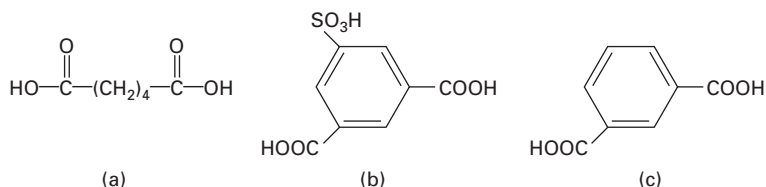
If EG is replaced by higher diols, a higher number of configurations will be formed in the chains. For example, in case of PBT the glycol residue will exhibit a *gauche-trans-gauche*-conformation [37]. With a growing number of methylene groups the chains will contain ‘shortened’ spatial conformations, composed of *trans*- and *gauche*-conformers (called α -forms) and ‘extended’ planar conformations, formed from *trans*-conformers only (called β -conformations). During deformation the β -forms will be elastically changed into extended α -forms. The copolymers based on PET always contain a relatively high number of benzene nuclei in the *para*-position, which makes the chains more rigid. Likewise the polar forces, generated by ester groups, hinder the mobility of chains at low temperatures [38].

Modification with isophthalic acid (see Fig. 9.4c) results in a 60° bending of polymer chains. This disturbs the straight zigzag structure of the chain portions and steric hindrances of an optimum chain arrangement are created. Up to an isophthalic acid content of 15% the viscosity of the copolymer melt changes little and hence the chain rigidity is not decreased. The reason is that the mean quadratic distance of chain ends, which is in direct proportion to the viscosity, is maintained [3].

A sodium salt of 5-sulfoisophthalic acid (see Fig. 9.4b) affects the steric arrangement more adversely. The voluminous polar sulfo-group increases the rigidity of polymer chains. This is evident from the steep increase in copolymer melt viscosity caused by even a small addition of this comonomer [3]. It appears that the rigidity is caused by the polar nature of the $-\text{SO}_3\text{Na}$ group.

Chain rigidity can be reduced either by aliphatic dicarboxylic acids or by aliphatic diols containing a greater number of methylene groups. The application of dicarboxylic acids is more efficient because they reduce the number of benzene rings per unit chain length more rapidly. Of particular interest are modifications with the so-called isomorphous dicarboxylic acids. These acids exhibit the same length of elementary unit as the terephthalic acid but a lower rigidity. Examples of such acids are cyclohexane-1,4-dicarboxylic acid and adipic acid (see Fig. 9.4a) [3]. If an optimum amount of the isomorphous modification component is used (between 2 and 4%), the chain regularity will not be markedly disturbed but the chain mobility will be increased. It leads to an increase of the fibers' drawing capacity. If an optimum amount of this component is exceeded, the particular effect will be lost and the isomorphous modification component will behave like an ordinary modification component. As the adipic acid content is increased, the melt viscosity will decrease, suggesting that the chain flexibility will increase. Increased chain flexibility leads to a reduced glass transition (T_g) temperature and improved dyeability [3]. On the other hand, however, dyeability can also be improved by combining increased rigidity with structure loosening. For instance, through combined modification with isophthalic acid and a sodium salt of 5-sulfoisophthalic acid, fibers can be dyed by disperse dyes at boil without carrier. However, neither of the two components itself is capable of increasing dyeability to such an extent.

It should be noted that most comonomers cause the non-regularity of polymeric chains which is dependent on the actual separation of comonomer units. If we assume a statistical nature for the distribution of comonomer groups, based on the Markov model of a two-phase chain [39], the average number of PET units n_E between two units containing the modification component is determined by the relation:



9.4 Modifying component: (a) adipic acid; (b) 5 sulfoisophthalic acid; (c) – isophthalic acid.

$$n_E = \frac{100}{n_K} \quad 9.2$$

where n_K is the molar percentage of comonomer. The ethylene glycol terephthalate, i.e. PET unit, has a length $L_{PET} = 1.075$ nm. It is then easy to determine also the length of the PET polymeric chain $L_p = n_E L_{PET}$ separating two units of the modification component.

Block copolyesters are composed from long flexible polyalkyleneglycol segments. The ethylene glycol $-(CH_2)_2-O-$ group has an average length of 0.501 nm. Poly(ethylen) glycole (PEG), having a molecular weight of 3000, has a degree of polymerization of about 68. The 'block' length of PEG is then 34.12 nm and this represents approximately the length of 32 PET units. At higher concentrations of PEG blocks the distances between individual blocks rapidly decrease. At the concentration of 32.97 (weight) % the block lengths of PEG and PET are the same. These very simplified calculations are based on the assumption of an ideal arrangement of copolymer chains in unlimited length. Real fibers contain, of course, segments of higher or lower local comonomer concentrations. Moreover, the polymer chains have a finite length. Corresponding to a polymerizing degree of 80 is an average PET chain length of 86 nm. It is evident, that some chains will not contain any modification component at all.

9.3.2 Effect of modification on the state of crystalline phase

The presence of a comonomer has influence on the rate of crystallization and whole crystalline structures. The following possibilities exist:

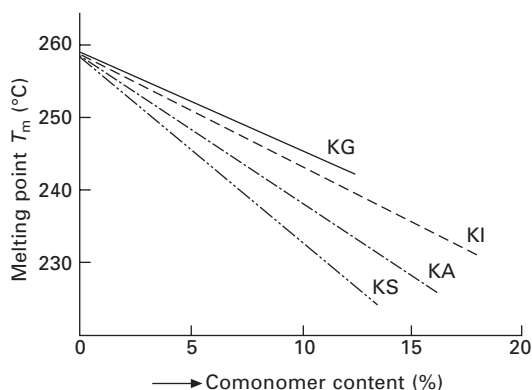
- mixed crystals are formed (the comonomer is built into the crystallites);
- crystallites are formed by the monomer units of the basic homopolymer only (comonomer units remain in the amorphous phase only);
- crystallization is prevented (in this instance, however, the copolyester is unsuitable for preparation of textile fibers);
- two independent crystalline structures are formed (this comes into consideration with block copolymers only).

It is evident that increasing the relative molecular mass of the polymer leads to a retardation of crystallization. But the temperature corresponding to the maximum crystallization rate, T_{cm} , does not change in practice [40]. The addition of a comonomer will shift T_{cm} towards lower values. Likewise the crystallization rate will generally be markedly decreased. Owing to the effect of a reduced T_g and shifted T_{cm} , the crystallization rate of copolymers can be even higher. Privalko [41] has found that T_{cm} [K] is related to the T_g of polymers T_g [K] by the empirical relation $T_{cm} = 1.26T_g$.

Isomorphous modification components increase the rate of crystallization when used at lower concentrations. But at higher concentrations above 5 molar% with adipic acid, even such modification components will decrease the crystallization rate. These conclusions are supported by the results of measurements of the dependence of the cold crystallization temperature T_c on the content of different comonomers [3]. The higher the value of T_c the more difficult will be the crystallization of a given system. Increasing isophthalic acid content leads to the marked increase of T_c . In copolyesters containing a sodium salt of 5-sulfoisophthalic acid, T_c increases proportionally to modifying component content. On the other hand, increasing content of adipic acid, DEG and PEG [42] decrease the T_c .

The equilibrium degree of crystallinity at a given temperature is affected by the presence of comonomers to a much lesser extent. Thus, for example, it needs 10% content of isophthalic acid to cause a slight decrease in equilibrium crystallinity [3]. A more distinct decrease in the equilibrium degree of crystallinity is caused by comonomers which increase the rigidity of chains (e.g. sodium salts of 5-sulfoisophthalic acid).

The different crystallization rates of copolymer and homopolymer can play an important role in the course of fiber production, mainly during drawing and setting in a tensioned state. The crystallization hinders relaxation and disorientation of the chains and can thereby affect significantly the final structure of crystalline and amorphous phases in the fiber. The addition of a comonomer, built in statistically into the homopolymer chain, results generally in a reduction of the melting point T_m (schematically see Fig. 9.5). It has been found that the compounds that are not introduced into the crystallites are DEG [39], PEG [42], sebacic acid [43] and adipic acid [43]. Mixed crystals are formed by isophthalic acid [8, 44] and by 1,3-propylene-*p*-



9.5 Schematic influence of various comonomers on the melting point T_m (KA adipic acid, KI isophthalic acid, KS sulfoisophthalic acid, KG glutaric acid).

hydroxybenzoic acid [45]. It is evident that mixed crystallites can be formed only by chemically related units of more or less similar dimensions [8].

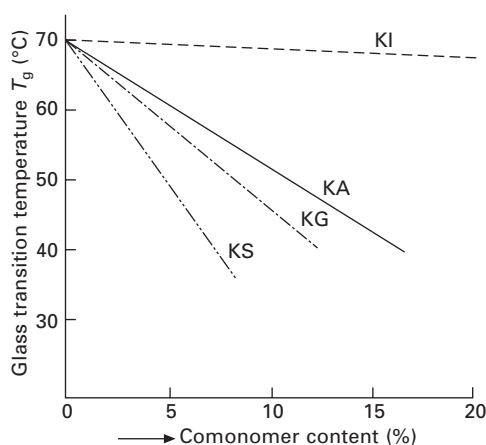
Owing to its voluminous polar side group, a sodium salt of 5-sulfoisophthalic acid will not be introduced into the crystallites. An example of a system in which two types of crystallites are formed is the PET/PBT copolymer [46].

9.3.3 Effect of modification on the state of amorphous phase

The majority of comonomers are not present in the crystallites but the amorphous regions always contain both components. This phase is characterized mainly by its mobility. Indirect information on the chain mobility in amorphous regions can be obtained from the values of T_g . The influence of various comonomers content on T_g is schematically shown in Fig. 9.6. The lower the values of T_g the lower will be the energetic barriers hindering mobility in the amorphous phase. A decrease in T_g is affected by [47]:

- a decrease of the total energy of intermolecular forces between polymer chains (this energy is proportional to the cohesions energy density, CED);
- growth of the flexibility of polymeric chains (flexibility is nearly independent of CED);
- growth of the symmetry of polymer chains.

Marcinčin and Romanov [48] described an empirical relationship between the T_g of copolymers and the CED. Most of the modification components



9.6 Schematic influence of various comonomers on T_g (KA adipic acid, KI isophthalic acid, KS sulfoisophthalic acid, KG glutaric acid).

cause the chain irregularities (reduction of the CED) and introduce flexible groups to the chains. The mobility of polymer chains is generally increased by the presence of ether link $-\text{CH}_2-\text{O}-\text{CH}_2$ [49]. On the other hand, the mobility of chains is heavily restricted by the presence of large side groups. Still more distinct is the effect of polar side groups [3].

The T_g is also influenced by structural fiber parameters and relative molecular polymer masses. Increase in relative molecular mass is accompanied by a hyperbolic increase in T_g . The effect of the growth of crystallinity is more sophisticated. At low proportions of the crystalline phase (below 30% in PET) a great number of small crystallites are formed and restrict the mobility of chains. This is accompanied by an increase in T_g . As soon as the amount of the crystalline phase exceeds a certain limit large crystallites begin to be formed. Owing to their relatively low number, the chain mobility is less affected and T_g decreases. In statistical copolymers the relation of T_g to the composition is generally not linear but passes through a maximum or a minimum.

In copolyesters, the relative number of the rigid benzene rings has a major influence on T_g . A modification replacing TPA will therefore reduce the T_g value much more markedly than modification replacing EG. With a growing number of methylene groups in the polyalkylene terephthalate chains, T_g will show a more or less hyperbolic decrease [50]. In a block polymer containing PEG, the decrease in T_g due to increase of modification component content is relatively small [51].

The non-symmetric modification components are represented by sodium salt of 5-sulfoisophthalic acid and isophthalic acid. A sodium salt of 5-sulfoisophthalic acid increases the value of T_g slightly (as compared with pure PET) but the presence of a greater number of DEG units in this copolyester reduce T_g markedly. The voluminous asymmetric sulfo-group strongly increases the polymer chain rigidity. Isophthalic acid will decrease the T_g value in copolyesters [52]. From the steric point of view both these modifications lose the amorphous phase structure, which results in improved dyeability.

9.4 Processing and structure evolution in polyester fibers

PET filament yarn and staple fibers are manufactured either by direct melt spinning of molten polymer from the polymerization equipment or by spinning of re-melted polymer chips. PET fiber spinning is carried out by using extruders, which feed the molten polymer under pressure through the spinnerettes. The rate of spinning is dependent on the cooling intensity and varies in wide range from 400 to 10 000 m/min. Fine fibers (<2 dtex) at intensive cooling can be spun at rate around 6000 m/min. For coarse fibers

(fishing lines, catgut diameter: 0.1–1 mm) the rate of spinning is 20–30 m/min only. Molten polymer ray solidification is induced by cooling with cold air. Depending on the desired product, post-spinning operations may include drawing, heat setting, crimping, lubrication and tearing or cutting.

9.5 Spinning

During the spinning process, PET melt is extruded and then wound up at a selected speed (standard is around 1200 m/min). The *discontinuous process* (cost-effective for smaller batches) of PET spinning uses the polyester chips as starting material. Sufficient drying and dry storage of chips are some of the most important parameters in the PET spinning. Even very small amounts of humidity considerably reduce the average degree of polymerization during melting. Only 0.01% H₂O in the PET chips causes a 10% decomposition of the melt [27]. In order to avoid a depolymerization as a result of hydrolysis during chip melting, it is important to continue drying until their moisture content does not exceed 0.005% [6, 27].

The *continuous process* is used for the production of standard fibers in larger batches. In this process the melt produced in the polycondensation reactor is directly delivered to the extruder. The spinning temperature is usually in the range of 280–300 °C (about 30 °C above melting temperature). Standard molecular weight PET (molecular weight 15 000 and 20 000) is spun at 280–290 °C, whereas ultra-high molecular weight PET is spun at 300 °C or above. The molecular weight is directly connected to various viscosity characteristics. The molten viscosity is approximately 2000–20 000 poise at 290 °C, depending on the average molecular weight. Because of high melt viscosity, effective melt spinning is limited to polymers with intrinsic viscosities $[\eta]$ not higher than 0.8–0.9 dl/g [53]. The intrinsic viscosity is connected with number-averaged molecular weight M_n of PET by Mark Houwink equation:

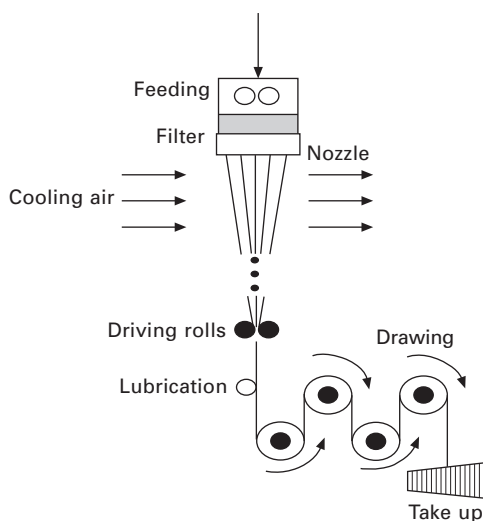
$$[\eta] = K M_n^a \quad 9.3$$

where $a = 0.898$ and $K = 5.41 \cdot 10^{-5}$ dl/g were found by regression for high molecular weight of PET and solvent dichloromethane/trifluoroacetic acid [54]. The molecular weight corresponding to intrinsic viscosity $[\eta] = 0.8$ dl/g is $M = 44\,000$ and for viscosity $[\eta] = 0.9$ dl/g is $M = 50\,200$.

The delivery pump must provide a pressure of about 100–200 bars to force the flow through the pack, which contains filtration media (e.g. sand) to remove any particles larger than a few μm . Standard spinning nozzles have holes of 0.1–1 mm in diameter. The polymer throughput per hole is usually in the range of 1–5 g/hole/min. The extrusion velocity, i.e. exit velocity from the spinneret v_B [m/min] depends on the amount of melt mass passing through hole, hole diameter and density of the melt. Typical values of v_B are about 10–30 m/min [27].

The process of PET melt spinning is shown in Fig. 9.7. After extrusion, the polymeric filament is solidified in the cooling chamber by the action of cold air. Heat is passed from polymeric filament to the surrounding air atmosphere by direct heat transfer and heat convection to the fiber surface. The speed of cooling is characterized by a coefficient of heat transfer c [$\text{W}/\text{m}^2/\text{K}$], which is for the fibers in the range of 33–800. Thermal conductivity is so small (around 0.01 [$\text{W}/\text{m}^2/\text{K}$]) that the difference in temperature inside the fiber and on the surface can be up to 30°C . Flexible linear macromolecules in the melt adopt a random coil-like configuration. In the dense melt, these coils interpenetrate each other and thus their diffusive motion is slow at temperatures above the melting point. The melt-quenching of the molten PET then leads to a locally regular structure. A ‘nodular’ structure is typical [3].

Owing to the take-up speed, pre-orientation of amorphous PET occurs. The speed of the molten polymer emerging from the spinneret is much less than the speed at the godet wheel (driving rolls in Fig. 9.7) and this stretching in the semi-molten state induces molecular order and orientation in the fiber. Stretching during spinning leads to a huge increase of the surface area per unit volume, which tends to reduce the chance of crystallization. On the other hand, stretching by spinning results in a molecular orientation and therefore accelerates crystallization. It depends on the spinning conditions which effect will dominate [55].



9.7 Process of PET melt spinning.

Depending upon the spinning speed various kind of fibers are obtained:

- *1000–1800 m/min LOY* (low oriented yarn). The fibers are amorphous and have to be drawn almost immediately. A semicrystalline structure is produced in drawn and annealed fibers.
- *1800–2800 m/min MOY* (medium oriented yarn). The fibers are amorphous and more oriented. They are used in combination with immediate drawing/annealing or texturing.
- *2800–4200 m/min POY* (pre-oriented yarn). These fibers are clearly not crystalline but they are oriented enough to support storing for several months without becoming brittle. They are generally used in technologies based on simultaneous drawing and texturing [56]. POY fibers are currently produced from PET at spinning speeds between 3000 and 3500 m/min.
- *4200–6000 m/min HOY* (highly oriented yarn). These fibers are partially crystalline and exhibit high orientation. They are not fully drawn. It was found that crystallization begins at a critical amorphous orientation of 0.18 [57]. The larger increase in amorphous phase orientation is due to the strong interaction between crystallites and surrounding amorphous matrix [57].
- *6000–10 000 m/min FOY* (fully oriented yarn). The fibers are sufficiently oriented and crystalline, of sufficiently low extension to break and of sufficiently high tenacity to be used for many purposes without further drawing. These products therefore eliminated the need for drawing, although not for all uses. There is a growing problem of diameter variation (unevenness) and gradual loss of strength due to increasing spinning speed.

It is interesting that the highest tenacity and modulus are best approached by a LOY plus high draw ratio route [58]. It was observed for LOY (spinning speed 500–2500 m/min) that after the simulated drawing the stress at break is a strongly decreasing function of spinning speed [59]. This is in accordance with Brody [60] finding that high speed spinning resulted in a broader or more non-uniform distribution of the chain contour length of tie molecules in the amorphous phase. The molecular orientation in the amorphous regions of the drawn LOY PET fibers is much higher than in high speed spun PET fibers [61]. In a typical LOY fiber spinning process the polymer viscosity increases exponentially along the spinning thread line as the polymer is transformed from a melt to a solid body.

Owing to increase of the spinning speed the increase of the fiber stress at break and decrease of the elongation at break occur. When the spinning speed exceeds 5000 m/min, the elongation at break is below 70% and the yield point in the stress–strain curve becomes less distinctive. The stress at break exhibits a maximum at a spinning speed of 6000–7000 m/min and

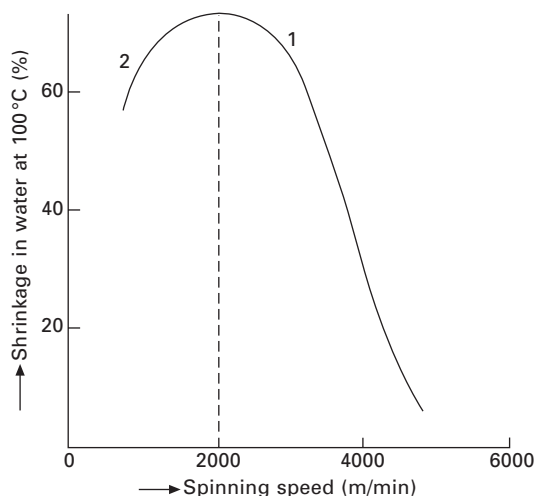
then decreases [62]. The elongation decreases monotonously with spinning speed and is less than 25% at a spinning speed of over 8000 m/min [62]. The birefringence Δn increases slowly up to a spinning speed of 2000 m/min and then quickly above a spinning speed of about 3000 m/min. The maximum value of $\Delta n = 0.12$ appears at a spinning speed of 7000 m/min and then decreases to $\Delta n = 0.08$ at a spinning speed of 9000 m/min [62]. An increase in winding speed up to 3500 m/min results in an increased orientation without any indication of crystallization [63]. At a winding speed of about 3500 m/min, flow-induced crystallization becomes apparent [64] while at speeds of 5000 m/min and higher, very well-developed crystals are detected [65]. Another feature of high speed spinning is non-uniformity of the fiber macro-structure, with more orientation and crystallinity near the fiber surface as a result of non-uniform solidification. Since fiber stresses become concentrated in the oriented regions, the taut molecules will break first, triggering rupture of the fiber before the unoriented molecules contribute much resistance. At higher spinning speeds, the loss of overall fiber strength and tenacity therefore results [66].

Detailed explanation of structural changes during high speed spinning of PET are presented by Nakajima [62]. As a result of the special molecular properties of POY, the temperature at which the heat induced crystallization occurs is about 30 °C lower than for LOY.

Higher spinning speed leads to the higher pre-orientation of chains. If the temperature is increased above the glass transition point T_g , then there is an increased reorientation of the amorphous (non-crystalline) molecules and shrinkage occurs. The shrinkage value increases with increasing amorphous orientation. If the spinning speed is further increased above 2000–3000 m/min, tension-induced crystallization occurs. This blocking increases the molecular reorientation of the amorphous phase, even at temperatures above T_g , and result is reduction of the shrinkage. The thermal shrinkage in boiling water therefore exhibits a maximum (around 60%) at a spinning speed of 2000–3000 m/min and then decreases to as low as 2–3% at a spinning speed of over 6000 m/min (see Fig. 9.8) [62].

Higher spinning temperature leads to the lowering of tenacity, increasing of deformation at break and lowering of orientation. These tendencies are quite the opposite when a small amount of poly(methylmethacrylate) is added to the PET [67]. This additive reduces the structure formation of PET at spinning speeds higher than 3000 m/min.

When PET is melt-spun at high speeds, the so-called ‘necking’ deformation in the threadline region occurs. This phenomenon is in fact the sudden reduction in fiber diameter detected by a sudden jump in the velocity in the necking zone. At a take-up velocity of 6000 m/min, the necking zone at distance of 140–150 cm from the spinneret was found. The temperature profile has a maximum about 160 °C at the end of this zone [68]. From investigation of



9.8 Typical spinning speed effect on fiber shrinkage in boiled water; Region 1 – POY and region 2 – LOY.

fiber diameter change at take-up speed of 4000 m/min, a necking deformation was identified in distance 40–47 cm from the spinneret [68]. Just before the neck formation, the viscosity suddenly decreases [69].

It is generally believed that the occurrence of necking is associated with the crystallization process. Stress-induced crystallization is an essential requirement for neck formation. The position of the neck moves closer to the spinneret as the deformation rate is increased. The actual position of the neck fluctuates and from diameter measurements a bimodal distribution appears [69]. Necking is also seen when the polymer intrinsic viscosity is increased [70].

High speed spinning requires considerable energy consumption, and manufacturing the take-up bobbin and operation safety are expensive. To obtain orientation-induced crystallization at speeds lower than that for the high speed spinning, super-cooled spinning was proposed [71]. This is achieved by setting the nozzle temperature to 265 °C, i.e. lower than the melting point of PET. The experimental results show that high orientation and high crystallinity can be achieved at a spinning speed of 2500 m/min, which compares favourably with a speed of 5000–6000 m/min in the high speed spinning [71].

To obtain high tenacity, high modulus PET fibers, the liquid isothermal bath (LIB) spinning process was developed [72]. For the normal LIB, the liquid bath was placed in the thread line at position which is 150–180 cm from the spinneret. The modified LIB process was developed with the intention of increasing the fibers' temperature prior to its entry to the hot liquid bath. The hot liquid reduces the fibers' cooling rate. It was found that heating the

fibers before entering the liquid bath induces uniform radial structure and an increase of deformability [73]. This process makes possible formation of high tenacity, high modulus PET fibers via melt spinning at high speeds (up to 5000 m/min). For the LIB process, the spin line stress within the liquid bath is enhanced by friction between the filament and the liquid. This leads to 'super-deformation' in the liquid bath, i.e. a neck-like deformation [72].

The as-spun fibers produced with the modified LIB process have high amorphous orientation, low crystallinity and relatively large crystallite size. Since these fibers have a large thermal shrinkage, they must be drawn and heat-treated [73].

In the melt spinning process of high molecular weight PET, the spin-line immediately below the spinning nozzle was heated by irradiating the carbon dioxide gas laser. In comparison with the fibers prepared without the laser irradiation, as-spun fibers obtained with laser irradiation showed higher elongation at break and higher tenacity [74].

One of most effective approaches for the production of PET fibers with improved mechanical properties is the utilization of high molecular weight polymers obtained usually by solid state polymerization. Because of extremely high viscosity, fiber formation of high molecular weight PET is often accomplished by solution spinning [75] or spinning with a plasticizer [76].

9.6 Drawing

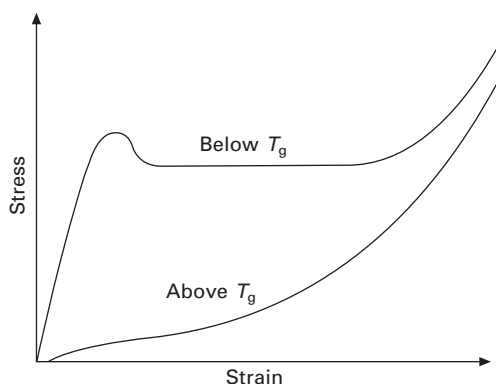
Drawing is an essential fabrication process to achieve well-oriented structures with appropriate mechanical properties. PET has relatively rigid molecules with a glass transition temperature higher than room temperature and therefore fibers in the as-spun state are generally *amorphous*. They have molecular orientation but only become crystalline with *oriented crystallites* when fully drawn. The presence of significant crystallinity in the fibers prior to drawing is detrimental. Free extension of the polymer chains is inhibited by crystallites which must be disrupted for molecular extension to occur during drawing. On the molecular level, drawing is accompanied by the transition of glycol fragments from twisted *gauche*-conformation to the extended *trans*-conformation.

Generally, during deformation, the orientation of PET increases with the increase of both draw ratio and stretching rate as a result of chain orientation and relaxation. At higher temperatures and low stretching rates, the chain mobility and chain slippage lead to the higher orientation which relaxes rapidly after end of deformation. The quickest relaxation step is viscoelastic relaxation between entanglements (tens of seconds), followed by chain retraction (hundreds of seconds) and then chain disentanglement (thousands of seconds). When amorphous PET is deformed near its T_g , relaxation

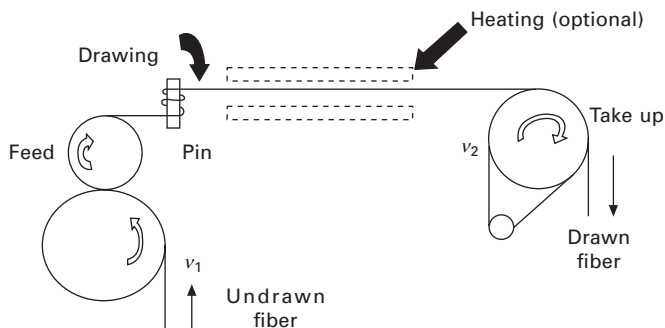
processes are connected with molecular weight, molecular weight between entanglements and inner friction coefficient [77].

Tensile deformation behavior of undrawn PET fiber is strongly dependent on temperature (see Fig. 9.9). When PET is deformed at a temperature above $T_g \sim 68^\circ\text{C}$, deformation takes place uniformly along the length. Below T_g , however, PET shows the phenomenon of necking. At a small extension of a few per cent a yield point appears and a sharp neck forms at some point. Subsequent extension then takes place at nearly constant load and involves thinning as the neck travels along the fiber.

This behavior leads to difficulties when the continuous drawing of fibers occurs. When fibers are drawn between two rollers running at different speeds (see Fig. 9.10) at temperatures below T_g (*cold drawing*), stable running can be achieved only by imposing a temperature gradient on the drawing filaments between the rollers so as to stabilize the position of the neck [78]. On the other hand, if drawing is carried out at temperatures above T_g (*hot drawing*),



9.9 Typical tensile stress-strain curves for undrawn PET at constant rate of deformation.



9.10 Pin drawing process.

the onset of drawing may be stabilized by a tension gradient imposed on the filaments by the first roller [79]. At intermediate temperatures, necking occurs only at high strain rates due to the strain-rate dependence of T_g . Long and Ward [80, 81] investigated tensile drawing and shrinkage force of PET. They found that by modeling deformed PET as a network, the properties of drawn material could be correlated with deformation histories. Gordon *et al.* [82] also observed that their results from two-stage uniaxial stretching of PET could be consistently interpreted using a molecular network model.

In both cold and hot drawing, the principle of drawing is the longitudinal tensile deformation of 20–2000% from starting length l_0 . The *draw point* where fiber drawing takes place is usually done by a stationary heated metal pin around which the fiber passed (see Fig. 9.10).

The industrial hot drawing process of a fiber involves passing the fiber over a series of rollers. The rollers rotate at specified constant angular velocities, each faster than the other. In a two-stage draw process, most of the drawing is provided in the first stage (between first and second roller) and a relatively smaller drawing effect is achieved in the second stage (between second and third roller). As the number of stages is increased, it is possible to keep each roller at a different temperature and induce the maximum possible draw ratio in each stage in order to obtain the maximum molecular orientation in the fiber [83].

In zone drawing and annealing, the molecular chains are oriented by localized heating which introduces a steep temperature gradient and a high strain rate [84]. Localized heating can be achieved using a CO₂ laser which allows accurate fixing of the drawing position without contact [85]. For preparation of high modulus PET fibers, vibrating hot drawing is very efficient [86]. A variety of drawing methods for improving mechanical properties of PET have been summarized by Kunugi and Suzuki [86].

The main parameter of the drawing process is drawing ratio, defined as the ratio of drawn fiber length l to the starting length l_0 .

$$\lambda = \frac{l}{l_0} = \frac{v_2}{v_1} \quad 9.4$$

In fact, the total drawing ratio λ is the product of partial drawing at individual stages of drawing $\lambda_1, \lambda_2, \dots$ i.e.:

$$\lambda = \lambda_1 \lambda_2 \dots = \frac{v_2}{v_1} \frac{v_3}{v_2} \dots \quad 9.5$$

where v_1 is the rate of the first drawing roller, v_2 is the rate of the second drawing roller and v_3 is the rate of the third drawing roller (for two stage drawing).

The maximum attainable draw ratio λ_m is estimated as the ratio of the extended chain length to the root mean square end-to-end distance of an

unperturbed random coil [87]. To predict the maximum attainable draw ratio as function of the molar mass M , the simple relation $\lambda_m \approx M^{0.5}$ can be used [87]. For isotropic amorphous PET, $\lambda_m \sim 3.45$ [88]. The assumption that the majority of the entanglements in PET will act as permanent crosslinks leads to the evaluation of λ_m from rubber elasticity theory in the form $\lambda_m \approx N_e^{0.5}$, where N_e is the number of statistical chain segments between entanglements [54].

Drawing is mainly influenced by: temperature, rate of deformation and presence of plastifying agents. Polymeric chains in LOY undrawn fibers are only slightly oriented. Polymeric chains in drawn fibers are mainly oriented parallel to the fiber axis (around 80–90% of chains). Drawing is therefore responsible for increasing fiber strength decreasing the deformation at break and causing the fibrous (fibrillar) structure. This new fibrillar oriented structure is deformed (plastically) as well. The crystallization rate is increased with draw ratio due to the so-called strain-induced crystallization effect. Ziabicki [89] has shown for the case of uniaxial tensile deformation that the half-time of crystallization $t_{0.5}(f_a)$ is related to mean orientation factor f_a .

$$\frac{t_{0.5}(0)}{t_{0.5}(f_a)} = \exp(Af_a^2 + Bf_a^2 + \dots) \quad 9.6$$

where $t_{0.5}(0)$ is the half-time of crystallization of unoriented PET and A , B are empirical constants. For small f_a the higher terms are often neglected ($B = 0$). There are two basic drawing processes: hot drawing and cold drawing.

Hot drawing (homogeneous) is carried out at drawing temperature T_D : $T_D > T_g$. For PET the minimum T_D is equal to 80 °C. The rate of drawing is increased by increasing drawing temperature or by using water as a heating medium. At hot drawing temperatures, the polymer is in a rubbery state, and the chains are free to move at a molecular level and can reorganize and reorient themselves under the mechanical stress of the drawing process. Orientation is here mainly due to sliding of chains. High temperatures require higher tensile stress to ensure an orientation. Increase of tensile stress leads to the increasing of melting temperature (e.g. polypropylene can be drawn at 180 °C, in spite of the fact that it melts at 173 °C). Drawing takes around 1–20 s. In the course of hot drawing, uniform fiber thinning occurs. Since the drawing process gives additional orientation to products, the draw ratio λ (3–6) varies according to the final end uses. For higher tenacities higher draw ratios are required. The shrinkage force σ_s induced by orientation during hot drawing can be expressed by a relation derived from theory of rubber elasticity [90]:

$$\sigma_s = N_0 kT (\lambda^2 - 1/\lambda) \quad 9.7$$

where T is temperature, k is the Boltzman constant and N_0 is the number of chains in unit volume of idealized network of chains.

The drawing process generates molecular orientation which can lead to strain-induced crystallization. Crystallinity induced by strain is strongly dependent on the strain rate, the temperature and the drawing conditions [91, 92]. Crystallinity may be developed during the hot drawing at the temperature range of 130–220 °C [93]. The so-called cold crystallization temperature T_c is 128 °C for PET [94]. Le Bourvellec *et al.* [95] found that crystallinity and crystallization kinetics depended on the degree of molecular orientation, i.e. PET deformed at higher temperatures crystallized more slowly because more molecular relaxation had occurred. It is interesting that strain-induced crystallization did probably not occur during drawing but was postponed until the moment when deformation stopped [96]. Crystallization can therefore occur during deformation at lower strain rates, with more crystallization occurring during drawing at low strain rates than at high strain rates. At the very high strain rates no crystallization would occur during drawing.

When the temperature of drawing is relatively high and the strain rates low, PET fibers will stretch without resultant orientation occurring. This is often denoted as flow drawing [97]. It has been suggested that under these conditions, molecular relaxation processes predominate over the orientation process. Consequently the drawing tension drops to low levels.

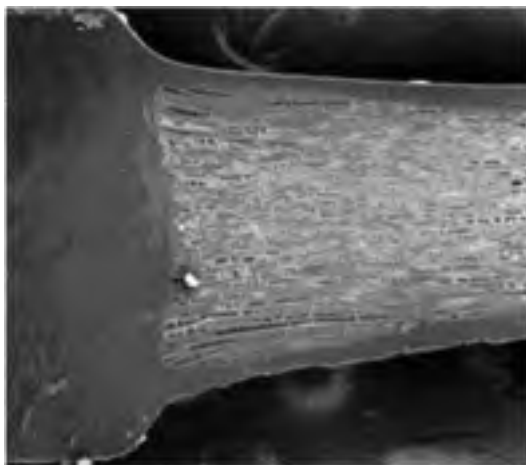
Dargent *et al.* [98] investigated the influence of water presence on the hot drawing process. It was found that water does not modify the degree of crystallinity of drawn PET but blocks the growth of a part of the crystallites and modifies their crystalline size. At a large draw ratio, the effect of water molecules on the orientation of the amorphous phase decreases and vanishes for approximately a draw ratio of 6. Water molecules have also an influence on strain-induced crystallization by shifting the crystallite size distribution to lower values.

The blowing hot air drawing at temperature of 220 °C and the maximum strain rate of 18.7 s⁻¹ was applied to PET fiber in order to produce fiber with improved mechanical properties [99]. The resulting fiber had degree of crystallinity of 44%. Despite the drawing at high temperatures close to the melting point, momentary heating at high temperatures promotes strain-induced crystallization and alignment of chains rather than the chain slippages [99].

Cold drawing (heterogeneous – adiabatic) at temperatures lower than T_g is characterized by huge plastic deformations at constant stress and the appearance of necking. The cold drawing process is quite exothermic. In the neck region the energy is dissipated into heat, viscosity is locally decreased and chain orientation occurs. In the case of semicrystalline polymers, melting of lamellar structures occurs as well. With increased drawing speeds the necking zone becomes more distinct because the drawing heat cannot

dissipate as quickly. Time of drawing is here very short, around 0.005 seconds only. The amorphous phase in drawn PET fibers that have not yet been thermally treated constitutes 90% or more of the structure. Their structure is in the form of a 'frozen' physical network with chain entanglements as knots. Cold drawing of PET amorphous material also induces formation of a highly ordered metastable mesomorphic form [100], which leads to a drastic increase of the packing density [101]. This mesomorphic form of PET corresponds to a solid mesophase characterized by parallel arrangement of chain axes and long-range positional order of a structural feature only in one dimension, i.e. along the chain axis and absence of any long-range order in the lateral packing of the chains [102]. This phase is stable at temperatures lower than T_g but highly unstable above T_g . When cold drawn fibers are heated above T_g (for amorphous PET it is about 70 °C in the dry condition and 50 °C in the wet) the mobility of the physical network is released and a mesophase readily transforms into a crystalline phase [103]. The result is an amorphous contraction and simultaneous crystallization into the normal crystalline (triclinic) form. It was also observed that crystallite size (ranging from 2.5 to 4.0 nm) is increased with draw ratio [91]. Oriented PET fibers have half-time of crystallization shorter than 0.01 s [104] and this process is in competition with shrinkage. Complete shrinkage is therefore usually obtained by shock heating only.

When sub- T_g physically aged, unoriented, amorphous PET fibers are cold drawn, high draw ratios could be achieved and an sheath/fibrillar core microstructure results. In the fibrillar core the slit-like voids of typical width 0.4 μm and length 5 μm can be seen (see Fig. 9.11). The slit voids of 1–2%



9.11 SEM micrograph of a longitudinal section through the neck region of an aged PET fiber (<http://www.irishscientist.ie/p186b.htm>).

from fiber volume appear to be formed at the instant when the fibrils are formed and simultaneously pulled apart by the extreme stress of cold drawing [105].

It has been shown that PET fibers can be treated with acetone or dimethylformamide/water solutions to plasticize the fiber, whilst creating an imperfect crystal structure that enhances drawability during cold drawing [106]. The resultant fibers can be drawn to higher draw ratios with the use of a two-stage draw technique resulting in 20% higher strength values. Use of subcritical (at pressure below critical value 72.8 atm) and supercritical CO₂ as a drawing media has similar effects as use of the above-mentioned solvents [107].

Rietsch *et al.* [108] studied tensile drawing of PET from 20 to 80 °C. Cold drawn PET was observed to neck at a natural draw ratio of 4.3, roughly independent of rate and temperature (rates ranged from 0.05 to 5 cm/min). Hot drawn PET, however, deformed uniformly. Sweeney *et al.* [109] found that necking would occur in PET below 60 °C and would not occur above 80 °C.

The necking phenomenon starts at the yield point where the engineering or nominal stress reaches a maximum before it drops as a result of localization of the plastic deformation. Plastic flow localization proceeds gradually up to a strain value that is called the natural draw ratio λ_p . Natural draw ratio is dependent on temperature and rate of deformation [110]. This parameter is dependent on the nature of the polymer:

- Stiff polymers (polystyrene, aramids) have $\lambda_p = 1.5\text{--}2.5$ (as for viscose).
- Semicrystalline polymers with lower stiffness as polyamides and PET have $\lambda_p = 3\text{--}6$.
- High crystalline flexible polymers as polypropylene and polyethylene have $\lambda_p = 5\text{--}10$.

The draw ratio has a major effect on fiber elongation and tenacity. High draw ratios give high tenacity fibers with higher modulus and lower extensions to break; low draw ratios give lower tenacities with much more extension. A semi-empirical rule connecting elongation to break ϵ_b and tenacity σ_b [cN/dtex] has been proposed

$$\sigma_b = K\epsilon_b^{-\alpha} \quad 9.8$$

where K and α are constants. Experimentally, $\alpha \approx 0.3$ and K is a measure of the inherent fiber strength and is related to the molecular weight. This parameter will also increase if, after drawing, heat setting is used to crystallize the oriented structure.

9.7 Heat treatment

The heat setting step usually accompanies the drawing process. The purpose of this step is:

- stabilization of fiber dimensions (reduction of shrinkage caused by chain retractions);
- relaxation of internal stresses in the fiber;
- creation or stabilization of the crystalline structure (the melting of small imperfect crystallites and the formation of more perfect larger ones).

The level of fiber tension and the heat setting temperature can both have significant effects on the final properties of fibers. Basically, there is a competition between two separate processes, i.e.

- Crystallization, starting in the oriented amorphous mesophase (extended chain crystallization) and then extending into low oriented amorphous phase (folded chain crystallization) [103].
- Shrinkage due to chain disorientation via bond rotation in amorphous regions, i.e. changes of amorphous chains conformation from the *trans* to *gauche* form.

The relative rates of these two processes are affected by tension and temperature mainly, thus a huge range of different fiber properties can be achieved.

Shrinkage varies strongly with the mode of treatment. If relaxation of stress and strain in the oriented fiber is allowed to occur through shrinkage during heat setting, then shrinkage at the textile processing stage is reduced and initial modulus is lowered. Heat setting with fixed fiber length, i.e. under tension during heat treatment, is less affected with change in modulus and reduced shrinkage values can still be obtained. In semicrystalline PET fibers ‘amorphous’ shrinkage takes place partially. The amount is determined by the orientation in the amorphous phase and the mean relative molecular mass of the polymer. Amorphous shrinkage can occur at low temperatures (less than 100 °C) only. Corresponding shrinkage forces lie in the region of 10 to 20 mN/tex. Another shrinkage mechanism is the so-called crystalline contraction. It occurs especially in differentially shrinkable fibers. This type of contraction is provoked by rearrangement of the crystalline phase connected with the formation of ‘perfect’ crystallites with folded chains. The rearrangement of the crystalline phase can occur at relatively high temperatures only (above 200 °C for PET) and its prerequisite is the presence of a greater number of less than perfect crystallites. This kind of structure is formed during setting under tension or in modified polyesters.

There are two basic ways of fiber setting:

- *Isotonic setting*, when the shrinkage of the fiber occurs as a result of chain retractions and relaxation of internal stresses. These changes are

stabilized by recrystallization. The orientation and strength of a fiber are decreased and elongation to break is increased. Practically, this type of setting is implemented in the free-state without limitation of dimensional changes (*annealing* or *slack heat setting*).

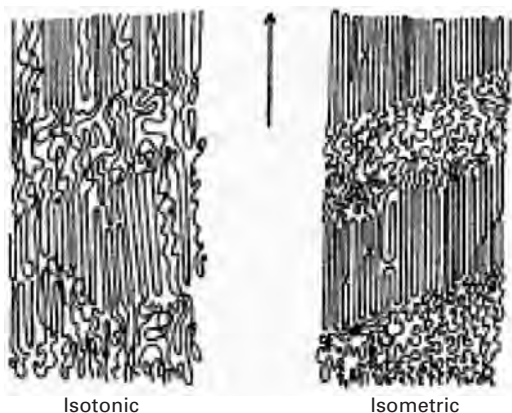
- *Isometric setting*, when there are no dimensional changes of fibers. The main mechanism is the relaxation of internal stresses associated with chain sliding and stress-induced crystallization. The orientation and strength of fibers are unchanged. This type of setting practically runs at a constant length, when the fibers cannot be deformed.

The semicrystalline structure appears mainly during thermal setting in isometric or isotonic state. The structural differences caused by these heat setting types are schematically shown in Fig. 9.12.

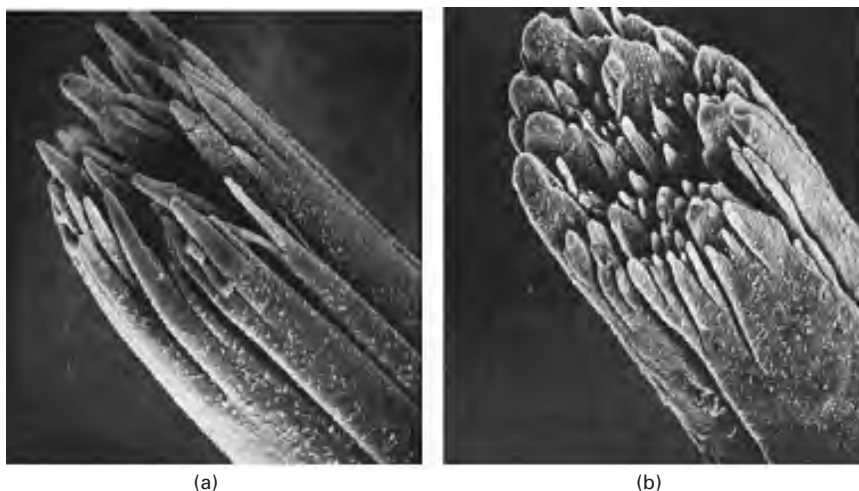
Fibers, after setting, have typically a degree of crystallinity about 0.4, orientation factor of the crystalline phase about $f_c > 0.95$ and orientation factor of the amorphous phase about $f_a = 0.6$. Basic structural units are relatively strong *microfibrils* having diameters of 10–15 nm and lengths of 10^3 nm. These units are assembled into *fibrils* having diameters of 30–45 nm. A very important role is played by taut tie molecules (TTM). The proportion of TTM is around 0.1–0.5. This phase is responsible for the mechanical properties of PET fibers.

In the presence of modification components, variations in crystallization rate and different retraction of chains in amorphous regions occur [3]. The setting is generally accompanied by microfibrils coarsening in the structure. It is demonstrated in Fig. 9.13, where the differences between fibrillar structure of the Tesil 35 (modified with 5-sulfoisophthalic acid) before and after heat setting are shown.

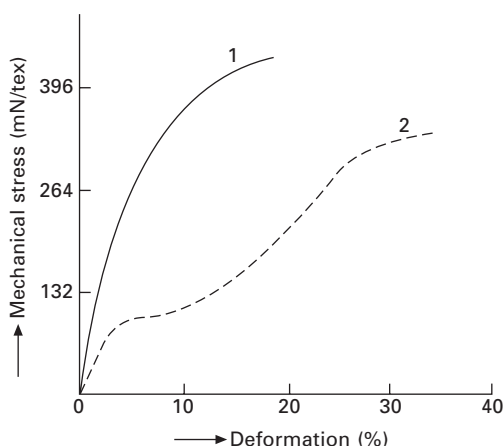
These structural differences are accompanied by differences in behavior. The marked differences are visible in the stress–strain curves. In Fig. 9.14,



9.12 Structural differences due to basic heat setting types.



9.13 Fibrillar structure of Tesil 35 (modified with 5 sulfoisophthalic acid): (a) drawn fiber with draw ratio 4.6; (b) drawn fiber after 10 min period of annealing at 160 °C [3].



9.14 Typical stress-strain curves of heat set fibers: curve 1 – isometric heat setting; curve 2 – free state heat setting.

the curves for a typical PET fiber after heat setting at 100 °C for a period of 60 seconds are shown [3]. Setting is accompanied by melting of the smallest, least perfect crystals and the formation of larger, more perfect crystals. This is in agreement with the rule-of-thumb, which defines the necessity to go to higher temperatures to achieve a new state, with the distribution of crystal size and perfection being shifted to higher values.

To secure the results obtained by setting it is therefore essential that the maximum temperature used in subsequent thermal treatments is 15–20 °C

lower than the setting temperature. The temperature used in subsequent aqueous treatments under pressure should be roughly 30 °C lower than the temperature of heat setting. This means that before high temperature dyeing at 130 °C, the material must be processed by heat setting at a temperature higher than 170 °C, for instance at 180 °C.

The heat setting effect in PET is highly time-dependent. The rate of setting increases rapidly with increase of temperature. The structural and morphological changes due to heat setting are presented in the review by Gupta [111].

9.7.1 Isotonic setting

Peszkin and Shultz [112] annealed PET fibers at temperatures ranging from 100 to 200 °C under a small tensile force. They observed that a competition existed between chain-recoiling (shrinkage) and crystallization. The crystallization kinetics increases with higher temperatures and higher tension. Chain orientation also increases with tension [112]. Heat setting of PET fibers under a higher tensile force provokes the crystallization in two stages [113]. In the first stage, nucleation starts and fibrillar crystallites grow as the fibers begin to elongate. Chain mobility in the amorphous phase is restricted gradually and reaches its asymptotic value. Concurrently, tensile modulus and tenacity increase markedly. In the second stage, a microstructure is created and the perfection of crystallites continues to increase. Fiber elongation during heat treatment reaches its asymptotic value. Simultaneously, the increasing trend in tensile modulus is stopped and reaches its asymptotic value [113].

High temperature (above 200 °C), high tension heat setting maintains a high level of orientation in the amorphous regions, hence high fiber modulus and relatively lower dyeing rate. The latter can be improved by reducing the heat setting temperature so that less crystallization occurs. If the fibers are heated with low tension, disorientation of the oriented amorphous regions occurs and the fibers are left with low shrinkage forces (and modulus) but high dyeability.

The three stage model of oriented PET structural changes during its isothermal crystallization was proposed in the work of Radhakrishnan and Kaito [114]. The first stage is thermodynamic relaxation, which occurs when the material is heated above its T_g . The second stage is the structural change of the oriented amorphous structure, where the degree of orientation increases from the nearly isotropic state and the *gauche*-conformation is transformed into the *trans*-conformation. Crystalline structure appears in the third stage, only after the orientation process is completed. The bundles of highly oriented tie chains in the amorphous phase (mesophase) are probably responsible for the first stage of crystallization (80–100 °C), the less ordered or non-oriented chains are responsible for the second stage of crystallization at temperatures above 140 °C [115].

9.7.2 Free ends heat setting (annealing)

Free ends annealing of PET fibers enhances dimensional stability of the material due to the relaxation of residual stresses. It has been observed [116] that up to an annealing temperature of approximately 180 °C, the number and size of the crystallites increase steadily. At temperatures above 180 °C the recrystallization process results in a further increase in crystallite size but a decrease in their number.

The overall shrinkage process of PET fibers with low orientation involves a rapid initial stage of rubber-like contraction of the molecular network, associated with disorientation in the amorphous phase, followed by a crystallization stage during which chain folding may occur. In the highly drawn samples with high orientation, however, crystallization can be extremely rapid, particularly at high temperatures, and shrinkage is hindered [117]. It was observed that during crystallization pushing of the DEG-rich chains portion to the amorphous region occurs. Result is the increase of DEG concentration in the amorphous region [25].

It was found that the degree of crystallinity increases with an increase in annealing temperature and then the amorphous density of PET decreases on free ends annealing, because the crystal density could be assumed to be constant [118]. The increase of the orientation of crystalline phase can be explained by the relaxation of the molecules in the amorphous region [119]. Some molecules in the amorphous regions relax during the heat treatment due to the removal of the residual stress and strain. This relaxation may accompany a longitudinal pulling of the crystallites along the fiber axis, followed by the improvement in the crystallite orientation.

As first published by Marvin [120], the amount of disperse dyes after isothermal sorption depends on the annealing temperatures of PET. This amount initially decreases as the annealing temperature increases and then increases over the value of the untreated control at higher annealing temperatures. The analysis of the experimental data leads to the conclusion that sorption sites are predominantly located in amorphous regions near crystal surfaces of PET [121].

Toda and coworkers [118] studied the amorphous structure change in PET due to free ends annealing under dry and wet conditions in the terms of amorphous density and dye uptake. The amorphous structure was classified into three parts. In the first region (to approx. 120 °C in water and approx. 145 °C in the dry state) the amorphous fraction density slowly decreases with proceeding crystallization. The molecular conformation of the amorphous chains and the free volume content of the amorphous region changed only subtly. In the subsequent second region (to approximately 170 °C in water and approximately 210 °C in the dry state) the amorphous fraction density decreases sharply. The state of the amorphous chains is changed from the *gauche* to the *trans*-conformation and the free volume content of the

amorphous region greatly increases with crystallization. In the last region (above approx. 170 °C in water and above approx. 210 °C in dry state) the amorphous fraction density increases significantly as crystallization proceeds. The increased free volume is partially converted to microvoids.

Owing to the structural changes during free ends annealing, the mechanical properties, such as the elastic modulus and yield strength decrease [122–124]. Gupta and Kumar [124] found that the free ends annealing of PET fibers at high temperature causes the crystalline and amorphous regions to be stacked in series, reducing the number of which will be the first to take up the load. Owing to the limited number of TTM, the stress concentration will be high and they will quickly yield. Furthermore, since free ends annealing reduces the amorphous orientation, the decrease of initial modulus results. Decrease of initial modulus leads to the drop of elastic recovery properties, such as wrinkle and crease resistance [125].

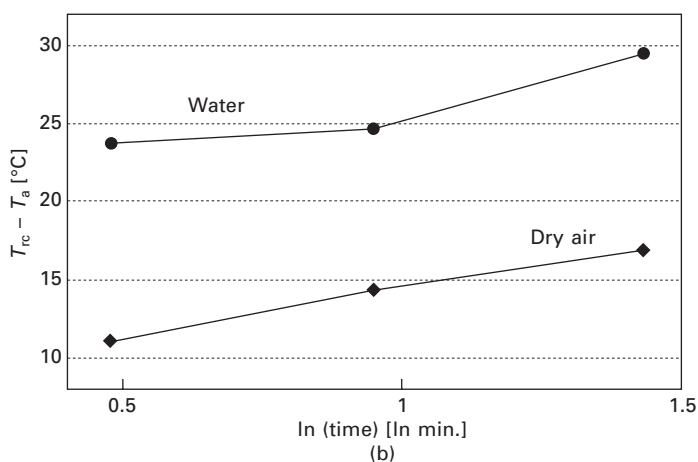
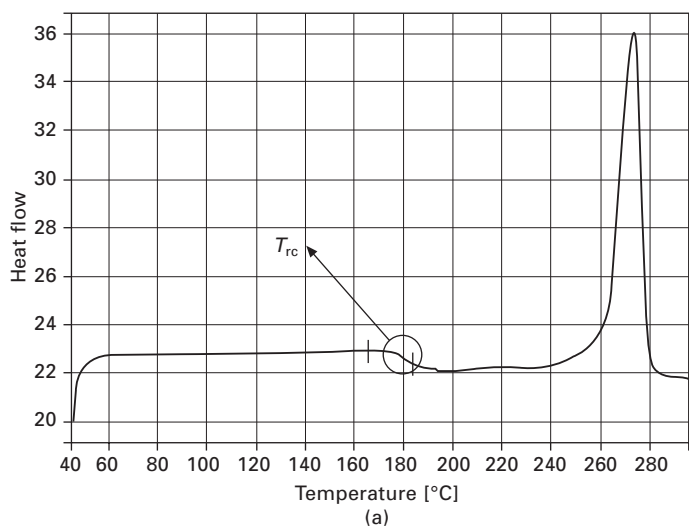
Suprisingly, the short-term heat treatment at 190 °C for 1.2 seconds increases the initial modulus, but the yield strength is decreased significantly. During the short heat treatment, the chains in PET fibers are relaxed and crystallized to some extent. The PET chains in the amorphous regions were also relaxed, promoting the formation of *micro-crystals*. These micro-crystals in the amorphous region can explain the increase in the initial modulus [125].

We have investigated the influence of free ends annealing temperature T_a on the thermal and mechanical behavior of recycled drawn PET fibers [126]. Figure 9.15(a), shows a typical DSC thermogram of polyester fibers after setting. The characteristic bend in the exothermic direction (circle on Fig. 9.15a) is an indicator of annealing temperature. Location of this bend is called effective setting temperature or start of recrystallization (T_{rc}). It was found, that values T_{rc} are about 15 or 20 °C higher than selected annealing temperature [127].

The T_{rc} temperature is directly proportional to the setting temperature and increases with the setting time. This is visible in Fig. 9.15(b), where the dependence between $T_{rc} - T_a$ and logarithm of heat setting time is shown. The presence of T_{rc} peak is explained by melting of small crystallites that are unstable to heat (melting energy is in this case around 8 kJ/mol) [3].

Figure 9.16 shows the dependence of the mean values of tensile strength and break elongation on annealing temperature. The tensile strength σ_b slightly decreases and deformation at break ε_b increases as setting temperature increases. The distribution of tenacity can be approximated by the two parameter Weibull distribution. Parameters of the Weibull distributions were practically unchanged by setting temperature [126]. The statistical nature of fiber break is therefore probably not dependent on the setting temperature.

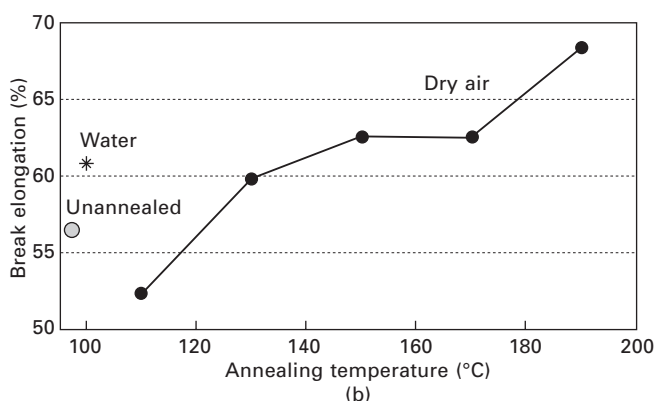
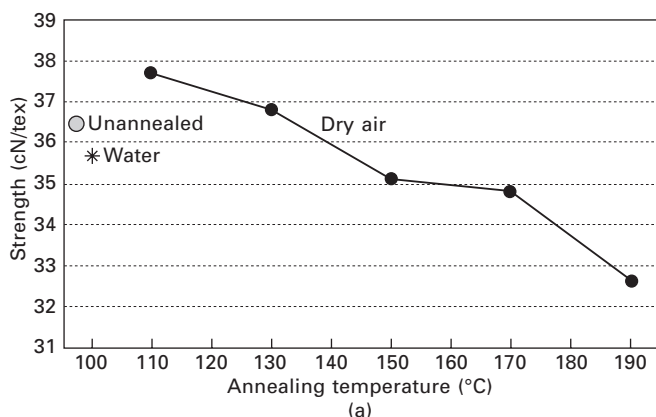
The surface of fibers and breaking zone were identified by scanning electron microscopy. Figure 9.30 (Section 9.11) shows the breaking zone of fibers before and after setting. Increasing of free ends annealing temperature leads



9.15 (a) Thermogram of polyester fiber (DSC) and T_{rc} indication; (b) dependence of $T_{rc} - T_a$ on time of free ends annealing.

generally to an increase of plastic flow portion at fiber break and corresponds to the increase of breaking elongation or deformation work to break.

Annealing with free ends allows the movement of microfibrils toward their position before plastic deformation and the material shrinks. The contour length of the tie molecules increases and the end-to-end distance decreases. This effect drastically reduces the fraction of the tie molecules in amorphous layer [128].



9.16 Influence of tensile strength (a) and deformation at break (b) on the free ends annealing temperature.

9.7.3 Isometric setting

Isometric, i.e. constant-length, conditions means that no macroscopic length changes during the heat treatment occur. Therefore, the entropic retractive forces in the fibers during the heat treatment appear. Then the whole molecular network is under tension, which supports processes such as breaking of the physical links of the stressed network and intermolecular slipping. When tension is applied during the heat treatment, it directly involves the orientation of the crystallite by pulling the crystallite in the loading direction. During isometric setting, the non-crystallizable fraction increases and the crystallizable fraction decreases with increasing of heat-setting temperature [129]. Under these conditions dimensional stability of the fibres can be achieved as well [130]. Based on the small-angle X-ray scattering data of PET it was found [131, 132] that during heat setting two distinct changes in the crystal morphology of the oriented PET occur. First,

there is a reduction in lattice and conformational defects, leading to the perfection of crystalline structure and the formation of larger, more perfect crystals. Secondly, there is formation of a new crystalline morphology in the form of folded chain lamellae, which grow perpendicular to the chain axis. These secondary crystallites formed during heat setting are qualitatively different and apparently much less stable than those formed during stretching [131]. Substantial disorientation due to relaxation of the tie chains connecting neighboring crystals was noted in fibers subjected to prolonged isometric heat setting [133]. However, no changes in crystal orientation were observed and a marked increase in tensile modulus for oriented PET held under stress was seen upon prolonged heat treatment [134].

Isometric heat setting does not reduce the fraction of tie molecules but relaxes them by increasing their contour length, without changing their end-to-end distance. If their number is sufficiently high, i.e. at a high draw ratio, they can slowly crystallize at room temperature and form axial crystal bridges. They very efficiently transmit the axial forces and prevent shrinkage during a new heat treatment [128].

9.8 Structure of polyester fibers

The fiber structure depends heavily on the process parameters of fiber formation such as spinning speed, drawing and heat setting. Final fiber structure depends considerably on the temperature, rate of stretching, draw ratio, relaxation and heat setting condition. The crystalline and amorphous orientation and the percentage of crystallinity can be adjusted significantly in response to these process parameters. The polymer structure is generally described in two hierarchical levels:

- the molecular level (molecular chains and their construction);
- the supramolecular level (crystalline and amorphous regions).

These two levels are determined by the chemical composition of the polymers. Theoretically, PET should contain hydroxyl (—OH) end groups only. But owing to the effect of various degradation reactions, such as hydrolysis and thermal oxidation, taking place during polycondensation or melting of PET, carboxyl (—COOH) end groups are also produced. In different PET fibers the acidity caused by these end groups ranges from 2×10^{-2} to 4×10^{-2} mol/kg [135]. Furthermore, carboxyl groups are responsible for additional degradation because they catalyze the hydrolysis of ester bonds. Therefore, when high strength industrial fibers (tire cords) are prepared, inhibitors are used to react with the carboxyl groups restricting the degradation process.

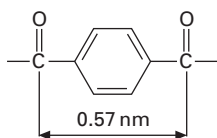
Owing to the effect of side reactions about 1.5–3% of DEG is always produced. DEG is introduced into the chains as a statistical copolymer. Finally, the PET fiber contains 1.4–3.8% of oligomers (cyclic trimer mainly) on average.

9.8.1 Molecular structure

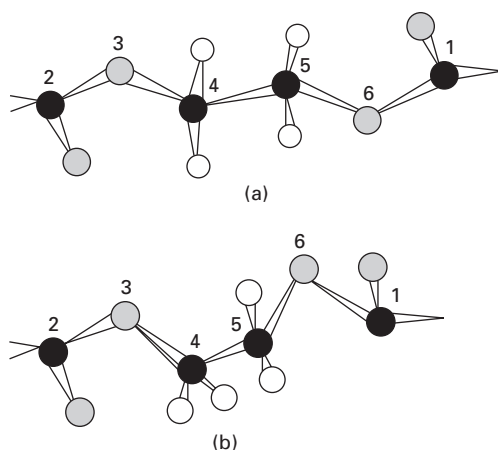
The PET fiber has rigid benzene rings in its backbone. Individual chains contain sequences of six aliphatic groups ($-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-$). Practically coplanar arrangement of the benzene rings, carboxyl and aliphatic molecular groups in the adjacent chains allow side-by-side arrangement. The geometrical structure of the terephthalate unit is shown in Fig. 9.17.

Cross-sectional area per single PET chain is relatively small, equal to the 0.217 nm^2 only [136]. The cohesion of PET chains is a result of hydrogen bonds and van der Waals interactions, caused by dipole interaction, induction and dispersion forces among the chains. The total magnitude of secondary forces in a PET unit is 1.37 kJ/mol . Of this, 1.02 kJ/mol is due to the disperse forces induced by the benzene rings. Thus the strength of PET fibers is determined in the first place by the rigidity of the benzene ring (the secondary van der Waals forces decrease with the sixth power of the distance) which forms an angle of only 12° with the plane of the ester bonds. The partial flexibility in the macromolecule of PET is mainly due to the ethylene group. The tendency to crystallize depends on forces of attraction. The interactive forces create inflexible tight packing among macromolecules showing high modulus, strength and resistance to moisture, dyestuffs and solvents. The unusually high melting point of PET (compared with aliphatic polyesters) is attributed to ester linkages. Because of this, PET is difficult to crystallize.

Rotation of chains around the $\text{C}-\text{O}-\text{C}$ bonds in the EG moiety of the repeat unit results in the formation of two conformers, a planar *trans*-conformer and a spatial *gauche*-conformer (see Fig. 9.18). *Trans*-conformation corresponds to the arrangement with the longest elementary unit. It is the state at which the so-called van der Waals distances between the chains and the individual groups in the chains are maintained. The van der Waals distances are distances at which the attractive and repulsive components of disperse forces are in equilibrium. The crystalline domains in PET contain solely *trans*-conformers, but both are present in the amorphous domains [138]. The *trans*-conformer is higher in energy than the *gauche* by approximately 28 J/g^{-1} [139]. This is small compared to the enthalpy of fusion, which has been estimated to be 140 J/g for fully crystalline PET [140]. The activation energy for transition between these conformers is 92 kJ/mol [141]. Conformation in the crystalline PET is totally *trans*, in the amorphous PET *trans* is around 14.5%. The quenched PET has 8.1% *trans* conformer only [142]. On the boundary of



9.17 Dimensions of terephthalate unit.



9.18 The glycol segment of PET in the (a) *trans* and (b) *gauche*-conformations [137].

the amorphous and crystalline regions are intermediate regions with slightly perturbed three-dimensional ordering, containing *trans*-conformations only. Thickness of these intermediate regions is about 1.03 nm [141].

Amorphous PET is assumed to be made up of a molecular network with entanglements as knots. The PET repeat unit contains six flexible units, the average length of which is $L = 0.268 \text{ nm}$ [143]. The corresponding molecular mass is $M_f = M_u/6 = 32 \text{ g/mol}$ where $M_u = 192 \text{ g/mol}$ is molecular mass of PET monomer unit. The projected length of the repeat unit in *trans*-conformation along the chain axis is $L_p = 1.075 \text{ nm}$ [138], so that the average projected length per flexible unit is $L_v = L_p/6 = 0.179 \text{ nm}$. The average molecular weight between entanglements was evaluated as $M_e = 1450 \text{ g/mol}$ [144]. The number of flexible units between entanglements is then $N_e = M_e/M_f = 45.32$ so that the extended length between entanglements is $L_e = L_v N_e = 8.11 \text{ nm}$ [88]. The number of monomeric units between entanglements is $N_m = M_e/M_u = 8$. Saunders *et al.* [137] computed the 10 monomeric units between entanglements. The value of $M_e = 1200 \text{ g/mol}$ was found by Lorentz and Tassin [88]. A very high value of $M_e = 3990 \text{ g/mol}$ was obtained from investigation of T_g depression due to PET chains extension in the glassy state [145]. Corresponding to $N_e = 124.69$, extended length between entanglements is $L_e = 22.32 \text{ nm}$ and number of monomeric units between entanglements is 21.

The repeat unit of PET (identity period) is 1.075 nm and is slightly shorter than the length of a fully extended chain (1.09 nm). The long repeat gives a strong tendency to form perfect crystalline arrangements. Daubeny *et al.* [138] found that the PET unit cell is triclinic with dimensions $a = 0.456 \text{ nm}$, $b = 0.594 \text{ nm}$, $c = 1.075 \text{ nm}$, $\alpha = 98.5^\circ$, $\beta = 118^\circ$ and $\gamma = 112^\circ$. The corresponding

crystalline density is $\rho_{\text{cPET}} = 1440 \text{ kg/m}^3$. The following unit cell dimensions are more precise: $a = 0.448 \text{ nm}$, $b = 0.585 \text{ nm}$, $c = 1.075 \text{ nm}$, $\alpha = 99.5^\circ$, $\beta = 118.4^\circ$, and $\gamma = 111.2^\circ$. This represents the crystalline density of $\rho_{\text{cPET}} = 1515 \text{ kg/m}^3$ [146].

The amorphous orientation in PET fibers is rather low (orientation factor 0.34–0.40), and the total *trans*-conformation fraction in PET fibers is nearly 0.80. The *trans*-conformation fraction in amorphous regions is about 0.64 [147]. The molar volume of PET $V_{\text{PET}} = 144 \text{ cm}^3/\text{mol}$. The amorphous density of PET $\rho_{\text{aPET}} = 1333 \text{ kg/m}^3$. The crystalline density of PET $\rho_{\text{cPET}} = 1440 \text{ kg/m}^3$. PET exhibits glass transition T_g (about $68\text{--}77^\circ\text{C}$), crystallization temperature ($180\text{--}190^\circ\text{C}$) and melting point (256°C). When amorphous PET is saturated by water, the reduction in T_g of 15°C occurs [148].

The cohesion energy DE_k of amorphous PET and copolymers can be calculated from the molar constant of attraction by molar contribution method [51]. For PET, the value $= 74.29 \text{ kJ/mol}$ was computed [3].

Typical PET has 40% crystallinity. Another factor for crystallization is the position of the benzene rings. If benzene rings are placed on the chain axis (c) then close packing of the molecular chains eases polymer crystallization. The elastic modulus of crystalline regions of PET in direction parallel with chain axis is 108 GPa. The calculated Poisson ratio is around 0.34.

9.8.2 Supramolecular structure

Polyester fibers may be considered to be composed of crystalline, oriented non-crystalline (mesophase, tie molecules) and non-crystalline (amorphous) regions. There is a maximum crystallization rate at 180°C for crystallization from the quiescent melt, which is independent of PET characteristics and measurement technique. The magnitude of the shortest half-times for crystallization is in the range of 16–50 s [2].

The quenched fiber does not show any development of crystallinity. As the crystallization of PET does not start until a temperature of 85°C is attained, the undrawn fibers (spun below 4000 m/min), which are relatively rapidly cooled below this temperature after extrusion from the spinning nozzle, are nearly amorphous. Drawing conducted at lower temperatures can give a highly oriented structure with a low level of crystallinity. However, as drawing is generally conducted at higher temperatures, the fibers exhibit a relatively high crystallinity (about 15% of crystalline phase). During subsequent tempering process additional crystallization takes place so that, eventually, commercial fibers are about 40% crystalline.

The triclinic unit cell of crystalline PET is equal to more than 98% of the theoretical extended length of the monomer repeat unit. There is a little molecular extensibility remaining in a PET crystal, resulting not only in a high modulus but also in a relatively short extension range over which the

crystal can be recovered elastically. The length of the polymer chain within a crystalline region is typically around 20 repeat units. The crystalline regions of PET are composed primarily of folded chain segments, so that the length of any given crystalline region is fairly small before being interrupted by an amorphous region. Crystalline regions are of different sizes and the size and distribution of these crystallites contribute to some fiber properties.

A number of basic structural models are required to represent the different states of the fiber: amorphous (no orientation) after extrusion, amorphous (oriented) after cold drawing, crystalline oriented after thermal treatment and after hot drawing, stretching and annealing. The crystalline oriented form can also be obtained by high speed spinning. It is important that the rate of crystallization for oriented fibers under tension is thousands of times faster than for unoriented melts.

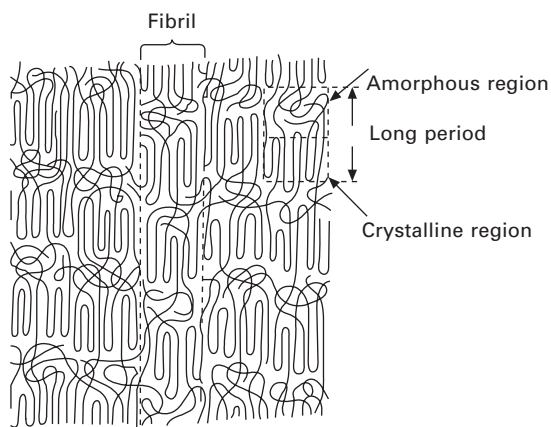
The basic structural element of all semicrystalline fibers is the microfibril. In PET fibers the microfibril thickness is around 10 nm and the length is comparable to that of macromolecular chains: around 1 μ m. Microfibrils are thin, long elements of elliptical cross-section. Microfibrils are composed of periodically repeated amorphous and crystalline sections, which are bridged by a great number of TTM. The fraction of TTM is between 10 and 30% of chains in the crystal lattice of the blocks [149]. It was experimentally proved, that with increasing of PET fibers orientation the amount of taut molecules increased markedly and due to increasing crystallization temperature the fraction of taut molecules decreased slightly [150].

The long period, i.e. the length of adjacent crystalline and amorphous sections, is around 15 nm. In PET fibers the crystallite axis is inclined to the microfibril axis at an angle of some 12°. A more detailed examination of wide-angle and small-angle X-ray scattering has shown that the crystallites in semicrystalline polymers differ from real polymer single crystals. Hosemann [151] assumed that the crystalline regions are made up of the so-called microparacrystallites, arranged in series and interconnected by tie molecules. Extensive experiments have shown that the difference in densities between the crystallites and amorphous regions in a microfibril is not more than 10%. This indicates a considerable amount of arrangement in the amorphous 'interfibrillar' regions, composed predominantly of tie molecules, the latter connecting adjacent crystallites. To a smaller extent, loops and free chain ends can be found in these regions [152]. The majority of disturbances in microfibrillar amorphous regions are caused by *gauche*-conformers which can be reversibly transformed into *trans*-conformers (elastic fiber deformation). Since a single molecular chain is passing through a number of crystalline and amorphous blocks in the fiber, the crystallites cannot be independent of the amorphous phase. The molecules in the crystalline regions are expected to participate in the recrystallization that occurs by the regular folding of the extended trans segments of the amorphous PET chains [153].

Individual microfibrils cluster into bundles called fibrils. A boundary of fibrils is weaker due to the presence of the ends of microfibrils. These point defects of the microfibrillar lattice make the surface of the fibril less uniform and thus decrease the degree of packing between fibrils. Hence, the boundary between fibrils permits shearing displacement and fails more easily than the boundary between the microfibrils of the same bundle, thus yielding longitudinal voids so characteristic for highly drawn fibrous material [154]. Because forces between fibrils are weak, they can be observed in fractured fibers. The fibrillar structure of drawn PET fibers is visible in Fig. 9.13 (see Section 9.6).

Fibrils are interconnected by interfibrillar tie chains. Owing to the effect of inadequate arrangement of fibrillar bundles the structure also contains inter-fibrillar amorphous regions. This so-called fibrous structure is the result of plastic deformations taking place during fiber drawing. In PET fibers it is formed when the draw ratio is greater than about 2 to 3. It has been found that the absorptive and mechanical properties of PET fibers are fundamentally influenced by the state of the inter-fibrillar amorphous phase [51, 52]. The latter is made up of tie chains, loops, free ends and chain entanglements too. In highly oriented polymers a part of the stretched tie chains forms inter-crystalline bridges exhibiting the same modulus as the crystalline phase [155]. They differ from the tie chains, especially at temperatures above T_g , when they perform the function of physical crosslinking. The tie molecules are sufficiently mobile at these temperatures and induce entropic elasticity. The microfibrils are mainly responsible for fiber stability.

On the basis of these findings Prevorsek [213] proposed a three phase structural model for polyester and polyamide fibers, which is shown in Fig. 9.19. This model comprises microfibrils containing alternate amorphous and crystalline regions; these are interconnected by an amorphous interfibrillar



9.19 Structural model of semicrystalline fibers.

phase, formed mostly by tie molecules. Each phase is characterized by its volume fraction and orientation.

The mobile phase in amorphous regions (MAP) of PET is rich in *gauche*-conformers, while the crystalline phase (CP) is in the *trans* form only [113]. Rigid phases in amorphous regions (RAF) are rich in *trans*-conformer [142]. RAF can be easily characterized by thermal analysis [156] as it does not participate in the glass transition of the amorphous phase. This rigid amorphous fraction represents the main part of the material in the fully crystallized PET (49%,). There exists a strong coupling between the RAF and the remaining amorphous phase [142].

9.9 Mechanical behavior of polyester fibers

Regular (linear) structures without the side chain groups are able to form crystalline order in polymeric materials. Some polymers, including PET, are in the amorphous state after solidification. During drawing and heat setting, semicrystalline oriented structures appear (see Section 9.6 and 9.7). These structures are reversible or non-reversible depending on further temperature and mechanical effects. The relationship between the mechanical properties and structure of polymeric fibers therefore strongly depends on processing conditions applied.

The relationship between molecular structure and mechanical behavior of amorphous polymers has been extensively studied [157]. The amorphous structure was usually described as physical network created by molecular chains with entanglements at nodal points. The structure of semicrystalline polymers is much more complex and beside the amorphous and crystalline portions mechanical behavior is strongly influenced by the presence of TTM fraction.

Some of concepts useful for amorphous polymers can to some extent also be applied to semicrystalline polymers [158]. The multiphase structure of these polymers often requires more complex models in which microstructural aspects, such as tie chains, degree of crystallinity and orientation are included.

In the first part of this chapter the basic types of fiber mechanical behavior models have been compared. To describe of stress–strain curves, parametric and nonparametric models are shown. The next part is devoted to the modeling of tensile strength and failure mechanisms of polyester fibers.

9.9.1 Models of fiber mechanical behavior

The modeling and interpretation of polymeric fiber mechanical behavior requires the creation of models characterizing at least the connection between the deformation, stress and time or temperature, respectively (phenomenological

models). More complex constitutive and multiphase models are based on the simplified assumption about deformation of some structural elements (phases). Structural models are based on the creation of a simplified fiber structure and the description of its response to the mechanical actions. In polymer fibers, modeling is complicated by the following:

- *Validity of the linear viscoelastic* behavior is very limited (strain limit for polymers in the glassy state is less than 1%). Most experiments are naturally beyond this limit. Parameters from classical viscoelastic models can no longer be considered as material constants and Boltzman's superposition law is not valid.
- *Permanent structural changes* of the fibers due to external forces occur. There are not only changes in orientation but frequently changes of the various phase portions (crystalline phase, the phase of taut tie chains). These structural changes obviously provoke changes in mechanical behavior (see, for example, strain hardening, etc.).
- *Polymeric fibers* have a long deformation/temperature history which is due to 'memory' effect to some extent reflected in the mechanical behavior.
- *Structural changes* which are reflected in the mechanical (viscoelastic) behavior of fibers are often not directly experimentally measurable but can usually be estimated on the basis of some models. This leads to a situation where mechanical models include a redundant number of parameters without proper physical interpretation.

It is thus clear that the mechanical description of non-linear viscoelastic semicrystalline materials (including fibers) will always be some approximation of real processes. According to this approximation, the mechanical models can be formally divided into four basic categories:

- continuum models;
- micromechanical constitutive models;
- structural models;
- multi-phase models.

These models are distinguished by the extent to which the fiber structure is taken into consideration. For direct treatment of experimental data the continuum and micromechanical constitutive models are very useful. These models are well suited to the macromechanical approach to the modeling of fiber rheology. The models from the multi-phase group need some additional quantitative information on structural elements. The most complex models, the structural models, represent micromechanical approach to the modeling of fiber rheology. In this case it is necessary to have complex information about structural elements and their mechanical behavior.

Continuum models

The continuum approach ignores the molecular nature of polymers and treats it in terms of laws of elasticity for solids and laws of fluid dynamics and viscous flow for liquids. Models of this group consider the fiber from the perspective of mechanical action as an homogeneous (non) linear viscoelastic body and fiber fine structure is neglected. The simplest (spring/dashpot) models are based on the formal ideas of linear viscoelasticity [159]. They are generally expressed by using linear differential equations with constant coefficients. The strain limit for linearity remains constant at about 1% throughout the glassy region, then increases very rapidly from 1 to roughly 50% as the polymers go through the transition region and reaches up to 100–150% when the polymers are in the rubbery region [160].

Large classes of models use various theories of nonlinear viscoelasticity for an homogeneous body [161]. The general multiple integral constitutive relations for a nonlinear viscoelastic material are given by the Green–Rivlin theory [159]. These constitutive relations are based on an expansion of multiple integrals with multivariable relaxation functions as kernels. For non-linear deformation of polymeric fibers, the appropriate adaptation of classical Boltzman integral was suggested by Leadermann [162].

A number of other approaches based on the theory of nonlinear viscoelasticity was published by Yannas [160]. Most of the rheological models of this type cannot be expressed analytically and are expressed by multiple integral equations with rather complicated kernels. The non-linear viscoelastic and viscoplastic constitutive model based on the generalized Boltzman integral proposed by Shapery [163] was successfully modified for modeling non-linear viscoelastic and viscoplastic behavior of polyester fibers [164].

Hall [165] proposed the empirical model of the stress–strain curves of the fiber, where stress is expressed as a combination of the functions of deformation and time (the principle of separability).

$$\frac{s(t)f_1(\mathbf{e})}{\mathbf{e}} = f_2(\mathbf{e}) + f(t) \quad 9.9$$

Nonlinearity is introduced by means of functions $f_1(\epsilon)$ and $f_2(\epsilon)$ which are equal to 1 and 0, respectively, if the behavior is linear. Hall found that the function $f_1(\epsilon)$ varied linearly with strain over the region of homogeneous deformation and was independent of the nature of the fiber type. The function $f_2(\epsilon)$ was found to be clearly nonzero.

The simplest standard linear viscoelastic body model (two springs and one dashpot) can be easily extended by using of nonlinear members. For polymeric fibers, Eyring three element model containing two springs and one nonlinear dashpot (plastic member) is often used. Non-linear behavior shows only a plastic member. The rate of deformation is here governed by the hyperbolic sine equation derived from the idea of plastic deformation

of polymer chains such as an activated process [166]. Generalization for the case in which more than one flow mechanism is involved in the flow process is presented in the work by Ree and Eyring [167]. A very simple procedure of non-linear viscoelastic modeling has been used relying on the replacements of dashpot and spring constants by functions of deformation or deformation rate (usually either polynomial or linear functions are used) [168]. The advantage is a virtually continuous transition from linear to nonlinear viscoelastic behavior.

Micromechanical constitutive models

These models frequently use a combination of springs and dashpots but these elements are characterizing the responses of fiber structural components. Part of the polymeric material is often approximated by a molecular chain network system created by the crosslinkages, which are assumed to be physically entangled points of molecular chains. In semicrystalline polymers the crystallites are acting as physical crosslinks. The more complex model of molecular chain network composed of crosslinks and sliplinks was proposed by Ball *et al.* [169] and modified by Sweeney and Ward [170]. In the affine models the numbers of entangled points remain constant during the deformation and only orientation occurs [171]. In the non-affine models a change in the number of entangled points is taken into account [172]. The constitutive equation obtained can well reproduce the tension and compression behaviors of polymers.

The idea of decomposing the total stress σ into elastic σ_e and a history-dependent component σ_v was used by Green and Tobolsky [173]. The corresponding models are composed of two parallel units with special responses. For a description of non-linear time-dependent behavior of rubber elastic materials, the model composed from two polymer networks acting in parallel was proposed by Bergstroem and Boyce [174]. First a network expresses the equilibrium response of the material (hyperelastic component) and the second network captures the time-dependent deviation from the equilibrium state (elastic component in series with plastic component).

Haward and Thackray [175] described the deformation processes in polymers with two parallel processes. The first process is due to the initial non-linear elastic response controlled by the secondary intermolecular interactions (e.g. van der Waals bonds). The second process originates from the entangled polymer network orientation which leads to entropic elastic effects at large strains. Based on these ideas, they created a simple three element constitutive model consisting of a Hookean spring (describing the initial elastic response) in series with a nonlinear (Eyring) dashpot (yielding behavior) and nonlinear Langevin type spring (describing strain hardening response) in parallel. The response of the Eyring dashpot representing the

rate and temperature-dependent plastic flow has the form

$$\frac{d\mathbf{e}}{dt} = \mathbf{k} \sinh(\mathbf{a} \mathbf{s}) \quad 9.10$$

where κ and α are constants. This equation was derived from the idea of plastic deformation as a temperature and stress activated process with a symmetric, simple energy barrier [176]. The parameter α (GPa^{-1}) is related to the minimum free volume per unit flow, V_f , by the relation:

$$\mathbf{a} = \frac{V_f}{2kT} \quad 9.11$$

where $k = 1.38 \times 10^{-23} \text{ J/K}$ is Boltzman constant and T is the temperature. The total activation energy $DE^\ddagger$, of this plastic flow (the height of the energy barrier) is related to the parameter according to the equation:

$$DE^\ddagger = RT \left[\ln \frac{V_f}{V_m} - \ln(\mathbf{k}) + \ln \frac{2kT}{h} \right] \quad 9.12$$

Here, V_m is the volume of an elementary flow unit, R is the universal gas constant, and $h = 6.626 \times 10^{-34} \text{ Js}$ is Planck's constant. For PET the value of V_m is usually equal to $2.912 \times 10^{-8} \text{ m}^3$, which corresponds to the volume of the elementary crystalline unit.

To obtain an analytical expression for stress-dependent viscosity, eqn. (9.10) is substituted into the relation:

$$\mathbf{s} = \frac{\mathbf{s}}{d\mathbf{e}/dt} = \frac{\mathbf{s}}{\mathbf{k} \sinh(\mathbf{a} \mathbf{s})} \mathbf{a} \frac{2\mathbf{s}}{\mathbf{k} \exp(\mathbf{a} \mathbf{s})} \quad 9.13$$

The approximation $\sinh(x) \approx \exp(x)/2$ valid for high values of x ($x > 3.5$), has been also used for description of deformation behavior near yield stress σ_y [177]. Equation (9.10) can be rewritten in terms of stress dependent on the strain rate:

$$\mathbf{s} = \frac{2kT}{V_f} \sinh^{-1} \frac{V_f}{2k} \frac{d\mathbf{e}}{dt} \mathbf{a} \frac{2kT}{V_f} \ln \frac{V_f}{2k} \frac{d\mathbf{e}}{dt} \quad 9.14$$

A plot of σ_y/T against $\ln(d\mathbf{e}/dt)$ produces a series of straight lines (each for one temperature), the slope of which is directly connected with activation volume V_f .

The modified Eyring-like model for prediction of yield stress has been published by Fotheringham and Cherry [178]. This model is based on the assumption that yielding involves a simultaneous cooperative motion of polymer chain segments. It is also assumed that there exists a structural parameter denoted as internal stress, σ_i , which reduces the yield stress σ_y . The resulting Eyring-like model has the form of hyperbolic sine function raised to the n th power:

$$\frac{d\mathbf{e}}{dt} = a_1 \sinh^n \left[\frac{V(s_y - s_i)}{2kT} \right] \quad 9.15$$

Here, n is a material parameter used to characterize the cooperative movement of the chain segments, V is the activation volume, k is the Boltzman constant and a_1 is thermally activated characteristic strain rate.

An empirical nonlinear rate and temperature-dependent plastic flow response has the form [155]

$$\sigma = K[1 - \exp(-\varepsilon/\varepsilon_0)] (d\varepsilon/dt)^m \quad 9.16$$

where K is the scaling factor, ε_0 , a viscoplastic parameter and m is the strain rate sensitivity coefficient determined experimentally. This plastic term was used as a part of three element model for prediction of true stress–true strain behavior of amorphous PET. A much simpler empirical power law approximating the rate of viscous flow [179] gives:

$$(d\varepsilon/dt) = K [\sigma/s]^M \quad 9.17$$

where K is a reference deformation rate, s is resistance to deformation and M is a sensitivity coefficient.

The rubber elasticity spring represents stretching of the molecular entanglement network of polymeric chains. In the case of limited extension of the chain between crosslinks, the appropriate form expressing the (entropic) retractive stress σ_r is [180]

$$\sigma_r = \frac{I_m E_h}{9} \left[L^{-1} \left(\frac{\hat{\mathbf{e}} \cdot \mathbf{I}}{\lambda_m} \right) - \frac{1}{I^{3/2}} L^{-1} \left(\frac{\hat{\mathbf{e}} \cdot \mathbf{I}_c}{\lambda_m \sqrt{I}} \right) \right] \quad 9.18$$

where E_h is the low-strain modulus, λ is the draw ratio of the ‘entropic spring’ and λ_m is the maximum allowable network draw ratio. $L^{-1}(x)$ denotes the inverse of Langevin function $L(x) = \coth(x) - 1/x$, which can be accurately approximated by the Padé approximation [181]:

$$L^{-1}(x) = x \frac{3 - x^2}{1 - x^2} \quad 9.19$$

Instead of the Langevin spring, the approximate relation to express the rubber elasticity has been proposed [182]:

$$\sigma_r = \frac{11}{14} \frac{\hat{\mathbf{e}} \cdot \mathbf{I}}{I^2} - \frac{1}{I^2} \frac{\hat{\mathbf{e}} \cdot \mathbf{I}}{I} + \frac{4.25}{14} \frac{\hat{\mathbf{e}} \cdot \mathbf{I}^3 + 4}{5I} - \frac{1}{I^2} \quad 9.20$$

where σ_r is computed in kg/mm². For large λ_m eqn. (9.18) reduces to the Gaussian equation [180] and

$$\sigma_r = C_r \frac{\hat{\mathbf{e}} \cdot \mathbf{I}}{I} - \frac{1}{I^2} \quad 9.21$$

where C_r is the elastic network modulus. It is interesting, that the expression of eqn. (9.21) in terms of true stress (σ_{tr}) leads to the form

$$\mathbf{s}_{tr} = C_r \frac{\hat{\mathbf{E}}}{\hat{\mathbf{I}}}^2 - \frac{1}{\hat{\mathbf{I}}} \quad 9.22$$

The strain dependence of the glassy polymers networks deformation can be also expressed by other non-Gaussian chain statistics [183]. For the plane-strain geometry, the rubber-like stress σ_r generated by the entangled polymeric chain network in the direction of loading is expressed in the form:

$$\mathbf{s}_r = \frac{\sqrt{n} E_h}{3 I_c} \frac{\hat{\mathbf{E}}}{\hat{\mathbf{I}}}^2 - \frac{1}{\hat{\mathbf{I}}^2} L^{-1} \frac{\hat{\mathbf{E}} \hat{\mathbf{I}}_c}{\hat{\mathbf{E}} \sqrt{n}} \quad 9.23$$

where E_h is the initial strain hardening modulus of the network, n is the number of 'rigid' entanglements between crosslinks providing limiting extensibility of a chain ($\lambda_m = \sqrt{n}$) and $\mathbf{l}_c$ is the stretch on each chain in the network $\mathbf{l}_c = \sqrt{(\mathbf{l}^2 + 1 + 1/\mathbf{l}^2)/3}$. The final model describing polymeric material deformation behavior can be then simply expressed as sum of $\sigma_r + \sigma_y$ where σ_y is yield stress [174].

Rubber-like behavior of a polymeric network can be approximated by a model composed of a basic cell containing eight non-Gaussian chains (Langevin springs). This model includes the cooperative nature of the network deformation. The response of this model to an uniaxial deformation is in the form [183, 184]

$$\mathbf{s}_r = \frac{G \sqrt{N}}{I \sqrt{3}} \frac{\hat{\mathbf{E}}}{\hat{\mathbf{I}}}^{L-1} \frac{\hat{\mathbf{E}} \sqrt{I^2 + 2/I}}{\hat{\mathbf{E}} \sqrt{3N}} - \frac{\hat{\mathbf{E}} I^2 - 1/I}{\hat{\mathbf{E}} \sqrt{I^2 + 2/I}} \frac{\hat{\mathbf{O}}}{\hat{\mathbf{O}}} \quad 9.24$$

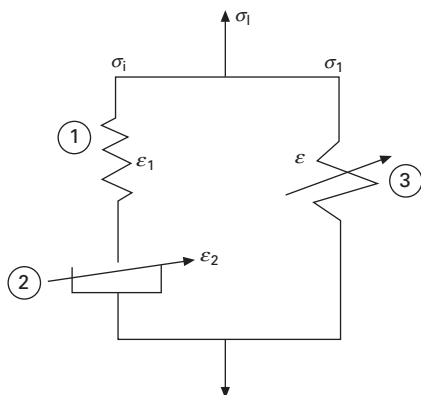
The parameter G is equal to the material shear modulus and N is a function of the stretch at break λ_b i.e.

$$N = \frac{\mathbf{l}_b^2 + 2/\mathbf{l}_b}{3} \quad 9.25$$

A three element model (see Fig. 9.20) containing one linear Hookean spring (1), one nonlinear spring with parabolic response (3) and Eyring type nonlinear dashpot (2) was proposed for modeling of viscoelastic behavior of PET and modified PET fibers [3]. The spring with parabolic response was derived from the idea that some flow units were transformed into plastic units during deformation [185].

$$\sigma = E_l (\epsilon - K_1 \epsilon)^2 \quad 9.26$$

The modulus E_l and a constant K_1 are parameters of this spring.



9.20 Non-linear viscoelastic model: 1 Hookean spring; 2 nonlinear dashpot; 3 non-linear spring [3].

The three element model, formally shown on Fig. 9.20 where the nonlinear spring is of the Langevin type, was used for the creation of a robust three-dimensional constitutive model describing the finite mechanical response of amorphous polymers over a wide range of temperatures and strain rates [186].

The use of a generalized non-linear Maxwell model for the description of tensile stress–strain curves of glassy polymers is described by Bauwens [182]. The model assumes that during the course of deformation, some structure initially present in the polymer is destroyed and that the initial spectrum of the Maxwell elements is converted to another spectrum.

The spring/dashpot models can be modified by adding other members to allow the inclusion of the process of irreversible destroying of some structures initially present in the polymer [187, 188]. The model, based on two distinct thermally activated rate processes (the model from Fig. 9.20 with one more parallel Eyring dashpots), for description of the double-yield-point tensile behavior of the polymers, was proposed by Spathis and Kontou [189]. Models of this type were successfully applied to describe the stress–strain behavior of several amorphous as well as semicrystalline polymers [190–192]. Common factors in these models are the application of rubber elasticity to model strain hardening and a stress dependent viscosity to describe the deformation kinetics [193].

The constitutive model for the viscoplastic behavior of a semicrystalline polymer was proposed by Drozdov and coworkers [194, 195]. A polymer is assumed as a network of chains bridged by permanent joints (entanglements or physical crosslinks on the surfaces of crystallites). The equivalent network is treated as an ensemble of meso-regions with various activation energies to separate active strands (mobile part of the amorphous phase) from their junctions. The spatial heterogeneity of a network is attributed to interactions

between amorphous regions and crystallites. A similar model for viscoelastic behavior at finite strain is described by Drozdov [196].

A model based on the molecular dynamics simulations of polymeric chains has been developed by Cook [197]. The model approximates the conformational motion energetic by a number of chains of particles that are connected by bonds with multi-welled potentials. Interactions between particles on adjacent chains are modeled by short range repulsive potentials. This model was applied for simulation of the stress–strain behavior of glassy polymers.

Structural models

Models of this group expressed macroscopic stress, deformation, time, behavior of fiber by using a combination of the mechanical behaviors of typical structural elements. This approach is generally referred to as micromechanical. There are a number of models that describe the mechanical behavior of typical structural elements such as tie chains [198, 199] and various other elements (folded chains, parallel chain bundles, meanders, etc.). Many models are based on the formal idea of a fiber as a composite structure. Arridge and Barham [200] used a fiber model composed of an amorphous matrix (partially oriented), in which needle-like fibrils oriented parallel to the axis of fiber were dispersed. Tension on fibrils is transmitted through shear deformation of the matrix. Fibrils that exceed a critical length (depending on the degree of deformation) are deformed plastically and shorter fibrils only elastically. This model was successfully used to describe the mechanical behavior of drawn polypropylene and polyethylene fibers [201]. The model of Gibson *et al.* [202] uses as the structural element the parts of polymer chains passing through more noncrystalline regions. These polymeric chains consist in fact of a continuous crystalline phase.

In the series model, the polymer fiber is replaced by a parallel array of identical fibrils which are subjected to a uniform stress along the fiber axis [203]. Each fibril consists of a series of oblong domains arranged end to end. In a domain the chains run parallel to the symmetry axis at an angle ϕ with the fiber axis. All domains in a fibril are assumed to be isotropic transverse to the symmetry axis and to have identical mechanical properties. In the modified series model, the mechanical properties of a domain belonging to the elastic extension of the fibril are the chain modulus and the modulus for shear between the chains. The series model implies that the fiber extension is governed by a sequential orientation mechanism. The model also indicates the importance of the initial orientation distribution of the chain axes for the deformation of the fiber [203].

In the Harland model [204] the idea of a three phase structure of the polymer composed of microfibrils mutually interconnected by tie chains, which are

located in the amorphous matrix, is used. This structure is replaced by networks which constitute binding points from crystallites mutually connected by tie chain links. The model takes into account the partial destruction associated with chains pull out of the crystalline phase. However, this model contains many experimentally undeterminable parameters.

Nagamura *et al.* [205] started from the three phase fiber model composed of two continuous phases (amorphous and crystalline) connected by tie chains of different lengths. These chains are gradually deformed until they break. The macroscopic stress of a deformed polymer is calculated by adding the stresses transferred by the amorphous phase and those transferred by various tie chains. This model includes experimentally undeterminable parameters such as the distribution of tie chain lengths. A model that accounts for the deformation-induced evolution of the structure of amorphous and crystalline phase was published by Oshmyan *et al.* [206]. A review of modeling approaches for oriented semicrystalline polymers is presented by Breese and Beaucage [207]

Multi-phase models

Unlike structural models, these multi-phase models assume that all structural phases of the fiber are continuous. Each phase is characterized by its mechanical characteristics, the volume fraction and a degree of orientation. For a simple two phase structure (amorphous and crystalline) of semicrystalline polymers there are two basic arrangements [208]. In the series *configuration* both phases have the same stress and deformation of each phase depends on its stiffness (Reuss average). In the *parallel arrangement* both phases have the same deformation and the stress in each phase varies (Voigt average).

In reality the distribution of stress or strain is somewhere between these two extremes. To overcome this problem, the contiguity parameter ξ as a means of interpolating between these two extremes was introduced [209]. The estimator of the value of a mechanical property P , of phase a , with an average orientation characterized by f has the form

$$P_a(f) = \frac{P_a^R(f)P_a^V(f)[1 + \xi]}{\xi P_a^R(f) + P_a^V(f)} \quad 9.27$$

The term $P_a^R(f)$ represents the value of the property P averaged over the all regions using the assumption of homogeneous stress (Reuss average) and $P_a^V(f)$ represents the corresponding average using the assumption of homogeneous strain (Voigt average). The quantity ξ is a contiguity parameter associated with the property, P . The value of $\xi = 0$ yields the Reuss average (constant stress). A value of $\xi \rightarrow \infty$ yields the Voigt average (constant strain).

Intermediate values of ξ generate averages between these extremes. In the case that the Voigt and Reuss averages are equivalent (e.g. for $f = 1$), $P_a(f)$ is independent of ξ . The property $P(f)$ of two phase system composed from phase a and b is then

$$P(f) = P_a(f) \frac{1 + \mathbf{x}cV_b}{1 - cV_b} \quad 9.28$$

where V_b is the volume fraction of the b -phase and

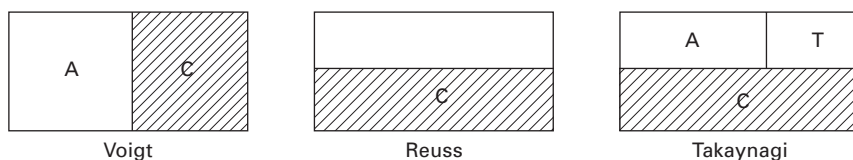
$$c = \frac{P_b(f) - P_a(f)}{P_b(f) + \mathbf{x}P_a(f)} \quad 9.29$$

Individual phases are denoted according to requirement $P_b(f) > P_a(f)$.

Takaynagi *et al.* [210] suggested a model for the description of the selected mechanical characteristics (modulus) of semicrystalline polymers, allowing the use of different phases (with regard to the volume fractions) see Fig. 9.21. In Militký *et al.* [211] the two limit Takaynagi models containing an amorphous phase, a crystalline phase and a phase of taut tie chains were proposed. An extension of this model, so that the tie chain phase is considered as a non-linear viscoelastic body, was published by Militký and Jansa [212]. The proper contiguity parameter $\mathbf{x}$ for the Takaynagi model (in fact two phase) was published by Lindenmeyer and McCullough [209]. Analysis of the viscoelastic response of semicrystalline fibers in terms of the Takaynagi model has been published [213, 214].

The advantage of multi-phase models is that they contain experimentally determinable characteristics (crystallinity degree, the orientation of various phases). On the other hand, they are highly simplified and they are suitable mainly for special cases such as the prediction of moduli and strength.

There is a whole range of ways how to describe the mechanical behaviors of polymeric fibers. A number of models are more descriptive and useful for specific cases only. On the other hand, the inclusion of structural information is allowed. It appears that there will be further development in this area and models will be created according to purpose or utilization.



9.21 Basic models of structural arrangements: A, amorphous phase; C, crystalline phase; T, phase of taut tie chains.

9.9.2 Environmental effects

Environmental factors, such as humidity, temperature, pH, ultraviolet radiation, and micro-organisms can affect the strength and the fracture processes in PET fibers. The strength decrease due to the influence of environmental effects depends on the mechanism of degradation. There are three limit situations [215]:

1. The polymer chains randomly break but practically no volatile material is produced until late in the degradation (*random scission*).
2. The decrease in molecular weight is proportional to the amount of volatile products and molecules which are volatile at the degradation conditions are progressively separated gradually from the chain ends (*depolymerization*).
3. Whole polymer molecules disappear. This occurs most frequently when the polymer molecule breaks to form macroradicals, which then decompose to form monomers in a reaction that is the exact reverse of the process which occurs during polymerization.

In reality, the degradation usually lies between these extreme situations. There are two main mechanisms of chain scission, i.e. depolymerization and random chain scission. Depolymerization occurs often during thermal degradation. Random chain scission is typical for hydrolytic degradation. In some situations, as in case of photodegradation, the chain scission mechanisms are combined with crosslinking [215]. The rate of chain scission due to environmental breaking of ester links in PET fibers increases with increasing of initial fiber carboxyl end group concentration, i.e. with decreasing molecular weight [216].

Hydrolysis

The number of ester links in starting PET material with degree of polymerization $DP = M_0/M_n$ is equal to $2DP$, where M_0 is molecular weight of PET and $M_n = 192$ is the weight of PET monomer unit. In a PET chain $N_{cg} = (DP - 1)$ accessible ester links are initially present. After environmental attack of time t , there will be $N_{cg} - N_b$ ester links resting where N_b is equal to the number of broken ester links at time t . The same weight of PET is now shared between $N_b + 1$ pieces, so the number average molecular weight M_t after time t is equal to the $M_0/(N_b + 1)$ and $N_b = M_0/M_t - 1$.

The rate of chain scission can be approximately expressed by the first order reaction scheme [217]:

$$\frac{dN_b}{dt} = K_s(N_{cg} - N_b) \quad 9.30$$

where K_s is rate constant of chain scission. After integration, the number of broken ester link due to chains scission can be obtained:

$$N_b = N_{cg} [1 - \exp(-K_s t)] \quad 9.31$$

The corresponding number average molecular weight M_t is then:

$$M_t = \frac{M_0}{1 + N_{cg}[1 - \exp(-K_s t)]} \quad 9.32$$

It is known that M_t is directly connected with the strength σ_B of PET fibers. The empirical equation $\sigma_B = a + b \ln(M_t + c)$ where a , b , c are constants, has been proposed [217]. The classical relation between strength σ_B of PET fibers and M_t has the form:

$$\sigma_B = A - B/M_t \quad 9.33$$

where A is the limit strength for $M_t \rightarrow \infty$ and B is the coefficient of sensitivity.

A more complex model based on the facts that water absorption, and thus chain scission, are only possible in the amorphous phase, so that it is necessary to consider the local concentrations of the water molecules in the amorphous phase is presented by Launay *et al.* [218]. For this model, the rate of chain scission is described by the equation:

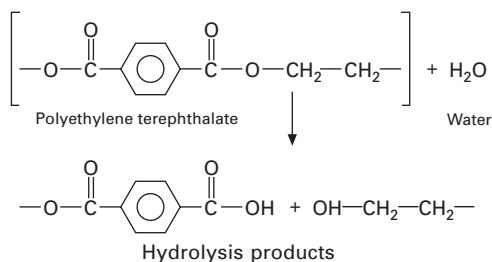
$$\frac{dN_b}{dt} = K_s(N_{cg} - N_b)(W_0 + cN_b) \quad 9.34$$

where constants $W_0 = 0.75$ mol/kg and $c = 0.179$ mol/kg were obtained from the experimental dependence between W and the number of chain scissions N_b , per unit mass of the amorphous phase [218].

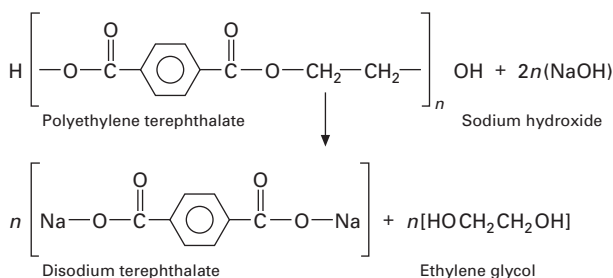
For practical use of technical PET fibers it is important to estimate strength loss due to hydrolysis. Generally, polyester fibers will hydrolyze over a wide range of pH. This reduces the polymer chain length and the strength of the fiber. The hydrolysis in neutral and acid conditions is due to the attack of H^+ ions. In acidic conditions the accelerated hydrolysis involves protonation of the in-chain oxygen atom of the ester group followed by reaction with water to produce equivalent amounts of hydroxyl and carboxyl end-groups. The macroscopic hydrolysis reaction can be written as in Fig. 9.22 [219].

It is known [6] that there are big differences in the effects of different acids, which may be attributed to different rates of diffusion into the polyester. The activation energy of the hydrolysis was estimated to be around 113 kJ/mol [217, 220].

Hydrolysis in alkaline conditions is different, since it involves OH^+ ion attack of carboxyl oxygen atom to randomly break the ester groups and produce equivalent amounts of hydroxyl and carboxyl end-groups. In case of voluminous ions as Na^+ , the hydrolysis reaction has the form shown in Fig. 9.23 [216].



9.22 Hydrolysis of PET in acid conditions.



9.23 Hydrolysis of PET in alkaline conditions.

Owing to the volume of Na^+ ions and the creation of bigger clusters with water molecules hydrolysis takes place on the surface only and results in the gradual removal of material from the surface of the fiber. For smaller alkaline species, such as NH_3^+ , diffusion into amorphous phases occurs and amorphous parts in fibers are predominantly removed.

The result of hydrolysis is a reduction of the length of the molecular chain, reduction of molecular weight and consequently a reduction of the tensile properties. For some alkalis (e.g. NaOH) the hydrolysis leads to the controlled reduction of fineness.

The hydrolytic attack of industrial PET yarns by water and mild solutions of acid or alkalis (in the pH range of 4 to 11) over the temperature range from 20 to 40°C is low. It was predicted that more than 90% of initial stress of break is retained after 10 years of exposition under these conditions. At room temperature, there will be little loss of strength for several centuries [217]. The hydrolytic scission of PET in saturated water steam above the glass transition temperature is autocatalysed by the carboxyl end- groups generated [216]. The reaction kinetics can be here described by the half-order rate equation [221].

Thermal degradation

The thermal degradation of PET proceeds by a random chain scission at ester linkages, although a radical mechanism has also been proposed. The

rate of chain scission can be here expressed by the zero order reaction [215] and number of broken ester links due to chains scission is given by the relation:

$$N_b = N_{cg}K_s t \quad 9.35$$

The rate of pyrolysis increases quickly in the presence of very small amounts of water. The presence of 0.007% (w/w) of water at 280 °C practically doubles the rate of PET chains scission in comparison with the dry state [222].

Acetaldehyde is always produced during the thermal degradation of PET at over 250 °C [19]. Jenekhe and Lin [223] carried out the pyrolysis of PET films in the temperature range of 250–600 °C. They considered a one-step decomposition reaction with a first order kinetic process. Yang *et al.* [224] obtained a value of 242 kJ/mol for the activation energy and $n = 1$ (first order process) for the thermal decomposition in nitrogen of the pure PET without stabilizers. Color changes during degradation have been attributed to the formation of polyenaldehydes from acetaldehyde and from a further breakdown of poly(vinyl ester)s. The formation of unsaturated ester and quinonoid species occurs [225].

The experimental results published by Montaudo *et al.* [226] provided strong evidence that cyclic oligomers were the primary pyrolysis products of PET (at about 300 °C). These oligomers further decompose by a hydrogen transfer reaction and generate open chain oligomers with olefin and carboxylic end-groups (at about 400 °C). The kinetics of weight loss during pyrolysis is described by Gullon *et al.* [227].

Photodegradation

The degree of changes during photodegradation depends on the wavelength spectrum of light and the atmospheric conditions [228]. Under the action of sunlight, polymer materials undergo a series of oxidative reactions that lead to chemical degradation. The light in the 290–400 nm wavelength range of sunlight can cause a photolysis of PET, mainly due to a remarkable decrease in molecular weight [229]. The increase of orientation and crystallinity of PET fibers decreases the rate of photodegradation [230].

An essential start of photodegradation is absorption of sunlight radiation and hence the reactions will be in the surface layers mainly. The first chemical step in photodegradation is usually homolytic bond scission to form free radicals. These radicals will normally react rapidly with any oxygen present. The photochemical reactions affecting photodegradation of PET proceed in two steps, a very rapid initial step, followed by a normal step. The rapid drop of molecular weight at the initial step has been associated with a concept of 'weak links' on the main chain [229]. The corresponding loss of molecular weight M_t after degradation time t is described by relation:

$$\frac{M_0}{M_t} - 1 = M_0 K_n t + \frac{M_0 P_w}{M_m} [1 - \exp(-K_w t)] \quad 9.36$$

where K_n and K_w are the rate constants of degradation of the ‘normal links’ and ‘weak links’, respectively, and P_w is the mean fraction of ‘weak links’ in molecular polymeric chains.

The photodegradation of PET is predominantly due to chain scission in the ester group. Carbon dioxide and carbon monoxide may be liberated. The carboxyl end groups are formed during PET photodegradation [231]. These carboxyl end groups act as catalyst to promote further degradation [232]. An alternative chain scission process is indicated by the fact that vinyl groups are formed in the degrading PET.

9.9.3 Analysis of stress–strain curves

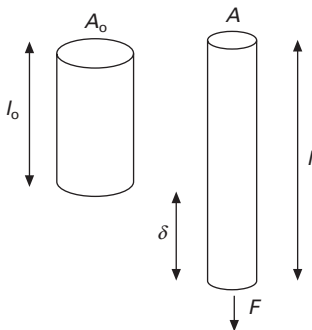
Stress–strain curves of fibers are determined by usage of dynamometers, which are available in every material testing laboratory. Let us start with straight fiber of cross-section area A_0 (diameter d_0) and length l_0 . After applying the load F the fiber is extended to the length l and shortened to the area A or diameter d (see. Fig. 9.24).

The engineering stress σ , engineering strain ϵ and draw ratio λ are defined by well known equations:

$$s = \frac{F}{A_0} \quad e = \frac{l - l_0}{l_0} = \frac{l}{l_0} - 1 \quad I = \frac{l}{l_0} = 1 + e \quad 9.37$$

The differential of draw ratio is then defined as $d\lambda = dl/l$. After integration the so called true strain ϵ_t can be obtained:

$$e_t = \int_{l_0}^l \frac{dl^*}{l^*} = \ln(I) = \ln(1 + e) \quad 9.38$$



9.24 Ideal geometry of fiber extension.

The important characteristics of material deformation are the so-called Poisson ratio ν , defined as the ratio of the relative transversal deformation ϵ_T and relative longitudinal extension ϵ :

$$\mathbf{n} = -\frac{\mathbf{e}_T}{\mathbf{e}} \text{ where } \mathbf{e}_T = \frac{d - d_0}{d_0} \quad 9.39$$

The change of cross-section area is then:

$$\frac{A}{A_0} = (1 - \mathbf{n}\mathbf{e})^2 \quad 9.40$$

and change of volume due to deformation is

$$\frac{V}{V_0} = (1 - \mathbf{n}\mathbf{e})^2 (1 + \mathbf{e}) \quad 9.41$$

For liquids and rubber the volume is not changed during deformation, i.e. $V/V_0 = 1$ (incompressible material) and $\nu = 0.5$. For the majority of fiber-forming polymers, the volume is increased due to extension (i.e. $V/V_0 > 1$) and then $\nu < 0.5$ (obviously $0.2 \leq \nu \leq 0.45$). In the case when volume is not changed during deformation, cross-section area is reduced according to relation:

$$\frac{A}{A_0} = \frac{l_0}{l} = \frac{1}{1 + \mathbf{e}} \text{ a } (1 - 0.5 \mathbf{e})^2 \quad 9.42$$

In Fig. 9.25(a) the comparison of functions $1/(1 + \epsilon)$ (dotted upper line) and $(1 - 0.5\epsilon)^2$ (solid lower line) is shown. The differences for small deformations (below $\epsilon = 0.1$) are sufficiently small. The values of V/V_0 computed from eqn. (9.41) for various deformations $\mathbf{e}$ are shown in Fig. 9.25(b). The deviations from theoretical value $V/V_0 = 1$ are not important for small ϵ . It can be stated that for sufficiently small deformations the values computed for constant $\mathbf{n}$ are fully acceptable. The true stress can be then expressed in the form

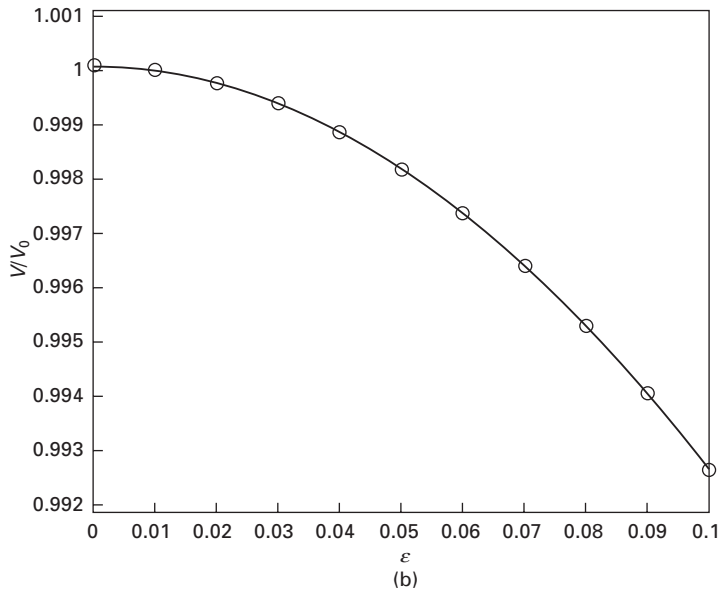
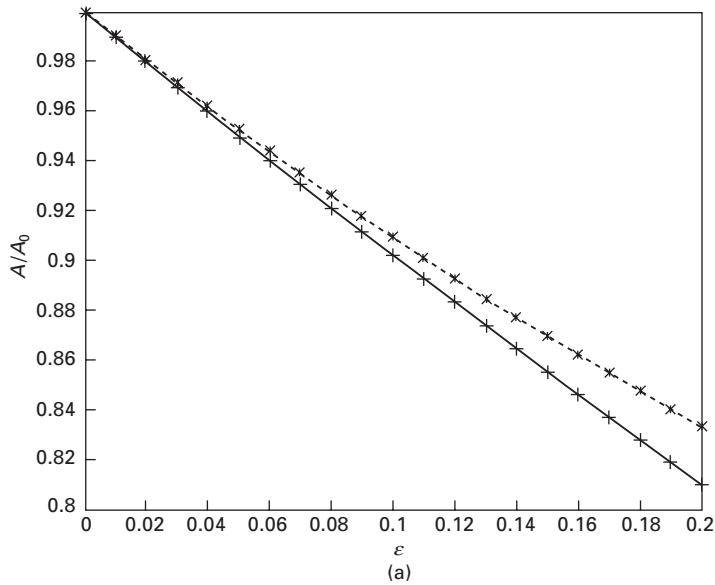
$$\mathbf{s}_t = \frac{F}{A} = \frac{\mathbf{s}}{(1 - \mathbf{n}\mathbf{e})^2} \quad 9.43$$

In practical applications the assumption of constant volume during deformation is used and true stress is expressed in the form:

$$\sigma_t = \sigma (1 + \epsilon) \quad 9.44$$

It is interesting that for linear true stress–true strain dependence $\sigma_t = E\epsilon_t$ for incompressible material, the engineering stress–strain diagram is a convex increasing curve:

$$\mathbf{s} = \frac{E \ln(1 + \mathbf{e})}{1 + \mathbf{e}} \quad 9.45$$



9.25 Comparison of functions expressing the dependence (a) of A/A_0 on ε and (b) of V/V_0 computed from eqn. (9.41) on ε .

where E is initial modulus for true stress–strain dependence which is equal to initial modulus of the engineering stress–strain curve because value of derivative $[\ln(x)/x] = 1/(x + 1)^2 - \log(x + 1)/(x + 1)^2$ for x approaching 1 is equal to 1. In case of polymer with constant Poisson ratio during deformation,

eqn (9.45) is replaced by the form:

$$\sigma = E(1 - \nu\varepsilon)^2 \ln(1 + \varepsilon) \quad 9.46$$

The shape of this function depends on the value of Poisson ratio (see Fig. 9.26a). As in the previous case, the initial modulus for true stress/strain dependence is equal to initial modulus of the engineering stress–strain curve.

For a larger elongation, it is better to use Poisson's logarithmic ratio ν_t defined by relation:

$$n_t = - \frac{d \, d/d_0}{dl/l_0} \quad 9.47$$

After integration in the limits (l_0, l) and (d_0, d) the following relation for the change of cross section area can be derived:

$$\frac{A}{A_0} = (1 + \varepsilon)^{-2n_t} \quad 9.48$$

The corresponding true stress is equal to:

$$\sigma_t = \sigma (1 + \varepsilon)^{2\nu_t} \quad 9.49$$

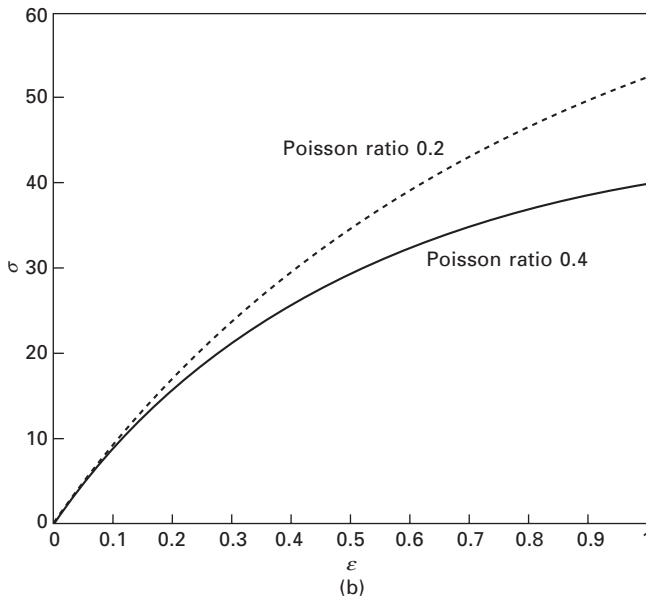
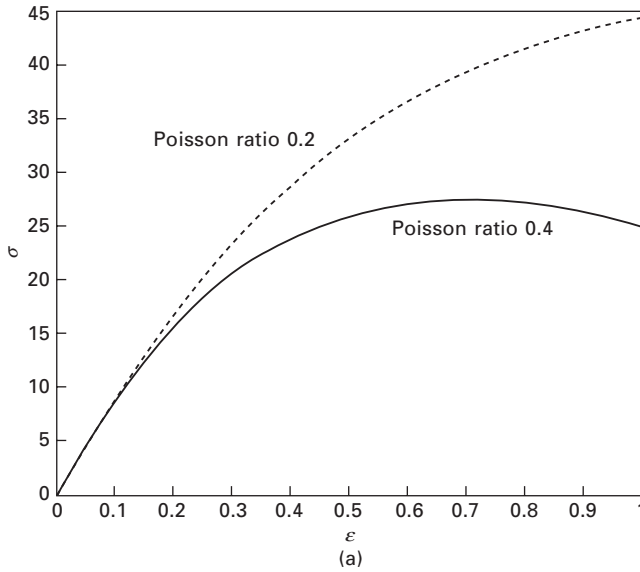
and corresponding engineering stress–strain curve for linear true stress–true strain dependence now has the form:

$$\sigma = (1 - \varepsilon)^{2\nu_t} \ln(1 + \varepsilon) \quad 9.50$$

The shape of this function depends also on the value of Poisson ratio (see Fig. 9.26b). The initial modulus for true stress–strain curve is equal to initial modulus of the engineering stress–strain curve as in previous cases. It was experimentally proved that the Poisson ratio decreased with increasing of tensile elongation [233].

The stress–strain curve models

The real true stress–strain curves of glassy polymers exhibit some typical characteristic stages of deformation. Initially the polymer shows a reversible, nearly elastic, deformation. At a certain amount of stress, deformation becomes irreversible, which is indicated by a yield point in the true stress–strain curves. After the yield point, a decrease in stress arises, which is denoted as strain softening. With proceeding deformation a strain hardening is observed by an increase in stress. In the last stages before break the destruction of the microstructural unit occurs. It is well known that the extent of strain softening depends on the thermal and mechanical history of the polymer. Strain softening can be reduced or even completely removed by a thermal or mechanical treatment [187]. Plastic deformation in glassy amorphous polymers is controlled by molecular motions on a segmental scale and can be recovered by a thermal annealing above T_g [234]. During strain hardening



9.26 Engineering stress–strain curves computed from (a) eqn. (9.46) for two Poisson ratios and (b) eqn. (9.50) for two Poisson ratios.

the entanglements control the modulus and the molecular weight controls the strength at break [193]. The reversibility of plastic deformation supports the idea that the entangled polymer network is responsible for the large strain behavior. The stress–strain response to large strains of amorphous polymers is therefore simply described by a neo-Hookean relation [235, 236].

$$s_t = s_y + E_y \frac{\hat{\epsilon}_t}{\hat{\epsilon}_y}^2 - \frac{1}{I} \quad 9.51$$

where E_y is the strain hardening modulus and σ_y is the yield stress. Haward [237] used a neo-Hookean relation based on the entanglement density in the amorphous phase to describe the of strain hardening behavior of semicrystalline polymers.

The true stress σ_t vs. true strain ϵ_t dependence (stress–strain curve) of semicrystalline fibers can be often represented by the empiric Ramberg–Osgood equation (see [238]):

$$\epsilon_t = \frac{s_t}{E} + \frac{\hat{\epsilon}_t}{EK} \quad 9.52$$

where K is strength coefficient and m is strain hardening exponent.

The Ramberg–Osgood model was used to represent the stress–strain behavior of a nanocomposite up to ultimate tensile strength. It was observed that there was a good correlation between K and yield stress σ_y .

For the true stress–strain relationship of crystalline polymers at elevated temperatures, Takayanagi and co-workers have proposed an empirical relationship [239]:

$$\log(\sigma_t/\sigma^*) \log(\epsilon_t/\epsilon^*) = -c \quad 9.53$$

where σ^* and ϵ^* are determined empirically by shifting the doubly logarithmic curves along both axes. The constant c is characteristic of polymer species, being independent of melt index, drawing temperature and deformation rate. For polyamide 6, the value of c was 0.175. σ^* decreased rapidly with temperature and ϵ^* was nearly independent of temperature.

Exponential, parabolic, hyperbolic and piecewise linear functions have been used to describe the constitutive behavior of materials [240]. Of these models, an exponential model of true stress–strain dependence in the form of

$$\sigma_t = a + b \exp(c \epsilon_t) \quad 9.54$$

is widely used [241]. Here the parameter a is the asymptotic true strain as true stress approaches infinity (assuming $c < 0$), b is the rate at which the material approaches its asymptotic strain, and c describes the curvature in the rate of approach to the asymptote. The simple piecewise nonlinear model for true stress–strain dependence description was published by Hutchinson and Neale [242].

$$\begin{aligned} \sigma_t &= k a \epsilon_t^b \text{ for } \epsilon_t \leq \epsilon_0 \\ \sigma_t &= k \exp(c \epsilon_t^2) \text{ for } \epsilon_t > \epsilon_0 \end{aligned} \quad 9.55$$

The variables a , b , c and ε_0 are related by the continuity of true stress σ_t and its first derivative with respect to strain at $\varepsilon_t = \varepsilon_0$; i.e. $b = 2c\varepsilon_0^2$ and $a = \exp(b/2)/\varepsilon_0^b$. Three phase empiric piecewise model for description of engineering stress–strain dependence of PET yarns was published in Serwatka *et al.* [243].

The true stress–strain behavior of amorphous PET can be analyzed by using a model composed from parallel viscoplastic σ_p and an orientational σ_{or} component connected in series with a Hookean spring [155]. The viscoplastic term is thermally activated and reflects mainly the strain rate sensitivity of the material. Its response is defined by eqn. (9.16). The orientational term represents the internal stress of the rubberlike network approximated by array of Langevin springs. Its response is defined by eqn. (9.24). The final model is modified to take into account the linear increase of crystallinity in PET during tensile deformation.

The sigmoid stress–strain curves can be expressed by a nonlinear model composed of a linear spring (modulus E_2), a Maxwell element (modulus E_1 , viscosity η) and a nonlinear spring with parabolic response ($\sigma = b\varepsilon^2$) in parallel. The linear spring in the model is used to describe the Hookean region in the tensile curve at lower strain, the Maxwell element to illustrate the viscoelasticity, and the nonlinear spring to characterize the nonlinear mechanical response:

$$\mathbf{s} = E_2 \mathbf{e} + b \mathbf{e}^2 = \mathbf{h} \mathbf{n} \left[1 - \exp \left(- \frac{\mathbf{E}}{\mathbf{A}} \frac{E_1 \mathbf{e}}{\mathbf{h} \mathbf{n}} \right) \right] \quad 9.56$$

where $\nu = d\varepsilon/dt$ is the rate of deformation. The asymptotic stress σ_{as} for sufficiently large strains has parabolic response $\sigma_{as} = E_2 \varepsilon + b\varepsilon^2 + \eta\nu$. In Plaseied and Fatemi [244], the stress–strain dependence for standard linear viscoelastic body model (which is in fact eqn. (9.56) for $b = 0$) was modified by using of nonlinear viscosity:

$$\mathbf{h} = \mathbf{h}_\infty + \frac{\mathbf{h}_0 - \mathbf{h}_\infty}{[1 + (c \, d\mathbf{e}/dt)^2]^d} \quad 9.57$$

where c and d are material constants. The viscosity decreases from its initial value η_0 at $d\varepsilon/dt = 0$ to η_∞ as $d\varepsilon/dt = \infty$.

A more complex, four element model (two springs and two dashpots with nonlinear responses) is used by Khan *et al.* [245].

Drozdov and Christensen [246] derived the constitutive model for the mechanical behavior of a semicrystalline polymer at small strains (below yield point, where the stress–strain curve is monotonously increasing). A polymer is assumed as a network of chains bridged by permanent joints (entanglements or physical crosslinks on the surfaces of crystallites). This network is replaced by an ensemble of meso-regions (MR) connected by

links (crystallites). Macroscopic deformation induces sliding of joints between chains and sliding of MR. The final constitutive equations have the form:

$$\mathbf{s} = E_0(\mathbf{e} - \mathbf{e}_{pl}) \left[\frac{\dot{\mathbf{e}}}{\dot{\mathbf{e}}_1} - a \frac{\dot{\mathbf{e}}}{\dot{\mathbf{e}}_1} - \exp \left(\frac{\mathbf{e} - \mathbf{e}_{pt}}{\mathbf{e}_1} \right) \right] \quad 9.58a$$

$$\frac{d\mathbf{e}_{pl}}{d\mathbf{e}} = a \left[\frac{\dot{\mathbf{e}}}{\dot{\mathbf{e}}_1} - \exp \left(\frac{\mathbf{e} - \mathbf{e}_{pt}}{\mathbf{e}_1} \right) \right] \quad 9.58b$$

The parameter a [0, 1] is the rate of sliding for a fully developed flow of joints. The strain, $\mathbf{e}_1$, characterizes transition to the steady viscoplastic flow and E_0 is the initial elastic modulus. The adjustable parameters E_0 , a and $\mathbf{e}_1$ can be found from experimental stress–strain curves [246]. A phenomenological constitutive model for expression of stress dependence on strain, strain rate and temperature has been proposed [247]. This constitutive model has capability to describe the entire range of deformation behavior of glassy and semicrystalline polymers, especially the intrinsic strain softening and subsequent orientation hardening.

Engineering stress strain dependence can be described by using of models from Section 9.9.1 usually by solving of governing differential equations. For three element model from Fig. 9.20, the differential equation determining the relationship between the stress, σ deformation ε and time t has the form:

$$\frac{d\mathbf{s}}{dt} = \frac{d\mathbf{e}}{dt} [E_0 + E_1(1 - 2K_1\mathbf{e})] - E_0\mathbf{k} \sinh [\mathbf{a}(\mathbf{s} - E_1(\mathbf{e} - K_1\mathbf{e}^2))] \quad 9.59$$

In the case when stress–strain curves are measured at a constant deformation rate $\nu = d\mathbf{e}/dt$, the solution of this differential equation leads to the relation:

$$\mathbf{s} = E_1(\mathbf{e} - K_1\mathbf{e}^2) + \frac{1}{2} \ln [R + S \tanh (K_4\mathbf{e} + K_5)] \quad 9.60$$

where

$$R = \mathbf{n}/\mathbf{k} \text{ and } S = \sqrt{1 + R^2} \quad 9.61$$

and

$$K_4 = \frac{\mathbf{a}\mathbf{k}E_0S}{2\mathbf{n}} \quad K_5 = \operatorname{argtgh} [(1 - R)/S] \quad 9.62$$

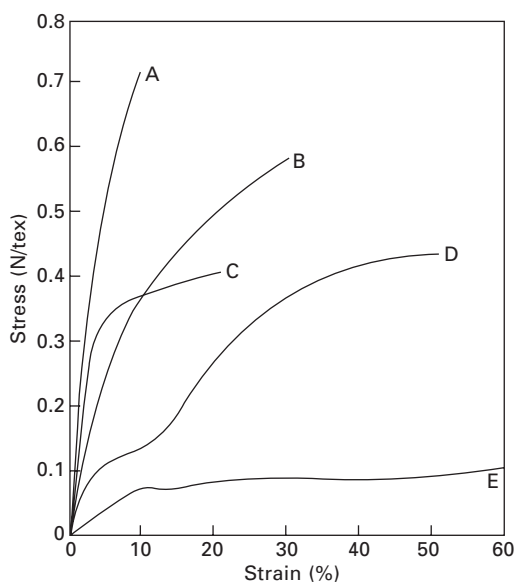
The model parameters α , κ , K_l , E_0 , E_l can be estimated from experimental data by nonlinear regression [248]. The estimated model parameters for heat-set PET fibers having a draw ratio of $\lambda = 5$ are: $\alpha = 13.9 \text{ GPa}^{-1}$, $\kappa = 7.2 \cdot 10^{-3} \text{ s}$, $K_1 = -3$, $E_0 = 5.6 \text{ GPa}$, $E_1 = 0.52 \text{ GPa}$, $\mathbf{DE}^x = 94.2 \text{ kJ/mol}$ and $V_f = 2.86 \cdot 10^{-27} \text{ m}^3$. Details about application of this model for modeling of modified PET fibers stress strain curves are in Militký *et al.* [3].

The large tensile deformation behavior of PET fibers at high temperatures can be described in terms of stretching springs and dashpots, approximating intermolecular resistance acting in parallel with network resistance (see Section 9.9.1). In this representation, the deformation of the crystalline phase is coupled with the amorphous phase through three different analog representations leading to the classical upper and lower bounds [179, 249].

Stress–strain curve characteristics

The shapes of stress–strain curves of fibers are generally dependent on their thermal and mechanical history, i.e. conditions of spinning, drawing and heat setting. The typical stress–strain curves of PET fibers and filaments are shown in Fig. 9.27. It can be seen that the filaments have a much higher initial modulus than the staple fiber. High tenacity filament and staple fiber have very high breaking strengths, but relatively low elongations. POY exhibits low strength but very high elongation at break.

The typical stress–strain curve shapes shown in Fig. 9.27 are maintained for all types of copolyesters as long as the fibers are tempered after drawing. The comparison of stress–strain curves for drawn polyalkylene terephthalate fibers is published in Ward and Wilding [50]:



9.27 Typical stress–strain curves for PET fibers: A, high tenacity filament; B, high tenacity staple; C, regular tenacity filament; D, regular tenacity staple; E, POY filament.

- The stress–strain curve of PET gives a continuously rising curve with a relatively high initial modulus.
- The stress–strain curve of PTT (polytrimethylene terephthalate – 3GT) has a sigmoidal shape with an inflection in the vicinity of a 5% deformation; the initial modulus is lower.
- The stress–strain curve of PBT (4GT) shows a marked ‘plateau’ in the region of 4 to 12% deformation. The initial modulus is close to that of PTT.
- After thermal annealing of fibers, the modulus of 2GT drops very appreciably (around 33%) and that of PTT and PBT actually increases (47% for PTT and 28% for PBT).

These deviations result from a different conformation of chains in higher polyalkylene terephthalates (the presence of the shortened form and transformation of the latter into the extended form). In PET a change in crystal lattice takes place in the deformation region of 4 to 12% [250].

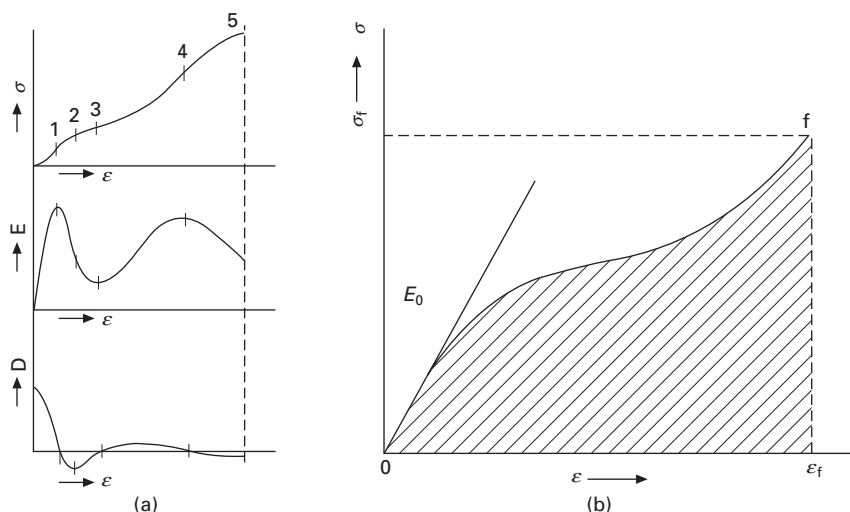
Stress–strain curves can be parameterized by characteristic points determined by smoothing and differentiation [251–253]. It is not necessary to find the approximation function $\sigma(\epsilon)$, in closed form, but smoothed (noiseless) data for graphical interpretation, numerical differentiation and integration are required. The purpose of numerical smoothing is to remove the random noise in experimental data and reconstruction of noiseless function $\sigma(\epsilon)$. A smoothing function $\sigma(\epsilon)$ must be continuous in a first two derivatives only. Therefore a non-parametric C^2 spline smoothing of the experimental stress–strain curve, determined by the couples σ_i, ϵ_i $i = 1..N$, is useful [248]. It has been shown that function $\sigma(\epsilon)$ from class C^2 , which minimizes combination of the smoothness of $\sigma(\epsilon)$ and its closeness to the experimental points, has the following properties:

- The function $\sigma(\epsilon)$ in each interval I_j $\mathbf{\sigma}(\epsilon_{i+1}, \epsilon_i)$ is a polynomial of at most third degree.
- At all locations ϵ_i , function $\sigma(\epsilon)$ is continuous in function values and in the values of the first two derivatives.

The full procedure of spline smoothing is described by Meloun *et al.* [248]. From smoothed function $\sigma(\epsilon)$ the shape of the first (modulus $E = d\sigma/d\epsilon$) and second (rate modulus $D = d^2\sigma/d\epsilon^2$) derivatives can be simply determined.

Figure 9.28 shows a typical smoothed stress–strain curve together with the courses of the modulus E and rate modulus D . From the extremes on the curves for E and D it is possible to exactly define five characteristic points on the stress–strain curve:

1. The point of the first maximum on the modulus curve (E). The corresponding modulus E_0 is used as the initial modulus characterizing the initial resistance to the deformation.



9.28 Typical characteristics points on the stress–strain curve: (a) smooth curve and its first two derivatives and (b) basic characteristic.

2. The point of the first minimum on the rate modulus curve (D). It corresponds to the yield point characterizing the start of marked plastic deformation. It is therefore related to the elastic recovery of the fibers.
3. The point of the first minimum on the modulus curve (E). It characterizes the region of maximum ‘strain softening’ in which secondary bonds break and shear deformations due to the stretching of tie chains take place.
4. The point of the second maximum on the modulus curve (E). It characterizes the region of maximum ‘strain hardening’. Most of the tie chains are already taut here and tensile deformation takes place in them.
5. Point of rupture. Before this point is reached, crystallites are disrupted and a nearly plastic flow takes place owing to the effect of the rupture of tie chains.

In order to completely characterize the stress–strain curves, the stress, deformation, modulus E , rate modulus D and deformation work (i.e. integral under $\sigma(\epsilon)$ curve) are determined at individual points. Some of these parameters are linked with the behavior of fibers in woven fabrics. For instance, the initial modulus E_0 is closely correlated with fabric handle and drape. The yield-point stress is related to creasing and recovery, whereas the total deformation work is linked with toughness [254]. The modulus corresponding to maximum strain hardening (see point 4) is supposed to be related to the maximum drawing to which the fiber was exposed. A growing distance between points 2 and 4 indicates a decrease of recovery power.

The most frequently used characteristics are the tenacity (tensile strength) and extension at break. These characteristics are dependent on the degree

of molecular orientation in the fiber, which is determined by the drawing and heat setting process. High draw increases tenacity and reduces breaking extension.

The initial modulus and fiber strength will increase with increasing of deformation rate. On the other hand, elongation will decrease [254]. The increase in the relative molecular mass will cause, in the first place, the modulus and strength to increase.

Initial modulus

The initial modulus is dependent on the orientation in the crystalline and amorphous phases and on the degree of crystallinity. The methods of its prediction from these known structural parameters have been reviewed [119]. In amorphous isotropic polyesters and copolyesters the initial modulus E_{ao} can be predicted by using the empirical expression [51]:

$$E_{ao} = \frac{3(1 - 2\nu)}{4.2058 \cdot 10^{-12} \gamma^{-3/2}} \quad 9.63$$

where γ is polymer surface tension (predictable by molar contribution method [51]) and ν is the Poisson ratio (for amorphous polymers in a glassy state is $\nu \approx 0.33$). For an isotropic amorphous PET in a glassy state the value $E_{ao} = 2.31$ GPa has been computed [3]. The presence of comonomer units in modified PET fibers is responsible for a decrease in the initial modulus.

Yield point

The yield point is determined practically by analysis of the derivatives of stress–strain curves. It corresponds to the first minimum on the first derivative of the stress–strain curve (see Fig. 9.28). The yield point for well-oriented fibers is in the range of 0.5–1.0% strain, whereas isotropic samples show a yield strain at about 2.2%. Unloading the fiber after the first extension up to a strain larger than the yield strain results in a small but permanent extension of the fiber. There is little variation in the yield strain, ϵ_y , for fibers made of different kinds of polymer [203].

The yield stress of amorphous polymers depends on time and temperature, a phenomenon known as physical aging. The yield is related, above all, to the orientation of the amorphous phase [119]. The higher the orientation factor of the amorphous phase, the higher will be the yield stress. The yield stress σ_y of glassy polymers exhibits viscous flow which can be expressed by Eyring type model modified for normal stresses [177].

$$\frac{\sigma_y}{T} = A \left[\ln \frac{\dot{\epsilon}}{A} + \frac{Q}{RT} \right] \quad 9.64$$

where T is the absolute temperature, $d\epsilon/dt$ is strain rate, Q is the activation energy, R is universal gas constant and A, B are parameters containing geometrical and entropic factors. The yield stress is found to increase with decreasing temperature and with increasing strain rate. The two-process Ree–Eyring model has been used to describe of amorphous PET yield behavior [255].

Rault [256] applied the compensation law to the yielding of amorphous and semicrystalline polymers. Accordingly, the yield stress has the form:

$$\sigma_y = \sigma_0 - \frac{T\sigma_0}{T_g} + \frac{kT}{V} \ln \frac{\dot{\epsilon}}{A e_0} \quad 9.65$$

where σ_0 , e_0 , and V are parameters. Parameter σ_0 may be associated with the athermal stress $\sigma_i(0)$ of the cooperative model described by Richeton [257]. The first term of this yield stress models exhibits a linear dependence on temperature. As mentioned by Rault [256], the ratio σ_0/T_g is found to be about 0.5 MPa/K for many thermoplastic polymers. The basic molecular theories of yield are reviewed by Stachurski [157].

It was found that the yield stress of amorphous polymers increases dramatically for the low temperatures as well as for the high strain rates. To describe this behavior, a model based on the cooperative model of Fotheringham and Cherry [178] and strain rate/temperature superposition principle of the yield stress was derived [258]. This model was extended to the temperatures above T_g .

The cooperative model for the yield behavior of semicrystalline polymers is proposed by Gueguen *et al.* [259]. The semicrystalline polymer is here considered as a two phase material, where the yield processes in the amorphous phase and in the crystalline phase are taken into account separately. The Takayanagi-type model is used to predict an effective activation volume and effective activation energy, which are then implemented in the cooperative model. This model has been used to describe the yield behavior of polyethylene and PET.

9.10 Tensile strength of polyester fibers

Generally, fiber strength is a rather sophisticated parameter. It will decrease as the degree of arrangement of the chain folds in crystallites rises [260]. The strength of drawn PET at a given draw ratio increases with increasing molecular mass [53, 54]. For PET, such molecular weight dependences are explained by the suppressions of disentanglement and relaxation of oriented molecular chains during deformation [54]. For many processes dealing with ultimate strength, like crazing or fracture, the molecular mass between entanglements, M_e , is probably more important molecular characteristics

[266]. As the orientation factor of the amorphous phase in PET fibers grows, the strength grows too [119].

In addition to the molecular mass, chemical composition of chains and the inter-chain cohesion forces, the strength is also influenced by the presence of different types of defects and heterogeneities. The strength has therefore a statistical nature and its distribution (the probability model) is related to the rupture mechanism.

The strength variability of fibers is usually described in the frame of weakest link model. This model assumes that the fiber can be replaced by a series of randomly assembled uniform strength links, of which the strengths are i.i.d. (independent, identically distributed) random variables with a common cumulative distribution function. Break occurs in link with smallest strength. Another model is simply described as a random defect model. This model considers the fiber to have some constant strength, upon which dimensionless, non-interacting, strength-reducing defects randomly occur. Choice of the model primarily depends on the proposed hypothesis regarding the nature of the strength variability of the particular fibers. Suitability of the proposed model to represent the fiber variability can then be evaluated by comparing predictions of the model with actual data. The probabilistic approach to the fracture of fibers is based on these assumptions [262, 263]:

- the fiber breaks at specific place with critical defect (catastrophic flaw) and fracture behavior is time-independent;
- defects are distributed randomly along the length of fiber (model of Poisson marked process);
- fracture probabilities at individual places are mutually independent.

It has been experimentally verified that the distribution function of the strength in PET and modified PET fibers can be well approximated by Weibull distribution [3, 264, 265]. It corresponds to the hypothesis of chains being ruptured at randomly distributed defective points when the fibers are deformed. The three parameter Weibull distribution function has the form:

$$F(s_f) = 1 - \exp \left[- \left(\frac{s_f - B}{A} \right)^C \right] \quad 9.66$$

The mean value $E(\sigma_f)$ and variance $D(\sigma_f)$ of fiber distribution are simple functions of parameters A , B and C :

$$E(s_f) = B + A \cdot \Gamma \left(\frac{1}{C} + 1 \right) + \frac{1}{C}$$

$$D(s_f) = A^2 \left[\Gamma \left(\frac{2}{C} + 1 \right) + \frac{2}{C} - \Gamma^2 \left(\frac{1}{C} + 1 \right) + \frac{1}{C^2} \right]$$

where $\Gamma(x)$ is gamma function. For $C > 3$ or $C \approx 1$ is approximately $\Gamma(x) = \frac{\hat{B}}{\hat{A}} + \frac{1}{C} \approx 1$ and then $E(\sigma_f) \approx A$. As C increases, the distribution is narrower and is increasingly similar to the normal (Gaussian) distribution. When the parameter C is large, the mean and variance can be approximated by the following expressions [266]:

$$E(s_f) = B + 1 - \frac{0.577}{C} + \frac{\pi^2/6 + 0.333}{2C^2}$$

$$D(s_f) \approx \frac{\pi^2}{6C^2}$$

For $C > 3.6$, the Weibull distribution is nearly symmetric and has a form very similar to a normal distribution. The expression for the coefficient of variation, which is in case of $B = 0$ is the function of parameter C only, is very interesting:

$$CV = \frac{\sqrt{D(s_f)}}{E(s_f)} = \frac{\left[\frac{\Gamma(\frac{\hat{B}}{\hat{A}} + \frac{2}{C}) - \Gamma^2(\frac{\hat{B}}{\hat{A}} + \frac{1}{C})}{\Gamma^2(\frac{\hat{B}}{\hat{A}} + \frac{1}{C})} \right]^{1/2}}{\frac{\hat{B}}{\hat{A}} + \frac{1}{C}}$$

For small C it is valid $CV = C^{-0.92}$ for $0.05 \leq C \leq 0.5$. These approximations are also interesting for the interpretation of Weibull parameters.

Estimation of Weibull parameters is based on the experimental strength values σ_{fi} , $i = 1 \dots N$. There are a lot of methods for the estimation of parameters A , B , C . [267]. The standard *maximum likelihood method* leads to the solution of three nonlinear equations [268]. If there is a possibility to estimate parameter B independently, the reduced strength data $\sigma_{rfi} = \sigma_{ji} - \hat{B}$, $i = 1 \dots N$ can be simply created. In this case, the *moment method* based on the comparison of first two moments leads to the estimation of the parameter C as solution of nonlinear equation [267]:

$$\bar{s}_f \left[\frac{\Gamma(\frac{\hat{B}}{\hat{A}} + \frac{2}{C})}{\Gamma^2(\frac{\hat{B}}{\hat{A}} + \frac{1}{C})} - 1 \right]^{1/2} - s_f = 0 \quad 9.67$$

where s_f is standard deviation of strength data. The parameter A is then estimated from:

$$E(\sigma_f) = \bar{\sigma}_f + \hat{B},$$

i.e.

$$\hat{A} = \frac{\bar{s}_f - \hat{B}}{\frac{\hat{B}}{\hat{A}} + \frac{1}{C}}$$

where $\bar{\sigma}_f$ is mean strength value of original data.

For a quick estimation of parameters A , C (in the case of known $\hat{B}$) it is attractive to use the so called $Q-Q$ graph enabling to check Weibull distribution acceptability for experimental data [268]. This graph is simply derived from the distribution function defined by eqn (9.69) replacing $F(\sigma_{fi})$ by order statistics $P_i \approx i/(N + 1)$ for $i = 1..N$ and replacing σ_{rfi} by ordered values (*empirical quantiles*) $\sigma_{rf(i)} \leq \sigma_{rf(i+1)}$. After substitution and rearrangements the final linear form

$$\ln [-\ln (1 - P_i)] = \ln (A) + C \ln (\sigma_{f(i)}) \quad 9.68$$

is obtained. The $Q-Q$ graph is then the dependence of $[-\ln(1 - P_i)]$ on the $\ln(\sigma_{f(i)})$. In case of validity of Weibull distribution with lower limit $\hat{B} = 0$, this dependence should be straight line with slope C and intercept $\ln(A)$ [248]. When lower limit $\hat{B} > 0$, the x axis of the $Q-Q$ graph should be $\ln(\sigma_{f(i)} - \hat{B})$. By using of standard linear regression, the parameters A and C can be roughly estimated [268]. Owing to the empirical quantiles $\sigma_{rf(i)}$ roughness and their nonconstant variances, the special treatment for refining of P_i can be used [269].

For quick and rough parameter estimation of three parameter Weibull models the moment-based method can be used. The main idea of this method is very simple. Based on the M sample moments and corresponding theoretical moments for selected strength distribution, the M nonlinear equations can be created. Their complexity is based on the suitable selection of moments [268]. Cran [270] used this technique to estimate the parameters in three parameter Weibull distribution. The Shape parameter C can be estimated from the relation:

$$\hat{C} = \frac{\ln(2)}{\ln(m_1 - m_2) - \ln(m_2 - m_4)} \quad 9.69$$

It is valid for estimating the lower limiting strength B :

$$\hat{B} = \frac{m_1 m_4 - m_2^2}{m_1 + m_4 - 2m_2} \quad 9.70$$

and estimation of scale parameter A is in the form:

$$\hat{A} = \frac{m_1 - \hat{B}}{\Gamma(1 + 1/\hat{C})} \quad 9.71$$

where $\Gamma(x)$ is Gamma function. In these relations m_r are special, so-called Weibull sample moments defined as:

$$m_r = \sum_{i=0}^{N-1} (1 - i/N)^r [x_{(i+1)} - x_{(i)}] \quad 9.72$$

For $i = 0$ this is formally $x_{(0)} = 0$. This very simple technique can be used for the rough estimation of strength distribution parameters. It is suitable for prediction of importance of parameter A in Weibull models [270]. For two parameter Weibull model $A = 0$ and C is estimated from:

$$C = \frac{\ln(2)}{\ln(m_1) - \ln(m_2)} \quad 9.73$$

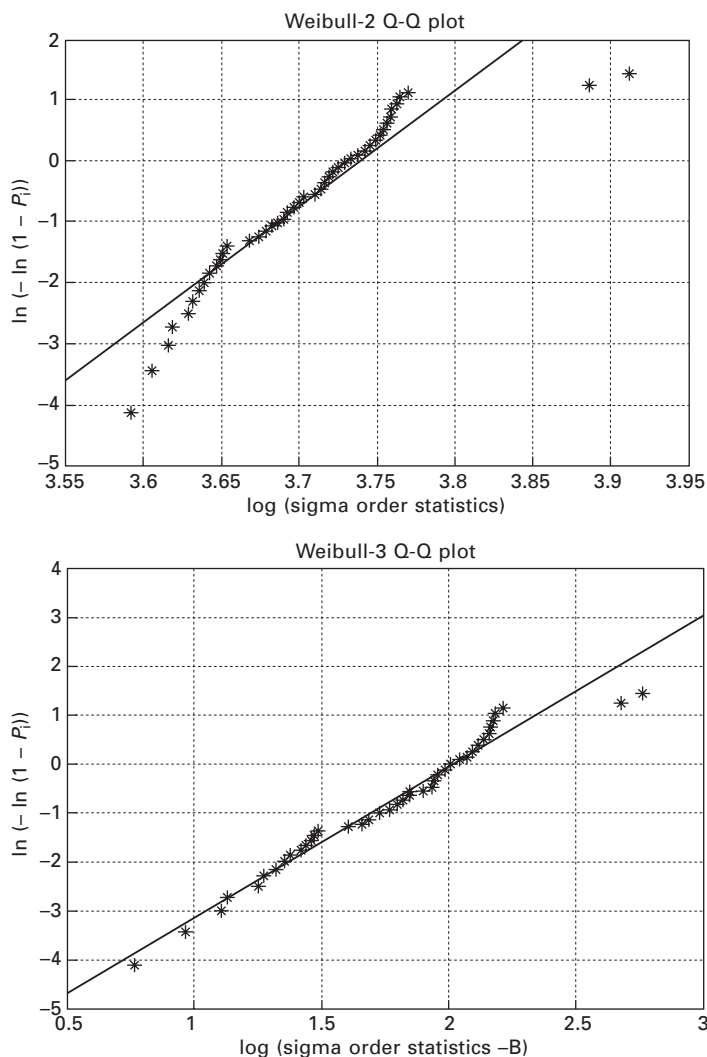
The assumption $B = 0$ is valid if A and C estimates for two and three parameter Weibull model are reasonable close. The properties of Weibull distribution and details about parameter estimation are given by Murthy *et al.* [266].

For industrial PET monofilament having a draw ratio of $\lambda = 5$, the $Q-Q$ graphs for checking 2 and 3 parameter Weibull distribution function of the strength are shown in Fig. 9.29. The corresponding estimators of parameter values computed from the Cran equations are: $\hat{B} = 34.19$ cN/tex, $\hat{A} = 7.51$ cN/tex $\hat{A}$ and $\hat{C} = 3.34$. It is important that the standard $Q-Q$ graph (valid for 2 parameter Weibull distribution) wrongly indicates the unsuitability of Weibull distribution (see Fig 9.29a). The simple way to overcome this problem is to use a $Q-Q$ graph with a modified x axis (valid for three parameter Weibull distribution) with parameter $\hat{B}$ computed from eq. (9.70) (see Fig. 9.29b).

It was evaluated that modified PET fibers prepared under comparable conditions exhibited lower mean fiber strength than did PET. This is obviously due to heterogeneity in the polymer chains caused by the presence of comonomer units. It was observed that in the range of technological comonomer concentrations the fiber strength was decreased almost linearly with increasing comonomer content [271]. The respective slopes of these relationships, indicating the decrease in strength corresponding to a 1% increase in comonomer concentration, are: 0.0118 GPa/mol% for isophthalic acid, 0.026 GPa/mol % for adipic acid, 0.055 GPa/mass% for polyethyleneglycol and 0.058 GPa/mol for sulfoisophthalic acid [271]. Although these values cannot be used for extrapolation they indicate the rate of decrease of the strength, especially for minor additions of comonomer.

Theoretical estimation of tensile strength is more complicated than the tensile modulus. Whereas tensile modulus reflects the average of the structure, tensile strength relates more to the weakest portion in the structure. Real (imperfect) fibers are partially crystalline and viscoelastic (mechanically irreversible). The *equivalent* fiber was defined as a reversible, Hookean fiber that behaves as a perfect fiber possessing the same bulk thermodynamic properties as the actual fiber [272]. Its modulus is that of the initial modulus of the real fiber, E_i , and its strength σ_T is the same as the real fiber. By analogy with the fusion theory, the σ_T is predicted from the relation:

$$\sigma_T = \sqrt{2XE_iW_r} \quad 9.74$$



9.29 Distribution function of PET fibers: x, experimental points, solid line – Weibull distribution.

where X is crystallinity and W_r is work to rupture. Imperfections such as crystallinity, morphology, draw ratio, orientation, molecular weight and molecular weight distribution have influence on the values of X and E_i . Ideally, the variation of σ_T with the product $\sqrt{X E_i}$ represents a line of slope $\sqrt{2 W_r}$ [272].

9.11 Failure mechanisms of polyester fibers

The failure behavior of semicrystalline polymers depends on a combination of yield stress, strain hardening and tensile strength. Owing to a rise in yield stress, the localization of deformation increases. Moreover, similar to amorphous polymers, the entanglement density plays an important role in the failure behavior of semicrystalline polymers, which was already suggested by Bastiaansen *et al.* [273] and Plummer and Kausch [274]. The entanglement density affects the strain hardening behavior of the polymers, which affects the amount of stabilizing of deformation in strain localization zones. The brittle failure of melt crystallized samples and more ductile response of a higher molecular weight indicate a strong influence of entanglements, thus strain hardening, in their attribution to the failure behavior [275]. The physics of ductile fracture exhibits the following three stages: formation of a free surface by interface decohesion, growth of the void by means of plastic strain and coalescence of the growing void with adjacent voids, forming a microcrack. When process of void nucleation is easy, the fracture behavior is controlled by the growth and coalescence of voids. These three steps, *nucleation*, *growth* and *coalescence* of voids, occur in highly stressed regions of the fiber [276].

Ductile behavior is characterized by a lowering of the slope of load deformation curve at the yield stress. Yield can be caused either by multiple crazes or by shear yielding. In the first case, crazes have to be initiated in a relatively large volume of the material in order to contribute significantly to the overall deformation. Shear yielding is the plastic flow without crazing. Crazing occurs in materials below T_g , while shear yielding can be observed in a wide range of temperatures but only if the critical shear stress for yielding is lower than the stress required for initiating and propagating of crazes [277].

The mechanical response of semicrystalline polymers is controlled by the number of tie molecules between the crystallites (see Section 9.8). When tie molecule density is high, crystallites shear occurs before the tie molecules fracture and a craze develops, which leads to the enhancing of polymer ductility. Any accidental local anisotropy in fibrous structure can lead to shear forces even under purely axial load, thus giving rise to longitudinal crack formation, which as a rule precedes the failure of the strained material. When the tie molecule density is low, the load transmitted through these links will produce brittle fracture [278].

There are two distinct effects influencing the process of material failure. One is the fiber morphology-dependent distribution and size of defects, which strongly influence the nucleation and growth of cracks [154]. The other effect is the inherent cohesiveness of the long chains in linear polymers, which resists plastic deformation and the separation of material during the formation

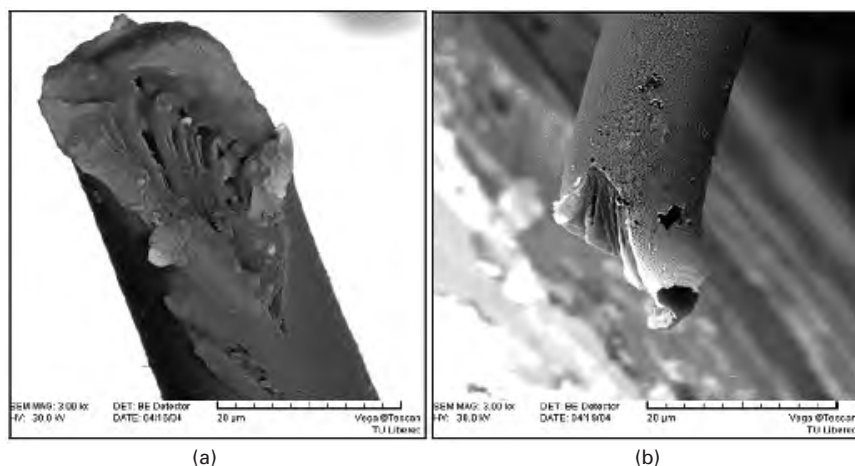
and propagation of cracks [279]. The fibrillar material has its weakest areas in the boundaries between adjacent microfibrils and fibrils, where the axial material connection by TTM with the rest of the sample is interrupted. Hence, the failure of the material is initiated at the ends of microfibrils. Here the usual axial connection by a great number of TTM is interrupted and amorphous layer is exhibiting a much smaller elastic modulus than the normal amorphous phase. Very likely this effect is preceded by opening a microcrack at the free end, which requires the rupture of a smaller number of chains than in a normal cross-section of a microfibril. The rupture of an adjacent microfibril leads to a microcrack extension in the lateral direction. Since the majority of free ends are located in the outer boundary of the fibrils, the microcracks formed by opening the point defects at the ends of microfibrils can coalesce by longitudinal growth along this boundary [280]. Interestingly, the ruptured molecules yield free radicals which can be monitored by electron spin resonance. The microcracks or microvoids can be visualized by special staining technique using OsO_4 [281]. As soon as one of the cracks reaches critical dimensions the catastrophic crack propagation leads to macroscopic failure [282].

Fracture studies on semicrystalline PET were published by Ward and coworkers [283, 284], who observed that in semicrystalline PET, fracture occurred by inherent flaws between amorphous and crystalline boundaries. Pecorini and Hertzberg [278] studied the effect of annealing and drying conditions on the fracture and fatigue behavior of PET and correlated their results qualitatively to the changes in the tie-molecule density. Gupta *et al.* [117] monitored the structural changes occurring during elongation up to fracture of uniaxially drawn, heat-set PET film samples by rapid scanning Fourier transform infra-red (FTIR) spectroscopy and identified chain uncoiling (lamellar separation) in the amorphous regions and longitudinal slip in the crystalline regions as the main deformation mechanisms in these materials. More recently, Van Den Heuvel *et al.* [285] identified molecular uncoiling by *gauche-trans* transitions as the major deformation mechanism when a technical PET yarn was axially stretched.

The tensile failure of PET fibers at slow rates of deformation can be decomposed to the two distinct stages [286, 287]:

- Initiation on (or near) the surface of the fiber, followed by slow growth of crack normal to the fiber axis with plastic deformation leading to crack opening ('V-crack').
- Quick catastrophic failure of the remaining area perpendicular to the fiber axis.

In Fig. 9.30 the breaking zones of non-annealed and annealed recycled PET fiber are shown [126]. The V notch is visible in the breaking zone of annealed sample. Walker *et al.* [288] found that extension of ductile thermoplastic



9.30 Breaking zone of recycled PET fibers and (a) before heat setting and (b) after setting at 200°C [126]

sheets leads to either V notches or characteristic ‘diamond’ cavities. Both features showed stable growth until a fracture. Under fast rate of deformation realized by pendulum, the broken ends left behind swell and have a mushroom shape. Hearle and coworkers explained appearance of this shape by localized adiabatic deformation [289]. Under specific cyclic loading conditions, quite different breaking zone morphology has been observed [286].

9.12 Conclusions

In this review, basic information is given about chemistry, fabrication technology and structure of PET and modified PET fibers. The main approaches to the modeling of tensile behavior of polymeric fibers focused on the PET are presented.

Despite the fact that PET and modified PET fibers have been widely investigated, there is still no complete way to predict the mechanical behavior and tensile failure based on the structure or manufacturing parameters. One of the main reasons is the complex character of changes during fiber manufacturing and modifications of structure during influence of stress field, temperature, time and environmental factors. Continuous effort is being made to investigate structural changes of fibers on-line but the information is only indirect and global. In fact, most of mechanical and failure properties are dependent on the local structure and therefore the use of statistically averaged information is speculative. Further information is obtainable from distribution of data or replacing the mean value by suitable quantiles [268].

9.13 References

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Tensile properties of polypropylene fibres

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Abstract: Polypropylene (PP) is a major fibre-forming polymer. However, processing and durability are restricted by a lack of control of its viscoelastic properties and by its low stability to oxidation. These difficulties have been progressively resolved in the past decades by a sharper control of synthesis conditions, i.e. of properties such as stereoregularity and molar mass distribution and by a better knowledge of oxidation and stabilization mechanisms. These research efforts allowed PP to be used in a very wide range of fibre applications, from disposable nappies to geotextiles.

Key words: polypropylene, structure, processing, mechanical properties, embrittlement, durability, stabilization.

10.1 Introduction

Polypropylene (PP) was known before the Second World War, but only in its non-crystalline (atactic) form which displays the characteristics of an unvulcanized rubber with the inconvenience of being practically unvulcanizable. Polypropylene became an industrially interesting polymer when Natta discovered a way to obtain a stereoregular structure using stereospecific catalysts in 1954. Polypropylene was thus the last commodity polymer (the others being polyethylene, poly(vinylchloride) and polystyrene) to appear on the market. Its fibre-forming properties were rapidly recognized. It was first used to replace vegetal fibres such as hemp in cordage. However, it progressively invaded other important markets (including carpets, filters) including cigarette filters, geotextiles, agriculture bays, camouflage technology, disposable nappies (diapers) and prosthetic mesh [1–5]. Overall world consumption of PP was about 42 million tons in 2005. One estimates an average increase rate of about 5% a year so that its consumption is expected to reach more than 50 million tons by the end of 2010 and PP fibres ranked in second place after polyester fibres [6, 7]. Its growth could be slowed down in the future, by the increase of petroleum prices and the revival of natural fibres but these trends are, in reality, very difficult to predict.

10.2 Polypropylene (PP) structure and properties

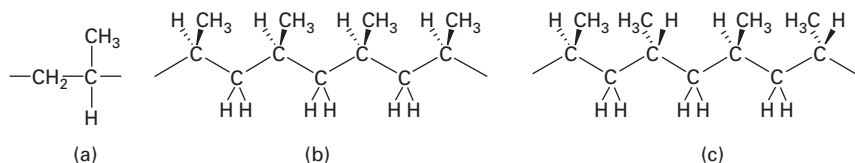
Polypropylene (PP) results from the polymerization of propylene. The structure of the repetitive unit is shown in Fig 10.1a. Some properties of the three PP isomers are provided in Table 10.1, and will be discussed in the following text. Among the possible chain configurations, only stereoregular ones (syndiotactic and isotactic PP, Figs 10.1b and 10.1c) are able to crystallize and have interesting mechanical properties. Isotactic PP is, by far, the most commonly used stereoisomer.

In isotactic PP, the equilibrium chain configuration is a helix having a period of three monomer units. iPP is able to crystallize into three distinct forms: α , β , γ , the most thermodynamically stable being the monoclinic (α) one. Hexagonal (β) and orthorhombic (γ) are developed under specific crystallization conditions. Crystalline unit parameters [38, 39], as well as crystal layer thickness [17] can be found in the literature, but they depend on processing conditions and will not be discussed here. Table 10.1 recalls values of melting temperature of an infinite crystal (about 190 °C). However, the melting point of a commercial PP is close to 165 °C (it is found to be lower for PP) and can be lowered by the introduction of comonomers. PP copolymers with melting points as low as 148 °C are used in fibres technology. The PP amorphous phase is characterized by a glass transition temperature close to 0 °C.

The respective densities of amorphous and crystalline phase of PP are 0.850 and 0.936. The melting enthalpy ΔH_M of the 100% α -crystalline phase is given with some scatter in the literature, but the most frequently accepted value is 209 kJ kg⁻¹ [40], which is higher than that of the β -crystalline phase [33–36]. It is also still considered that ΔH_M for a 100% crystalline PP is higher for iPP than for sPP [30–31].

Its apolar character makes PP hydrophobic (water equilibrium concentration lower than 0.1%), not easily wettable or dyeable. In contrast, it is easily washable. The surface polarity can be improved by a wide variety of treatments generally consisting of superficial oxidation [41] or plasma treatment [42, 43].

Owing to its hydrocarbon structure, especially the presence of a tertiary



10.1 Polypropylene structure: repetitive unit (a), isotactic stereoisomer iPP (b) and syndiotactic stereoisomer unit sPP (c).

Table 10.1 Physicochemical properties of atactic, isotactic and syndiotactic PP [8–38]

	Atactic PP			Isotactic PP			Syndiotactic PP	
Density (g cm^{-3})	0.854–0.863		[8]	0.850 0.931–0.936 0.921–0.931	amorphous phase [9] α crystalline phase [9, 10] β crystalline phase [9, 10]		0.856 [11] 0.93 [11]	
Thermal expansion coefficient ($10^4 \text{ }^\circ\text{K}^{-1}$)	6.1–9.4	80–120 °C	[8]	1.4–1.5		[12]		
Glass transition temperature K	238–283		[13–15]	263–283	DSC	[15–17]	270–278	[18, 19]
Mark–Houwink parameters $K (\text{ml g}^{-1})$	2.7×10^{-4}	benzene (23 °C)	[20]	1.1×10^{-4}	decaline	[21]		
a (none)	0.71		[20]	0.80		[21]		
Solubility parameters ($\text{MPa}^{1/2}$)	15.14		[22]	15.11–18.8		[22, 23]		
Heat of fusion (J g^{-1})				138–209 113–170	α crystalline phase [24–31] β crystalline phase [33–37]		109–207	[29–31]
Melting temperature (K)				459–465	α crystalline phase	[22, 38]		

C—H bond, PP is relatively sensitive to thermal and photochemical oxidation. It cannot be processed, stored or used without stabilizers [44].

There is a wide variety of polymerization processes differing by the physical state of the monomer (gas or liquid) and the nature of catalysis (Ziegler–Natta, metallocene...) [45]. The polymerization conditions determine the degree of chain stereoregularity, the molecular weight distribution, the powder morphology and, finally, the comonomer content and its distribution into the chains.

10.3 Polypropylene (PP) fibre processing

There is also a wide variety of fibre processing methods for PP. Melt spinning is a common method in which fibres are extruded through a die and then drawn [46]. Two processes can be distinguished, depending on the crystallization rate: short spinning (fast crystallization) and long spinning (relatively slow crystallization). In long spinning, drawing is mostly possible from the molten state. In short spinning, drawing is mostly performed in the solid state. Using a second drawing stage in the solid state, it is possible to obtain very high strength fibres (620 MPa, e.g. 15 times the strength of PP samples). The relatively low melting point of PP allows nonwoven cloth to be made from staple PP fibres by welding them together without the aid of chemicals and this is interesting for certain applications, for instance in nappies.

Melt spinning requires a relatively low viscosity, e.g. a melt index typically higher than 10 dg min^{-1} [47]. Classical Ziegler–Natta PP grades cannot be processed at high spinning rates due to their wide molar mass distribution (MMD). In the 1980s, polymers with sharper MMD were obtained using controlled peroxide initiated thermal degradation [48]. At the end of the 20th century, metallocene catalysis allowed the polymer polydispersity to be controlled during its synthesis, leading to an increase in spinning rates and in fibre toughness [49, 50].

It is noteworthy that, compared with classical polar fibres-forming polymers such as polyamides or poly(ethylene terephthalate) (PET), PP must have higher average molar mass (typically $M_w > 100 \text{ kg mol}^{-1}$) to have good mechanical properties (see below). As a result, PP is more viscoelastic than polyamides and PET in the molten state, which conveys some advantages and drawbacks. An advantage is that the viscoelastic behaviour enables the creation of fibres of very small diameter (few micrometers) at very high rates. The drawback is that viscoelasticity is responsible for the shear rate dependence and possibly die resonance, e.g. a periodic diameter fluctuation, and melt fracture above a critical shear rate. These defects can be avoided with a rigorous control of rheological properties, which is only possible with a no less rigorous control of MMD.

Another common industrial method of PP fibres processing is the melt

blown process in which short fibres (3–7 mm) are blown at high temperature (50–100 °C above the melting point) and high rates (6000 m min⁻¹) leading to nonwoven clothes in which the cohesion results from the entanglement of fibrils. This process needs very high fluidity PP grades.

10.4 Initial tensile properties

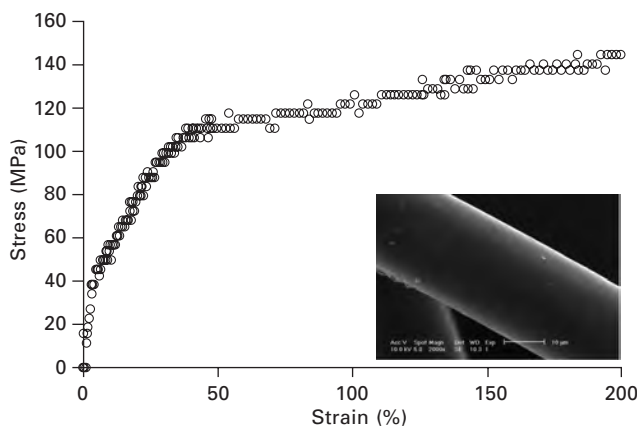
Usually, mechanical properties of fibres are evaluated by tensile testing (see Chapter 2). From this test, different mechanical properties can be assessed: Young's modulus, stress at yield and strain at break. Typical values [51] depending on draw ratio, are given in Table 10.2. These properties depend on the temperature and the deformation rate used for the test, PP molar mass, chain orientation and crystalline morphology. The latter characteristics are sharply dependent on the processing conditions [52]. As has been previously shown, there are several processing methods: gravity spinning, melt spinning and melt blowing. Furthermore, for each processing conditions, different parameters values as temperature, pressure, extrusion rate and draw ratio lead to different crystalline morphologies.

10.4.1 Stress–strain curve

In order to illustrate the mechanical behaviour of PP fibres, a stress–strain curve is shown in Fig. 10.2. This curve characterizes the mechanical behaviour of a PP geotextile fibre having a diameter close to 30 mm loaded with at a constant crosshead displacement rate of 50 mm min⁻¹ and using a 100 N cell. In the same manner as with isotropic PP samples, the initial part of the curve exhibits a pseudo-linear behaviour followed by a yield. This yield corresponds to the beginning of plastic deformation associated to a necking process. The necking process is often more diffuse than in isotropic PP samples so that no knee can be observed on the stress–strain curve. In this case, yield stress (σ_y) value can be assessed as the beginning of nonlinear behaviour.

Table 10.2 Tensile properties as a function of draw ratio for iPP and sPP having similar molar masses [51]

	Tensile modulus (GPa)		Tensile strength (MPa)		Strain at break (%)	
	iPP	sPP	iPP	sPP	iPP	sPP
Draw ratio $\lambda = 4$	3	0.8	200	130	150	100
Draw ratio $\lambda = 7$	6	1.7	400	280	50	50
Draw ratio $\lambda = 10$	15.5	–	600	–	20	50



10.2 Typical stress-strain curve for a PP fibre obtained by melt spinning (diameter of 30 μm).

10.4.2 Mechanical properties

Compared to iPP samples, the mechanical properties of fibres show higher Young's moduli (E) and yield stresses (σ_y) but lower strains to failure (ϵ_R). However, depending on processing methods and conditions, the Young's moduli of PP fibres can be quite different. For instance, the methods based on melt spinning and drawing under peculiar conditions (slow stretching in a tensile testing machine or in an oven) lead to elastic modulus values in the range from 10 to 22 GPa, whereas, by using solid state extrusion (hydrostatic extrusion, die drawing followed by slow stretching or spinline stress), elastic modulus values range from 17 to 20 GPa [53].

This increase of modulus is often attributed to a specific oriented morphology called shish-kebab. Indeed, for the melt spinning process for instance, macromolecules are highly extended prior to crystallization and the latter, when it occurs, does not change the macromolecular orientation. In these conditions, lamellar surfaces would be normal to the fibre direction leading to high modulus. According to this, many modelling approaches have been proposed to relate the elastic properties of crystalline phase to the elastic modulus of the PP fibre [54]. The crystalline phase and degree of orientation are responsible for the increase in yield stress: typically its value can reach up to 100 MPa compared with 27 MPa for iPP.

For ultra high molecular weight PP (UHMW-PP), a maximum modulus value of 40.4 GPa has been obtained by Matsuo *et al.* by using the gel-casting method [55]. This value approaches the theoretical crystal modulus of iPP (35–42 GPa) [56].

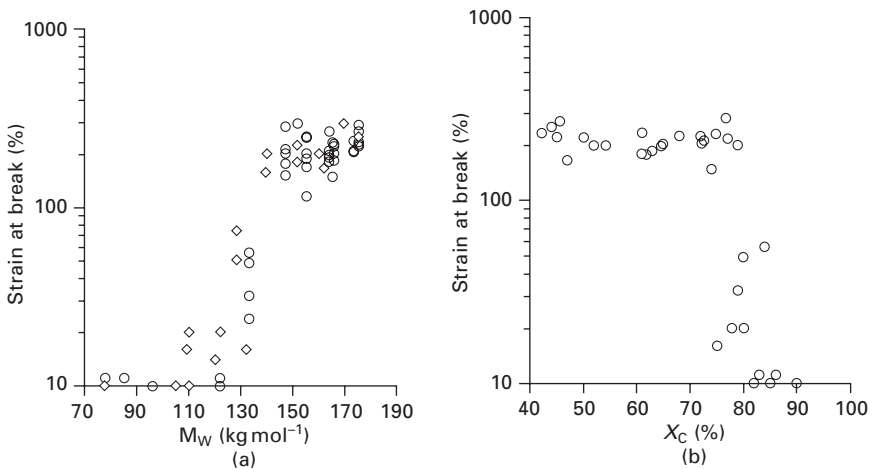
Finally, fibres of sPP display a rubber-like mechanical behaviour when fibres are submitted to successive elongation and relaxation cycles [57, 58].

This is the most important characteristic and unusual physical property for s-PP fibres. For the latter, the maximum achievable tensile modulus value is remarkably lower than for iPP, since the latter is characterized by higher crystal modulus, crystallinity ratio and drawability compared with the former. As a result, the maximum tensile modulus of oriented sPP is close to 3 GPa.

10.4.3 Fracture properties

Fracture properties of iPP fibres depend on such intrinsic parameters as molar mass, crystallinity ratio, morphology and orientation. This latter is linked to processing conditions especially draw ratio. This aspect has been extensively studied in the literature [21]. But these properties are also highly dependent on defects induced by the processing at the surface or in the core of the fibre. Classically, stress at break is close to 150 MPa and values of strain to failure range from 150 to 300%. An annealing process would lead to an increase in failure stress but to a decrease of strain to failure.

In the case of fibres made by melt spinning, it has been observed that strain to failure is determined by the spinline stress provided that the weight average molecular molar mass is higher than 180 kg mol^{-1} [59]. Below this critical value, fibres fail in a brittle manner with a strain at break close to 10% and without strain hardening. Figure 10.3(a) shows strain to failure as a function of weight average molar mass for fibres having different molar masses: below 150 kg mol^{-1} , fibres are brittle. It is noteworthy that a molar mass decrease is always accompanied by a crystallinity ratio increase (Fig. 10.3b) [60].



10.3 Strain at break as a function of weight average molar mass M_W (a) and as function of crystallinity ratio X_C (b).

Fracture properties, i.e. stress and strain and break, are often interpreted by using the tie molecule concept. Indeed, it has been common to consider that the fibre structure is based on 'microfibrils' or 'nanofibrils'. These fibrils are formed from shish-kebab structures as previously seen. In order to obtain good fracture properties, the crystalline regions have to be interconnected by chains or entangled chains through amorphous region, called 'tie molecules' [61]. In the case of melt spun fibres, it can be assumed that a lack of interconnections is responsible for brittle failure below the critical molar mass close to 150 kg mol^{-1} .

10.5 Fibre durability

10.5.1 Failure processes

Fibre failure can result from mechanical loading, from physical polymer-solvent interactions, or from chemical interaction between the polymer and reactive species (water, oxygen, etc.) present in the environment or from a combination of these cases. Mechanical failure can result from creep, fatigue or accidental overloading resulting from instance from earthquake in the case of geotextiles. Efficient rules for mechanical design are in principle available [62–64] to avoid anomalous mechanical failure.

Polymer-solvent physical interactions can considerably reduce the time to failure when the material is submitted meanwhile to mechanical loadings [65]. In the case of PP, however, polymer-solvent interactions are strongly limited by the apolar character of the polymer and by its crystallinity. It is well known that PP is soluble only at high temperature, i.e. practically in molten state, in a small number of aromatic solvents. PP fibres cannot be recommended in applications where they are submitted to mechanical loading in the presence of aromatic chlorinated solvents.

Chemical interactions between PP and reactive species present in the environment are sharply determined by the hydrocarbon structure of the polymer. This type of structure is totally unreactive with water and with most of the water soluble species: acids, bases, salts, except the case of oxidizing ones such as nitric acids, potassium permanganate, hydrogen peroxide, etc.

The only significant ageing process in PP is thus oxidation with the above-mentioned reactants, or simply with atmospheric oxygen. The remainder of this section will be devoted to oxidation and its consequences on mechanical behaviour of PP fibres.

10.5.2 Oxidation mechanisms

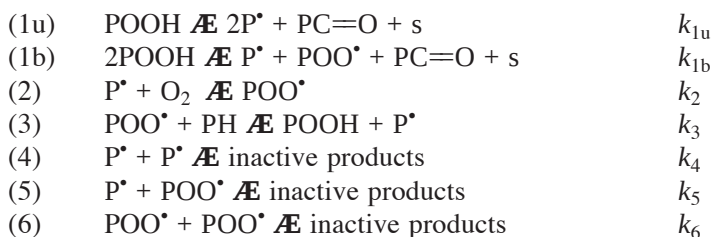
After the pioneering works of Semenov in the former USSR [66] and Bolland and Gee in England [67, 68], it was widely recognized that oxidation occurs

through a radical chain mechanism. Its main particularity is the formation of hydroperoxides (POOH) which decompose easily to give new radicals inducing thus a catastrophic auto-acceleration of the reaction. The propagation of the radical chain involves two steps: first the oxygen addition to an alkyl radical ($P^\bullet$) to give a peroxy radical ($POO^\bullet$) and second the abstraction of a hydrogen to the substrate to give a hydroperoxide and a new alkyl radical. The second step is at least one million times slower than the first one so that it plays a key role in the oxidation kinetics.

The PP monomer units contain a tertiary C—H bond that is especially reactive in hydrogen abstraction processes. It partially explains the relatively high sensitivity of the polymer to oxidation. Another very important characteristic of PP oxidation is that termination by bimolecular combination of peroxy radicals is not very efficient, that contributes to increase the oxidizability of the polymer.

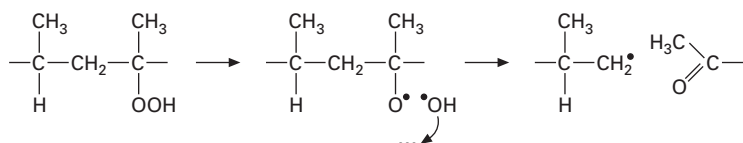
Hydroperoxide decomposition can be unimolecular (1u) or bimolecular (1b) and catalysed by transition metals (Ti, Cu, Fe, Cr, Co, etc.). In all the cases, it produces alkoxy radicals of which the peculiarity is to rearrange easily by β -scission (see Fig. 10.4).

As will be seen below, chain scission is the direct cause of embrittlement. Finally, most of the important features of PP oxidation can be predicted from a standard mechanistic scheme:

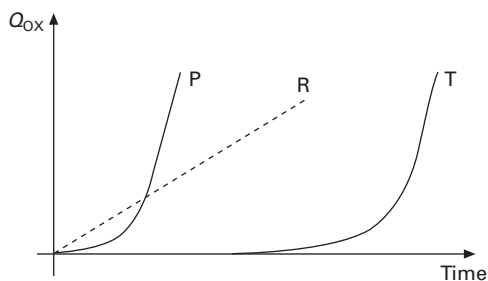


The kinetic behaviour depends essentially on initiation mode, as illustrated by Fig. 10.5.

In the case of radiochemical ageing at relatively high dose rate, initiation results essentially from polymer radiolysis. Hydroperoxide decomposition can be indeed neglected for short exposure times at low temperatures. In this case, oxidation proceeds at a constant rate.



10.4 Mechanism of hydroperoxide decomposition leading to carbonyl and chain scission.



10.5 Shape of oxidation kinetic curves (for instance Q_{OX} is the quantity of absorbed oxygen) in case of radiochemical (R), photochemical (P) and thermal (T) oxidation at low temperature, typically in solid state.

In the case of thermal ageing at low temperature, since k_{lu} is relatively low, the hydroperoxide concentration rapidly reaches a level at which bimolecular decomposition becomes predominant. In this case, oxidation kinetics displays an induction period followed by a catastrophic auto-acceleration. Whatever the chosen endlife criterion, lifetime is always of the order of the induction time.

In the case of photochemical ageing, with the commonly used light intensities, hydroperoxides react by the unimolecular mechanism with a k_{lu} value several orders of magnitude higher than for thermal ageing at the same temperature. As a result, induction time is reduced to zero and auto-acceleration is considerably less marked than in thermal ageing.

10.5.3 Oxidation-induced embrittlement

Embrittlement due to oxidative ageing results from the loss of polymer capacity to undergo plastic deformation. It occurs suddenly, which indicates the existence of a critical state separating ductile and brittle regime of deformation. The following most probable causal chain can be ascribed: oxidation $\rightarrow$ chain scission in the amorphous phase $\rightarrow$ molar mass decrease $\rightarrow$ easier chain disentanglements $\rightarrow$ chemical crystallization $\rightarrow$ embrittlement.

At the present state of our knowledge, it is difficult to choose between two embrittlement mechanisms: a purely micromechanical one in which the key factor would be a critical interlamellar distance l_a or a molecular mechanism in which the key factor would be a critical concentration of tie chains interconnecting crystalline lamellae. In both cases however, for a given starting morphology, this critical state corresponds to a critical value of the weight average molar mass: $M_w = M_c$. For PP, M_c is of the order of 200 kg mol^{-1} for quasi-isotropic samples and 150 kg mol^{-1} for fibres.

10.5.4 Stabilization

Since oxidation almost always results from a radical chain process with a relatively low initial rate and high initial kinetic chain length (number of propagation events per initiation event), it is possible to envisage efficient ways for its inhibition:

- Radical scavenging (i.e. chain interruption) by aromatic amines, hindered phenols or hindered amines of the tetramethylpiperidine type (hindered amine stabilizer – HALS).
- Decrease of the initiation rate by hydroperoxide destruction by non-radical way, using sulphides or phosphites, and suppression of eventual catalytic effect of metallic impurities using metal chelatants.
- In the specific case of photo-oxidation: decrease of the photo-initiation rate using UV absorbers (even if they are not very efficient in thin samples), pigments such as TiO_2 with adequate surface treatments (so as to avoid a deleterious photocatalytic effect) or quenchers to deactivate photo-excited states responsible for photo-initiation. Polyolefin stabilization has an abundant literature [69–76]. Very efficient blends, exploiting the synergistic effects between distinct stabilizer families, are commonly used.

10.5.5 Lifetime prediction methods

Unstabilized PP cannot be processed or even stored at ambient temperature for more than a few years, even in the dark. Considerably longer lifetimes can be obtained with adequately chosen stabilizer systems. Lifetimes in the order of 100 years are, for example, expected in the case of PP geotextiles used in civil engineering. The problem, for users, is to try to determine this lifetime from accelerated ageing tests. Two ways are possible: the empirical way in which one key condition is a good simulation of natural ageing conditions, and the scientific way in which the key condition is a good scientific model to represent ageing effects. The empirical way has largely predominated since the 1950s, despite its low reliability [77–80]. The emergence of numerical tools to solve very complex kinetic schemes has recently given an impulse to the scientific method [81]. In this latter case, accelerated ageing tests are not aimed at simulating natural ageing but only at identifying kinetic parameters of the model. It appears then that tests at variable oxygen pressures, which were rarely used in the past, are especially interesting [82].

10.6 Conclusions

As soon as the method for its stereospecific synthesis was discovered, half a century ago, polypropylene appeared to be a very interesting fibre-forming

polymer because of its low cost, easy processability, hydrophobicity and relatively high tenacity. Considerable worldwide efforts in the mean time have allowed the degree of stereoregularity to be better controlled and the molar mass distribution to be more sharply defined so reducing its susceptibility to oxidation, which is the weakest characteristic of PP. As the same time, new processing methods taking advantage of the peculiarities of the PP rheological behaviour, especially its high viscoelastic character in the molten state, have been created. As a result, a wide variety of PP fibres, offering a broad range of diameters, stiffnesses, tenacities, photo and thermal stabilities, etc., is now available on the market. It is thus not surprising to find PP fibres in an unequalled variety of applications, from geotextiles to nappies.

10.7 References

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Tensile fatigue of thermoplastic fibres

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Abstract: Nylon and polyester fibres find many uses which subject them to cyclic tensile loads. Under specific cyclic loading conditions these fibres can fail by a fatigue process, which can be identified from their fracture morphologies. Fatigue failure only occurs when the minimum cyclic load is below a threshold level. Fatigue failure can therefore be avoided by increasing the overall loading on the fibre. Fatigue crack initiation has been observed to be associated with small particles within the fibres which are added to aid the manufacturing process. Crack initiation becomes generalised throughout the fibres and failure morphologies more complex as the temperature increases.

Key words: thermoplastic fibres, fatigue, fracture morphologies, effect of structure, effect of temperature

11.1 Introduction

Fine diameter thermoplastic fibres, principally polyamide and polyester fibres, are used for traditional textile applications as well as in advanced technical structures. The failure of the fibres due to the repeated loading of the fabric or structure can, in some cases, have serious consequences and the mechanisms leading to unexpected fatigue failures have to be understood and taken into account for many applications.

The fibres which will be discussed in this chapter will be melt spun thermoplastic polyester (polyethylene terephthalate, PET, and polyethylene naphthalate, PEN) and nylon (polyamide 6 and 6.6) fibres. PET fibres are the most widely used and produced fibres throughout the world. Polyamide (PA) fibres were the first synthetic fibres to be produced and are the second most used and produced type of synthetic fibre. Both types of fibre find wide use in apparel and in high performance technical structures such as tyres, cables such as mooring ropes, parachute cords and belt drives. There are many other examples of course. The desirability of avoiding unexpected failure, due to fatigue, in the latter structures should be obvious. These types of fibres fail by fatigue under certain types of cyclic tensile loading. The distinctive fracture morphologies, which occur when fibres fail in fatigue, can be used for diagnostic purposes and allow an insight into the mechanisms controlling this behaviour. The understanding of the fatigue processes in these fibres

can suggest ways of reducing or eliminating the probability of unforeseen failures.

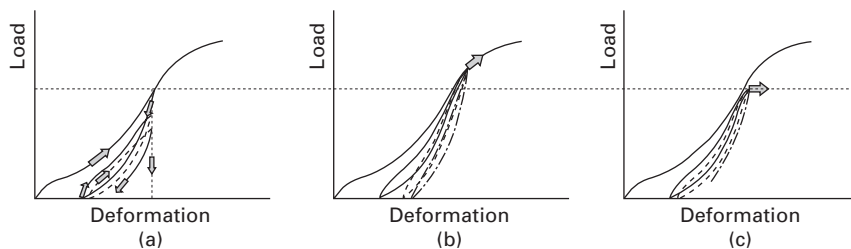
PET and PA fibres are drawn from the melt and the act of drawing aligns the fibre molecular structure, enhancing the fibres' properties and making them anisotropic. An undrawn fibre would have low rigidity and strength but high elongation. It would also show exaggerated plastic deformation which would not allow it to be used for most applications. The alignment of the molecular structure, during drawing, means that more of any load applied to the fibre is supported by molecules which are parallel to the fibre axis. This means that their deformation is controlled by the rigid first order covalent atomic bonds in the molecular skeleton backbone rather than more compliant secondary bonds, such as hydrogen and van der Waals forces, which determine intermolecular linkages. This process of making the fibre, from the molten polymer, does not lead to a perfect alignment of the molecular structure. The molecules are not all arranged parallel to the fibre axis. If this were the case, the rigidity of such fibres would be much greater. For this reason other manufacturing processes have been used to produce fibres with their macromolecules aligned much more parallel to the fibre axis and the results are truly amazing increases in mechanical and often heat resistance properties. This type of fibre is used for technical apparel and high performance fibre reinforced composites. These fibres are usually made by a liquid crystal process in which molecular alignment occurs intrinsically due to atomic bonding within, usually, a solution and the locally aligned molecules are then arranged naturally parallel to the fibre axis during passage through a spinneret. Fatigue can be an issue with these fibres but has been less studied than for thermoplastic fibres treated in this chapter. One reason is the high anisotropy of liquid crystal spun fibres which leads to extremely complex fibrillated failures, which are difficult to interpret. Such fibres are discussed in Chapter 12.

11.2 Principles of tensile fatigue

Fibres are long fine structures. Conventional thermoplastic fibres have diameters usually in the range of 5–40 mm and the technical fibres which will be discussed here have diameters around 10–25 mm. This can be compared with the diameter of a human hair, which is about 80 mm. Their fineness means that even the stiffest fibres in tension are very flexible in bending. The bending stiffness is a function of the reciprocal of the fibre diameter to the fourth power. Although there are ways of getting around the buckling of fibres in compression, most evaluation of fibres is in tension (Bunsell and Schwartz, 2000). The tensile fatigue evaluation of fibres presents particular difficulties as the tests are not quick to undertake and the fibre properties change throughout the test.

The study of the fatigue behaviour of materials, in general, began in earnest in the 1950s, due to major problems encountered by the first civilian jet airliners, although the failure of metal structures under cyclic loading had been encountered since the early days of the Industrial Revolution. Metals, however, have an elastic region in which a cyclic strain of the material induces a cyclic stress. The two are in phase as the material is in its elastic domain and this means that the standard way of fatigue testing metals is to apply a cyclic deformation which induces an in-phase cyclic load, related by Hooke's law, and neither is varied throughout the test. It can be noted that in most applications a material is subjected to a cyclic load, rather than a cyclic strain.

Attempts to evaluate the fatigue characteristics of organic fibres initially used the same type of test as was being used to test metals. That is to say, a cyclic deformation was applied to the fibre. As the fibres were not purely elastic, the plastic deformation produced on each cycle led to an ever increasing length, resulting in a reduced load amplitude experienced by the fibre and eventually its complete buckling. This type of simple extension cycling is shown schematically in Fig. 11.1(a). In this test the fibre either fails in the first cycle or not at all as the maximum loading levels quickly fall. A more complicated version of this test, designed to avoid the accumulation of plastic deformation, is accumulated extension cycling and the results are shown in Fig. 11.1(b). In this test the fibre is held vertically and the plastic deformation produced on each strain cycle is removed by opening the bottom grip. A small weight attached to the bottom end of the fibre, which passes through the lower grip, pulls the fibre taut. The grip closes and the fibre is taken through another strain cycle. This means that the volume of fibre being tested is progressively decreased so that although the maximum displacement imposed does not change, the fibre is progressively taken up its stress-strain curve. With this second type of test, the fibre ultimately fails but it can never be clear if the break is due to a fatigue process or just because the end of the stress-strain curve has been reached. The optimal way of conducting a fatigue test on an inelastic fibre is to monitor the maximum cyclic load and maintain it constant (Hearle, 1967). This requires a machine capable of adapting the loading conditions on the fibre as it creeps and deforms plastically as shown in Fig. 11.1(c) (Bunsell *et al.*, 1971). The fibre does continue to deform by creep but this can be evaluated by constant load tests. Failure by creep under cyclic conditions, during which the fibre is subjected to the maximum load for only a brief part of the cycle, would be expected to occur after longer times than that observed if the maximum cyclic load were applied constantly. It is this maximum load cycling technique which has revealed the fatigue process in organic fibres (Bunsell and Hearle, 1972).



11.1 Different ways of conducting tensile fatigue tests: (a) simple strain cycling; (b) cumulative extension cycling; (c) maximum load cycling. The grey arrow shows how the maximum cyclic load on the fibre varies throughout the test ((a) falling in, (b) increasing and (c) remaining constant).

11.3 The tensile and fatigue failures of thermoplastic textile fibres produced by melt spinning

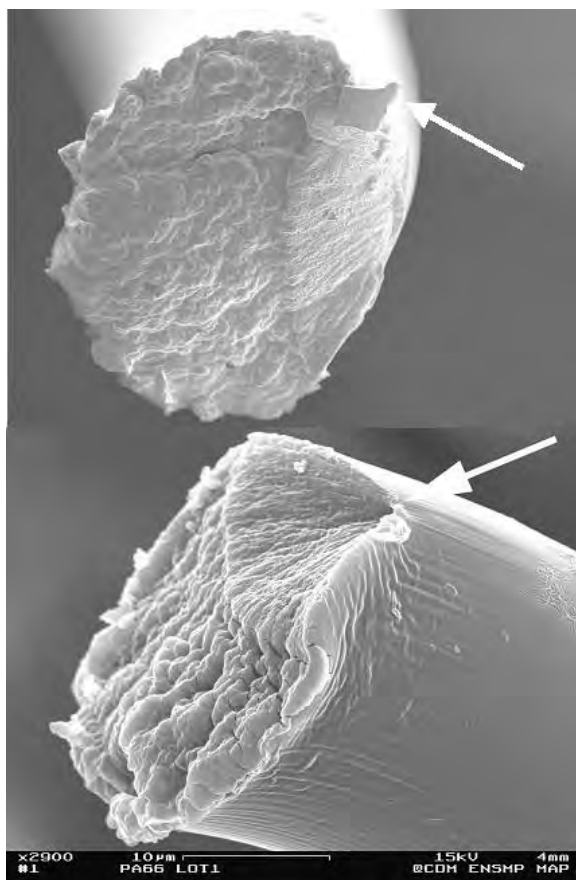
11.3.1 Fatigue fracture morphologies

The most striking feature of the fatigue failure of this class of fibres is their fracture morphology, which is very distinctive and different from tensile or creep failures. Figure 11.2 shows the complementary ends of a PA6.6 fibre broken in tension. The arrows show the region of crack initiation. Figure 11.3 shows a PA6.6 fibre undergoing tensile failure. The crack has initiated at the surface and can be seen to have developed across the diameter of the fibre. As the crack propagation is slow, or stable, the plastic deformation ahead of it results in its opening. When the remaining load-bearing cross-section can no longer support the load, the fibre fails, resulting in two similar complementary fracture surfaces.

The type of failure shown in Fig. 11.2 is characteristic of tensile and creep failure of PA6, PA6.6, PET and PEN fibres. There are two obvious regions of crack propagation (Hearle *et al.*, 2000). From the region of crack initiation there is a bevelled zone, resulting from a phase of slow crack growth during which the plastic deformation ahead of the crack leads to an opening of the crack. The load-bearing cross-section of the fibre is reduced by the advance of the crack and finally fails in an uncontrolled manner, resulting in a fracture zone normal to the fibre axis direction.

The fatigue failure of the same type of PA6.6 as shown in Fig. 11.2 but tested at 50 Hz at 21 °C is shown in Fig. 11.4. The choice of 50 Hz as a testing frequency was made as many technical structures such as tyres and parachute cords experience cyclic loadings at such a frequency.

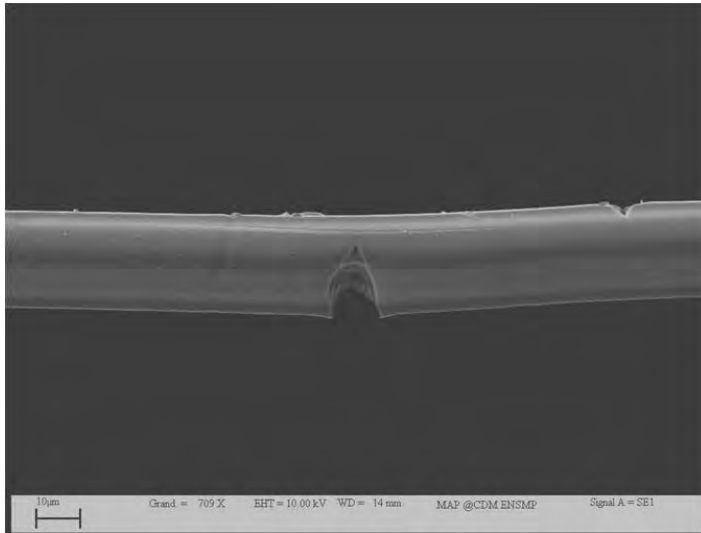
In fatigue, the difference in fracture morphology from that obtained in tension or creep is very clear. Crack initiation, as in tensile failure is in the region of the fibre surface but instead of progressing across the fibre, the



11.2 Complementary ends of a PA6.6 fibre broken in tension, at room temperature. The arrows show the region of crack initiation. The diameter of the fibre was $27\mu\text{m}$.

crack begins to run along the fibre at a slight angle to the axial direction. It can be seen from Fig. 11.4 that the break leaves a concave impression on the end from which the tongue of material is removed. This is different from the convex surface seen in the case of peeling of the fibre. When the load-bearing cross-section is sufficiently reduced, the PA fibre fails from the root of the fatigue crack by a tensile mechanism, as can be seen from the circled right image in Fig. 11.4, in which the two regions of tensile failure can be observed at the point of final failure.

Exactly similar tensile and fatigue behaviours are seen with PA6 fibres with indistinguishable fracture morphologies seen in both types of nylon fibre. This is a remarkable feature of the tensile fatigue of these thermoplastic fibres that the angle of fatigue crack penetration seems to be common amongst the



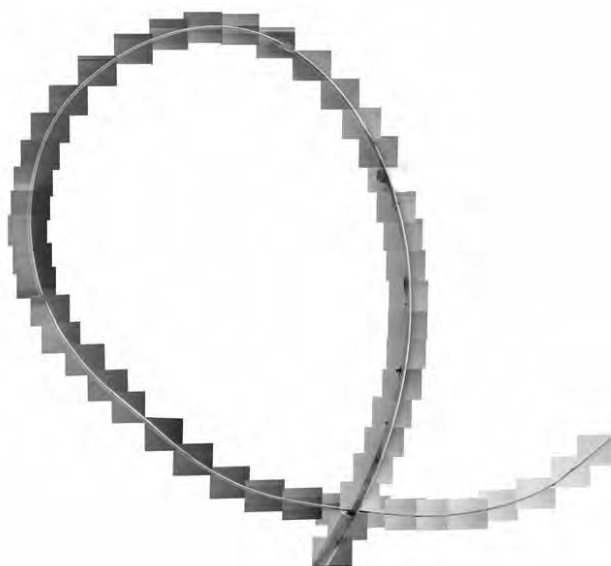
11.3 Complementary ends of a PA6.6-A fibre broken in fatigue, at room temperature, after cycling from zero load to 80% of simple tensile strength at 50 Hz.



11.4 The tongue end of a PET fibre broken at room temperature at 50 Hz revealing the very long crack development before failure. The diameter of the fibre was 18 μm and the length of the crack was 2.4 mm.

polyamide fibres and independent of draw ratio. The angle is different, as we shall see, from that observed with the polyesters, both PET and PEN, which themselves share a common type of fatigue crack growth. The polyamide and the polyester fibres share many characteristics in their fatigue behaviour but the striking differences between the angles of fatigue crack penetration into the fibre must reflect some intrinsic difference, perhaps at the level of the molecular structure or morphology. This has yet to be fully understood.

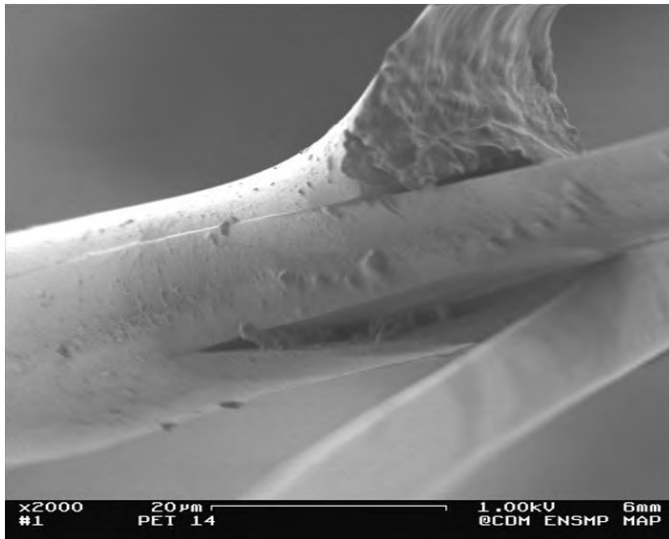
Analogous fatigue behaviour, at room temperature, to that observed with polyamide fibres is seen with polyester (PET and PEN) fibres both in tension and fatigue; although, as mentioned above, some differences, in the angle of crack penetration into the fibre and also final failure, occur in the latter cases. The failures of PET fibres in tension or creep give very similar fracture morphologies to that shown for PA fibres in Fig. 11.2. In room temperature fatigue, the same scenario of initiation near the surface followed by propagation along the fibre, gradually reducing the load-bearing cross-section is again observed. However the angle of propagation is smaller than in the PA fibres, leading to a longer crack before the load-bearing section is sufficiently reduced to cause failure, as can be seen in Fig. 11.5, which shows a highly drawn technical PET fibre of 18 mm diameter which has failed in fatigue. The final failure stage of a PET fibre, which breaks in fatigue, occurs behind the fatigue crack tip by a creep process. The initiation of the final creep failure phase does not occur from the fatigue fracture surface but



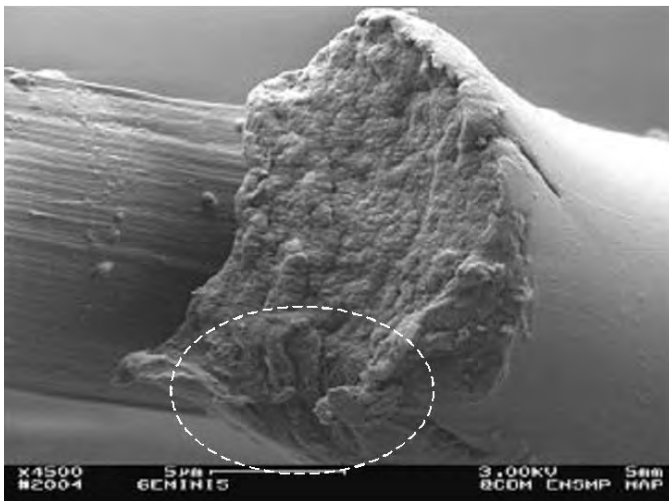
11.5 Final failure by fatigue of a PET fibre occurs behind the fatigue crack tip by a creep process.

from near the apparently undamaged fibre surface, as shown in Figs 11.6 and 11.7.

The failures of PEN fibres in tension and fatigue seem identical to those



11.6 The final failure stage of room temperature fatigue failure in PET fibres occurs from the surface of the fibres, as shown circled, and not from the fatigue fracture surface, as in PA fibres.



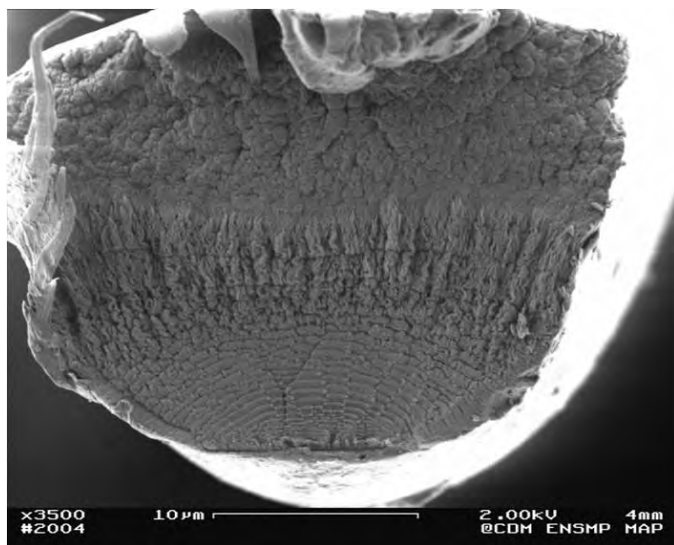
11.7 Striations showing step by step advancement of a fatigue crack in a PEN fibre subjected to loading at 50 Hz at room temperature leading to a superficially creep type failure morphology (Lechat *et al.*, 2006).

of PET fibres and the same long breaks are seen under cyclic loading which leads to fatigue (Lechat *et al.*, 2006). However the PEN fibres do show a mechanism, which may exist in PA and PET fibres but is less easily observed in these latter fibres. Under certain cyclic loading conditions PEN fibres fail with an apparent creep fracture morphology; however, a closer inspection of the slow crack growth zones reveal that a step by step growth of the crack has occurred, shown as a series of striations (Lechat *et al.*, 2006). The striations can be seen in Fig. 11.8.

Close inspection of fracture morphologies of PET fibres, originally interpreted as being due to creep under cyclic loading conditions has revealed that faint striations, similar to those seen in PEN fibres, can sometimes be observed. It is not known why the striations are so much more obvious in PEN fibres but their identification suggests the possibility of another type of fatigue crack growth in fibres. Another explanation would be that the striations are due to arrested slow tensile cracks which stop as the load falls, due to the cyclic form of loading, only to continue propagation at the next load cycle. Fatigue tests at varying frequencies would allow a fuller understanding of this type of failure but have yet to be carried out.

11.3.2 Loading conditions leading to fatigue failure

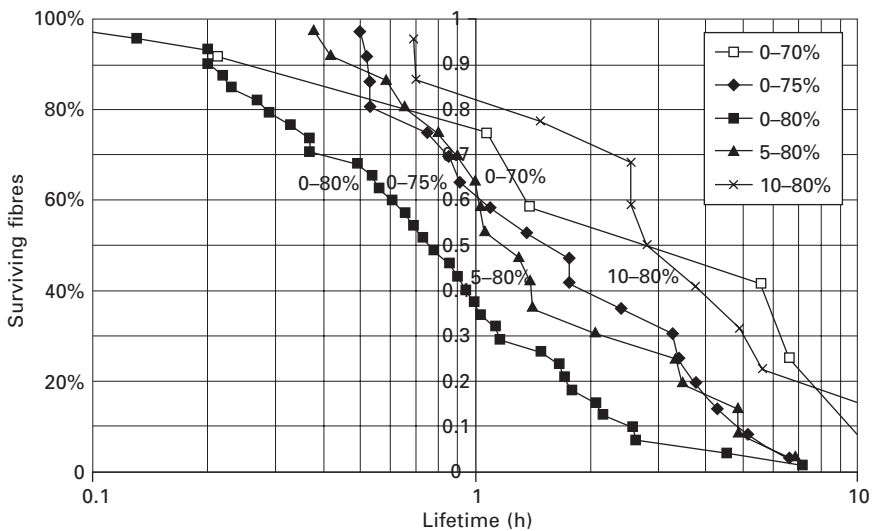
There are loading criteria which must be fulfilled if the fibres are to fail by fatigue. It seems likely that the fibres have to be subjected to a certain cyclic



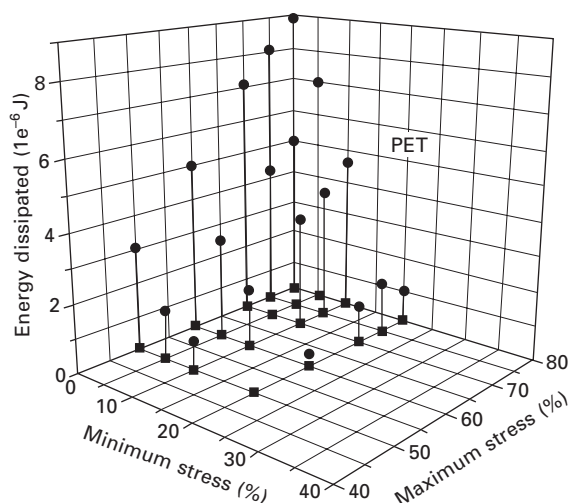
11.8 The survival graphs of PET fibres subjected to different maximum and minimum cyclic loads. The median lifetime is defined as that which produces 50% survival rates (Le Clerc *et al.*, 2006a).

load amplitude for fatigue failure to occur although a minimum amplitude level has not been determined. However, what is clear in all of the fibres so far discussed is that the minimum cyclic load has to be below a certain level, but not necessarily zero, for fatigue failure to occur. Figure 11.9 shows the effects of increasing the maximum cyclic load and also on increasing the minimum load on PET fibres subjected to fatigue loading at 50% at room temperature. It can be seen that increasing the maximum load, from 70% of simple tensile breaking load to 80%, reduces median lifetimes, as would be expected. However, if the maximum load is kept at 80%, increasing the minimum load from 0 to 10% of breaking load increases the median lifetime to the same as when the fibre is cyclically loaded from 0 to 70% of breaking load (Le Clerc *et al.*, 2006a).

The loading levels shown in Fig. 11.9 are rather high and have been used so as to obtain failures in reasonable times. The fatigue process has been seen to be related to the internal damping which occurs during cycling and Fig. 11.10 shows how this energy dissipation is affected by changes of both the minimum and the maximum load levels (Le Clerc *et al.*, 2006a). It can be seen that, for any given loading condition, as the minimum stress is increased the dissipated energy falls quickly but as the maximum stress is reduced the dissipated reduces much less quickly. This suggests that although there is a minimum load cut off level above which fatigue is inhibited, reducing the maximum stress only increases lifetimes but does not prevent ultimate fatigue



11.9 The survival graphs of PET fibres subjected to different maximum and minimum cyclic loads. The median lifetime is defined as that which produces 50% survival rates (Le Clerc *et al.*, 2006a).



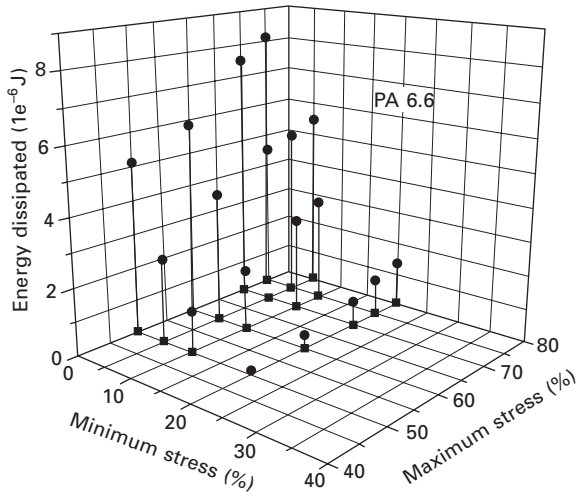
11.10 Energy dissipation during cyclic loading of PET fibres as the minimum and maximum stresses are varied (Le Clerc *et al.*, 2006b).

failure. Similar effects of changing loading parameters are also observed when testing PA fibres, as is shown in Fig. 11.11.

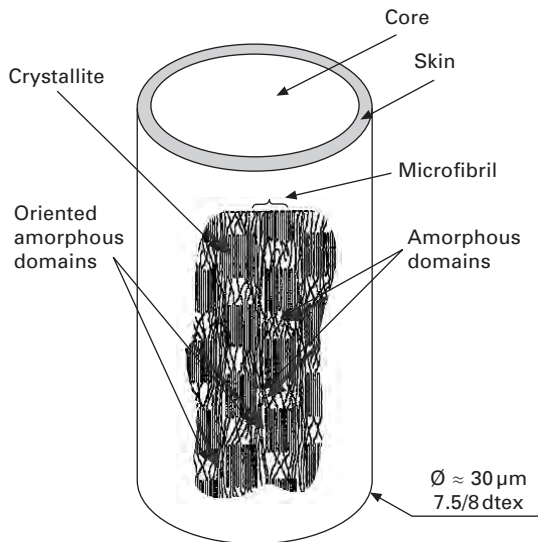
11.4 Mechanisms involved in fibre fatigue

The long fatigue cracks developed in the fibres which have so far been described are a reflection of the anisotropy of their molecular structures, although the distinctive angles of penetration seen between the two main families of fibres, PET and PA, are not fully understood. It is likely that this angle is related to the long periods of the molecular morphology found in each type of fibre. The structure of a fibre is complex, as is shown schematically for a PA6.6 fibre (Fig. 11.12). The structure of a PET fibre is thought to be very similar although perhaps showing greater groupings of the nanofibrils into larger fibrils, which may explain the longer breaks observed in fatigue.

These fibres are spun and drawn from the melt at very high speeds, 3000–7000 m/min. On leaving the spinneret the material is near its melting point, around 260 °C and is quickly cooled. Cooling is most intense at the surface of the fibre, which is the region which first solidifies. Shortly afterwards, the core of the fibre also cools and contracts. This results in residual stresses across the fibre section with the surface being put into compression with respect to the core. The residual stresses have been measured by Raman spectroscopy and can be very significant (Marcellan *et al.*, 2004). Cooling also produces a skin which can be observed by transmission optical microscopy and on scanning electron micrographs of fracture surfaces. At the molecular



11.11 Energy dissipation during cyclic loading of PET fibres as the minimum and maximum stresses are varied (Le Clerc *et al.*, 2006b).

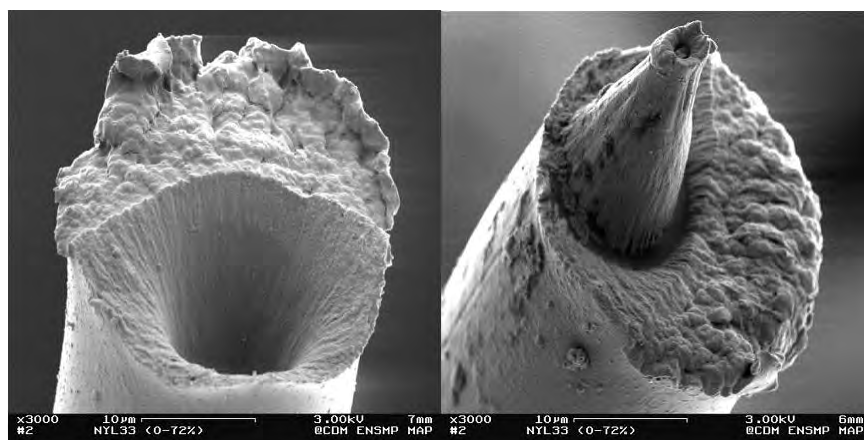


11.12 Macro and nano-structure of a PA 6.6 fibre (Marcellan *et al.*, 2004).

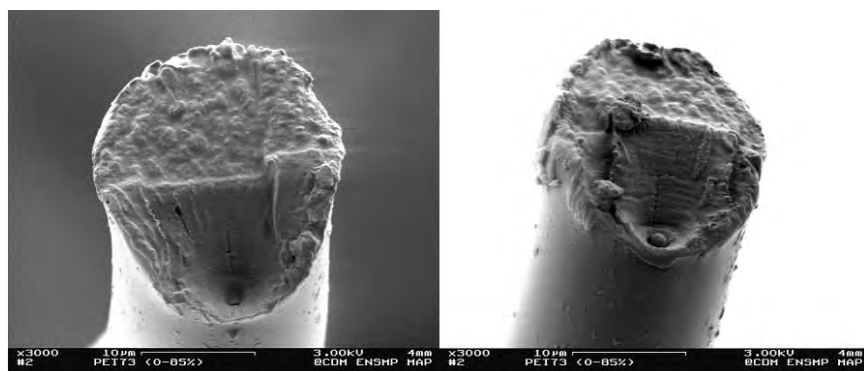
level the macromolecules are generally thought as being folded in compact crystalline regions, making the structure semicrystalline. The molecular structure is arranged in fibrils and possibly bundles of fibrils which must influence fatigue crack growth.

The fibres also contain materials other than the polymer. These are added to the polymer before extrusion and drawing for a variety of reasons. For

example, antimony is added as a catalyst to aid polymerisation in PET, and bromine is added, often carried on flake glass, as an antioxidant or flame retardant material, in PA. These small inclusions are usually less than 1mm in size but they are very significant in initiating crack growth in fatigue or possibly even under simple tensile or creep loading. Occasionally large particles can initiate failure from within the fibres when tested at room temperature. In this case the failure morphologies are conical, as can be seen in Fig. 11.13 (Herrera Ramirez and Bunsell, 2005, 2006). Figure 11.14 reveals a particle, which has been identified as antimony, still in place in one



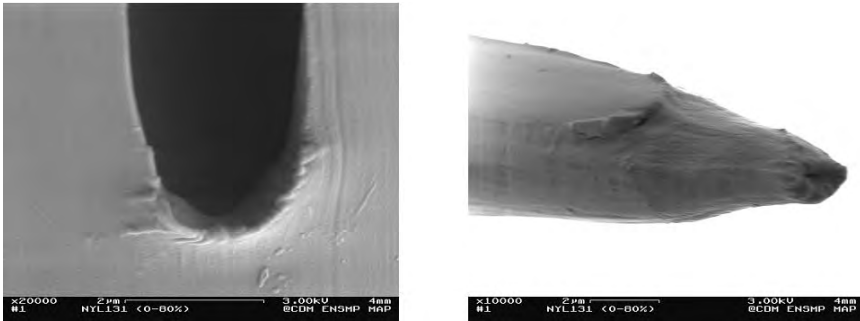
11.13 Both broken ends of a PA 6.6 fibre broken at room temperature in fatigue at 50Hz showing crack initiation inside the fibre. The small crater at the tip of the cone reveals the origin of the crack as an inclusion (Herrera Ramirez and Bunsell, 2006).



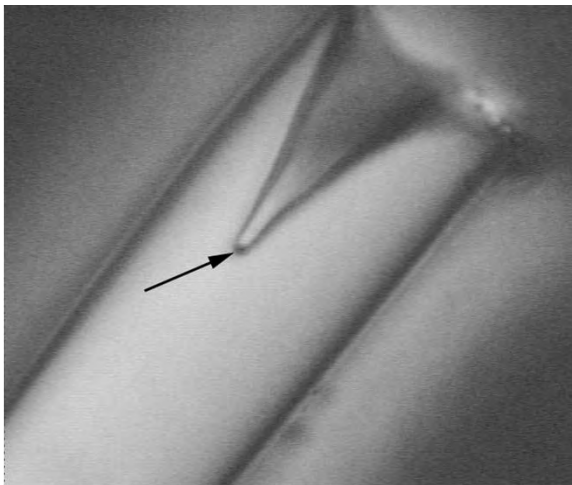
11.14 Both ends of a PET fibre, showing a classical tensile or creep fracture morphology, the crack having been initiated by an antimony particle of about 1µm in size (Herrera Ramirez and Bunsell, 2006).

of the two complementary fracture surfaces of a PET broken apparently in creep. Figure 11.15 shows the tip of the tongue obtained after the fatigue of a PA6.6 fibre together with the complementary initiation point. The break has clearly been initiated just under the fibre surface by a particle.

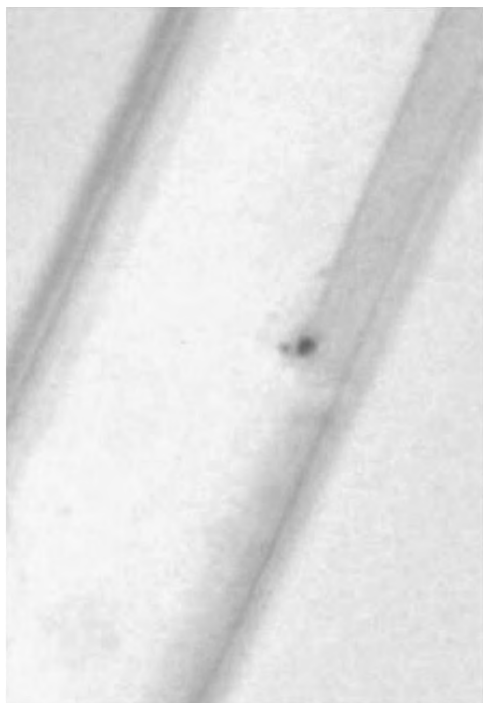
An examination of the fibres before testing reveals the presence of the particles and there seems always to be a particle or several particles in the initiation regions of fatigue cracks (Le Clerc *et al.*, 2006b). Figures 11.16 and 11.17 show such particles at the crack initiation point in, respectively, a PA6.6 fibre and a PET fibre, which had failed in fatigue at room temperature.



11.15 Complementary initiation points of a fatigue break of a PA 6.6 fibre showing that the initiation was by a particle which has left a crater in the tongue end of the break (Herrera Ramirez and Bunsell, 2006).



11.16 A particle revealed by transmission optical microscopy at the point of initiation of a conical fatigue crack in a PA6.6 fibre tested at room temperature.

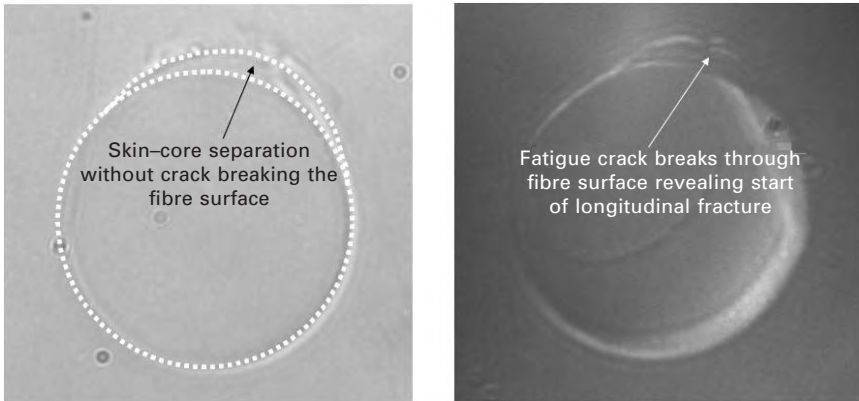


11.17 A particle is shown, by transmission optical microscopy, at the crack initiation point in a PET which has failed in fatigue at room temperature.

At room temperature, it is usually only the particles situated at the interface between the fibre skin and the core of the fibre, about 1 mm under the surface, which initiate cracks. Clearly the interface represents a weakened boundary within the fibre and the presence of these particles further weakens the fibre. The polymer, when drawn from the melt, undergoes considerable extension but the hard inclusions do not. This results in a region before and after each particle in which the polymer experience different deformation from that of the rest of the fibre. This must create a weakened zone, which when it is at the skin–core boundary can initiate fatigue cracks and possibly other types of failure.

Figure 11.18 shows two successive sections of the initiation region in a PA6.6 fibre. The presence of a particle at the skin–core interface initially induces a debonding, which may be visible on the fibre surface by the presence of some irregularity. The skin is then broken and this is seen as the beginning of the longitudinal fatigue crack.

It should be noted that surface damage or irregularities are not the causes of the crack initiation but rather the disturbance, inside the fibre, due to the



11.18 Microtomed sections of the initiation region of a fatigue crack, obtained at 21°C and 50% rh, in a PA6.6 fibre of 26 µm in diameter, revealing that initially the skin becomes separated from the core (left) and then the fracture breaks through the skin to appear as the initiation point of the longitudinal fatigue crack.

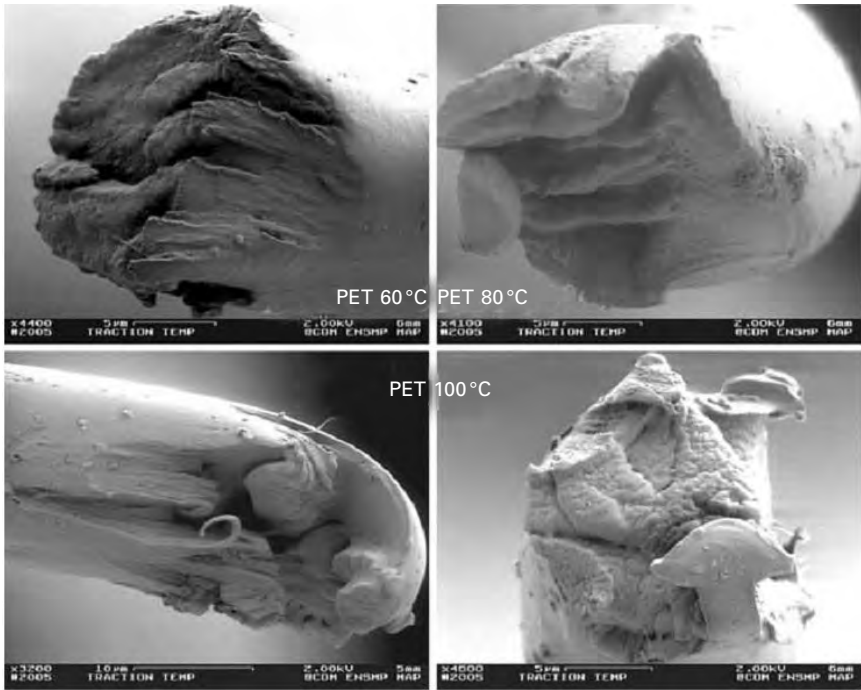
presence of a particle. When the fatigue crack has begun to propagate, its path can be influenced by other particles and it can be seen to be deviated so as to pass preferentially through regions near particles.

11.5 Tensile and fatigue failure at elevated temperatures and in structures

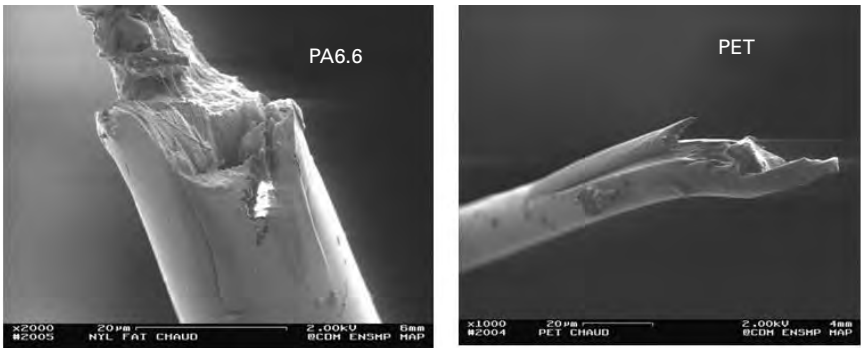
The appearance of the fracture morphologies of PA or PET fibres is seen to change as the temperature of the environment in which they are tested is increased. In tensile tests, the fracture morphologies become less crisp and sometimes more complex, as is shown in Fig. 11.19.

Around the glass transition temperature (T_g) the fatigue fracture morphologies of both PA and PET fibres show two distinctive types of failure. The familiar long fatigue fractures found at room temperature are evident but increasingly, as the temperature rises, another complex, truncated fatigue morphology, becomes the dominant feature of the fibre breaks, as shown in Fig. 11.20. Above T_g only the truncated fatigue breaks are found.

These types of fracture morphologies are also found in fibre bundles which are cycled at 50 Hz at room temperature. The temperature of the bundles has been found to increase above T_g due to the poor heat dissipation of the fibres so that even if the surrounding environment is at room temperature the fibres inside the bundle experience large increases in temperature and fail by the truncated fatigue process (Le Clerc *et al.*, 2006a). For the same reason these breaks have also been observed with fibres removed from rubber which



11.19 The tensile fracture morphologies of the fibres become more rounded and complex with increasing temperature, as is illustrated here with PET fibres.



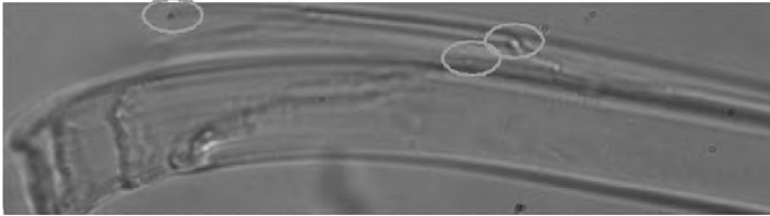
11.20 Examples of high temperature fatigue breaks found in PA6.6 and PET.

had been reinforced with PET and PA6.6 fibres and subjected to fatigue tests.

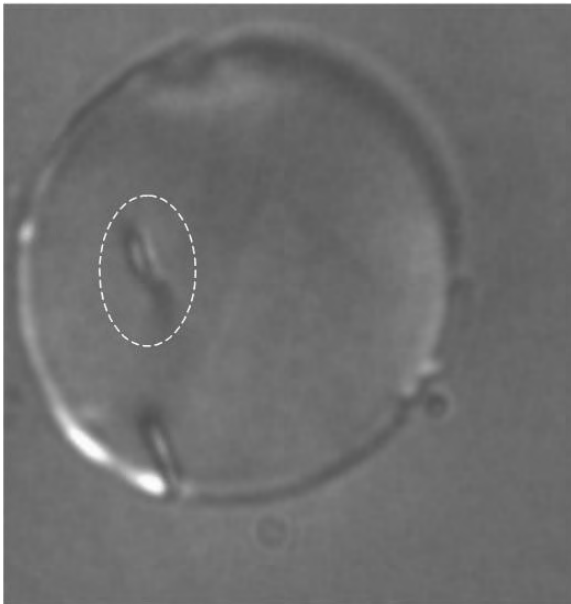
An examination of these complex breaks by transmission optical microscopy reveals that multiple breaks are initiated at high temperatures and throughout the body of the fibre. Figure 11.21 shows such a micrograph which again

reveals that crack initiation is associated with the presence of particles. At higher temperatures however, the fractures can be initiated throughout the volume of the fibre. Figure 11.22 shows a section of a PET fibre fatigued at 120°C and reveals an internal crack which, successive microtomed sections show, does not exit at the fibre surface (Le Clerc *et al.*, 2007).

The processes involved are an extension of the mechanisms seen at room temperature as initial damage is still seen at the fibre–core interface but the presence of particles within the body of the fibre initiates additional crack propagation. It has been seen that these internal cracks do not necessarily exit



11.21 Optical micrograph of a truncated fatigue fracture of a PET fibre, tested at 80°C, revealing several inclusions associated with the break.



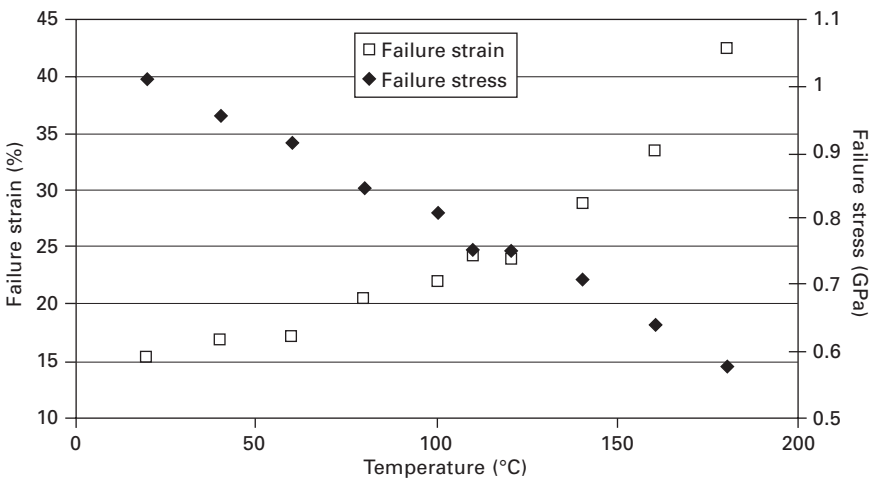
11.22 At temperatures around T_g and above a majority of fatigue breaks in PET and PA6.6 show complex truncated fatigue breaks. Some cracks can be seen to occur inside the fibre and do not exit at the surface (Le Clerc *et al.*, 2007).

at the fibre surface but clearly weaken the fibre. That the cracks do not reach the fibre surface means that there is no significant shear stress generated at the crack tip so that propagation along the fibre is limited. This explains the shorter conical breaks seen by Herrera-Ralmirez and Bunsell (2005, 2006). As has been demonstrated it is likely that several independent cracks can be initiated within any given length of fibre. Eventually these cracks coalesce and the complex truncated fatigue break occurs.

It seems likely that the increased temperature reduces transversal bonds between microfibrils making up the fibres so that the weak interface, provided by the skin–core boundary, is no longer unique and failure can be initiated throughout the body of the fibre encouraged by the presence of inclusions.

The truncated fatigue breaks observed in this study resemble exactly the fibre breaks taken from fatigued composite disk specimens consisting of the fibres embedded in a rubber matrix, as reported by Yabuki *et al.* (1986), Winkler (1991) and Naskar and Mukherjee (2004). It is clear that in this type of test, the fibres are subjected to large temperature increases due to internal damping and the poor heat transfer properties of the fibres and the rubber. The appearance of the fatigue breaks is then that of the truncated fatigue morphologies rather than those observed with single fibres tested at room temperature, for which heat exchange with the surrounding environment has been calculated to be of the order of only several degrees Celsius.

The simple tensile failure stress and strain to failure of the PET fibres tested in fatigue vary as shown in Fig. 11.23. It can be seen that the failure stress is markedly different at 80 and 120 °C from that at room temperature.

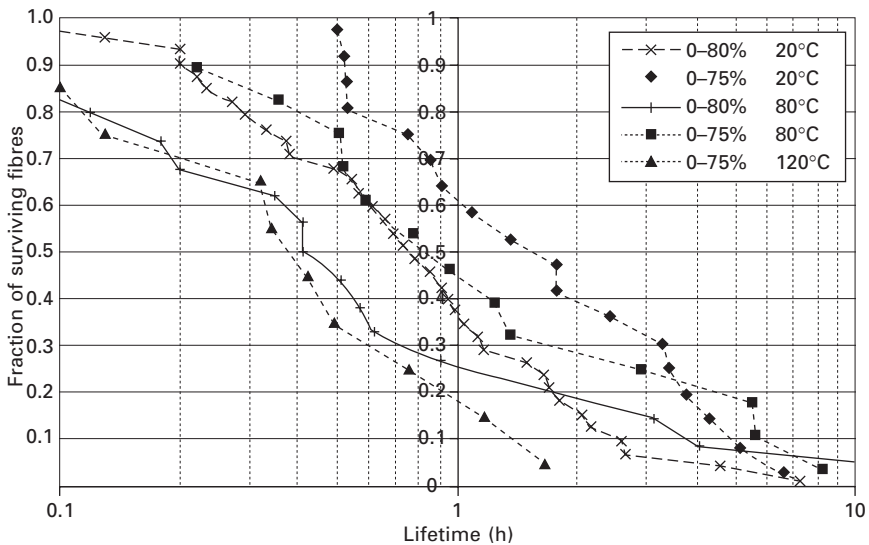


11.23 The failure strains and stresses of PET fibres as a function of temperature (Le Clerc *et al.*, 2006a).

This can be of great importance if the fibres are thought to be at a lower temperature but because of internal heating, and poor heat dissipation, which may occur in fibre structures, they are really at a much higher temperature. In this case the fibres can be more susceptible to the fatigue process than would be the case if they were at lower temperatures. It can also be seen from Fig. 11.23 that the strain behaviour of the fibre also varies with temperature but this is of lesser importance in the fatigue process.

These observations should be borne in mind when examining the fatigue results shown in Fig. 11.24 for which the percentages given are those of the maximum cyclic load compared with the simple tensile breaking load at that temperature. It should be noticed that the lifetimes decrease with temperature, although raising the minimum load is still found to increase lifetimes at any given temperature. The principal reason why lifetimes are reduced is that the final failure process in the fatigue of PET fibres is governed by the creep of the reduced load-bearing section of the fibre. Creep is thermoactivated and its rate is increased with temperature.

Truncated fatigue failures have been observed at room temperature in PA6.6 fibres which had been immersed in hot water and then tested at room temperature (Nasri *et al.*, 2002). Significantly, these fibres absorb water and as they do the T_g falls and can fall below room temperature. In this case it seems that the fibres were above their glass transition temperature and the fatigue failure resembled those obtained at high temperatures.



11.24 Fatigue lifetimes of PET fibres as a function of temperature and stress level (Le Clerc *et al.*, 2006a).

11.6 Conclusions

The most widely used and produced organic fibres, polyester and nylon fibres, fail by a tensile fatigue process which produces a distinctive type of fracture morphology, very different from that obtained with other types of loading. Fatigue failures require sufficiently large cyclic load amplitudes but a necessary criterion is that the minimum cyclic load must be lower than a critical load threshold. The mechanisms which control this behaviour are complex and the macrostructures of the fibres, which have been shown to have skin-core structures, are important in the initiation of fatigue breaks, at room temperature. The role of small, hard inclusions in the fibres has been shown to determine the point of initiation of the fatigue cracks which then run along the fibre, gradually reducing the load-bearing cross-section until failure occurs. The angle of penetration of the fatigue cracks is common to the polyester fibres and seemingly independent of draw ratio. This angle is smaller than that seen with fatigued PA fibres and leads to longer fatigue cracks. At higher temperatures the crack initiation is found to occur at inclusions throughout the thickness of the fibre. This produces truncated failures similar to those found when the fibres in reinforced rubber are examined after fatigue tests which lead to failure of the composite.

11.7 Acknowledgements

This chapter refers to works in a number of research establishments and countries but could not have been written without the contributions of a considerable number of research students who have worked with the author of this chapter. Some of these students are mentioned in the references below but by no means all. Thanks must go to all of them for throwing light on a fascinating and difficult subject.

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Liquid crystalline organic fibres and their mechanical behaviour

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Abstract: Synthetic fibres based on liquid crystalline polymers can be divided into three main categories: aromatic polyamides, aromatic heterocycles and aromatic copolyesters. In this chapter, commercially available liquid crystalline fibres are described in terms of their polymer synthesis, production techniques (fibre spinning, heat treatments) and final properties (thermal, mechanical, chemical and environmental stabilities). Finally some industrially relevant applications of liquid crystalline synthetic fibres are presented.

Key words: liquid crystalline fibres, aromatic polyamides, aromatic heterocycles, aromatic copolyesters, mechanical properties.

12.1 Introduction

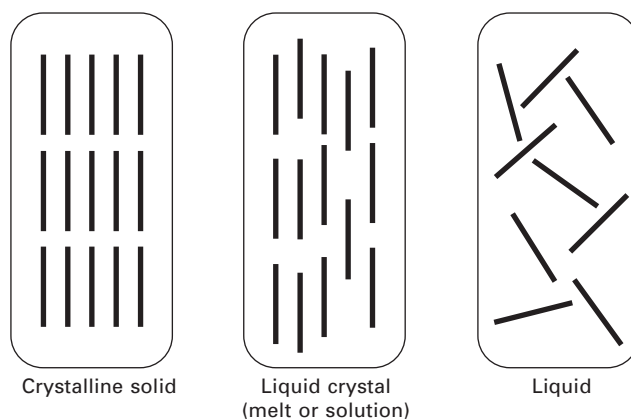
Modern fibres based on liquid crystalline (LC) polymers manifest outstanding tensile mechanical properties. They can reach a tensile modulus of up to 300 GPa and tensile strength of up to about 6 GPa (Table 12.1). Moreover, they are characterized by low density, in the range of 1.38–1.56 g/cm³, which implies impressive specific properties.

First predictions of the existence of liquid crystals date back to the 1950s (Onsager, 1949; Flory, 1956). As depicted in Fig. 12.1, LC phases display some features common to a three-dimensionally ordered crystal, and some others typical of a disordered isotropic fluid (Ciferri and War 1979; Tadokoro, 1979; Blumstein, 1985; Nakajima, 1994; Hearle, 2001; Wang and Zhou, 2004; Sperling, 2006). Crystalline solids are ordered in three dimensions, while liquids are entirely disordered: liquid crystals lie between these two extreme cases, i.e. they exhibit long-range order in one or two dimensions, but not in all three. From a general point of view, both small molecules and macromolecules may exhibit LC behaviour. The molecular asymmetry is the most important requirement for a macromolecule in order to originate the various possible LC phases (called mesophases). This asymmetry can be manifested either as rods of axial ratio greater than about 3, or thin platelets of biaxial order. Another fundamental requirement is a sufficiently high chain

Table 12.1 Tensile properties of representative liquid crystalline, inorganic and conventional organic fibres (Technical Datasheets; Kozey *et al.*, 1995)

Fibre/trademark	Company	Density (g/cm ³)	Tensile modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
Kevlar 29	DuPont	1.44	71	2.9	3.6
Kevlar 49	DuPont	1.44	112	3.0	2.4
Kevlar 149	DuPont	1.45	143	2.3	1.5
Nomex	DuPont	1.38	11.6	0.59	28.0
Twaron	Teijin Aramid	1.44	70	3.2	3.3
Twaron HM	Teijin Aramid	1.45	103	2.8	2.5
Technora	Teijin Aramid	1.39	73	3.4	4.6
Teijinconex	Teijin Aramid	1.38	7.9–9.7	0.61–0.67	40.0
Teijinconex HT	Teijin Aramid	1.38	11.6–12.2	0.73–0.85	25.0
Armos	Ltd Lirsot	1.43	150–160	4.5–5.5	2.5–3.5
SVM	ASRIPF	1.43	135–150	4.0–4.5	3.0–3.5
Terlon	ASRIPF	1.46	130–160	2.5–3.5	2.5–3
PBI	PBI Perf. Products	1.40	5.6	0.4	30
PBZT		1.58	200–300	2.6–3.9	1.5–3.5
Zylon AS (PBO)	Toyobo	1.54	180	5.8	3.5
Zylon HM (PBO)	Toyobo	1.56	270	5.8	2.5
M5 (PIPD)	Magellan	1.70	330	5.5	1.5
Vectran NT/ Vectran M	Kuraray	1.40	52	1.1	2.0
Vectran HT/ Vectran HS	Kuraray	1.41	75	3.2	3.3
Vectran UM	Kuraray	1.40	103	3.0	n.a.
Nylon (polyamide)	DuPont	1.14	5.5	1.0	18.3
Dacron (polyester)	DuPont	1.38	13.8	1.1	14.5
Spectra 900 (UHMWPE)	Honeywell	0.97	70	2.4	4.0
Spectra 1000 (UHMWPE)	Honeywell	0.97	105	3.1	2.5
E-glass		2.55	72	1.5–3.0	1.8–3.2
S-glass		2.5	87	3.5	4.0
S2-glass		2.49	86	4.0	5.4
Carbon		1.8–2.0	140–820	1.4–7.0	0.4–2.1
Steel		7.86	210	0.34–2.8	>1.0

stiffness, that could be evaluated by a persistence length, formally defined as the length over which correlations in the direction of the tangent of the macromolecule are lost. While macromolecules in conventional polymers have a persistence length in the order of some nanometres (for example, 0.58 nm for polyethylene and 1.0 nm for flexible aliphatic polyamide 6,6), macromolecules in liquid crystalline polymers (LCPs) can reach several tens of nanometres. Aromatic polyamides have persistence lengths in the order of 20–40 nm (Adams *et al.*, 2003), aromatic heterocycles in the order of

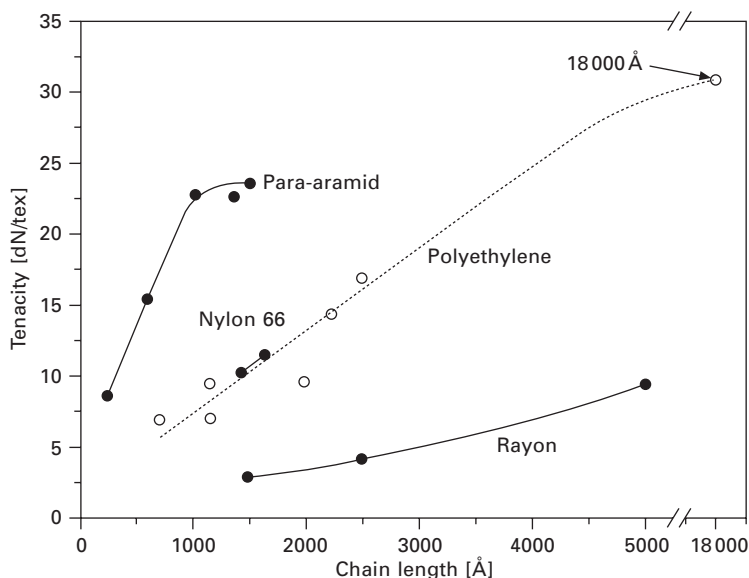


12.1 Structure of solid crystal, liquid crystal and liquid.

50–70 nm (Wong *et al.*, 1978; Crosby *et al.*, 1981), and aromatic polyesters in the order of 30–80 nm (Flory, 1980; Bicerano, 1998). Liquid crystals can be divided into thermotropic and lyotropic. In fact, the liquid crystalline behaviour may occur either in the diluted state (lyotropic liquid crystals) in a critical concentration range, or in the molten state (thermotropic liquid crystals) in a proper temperature range.

Lyotropic and thermotropic LCPs are probably the ideal precursors for preparing fibres. In the diluted or molten states the degree of uniaxial orientation is typically very high and the extensional flow that is associated with the extrusion process orients the mesophases in the flow direction. Both lyotropic and thermotropic LCPs are currently used for fibre production. By exploiting the characteristic anisotropy of LCPs, very high orientation can be reached during the process of fibre production. Nevertheless, the outstanding mechanical properties of LC fibres can be reached only if polymers with a sufficiently high molecular weight are used (Schaeffgen, 1983). In fact, as documented in Fig. 12.2, the fibre tenacity markedly depends on the chain length.

The industrial development of high performances fibres based on LCPs started in the early 1960s with the patents of DuPont on aromatic polyamides (Hill *et al.*, 1961; Kwolek *et al.*, 1962). Modern fibres based on LCPs can be divided into three classes: (i) aromatic polyamides, (ii) aromatic heterocycles, which possess lyotropic behaviour, and (iii) aromatic copolyesters, which display thermotropic behaviour. In this chapter, commercially available LC fibres will be described in terms of their production (polymer synthesis, fibre spinning, heat treatments) and properties (thermal, mechanical, chemical and environmental stabilities).

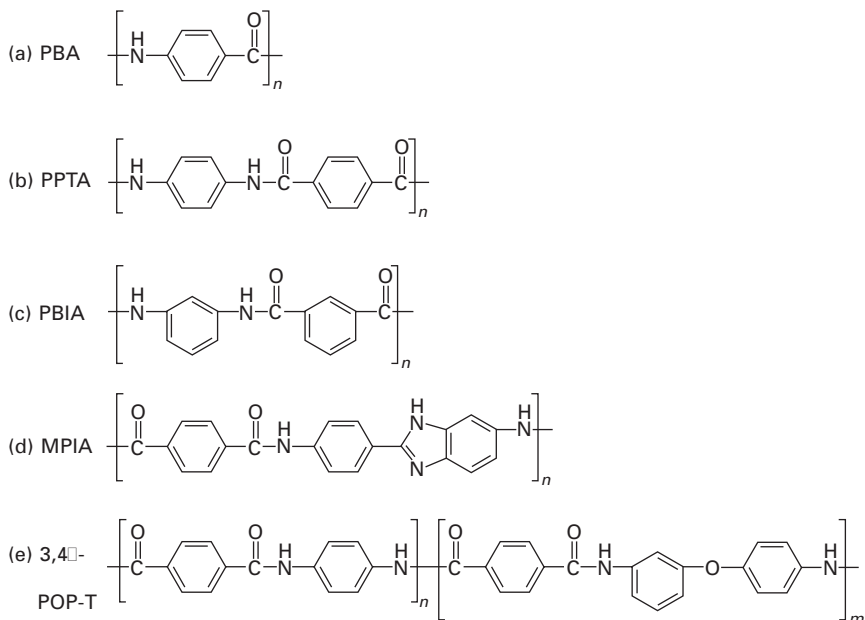


12.2 Tenacity as a function of number average chain length for various fibres (Schaeffgen, 1983).

12.2 Liquid crystalline (LC) aromatic polyamide fibres

Aromatic polyamide fibres, commonly known as aramid fibres, are obtained from polyamides containing aromatic rings along the main chain: unlike aliphatic polyamides, most of amide linkages are attached directly to two aromatic rings. Typically, the aromatic units are phenylene or naphthalene rings or, in some cases, heterocyclic rings. Since the free chain rotation around the phenylcarbonyl and phenylamide bonds is impeded (as opposed to the highly flexible aliphatic chains), these macromolecules have a rod-like behaviour. Figure 12.3 proposes several examples of the most relevant aromatic polyamides currently used for fibre production.

From a general point of view, the aromatic polyamides can be classified in relation to the position of the chain-extending bonds on the aromatic rings. It is therefore possible to identify *para*-aramids and *meta*-aramids. Examples of the *para*-aramids are poly(1,4-benzamide) (PBA), poly-*p*-phenylene terephthalamide (PPTA) and poly-*p*-phenylene-benzimidazole-terephthalamide (PBIA), while a noticeable example of the *meta*-aramids is poly-*m*-phenylene isophthalamide (MPIA). The previous examples refer to homopolymers, the use of various monomers enables the creation of copolymers and therefore the extension of the composition to other relevant precursors such as co-poly-*p*-phenylene/3,4'-oxydiphenylene ether terephthalamide (3,4'-POP-T) which is based on PPTA.



12.3 Structural formulae of the most important aromatic polyamides that are available in the reference literature and on the market as commercial brands.

Examples of commercial fibres based on these polymers are *PRD-49* (DuPont, USA), the early versions of which were based on PBA and which is no longer available; *Kevlar* (DuPont, USA) and *Twaron* (Teijin Aramid, Japan) previously of Akzo Nobel (Netherlands) which are based on PPTA; *Nomex* (DuPont, USA) and *Teijinconex* (Teijin Aramid, Japan) which are based on MPIA; *Technora* previously known also as *HM-50* (Teijin Aramid, Japan), which is based on 3,4'-POP-T copolymer; and *Kermel* (Kermel, France) previously of *Hoechst AG* (Germany) and *New Star* (Yantai, China), which are both based on unspecified *meta*-aramids. In addition, the Russian company Tverchimvolokno and the All-Russian Scientific Research Institute of Polymeric Fibres (ASRIPF) developed *Armos* (Ltd Lirsot, Russia) and *SVM*, previously known also as *Vniivlon* (ASRIPF, Russia), which are based on PBIA (Gerzeski, 1989), and *Terlon* (ASRIPF, Russia), which is based on a PPTA-based copolymer different from that used for *Technora*.

12.2.1 Fibre production

Polymer synthesis

The synthesis of PBA and PPTA was developed in the early 1960s by Kwolek and co-workers at DuPont (Kwolek *et al.*, 1962; Kwolek, 1971, 1972, 1974;

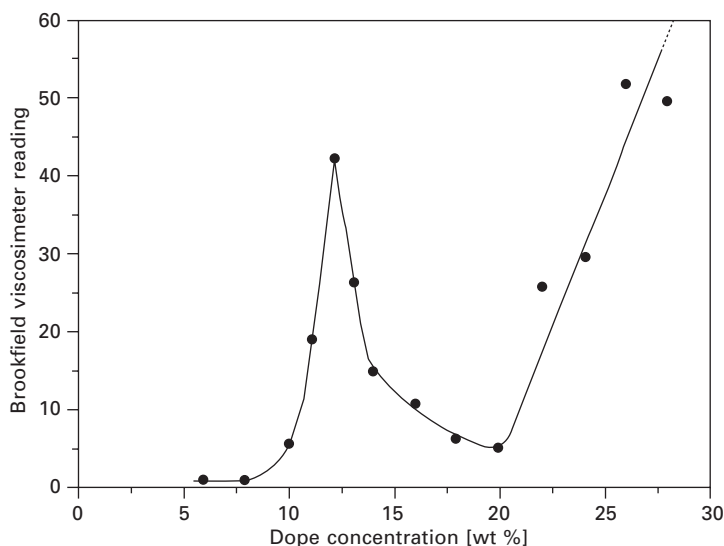
Hill *et al.*, 1961). In particular, the synthesis of PPTA (Yang, 1989) involves the condensation of *p*-phenylenediamine (PPD) and terephthaloyl chloride (TCL) with acid chloride (Bair *et al.*, 1977; Kwolek *et al.*, 1977). These reactants are dispersed in a suitable solvent such as *N,N*-dimethylacetamide (DMAc), tetramethyl urea (TMU) or *N*-methyl-2-pyrrolidone (NMP) in the presence of salts such as CaCl_2 or LiCl (Morgan, 1977). The polymerization is generally conducted at low temperature (often below 50°C) and the resulting polymer is separated by precipitation in water, collected and subsequently washed and dried. Moreover, reactants and solvent must be accurately purified prior the synthesis, otherwise the impurities (particularly water) may greatly reduce the molecular weight.

From a general point of view, the molecular weight depends on the solvent, the monomer concentration and the salts. Under typical polymerization conditions, the resulting number average molecular weight (M_n) is of the order of 20 000, the weight average molecular weight (M_w) 50 000 with a polydispersity index of 2–3. These values, which correspond to a degree of polymerization of 50–80, a chain length of 108 nm and an inherent viscosity of 4 dL/g (Arpin and Strazielle, 1977; Irwin, 1984; Ogata *et al.*, 1984), are of the same order of magnitude of those commonly encountered for aliphatic polyamides.

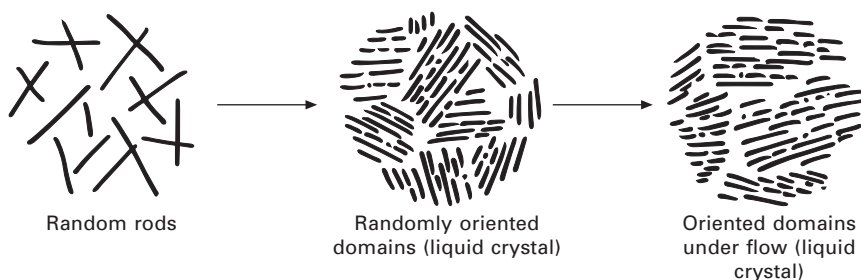
Fibre spinning

Aromatic polyamides cannot be melt-processed because they decompose before a melting temperature is reached, which is located over 400°C for most of these polymers (Yang, 1989). Consequently, aramid fibres are generally spun from polymer solutions. When the polymer concentration exceeds a critical limit in the solution (5–10 wt%), a phase separation generally occurs between anisotropic liquid crystalline and isotropic phases. In other words, aromatic polyamides are lyotropic LCPs, since they form ordered mesophases in concentrated solutions. The critical concentration depends on the polymer molecular weight, the type of solvent (i.e. polymer–solvent interaction) and temperature (Yang, 1989).

PPTA forms anisotropic solution in strong acids such as sulphuric acid, chloro- and fluorosulphuric acids, and hydrogen fluoride even at very high concentrations (20 wt% or higher) above $\sim 70^\circ\text{C}$ (Blades, 1973, 1975; Close *et al.*, 1983). In Fig. 12.4 the shear viscosity of PPTA/ H_2SO_4 solution at 70°C is reported as a function of the dope concentration, while Fig. 12.5 schematically represents the evolution of the solution structure at different concentrations. At low concentration (below $\sim 8\%$), rod-like PPTA molecules are randomly oriented in an isotropic dilute solution and the viscosity increases as the concentration increases. When the concentration approaches a critical value ($\sim 12\%$), the molecules pack close together and rearrange



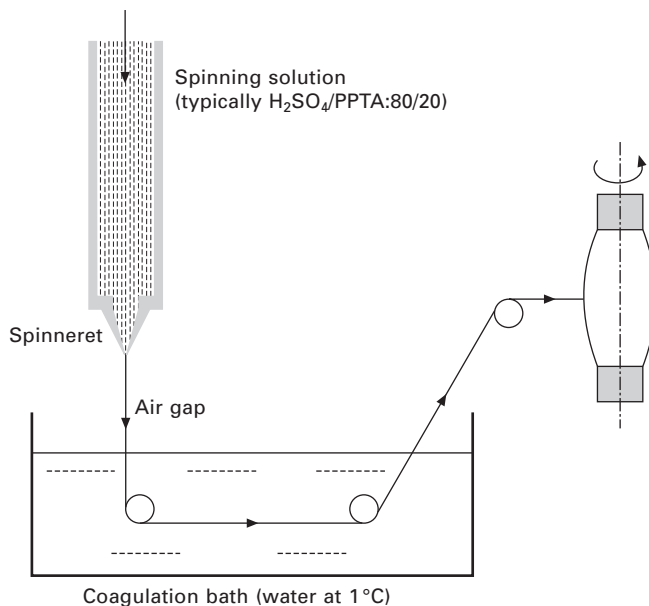
12.4 Bulk viscosity as a function of dope concentration for PPTA/ H_2SO_4 solution at 70 °C (Close *et al.*, 1983).



12.5 Liquid crystalline structure of PPTA/ H_2SO_4 solution.

in small domains, which remain randomly oriented. The anisotropy of the solution (i.e. the LC domains) progressively increases. When the solution is under flow, shear and elongational stresses induce an orientation of the LC domains in the flow direction: in this way the viscosity of the solution decreases when the concentration increases. At higher concentrations (above ~20%), the viscosity increases again, and the polymer is almost entirely in an LC state. This behaviour is maintained up to a temperature of about 120 °C; above that the polymer degrades and the solution shows a decrease of both anisotropy and viscosity.

Filaments of LC aromatic polyamides are usually formed by a *dry jet-wet spinning* process, originally developed in the 1970s (Bair and Morgan, 1972; Blades, 1973, 1975; Bair, 1974). As depicted in Fig. 12.6, the polymer



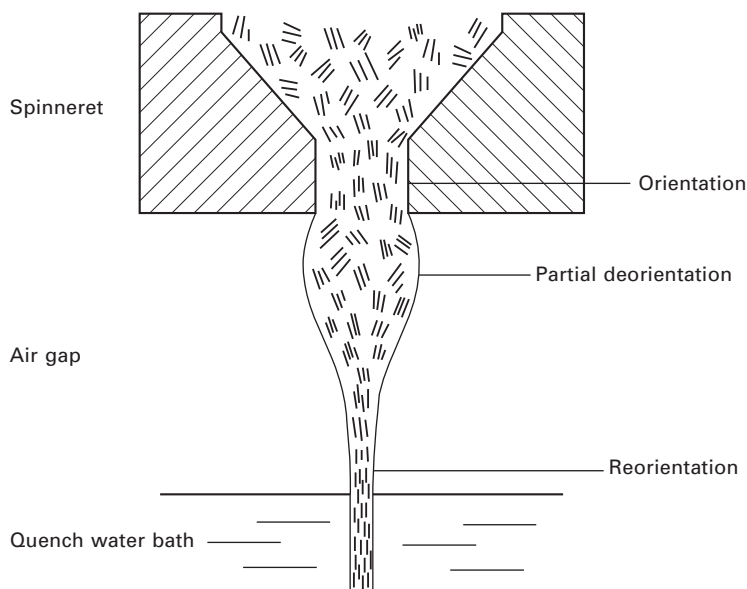
12.6 Schematic representation of the dry jet-wet spinning process.

solution is extruded through a spinneret through an air gap into a coagulating bath. The cold water bath also contains a base to neutralize and remove the retained acid. In a typical process, a solution of 20 wt% of PPTA in sulphuric acid (normally undiluted) is extruded at temperature lower than 90 °C at a rate between 0.1 and 6 m/s into a cold water bath (~1 °C) with an air gap (of 10–15 mm) between the spinneret tip and the bath. Afterwards the as-spun fibres are washed and dried and subsequently post-treated.

In comparison to the wet spinning process used for the conventional organic fibres, where the spinning nozzle is immersed in the coagulation liquid, the air gap of dry jet-wet spinning process induces a higher degree of molecular orientation and hence an improvement of the mechanical properties. For example, Blades (1973) reported values of 173 gpd¹ for the modulus and 7.0 gpd for the tenacity of as-spun PPTA fibres produced by a wet spinning, while values of 750 gpd and 26 gpd, respectively, were reported for fibres produced by a dry jet-wet spinning.

As depicted in Fig. 12.7, the LC domains are randomly oriented in the polymer solution. The shear flow in the capillary hole induces an orientation of the LC domains, which undergo a partial deorientation at the capillary exit. The following spinning tension in the air gap induces a filament contraction and a reorientation. Consecutively the precipitation in the quench water bath freezes the structure in a highly oriented state.

¹ 1 gpd (grams per denier) = 88.26 $\frac{\text{N}}{\text{cm}^2}$ density (in g/cm³) MPa.



12.7 Structural development during fibre spinning.

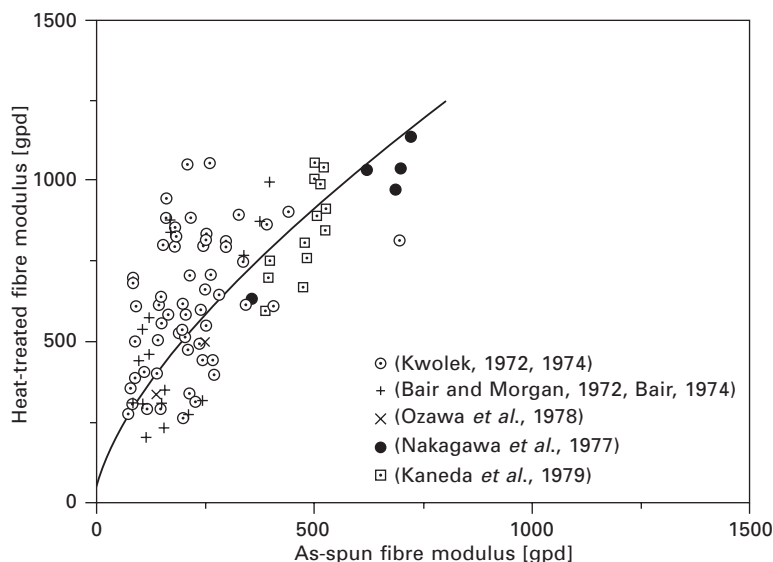
The importance of the orientation induced during the spinning process clearly emerges when the effects of the solution concentration on the mechanical properties are considered. In fact, the mechanical properties are significantly improved only if the solution concentration is significantly higher than the critical concentration so that a LC phase is obtained. Kwolek *et al.* (1977) spun solutions of tetramethylurea–LiCl (6.5 wt% of salt) as solvent and PBA with inherent viscosity 2.1 dL/g at different concentration. When the concentration was 4.6 wt%, no LC phase was separated (i.e. the solution was isotropic), and the tensile modulus of the resulting fibres was 182 gpd and the tenacity 4.4 gpd; when the concentration was raised to 5.8 wt%, small amount of LC phase separated, and the modulus increased to 330 gpd and the tenacity to 8.5 gpd; finally, when the concentration was 6.8 wt%, large amount of LC phase was separated, and the modulus reached 424 gpd and the tenacity 9.7 gpd. Concurrently, the orientation angle (that is the bulk average angle between the crystallites and the fibre axis) progressively decreased from 33 to 20 and 16 degrees.

Even if the use of three or more monomers (i.e. additional moieties in the main chain) could reduce the chain rigidity, aromatic co-polyamides could maintain interesting mechanical properties and have improved solubility. In the literature (Yang, 1989; Wang and Zhou, 2004) there are several examples of high strength fibres based on PPTA segments. Technora is a copolymer based on PPTA monomers and 3,4'-diaminodiphenylether (3,4'-ODA) as third monomer (Ozawa *et al.*, 1978). It is characterized by a fully extended

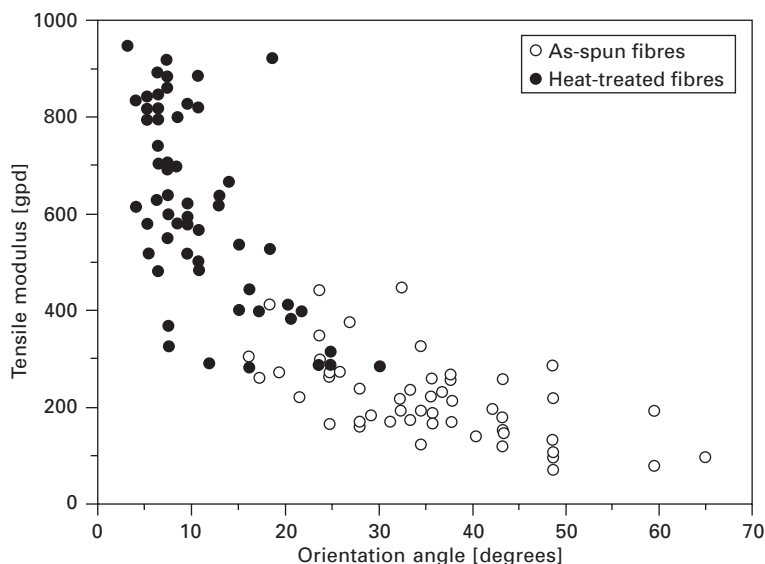
linear chain conformation, with a lower rigidity with respect to PPTA homopolymer. The higher flexibility reflects in a decomposition temperature lower than PPTA (500 °C instead of 550 °C) and an improved solubility. For this reason, a normal isotropic solution can be spun by ordinary wet spinning method followed by drawing at high draw ratio (6–10) and dried at 500 °C. While the high draw ratio applied during the spinning process develop a highly oriented structure, drying at high temperature promotes intermolecular rearrangement within the fibre. In this way post-drawing is not necessary: in fact, Technora fibres are characterized by a modulus of (570 gpd) and tenacity (25 gpd) similar to rigid-chain aramids.

Heat treatment

Heat treatments of as-spun aramid fibres under tension at high temperatures (150–550 °C) for a short period of time induce an increase of the orientation and crystallization of the polymer chains and a consequent enhancement of the mechanical properties. For example, Rao *et al.* (2001a, b) showed that the application of both high temperatures and tension are fundamental to induce rearrangements of the crystalline microstructure and an enhancement of the mechanical properties of *Kevlar*. Figure 12.8 shows that the modulus generally increases after heat treatment for several *para*-aramid fibres, while Fig. 12.9 shows the modulus increasing when the orientation angle decreases in the case of PBA fibres spun under different conditions and successively



12.8 Heat-treated fibre modulus as a function of as-spun fibre modulus.



12.9 Tensile modulus as a function of orientation angle of PBA fibres (Kwolek, 1972).

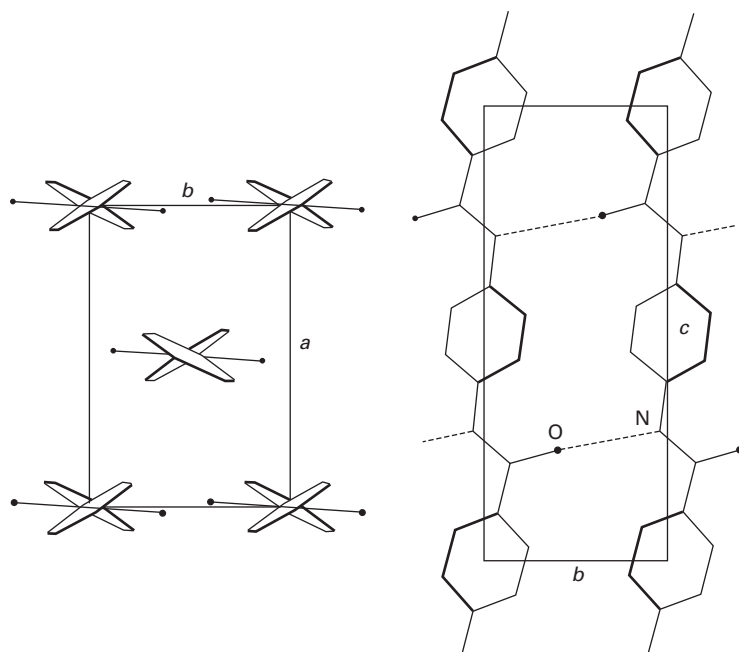
heat-treated (Bair and Morgan, 1972; Kwolek, 1972, 1974; Bair, 1974; Nakagawa *et al.*, 1977; Ozawa *et al.*, 1978; Kaneda *et al.*, 1979). Kevlar 149 is a hot-drawn version of Kevlar 29 and the modulus increases from 71 to 143 GPa. X-ray diffraction analysis shows that the heat treatment induces an increase of the apparent crystallite size (ACS) from 52 to 58 Å (Blades, 1973, 1975) and a reduction of the axial crystal orientation angle from about 15–20° to 10° or less (Schaeffgen *et al.*, 1979; Panar *et al.*, 1983; Schaeffgen, 1983; Kwolek *et al.*, 1988).

12.2.2 Structure

The unique mechanical properties of aramid fibres are related to their peculiar microstructure characterized by several features such as fibrils, radial pleated sheets and skin–core differentiation.

Crystalline structure

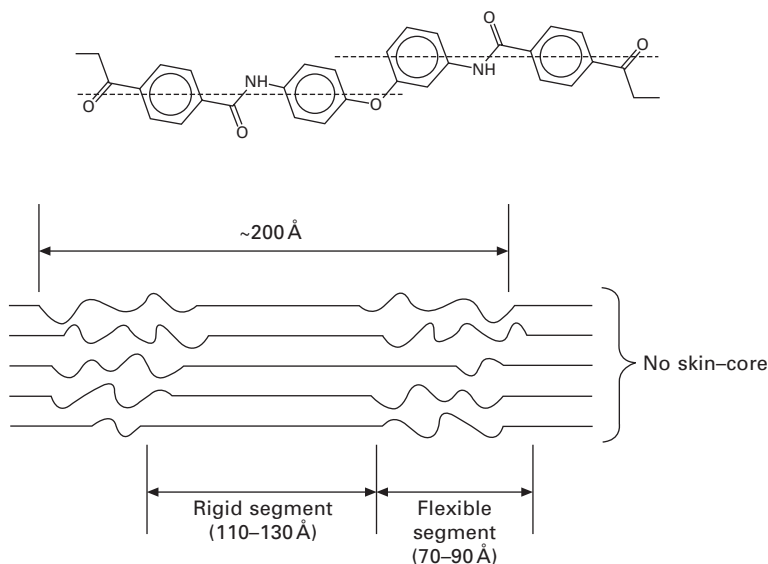
X-ray diffraction analyses reveal that Kevlar fibres are highly crystalline with polymer chains markedly oriented along the fibre axis. The amorphous phase is virtually absent and a very small fraction (few per cent) of un-oriented crystalline component is present (Panar *et al.*, 1983). Northolt and Van Aartsen (1973) and Tashiro *et al.* (1977) proposed a centred monoclinic (pseudo-orthorhombic) unit cell (Fig. 12.10), the dimensions of which



12.10 PPTA crystal lattice (Yang, 1988).

are $a = 7.87 \text{ \AA}$, $b = 5.18 \text{ \AA}$ and $c = 12.9 \text{ \AA}$ (fibre axis). In particular, the characteristic orientations and distances of the various segments permit the formation of strong hydrogen bonding between the nitrogen and oxygen of the amide groups in neighbouring chains. Moreover, the structure markedly depends on the processing parameters, as previously shown for the case of the heat treatments that may induce relevant changes of crystallite quality and orientation.

Technora fibres are based on the 3,4'-POP-T copolymer. The third monomer, i.e. 3,4'-diaminodiphenylether, is characterized by a crankshaft configuration that induced a relatively linear conformation through C—O—C bridging between the two phenyl groups (Fig. 12.11). The effect is that high orientation can be achieved and hence high mechanical properties. X-ray diffraction analyses (Blackwell *et al.*, 1987) revealed a high degree of molecular orientation and a lower crystallinity in comparison to PPTA-based fibres such as Kevlar. Imuro and Yoshida (1986) proposed the existence of two randomly distributed regions inside the fibres (Fig. 12.11). While the first region is composed of PPTA rigid chain segments and can crystallize, the other region is composed of flexible chain segments containing large amounts of the third monomer (3,4'-POP-T segments) which cannot crystallize and forms hydrogen bonding.

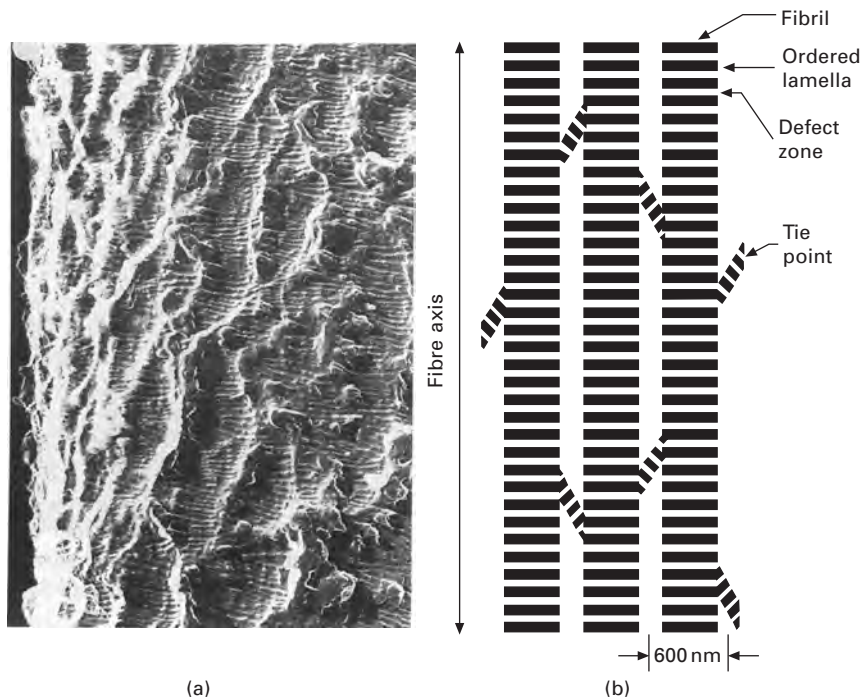


12.11 Structure of 3,4'-POP-T (top) and scheme of Technora fibre structure (bottom).

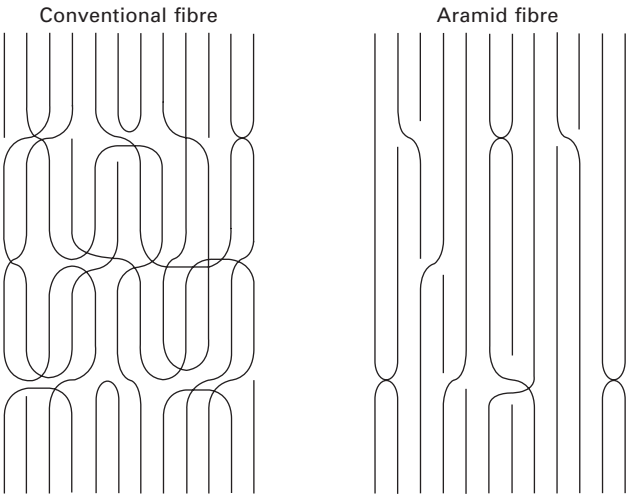
Fibrillar structure

The crystalline structure of aramid fibres is arranged to form ordered lamellae (Fig. 12.12), i.e. stacks of platelets with approximately 35 nm spacing perpendicular to the fibre axis and separated by defect layers (Schaeffgen *et al.*, 1979; Panar *et al.*, 1983; Schaeffgen, 1983). Moreover, X-ray diffraction analysis (Barton, 1983; Panar *et al.*, 1983) revealed a crystalline correlation length (i.e., the statistical average distance along the fibre axis where the polymer chains maintain the structural perfection) of 80–100 nm for Kevlar. In other words, the crystalline correlation length is higher than the long-range periodicity: this fact is in contrast with the microstructure observed for conventional fibres. In this case, the values of the long periodicity (e.g., 10 nm for nylon and 13 nm for polyester) are markedly higher than the crystalline correlation length (e.g., 6.8 nm for nylon and 5.9 nm for polyester) which represents the thickness of crystalline lamellae.

The difference between conventional fibres and LC aramid fibres is explained by the model depicted in Fig. 12.13. Unlike conventional fibres, the highly extended chains of LC aramid fibres pass through adjacent crystalline layers, while a minimal amount of chain bends and possibly half the chain ends are contained in alternating defect layers. In other words, there is a significant chain continuity, and the chains are largely extended across the defect zone. In fact, as shown by X-ray diffraction analyses, the chains in the defect zones are not forming an amorphous phase as in conventional fibres.



12.12 Fibrillar structure model (left) and TEM micrograph of etched surface of a Kevlar fibres (right) (Yang, 1988). Reprinted with the permission of Elsevier.

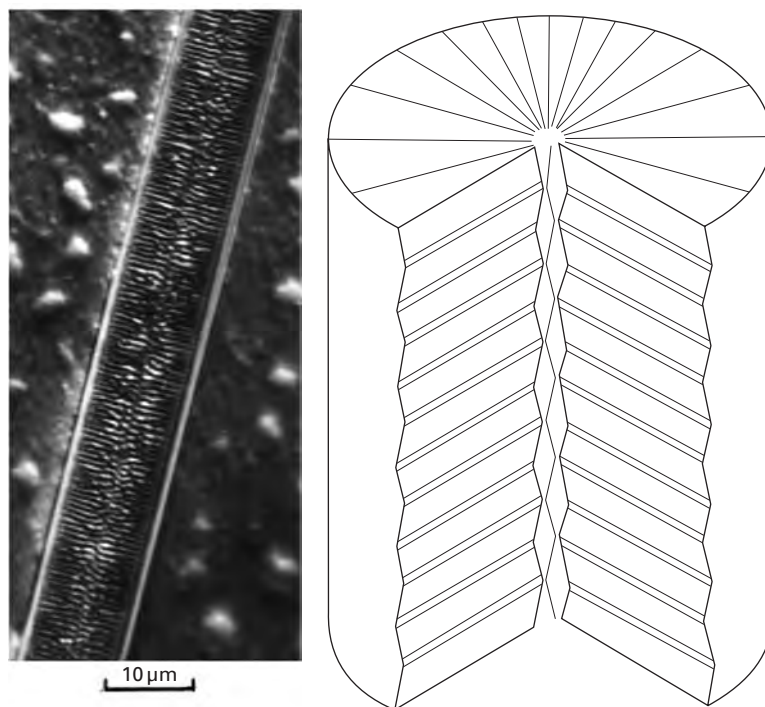


12.13 Comparison of *para*-aramid fibre structure with that of conventional fibres.

The lamellae are loosely connected as microfibrils (about 600 nm wide) with random tie points between fibrils (Dobb *et al.*, 1977; Donald *et al.*, 1983; Schaefgen, 1983). As reported before, the lamellae are separated by defect zones with about 35 nm spacing. Fig. 12.12 proposes a scheme of the fibre structure and a micrograph of a surface replica of an etched fibre, revealing the fibrillar structure of Kevlar fibres. The fibrillar structure is superimposed on the crystalline structure.

Pleated structure

Figure 12.14 includes an optical polarized micrograph of Kevlar fibres that reveals the presence of a 'pleated' structure shown as a series of transverse bands with a periodicity of 500–600 nm (Dobb *et al.*, 1977; Hagege *et al.*, 1979; Li *et al.*, 1983; Shahin, 2003). This radial-sheet structure consists of alternated bands in each sheet arranged at approximately equal but opposite angles (about 170°) to form pleats (Fig. 12.13). Donald *et al.* (1983) observed that this supramolecular structure is a characteristic feature of oriented LCPs



12.14 Optical micrograph in polarized light (left) (Shahin, 2003) and scheme of pleat structure for PPTA fibre (right) (Yang, 1988). Reprinted with the permission of John Wiley Sons Inc. and of Elsevier.

in general. The physical reasons behind this arrangement are not yet fully understood. Yang (1988) suggested that the stress relaxation and differential expansion of a fibre core within a solidified fibre skin during initial quenching may cause the observed periodic pleating. The pleated sheet structure is also superimposed on the fibrillar structure. Moreover, it is expected that the pleated structure may have a strong effect on tensile mechanical properties (especially the modulus).

Skin–core structure

In addition to the previous features, aramid fibres also present a skin–core structure. The surface fibrils are uniformly oriented in the axial direction, while the fibrils in the inner core are imperfectly packed (Panar *et al.*, 1983). This feature clearly emerges from the polarized light optical microphotograph reported in Fig. 12.14, where the surface regions appear to be markedly different from the core. Skin and core regions differ also in terms of density, void content and fibrillar orientation. From a practical point of view, Provost (1979) found that the surface cannot be dyed unlike the core: for this reason, partial surface defibrillation or damaging of the fibres can improve their dyeability. Moreover, Panar *et al.* (1983) showed that plasma etching has a selective action on the skin and on the core when open fibre ends were exposed. Interestingly enough, Graham *et al.* (2000) evaluated the nanomechanical properties of Kevlar 49 fibres by using interfacial force microscopy (IFM). The core and the skin regions were found to possess elastic moduli of 60.8 and 13.4 GPa, respectively.

12.2.3 Properties

Physical and thermal properties

Generally speaking, aramid fibres possess a typical yellowish or golden look due to the presence of the aromatic groups. While unsubstituted polymers (e.g. PPTA, MPIA) have a density of 1.43–1.46 g/cm³, substituted polymers are characterized by lower density values in the range 1.2–1.4 g/cm³ because the substituted groups reduce the packing factor (Takatsuka *et al.*, 1977; Chaudhuri *et al.*, 1980). By considering a typical diameter of 12 μm , these values correspond to a linear mass density of about 1.7 dtex.

The aromatic rings in the backbone chain induce high thermal stability. While the glass transition temperatures are only reported in few cases and always at very high temperatures (over 370 °C for PPTA and 255–260 °C for polymers containing pendant substituents and *meta*-oriented phenylene segments), the melt temperature of unsubstituted polymers such as PPTA and MPIA was not detected (Takatsuka *et al.*, 1977; Chaudhuri *et al.*, 1980). In fact, they generally degrade before reaching a melting point. Moreover, Rao

et al. (2001a) found three distinct transitions at about 100, 200 and 350 °C in dynamic-mechanical tests and investigated them also by X-ray diffraction measurements. While the first transition is associated with the removal of water from the intercrystalline region, the second transition (**b**-relaxation) is related to cooperative rearrangements of the crystalline structure. Finally, the **a**-relaxation at 350 °C corresponds to the glass transition. Thermogravimetric analysis in nitrogen has shown that PPTA homopolymer-based fibres (Kevlar) are stable up to about 550 °C, while PPTA copolymer-based fibres (Technora) are stable up to about 500 °C (Takatsuka *et al.*, 1977; Chaudhuri *et al.*, 1980; Yang, 1988). On the other hand, most unsubstituted aromatic polyamides are stable up to temperatures in the order of 400–500 °C, while chloro, methyl and other substituted polyamides may reach 300–400 °C. Moreover, thermogravimetric analysis in air have shown that Kevlar begins to lose weight at above 350 °C in air, with complete decomposition generally occurring between 427 and 482 °C (Penn and Larsen, 1979; Yang, 1993; DuPont, 2008).

In addition, aramids possess good flame resistance, but they can eventually be ignited if a flame is present (Technical Datasheets; Yang, 1989). Kevlar fibres do not sustain combustion but char at about 427 °C (Yang, 1988), while Technora presents an ignition point at about 650 °C (Yang, 1988).

Finally, aromatic polyamides are characterized by excellent dimensional stability manifesting very low high temperature shrinkage and thermal expansion coefficient (Technical Datasheets; Yang, 1988). The longitudinal thermal expansion coefficient of commercial *para*-aramid fibres is negative in the range of -3 to $6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, while it is positive in the range of 15 – $20 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ in the case of *meta*-aramid base fibres. On the other hand, the transversal thermal expansion coefficient is positive and larger, being about $6 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$.

Mechanical properties

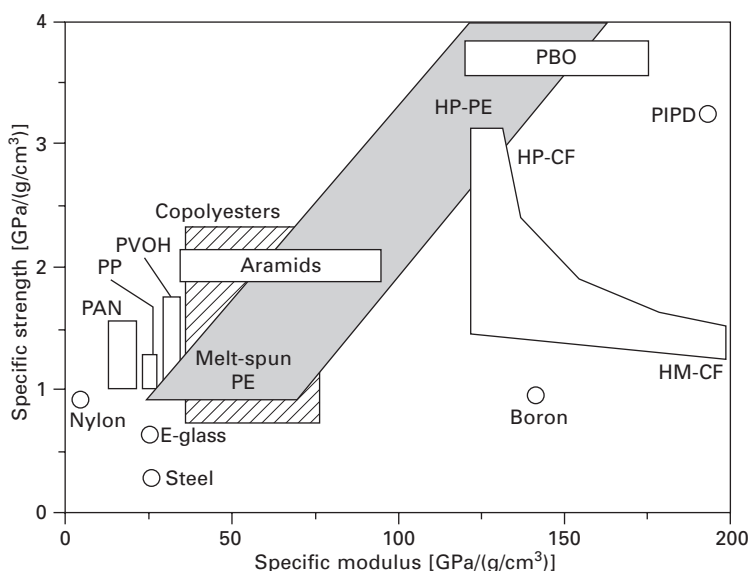
Tensile

In general, aramid fibres possess remarkable specific mechanical properties. As reported in detail by Yang (1989), the various types of aramid fibre have initial tensile modulus in excess of 39 GPa and tensile strength in excess of 1.3 GPa. These values markedly change as a function of the type of polymer, microstructure, spinning conditions and heat treatments. Table 12.1 summarizes the most relevant tensile mechanical properties of several commercially available aramid fibres, and, for the sake of comparison, those of other types of industrially relevant fibres. As reported in Table 12.1, *para*-aramid PPTA homopolymer-based fibres (such as Kevlar and Twaron) have tensile initial moduli between 70 and 142 GPa and tensile strengths between 2.3 and 3.2 GPa. These remarkable properties are mainly related to the structure

developed during the spinning process. In fact, the rigid-rod chains are almost completely aligned along the drawing direction. By finding the ratio of the mechanical properties of aramid fibres to the corresponding densities (also reported in Table 12.1) specific values can be obtained. Figure 12.15 proposes a chart with the specific values of the tensile moduli and strengths for several types of fibres: aramid fibres undoubtedly show specific tensile mechanical properties higher than several other industrial fibres such as steel and glass fibres, and comparable to those of UHMWPE and carbon fibres. Furthermore, these specific mechanical properties are much higher than those manifested by traditional nylon and polyester organic fibres.

Unlike *para*-aramid fibres, *meta*-aramid-based fibres (such as *Nomex* and *Teijinconex*) contain crooked chains that can flex and rotate even in pure tension. As a result, these fibres are much less rigid and strong than *para*-aramids: their initial modulus is typically of the order of 10 GPa and the tensile strength of the order of 600 MPa. On the other side, they are easier to produce and hence are less expensive.

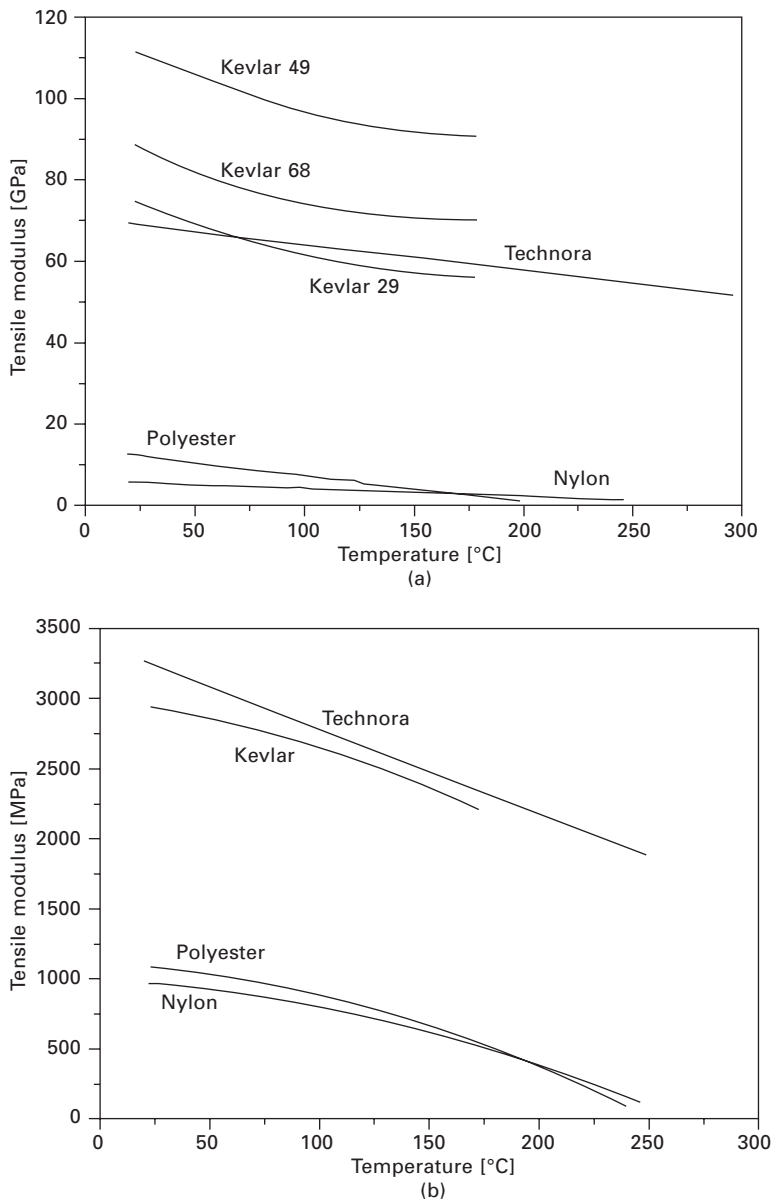
Technora fibres consist of a PPTA-based copolymer containing ether linkage —O— in the backbone. Owing to this chemical structure Technora fibres possess modulus values intermediate between the low and high modulus PPTA-based fibres. Furthermore, the tensile modulus can be increased by additional cyclic rings which enhance the stiffness of the polymer chains. Examples are PBIA-based fibres (*Armos* and *SVM*) which contain heterocyclic



12.15 Specific strength and specific modulus of several type of fibres (HP = high performance, PAN = polyacrylonitrile, PVOH = polyvinyl alcohol, PP = polypropylene, PE = polyethylene).

rings such as benzimidazole. *Armors* fibres can reach a modulus of 157 GPa and a tensile strength of 4.6 GPa.

The effect of temperature on modulus and tensile strength is reported in Fig. 12.16a and 12.16b, respectively, where Kevlar and Technora fibres are

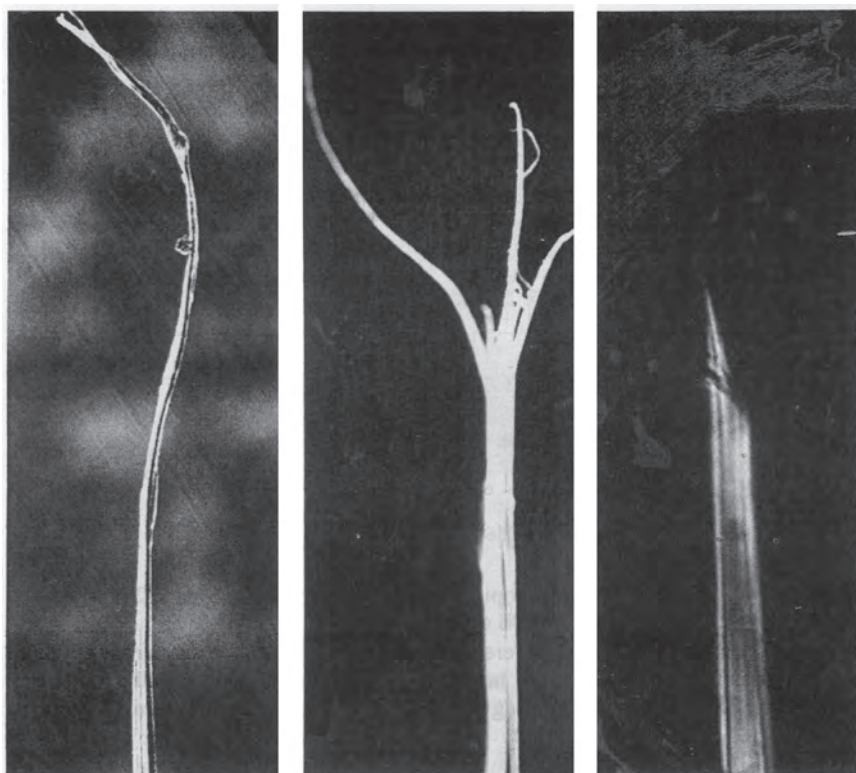


12.16 Modulus (a) and tensile strength (b) as a function of temperature for several para-aramid fibres and for two conventional polymer fibres (Technical Datasheets).

compared with traditional organic fibres based on nylon and polyester. In all cases the investigated properties decrease as the temperature increases, but aramid fibres appear to be much more stable than nylon and polyester fibres over the entire temperature range. From room temperature to 180 °C, *para*-aramid fibres manifest a 15–25% decrease of the modulus and a 30–35% decrease of the tensile strength (Technical Datasheets). Furthermore, even if the absolute values of modulus and tensile strength are constant for a steel wire from room temperature to 300 °C, the *para*-aramid fibres maintain higher specific properties over the same temperature range. In addition, at cryogenic temperatures (i.e. –196 °C), the modulus of Kevlar 29 slightly increases, while the tensile strength does not change significantly (Technical Datasheets).

The tensile mechanical properties of aramid fibres are also influenced by the strain rate. Experimental measurements have revealed that an increase in strain rate of more than four orders of magnitude (i.e. from 0.001 67 to 80 s^{–1}) induced a reduction of only 15% of the tensile strength (Abbott *et al.*, 1974). On the other hand, Wang and Xia (1999) found that both modulus and strength of Kevlar 49 increased by 23 and 30%, respectively, as the strain rate increased from 140 to 1350 s^{–1}.

The tensile stress–strain curves of aramid fibres remain almost linear up to failure. Some information on the failure mechanism under tensile loads of aramid fibres can be obtained by analysing the morphology of the fracture surfaces (Yang, 1988). The first micrograph of Fig. 12.17 shows the ‘pointed break’ morphology where the fibre diameter gradually tapered until the break point was reached (from 12 to 2 mm). This fracture behaviour is typically induced by tests performed at slow strain rates. This morphology is associated to highly crystalline and oriented structure, and it is generally associated to high modulus and strength values. On the other hand, the last micrograph of Fig. 12.17 shows a ‘kink band break’ morphology where the fibre diameter shows little or no reduction. In this case, the presence of kink band defects (that represent structural discontinuity) induces premature failure. The central micrograph of Fig. 12.17 shows the most common ‘fractured break’ morphology, where the fibre diameter manifests a drastic reduction in the fractured zone (from 12 to 4.5 mm). In this case, the slippage between the fibrils under load and the step-wise fibrillar breaks produce uneven and jagged morphology in which the fibres are fibrillated and split at the breaks. In certain cases, long, helical ribbons of fibrils in fractured bare yarns can be observed because of eddy flow of spin solution through spinning nozzle (Konopasek and Hearle, 1977). From a general point of view, initiation and intensity of the fibrillation are a function of the internal fibre stress arising during the manufacturing conditions. Morgan *et al.* (1983) proposed that the fracture process begins on the fibre skin, where splitting of a highly ordered fibrillar structure may take place. Subsequently, the partial transverse



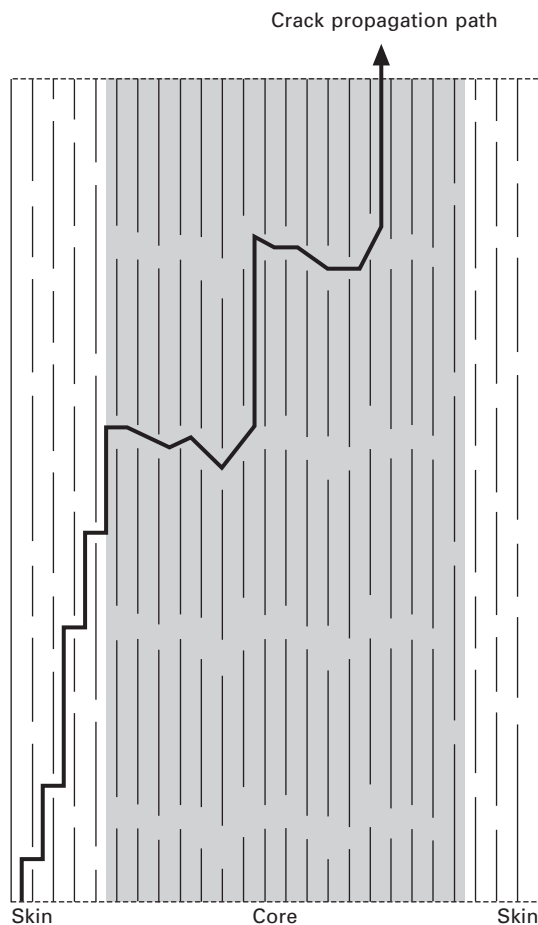
12.17 Tensile break mode of Kevlar fibre: pointed break (left), fractured break (centre) and kink band break (right) (Yang, 1988).

skin fracture propagates crosswise in the core region through the lamellar structure until reaching the core failure when two cracks meet (Fig. 12.18). This fracture mechanism, also called defibrillation, requires a great amount of energy because of the progressive and extensive internal damage of the fibres.

The statistical characterization of the brittle fracture behaviour of aramid fibres is mostly based on the classical (two-parameter) Weibull distribution (Chiao *et al.*, 1977; Lafitte and Bunsell, 1982; Wagner *et al.*, 1984; Bunsell, 1988; Minoshima *et al.*, 2000). In particular the cumulative distribution function $F(\sigma)$, which represents the failure probability for an applied stress σ , has the following expression:

$$F(s) = 1 - \exp \left[- \left(\frac{s}{a} \right)^b \right]$$

where a and b are the scale and shape parameters, respectively. The shape parameter describes the dispersion of the strength values and it increases as

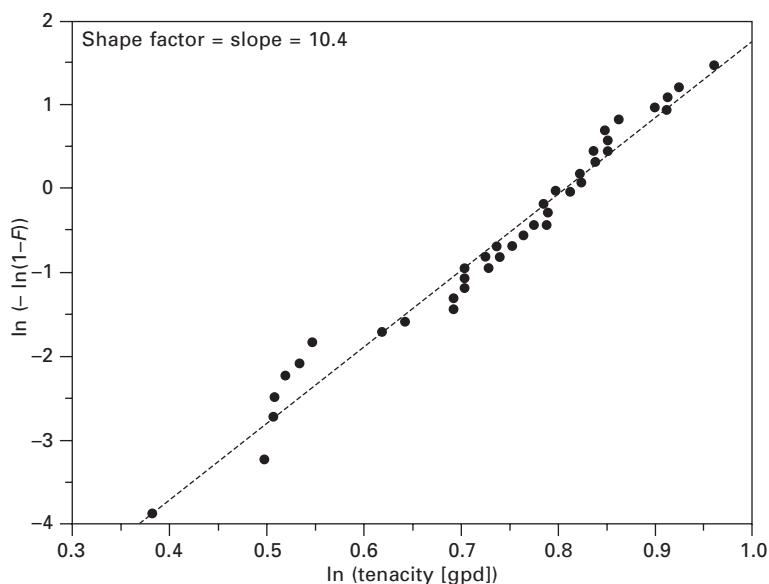


12.18 Tensile failure mechanism of PPTA fibre.

the dispersion of the strength values decreases. Typical values are 2–5 for carbon fibres and 4–6 for glass fibres. As shown in Fig. 12.19, Wagner *et al.* (1984) found a good fitting of the experimental values for the strength data of Kevlar 29 using the Weibull distribution, obtaining a shape parameter of 10.4. In general, for aramid fibres a shape parameter in the range 8–10 has been reported (Chiao *et al.*, 1977; Lafitte and Bunsell, 1982; Wagner *et al.*, 1984; Minoshima *et al.*, 2000).

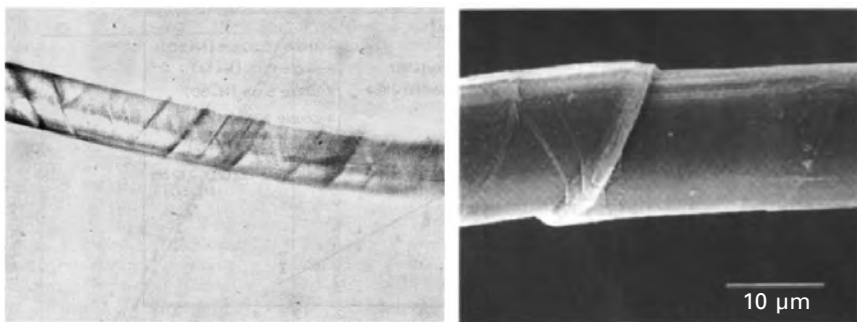
Compression, bending and torsion

Being aramid fibres, based on extended rigid-rod chain, a highly anisotropic structure is expected. In fact, the polymer chains are laterally connected only by relatively weak van der Waals forces and hydrogen bonding. Also the fibrils

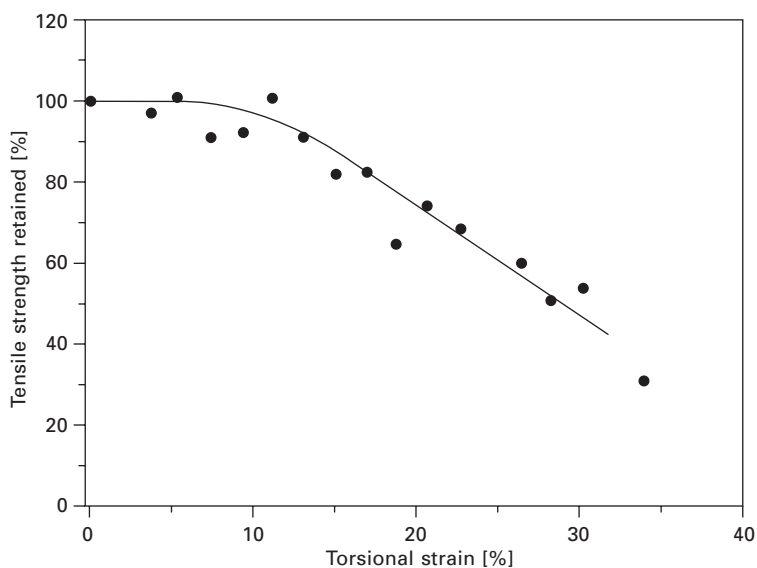


12.19 Weibull distribution function for the tenacity of Kevlar 29 fibres (Wagner *et al.*, 1984).

possess relatively weak lateral connections. In this way, fibres tend to split into microfibrils when tested under compression or bending configurations. Kinking or micro-buckling phenomena induce a reduction of the compressive strength in comparison to the tensile strength. Deteresa *et al.* (1982, 1984) found that Kevlar 49 has a compressive strength which is only one-fifth of that in tension (i.e. 0.7 vs 3.4 GPa). In the case of bending, yielding occurs at a relatively low strain of about 0.75% (Greenwood and Rose, 1974). Axial compression and severe bending may induce plastic deformation: Dobb *et al.* (1981) and Takahashi *et al.* (1983) showed the formation of kink bands at 55–60° to the fibre axis when the compressive strain reached about 0.5% (Greenwood and Rose, 1974), consistent with compressive yield stress. Figure 12.20 presents two micrographs, obtained with cross-polarized optical and scanning electron microscopes, of localized bands in the compressed region of a bent fibre. The phenomenon is more and more evident as the modulus-to-strength ratio of the fibres increases (as for example from Kevlar 29 to Kevlar 49). Moreover, kinking and micro-buckling irreversibly damage the fibres (Deteresa *et al.*, 1982, 1984). The application of a compressive deformation of about 3% brings a reduction of the tensile strength of about 10%. In a similar way, the application of torsional shear strain higher than 10% on Kevlar 49 fibres induces the loss of more than 10% of tensile strength as evidenced in Fig. 12.21. Even if the shear properties are much lower than the tensile ones, they are still greater than those of conventional organic



12.20 Kink bands in Kevlar fibres at optical microscope in cross-polarized light (left) (Yang, 1988) and (right) at scanning electron microscope (Kozey *et al.*, 1995) (b). Reprinted with the permissions of Elsevier and of Materials Research Society.

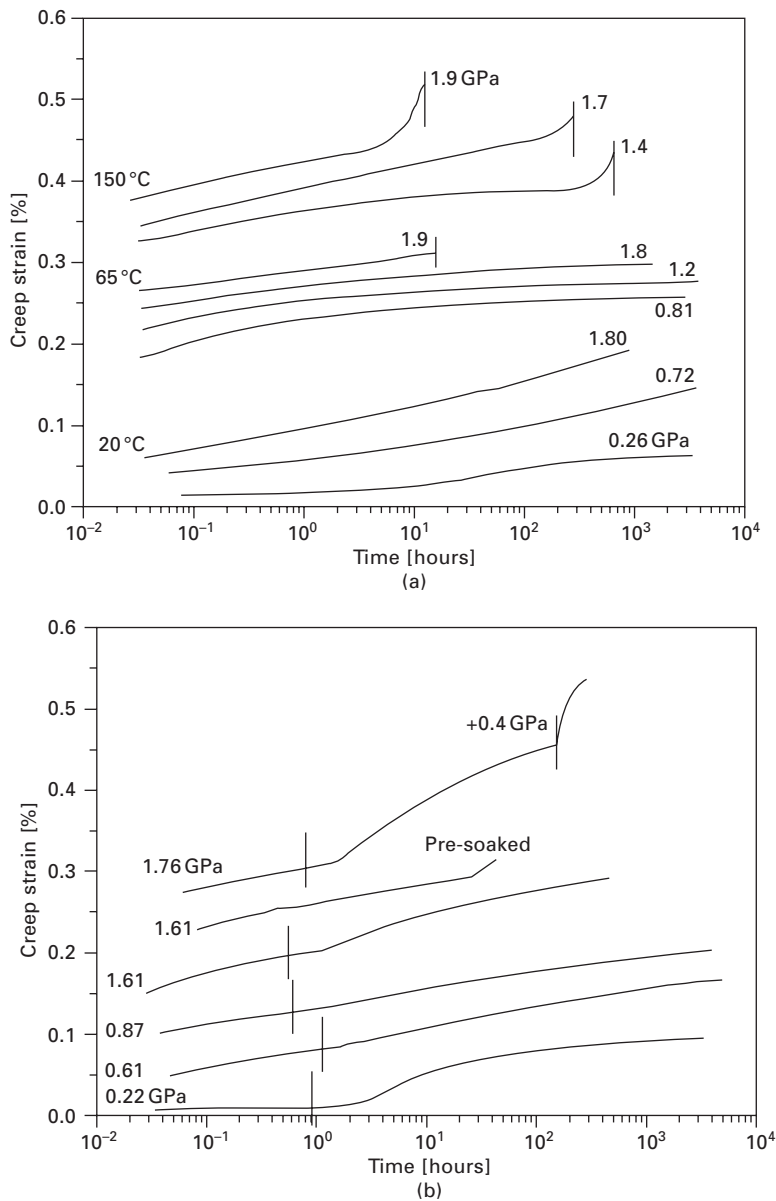


12.21 Tensile strength retention as a function of torsional strain for Kevlar 49 fibres (Deteresa *et al.*, 1984)

fibres. For example Kevlar 49 possesses a shear modulus of 1.8 GPa while the shear modulus of nylon fibres is 0.33–0.48 GPa, that of polypropylene fibres is 0.75 GPa and that of polyester fibres is 0.85 GPa. Similar results are found for the ultimate shear properties. For example, Kevlar 49 has an apparent shear strength of only 180 MPa.

Creep

Aramid fibres generally show limited deformation under creep conditions. Figures 12.22a and 12.22b report the creep strain as a function of time under tensional creep stresses from 0.26 to 2.0 GPa at 20–110 °C for Kevlar 49. Even



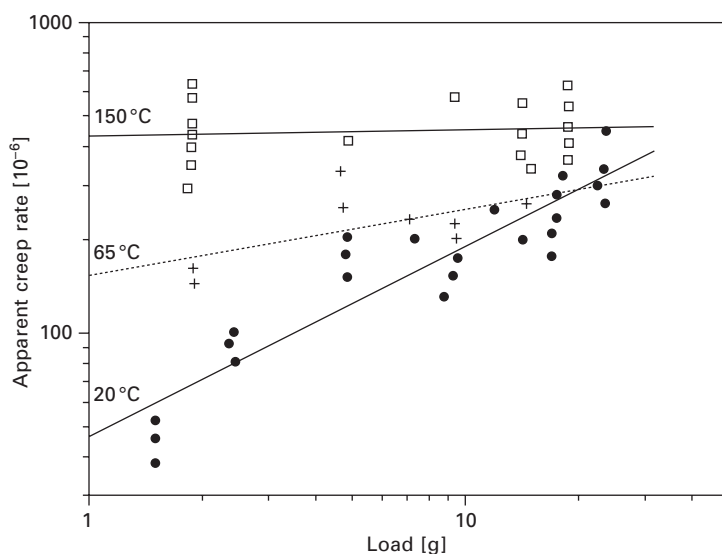
12.22 Creep strain of Kevlar 49 fibres in air (a) and in water at 20 °C (b) (Cook *et al.*, 1982).

if the creep strain increases with increasing temperature and stress, total creep in 10000 hours remains less than 0.5% (Cook *et al.*, 1982). Analogously, in the case of Technora fibre, creep deformation is limited between 0.25 and 1.5% in the temperature range 20–150 °C under tensional stresses of 0.12–0.62 GPa for 24 hours. Nevertheless, the strain values are greater than those manifested by Kevlar fibres under similar conditions. The presence of absorbed water generally decreases the creep stability. However, even if the behaviour of dry fibres was better, creep tests in water at 20 °C for Kevlar 49 under tension stresses of 0.22 to 1.76 GPa showed that the total creep strain in 10000 hours remained lower than 0.5% (Cook *et al.*, 1982).

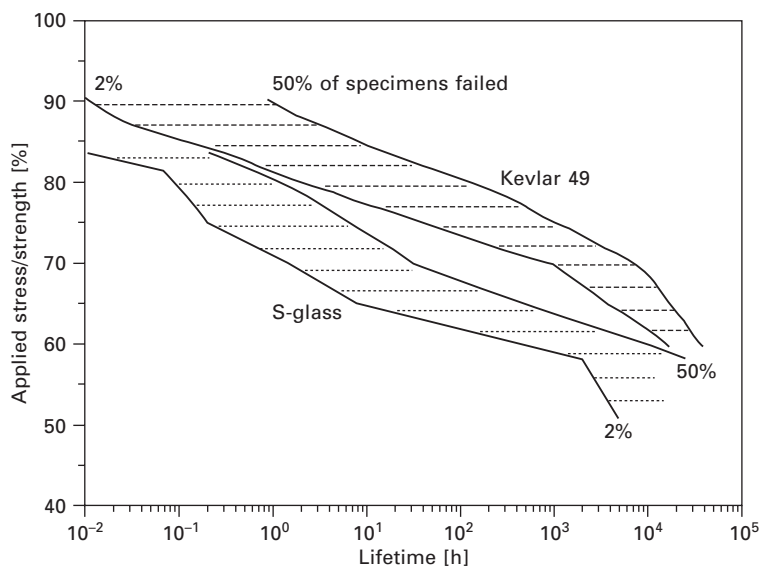
The creep strain of aramid fibres generally follows a linear trend with logarithmic timescale until the failure of individual fibres is first detected. Figure 12.23 shows the acceleration of the apparent creep rate as the applied load and testing temperatures are increased (Ericksen, 1985).

Besides creep phenomena, aramid fibres may also present stress relaxation (Bunsell, 1975; Cook *et al.*, 1982). For initial stresses in the range 0.14–1.0 GPa, Cook *et al.* (1982) evaluated a stress relaxation at room temperature of about 6–8% in the time interval 0.1–300 s for Kevlar 49. Analogous behaviour was observed for Technora (Technical Datasheets).

In addition, aramid fibres suffer from a stress rupture phenomenon, i.e. failure of the fibre under sustained tensile loads with little or no accompanying creep. Figure 12.24 shows the lifetime at different loading for Kevlar 49 and S-glass fibres. For *para*-aramid fibres somewhat better performances



12.23 Apparent creep rate as a function of load for Kevlar 49 fibres (Ericksen, 1985).

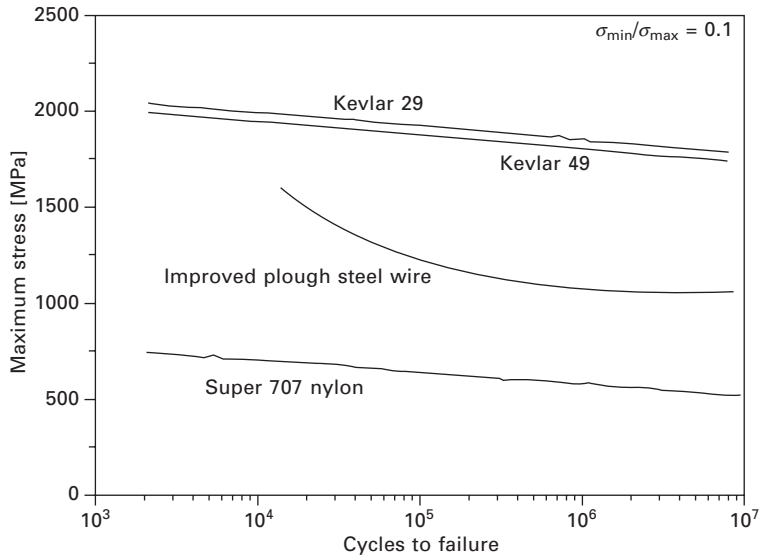


12.24 Stress-rupture behaviour of epoxy-impregnated Kevlar 49 fibres compared with that of epoxy-impregnated S-glass fibres (Chiao *et al.*, 1976).

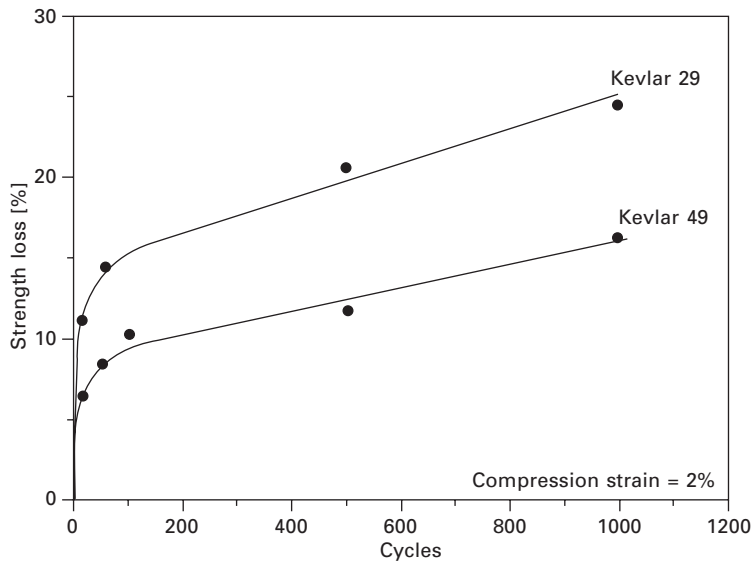
are reported. It is important to underline that strength retention data of the fibres cannot be used to estimate the behaviour of the resulting composites, but direct tests are needed (Chiao *et al.*, 1976; Chiao *et al.*, 1977; Chiao and Chiao, 1982).

Fatigue

Para-aramid fibres possess outstanding resistance to cyclic loading conditions (Fig. 12.25). In particular, Kevlar and Technora have a fatigue resistance which, some claim, is better than carbon fibres (Yang, 1993). Bunsell (1975) reported that Kevlar 49 fibres fibrillated but did not fail unless the maximum applied load was greater than 80% of the tensile strength. As depicted in Fig. 12.26, for Kevlar fibres Dobb *et al.* (1981) showed an initial rapid loss of residual strength under cyclic bending fatigue followed by a progressive damage linearly, depending on the number of fatigue cycles. The effect of the testing conditions on the fatigue life of Kevlar 29 fibres, i.e. maximum load and load amplitude, was analysed by Lafitte and Bunsell, (1982). Figure 12.27 summarizes the effect of the load amplitude in comparison to creep loading (zero load amplitude). The plot clearly shows how the lifetime decreases as the stress amplitude increases. The slope change observed for the data acquired under non-zero amplitude tests could be attributed



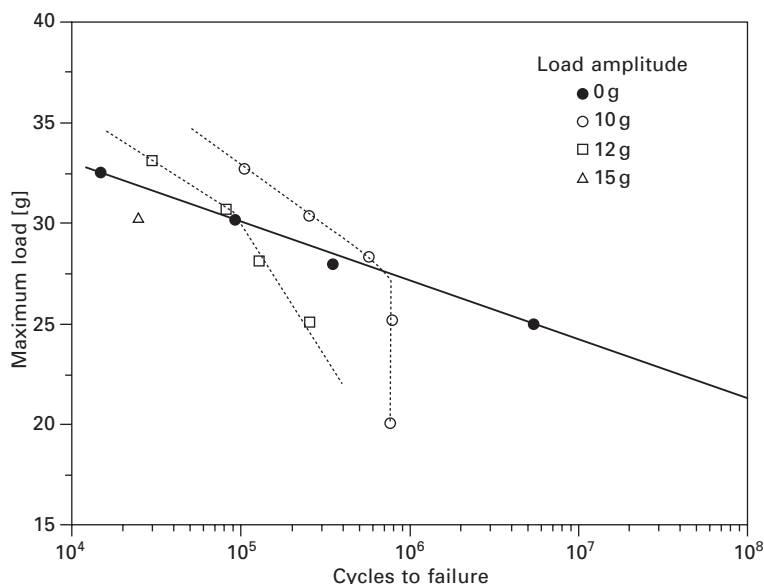
12.25 Comparison of tension–tension fatigue behaviour for several yarns and wire (Horn *et al.*, 1977).



12.26 Tensile strength loss as a function of the number of bending cycles for Kevlar fibres (Dobb *et al.*, 1981).

to different failure mechanisms. In the lower loads region a creep-induced failure prevails, while at higher loads fatigue failure occurs.

As with all other mechanical properties, the fatigue behaviour also markedly depends on the moisture content of the fibres. Minoshima *et al.* (2000)



12.27 Effect of load amplitude and maximum applied load on lifetime of Kevlar 29 fibres (Lafitte and Bunsell, 1982).

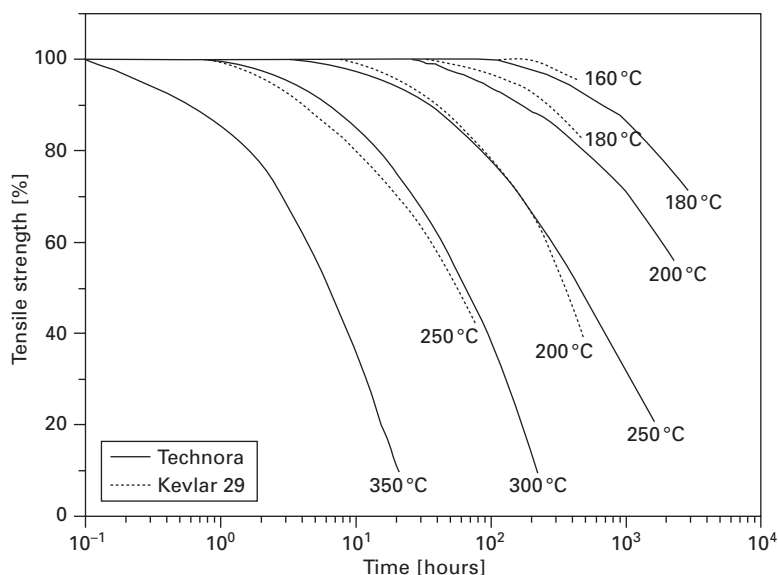
tested Kevlar 49 fibres in air and under vacuum. The fatigue strength in air is lower because of adsorbed water that is in the order of 3–4%. Finally, it is worthwhile to observe that the morphology of the fracture surfaces of fibres failed under creep and fatigue loading conditions is characterized by features similar to those described in the case of quasi-static tensile failure (Yang, 1988; Minoshima *et al.*, 2000).

12.2.4 Chemical and environmental effects

The performances of LC aramid fibres are markedly affected by the environmental conditions. This section briefly describes the degradation effects induced by exposure to elevated temperature, moisture, chemicals and ultraviolet radiation.

Temperature

The permanence at high temperatures induces a progressive degradation of the mechanical properties of aramid fibres. In Fig. 12.28 the strength retention of Kevlar 29 and Technora fibres is reported as a function of exposure time at temperatures ranging from 160 to 350 °C. As expected, the kinetics of the strength degradation process is accelerated as the temperature increases. For example, for a given treatment time of 48 hours in dry air,



12.28 Strength retention of Kevlar 29 and Technora fibres following elevated temperature exposure (Technical Datasheets).

Kevlar lost almost 16% of its initial strength at 180 °C, 50% at 400 °C and 100% at 455 °C (Technical Datasheets). For this reason, the maximum continuum service temperature of *para*-aramid fibres is typically limited to about 150–175 °C.

Moisture

As with more conventional aliphatic polyamides, LC aramid fibres adsorb a certain amount of water. The equilibrium moisture content depends on the chemical composition and the microstructure. For example, the water adsorption is quite high for SVM (5%), Kevlar 29 and Twaron (7%), moderate for Kevlar 49 and Twaron HM (3.5–4.5%), and reasonably low for Armos, Technora (2–3%) and Kevlar 149 (1%) (Technical Datasheets; Penn and Larsen, 1979; Yang, 1989). Moreover, the equilibrium moisture content is directly proportional to the relative humidity of the environment: in the case of Kevlar 49, the adsorbed moisture increases from 3.4% at 50% R.H. to 6.2% at 96% R.H. (Technical Datasheets; Smith, 1980). Penn and Larsen (1979) suggested that the mechanism of water adsorption is markedly affected by the impurities (e.g. the salts) and the fine structure of the fibres.

The adsorbed moisture plays a significant role in determining the mechanical tensile properties. Mimoshima *et al.* (2000) showed that the strength of Kevlar 49 fibres is higher under vacuum than in air, because of adsorbed water that is about 3–4%. Wu (1980) reported the mechanical properties of composites

made of Kevlar 49 and epoxy resin tested at 23 °C in a dry environment and conditioned at 52% R.H. The tensile strength in the longitudinal direction decreased by about 13%, the off-axis properties (longitudinal compression, transverse tension and compression, and in-plane shear) drastically decreased by about 28–49%. A somewhat higher moisture sensitivity is reported for Kevlar in comparison to Technora fibres (Peters, 1998). It is worth noting that the original mechanical properties can be restored upon removal of the moisture.

Chemicals

In general, aramid fibres are exceptionally stable in several highly corrosive environments (Technical Datasheets; Horn *et al.*, 1977; Bunsell, 1988). Table 12.2 briefly summarizes the environmental stability (evaluated as strength retention) of aramid fibres in contact with several chemicals. From a general point of view, most organic solvents have no or only little effect, most aqueous salt solutions no effect at all, whilst strong acids and bases (especially at elevated temperatures or high concentrations) have more intense effects.

Moreover, co-polymer-based Technora fibres show better acid and alkali resistance than PPTA-based fibres such as Kevlar, probably because the very high purity of the parent polymer. The higher hydrolytical stability of Technora is especially evident for seawater and steam exposure. Figure 12.29 reports the strength retention of Technora and PPTA fibres after 100 hours of exposure at 100–200 °C saturated steam. While PPTA shows a drastic drop at about 100 °C, Technora is stable up to 140 °C with a slower degradation rate.

UV radiation

Aramid fibres are strong ultraviolet (UV) adsorbers. After long-term exposure, the yellow or golden colour turns to orange and eventually brown. This degradation process takes place only in the presence of oxygen, but it is not enhanced by moisture or atmospheric contaminants (Technical Datasheets). Bare 1667 dtex Kevlar 29 showed 71% strength retention after 1 month of outdoor exposure in Wilmington (DE, USA) and 43% after 4 months (Yang, 1993). For this reason, aramid fibres need to be protected from UV exposure, for example by appropriate coatings. Since the *para*-aramids are self-screening, UV protection may also be reached simply by sacrificial fibres, with or without a binding matrix. Consequently, the strength retention of aramid fibres is proportional to their thickness. In fact, while very thin Kevlar 49 fabric showed strength retention of 51% after 5 weeks of exposure to Florida sunlight, thicker ropes with a diameter of 13 mm showed strength

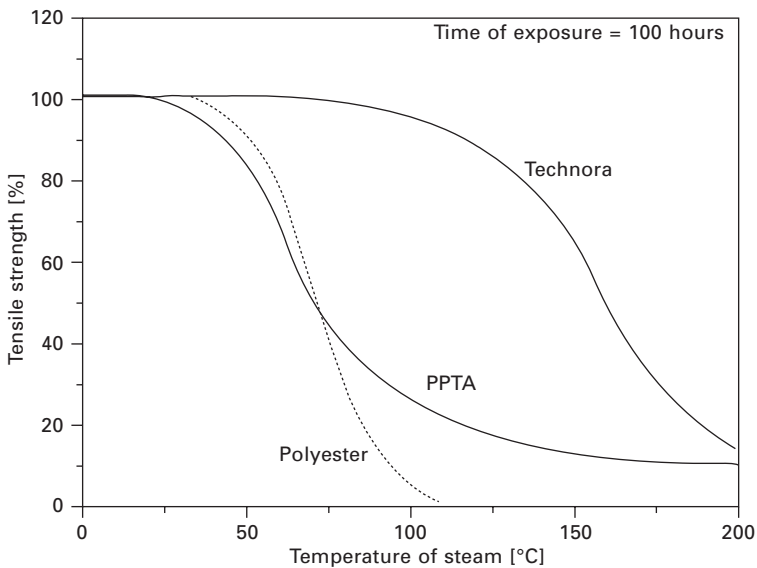
Table 12.2 Stability of Kevlar (K) and Technora (T) fibres in various chemicals (Technical Datasheets)

Chemicals	Conc. ^a (%)	Temp. ^b (°C)	Time (hours)	Effect on breaking strength ^c				
				None	Slight	Moderate	Appreciable	Degraded
Acids								
Acetic	40	21	1000		K			
	40	95–99	100	T			K	
Formic	90	21	100	K				
	90	95–99	100		T			K
Hydrochloric	20	20	100	T				
	10	71	10					K
Nitric	10	20–21	100	T			K	
Phosphoric	10	20–21	100	K,T				
	10	21	1000		K			
	10	99	100				K	
Sulphuric	10	99	10				K	
	20	95	100	T				
	40	95	100	T				
Alkalis								
Ammonium hydroxide	28	21	1000	K				
Sodium hydroxide	10	21	1000				K	
	10	95–99	100			T		K
Portland cement	saturated	95	100	T				
	saturated	180	15			T		
Organic solvents								
Acetone	100	Boil	100	K				
Benzene	100	20	784	T				
	100	21	1000	K				
Carbon tetrachloride	100	Boil	100			K		
Ethylene chloride	100	20	1000	T				
Ethylene glycol/water	50 / 50	99	1000			K		
Ethylene glycol	100	95	300	T				
Gasoline	100	20	784	T				
Gasolide-lead	100	21	1000	K				
Methyl alcohol	100	21	1000	K,T				
N-Methyl pyrrolidone	100	95	100				T	

Table 12.2 Continued

Chemicals	Conc. ^a (%)	Temp. ^b (°C)	Time (hours)	Effect on breaking strength ^c				
				None	Slight	Moderate	Appreciable	Degraded
Other								
Sodium chloride	3	21	1000	K				
	10	99	100	K				
	10	121	100				K	
Seawater	100	95	1000	T				
Seawater (New Jersey)	100	–	1 year	K				
Steam	100	120	400	T				
	100	150	48			K		
	100	150	100	T				
	100	200	100					T
Water, tap	100	99	100	K				

^a Concentration.
^b Temperature.
^c None, 0–10% strength loss; slight, 11–20% strength loss; moderate, 21–40% strength loss; appreciable, 41–80% strength loss; degraded, 81–100% strength loss.



12.29 Hydrolytic resistance of Technora and PPTA fibres in 100–200 °C saturated steam (Technical Datasheets).

retention of 69% after 24 months under the same conditions (Technical Datasheets).

12.3 Liquid crystalline (LC) aromatic heterocyclic fibres

Heterocyclic polymers with a lyotropic LC behaviour are characterized by wholly aromatic molecular structures with fused heterocyclic rings along the main chains. In more detail, they can be classified into three main categories: polybenzazole, polybenzimidazole and polypyridobisimidazole. Figure 12.30 summarizes the most relevant examples of this class of LC fibre.

Poly(2,2'-(*m*-phenylene-5,5'-bibenzimidazole) (PBI) is the most prominent example of polybenzimidazole: in fact, PBI fibres were commercialized by Celanese in 1983 and they are a trademark of PBI Performance Products (USA). Unfortunately, the *meta*-substitution gives a non-linear shape to the main chain: as a result, the tensile properties are broadly the same as conventional fibres (with a modulus of 5 GPa and a tensile strength of 400 MPa) (Coffin *et al.*, 1982). Nevertheless, PBI fibres are appreciated for the excellent thermal and chemical stabilities induced by the aromatic structure.

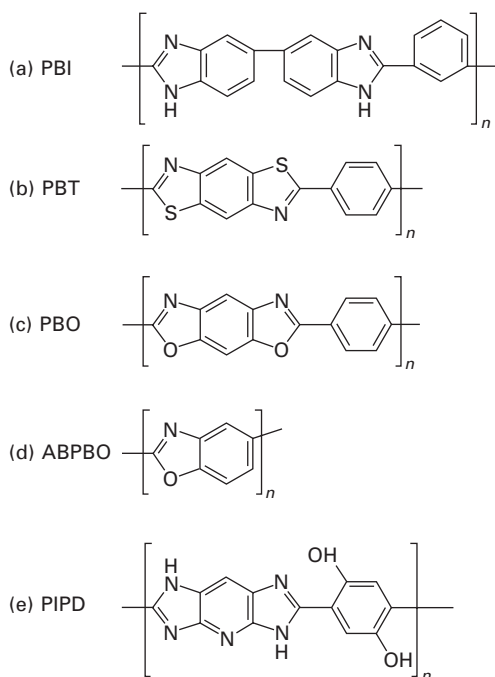
Polybenzazole polymers include poly(*p*-phenylene-2,6-benzobisoxazole) (PBO, aka PBZO), poly(*p*-phenylene-2,6-benzobisthiazole) (PBZT, aka PBT) and poly(2,5(6)-benzoxazole) (ABPBO). PBO and PBZT fibres were first developed by the US Air Force in the 1960s and 1970s, and are characterized by excellent mechanical properties. However, because the high production cost of PBZT, only PBO fibres were introduced in the industrial market with the trademark *Zylon* (Toyobo, Japan) since 1998.

Finally, poly(diimidazo pyridinylene dihydroxy phenylene) (PIPD) is the most important type of polypyridobisimidazole. Developed in the 1990s by Akzo Nobel, PIPD fibres are also known with the trademark M5, the property of Magellan (USA), a company tightly partnered with DuPont.

12.3.1 Fibre production

Polymer synthesis

The synthesis of PBO and PBZT (Wolfe and Loo, 1980; Wolfe and Arnold, 1981; Wolfe *et al.*, 1981a, 1985a, b, Wolfe and Sybert, 1987; Wolfe, 1988; Arnold and Arnold, 1994) is typically conducted via polycondensation of aromatic tetra-amines and terephthalic acid (TA) or TA derivatives (e.g. terephthaloyl chloride) in polyphosphoric acid (PPA). 4,6-Diamino-1,3-benzenedithiol dihydrochloride (DABDO) is used as a monomer in PBO synthesis, while 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) is used for PBZT synthesis. Before the polymerization, amino hydrochloride



12.30 Structural formulae of the most important heterocyclic polymers that are available in the reference literature and on the market as commercial brands.

monomer and PPA are heated at 60–130 °C for 3–24 hours (under vacuum or in an inert gas) to allow the dehydrochlorination that is necessary for the complete activation of the amino monomer. TA can be added before or after the dehydrochlorination; moreover, after the process, an additional amount of phosphorus pentoxide (P_2O_5) and/or PPA is required to obtain a stirrable mixture. Afterwards, the reactant mixture is heated at 100–150 °C for a few hours to remove the last traces of hydrogen chloride, to wet the terephthalic acid, and to initiate the polymerization reaction. Subsequently, the reactant mixture is heated at a temperature higher than 150 °C (typically between 190 and 200 °C) for several hours (up to 48 h) until the completion of heterocyclization is reached. It is important to note that PPA acts as catalyst and not only as solvent during the condensation of amine monomer with TA to directly form the benzobisazole macromolecules. The main problem during the early development stage was related to the difficulty of obtaining a molecular weight sufficiently high to guarantee elevated mechanical properties. The purity of monomers and solvent, especially for the amine monomer, is a critical issue: a high molecular weight must be attained. For this reason, the methods of production and purification of the amine monomer are of great

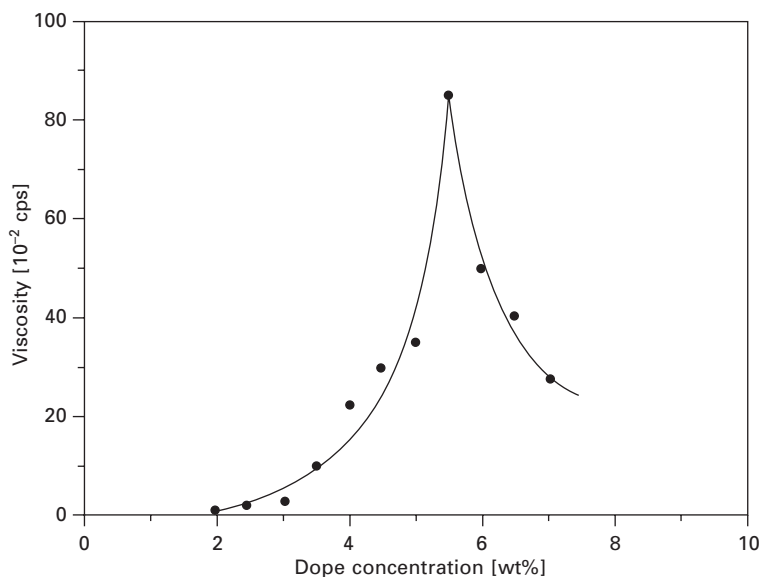
importance and very expensive (Wolfe and Loo, 1980; Wolfe *et al.*, 1985a, b; Wolfe and Sybert, 1987; Lysenko, 1988). Moreover, another critical issue to enhance the molecular weight is the dimension of TA aggregates: they must be small enough (less than 10 nm) to be completely dissolved in the reaction mixture. If these conditions are satisfied, the resulting polymer is characterized by an inherent viscosity of the order of 30–50 dL/g, corresponding to a weight-average molecular weight of about 40 000–60 000 g/mol and chain length of about 210 nm.

On the other hand, the synthesis of PIPD (Wolfe, 1988, So *et al.*, 1995; So and Heeschen, 1997) is conducted by polycondensation on 2,3,5,6-tetraaminopyridine (TAP) hydrochloride and 2,5-dihydroxyterephthalic acid (DHTA) in PPA as solvent. As for the synthesis of PBO and PBZT, a preliminary dehydrochlorination (several hours at about 100 °C) is necessary for the complete activation of TAP monomer. Subsequently, the polymerization process is conducted at 140–180 °C for 4–5 hours. If the degree of purity of the monomers is high enough, inherent viscosity of about 50 dL/g or more can be reached, corresponding to a molecular weight of the order of 60 000–150 000 g/mol.

Fibre spinning

PBO and PBZT manifest lyotropic behaviour like polyaramides. They have no melting point (i.e. they decompose before melting) and form an LC phase in strong protic acids such as PPA, methanesulphonic acid (MSA), chlorosulphonic acid, 100% sulphuric acid, and trifluoroacetic acid (Wong *et al.*, 1978; Berry *et al.*, 1981; Choe and Kim, 1981; Wolfe and Arnold, 1981, Wolfe *et al.*, 1981a, 1981b, Hu *et al.*, 2003). Figure 12.31 shows the viscosity of PBO–H₂SO₄ solution at 70 °C as a function of dope concentration: PBO molecules form a liquid crystal phase in 100% sulphuric acid at about 5.5wt %.

Dry jet–wet spinning is used to produce PBO and PBZT fibres (Allen *et al.*, 1983; Wolfe *et al.*, 1985a; Wolfe and Sybert, 1987; Jiang *et al.*, 1996; Chae and Kumar, 2006). The polymer solution is prepared by dissolving isolated polymer into MSA or by directly using the PPA polymerization solution. The different solvents do not induce significant differences in terms of mechanical properties of the resulting fibres (Allen *et al.*, 1981b). PPA-based solutions for dry-jet wet spinning typically have a concentration of 10–15 wt% in the temperature range of 100–170 °C. Chenevey and Helminiak (1986) have shown how polymers with a viscosity lower than 10–14 dL/g resulted in fibres with poor mechanical properties. Only with a viscosity of 20–30 dL/g or higher were the fibres obtained with a suitable spinning speed and with satisfactory mechanical properties, being of an intrinsic viscosity of about 50 dL/g as the optimal value.



12.31 Viscosity as a function of dope concentration for PBO-H₂SO₄ solution at 70°C (Choe and Kim, 1981).

Water at room temperature is normally used as a coagulation bath. Nevertheless, other coagulation baths (such as dilute phosphoric acid solution, MSA aqueous solution, methanol, ammonium hydroxide and iodine/ethanol solution) were considered. From a general point of view, the composition and temperature of the coagulation bath influence the structure and mechanical properties of the fibres (Choe and Kim, 1981; Rakas and Farris, 1990). The importance of the coagulation bath was shown by the non-aqueous coagulation system developed by Toyobo (Kitagawa *et al.*, 1999, 2000). In fact, a slow coagulation process during fibre production resulted in a better control of the structure of the fibre and in an increase of the tensile modulus from 280 to 360 GPa.

The production of PIPD-based *M5* fibres is conducted by conventional air gap wet-spinning (Lammers *et al.*, 1998; Northolt *et al.*, 2002). The as-polymerised solution of polymers with a dope concentration of about 18 wt% is spun at 180–190°C in air into a coagulation bath (water or dilute phosphoric acid). Subsequently, PIPD fibres are washed to a low phosphorus content and dried.

Heat treatment

Dry jet-wet spinning is usually followed by a heat treatment under tension to enhance the molecular orientation and, consequently, the mechanical

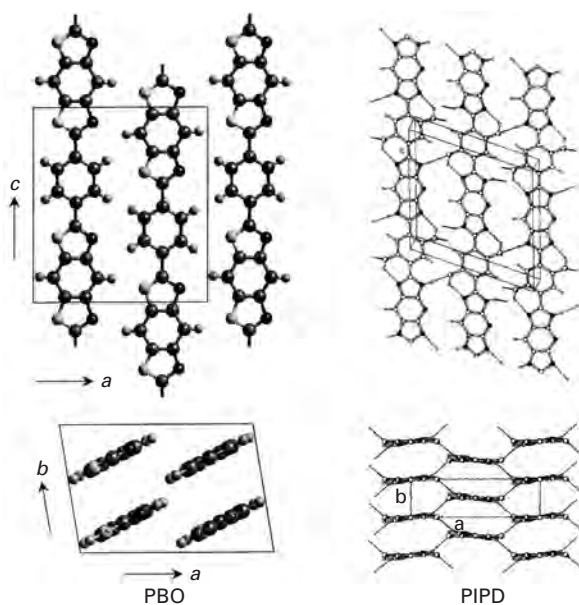
properties of the fibres. In a typical treatment, PBO fibres are drawn under tension at temperatures of 500–700 °C in nitrogen for a few seconds (Wolfe *et al.*, 1985a; Wolfe and Sybert, 1987). Allen *et al.* (1985a,b) investigated the effect of the heat treatment under tension for PBZT. Optimal conditions resulted in a temperature range of 630–680 °C, tension of 150–200 MPa and residence time of less than one minute. In this case, the modulus increased from 150 to 300 GPa and the tensile strength from 1.6 to 3 GPa. Figure 12.32a, b documents the effect of the treatment parameters (temperature and applied stress) on the modulus and strength of PBZT fibres.

In the case of PIPD fibres, heat treatment is conducted by drawing (at a few per cent strain) at high temperature (>400 °C) under stress for short times (approximately 20 seconds) under nitrogen gas (Klop and Lammers, 1998; Lammers *et al.*, 1998). In this way, the mechanical properties can be substantially improved. The modulus of PIPD fibres increased from 150 to 330 GPa after an heat treatment at 400 °C, and, concurrently, the strength improved from 2.5 to 5.5 GPa.

Structure

PBO and PBZT fibres are characterized by an extremely high crystallinity content (approaching 100%) and a strong orientation with a small number of defects (such as chain ends, chain bends and voids). Both fibres have a crystal structure consisting of a monoclinic unit cell (as depicted in Fig. 12.33) with $a = 1.12$ nm, $b = 0.35$ nm, $c = 1.20$ nm, and $\beta = 101^\circ$ in the case of PBO and $a = 1.17$ nm, $b = 0.35$ nm, $c = 1.25$ nm, and $\beta = 93^\circ$ in the case of PBZT (Fratini *et al.*, 1989; Tashiro *et al.*, 1998; 2001; Takahashi and Sul, 2000).

As reported by Sawyer *et al.* (1992, 1993), SEM and TEM micrographs of tensile fractured or compressively peeled fibres, and X-ray diffraction experiments concurrently indicate a fibrillar structure for PBO and PBZT fibres. Figure 12.34 shows a structural model of PBO fibres proposed by Kitagawa *et al.* (1998, 2000), Davies *et al.* (2001, 2003); Ran *et al.* (2002). The fibrils run parallel to the fibre axis with voids between them. Such fibrils consist of PBO molecules highly oriented along the fibre axis, with the a -axes of the crystals radially aligned across the fibre. The voids are elongated along the fibre axis originating from the large contraction during coagulation. Moreover, a skin–core differentiation is evident, being the surface region (< 0.2 mm) practically void-free. The extent of the skin–core differentiation mainly depends on the processing conditions, which regulate the solvent diffusion and fibre coagulation. Similarly, Allen *et al.* (1981a) revealed that PBZT fibres are also characterized by a similar fibrillar structure. Moreover, Hancock *et al.* (1980) found that microvoids were more pronounced in the case of PBZT fibres spun from MSA (in the order of 5 to 20 % by volume) than in the case of PBZT fibres spun from PPA.

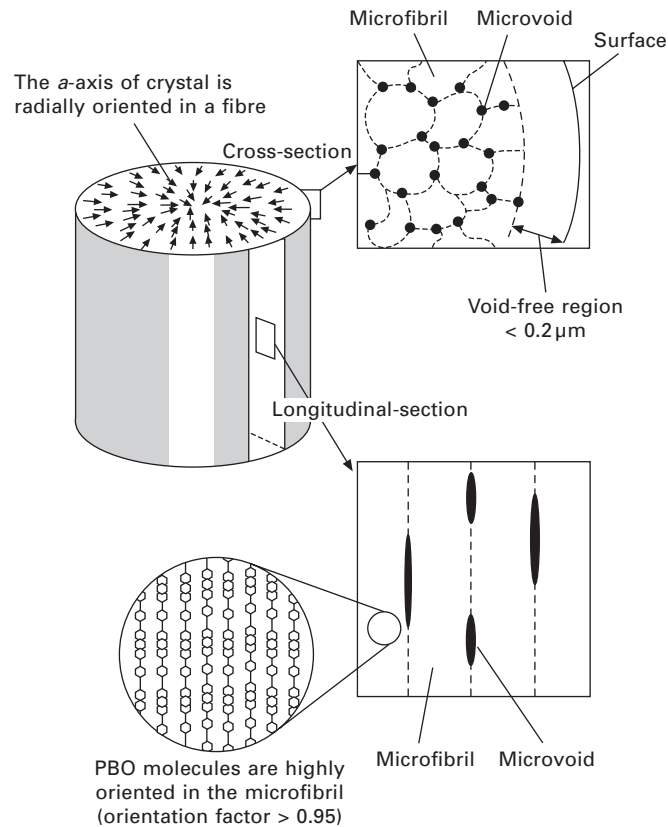
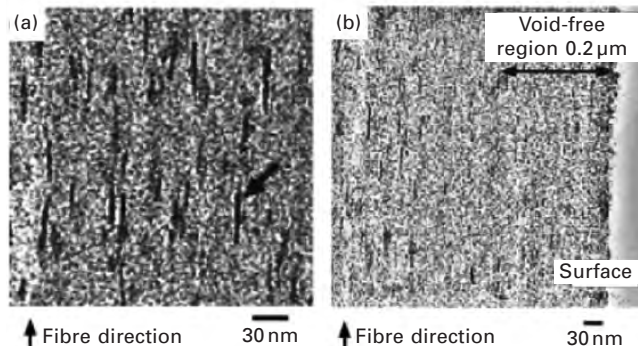
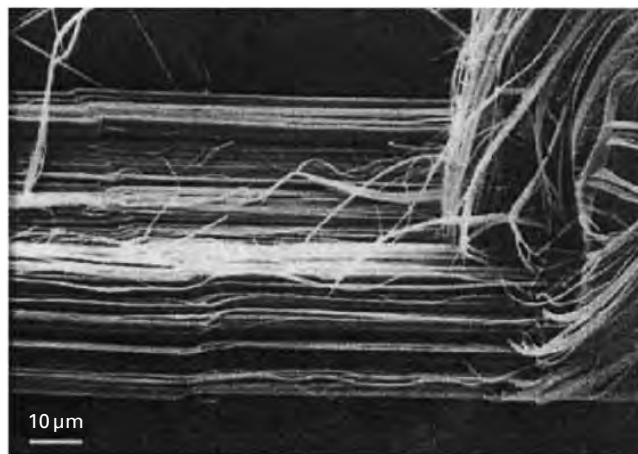


12.33 Crystal structure of (left) PBO (Tashiro *et al.*, 1998) and (right) PIPD (Klop and Lammers, 1998).

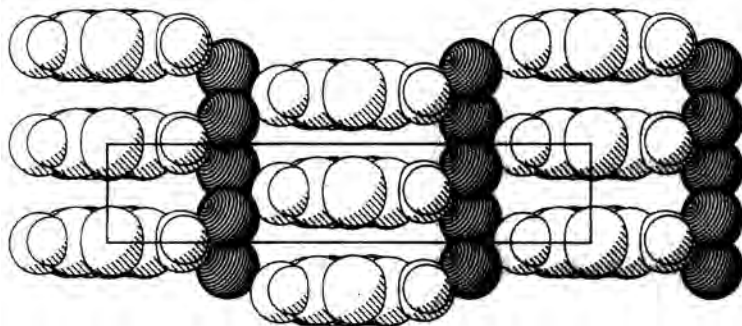
1991) observed an increase of the crystal size, more pronounced in the lateral direction rather than along the fibre axis, for both PBO and PBZT fibres. For example, Krause *et al.* (1988) found that crystallites were 5.2 nm long and 5.4 nm wide for as-spun PBO fibres, while they were 5.7 nm long and 10.6 nm wide for heat-treated PBO fibres. Moreover, the enhancement of crystallite orientation is shown by the Herman's orientation factor that increase from 0.87–0.95 of as-spun PBO fibres (PBO AS) to 0.93–0.99 of heat treated PBO (PBO HM) and PBZT fibres (Allen *et al.*, 1985a,b; Chae and Kumar, 2006).

Unlike PBO and PBZT chains, which interact only by weak van der Waals interactions, PIPD chains are characterized by rather strong interactions (Allen *et al.*, 1985a,b, Krause *et al.*, 1988; Adams *et al.*, 1989; Martin and Thomas, 1991). When PIPD fibres are spun from the polymer solutions, the formation of fibres with crystal solvate structures of PIPD-PPA take place. Subsequently, after coagulation, PIPD fibres assume the form of a two-dimensional crystal hydrate structure that contains 21 wt% of water molecules. The as-spun PIPD fibres (M5 AS) are characterized by a modulus of 150 GPa and a rectangular crystalline unit cell with dimensions $a = 16.85 \text{ \AA}$ and $b = 3.38 \text{ \AA}$, as depicted in Fig. 12.35.

During the heat treatment, the water molecules are removed from the system. Heat-treated PIPD fibres (M5 HT) are characterized by improved lateral molecular packing, molecular orientation and tensile modulus (330 GPa).



12.34 SEM micrograph of peeled PBO fibre (Chae and Kumar, 2006) (left, top), TEM images of microvoids containing region and void-free region (left, down), and structural model of PBO fibre (Kitagawa *et al.*, 1998) (right). Reprinted with the permission of John Wiley Sons Inc.



12.35 The hydrate crystal structure of as-spun PIPD fibres viewed along the chain axis. The water molecules between the chains are indicated by dashed filler circles (Klop and Lammers, 1998).

The crystal hydrate structure is transformed into a water-free structure with a monoclinic unit cell whose dimensions are $a = 12.60 \text{ \AA}$, $b = 3.48 \text{ \AA}$, $c = 12.01 \text{ \AA}$ and $\beta = 108.6^\circ$. Intramolecular $\text{O-H}\cdots\text{N}$ hydrogen bonds contribute to the rigidity of the polymer chains, intermolecular $\text{N-H}\cdots\text{O}$ hydrogen bonds form a bidirectional hydrogen network in which each polymer chain is linked to its four axially shifted neighbours as depicted in Fig. 12.35. Like PBO and PBZT, PIPD fibres are characterized by a fibrillar structure (Cunniff *et al.*, 2002).

12.3.2 Properties

Physical and thermal properties

From a general point of view PBO and PBZT fibres are characterized by high thermo-oxidative stability. Thermogravimetric analysis on PBO fibres reveals that the onset of degradation occurs at about 650°C in air, and at more than 700°C in a non-oxidative atmosphere (Denny *et al.*, 1989; Kuroki *et al.*, 1997; Clements, 1998; Bourbigot *et al.*, 2001). In the case of PBZT fibres the onset of degradation occurs at about 620°C in air and at more than 680°C in a non-oxidative atmosphere (Denny *et al.*, 1989; Kuroki *et al.*, 1997; Clements, 1998; Bourbigot *et al.*, 2001). These values are about 100°C higher than the corresponding temperature of *para*-aramid fibres. Moreover, in order to obtain complete degradation (i.e. no residual weight) a temperature of 800°C in air for both PBO and PBZT fibres must be reached. Both PBO and PBZT degrade before the melting or glass transition processes can occur. On the other hand, the onset of thermal degradation for PIPD-based M5 fibres in air is about 530°C (Northolt *et al.*, 2002).

The high thermo-oxidative stability of PBO and PBZT fibres is also evident during isothermal ageing (Wolfe, 1988; Denny *et al.*, 1989; Clements, 1998). After 200 hours at 316°C in air, no weight loss is observed, at 343°C

approximately 90% of the initial weight is retained, and at 370 °C over 70% of the initial weight is retained, corresponding to a weight loss rate of 0.06% per hour.

In addition, PBO and PBZT fibres possess exceptionally good fire resistance (Helminiak, 1979; Choe and Kim, 1981; Wolfe, 1988, 1989; Kim *et al.*, 1993; Bourbigot *et al.*, 2002, 2003). They are intrinsically non-combustible with very little toxic combustion products in case of fire. When directly exposed to a flame, they char, but do not support combustion.

Finally, PBO and PBZT fibres are characterized by negative axial coefficients of thermal expansion (CTE). CTE has a value of -1 to 2.5 ppm/°C for PBZT fibres (Im *et al.*, 1991) and of about -6 ppm/°C (Helminiak, 1979) for PBO (Zylon HM) fibres.

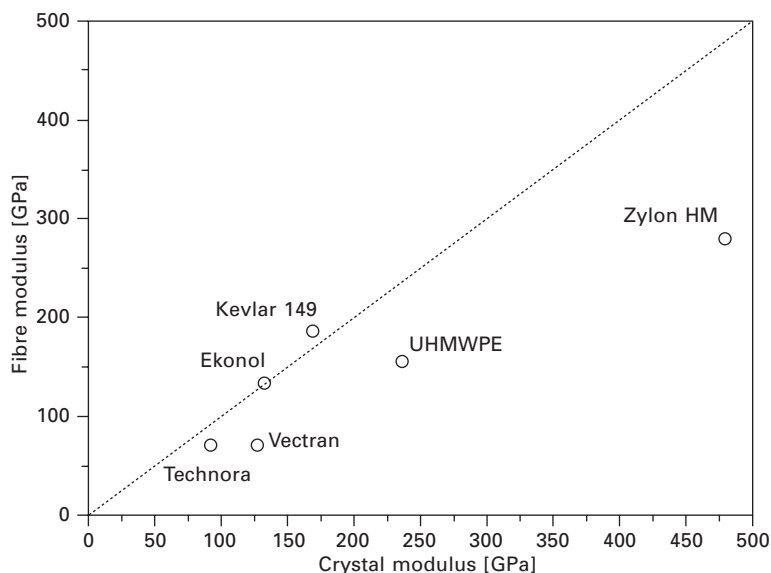
Mechanical properties

Typical tensile properties of PBZT, PBO and PIPD fibres are presented in Table 12.1. It can be noticed that their modulus and strength values are markedly higher than *para*-aramid fibres.

From a general point of view, modulus and strength depend on polymer molecular structure and weight (as mentioned before), processing and post-processing conditions. Zylon AS, Zylon HM and Zylon HM+ represent commercial trademarks for PBO-based fibres with different processing conditions. Zylon AS represents an as-spun PBO fibre with a modulus of 180 GPa, Zylon HM is the same fibre after a proper heat treatment which increases the tensile modulus up to 270 GPa. Zylon HM+ is a PBO-based fibre produced through a non-aqueous coagulation system: in this case the modulus reach 350–370 GPa (Krause *et al.*, 1988; So, 2000; Kitagawa *et al.*, 2001).

A theoretical limiting tensile modulus for PBO fibres, related to the rigidity of the crystal lattice, of about 460–480 GPa can be estimated from X-ray diffraction measurements (Day *et al.*, 1987; Lenhert and Adams, 1989; Tashiro and Kobayash; 1991; Nishino *et al.*, 1995; Kitagawa *et al.*, 2000; Kitagawa and Yabuki 2000). Figure 12.36 shows that the modulus of commercial PBO fibres could be further improved since the distance from the maximum theoretical value of the crystal modulus is wider than that of other high performance organic fibres.

As reported in Table 12.1, PBO fibres possess better tensile mechanical properties than PBZT fibres. In fact, while PBO fibres present a tensile modulus of 270 GPa and a tensile strength of 5.8 GPa, PBZT fibres can reach a modulus of 320 GPa and a strength of 3.9 GPa (Allen *et al.*, 1985a; Kozey *et al.*, 1995). This is probably related to the higher coplanarity in PBO fibres between the 1,4-phenylene ring and the plane of the heterocyclic moiety, which results in a higher packing density (Wang and Zhou, 2004). The



12.36 Macroscopic fibre modulus as a function of crystal modulus for various fibres (Kitagawa *et al.*, 2000).

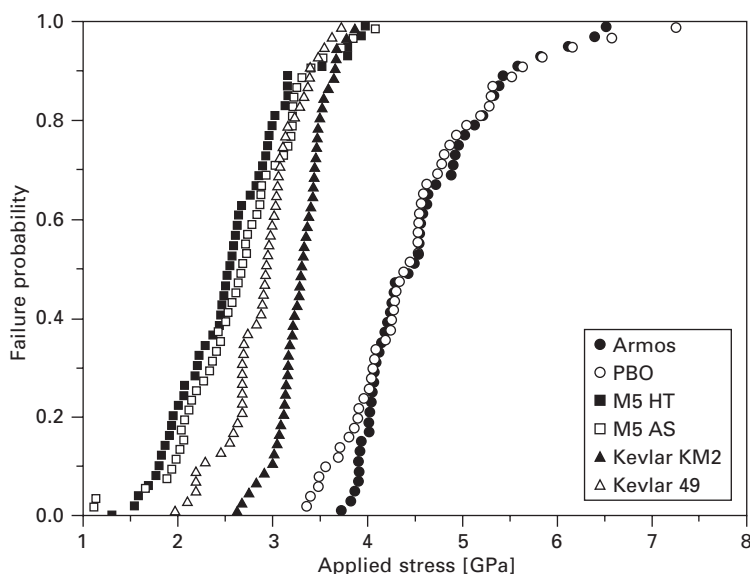
importance of the microstructure also emerges when considering ABPBO fibres (Fig. 12.30). The kinks in the main chain reduce its chain stiffness in comparison to PBO and PBZT: as a result, the modulus is 140 GPa, the strength 3.1 GPa and the elongation at break 2.9% (Krause *et al.*, 1988). On the other hand, ABPBO is characterized by high thermal stability due to the presence of the aromatic rings. In addition, Zylon HM fibres have good tensile creep properties. Chae and Kumar (2006) predicted a failure time of 19 years for a failure stress of 60% of the static strength. The apparent creep rate is 3.2×10^{-4} and 1.1×10^{-4} for Zylon AS and Zylon HM fibres, respectively, under a constant load of 50% of the breaking strength. These values are similar or even lower than those evaluated for *para*-aramid fibres ($2.5\text{--}5.0 \times 10^{-4}$).

PIPD fibres are also characterized by outstanding tensile mechanical properties. M5 HT fibres present a modulus of 330 GPa, a strength of 5.5 GPa and an elongation at break of 1.7%. These values depend on the processing conditions. The as-spun PIPD fibres have modulus of 150 GPa, strength of 2.5 GPa and elongation at break of 2.7%. After a heat treatment at 200 °C the tensile modulus increases up to 280 GPa, the strength up to 3.8 GPa and the elongation at break decreases to 1.5%. Finally, heat treatment at 400 °C improves the tensile modulus up to 330 GPa, the strength up to 4.1 GPa and an elongation at break up to 1.4% (Lammers *et al.*, 1998; Sirichaisit and Young, 1999; Northolt *et al.*, 2002). Moreover, theoretical analyses indicate

a chain modulus of 553–578 GPa, which is in relatively good agreement with the crystal modulus of 510 GPa estimated by X-ray diffraction (Hageman *et al.*, 1999).

As previously reported for aramid fibres, LC aromatic heterocyclic fibres also fail in a brittle manner under tension with a large scatter of the strength values. As reported in Fig. 12.37, the strength of PBO fibres has an average value of 5.8 GPa with peak values in excess of 7 GPa (Beers *et al.*, 2001; Leal *et al.*, 2007). In the case of M5 fibres (both M5 AS and M5 HT), the shape parameter of the cumulative Weibull distribution of the strength values is in the range 4–5, i.e. that is similar to E-glass fibres. On the other hand, PBO fibres reach values of about 6–7 and PBZT fibres values of about 7–10. In any case the shape parameter appears to be slightly lower than that of Kevlar fibres which is in the range 8–14 (Sahafeyan and Kumar, 1995; Leal; *et al.*, 2007).

While tensile properties are related to covalent bonds in the aligned polymer chains, compressive and shear properties mostly depend on the interchain bonds. PBO and PBZT fibres are characterized by weak van der Waals interactions between the chains: as a result, PBO and PBZT fibres show a compressive strength of 200–400 MPa and of 300–400 MPa, respectively (Technical Datasheets; Allen *et al.*, 1983; Kumar and Helminiak, 1988; Kozey *et al.*, 1995; Kitagawa *et al.*, 2001). These values represent only a small fraction (approximately 10–15%) of the axial tensile strength.

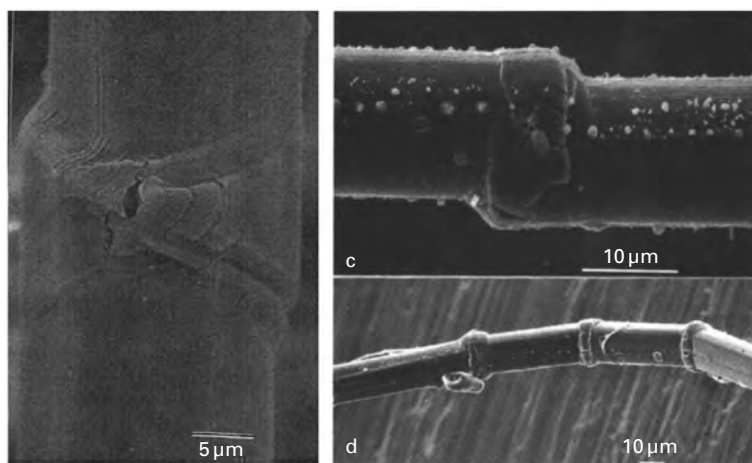


12.37 Cumulative probability of failure for several fibres in tensile test (Leal *et al.*, 2007).

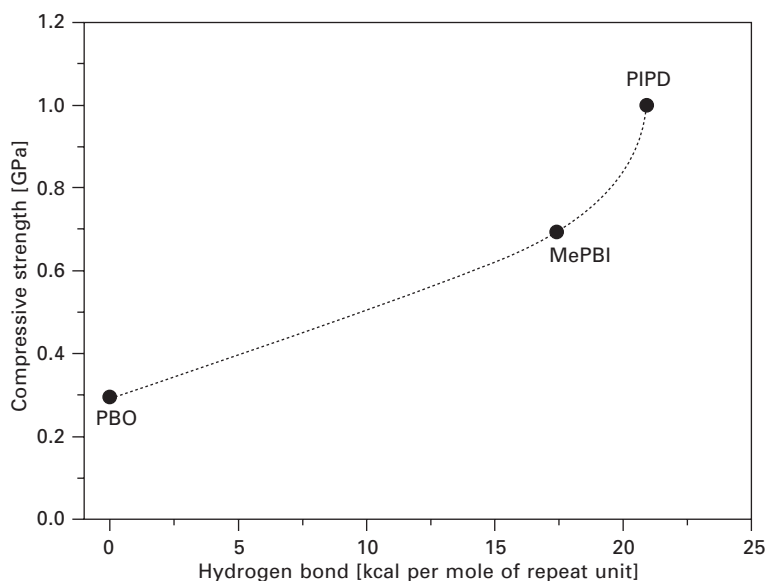
These compressive strength values are comparable to those of conventional organic fibres, but remarkably lower than those of carbon fibres (1–3 GPa), and inorganic fibres such as boron, alumina and silicon carbide fibres that can reach 7 GPa. On the other hand, unlike carbon and inorganic fibres, PBO and PBZT fibres do not present catastrophic failure under compressive stress, but they gradually fail via kinking, as depicted in Fig. 12.38.

From a general point of view, the compressive properties depend on the type and degree of intermolecular interactions present in the fibres (Deteresa *et al.*, 1988; Northolt and Sikkema, 1991; Hu *et al.*, 2000; Northolt and Batussen, 2002; Chae and Kumar, 2006). Figure 12.39 shows as the compressive strength increases as the energy of the hydrogen bonds increases for heterocyclic rigid-rod polymer fibres. PAN-based carbon fibres show a much higher compressive strength (above 2 GPa) due to the presence of covalent bonding between the graphitic planes. As previously described, the polymeric chains in Kevlar fibres are hydrogen bonded in a single direction. As a result, compressive strength is in the order of 400 MPa. Moreover, the pendent hydroxyl groups of PIPD, which create a two-dimensional network of intermolecular hydrogen bonds, drastically improve the compressive strength that reach a value of 1.7 GPa (Lammers *et al.*, 1998; Sirichaisit and Young, 1999; Hu *et al.*, 2003).

Similarly, the shear modulus G is another property that is strictly dependent on the interchain bonds. In the case of PBO and PBZT, the G value is about 1 GPa (Mehta and Kumar, 1994), while it increases to about 2 GPa for Kevlar (Deteresa *et al.*, 1984) and 5.9–7 GPa for PIPD (Lammers *et al.*,



12.38 Kink bands for PBO (Chae and Kumar, 2006) (left) and PBZT (Kozey *et al.*, 1995) fibres under compression (right, top) and bending (right, bottom). Reprinted with the permission of John Wiley Sons Inc. and of Materials Research Society.



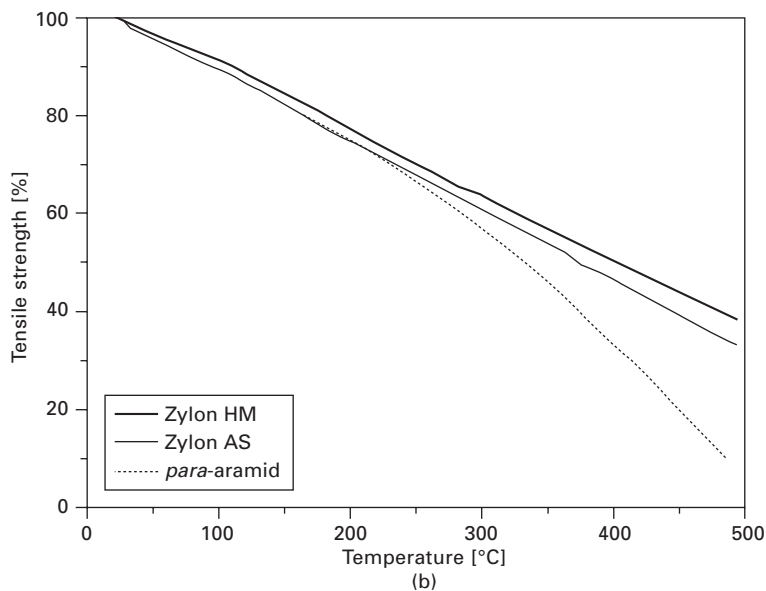
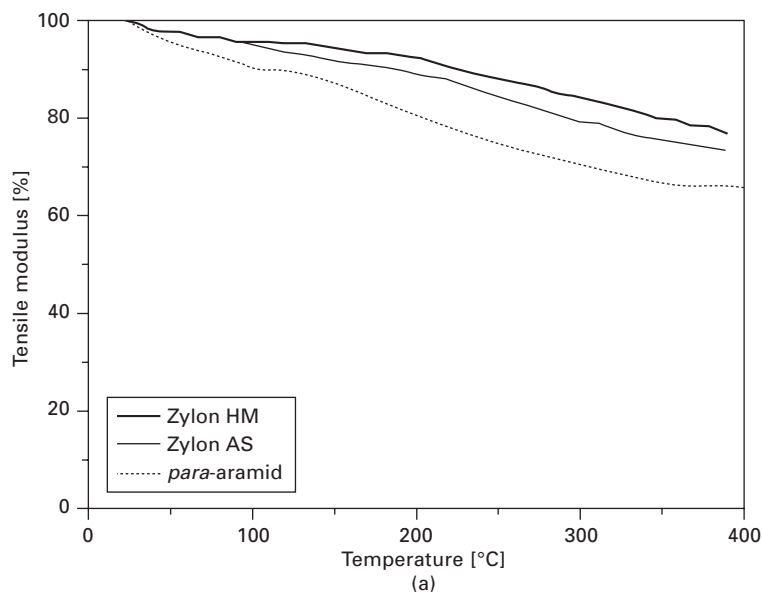
12.39 Compressive strength as a function of hydrogen bonding for heterocyclic rigid-rod polymer fibres (Chae and Kumar, 2006; Hu *et al.*, 2000).

1998; Sikkema, 1998; Northolt and Baltussen, 2002). As a comparison, the shear modulus of conventional organic fibres is generally in the range of 0.5–1 GPa, and 4–16 GPa for carbon fibres.

The mechanical properties of PBO and PBZT are influenced by the temperature, even if to a lower extent with respect to aramid fibres. As depicted in Fig. 12.40, tensile moduli and tensile strengths of PBO-based Zylon HM fibres decrease as the temperature increases. The modulus and strength at 400 °C are about 75% and 50% of the corresponding values at room temperature. In the case of heat-treated PBZT fibres, modulus and strength values at 250 °C are about 80% and 70% of the corresponding values at room temperature (Uy and Mammone, 1988). Similarly, the shear moduli of PBO and PBZT fibres show only a slight decrease in the range of 0–150 °C (Mehta and Kumar, 1994).

Chemical and environmental effects

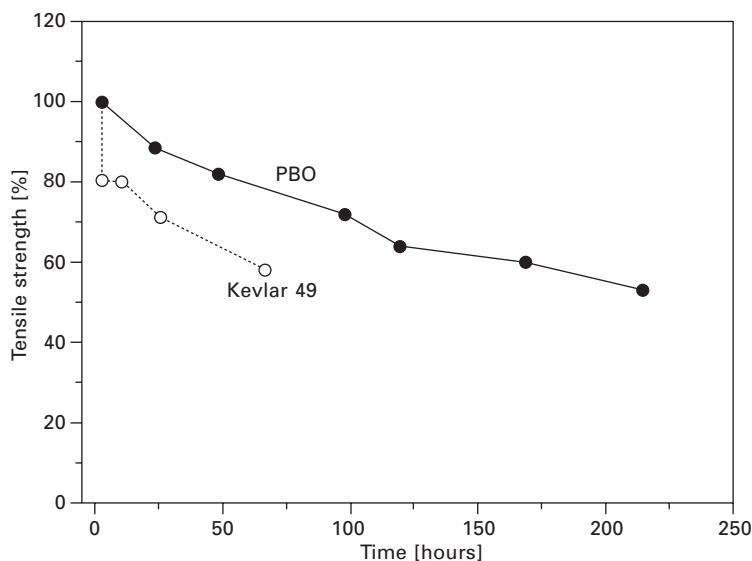
The strength retention of PBO and PBZT fibres after prolonged high temperature exposure is improved in comparison to *para*-aramid fibres. While the strength of PBO fibres is not affected by being held at 300 °C in an inert atmosphere, exposure at 300 °C in air causes a reduction of 25% in strength, as depicted in Fig. 12.41 (Jiang *et al.*, 1996). For PBZT fibres, Uy



12.40 Tensile modulus (a) and tensile strength (b) retention as a function of the temperature for PBO-based Zylon fibres (Technical Datasheets).

and Mammone (1988) found no loss of strength after an exposure at 300 and 450 °C for 65 hours in air.

PBO-based Zylon AS and Zylon HM fibres display moisture adsorption of

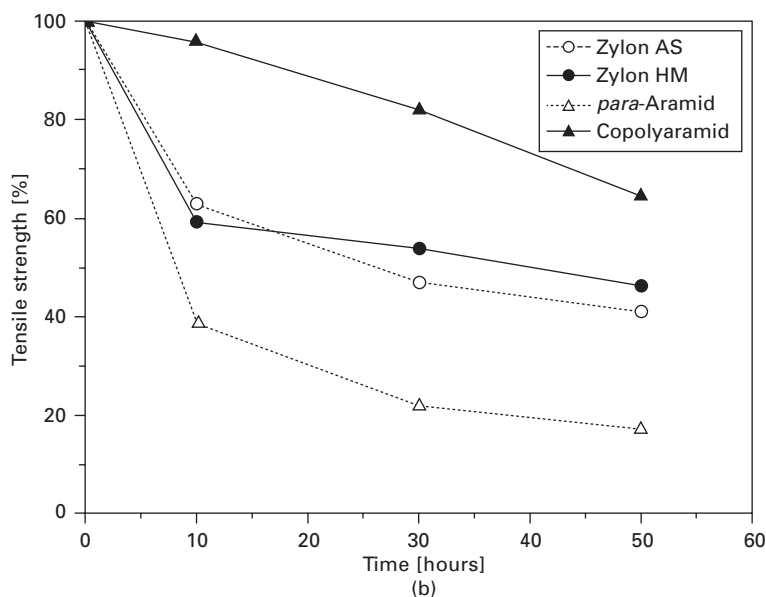
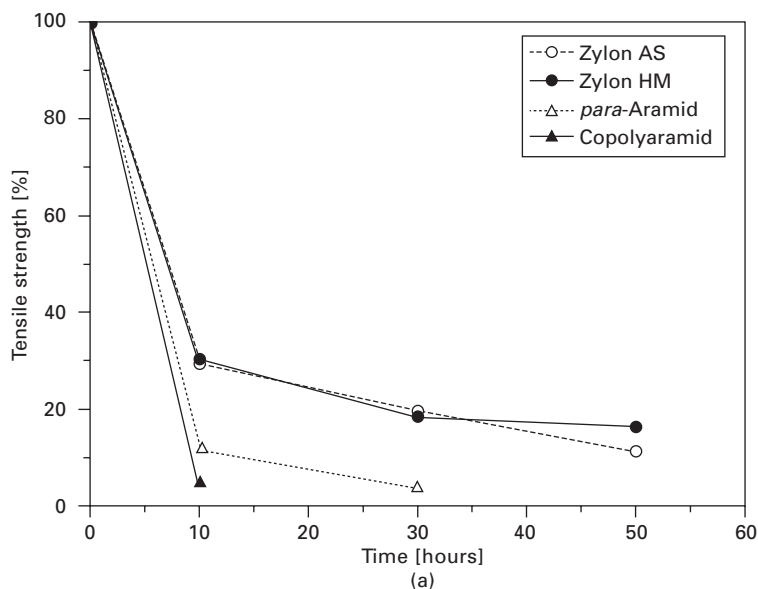


12.41 Strength retention for PBO and Kevlar 49 fibres as a function of time when exposed at 300°C in air (Jiang *et al.*, 1996).

2.0% and 0.6% (Clements, 1998), respectively. Even if PBO fibres are highly resistant to hydrolysis in comparison to *para*-aramid fibres, the combination of humidity and high temperature can drastically impair the tensile strength, as depicted in Fig. 12.42. Exposure to saturated steam for 50 hours at 250 °C causes the strength to decrease below 20% of its room temperature value. On the other hand, PIPD-based M5 fibres show very high resistance to humidity at elevated temperatures. In fact, as documented in Fig. 12.43, the strength of M5 yarns exposed to elevated temperature (82 °C) and humidity (85% RH) up to 11 weeks is almost unchanged, while Zylon yarns lost over 20% of their initial tensile strength (Cunniff *et al.*, 2002).

PBO fibres are also very sensitive to ultraviolet and visible light. Exposure to UV radiation induces sharp drops of the tensile strength in the initial stage as depicted in Fig. 12.44. Similarly, a one month exposure to two 35 W fluorescent lamps placed 150 cm from the sample resulted in a reduction of the PBO fibre tensile strength to nearly 70% of its original value. On the other hand, PIPD-based M5 fibres display very high resistance to visible and ultraviolet light. After exposure to a Zenon lamp for 100 hours, the tensile strength of M5 yarns remained unchanged, whilst the tensile strength of Zylon yarns decreased by 35% (Cunniff *et al.*, 2002).

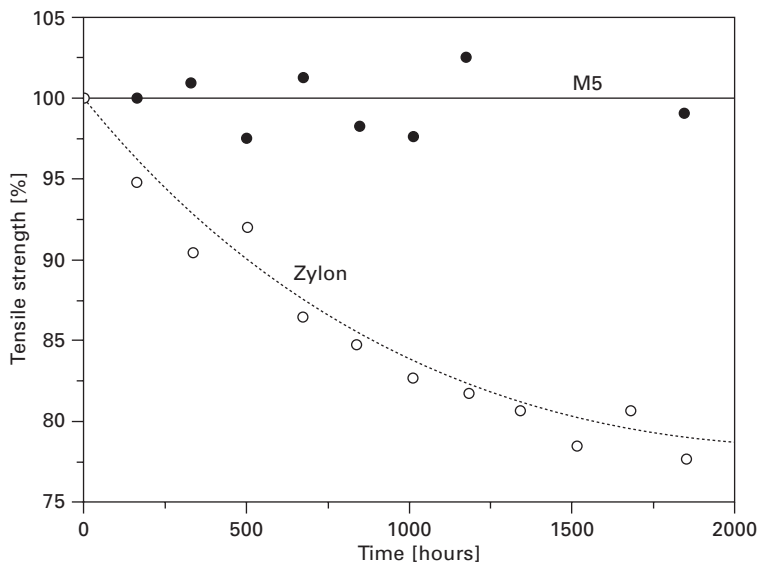
PBO fibres are generally highly resistant to chemicals at room temperature, but they are quite sensitive to exposure to strong acids and bases at high temperature (Wolfe, 1988).



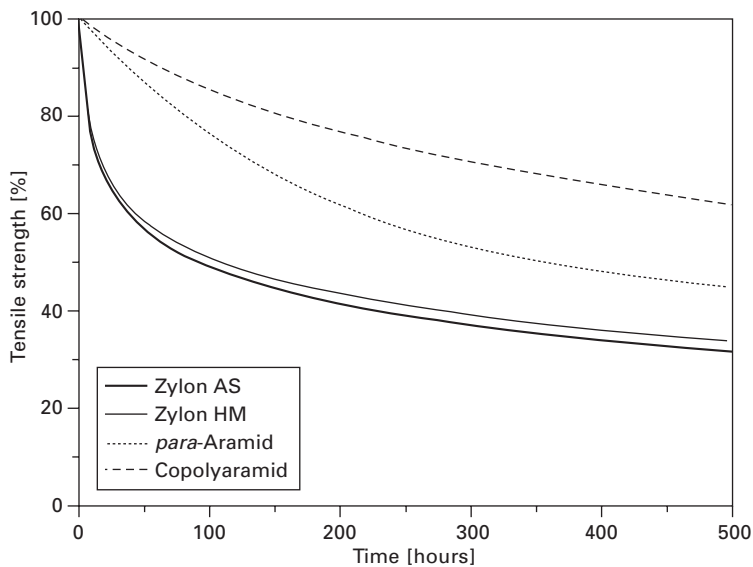
12.42 Tensile strength retention in PBO and aramid fibres in saturated steam at 180°C (a) and 250°C (b) (Technical Datasheets).

12.4 Liquid crystalline (LC) aromatic copolyester fibres

Thermotropic LC polymers are characterized by a molecular structure with a high degree of linearity and rigidity that allows the formation of ordered



12.43 Tensile strength loss of PIPD-based M5 and PBO-based Zylon fibres after exposure to 82 °C and 85% RH (Cunniff *et al.*, 2002).



12.44 Tensile strength retention in PBO and aramid fibre as a function of UV exposure time (Technical Datasheets).

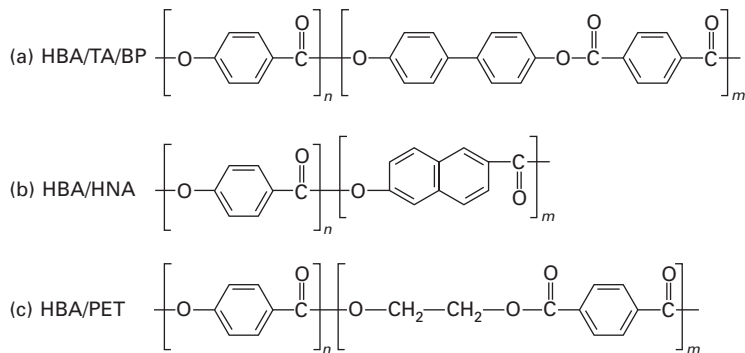
phases over a wide temperature range. Owing to their ability to maintain molecular orientation at high temperatures, these polymers may be melt-processed into strong fibres. Moreover, the melt processing allows the

use of these polymers as self-reinforcing plastics to produce extruded or injection-moulded articles.

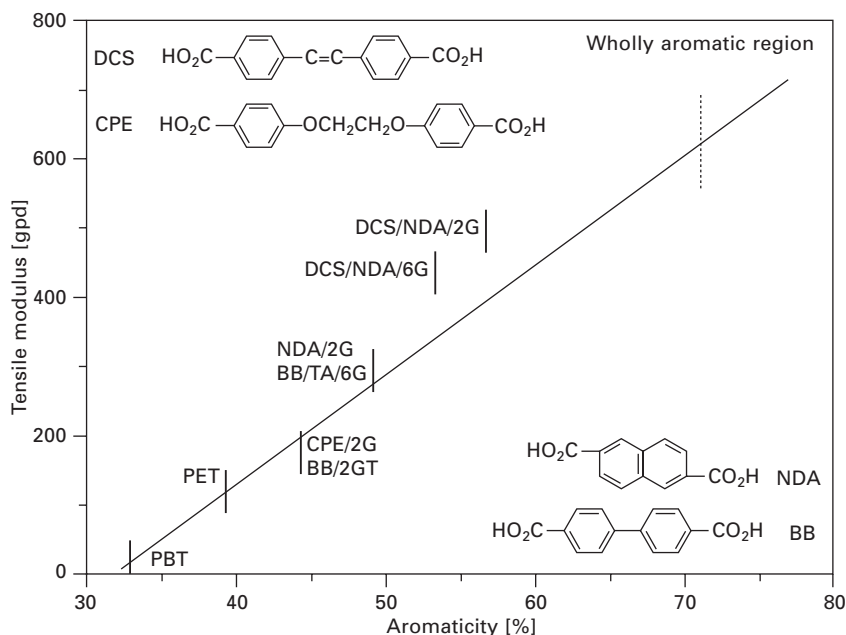
Although several molecular structures give rise to thermotropic liquid crystallinity, the aromatic polyester and copolyesters are the only ones which have been successfully prepared at an industrial scale. Figure 12.45 shows some example of aromatic polyesters and copolyesters with thermotropic LC behaviour. Moreover, although several aromatic copolyesters are commercially available, only Vectran (Kuraray, Japan), a copolymer of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, has been successfully developed as a high performances fibre.

The development of thermotropic polymers based on aromatic polyesters and copolyesters began in the late 1960s and it was mainly conducted by Economy (Carborundum Co.), Jackson Jr (Eastman Kodak) and Calundann (Hoechst Celanese). The interest in aromatic polyesters and copolyesters is mainly driven by the correlation existing between the mechanical properties and the degree of aromaticity in the polymer structure, that could be defined as the ratio of the number of sp^2 hybridized carbons to the total number of atoms in the repeat unit (Calundann *et al.*, 1988). In fact, as shown in Fig. 12.46, the tensile modulus of the fibres increases as the degree of aromaticity increases. Moreover, while conventional fibres based on polyesters such as poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) have low degrees of aromaticity and low tensile moduli (up to 200 gpd), only wholly aromatic polyesters fibres can reach moduli in excess of 600–700 gpd.

Homopolymer aromatic polyesters are characterized by very high melting points. As a result, they decompose before forming thermotropic mesophases. For example, poly(*p*-hydroxybenzoic acid) (PHBA), has a melting point of about 610 °C. Similarly, the polymer based on TA and hydroquinone (HQ)



12.45 Structural formulae of the most important aromatic polyesters and copolyesters that are available in the reference literature and on the market as commercial brands.



12.46 Effect of polyester aromaticity on fibre tensile modulus (Calundann *et al.*, 1988).

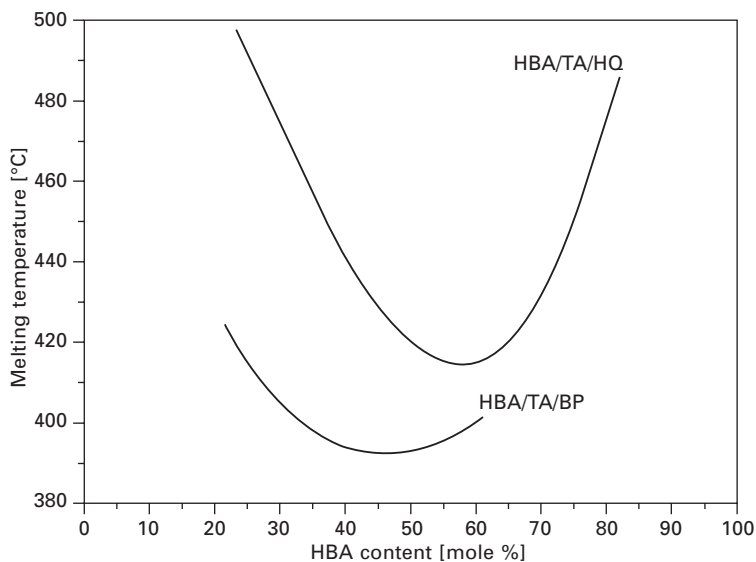
has a melting point of about 600 °C. On the other hand, their decomposition temperature is about 400–450 °C. As a result they are not melt-spinnable and not injection-mouldable.

To enhance the melt-processability of wholly aromatic polyesters, it is therefore necessary to depress their melting temperature. To achieve this result, additional monomeric units with somewhat less linearity and higher flexibility can be added during the polymerization process (East *et al.*, 1982; Huynh-Ba and Cluff, 1985). Aliphatic segments noticeably reduce the melting point because of their intrinsic lower rigidity. For example, PET/HBA shows a minimum in the melt viscosity at 275 °C for a HBA content of about 60–70 mole% because of the highly oriented nematic melt structure (Kuhfuss and Jackson, 1973; Jackson and Kuhfuss, 1976). These polymers are commercialized with the trademarks of *Rodrun* (Unitika, Japan) and *X7G* (Eastman Kodak, USA). Even if these polymers are melt-processable, they are not used for fibre production because the elevated PET content excessively lowers the final mechanical performance.

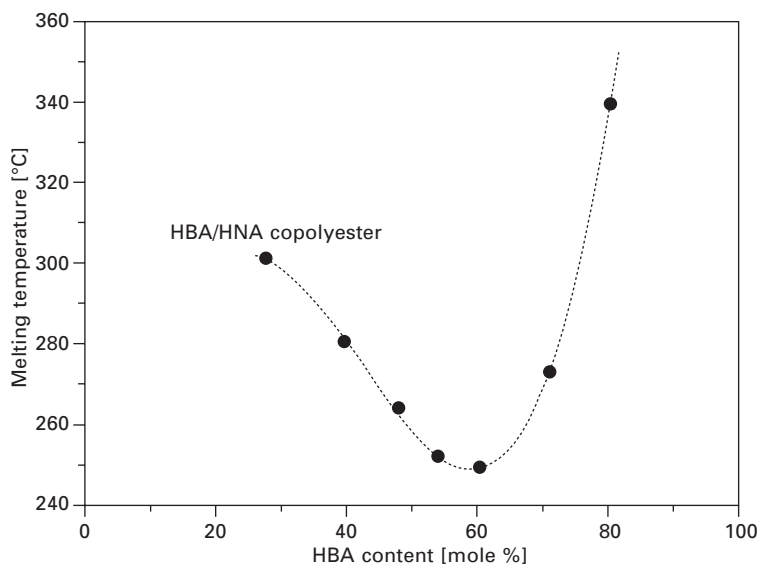
Alternatively the copolymerization of aromatic comonomers such as HBA, TA, HQ, 4,4'-biphenol (BP) and similar could be used. On the one hand, they act as mesogenic units that enhance the order of the polymer chains and the melt anisotropy. On the other hand, they produce random copolymers that may disrupt the crystalline order thus depressing the melting temperature.

Figure 12.47 shows the effect of composition on the melting temperature of wholly aromatic copolyesters based on HBA, TA and BP. For an HBA content of 42 mol%, the melting point reaches a minimum at about 395 °C (Cottis *et al.*, 1972). Copolyesters with this composition were commercialized with the trademarks of *Ekkcel* (Sumitomo Chemical, Japan) and *Xydar* (Solvay Advanced Polymers, Belgium). Both of them are injection-mouldable at about 400 °C; unfortunately this temperature is not compatible with common melt spinning equipment (Cottis *et al.*, 1972). By changing the ratio of the monomers for HBA/TA/BP copolyester, Sumito Chemical (Japan) developed a polymer with a melting point lower than 350 °C and the relative melt-spun fibres were commercialized under the trademark *Ekonol* (Ueno *et al.*, 1985).

Similarly, Hoechst-Celanese (USA) developed polymers based on parallel offset or ‘crankshaft’ geometry provided by 2,6 functionally di-substituted naphthalene monomers (Calundann, 1979, 1980; Calundann *et al.*, 1988). In particular, most of the efforts were focused on a copolymer based on HBA and 6-hydroxy-2-naphthoic acid (HNA) that was commercialized in 1985 under the trademark *Vectra*. Since 1986, Hoechst-Celanese and Kuraray (Japan) have jointly investigated the use of Vectra for fibre production which was finally commercialized under the trademark *Vectran*. Hoechst-Celanese licensed the fibre technology to Kuraray that entirely acquired the Vectran production in 2005. As depicted in Fig. 12.48, the HBA/HNA copolymer



12.47 Effect of the composition on the melting temperature of HBA/TA/BP copolyester (Cottis *et al.*, 1972).



12.48 Effect of the composition on the melting temperature of HBA/HNA copolyester (Calundann, 1979, 1980).

presents a minimum of the melting point at about 245 °C for an HBA content of about 60 mole%.

12.4.1 Fibre production

Polymer synthesis

As for most thermotropic polyesters and copolyesters, the HBA/HNA copolymer is obtained by a polycondensation reaction (Calundann, 1979; Calundann *et al.*, 1988). In particular, the process is conducted through conventional melt acidolysis starting with the acetoxy derivatives of the hydroxyl-containing monomers. Acetylated monomers are heated at about 200 °C and inert gas is fluxed until a clear melt forms. Subsequently, the system is heated to 250–280 °C for 0.5–3 hours to remove the acetic acid previously formed. The result is a turbid fluid dispersion consisting of the melt copolyester. The polymerization can be carried out with or without added catalyst. HBA and HNA monomers have a random distribution along the polymer chain because they possess about the same reactivity (Calundann, 1979; Gutierrez *et al.*, 1983).

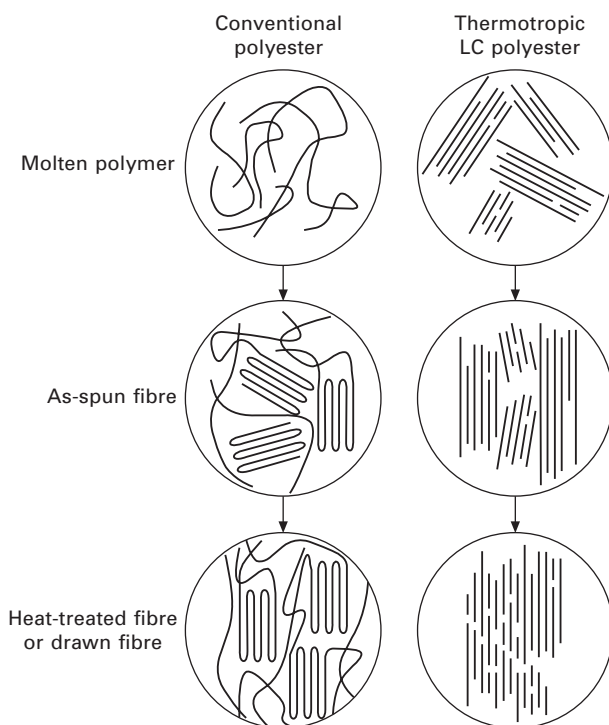
Fibre spinning

The spinning process of thermotropic LC polymers is typically conducted through conventional melt-spinning extrusion. During extrusion through very

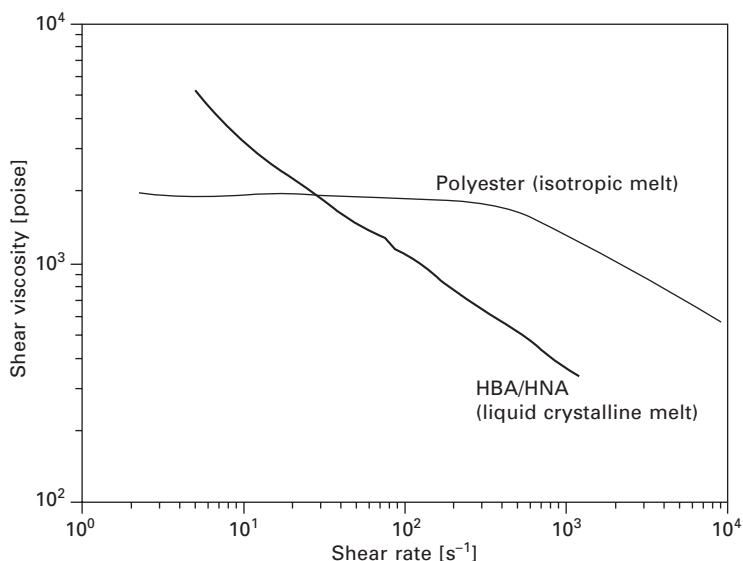
small holes, the shear flow induces an alignment of the LC domains in the flow direction: in this way, the extruded fibre is characterized by a highly oriented structure as depicted in Fig. 12.49.

Rheological behaviour of melt copolyester is highly dependent on the shear rate over a wide range of shear rates. As reported by Calundann and summarized in Fig. 12.50, the viscosity of the HBA/HNA copolymer melt continuously decreases following a power law with no sign of a zero-shear viscosity plateau typical of conventional polyesters (such as PET) (Calundann *et al.*, 1988). In particular, the power-law exponent is about -0.5 for HBA/HNA copolymer melt, while it generally lies between -0.4 and -0.7 for several copolyesters.

Most thermotropic polymers used to fibre spinning are characterized by melting points in the range 275 – 375°C with degradation temperatures between 340 and 450°C (Williams, 1982). Consequently, typical spinning processes are conducted at extrusion temperatures of 280 – 400°C for polymer with inherent viscosities of 1.5 – 5 dL/g . The fibres are collected from spinneret holes with diameters of 0.127 – 0.254 mm at a draw speed of 90 – 1800 m/min



12.49 Schematic diagram of the fibre formation during melt-spinning extrusion process.

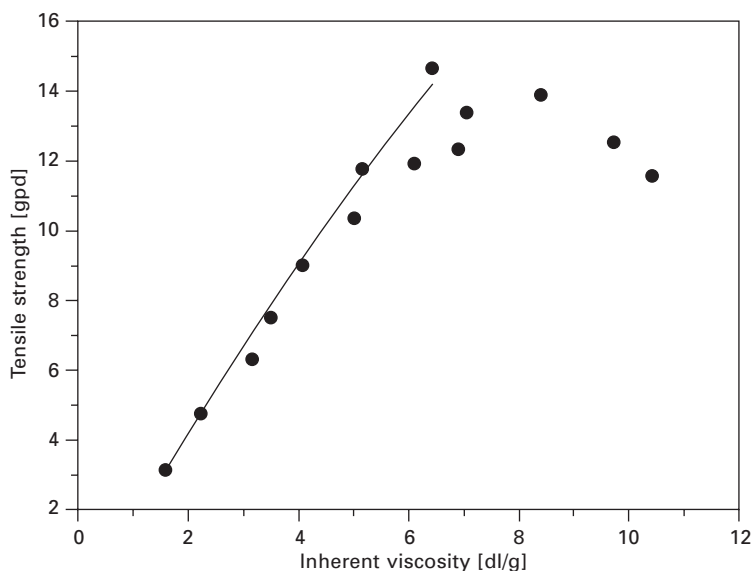


12.50 Viscosity as a function of shear rate for isotropic polyester and for anisotropic HBA/HNA polymer melts (Calundann *et al.*, 1988).

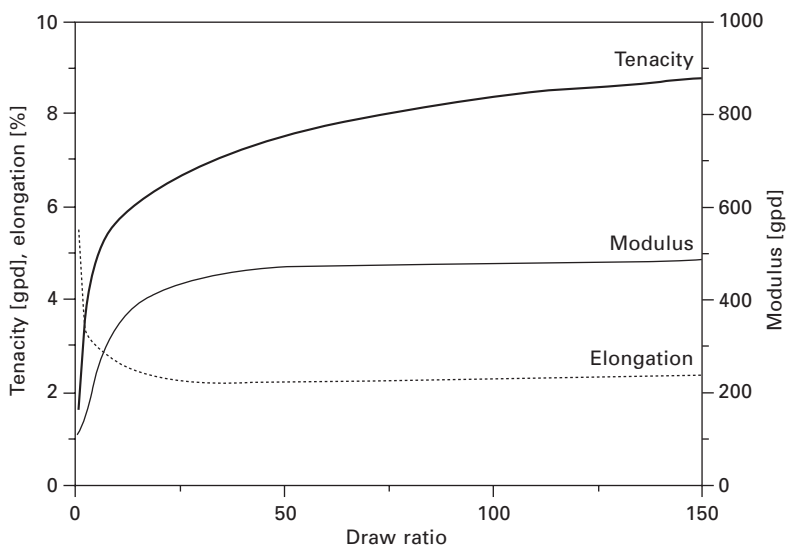
in air or in an inert atmosphere (Pletcher, 1976; Adams and Farrow, 1993; Yang and Allen, 1994; Clements, 1998).

The mechanical properties of as-spun fibre strongly depend on the polymer molecular weight. From a general point of view, the tensile strength of as-spun fibre increases as the polymer's inherent viscosity increases (Calundann and Jaffe, 1982; Yang, 1989). Moreover, as evidenced in Fig. 12.51, the tensile strength of an as-spun fibre reaches a maximum of 15 gpd with an inherent viscosity of 7 dL/g and then decreases because a stable spinning process becomes problematic due to high viscosity. As a result, an optimum viscosity of about 5–7 dL/g can be determined that yields to fibres with a modulus of 600 gpd, a strength of 12 gpd and an elongation at break of 2%.

As depicted in Fig. 12.52, the draw ratio during the melt spinning process markedly affects the mechanical properties of as-spun fibres (Acierno *et al.*, 1982; Muramatsu and Krigbaum, 1986; Calundann *et al.*, 1988). For a copolyester of HBA and naphthalene-based monomer, the tensile strength continuously increases with the draw ratio, while tensile modulus reaches a limiting value for draw ratios exceeding about 50. For fibres obtained from a HBA/HNA:58/42 copolymer spun at 260 °C or 280 °C, Muramatsu and Krigbaum, (1986) reported a tensile modulus increasing with the draw ratio until reaching a plateau value of about 425 gpd at a draw ratio of 135. In the case of fibres spun at 250 °C, the same authors found that modulus increases slowly with the draw ratio until a limiting value of about 220 gpd for a draw ratio of 60. On the other hand, as reported by Acierno *et al.* (1982) tensile



12.51 Relationship between polymer inherent viscosity and strength of thermotropic as-spun fibre (Calundann and Jaffe, 1982).



12.52 Mechanical properties as a function of draw-down ratio for copolyester of HBA and naphthalene-based monomer (Calundann *et al.*, 1988).

modulus and strength continuously increase for PET/HBA:40/60 copolyester up to draw ratio of 300 with higher values as the extrusion temperature increases. In general, as revealed by X-ray analysis (Calundann *et al.*, 1988),

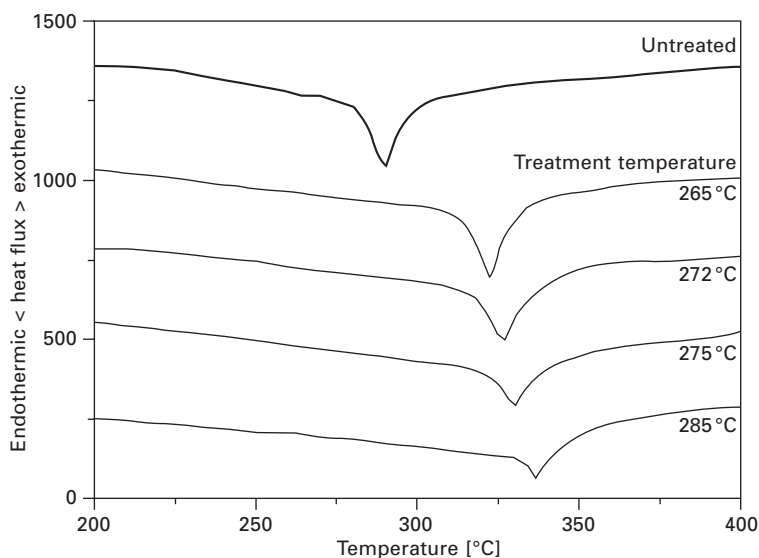
the enhanced properties are mainly related to elongational deformation imparted during the melt-drawing stage rather than shear deformation taking place during capillary flow in the spinning jet (despite high shear rates in the order of 10^4 s^{-1} are reached).

Heat treatment

The properties of as-spun fibres could be improved through a proper heat treatment in inert atmosphere at 170–320 °C for long periods of time (from 10 minutes to 30 hours) under little or no tension (Pletcher, 1976; Yang, 1989; Adams and Farrow, 1993; Clements, 1998).

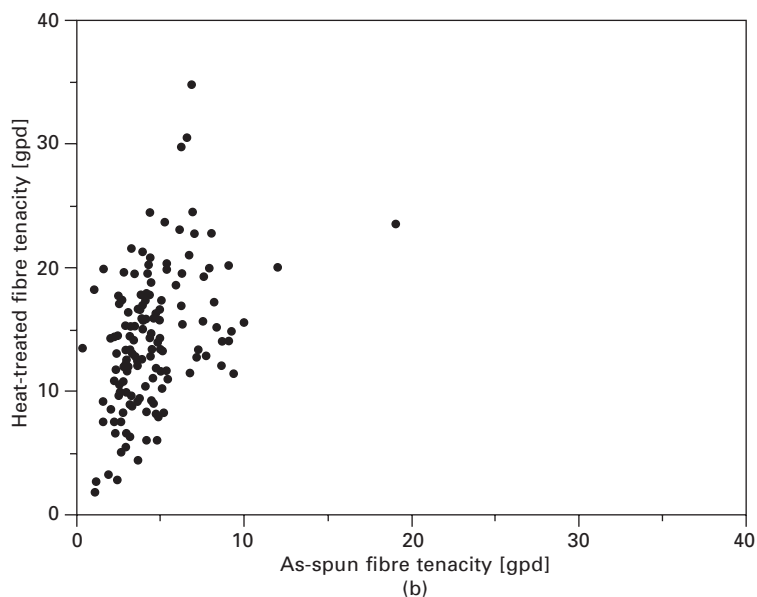
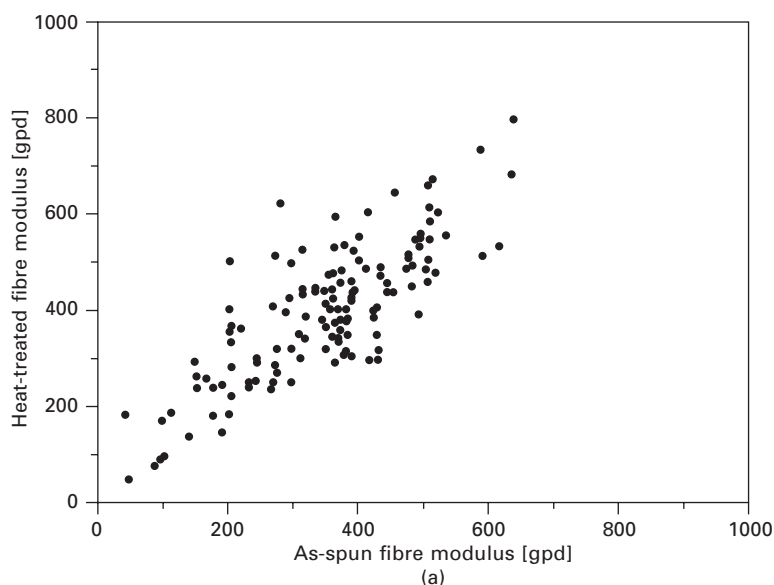
The heat treatment is typically conducted at a temperature 10–20 °C below the melting point to avoid filaments sticking. On the other hand, taking into account that the melting point increases during the heat treatment, the treatment temperature can be even slightly higher than the original melting point of the polymer. As depicted in Fig. 12.53, the endothermic peak of calorimetric curves shifts to higher temperatures as the heat treatment temperature rises (Sarlin and Törmälä, 1991; Nakagawa, 1994).

While the tensile moduli of most LC copolyesters are not significantly improved by the heat treatment (with values in the range 300–1000 gpd), heat treatment does induce strong improvements of tensile strength from about 10 gpd for as-spun fibres to values in excess of 20 gpd, occasionally reaching 40 gpd, for heat treated fibres. Elongation to break increases from

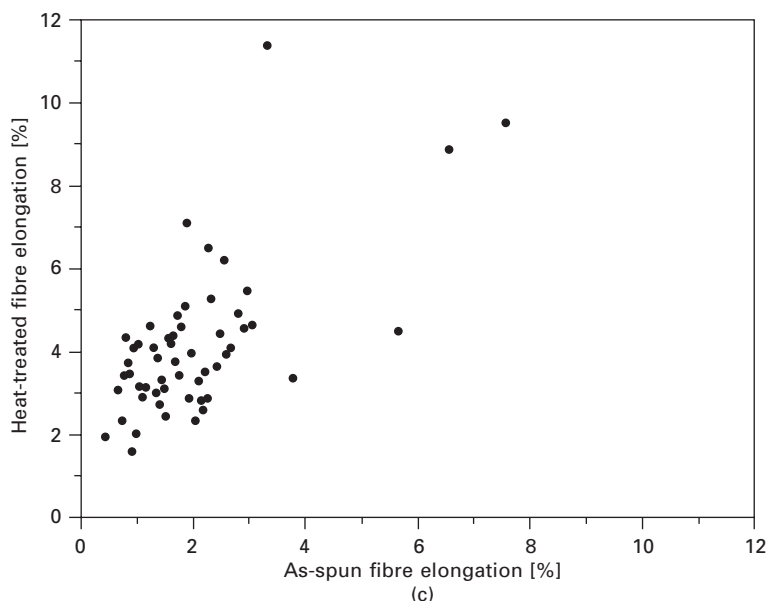


12.53 Calorimetric curve of heat-treated copolyester-based fibres (Nakagawa, 1994).

1–3% to 2–5% after the thermal treatment (Yang, 1989; Yang and Allen, 1994). This behaviour is summarized in Fig. 12.54. Also thermally treated HBA/HNA:75/25 copolymer fibres show only a little change of modulus,



12.54 Effect of heat treatment on fibre mechanical properties for thermotropic aromatic copolyesters: tensile modulus (a), tenacity (b) and elongation to break (c) (Yang, 1988).

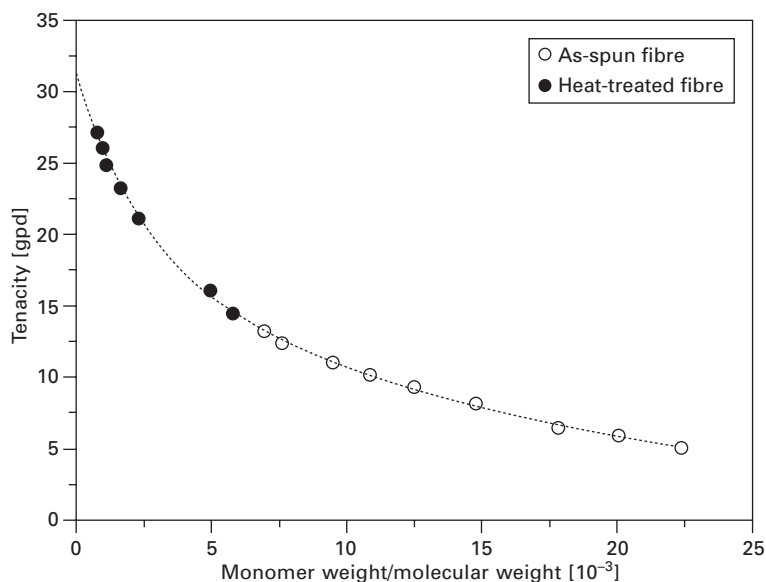


12.54 (Continued)

but a marked increase of strength and melting point. The modulus is 541 gpd and the tenacity 12.1 gpd for as-spun fibre, changing to 550 gpd and 20.0 gpd for heat-treated fibre, respectively (Calundann, 1979). However, the thermal treatment on as-spun HBA/HNA/BP/TA and HBA/IP/BP/TA fibres (in which HNA or IP is only a minor component) induces an increase of strength, melting point and modulus. In particular, as-spun fibres of HBA/HNA/TA/BP:60/5/15/20 copolymer possess moduli of 410 gpd and a tenacity of 5.5 gpd. After heat treatment, the modulus drastically increases to 1420 gpd and the tenacity to 30.8 gpd (Ueno *et al.*, 1985).

During the high temperature treatment the molecular mobility is increased, therefore crystal perfection, degree of molecular orientation and molecular weight improve. In particular, the higher molecular mobility allows solid-state polymerization, thereby increasing the molecular weight. As depicted in Fig. 12.55, the increase of strength is related, most of all, to solid-state polymerization rather than orientation enhancement (Muramatsu and Krigbaum, 1986; Calundann *et al.*, 1988; Nakagawa, 1994). For example, heat treatment induced an increase of weight average molecular weight from 38 400 to 145 000 g/mol for HBA/HNA copolymer (Nakagawa, 1994).

Moreover, heat treatment effectively improves the fibre properties only if the draw ratio is high enough. Muramatsu and Krigbaum (1986) reported that for HBA/HNA:58/42 copolymer fibre spun at 260 °C and subsequently heat treated at 231 °C, the mechanical properties were not significantly changed with a draw ratio of 5.8. On the other hand, the mechanical properties were



12.55 Relationship between fibre tenacity and inverse number-average molecular weight (Calundann *et al.*, 1988).

markedly enhanced for fibres drawn at a ratio of 68. In particular, a minimum draw ratio of about 45 was found to be critical for effectively improving the mechanical properties of the resulting fibres. At the same time, they observed that heat treatment for 10 hours at 231 °C (on fibres obtained with a draw ratio of 68) induced an increase of the inherent viscosity from 7.5 to 10 dL/g and an increase of the melting point from 247 to 268 °C.

Structure

X-ray analysis on HBA/HNA copolyester (Blackwell and Gutierrez, 1982; Blundell, 1982; Gutierrez *et al.*, 1983; Stamatoff, 1984; Chivers *et al.*, 1985) reveals a random comonomer sequence along macromolecules highly oriented in the spinning direction. Moreover, the parallel arrays of polymer chains are characterized by relatively weak interchain interactions. As-spun fibres have pseudo-hexagonal oriented nematic structures that rearrange in a well-defined orthorhombic structure after heat treatment.

The fibre microstructure depends on polymer composition and processing conditions. In general, similarly to lyotropic LCP fibres, a highly oriented fibrillar structure is observed with macrofibrils of about 5 μm , fibrils of about 0.5 μm and microfibrils of about 0.05 μm , in diameter. A skin-core morphology can be detected also for LC aromatic copolyester fibres, with a skin layer about 1 μm for fibre with a diameter of 10–20 μm (Ueda, 1987).

Moreover, banded structures with striations lying perpendicularly to the fibre axis, are observed under polarized light (Donald *et al.*, 1983).

12.4.2 Properties

Physical and thermal properties

Most aromatic copolyesters possess a density of about 1.4 g/cm^3 (Calundann *et al.*, 1988). Vectran fibres have a density of $1.40\text{--}1.41 \text{ g/cm}^3$ depending on processing conditions.

Similar to aramid and heterocyclic fibres, Vectran fibres are characterized by high thermal stability. Thermogravimetric analysis shows 20% weight loss at a temperature higher than 450°C and 50% weight loss at a temperature of 550°C (Technical Datasheets; Fette and Sovinski, 2004). Nevertheless, the maximum in service temperature is related to the melting that occurs at about $270\text{--}330^\circ\text{C}$ depending on heat treatment, as previously described.

Vectran fibres are characterized by a low, negative coefficient of thermal expansion (CTE). From -150 to 145°C , CTE has a value of $-4.8 \times 10^{-6}^\circ\text{C}^{-1}$, which increases to $-14.6 \times 10^{-6}^\circ\text{C}^{-1}$ in the temperature range $145\text{--}200^\circ\text{C}$ and to $-26.7 \times 10^{-6}^\circ\text{C}^{-1}$ in the temperature range $200\text{--}290^\circ\text{C}$. While CTE value is comparable to that of aramid fibres up to 145°C , at higher temperature aramid fibres shows CTE values lower than those of Vectran fibres.

Mechanical properties

The mechanical properties of aromatic copolyesters strongly depend on polymer composition, molecular weight, spinning and heat treatment conditions. Indicative ranges for the tensile properties of as-spun fibre are $42\text{--}650 \text{ gpd}$ for the modulus, $1\text{--}12 \text{ gpd}$ for the tenacity and $1\text{--}3\%$ for the elongation at break. After heat treatment, these values generally increase to $480\text{--}1200 \text{ gpd}$ for the tensile modulus, $3\text{--}35 \text{ gpd}$ for tenacity and $2\text{--}5\%$ for the strain to failure (Yang and Allen, 1994). For these polymers the theoretical crystal modulus is in the range of $180\text{--}250 \text{ GPa}$ (i.e. roughly $1400\text{--}2000 \text{ gpd}$), the exact value depending on the actual composition (Treloar, 1960).

Vectran fibre is based on HBA and HNA monomers. Table 12.3 summarizes the effect of the HBA/HNA molar ratio and heat treatment on fibre properties. A molar ratio of 3/1 represents the best balance between mechanical properties and melt processability (related to the melting point). Table 12.1 reports the mechanical properties of the commercially available Vectran fibres. The modulus is in the range $50\text{--}100 \text{ GPa}$, whilst the strength ranges from 1 to 3 GPa , depending on the processing conditions. The shear modulus is very low, with values of 0.6 GPa at room temperature and 0.15 GPa at 150°C for Vectran HS fibre (Mehta and Kumar, 1994). Similarly to aramid and heterocyclic LCP fibres, the Weibull distribution can be adopted to

Table 12.3 Tensile properties of fibres based on HBA/HNA copolymers (Calundann, 1979). AS, as-spun fibre; HT, heat-treated fibre

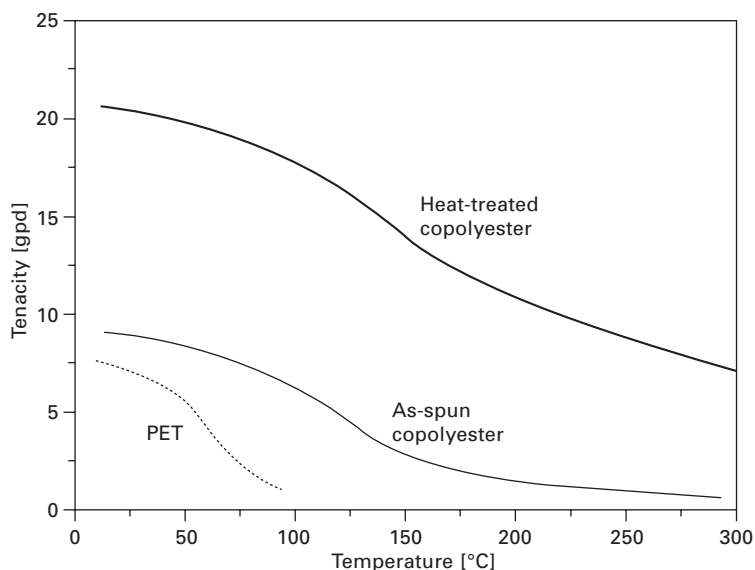
HBA:HNA molar ratio	Melting point (°C)	Process	Modulus (gpd)	Strength (gpd)	Elongation (%)
75/25	302	AS	541	12.1	2.8
		HT 250 °C, 90 h	550	20	5
70/30	275	AS	490	9.1	2.5
		HT 250 °C, 40 h	485	14	3.0
60/40	245	AS	597	9.2	2.2
50/50	260	AS	513	10.1	2.6
		HT 250 °C, 90 h	500	15.6	4.0
40/60	263	AS	742	7.2	1.3

characterize the statistical behaviour of the tensile failure of Vectran fibres (Miwa *et al.*, 1996; Pegoretti *et al.*, 2006a). Pegoretti *et al.* (2006a) found shape parameters of 8.28 for Vectran M (as-spun) fibre and 6.13 for Vectran HS (thermally treated) fibre. These values are higher than those commonly reported for E-glass (2–5) and carbon fibres (4–6), but lower than those of aramid fibres (8–14). The same authors reported a Weibull scale parameter for Vectran M (untreated) and Vectran HS (thermally treated) fibres of 1309 and 3374 MPa, respectively (Pegoretti *et al.*, 2006a), at a reference length of 25 mm.

Ekonol fibre (which is based on HBA/TA/BP and HBA/HNA/TA/BP copolyesters) also possesses very interesting mechanical properties. For these fibres Economy reported a tensile modulus of 165 GPa, strength of 3.8 GPa and elongation to break of 3.0% (Economy, 1989).

In contrast, the properties of PET/HBA copolyesters are markedly lower than those of wholly aromatic copolyesters (such as HBA/HNA or similar). Moreover, the control of the segment distribution of the copolyesters is problematic: as a result, substantially inferior mechanical properties were obtained (Wang and Zhou, 2004). The compositional control was enhanced by Unitika (Japan): the resulted fibre based on *Rodrun LC-5000* had a tensile modulus of 9.8 GPa, a strength of 220 MPa and an elongation to break of 4.5% (Suenaga, 1990). Mehta and Deopura (1993) reported a modulus of 12.0 GPa and a strength of 175 MPa for fibres obtained from PET/HBA:40/60 copolymer, while a modulus of 26.7 GPa and a strength of 315 MPa has been reported in case of PET/HBA:20/80 copolymer.

Figure 12.56 shows the effect of the temperature on the strength of HBA/HNA copolymer fibres that continuously decreases starting from room temperature. Nevertheless, the HBA/HNA copolymer fibre possesses a much better thermal stability in comparison with conventional polyester fibres such as PET over the whole range of temperature. In fact, while PET fibres can lose much of their mechanical properties above the glass transition temperature (i.e. around 70–80 °C), Vectran fibres maintain interesting properties practically

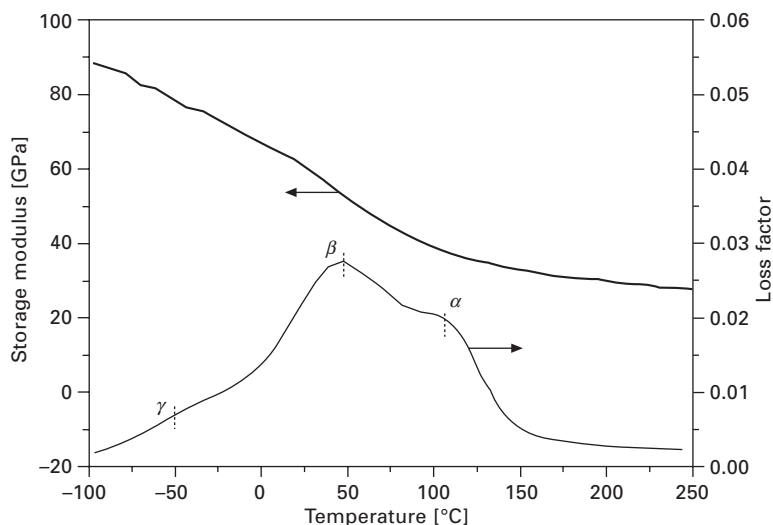


12.56 Tenacity as a function of the temperature for HBA/HNA copolymer and PET fibres (Calundann *et al.*, 1988).

up to the melting point, typically in the range 275–375 °C. Moreover, the importance of the heat treatment also clearly emerges from Fig. 12.56.

The effect of temperature on the mechanical properties of HBA/HNA copolymer and Vectran fibres can be better understood by considering their dynamic mechanical behaviour (Wellman *et al.*, 1981; Eichenauer and Kjung, 1992; Menczel *et al.*, 1997). As depicted in Fig. 12.57, three main relaxation phenomena can be observed on the dynamic mechanical thermal analysis thermogram: an α relaxation at 110 °C, a β relaxation at about 40 °C and a γ relaxation at –50 °C (Beers *et al.*, 2001). The γ relaxation is related to reorientational motion of *p*-phenylene groups, while β relaxation arises from reorientational motion of 2,6-naphthalene groups. Since the bonds at 2- and 6-positions are not collinear, this motion requires cooperative motion in neighbouring chain units. The α relaxation is a highly cooperative transition, similar to a glass transition to which corresponds a large decrease of strength and modulus. Nakagawa (1994) showed that heat treatment induced a shift of the α relaxation temperature for HBA/HNA copolymer from 88 °C for as-spun fibre to 97 °C for heat-treated fibres. Moreover, the intensity of α and γ relaxations can be significantly reduced with annealing.

Vectran fibres are characterized by excellent creep behaviour. Clements (1998) showed creep phenomena only when fibres were tested for 2760 hours under a high constant stress of 50% of tensile strength. Fette and Sovinski (2004) found that the apparent creep rate (defined as the slope of the creep strain with time in logarithm scale) of Vectran fibre is much lower than that of



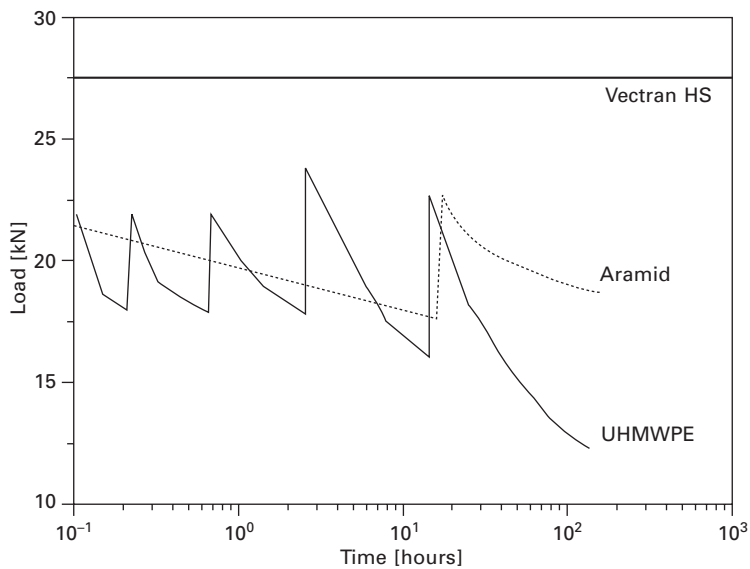
12.57 Dynamic mechanical behaviour of HBA/HNA copolymer: storage modulus (E') and loss factor ($\tan\delta$) as a function of the temperature (Wellman *et al.*, 1981).

Kevlar fibre during tests conducted at room temperature for 90 hours. In detail, Vectran fibre had an apparent creep rate of 0.0003%/log(hours) at a stress of 50% of tensile strength, whilst Kevlar fibre presented an apparent creep rate of 0.0015%/log(hours) at a stress of 34% tensile strength. Moreover, Vectran fibres do not present significant relaxation phenomena (in contrast to aramid and UHMWPE) as depicted in Fig. 12.58 (Fette and Sovinski, 2004).

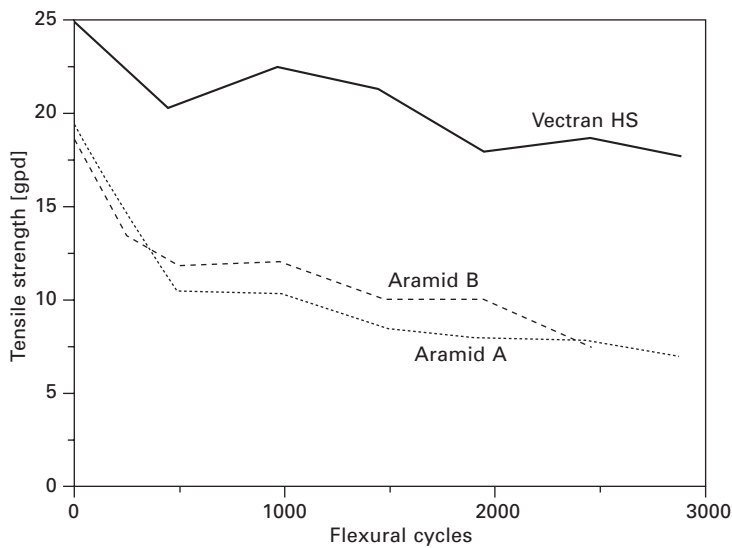
In general, Vectran fibres are characterized by an excellent behaviour under cyclic loading as depicted in Fig. 12.59. Under a flexural fatigue test, Vectran HS braid underwent a reduction in strength of 10% after one million cycles and maintained this strength level up to five million cycles. In contrast, Kevlar 29 braid suffered a strength reduction of 30% under the same conditions (Beers and Ramirez, 1990). The progressive loss of mechanical properties is related to the formation of kink bands that can be viewed as dislocations caused by buckling and breaking of the stiff polymer chains (Dobb and McIntyre, 1984; Sawyer and Jaffe, 1986; Sawyer *et al.*, 1992, 1993). The superior fatigue behaviour of Vectran fibres derives from the higher energy required in kink-band formation compared with aramid fibres.

Chemical and environmental effects

Vectran fibres are characterized by better resistance to repeated exposure at elevated temperature compared with aramid fibres. For example, exposure



12.58 Stress relaxation phenomena for Vectran, para-aramid and UHMWPE fibres (Fette and Sovinski, 2004).



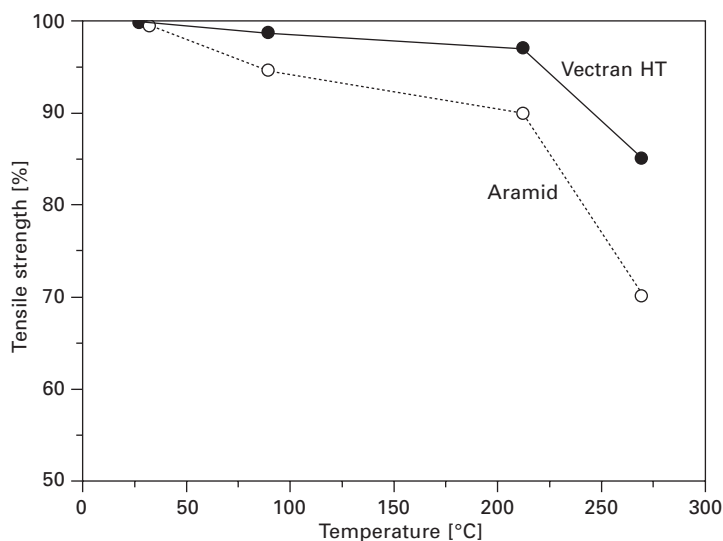
12.59 Tensile strength during flexural fatigue test on Vectran and aramid fibres (Technical Datasheets).

at 195 °C for 30 eight-hour cycles induced no strength loss for Vectran fibres, but considerable strength loss for *para*-aramid fibres. Vectran fibres retain their strength for short periods, but they gradually lose their strength over extended time. Exposure at 195 °C for 30 days induced a 24% loss of

strength (Beers *et al.*, 2001). Figure 12.60 confirms the better tensile strength retention of Vectran over aramid fibres after 24 hours exposures at various temperatures.

In spite of the presence of ester linkages, Vectran fibres are hydrolytically stable and present reduced water sorption. Dry fibres absorb less than 0.1% moisture under ambient conditions (Clements, 1998). Moreover, the absorbed water does not reduce the mechanical properties of Vectran fibres, as no strength loss was reported after one month immersion in water at 50 °C (Calundann *et al.*, 1988).

From a general point of view, wholly aromatic polyesters possess good chemical resistance. In the presence of organic solvents and in acidic environments, they have good strength retention with long exposures, while they show poor resistance to alkaline conditions. Moreover, this behaviour strongly depends on the composition: the chemical resistance is poorer for fibres containing *m*-phenylene moieties (Calundann *et al.*, 1988). Vectran fibres are resistant to organic solvents (as, for example, acetone, benzene and toluene), acids at less than 90% concentration and bases at less than 30% concentration depending upon time and temperature of exposure. They also perform better than aramid fibres: for example, after exposure for 10 hours in 10% sulphuric acid at 100 °C, Vectran HT fibres had strength retention of 96% and *para*-aramid fibres of only 40%. In addition, after exposure for 10000 hours in 10% sulphuric acid at 50 °C, Vectran HT fibres had strength retention of 82% and *para*-aramid fibres of only 12%.



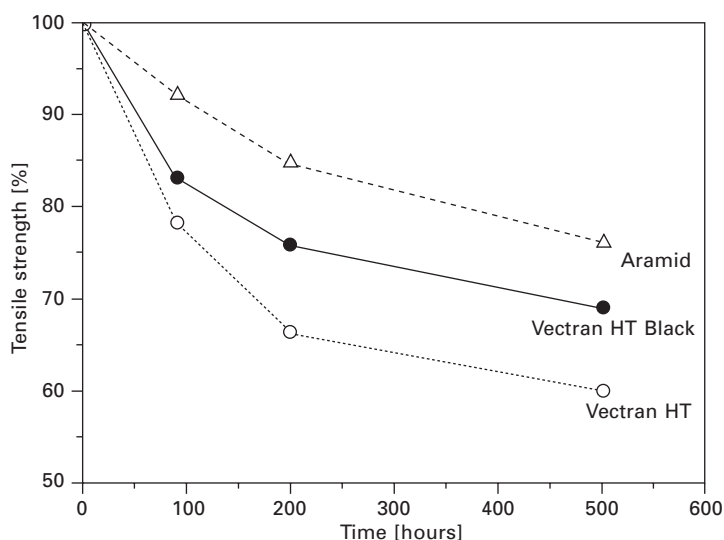
12.60 Strength retention at room temperature after exposure at elevated temperature for 24 hours (Technical Datasheets).

Similarly to aramid fibres, Vectran fibres have poor resistance to UV exposure. Therefore, when exposed to UV over extended periods of time, they need protection. As depicted in Fig. 12.61, Vectran fibres are more prone to UV degradation than aramid fibres: the UV resistance can be improved by adding carbon black or other protective pigments.

12.5 Applications and examples

The unique combination of properties, such as high specific strength and stiffness combined with toughness and creep resistance, renders LC organic fibres very attractive for several applications, such as ropes, cables and fabrics or as reinforcing fibres for composite materials (Yang, 1988; Clements, 1998; Brew *et al.*, 1999; van der Jagt and Beukers, 1999; Beers *et al.*, 2001; Rebouillat, 2001; Huang *et al.*, 2002; Park *et al.*, 2003).

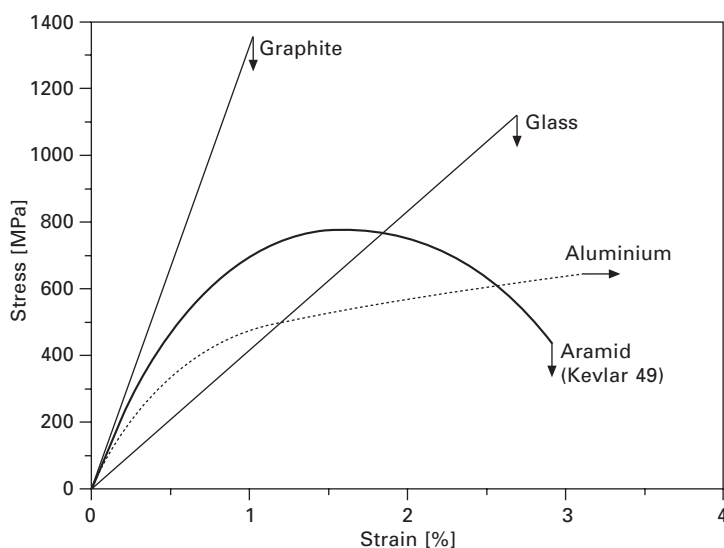
The good performances of aramid, copolyester and heterocyclic polymer fibres mean that they are quite extensively used for the manufacturing of woven fabrics. Examples for application are multilayered bulletproof jackets (toughness), protective clothing for fire fighters (fire resistance), industrial gloves (abrasion, cut and heat resistance), knee and elbow protections for motorcycle suits (abrasion resistance), sailcloth and inflatable structures (flex/fold ability, dimensional stability and tear strength). These fibres are also used for the manufacture of ropes and cables where dynamic applications require resistance to fibre-to-fibre abrasion, good bend-over-sheave, no creep and cut resistance. Examples are towed arrays/streamers for off-shore exploration,



12.61 Strength retention after UV radiation exposure of Vectran fibres (Technical Datasheets).

halyards for racing yachts, restraint lines for race cars, long lines for tuna fishing, marine cables, fishing nets, towing ropes, cargo tie downs, slings, bicycle brake cables and optical fibre reinforcement.

Because of their high strength and toughness, fire and cut resistance with lower weight, composites based on aramid, copolyester and heterocyclic polymer fibres (as Kevlar, Vectran and Zylon) find several applications in ballistics products (helmets, tank panels and other military components), civilian and military aircrafts, pressure vessels, missile cases and so on. Similarly, the necessity of higher performance (strength, vibration damping, creep, abrasion and impact resistance) and lower weight even with higher cost allows the use of these composites for sport and leisure goods as canoes, kayaks, racing shells, small boats, bow strings, hockey sticks, bicycle forks, tennis rackets/strings and so on. The potential benefits of LCP fibres on the mechanical properties can be seen by examining Fig. 12.62 and Table 12.4. Aramid fibres, as all the other LC fibres, are intrinsically more 'ductile' than carbon fibres: as a result, fibre reinforced composites show a relative improvement of ductility in terms of stress–strain curves. Moreover, as reported in Table 12.4, tensile modulus and tensile strength can reach values comparable to or even higher than those of glass or carbon fibre reinforced composites. These values are more and more interesting when the lower densities of the resulting composites are taken into account. However, compressive behaviour represents the limit because of the low values of compressive strength: in particular, compressive loads have to be avoided



12.62 Stress–strain curves of aluminium and various fibre reinforced unidirectional composites based on epoxy resin matrix (Technical Datasheets).

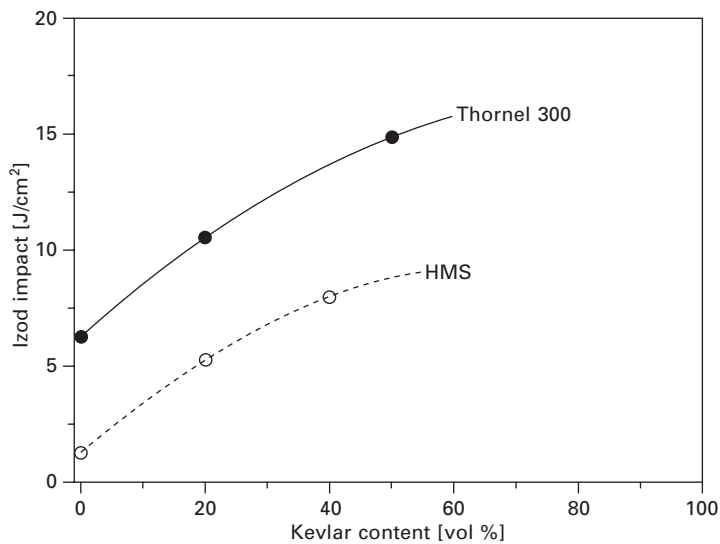
Table 12.4 Typical properties of reinforced composites based on liquid crystalline fibres and conventional inorganic fibres (Technical Datasheets; Yang, 1988; Brew *et al.*, 1999; Park *et al.*, 2003)

Properties	E-Glass	Carbon HM370	PPTA Kevlar 49	PBO Zylon HM	PIPD M5
Fibre volume fraction	0.6	0.6	0.6	0.77	0.5
Density (g/cm ³)	2.08	1.60	1.38	1.46	1.43
Tensile modulus (MPa)	39	224	76	205	138
Tensile strength (MPa)	1100	1730	1400	3300	1800
Compressive strength (MPa)	600	1400	280	150	620
Interlaminar shear strength (MPa)	83	84	90	30	57

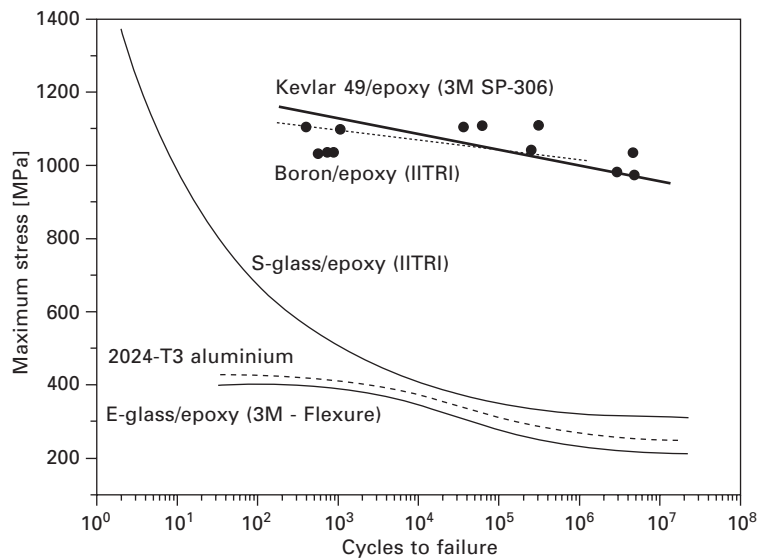
for composites based on the PBO fibre in the case of structural applications because their poor off-axis properties. The main advantage of the use of LCP-based fibres as reinforcing fillers in composite materials is depicted in Fig. 12.63 where some data regarding the impact behaviour of hybrid carbon–Kevlar composites are presented. Hybridization with Kevlar fibres markedly improves the impact resistance of the composites produced either with high modulus or with high tenacity carbon fibres. As a consequence, LCP fibres found extended applications in the field of the hybrid composites (Lubin, 1982) where (at least) two types of fibres are used (e.g. LCP/glass or LCP/carbon fibres). The addition of more than one type of fibre is essentially related to the effort to overcome the drawbacks of the use of only one type of fibre. In fact, while LCP fibre reinforced composites are characterized by poor compressive properties, carbon fibre reinforced composites have high cost and brittle failure and glass fibre reinforced composites have low stiffness. In addition Kevlar-epoxy composites display exceptionally high fatigue resistance, as evidenced in Fig. 12.64.

Aramid fibres are also widely used to reinforce rubber goods (as pneumatic tires, belt, hoses, athletic shoes, aircraft evacuation slides and life rafts), whilst copolyester fibres for medical applications (as, for example, catheters and control cables) where abrasion resistance, no creep and gamma sterilization are required. Moreover, copolyester fibres can be used in non-woven papers as insulating papers and speaker cones because their dielectric properties, vibration damping, low moisture absorption and tear strength.

Finally, it is worthwhile mentioning a recent new application of thermotropic LC fibres for the manufacturing of new single polymer composites, i.e. composite materials in which both the reinforcing (fibres) and the continuous (matrix) phases are polymers with the same chemical composition (Pegoretti *et al.*, 2006a, 2006b; Kalfon-Cohen *et al.*, 2007). One of the intended advantages of these composite materials is that strong and stable interfaces could be naturally produced, since the two phases are of identical chemistry. Another important advantage of a single polymer phase over traditional composites is the enhanced end-life recyclability that can be achieved by using the same polymer for both fibre and matrix phases.



12.63 Impact strength of unidirectional hybrid composites based on Kevlar 49 and two carbon fibres (Technical Datasheets).



12.64 Fatigue behaviour under tension–tension load of unidirectional composites and aluminium (Technical Datasheets).

12.6 References

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The manufacture, properties and applications of high strength, high modulus polyethylene fibers

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Abstract: High modulus polyethylene fibers (HMPE) are used in wide variety of applications due to their high strength and low density combined with good mechanical and chemical properties. In this chapter an overview is given of the gel-spinning manufacturing process, the characteristics of commercially available types and a number of properties. The major processing techniques of HMPE fibers are discussed and the versatility of this fiber is demonstrated in a description of HMPE-specific properties for its main application areas.

Key words: ultra-high molecular weight polyethylene, high modulus polyethylene, high performance polyethylene, fiber, property, application, Dyneema®, Spectra®.

13.1 Introduction

Gel-spun polyethylene fibers are ultra-strong, high modulus fibers that are based on the simple and flexible polyethylene molecule. They are called high strength, lightweight polyethylene fibers, high modulus polyethylene (HMPE) fibers, high performance polyethylene (HPPE) fibers or sometimes extended chain polyethylene (ECPE) fibers. The gel-spinning process uses physical processes to make available the high potential mechanical properties of the molecule.

Because of low density and good mechanical properties, the performance on a weight basis is extremely high. The chemical nature of polyethylene remains in the gel-spun fiber and this can both be positive and a limitation: abrasion and fatigue properties are very high but the melting point limits certain application areas. Nowadays the versatile HMPE fibers are widely used in ballistic protection, marine and offshore, fishing, sports, forestry, hoisting, cut resistance, aviation, medical and in a variety of composite applications.

13.2 Manufacture

13.2.1 Molecular character

Gel-spun HMPE fibers are produced from polyethylene, $(-\text{CH}_2-)_n$, with an ultra-very high molecular weight (UHMW-PE), typically $M_w > 10^6 \text{ g mol}^{-1}$. This material is chemically identical to normal high density polyethylene (HDPE), but the molecular weight is higher and in the range that is used in abrasion-resistant engineering plastics.

Unlike other high performance fibers, the molecules in HMPE fibers are not 'preformed' to form high tenacity and modulus fibers. In aramids and comparable fibers, the molecules tend to form rod-like structures and these need only be oriented in one direction to form a strong fiber. UHMW-PE has much longer and flexible molecules and only by physical treatments can the molecules be forced to take over the straight (extended) conformation and orientation in the longitudinal axis.

All the physical and chemical properties of polyethylene remain in the fibers. The differences result from the high fiber extension (stretching), high orientation and the high crystallinity. One of which is the highly anisotropic character in terms of strength and stiffness. The still present weak lateral (van der Waals) bonds between the molecular chains make low transverse strength and creep vulnerability as intrinsic characteristics, although the latter can be improved by the use of a branched base polymer.

13.2.2 Gel-spinning

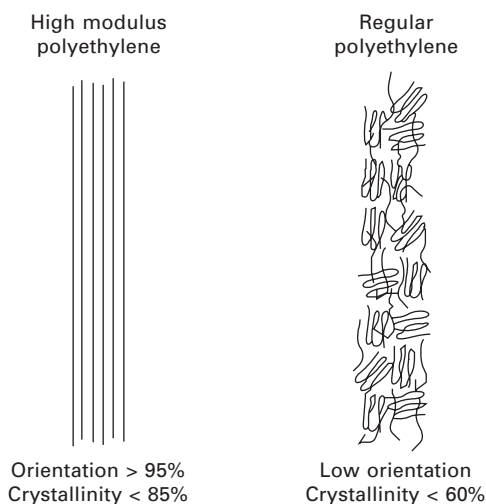
HMPE fibers are commercially produced under the trade names Dyneema® by DSM Dyneema BV in the Netherlands and USA, and by Nippon Dyneema Co., Ltd (a Toyobo/DSM joint venture) in Japan, and under the trade name Spectra® by Honeywell Specialty Materials in the USA. Especially developed for medical applications, Dyneema Purity® is produced by DSM Dyneema BV.

What a super-strong polyethylene fiber should look like was already available in the 1930s from the ideas of Carothers, but it took almost half a century to produce HMPE fibers (Carothers and Hill, 1932). The basic theory of how to produce a super-strong fiber from a polymer such as UHMW-PE is easy to understand. In normal polyethylene the molecules are not oriented and are easily torn apart. To make strong fibers, the molecular chains must be straightened, oriented and crystallized in the direction of the fiber. Furthermore, the molecular chains must be long to have sufficient interaction for load transfer and for this reason polyethylene with an ultra-high molecular weight is used as the starting material. Usually straightening and orientation are realized by drawing the fiber. The problem is that spinning these fibers from the melt is almost impossible due to the extremely high

melt viscosity. Furthermore, the drawing of a melt-processed UHMW-PE is possible only to a very limited extent owing to the very high degree of entanglement of the molecular chains. In the gel-spinning process these two problems are solved: the molecules are dissolved in a solvent and spun through a spinneret. In the solution the molecules become disentangled and remain in that state after the solution is spun and cooled to give filaments. Because of its low degree of entanglement, the gel-spun material can be drawn to a very high extent (super-drawn). As the fiber is super-drawn, a very high level of macromolecular orientation is attained (Fig. 13.1), resulting in a fiber with a very high tenacity and modulus.

In 1979 DSM invented and patented the fiber and the gel-spinning process to produce it (Smith and Lemstra, 1979). Several further patents concerning this process have been filed in later years. Dyneema® fibers have been in commercial production since 1990 at a plant in Heerlen, the Netherlands. The production of Dyneema® fibers demands relatively little energy and uses no aggressive chemicals. DSM has a joint venture agreement with Toyobo Co. for commercial production in Japan. In the USA, DSM has granted a license to Allied Signal, now Honeywell. The latter produces the Spectra® fiber at Petersburg (VA).

Since the start of commercial production, the performance of the Dyneema® and Spectra® fibers has been improved considerably. New grades have been introduced and a significant potential for further improvements is still present. Gel-spinning of HMPE fibers is a process that hinges on mechanical and physical parameters, not on chemistry. This makes it relatively easy to produce a wide range of fiber grades. The gel-spun fibers are characterized by



13.1 Macromolecular orientation of HMPE and regular PE.

a high degree of molecular chain orientation and a high level of crystallinity (up to 85%). This gives the fibers their unique properties.

Gel-spinning process

Figure 13.2 shows a diagram of the gel-spinning process (Jacobs and Mencke, 1995).

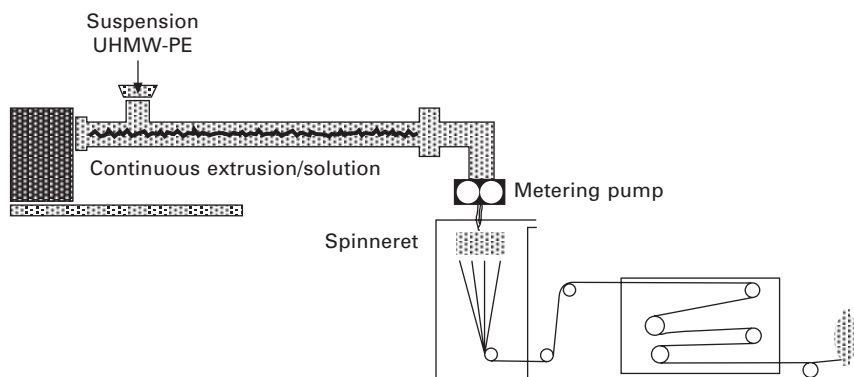
These are the main steps in the process:

- The continuous extrusion of a solution of UHMW-PE.
- Spinning of the solution, gelation and crystallization of the UHMW-PE. This can be done either by cooling and extraction or by evaporation of the solvent.
- Super-drawing and removal of the remaining solvent gives the fiber its final properties.

In the gel-spinning process, not only do all the starting parameters have an influence on the final properties of the fiber, the different process steps also influence all the following stages in the production of the fiber. Starting from the same principles, each fiber manufacturer may use very different equipment to produce comparable fibers (Kavesh and Prevorsek, 1983).

Feedstock polymer

Polyethylene is a flexible polymer with a very weak interaction between the molecular chains as only the van der Waals forces are active. This interaction is so weak that for strong fibers, ultra-long chains with high overlap lengths are required. The starting material for the HMPE fibers is polyethylene with a weight average molecular weight of one million or more. The higher the molecular weight, the higher the strength that can be obtained. Improvements



13.2 Gel-spinning process.

in equipment and processing parameters have made it possible to increase the molecular weight over the years.

Both the average molecular weight and the molecular weight distribution are critical parameters. Chains that are too long hinder the drawing step due to entanglements; short chains are less effective in the transfer of the load in the final fiber. Side groups on the chains also interfere with the drawing; however, it has been shown that a limited number of branches result in a better performance in terms of creep behavior.

Spinning solution

With long-chain, flexible polymers the high orientation required can be obtained by drawing the fiber up to a very high draw ratio (50–100 times). Melt-processed UHMW-PE can be drawn up to five times only, as the interaction between the molecular chains is too high because of the molecular entanglements. In solution, the molecules disentangle but there remain a number of crossovers determined by the concentration and the length of the molecules. The flexible molecules take on a roughly spherical shape with a diameter proportional to the cubic root of the molecular weight. For the UHMW-PE chains the diameter of such a ball is about 1% of the total chain length.

As soon as strain is applied when the solution is pressed through the spinneret, the molecules are forced into a more straightened form. This is the first step in the orientation process and the geometry of the holes in the spinneret has been thoroughly studied in DSM's research into improvements to the properties of the Dyneema® fiber.

For maximum fiber strength, the polyethylene molecules should be as long as possible. From an economic point of view the concentration of the solution should be as high as possible. However, these two factors together result in a solution that has a viscosity that is far too high to spin. Careful optimization of these parameters is an essential part of the process.

Gelation and crystallization

The solvent used in the polyethylene gel-spinning process should be a good solvent at high temperatures ($>100^{\circ}\text{C}$) but at lower temperatures ($<80^{\circ}\text{C}$) the polymer should easily crystallize from the solution. After the spinneret, the solution is cooled in the quench, the solvent is removed and a gel fiber is formed. This can be done by evaporation or by extraction of the solvent.

From a diluted solution, polyethylene crystallizes in the form of flat crystals of about 20 nm thickness, in which the chains are neatly folded. In these crystals the C-axis or chain axis is perpendicular to the crystal (lamella) surface. The crystal structure is orthorhombic, which implies that the crystal

axes are at right angles, two by two. The theoretically attainable modulus and tenacity of fibers can be derived from those of these polyethylene crystals.

The spatial structure of the polyethylene molecules at the moment of crystallization is critical for obtaining good draw-ability. This spatial structure is determined by the number of entanglements in the solution, the shape of the spinneret and, of course, the conditions in the quench. Together these parameters determine the necessary overlap of several different molecular chains in a single lamella. Control of the molecular overlap is a critical factor determining the draw-ability.

Between a single crystal and a fiber there is quite a long way to go. Lamellar crystals with folded chains do not form suitable building blocks for a strong fiber. Long, thread-like crystals (fibrils) with extended chains are much better suited for this purpose. After the removal of the solvent, the fibers consist of microcrystalline crystals embedded in non-crystalline material. In the subsequent drawing stage, the apparently random crystals and most of the non-crystalline material is transformed into a highly crystalline, highly oriented fiber.

Drawing

The final properties of the fiber in the gel-spinning process are achieved in the super-drawing stage. All the preceding steps are needed to make this possible. The strength and modulus are directly related to the draw ratio. The maximum attainable draw ratio appears to be related to the molecular weight and the concentration. The attainable draw ratio increases with decreasing concentration, but for each molecular weight there is a minimum concentration below which drawing is not possible, owing to insufficient molecular overlap.

The explanation for this drawing behavior is generally sought in the number of chain-chain entanglements. In a melt or in a concentrated solution of polyethylene with a very high molecular weight, there is a high concentration of entanglements. This makes it impossible to achieve a high draw ratio with the corresponding properties. On the other hand, if no entanglements are present due to too low a concentration, the gel fiber will break. The elasticity is then too low and the forces in the spinning process cannot be passed on over a great length. The fiber will break before it is drawn. A very low concentration is, of course, not of interest in a commercial process, but a trade-off has to be made between two conflicting parameters: a high molecular weight to reach a higher tenacity and a high concentration in order to keep the process feasible.

13.2.3 Other UHMW-PE fibers and films

An alternative method is to melt-spin polyethylene and super-draw the solid fiber. The resulting strength is about half that of gel-spun HMPE and creep properties are worse (McKenna *et al.*, 2004). A fiber of this type, Certran® produced by Celanese, was used in ropes but failed to be competitive. Another solid-state extrusion process is to compress UHMW-PE powder, followed by rolling and ultra-drawing. The strength is about 70% of gel-spun HMPE fibers. Tensylon® fiber or tape is produced by BAE Systems.

13.3 Fiber characteristics

13.3.1 Fiber form

HMPE fibers are produced as a multifilament yarn. The titer of the single filaments varies from about 0.3 denier per filament (dpf) (0.44 dtex) to almost 11 dpf (12 dtex). Tenacity of one filament may well be over 5 N/tex, and the modulus can be over 120 N/tex.

Most fiber grades have a more or less circular cross-section of the individual filaments (Fig. 13.3a) but also bean- or kidney-shaped (Fig. 13.3b) as a result of the fast evaporation of the solvent during spinning. The fiber skin is smooth.

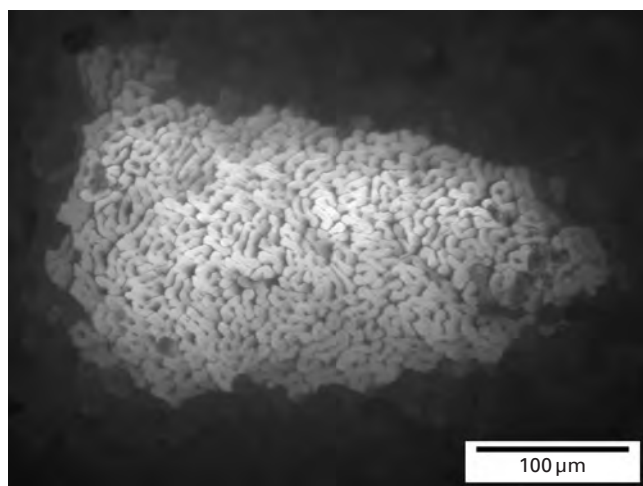
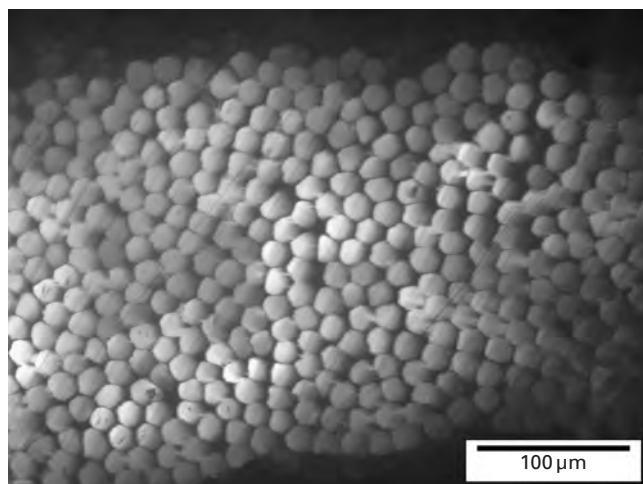
13.3.2 Structure and morphology

The fiber is highly crystalline; the crystallinity is typically >80%. The crystal domains, mainly orthorhombic with a small contribution of monoclinic, are highly extended in the fiber axis direction. The crystal domains are organized in nano- or microfibrils, which in their turn form macrofibrils. The larger part of the non-crystalline fraction is in the form of an interphase that is characterized by a high density, a high orientation and restricted mobility of the molecular chains.

13.3.3 Commercially available fibers

The product portfolio for Dyneema® and Spectra® at the end of 2007 is shown in Table 13.1. The reported physical properties are representative of published information from the fiber manufacturers (DSM, 2007; Honeywell, 2007; Toyobo, 2007). These values are influenced by testing methods and hence the direct comparison of properties is not always correct.

The Dyneema® NM types are 100% HMPE stretch broken fibers, spun to staple yarns. These are mainly produced for knitted and woven cut resistance clothing. The Dyneema Purity® types are developed especially for medical applications.



13.3 Cross sections of (a) 1760 dtex Dyneema® SK75 fiber and (b) 440 dtex Dyneema® SK65 fiber.

13.4 Properties

13.4.1 Tensile properties

The primary properties of the HMPE fibers are high strength and high modulus in combination with low density. The density of $970\text{--}980\text{ kg/m}^3$ is typical for highly crystalline linear polyethylene making HMPE fibers float on water.

Whereas the strength and modulus are already very high in engineering units (GPa), the combination with the low density makes the specific strength

Table 13.1 Commercially available high modulus polyethylene fibers

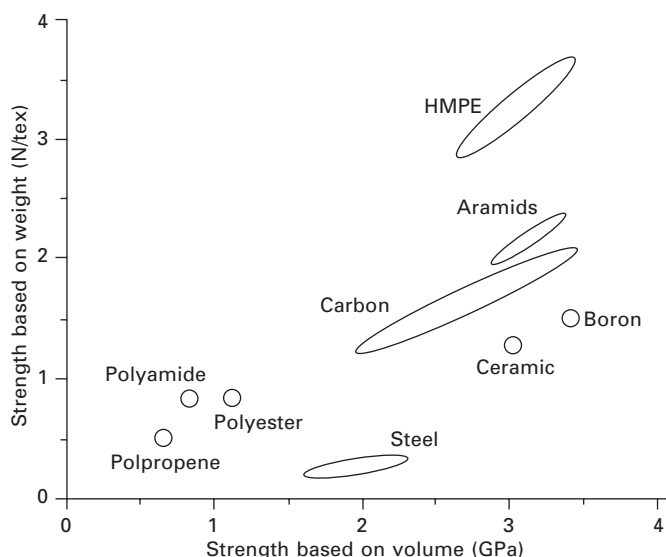
	Filament		Fiber linear density		Tensile strength			Tensile modulus			Elongation to break
	Diameter	Linear density	den	dtex	g/den	N/tex	GPa	g/den	N/tex	GPa	%
	mm	den									
DSM Dyneema (DSM, 2007)											
Dyneema® SK25	16	1.7	675	750	25	2.2	2.2	608	54	52	3.5
Dyneema® SK60	12	1.0	400–600	440–660	28–35	2.5–3.1	2.4–3.0	759–1080	67–95	65–93	3.5
Dyneema® SK62	17–21	2.0–3.0	400–2400	440–2640	33–35	2.9–3.1	2.8–3.0	974–1169	86–103	83–100	3.5
Dyneema® SK65	12	1.0	100–1200	110–1320	34–38	3.0–3.4	3.0–3.3	1082–1158	96–102	93–100	3.5
Dyneema® SK75	17–21	2.0–3.0	100–2400	110–2640	38–45	3.4–4.0	3.3–3.9	1267–1552	112–137	109–132	3.5
Dyneema® SK78	17–21	2.0–3.0	1600–2400	1760–2640	38–40	3.4–3.5	3.3–3.4	1267–1314	112–116	109–113	3.5
Dyneema Purity® SGX	17	2.0	50–400	55–440	36–37	3.2–3.3	3.1–3.2	1133–1246	100–110	97–107	3.5
Dyneema Purity® TG	12	0.9	23	25	43	3.8	3.7	1400	125	120	3.4
Dyneema Purity® UG	11	0.5	100–400	110–440	44–46	3.9–4.1	3.8–4.0	1473	130	126	3.3
Dyneema® NM22			400	440	17	1.5	1.5				
Dyneema® NM44			200	220	17	1.5	1.5				
Toyobo Co. (Toyobo, 2007)											
Dyneema® SK60 (Japan only)	12	1.0	50–1600	55–1760	29	2.6	2.6	895	79	79	3–5
Dyneema® SK71 (Japan only)	12	1.0	50–400	55–440	40	3.5	3.5	1246	110	110	3–5
Honeywell Specialty Materials (Honeywell, 2007)											
Spectra® fiber 900	38–40	10–10.8	650–4800	722–5333	26–31	2.3–2.7	2.2–2.6	850–920	75–81	73–79	3.6–3.9
Spectra® fiber 1000	23–28	3.6–5.4	215–2600	239–2888	34–38	3.0–3.4	2.9–3.3	1135–1320	100–117	97–113	2.9–3.5
Spectra® fiber 2000	19–23	2.5–3.6	100–180	111–200	38–39	3.4	3.3	1320–1450	117–128	113–124	2.5–3.6

or tenacity and specific modulus extremely high. The tenacity is 10 to 15 times that of good quality steel and the modulus is second only to that of special carbon fiber grades and high modulus poly(p-phenylene) benzobisoxazole (PBO). Elongation at break is relatively low, as for other high performance fibers, but owing to the high tenacity, the energy to break is high.

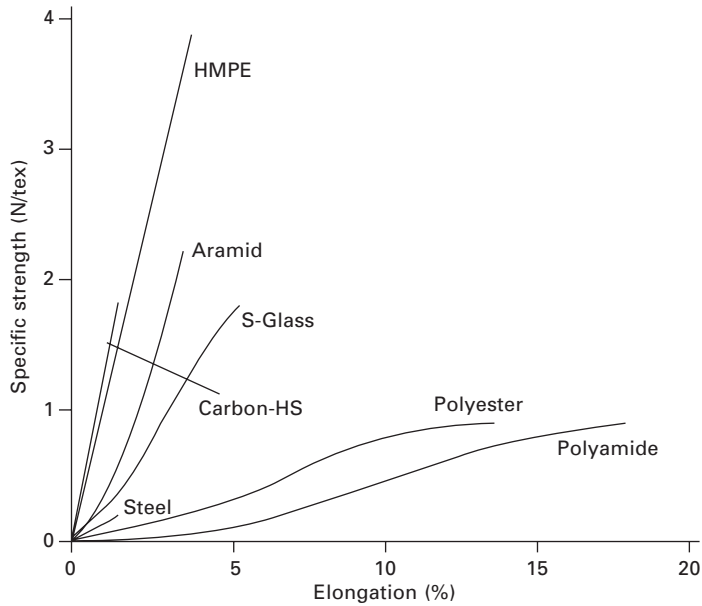
Figure 13.4 gives fiber strength in textile units (N/tex) and in engineering units (GPa). Textile units relate the strength to the weight of the fiber whilst engineering units refer to the cross-section and the volume of a fiber. It is clear from this diagram that the combination of low density and high strength makes HMPE fibers unique products. The diagram also shows that HMPE fibers are not only first choice in weight saving, but that their use can also give volume saving.

In Fig. 13.5 the specific strength and the elongation of various fibers are shown. Owing to their high modulus combined with elongation to break, HMPE fibers can absorb a large amount of energy. The work to break on a weight basis outperforms carbon and aramid fibers by a factors of 8 and 2 respectively (Lemstra *et al.*, 1987; Peijs *et al.*, 2000).

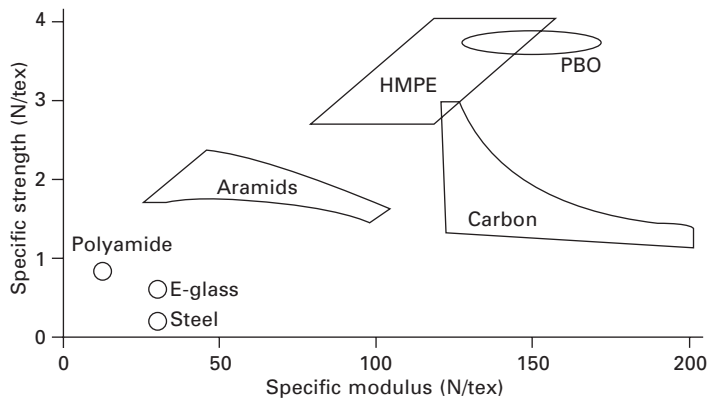
Figure 13.6 shows the specific strength versus the specific modulus and illustrates why HMPE fibers give veritable high performance. The high specific modulus is especially relevant in ballistic protection. The sonic velocity in the fiber determines the speed of spreading energy on ballistic impact and is calculated as the square root of the specific modulus. In Fig. 13.7 typical tenacity–strain curves of HMPE fiber types are shown.



13.4 Strength based on weight vs strength based on volume of various fibers.



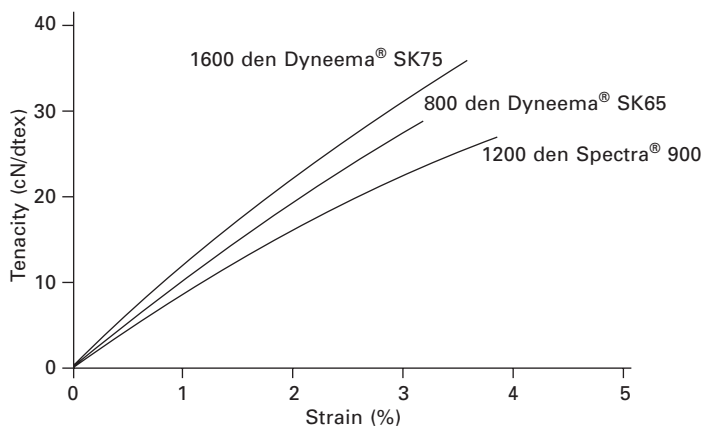
13.5 Fiber stress–strain curves.



13.6 Specific strength vs specific modulus for various fibers.

13.4.2 Compressive strength

UHMW-PE has a structure with low lateral (van der Waals) interaction between the adjacent chains. This results that in contrast to their high tensile strength, HMPE fibers have a low compressive yield strength of approximately 2–3% of their tensile strength, limiting their applicability in composites.



13.7 Typical tenacity–strain curves of HMPE fiber types.

Under compression loading kink bands (localized compression failures) are formed in the filaments (Fig. 13.8) (Noglić, 2003) due to buckling and slippage of the polymer chains. The kink bands disappear almost completely after subsequent tensile loading, hardly affecting tensile strength (Peijs *et al.*, 2000).

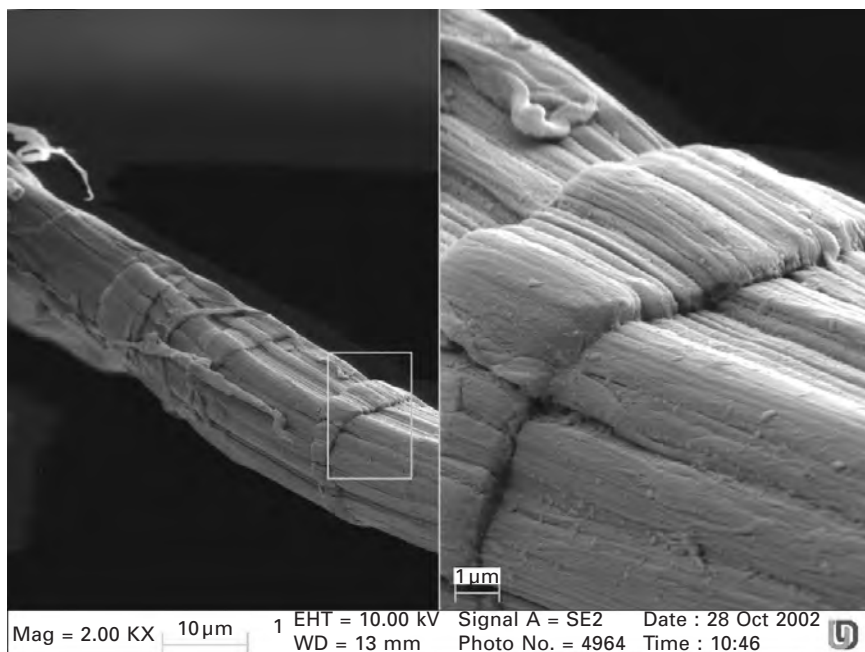
13.4.3 Mechanical properties in the transverse direction

As all the chains in the fiber are aligned in the fiber direction, the mechanical properties are highly anisotropic. In the transverse direction the modulus and strength are much lower than that in the fiber direction. Table 13.2 gives estimated values.

13.4.4 Thermal resistance

Depending on the conditions, HMPE fiber has a melting point between 144 and 152 °C. In a constrained condition, e.g. embedded in a polymer matrix as in composites, melting of the fiber is at a higher temperature and depends on the constraints on the fiber of the surrounding matrix.

The tenacity and modulus decrease at higher temperatures but increase at sub-ambient temperatures (Figure 13.9). Typically for long duration exposure HMPE yarns should not be used over 70 °C. Brief exposure to higher temperatures, but below the melting temperature, will not cause any serious loss of properties. When constrained to a constant length, the temperature resistance is improved. Short duration temperature exposure is limited to 130 °C for a non-constrained fiber and 145 °C for a constrained fiber. Because of their high crystallinity HMPE fibers do not show a clear glass–rubber transition temperature. At $T = -125^{\circ}\text{C}$ a weak glass–rubber



13.8 REM photograph of kink bands in an HMPE filament (Nogliki, 2003).

transition is shown which hardly has any effect on the mechanical properties. The fiber can be used from cryogenic conditions up to a temperature of 70 °C.

The mechanical properties of HMPE fibers are influenced by the temperature and strain rate. Figure 13.10 (Peijs *et al.*, 1994) shows a decrease in strength and a transition from elastic failure to viscoplastic failure at increasing temperatures or decreasing strain rates. The tenacity and modulus are usually tested around 1% per second, so below about 100 °C breakage will always be in the elastic failure range.

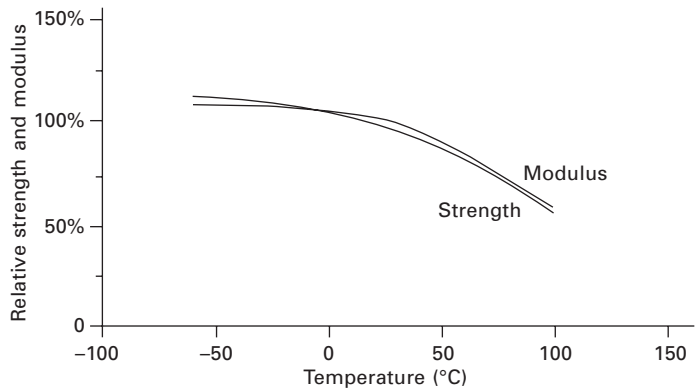
Large HMPE rope applications subjected to heavy cyclic loaded conditions, e.g. high frequency cycling with high load amplitudes, can experience a temperature increase due to hysteresis and internal friction. The energy loss of cyclic loaded HMPE fibers is dependent upon the temperature and at 70 °C it is approximately five times higher than at room temperature. The combination of load range, frequency and environment will determine whether a rope increases in temperature. As a practical limit for cyclic loaded HMPE rope applications an internal rope temperature of 70 °C could be taken. Solutions of using a limited quantity of ePTFE fibers or applying special developed coatings proved to be successful in bending fatigue tests in reducing the internal heat generated by friction between rope strands and in this way increasing the fatigue lifetime.

Table 13.2 Typical properties of various Dyneema® fibers (van Dingenen, 2001; Peijs *et al.*, 2000; Karacan, 2005; EDG, 1999)

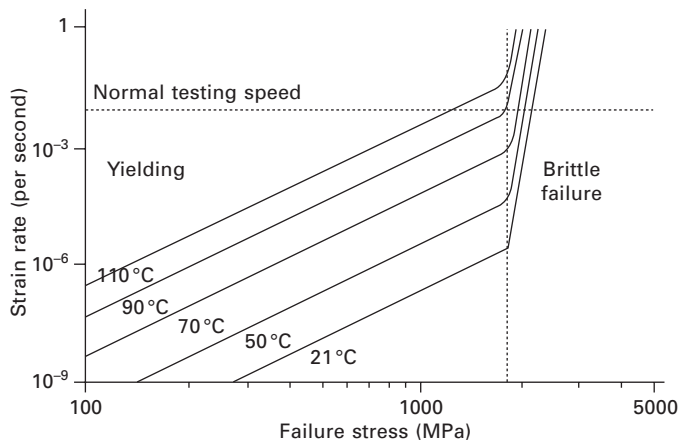
	Axial	Transverse
Physical		
Natural color	White	
Density (kg/m ³)	970–980	
Crystallinity (%)	< 85	
Equilibrium moisture regain	None	
Water pick-up (soaked)	None	
Boiling water shrinkage (%)	<1	
Limited oxygen index (%)	<20	
Hysteresis loss factor (23°C, 5 Hz)	0.02	
Friction coefficient (yarn-on-yarn)	0.05–0.07	
Mechanical		
Tensile strength (GPa)	3.6	0.03
Modulus (GPa)	116	3
Compressive yield stress (GPa)	0.1	0.05
Elongation at break (%)	3–4	–
Work to break (MJ/m ³)	45–70	–
Thermal		
Melting point (°C)	144–152	
Decomposition temperature (°C)	>300	
Coefficient of linear thermal expansion (K ⁻¹)	–12 $\times 10^{-6}$	
Specific heat (J/kg K)	1850	
Thermal conductivity (W/m K)	20	0.2
Electrical		
Resistance (Ω)	>10 ¹⁴	
Dielectric strength (kV/cm)	900	
Relative dielectric constant (22°C, 10 GHz)	2.2	
Dielectric loss factor	2 $\times 10^{-4}$	
Acoustic		
Sound speed (m/s)	10–12 $\times 10^3$	2 $\times 10^3$
Optical		
Refractive index	1.59	1.53
Birefringence	0.06	
Ultraviolet visibility (UV)	Transparent	
Eye visibility (VIS)	Transparent	
Near infrared visibility (NIR)	Highly transparent	
Infrared visibility (IR)	Highly transparent	
Radar visibility	Highly transparent	

13.4.5 Shrinkage

Owing to the high chain extension HMPE fibers show a high axial heat conductivity and a negative coefficient of linear thermal expansion. When given sufficient mobility, the chains will contract in order to return to the thermodynamically preferred coiled conformation. Shrinkage is negligible below 100 °C, and will occur mainly between 120 and 140 °C. If the fiber is



13.9 Strength and modulus of Dyneema® SK76 fibers as function of temperature.



13.10 Effect of temperature and strain rate on the failure stress of Dyneema® SK60 fiber (Peijs *et al.*, 1994).

constrained, it will develop significant shrinkage forces (up to approximately 0.1N/tex) (Govaert and Lemstra, 1992).

13.4.6 Effects of water

Polyethylene is not hygroscopic and does not absorb water. The fibers have a very low porosity; therefore water absorption in the fiber is negligible. However, multifilament yarns used as strands in a rope or in a fabric typically have 40% void and show some capillary action. If that is not acceptable, water repellent additives should be used.

Polyethylene fibers do not swell, hydrolyze or otherwise degrade in water, seawater or moisture. Properties such as tension fatigue, yarn on yarn

abrasion and bending fatigue may improve through contact with water. This is attributed to the cooling or lubricating effect of the water during those tests.

13.4.7 Chemical resistance

HMPE fibers are produced from polyethylene and do not contain any aromatic rings or any amide, hydroxylic or other chemical groups that are susceptible to attack by aggressive agents. The result is that polyethylene and especially highly crystalline, high molecular weight polyethylene is very resistant to chemicals, acids and alkali environments. Table 13.3 (AmSafe, 2007; DSM, 2008) gives examples of the effect of chemicals on HMPE fibers.

HMPE fibers, being of a polyolefinic nature, are sensitive to oxidizing media. In strongly oxidizing media, fibers will lose strength very fast. In normal air the fiber is stable for many years.

13.4.8 Biological resistance

The biological resistance of the fiber is that of high density polyethylene. The fiber is not sensitive to attack by micro-organisms (Table 13.4) (AmSafe, 2007).

13.4.9 Viscoelasticity

Polyethylene is a viscoelastic material, that is, the properties depend significantly on such variables as temperature, time and loading history. One characteristic is that the mechanical properties of HMPE fibers such as tensile strength (or tenacity), tensile modulus and elongation at break depend on the temperature and the strain rate. At high strain rates, or at low temperatures, both modulus and strength are significantly higher than the values given in the tables above. In Fig. 13.11 results are presented of 0.05–350%/s strain rate tests. This higher range is more representative for the behavior of HMPE yarns used in anti ballistic materials.

Another characteristic is that the fiber is sensitive to long-term static loads and will elongate proportionally with time, resulting a higher strain at rupture. This phenomenon is generally known as creep, and is a process in which the long molecular chains slide along each other.

The creep of HMPE fibers is influenced by the ambient temperature and the applied load. Very high loads or a high temperature will accelerate the irreversible creep. Over a considerable amount of time, the creep rate is constant and ultimately the fiber will fail (Fig. 13.12). Three regimes are characterized by the different behavior of the creep rate. In regime I the creep rate reduces to a plateau level; the elongation is reversible. In regime II the

creep rate increases slightly; the elongation is irreversible. In regime III the molecular chains start to break. High strains cause necking in the filaments (Fig. 13.13; Noglik, 2003), increasing local stress that further accelerates the strain until breakage. The time at which an HMPE fiber application should be discarded is dependent upon load, temperature and rope weight. Based on extensive testing, DSM Dyneema has developed a tool to predict creep rate and creep elongations, as well as to estimate creep lifetime of all its commercial HMPE fiber types (Smeets *et al.*, 2001; Vlasblom and Bosman, 2006).

Creep values are not the same in all HMPE fibers but depend on choices made in the production process. Compared to all commercially available regular HMPE fiber types, Dyneema® fibers prove to have the lowest creep rate, with the Dyneema® SK78 the best performer in terms of creep rate and lifetime. Dyneema® fibers offer a low creep rate at a low rope weight (Table 13.5). Other HMPE fiber types can obtain the combination of high rope strength and good creep performance only with a higher rope weight.

Dyneema Purity® UG fiber, developed especially for medical applications, is the overall best performer on creep resistance.

13.4.10 Abrasion resistance

The UHMW-PE used for HMPE fibers is also a well-known engineering plastic. As such it is especially used for its superior wear and abrasion resistance, so it is not surprising that the HMPE fibers also have good abrasion resistance.

In ropes, there are two types of abrasion: external and internal abrasion. In long-term, cyclic loaded use, the rubbing of rope strands on each other can cause fibrillation of the fiber or develop cracks across fibers, resulting in a loss of strength. In addition to other factors, the coefficient of friction of the fiber is important. Compared with other synthetic fibers, HMPE fibers have a very low coefficient of friction. This results in good fiber-to-fiber abrasion resistance without the use of lubricants or marine finishes, as is used on polyester fibers. A wet yarn-on-yarn abrasion test according to Cordage Institute CI1503, which is comparable to ASTM D6611, showed that inter-wrapped Dyneema® fiber outperforms other high modulus fibers (Fig. 13.14). Internal abrasion can be highly influenced by the presence of water (cooling).

Still, the most common causes of rope failure are external damage through surface abrasion and rope cutting. For a rope cover, the ability to resist external abrasion depends on the fiber (type and applied finish or coating), the cover construction (twist levels, braiding angles), the rope (construction and tension), the surface (abrasive nature) and the condition (wet or dry, sliding speed). There are no industry-wide standards to determine external

abrasion or cutting of ropes. Results of a rotating spoke wheel test (Fig. 13.15) and a steel wire sawing test (Fig. 13.16) show that covers made with Dyneema® fiber provide excellent resistance against these sources of deterioration (Table 13.6).

Table 13.3 (a) Chemical resistance of various Dyneema® fibers (DSM, 2008); (b) Aviation fluids susceptibility of Dyneema® SK75 fiber (AmSafe, 2007)

	++ None 0–10%	+ Slight 11–20%	+/- Moderate 21–40%	– Appreciable 41–80%	– Degraded 81–100%
Loss in tensile strength					
Tensile strength and chemical exposure					
Chemical	Concentration [%]	Conditions Temperature [°C]	Exposure time [h]	Effect on tensile strength	
Inorganic acids					
Hydrochloric acid	10	20	5000	++	
Nitric acid	10	20	5000	++	
Sulfuric acid	0.24	60	168	++	
Organic acids					
Glacial acetic acid	100	20	5000	++	
Alkalis					
Ammonium hydroxide	28	20	5000	++	
Calcium hydroxide	0.25	60	168	++	
Sodium hydroxide	10	20	5000	++	
Strong oxidizing agent					
Kalium permanganate	0.6				
In sulfuric acid	25	23	720	+	
Organic compounds					
Acetone	100	20	5000	++	
Ethanol	100	20	5000	++	
Oil	100	20	4320	++	
	100	40	4320	++	
	100	80	4320	++	
	100	20	4320	++	
Petrol	100	40	4320	++	
	100	80	4320	++	
	100	20	5000	++	
Toluene	100	20	5000	++	
Trichloromethane	100	20	5000	++	
Miscellaneous					
Distilled water	100	20	5000	++	
Seawater	100	20	5000	++	
Detergent in aqueous solution	30	20	5000	++	

Table 13.3 Continued

	++ None 0–10%	+ Slight 11–20%	+/– Moderate 21%–40%	– Appreciable 41–80%	– Degraded 81–100%
Loss in tensile strength					

Tensile strength and chemical exposure following
procedure RTCA DO160E Section 11

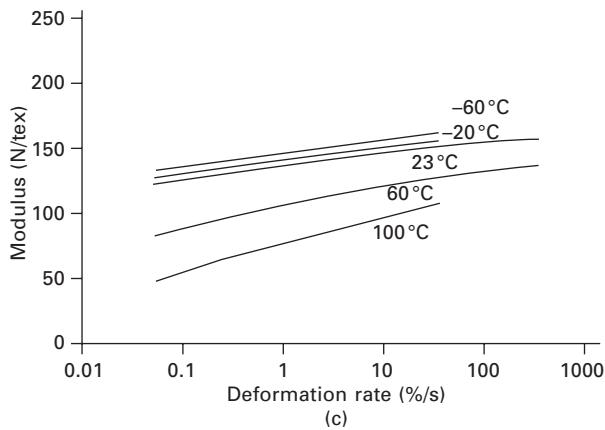
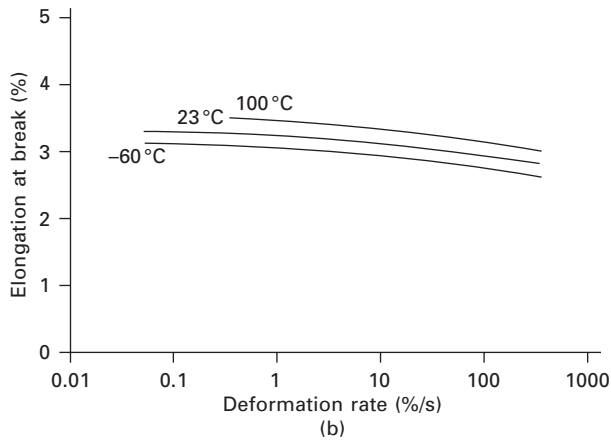
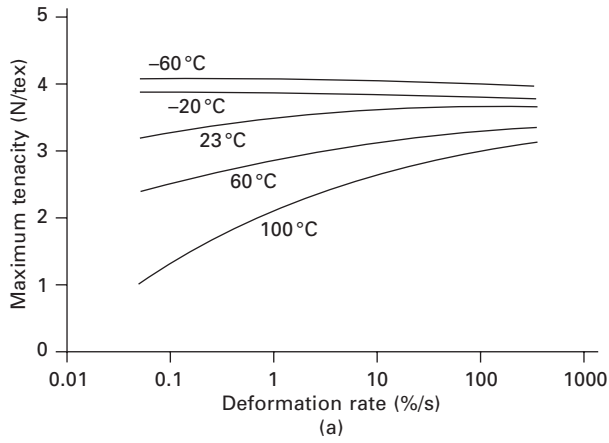
Chemical	Concentration [%]	Conditions Temperature [°C]	Wetting cycle [h]	Storage at 65 °C[h]	Effect on Tensile strength
Aviation Jet A fuel (ISO 1817 test liquid F)	100	40	24	160	++
Hydraulic fluid (ISO 1817 test liquid 103)	100	70	24	160	++
Lubricating oil (ISO 1817 test liquid 101)	100	70	24	160	++
Solvents & cleaning fluid (Isopropyl alcohol)	100	50	24	160	++
De-icing fluid (Ethylene glycol)	100	50	24	160	++
Insecticide (Pyrethroid pesticide)	0.92	23	24	160	++
Fire extinguishant (Protein) (Fluoroprotein)	100	23	24	160	++

Table 13.4 Fungal resistance test following standard RTCA DO 160D Section 13
(29 °C, 99% RH, 28 days) on Dyneema® SK75 fiber (AmSafe, 2007)
Observation levels

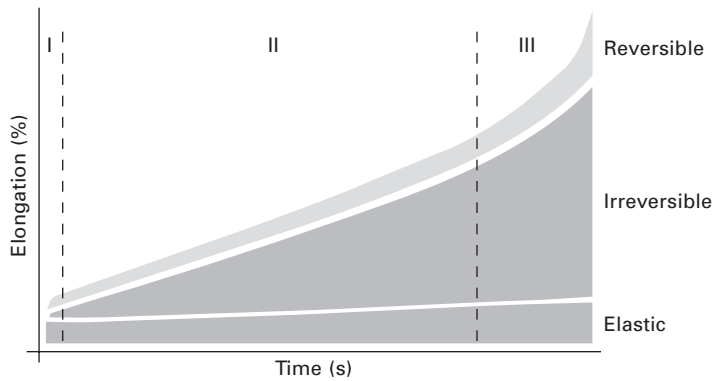
Observation	0	1	2	3
Microscope with nominal magnification of approximately 50×	No growth visible	Growth clearly visible		
Naked eye		Growth not, or hardly visible	Growth plainly visible but covers less than 25% of the test surface	Growth plainly visible and covering more than 25% of the test surface

Fungal resistance (29 °C, 99% RH, 28 days)

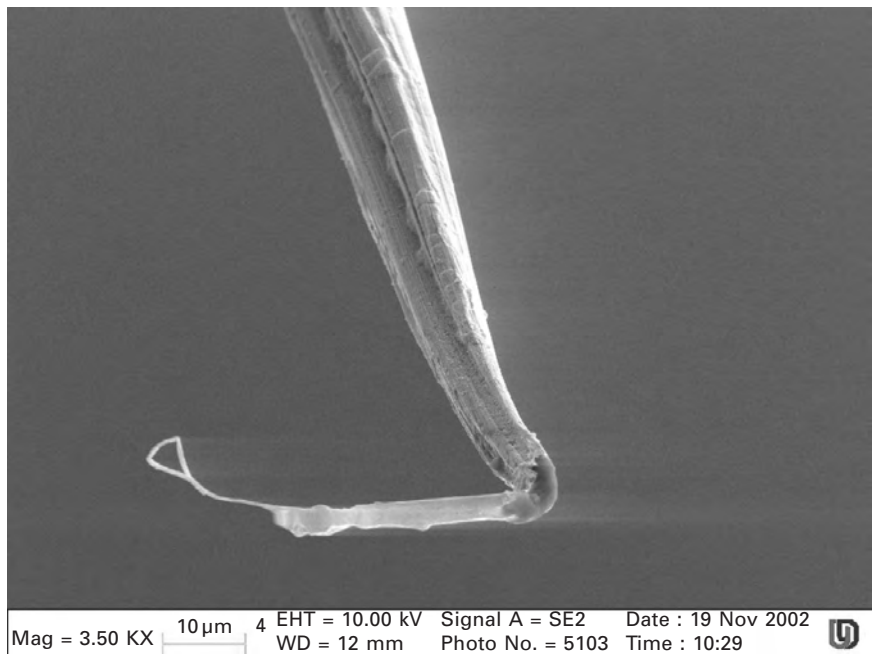
Fungi	Observation
<i>Aspergillus niger</i>	0
<i>Aspergillus flavus</i>	0
<i>Aspergillus versicolor</i>	0
<i>Penicillium funiculosum</i>	0
<i>Chaetomium globosum</i>	0



13.11 Dyneema® SK76 fiber versus strain rate, at different temperature levels; (a) tenacity; (b) elongation at break; and (c) modulus.



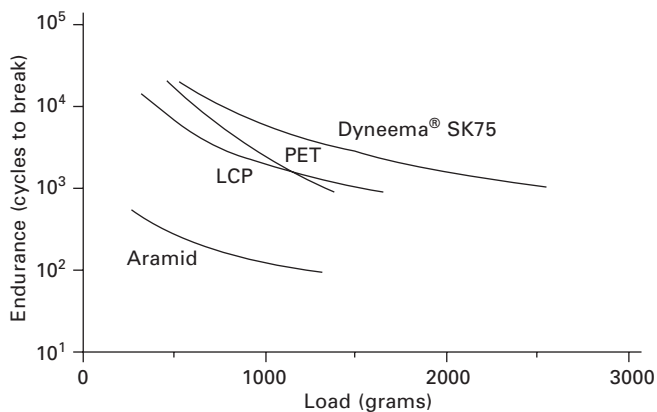
13.12 Typical HMPE creep curve.



13.13 Reduced cross-section on the tip of a broken, creep-loaded HMPE filament (Nogliki, 2003).

Table 13.5 Comparing creep resistance of Dyneema® and other HMPE fiber types in a 100 tonnes break strength rope

Fiber type	Rope weight (100 tonnes BS)	Creep load	Temperature	Creep rate	Creep lifetime
Dyneema® SK78	650 g/m	200 kN	16 °C	0.5%/yr	15 years
Dyneema® SK75	650 g/m	200 kN	16 °C	2.3%/yr	7 years
Other HMPE fibers	1360 g/m	200 kN	16 °C	5.5%/yr	Unknown



13.14 Wet yarn-on-yarn abrasion test results of HMPE vs polyester, liquid crystalline polymer (LCP) and aramid fibers.



13.15 Cover surface abrasion test using a rotating spoke wheel.



13.16 Rope cover sawing test using a steel wire.

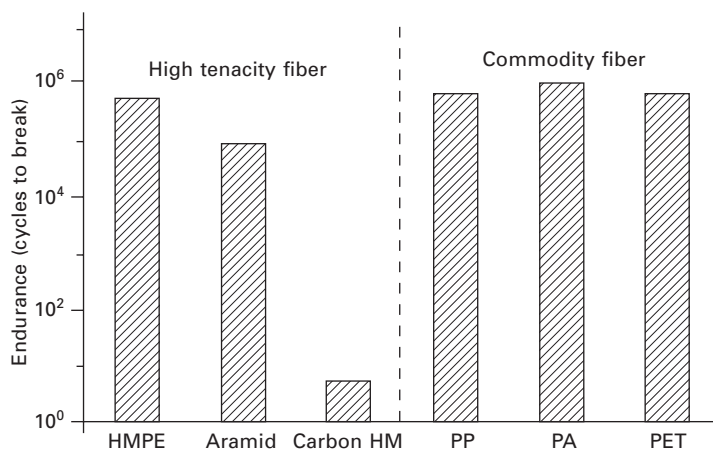
Table 13.6 Abrasion and cutting protection performance of rope covers with different fibers

Abrasion and cutting protection performance levels						
Rope protection performance of covers			0	+	++	
			Reference	Good	Excellent	
Increase in cycles to failure			1%	5%	>10%	
Abrasion and cutting resistance						
		Dyneema® SK75	LCP	PBO	Aramid	PET
External abrasion resistance	Dry	++	++	++	+	0
	Wet	++	++	+	0	0
Cutting resistance	Dry	++	+	0	0	0

13.4.11 Fatigue

Flexural fatigue

Fatigue is very important in, for example, rope applications. HMPE fibers are the first high performance fibers that not only have a high tenacity but that also have tension and bending fatigue properties comparable with the



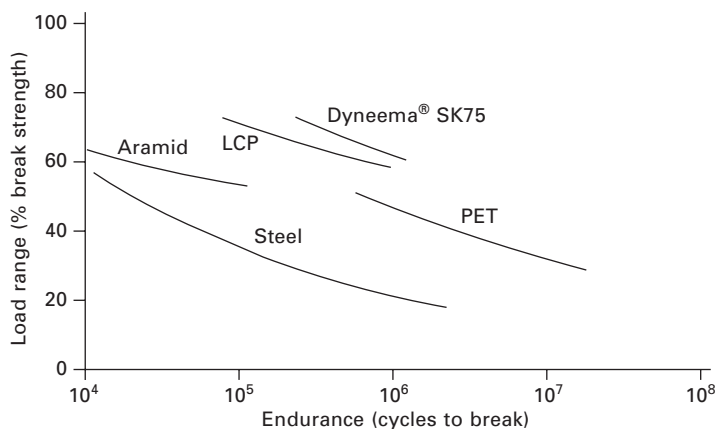
13.17 Flexural fatigue life tested on Folding Endurance tester at 0.4 g/den tension and 270° flex angle.

commonly used polyamide and polyester grades in ropes. Carbon fibers and glass fibers have a high modulus and a elastic failure mode, but HMPE fibers demonstrate that this is not an obvious combination. HMPE fibers have a high modulus but still are flexible and have a long flexural fatigue life tested on a folding endurance tester (Fig. 13.17). Good flexural fatigue resistance is related to low compressive yield stress.

Tension fatigue

In tension fatigue testing, a rope is repeatedly loaded in tension, resulting in inter-fiber abrasion and filament breakage, leading to a loss of strength. The deterioration rate is dependent on the applied mean load level and the range of loading. The HMPE fiber is quite resistant to repeated axial loading, even if the loading is partly in compression as in bending fatigue. Because of the low friction coefficient and good abrasion resistance, internal abrasion is usually negligible.

An overview based on several studies (Fig. 13.18) (Casey, 1994, 2003; OTO, 1998; Banfield *et al.*, 2005) shows a longer tensile fatigue life of braided ropes made from Dyneema® fiber than LCP, polyester, aramid and steel in wire-rope constructions. Aramid fibers suffer severe abrasion damage compared to Dyneema®, LCP and polyester fibers because of their high friction coefficient, especially when tested wet. Besides fiber properties, rope construction also influences fatigue life performance. In general, the fatigue life of laid ropes is lower than braided ropes, when comparing at same relative load levels (e.g. percentage of break strength). In case fatigue load is expressed as a specific load (force per amount of material, e.g.



13.18 Tensile fatigue life compared. All synthetic ropes were tested in a wet condition at the National Engineering Laboratory (Casey, 1994, 2003; OTO, 1998; Banfield *et al.*, 2005).

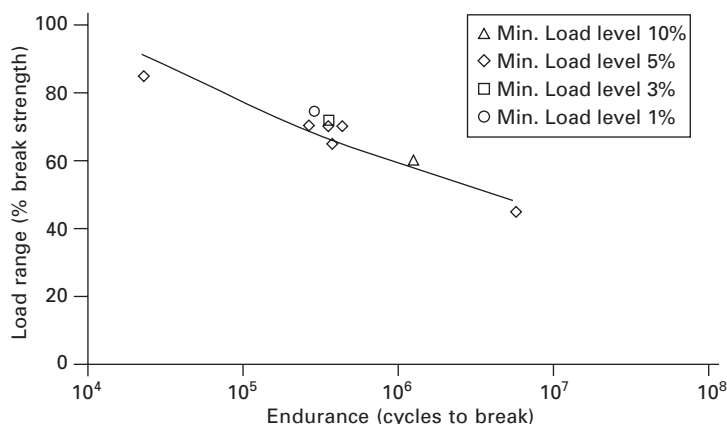
N/tex), the difference between constructions is far less pronounced (Hoppe, 1997).

The worst condition in fatigue loading is complete or nearly complete unloading (0% to 5% of breaking strength) of a rope in each tension cycle. Although the rope as a whole is under tension, the components can go into compression, e.g. due to rope twisting, non-uniform load sharing or relative movement between rope and jacket. Compared with other fiber types, HMPE is, like polyester, not sensitive to this. The fatigue lifetime of ropes made with Dyneema® was not influenced by reducing the minimum tension (Fig. 13.19). A minimum quasi-static tension of 2% break strength may be considered for HMPE ropes, identical to polyester ropes, while for aramid ropes, which are sensitive to compression failure, a minimum dynamic tension of 10% break strength is to be maintained (Bureau Veritas, 2007).

The relatively low melting temperature makes the fiber sensitive to high temperatures. Under fatigue loading a rope will experience hysteresis, a process which causes warming of the rope. The balance with energy loss to the environment determines whether the rope will stand a long-lasting test. High-speed loading and relaxation may lead to high temperatures, but even a thick rope immersed in water may stand the test without any difficulty, as has been shown in, for example, offshore mooring.

Bending fatigue

In running rope applications HMPE fiber ropes run over sheaves under a combined tensile and bending load. Rope fibers and the strands move relative to each other and cause internal abrasion. The rope construction has a great



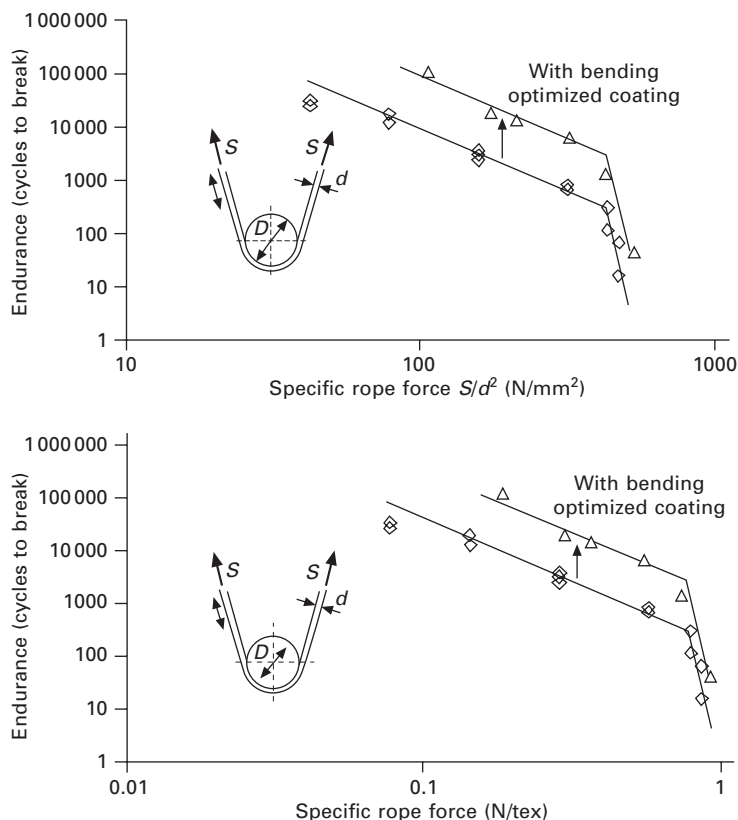
13.19 Tensile fatigue of ropes with Dyneema® SK75 generated with a minimum load level of 5% BL compared with fatigue results generated with other minimum load levels.

influence, but as HMPE fibers have a low friction coefficient and good abrasion resistance the results are comparable with those from commonly used synthetic fiber ropes and far higher than other high tenacity fibers like aramids and carbon fibers. The outcome of standard bending tests as performed in wire rope research is shown in Fig. 13.20 (Vogel, 1998; IFT, 2008a). The bending cycles up to breakage N is plotted versus the specific rope force S/d^2 (in N/mm^2) as known in steel wire rope research, and additionally versus the rope specific force in N/tex . The change in slope indicates the transition of fatigue breakage to forced breakage. The tests were carried out with a ratio of the sheave diameter D to the nominal rope diameter d of $D/d = 10$. Recent bending over sheaf tests on ropes made of Dyneema® SK75 using an improved coating technology showed 10–15% higher cycles to failure than steel wire ropes (IFT, 2008b).

Bending fatigue life of HMPE fiber ropes can also be improved by means of hybrid rope constructions. Testing showed that an 80 mm coated rope made with Dyneema® and a limited quantity of ePTFE fiber withstood more than twice the number of bend cycles of steel wire (Kelley and Gibson, 2007). An advantage of these improved durability rope types is that they can be used on a smaller sheaf, which enables a smaller footprint of lifting systems.

13.4.12 Resistance to light and other radiation

For HMPE fibers no special precautions are necessary during processing or storage. However, light resistance may become limiting when the material is exposed to UV light continuously or for a prolonged time. After UV



13.20 Bending fatigue cycles to break of 8 mm diameter braided rope samples ($D/d = 10$) made with Dyneema® SK75 versus the specific rope force S/d^2 in N/mm² and in N/tex (Vogel, 1998; IFT, 2008a).

exposure, HMPE fibers show a slight increase in modulus and a decrease in tenacity and elongation at break.

Tested according to ISO 4892, the sensitivity to a combination of UV and high temperature, generated by xenon arc lamps, showed half-strength values for HMPE fiber types in the range of 1000–1900 hours. Because of the nature of this test, not all tenacity loss can be described to the influence of UV-induced oxidation.

The UV degradation mechanisms can differ between polymer types, making a direct comparison between different fibers under laboratory conditions difficult. Although the UV exposure is better defined under a laboratory condition, these tests are often less representative of actual use, while real life outdoor tests are more valuable but take a long time.

The retention strength of HMPE applications subjected to UV exposure is dependent upon thickness, construction and use of protective measures such

as coatings or non-load-bearing jackets. Ultraviolet radiation only penetrates to shallow depths, causing small diameter non-covered ropes to be affected much more than large diameter ropes. In addition, open constructions such as eight-strand plait are affected more than 12-strand braided rope constructions. An outdoor exposure of small diameter rope samples made with Dyneema® showed over 10 years a logarithmic decay to 40% retention strength. Experience shows that larger diameter oil tanker mooring lines made with Dyneema® fiber, used over 20 000 mooring hours in 10 years time, had retention strengths of at least 75-90% despite the influences of weather, abrasion or tensile loading. Also a comparable mooring application made with Spectra® fiber showed excellent retention strengths after 13 years of service (Davis *et al.*, 2006).

Exposure to high energy radiation, as e-beam or gamma radiation, will result in chain scission and a reduction of tenacity. The effect is significant for doses of 100 kGy; however, the fibers retain a useful tenacity up to a dose of 3 MGy.

13.4.13 Accelerated thermal-oxidative aging

Accelerated aging during 8 weeks at 65 °C showed an increase of the strain at break, described to the thermal relaxation of the UHMW-PE chains, little variation of the tenacity and a modulus retention of 92%, confirming that Dyneema® fibers do not lose their specific energy absorption capabilities (Chabba *et al.*, 2007). Eight weeks at 65 °C will accelerate the aging to the level of five years at 35 °C.

Accelerated aging during 30 days at 80 °C and 50 bar pressure following ISO 13438 (Geotextile) showed 69% strength retention indicating that Dyneema® fibers will withstand oxidation in soil for far more than 25 years (BAM, 2004).

13.4.14 Electrical properties

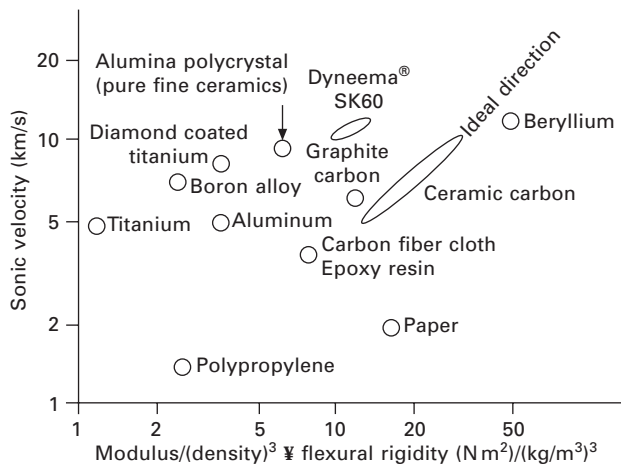
Polyethylene is an insulator and has no groups with dipole character. The fiber is characterized by a high resistance, low dielectric constant and a very low dielectric loss factor (Table 13.2). Fibers contain a small fraction of spin oil of a hydrophilic nature. For applications where the electrical properties are important, the spin finish should be removed.

13.4.15 Acoustic properties

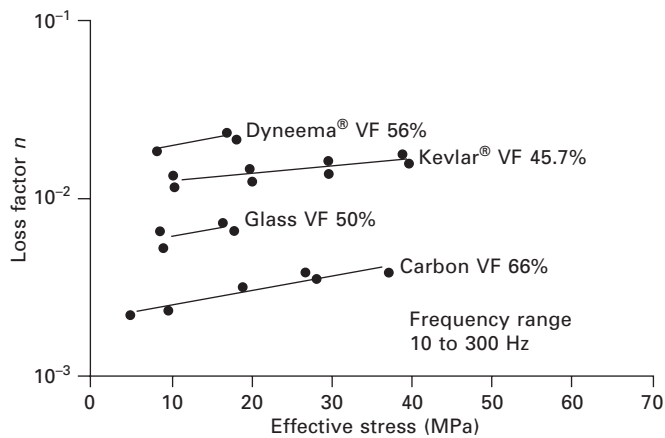
As with all mechanical properties, the acoustic properties are strongly anisotropic. In the fiber direction the sonic velocity, defined as the square root of the specific modulus, is much higher than in the transverse direction

(Table 13.2). The acoustic impedance, the product of density and transverse sound speed, is near that of water. A high sonic velocity in combination with a high modulus is required for loudspeaker cones (Fig. 13.21) (Kirschbaum *et al.*, 1987).

Mechanical damping losses are significant in both the longitudinal as well in the transverse direction. In the range of 10–300 Hz the loss factor of HMPE composites is approximately a factor 10 higher than that of carbon fiber composites (Fig. 13.22) (Kirschbaum *et al.*, 1987).



13.21 Sonic velocity versus flexural rigidity of composites for speaker cones (Kirschbaum *et al.*, 1987).



13.22 Loss factor of fiber reinforced composites (Kirschbaum *et al.*, 1987).

13.4.16 Optical properties

HMPE fibers are optically opaque. Owing to the stretching process of the fiber, the fiber molecules are mainly oriented parallel to the fiber axis and will perform birefringence. Birefringence is defined as the difference between the refractive index for light polarized parallel to the fiber axis and that for light polarized perpendicular to the fiber axis (Table 13.2) (Karacan, 2005).

Low infrared absorption coefficient and high thermal conductivity also make the fibre invisible to thermal imaging devices. The low reflectivity of radar waves results in a reduced visibility for radar sources.

13.4.17 Flammability

All polymeric materials are combustible and their behavior when exposed to heat and fire differs less than it often seems to do. Thermoplastics normally melt first and then decompose. In the end the gases from the decomposition start burning. Thermosets do not melt but start decomposing. The decomposition temperature and the ignition temperature of the gasses are usually in the same range as for thermoplastic polymers. HMPE fibers are made of polyethylene, a thermoplastic material that melts at about 150°C and decomposes over 300°C. Aramid fibers are thermosets. There is no melting point and gas emission starts at about 400°C.

Having an limited oxygen index (LOI) index lower than 20, HMPE fibers will burn slowly if ignited in atmospheric conditions. Testing flammability of a horizontal mounted fabric, following the automotive industry standard FMVSS 302, or vertically mounted, following the aviation industry standard FAR 25.853b, shows that in contact with a flame the fabric shrinks away from the flame without ignition or dripping. The sample is qualified as being self-extinguishing upon removal of the flame.

A vertically mounted ballistic panel made from fabric layers of Dyneema® passes DIN-4102 flammability tests where a flame is placed under an angle of 45°. Only a small dent is seen where the fabric layers locally shrunk away from the flame.

In case of fire toxic and/or corrosive decomposition products such as carbon monoxide, carbon dioxide, (dense) black smoke, aldehydes, organic acids may be formed. The toxicity of the gases in a fire depends on the composition of the substrate. If the material contains nitrogen, sulfur or chlorine (or any other halogen), such as polyamides and aramids, the gases are always toxic. If these chemical elements are not present, toxicity fully depends on the conditions in the fire. The conditions in the fire are by far the main parameters for the development of toxic gases. The local temperature and oxygen concentration determine which gases are produced.

13.4.18 Toxicity

Polyethylene is regarded as biologically inert. Dyneema® fibers are IARC classified 3 (not classifiable carcinogenic to human) based upon its length weighted geometric mean diameter in the range 17.93–18.32 μm . The observed diameter of the Dyneema® fibers is too large to produce respirable fibers, meaning they will never reach the deeper part of the respiratory tract and fibrogenic or carcinogenic effects on the lung will not occur.

Dyneema Purity® fibers have been specially designed to obtain the highest level of quality and purity, as required for use in medical devices and are fully biocompatible according to ISO 10993.

13.5 Processing

13.5.1 General precautions

HMPE fibers are continuous multi-filament yarns with a low elongation at break, making them more vulnerable to length differences than most other synthetic materials. Differences in length of fibers or filaments will result in uneven stress distribution over the filaments, causing damage or premature breakage.

In processing HMPE fibers into symmetric structures an accurate control over the tension and the length of the fibers is important. In the construction, the fibers should be of equal length in order to share load evenly. The tension in the fibers should be as constant as possible; therefore the creel should be stiff to avoid vibrations in the fibers. The path from creel to twister should be as linear as possible to prevent shifting of the fiber construction.

Passing the fiber through guides with too high pressures on the contact surface could also damage the structure by shifting of filaments or even filament breakage. The high tenacity HMPE fibers may cause damage and wear to guides and other contact points. These worn-out eyes damage the fibers. Highly wear-resistant contact points are recommended.

Fluff building and tucked up fibers before the inside corner of the eyelet are indications of fiber structure damage. To overcome this, lower tensions should be applied and preferably rolling guides (ceramic treated) should be used over fixed guides and pig-tails.

13.5.2 Fiber processing, blends and fusing

All HMPE fibers are produced as multifilament fiber and by far the largest part is used as such. Standard machinery can be used for twisting and twining HMPE fibers into applications. To obtain an even load sharing in a construction, twisting should be performed with even tensions and in

following production steps the same twist angles should be used to obtain similar twist losses.

The achieved tenacity of a construction depends upon the number of assembled yarns and the twist level. An empirical correlation from the English wool industry, the so-called *k*-factor, used to estimate the influence of twisting, is described as:

$$k = \frac{\text{twist level}_{(t/m)} \cdot \sqrt{\frac{\text{yarn count}_{(\text{dtex})}}{\text{density}_{(\text{kg/dm}^3)}}}}{3025}$$

The influence of the twist on an HMPE fiber is shown in Table 13.7. The strength is retained at a rather stable high level between an effective twist of $k = 0.4$ – 0.9 . An optimum twist level of $k = 0.8$, where minimal tenacity is lost, would result in 40 to 60 turns/meter for a 1760 dtex fiber. Compared with other materials these optimum twist levels result in very loose constructions. A coating over the construction could be considered to overcome this.

HMPE fibers can be cut to long or short staple or can be stretch broken. Short staple yarns can be processed using open-end and ring spinning, the latter producing spun yarn with superior properties. Long staple yarns and stretch broken yarns can be spun on wool spinning equipment (three cylinder spinning). Both short and long yarns can be combined with other yarns to form blended yarns. A large number of yarn blends have been produced for different applications but most for cut protection. Both filament yarns and long and short staple yarns can be used.

A unique property of HMPE fibers is the ability to be fused into monofilament-like products or tapes. In a strictly controlled way, HMPE fiber is heated in an oven to a temperature of about 150°C , so that the outer layers of the fibers are fused together while the fibers are stretched to avoid too much tenacity loss. These monofilament-like products found their use in sport fishing lines (Veillat and Dirks, 2003).

Table 13.7 Influence of twist on Dyneema® SK60 fiber

<i>k</i> -factor	440 dtex twist level (t/m)	1760 dtex twist level (t/m)	Tenacity (%)
0	0	0	100
0.57	80	40	104
0.85	120	60	104
1.13	160	80	96
1.7	240	120	85
2.83	400	200	65

13.5.3 Rope making

HMPE fibers are flexible and can be very well processed in all types of rope applications. During processing HMPE fibers must be kept under constant tension and path length differences must be avoided to obtain a high strength. The high tenacity and low elongation properties of this fiber puts some requirements on the contact points.

These should be hard, preferably rolling and certainly not worn out.

Constructions

Laid ropes have a higher breaking strength than braided ropes but are less flexible in handling. The ropes are torque unmatched (rotate under load). In highly dynamic loaded applications (much bending, changing tension loads, much handling) braided or plaited constructions are often preferred in torque matched (8 and 12-strand) constructions. To obtain a more stable construction the hollow 12 $\times$ 1 construction can be filled with a non-load-bearing material such as polyester. When produced with a braided cover, damage to the load-bearing strands can be prevented. Core–cover braids with HMPE as load-bearing core and polyester in the cover are in common use, but for a higher abrasion resistance HMPE fiber could also be considered as a cover material.

Rope strength

Table 13.8 compares the strength, diameter and weight of synthetics and steel for various rope diameters. In the table, strength values of same constructions have been determined by examining published data of various rope manufacturers. Ropes made from general-purpose synthetic polymers (polyamide, polyester) almost double in size to obtain a comparable strength as ropes made with Dyneema® SK75. Ropes made with other high modulus, high tenacity fibers (aramid, LCP) have 50–80% more weight. Compared with general-purpose steel wire ropes, the strength and diameter of ropes made with Dyneema® are roughly the same, yet their weight is a factor of 8 less. Many kinds of steel wire rope have already been replaced by HMPE, for instance in electricity cable pulling and forestry. It gives users the benefit of a much lower weight and all speed and handling benefits resulting from that.

Rope stiffness

Rope load–extension curves are non-linear and can change during use. For mooring calculations several linear elastic stiffness values are used, with as

Table 13.8 (a) Strength and weight for various diameter ropes; (b) Diameter and weight for various rope strengths

	12 strand braided synthetic rope						Steel wire rope		
	Dyneema®		Commodity fiber types		High tenacity fiber types		180	200	
	SK62	SK75	PET	PA	Aramid	LCP	kp/mm ²	kp/mm ²	
(a) Diameter (mm)									
12	127	142	37	33	148	142	84	113	Break strength (kN)
24	417	493	124	134	485	465	350	452	
96	4745	5819	1877	1767	5800	6206	5892	7167	
12	8	8	11	9	12	13	53	65	Linear density (kg/100 m)
24	30	31	47	37	45	47	227	257	
96	477	461	694	583	704	793	3896	3988	
(b) Break strength (kN)									
150	13	12	26	26	12	13	16	14	Diameter (mm)
500	26	24	48	49	24	24	28	25	
6000	110	98	180	181	98	95	97	88	
150	10	9	52	43	12	14	96	86	Linear density (kg/100 m)
500	38	32	181	153	46	51	324	283	
6000	615	474	2410	2068	733	765	3968	3345	

minimum the post-installation stiffness and as maximum the storm stiffness. Rope stiffness is dependent upon construction, frequency, amplitude, mean load level and fiber type, and thus measured values mentioned in literature can differ (Table 13.9) (EDG, 1999; Davies *et al.*, 2002; Marlow, 2005). As an approximation can be taken that HMPE rope stiffness is higher by a factor of 3 than polyester ropes.

Heat-set ropes

HMPE ropes used in static loaded applications show a characteristic plastic deformation called creep. This plastic deformation allows HMPE ropes and nets to be post drawn at elevated temperatures (also called heat-set) to remove the extra elongation that is introduced during the production by which the load distribution between rope components is improved, and as such the tenacity property is enhanced (Hogenboom and Dirks, 1990). During this process HMPE rope applications need to be kept under tension to fixate the structure. While heat-setting the rope is forced to elongate around 8–10% in a time dependent upon the temperature and the applied tension by which the absolute rope strength is increased by 20% while the rope diameter reduces up to 5%. Several rope and net manufacturers have heat-set HMPE ropes in their collection. In practice this process is limited to 40 mm diameter rope sizes because of the high load involved to heat-set larger sized HMPE ropes.

The improved orientation of the fiber in the rope due to the heat-set process shows a reduction in creep rate compared with non heat-set ropes, in both relative load (percentage of break strength) and in specific load (MPa or N/tex) conditions, without having a negative effect on creep lifetime. Fatigue cycling of heat-set ropes at the same relative load level as non-heat-set ropes will show a higher deterioration due to the higher load (in kN) on the heat-set ropes. When seen against the specific load (N/tex), the heat-set ropes give at least equal results than the non-heat-set ropes. It is dependent upon the application whether heat-set ropes (ease of handling, lower weight, lowest volume, highest tenacity) or non-heat-set ropes (longest fatigue lifetime, higher weight and volume) should be used.

Table 13.9 HMPE rope stiffness data as factors of break strength

Stiffness		Engineers' Design Guide (EDG, 1999)	Marlow brochure (Marlow, 2005)	OTC paper (Davies <i>et al.</i> , 2002)
Quasi-static	Post-installed	35 % BS	60 % BS	56 % BS
Dynamic	Intermediate	35–70 % BS	85 % BS	{ 59 % 0.54 % mean load (%)
	Storm	70 % BS	106 % BS	

13.5.4 Netting

Normally fishing nets are made by knotting braided or plied HMPE yarns to form net panels that are used to build, for example, a trawl net. Single knots in HMPE nets may lead to knot slippage owing to the slippery nature of the fibers so double knots can be used. Coating of twines is advised for a stable net construction. Lago® 45, a synthetic polymer-based anionic polyurethane marketed by I-coats NV, was especially developed for HMPE fibers in net applications.

Knot strength

In fishing gear, the wet knot strength is of more importance than the fiber tensile strength. Although HMPE fiber has a low relative knot strength, its absolute value is still a factor higher than other fiber wet knot strengths of braided twines used in fishing nets (Table 13.10).

Knot tensile fatigue failure is affected by fiber-to-fiber interaction with the twine, but the external damage from twine-to-twine abrasion at the neck portion of the knot is the major factor in knot fatigue failure. Knotted HMPE netting twines showed highest fatigue properties compared with regular polyethylene and polyamide, described by its low elongation (Wanchana *et al.*, 2002).

Heat-set nets

Heat-setting is common practice with HMPE nets for the same reasons as with ropes, but also to improve the knot strength by which the load is evenly shared between the filaments going into the knots. Heat setting of a coated net will also reduce knot slippage which stabilizes the mesh-size (Table 13.11).

Table 13.10 Estimated twine linear density and diameter for 2.5 kN knot strength of various materials

	Linear density (g/m)	Diameter (mm)
Polyethylene	23.8	6.9
Polyamide	18.2	5.2
Polyester	22.2	5.2
Dyneema® SK60	8.3	4.4
Dyneema® SK75	5.0	3.3

Table 13.11 Knot strength and knot slippage on 3 mm diameter Dyneema® SK75 braid of break strength 2.6 kN/(g/m)

Coating Heat-set	No No	No Yes	Lago 45 Yes	PUR Yes	
Knot strength	0.9	1.25	1.25	1.25	kN/(g/m)
Knot slippage	0.05	0.05	0.12	0.2	kN/(g/m)

Knotless nets

In knotless nets (Raschel and Ultra Cross techniques), the panels are produced directly from the fiber and twines without the intermediate step to produce separate panels which together are formed into a net. Raschel net meshes are knitted together instead of the traditional knotted process. An Ultra Cross net is a four-strand, braided continuous filament net used for heavy duty commercial fishing applications. Both these nets have a higher knot strength than conventional knotted HMPE nets.

13.5.5 Textile processing

HMPE fibers should be typically loaded linearly to obtain a high strength efficiency. Although knitted fabrics are not strength efficient, HMPE knitted fabrics are widely used in, for instance, cut protection gloves and Raschel-type nets. For protective clothing HMPE fibers are used in a wide variety of engineered yarns, spun yarns or a combination of both. Knitting of these yarns does not require any special equipment. The fiber is most suitable for spun yarn manufacturing, be it pure or blends with, for example, polyamide or polyester. It is also used extensively in engineered yarns, especially in combination with fiber glass and steel fiber (core spun yarns). These combinations achieve the highest levels of cut resistance while preserving comfort and sensitivity. HMPE fiber is suitable for use in coated gloves in combination with stretch yarns, like Lycra®, and is also knitted in combination with cotton to improve wearing comfort or to reach certain specifications economically.

HMPE fibers can be very well processed by means of weaving, e.g. for sailcloth. When weaving HMPE fibers, the main concern is to minimize the loss of tenacity and modulus. The aerial density and the construction of the fabric influence the performance of the final product. Owing to the low filament coherence, a shifting of filaments might occur during weaving, resulting in a loss of strength. Options to improve the bundle integrity include twisting the fibers before processing or applying an additional finish to the fiber. For ballistic appliances the weaving technique shows poorer properties because of the elongation within the construction elongation and the tendency of the fibers to shift aside upon bullet impact.

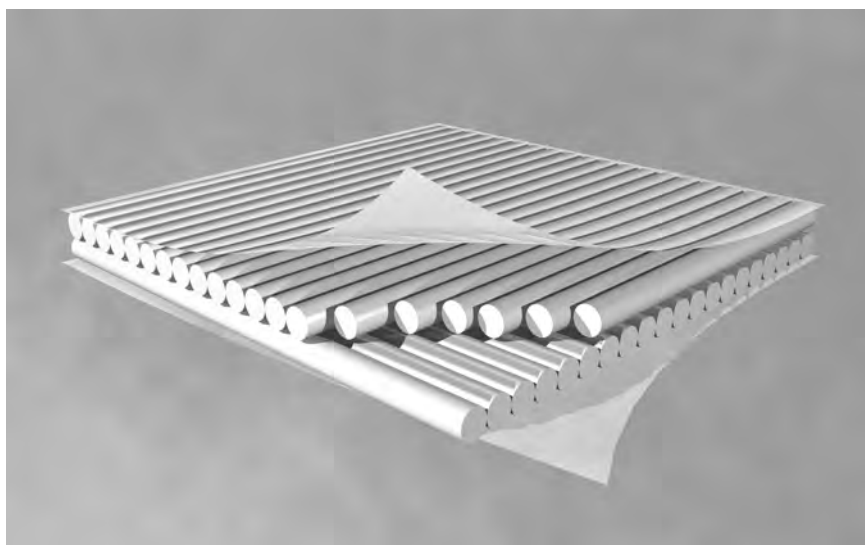
HMPE fiber is well suited for use in flexible composites or laminates. The most common use is in laminated sails using a scrim or an open fabric and polyester film. The fiber or the fabric can be corona or plasma treated to improve the adhesion of the matrix to the fiber. The matrix material is normally an epoxy or a polyester resin. The curing temperature should not exceed 120°C.

Laminate constructions made of a stack of alternating unidirectional layers (Fig. 13.23), in which HMPE fibers lie parallel to each other and are bonded by various thermoplastic matrices are used in ballistic protection (police vests, lightweight armor panels). This patented system is produced by licensed companies and gives a far better protection at the same weight than fabrics.

13.5.6 Additional processing steps

Owing to their chemical inertness and high crystallinity, dyeing high strength polyethylene fibers is extremely difficult although color can be added during the fiber spinning process. Particle size, shape, hardness and quantity might influence abrasion resistance negatively. Other methods, such as dyeing in subcritical carbon dioxide, showed a limited success because of the low color stability.

Another disadvantage of the excellent chemical stability, the absence of polar groups and the low surface energy of HMPE fibers is the low bond strength with a polymer matrix. Introduction of functional oxygen-containing



13.23 Dyneema® UD construction.

groups, i.e. hydroxyl, carbonyl and carboxyl, by oxidizing surface treatments can be effective in raising the bond strength up to a factor of three. This effect is low when compared with aramid, carbon or glass fiber composite systems, and is ascribed to the highly anisotropic character (poor shear strength) of HMPE filaments. The reduction in tensile strength by plasma treatment is generally less than 10% (Peijs *et al.*, 2000).

13.6 Applications

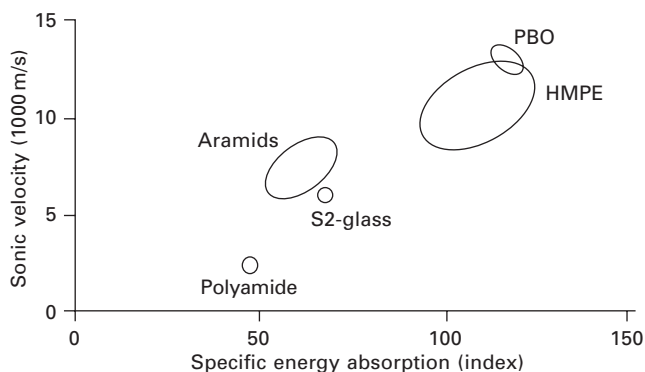
In the first decade of commercial production, HMPE fibers were mainly used for ballistic protection, marine ropes, nets and leisure products. The versatility of this fiber resulted in a further use in protective clothing, hoisting slings and recently in a number of aviation and medical applications.

13.6.1 Ballistic applications

Because of their high energy absorption at break, HMPE fibers are used in applications for civil, law enforcement and military personnel where low weight needs to be combined with high protection against mechanical threats. The mechanisms of energy absorption at ballistic speeds are important in ballistic protection. The primary factors that determine the weight needed to stop a projectile are the specific energy absorption, determined by the tenacity and elongation, and the sonic velocity of fibers, determined by the specific modulus, indicating the area of the fabric to be involved in stopping the projectile. HMPE fiber has a very high score in these two properties (Fig. 13.24) (Jacobs and van Dingenen, 2000).

Woven fabrics

Woven fabrics are traditionally used for ballistic protection in products as



13.24 Energy absorption and sonic velocity in ballistic fibers.

fragment-resistant vests, helmets, panels and spall liners for use in military and civilian vehicles. The fabric can be impregnated or laminated with various matrix systems. The application determines the fabric style, the number of layers and the type of matrix system.

Non-wovens

Needle-felt HMPE fiber non-woven material is designed primarily to protect against bullet fragments. It is mainly used in bomb blankets, bomb tents and bomb disposal suits but also in special designed vests for hunters.

Unidirectional sheets

Alternating unidirectional layered HMPE constructions (Fig. 13.23) stop bullets much more effectively than woven fabrics. In the unidirectional construction, a larger part of the sheet is involved in the absorption of energy. At ballistic impact of a fabric, the spread of energy in the fibers is hindered by reflections of the shock waves at the crossover points of the yarns.

HMPE fibers are used both for 'soft' and 'hard' ballistic protection. Soft ballistic protection is used in vests for the police and military, and protects against fragments and handgun ammunition. The unidirectional construction and the high modulus of the HMPE fiber results in less back face deformation by which the body trauma is reduced. In police vests the unidirectional form is used as such or in combinations with woven fabric from low titer HMPE or other fibers. The HMPE fiber unidirectional sheets have excellent chemical resistance and do not require treatment with water-repellent agents as other materials used in bullet-resistant vests. In addition to the ballistic protection, comfort is an important attribute. HMPE fibers result in the lightest, flexible and most comfortable vests in its class.

Helmets and lightweight panels are hard armor. The low-weight military helmets protect against fragments from bombs and grenades and handgun ammunition while offering maximum comfort. Using UD sheets, helmets can also provide protection against rifle threats. The armor panels can protect against highly penetrating military rifle ammunition and can be incorporated in vests, in civil cars and lightweight (military) vehicles. Inserts can be molded into complex shapes for accurate and secure fittings, easy to install and remove and are used mainly by police SWAT teams and military in combat. In military helicopters and civilian aircraft cockpit doors HMPE fiber panels are used to provide ballistic protection from small arms. In naval ships and patrol boats as main armor material because it is water resistant, lightweight and strong. The HMPE hard armor insert or vehicle panel can also be combined as a backing material with a steel or ceramic strike face to create superior protection.

13.6.2 Rope applications

An HMPE fiber is very suitable for products in a marine environment. The low weight and high strength make it possible to produce heavy duty ropes with very special characteristics. HMPE worked-in ropes float on water, are flexible, all contributing to an easy handling and have an elongation of less than 2.5% at break. This is close to steel wire and much less than polyester or nylon ropes. The fiber is strong and does not lose its tenacity in water, does not rot, has good UV resistance and is not affected by seawater. Abrasion resistance and fatigue are excellent to any standard, so it is not surprising that ropes, twines and nets were among the first products to be made of these fibers.

Towing arrays

In the seismic industry HMPE ropes are used in towing arrays because the high strength, low diameter ropes reduce the drag. The low elongation and the floating character of the ropes give a high degree of accuracy to the system. A high level of tension and bending fatigue resistance offers an extended service life.

Mooring and tugging ropes

The trend towards larger ships such as liquefied natural gas (LNG) carriers, oil tankers, bulk carriers and container carriers results in mooring ropes having a higher breaking load specified. The traditionally used steel wire mooring ropes become too heavy and difficult to handle, and conventional synthetic mooring ropes like polyamide and polyester are too bulky and too heavy. Also this increasing size of ships results in larger and more powerful tugboats. HMPE is recognized as the ideal fiber to meet this need for stronger, lightweight, safe to handle and durable mooring and tugging ropes.

Deep sea installation ropes

HMPE ropes contribute to the continuous quest to work in deeper waters. Capable of replacing steel wire size for size, a rope with Dyneema® fiber is only 15% of the weight and submerged in water it is weightless. The full capacity of the winch is available for lifting at every water depth. Especially designed ropes for bending applications are available to be used in heave compensation systems.

Mobile drilling unit (MODU) mooring ropes

DSM Dyneema has introduced a special fiber type for improved service life in applications that are subjected to long-term static loads. With extended creep life and excellent tension fatigue properties Dyneema® SK78 is the only HMPE fiber that has been type approved by Bureau Veritas and American Bureau of Shipping (ABS) to be used for MODU mooring systems. Compared with polyester mooring ropes, these HMPE ropes have a much smaller diameter that offers three times as much length on the installation winch. The low weight results in easy handling and reduced installation and hook-up time.

Hoisting slings

HMPE hoisting slings can be made from a rope, from narrow fabric or wound from yarns or twines. Advantages over steel wire are the light weight, resulting in an easy, fast and safe handling and the reduced risks of damaging the load or endangering the crew handling them. Compared with slings of other synthetic fibers, HMPE hoisting slings are smaller in size and lower in weight. Adding an HMPE cover to the sling provides good cut and abrasion resistance, giving protection in heavy duty lifting applications.

13.6.3 Net applications

Nets made from HMPE fibers are primarily used for commercial-scale fishing in both wild catch and aquaculture. In general, the low weight and high strength of HMPE nets and ropes result in easier handling, whereas the abrasion resistance and resistance to (sea) water enhances the lifetime compared to other materials. The abrasion resistance can even be further improved by applying proper coatings.

Wild catch

HMPE fiber is capable of replacing traditional polyamide fiber in netting twines with up to a factor 2 diameter reduction, resulting in a lower net weight and a reduced drag resistance. In the ropes, HMPE fibers are used in bridles, Gilson lines, rib lines and warp lines, where they reduce weight. This improves the efficiency of the fishing operation by means of increased towing speed, reduced fuel consumption or use of larger nets.

Aquaculture

The high demand for fish puts a lot of pressure on the aquaculture industry to increase the capacity. Compared with traditional polyamide, HMPE

containment nets are only up to a third of the weight and have smaller twine diameters which can reduce fouling on the nets. It results in an improved freshwater flow and a reduced drag from current and waves and by such improves the net stability and fish health. The high bite resistance of HMPE fiber reduces the number of fish escapes and net repairs. To keep predators, such as seals, sea lions and sharks away from the cages, additional nets are placed around a site. The special predator net constructions are based on HMPE combining high knot strength together with the high bite, cut and abrasion resistance.

Other net applications

Besides commercial scale fishing net applications, HMPE is also used in nets in aviation industry, offering more strength than traditional materials at much lower weight and water absorption resulting in fuel saving, or an increase in cargo per flight. Higher durability translates itself into lower repair costs and a reduced inventory. Amongst other net applications where HMPE has proven its advantages is a vehicle arresting system comprising of a spiked net made of Dyneema® fibers that becomes tangled in the front wheels while bringing a vehicle to halt. The high strength property of HMPE contributed to a lightweight, man-portable system (AmSafe, 2008).

13.6.4 Leisure applications

The primary reason for choosing HMPE in leisure applications is the low stretch of this fiber leading to optimal control.

Fishing lines

Very thin, ultra-strong braided HMPE angling lines were a major change in sport fishing after many years of polyamide monofilament. The line diameter is less than half that of other lines at equal strength, resulting in lower visibility, less resistance in guides of the rod and water and the ability to spool more on the reel. All are contributing to more accurate casts and greater distance. The low elongation ensures that the angler will 'feel the fish bite' and will have the ability to respond instantly. After being knotted (Table 13.12) the remaining strength of an HMPE angling line is double that of conventional lines.

Yachting ropes

Running rigging is an essential part for the overall performance of a yacht. It normally consists of a core–cover construction with a braided load-bearing

Table 13.12 Knot strength and loop strength of various fibers

	Knot strength		Loop strength	
	Absolute (N/tex)	Relative (%)	Absolute (N/tex)	Relative (%)
HMPE	1.1–1.7	35–55	1.3–2.0	40–65
Aramid	0.6–0.8	30–40	0.9–1.5	40–75
PET	0.4–0.5	50–60	0.6–0.7	70–75
PA-6	0.5–0.6	60–65	0.6–0.7	70–75
PP	0.4–0.5	60–70	0.6–0.7	85–95

core and a colored polyester cover. For racing yachts, strength is important to ensure that the ropes will not fail under extreme conditions. These boats are geared to the use of lightweight materials wherever possible. The stability of the yacht can be improved by maximizing strength and minimizing weight of halyards. Reducing weight in the mast causes a less violent impact with waves, resulting in lower loss of speed and less heel of the boat. This enables the use of a larger sail area giving more power and speed to the yacht. The low stretch of HMPE gives an accurate and stable positioning of sails by which the wind force is more efficiently converted into speed. The lines run smoothly through the blocks and sheaves while resisting kinking and hocking. Compared with steel wire halyards, those made of HMPE are softer on hands and gear. Owing to its reliability and durability, HMPE halyards are standard in long-distance sailing contests.

Sails

HMPE sails are mainly used for the main sail and foresails. An enhanced sailing performance, resulting from the strength-to-weight ratio and low stretch of HMPE fibers, is allowed by a lighter design without risks of loosing shape. An advantage of this is the greater speed and easier sail handling for sailors, particularly in racing. The high durability and good flex fatigue properties allows sails to be used over a longer period of time compared to conventional membrane sails with for example, carbon or aramid fibers. Unlike carbon fiber, HMPE is nearly transparent to onboard radar energy, making it the material of choice, for example, for single handed offshore races.

Kite lines

The low stretch of HMPE fiber in sport kite lines offers a quickly transfer of control inputs to the kite. The low friction allows the kite to remain controllable with several twists in the line.

Other leisure applications

The excellent impact resistance and vibration damping capability make it suitable for sporting goods such as archery bow strings and waterskis. It has also found its use to reinforce laminates in balloons.

13.6.5 Protective clothing

HMPE fibers offer a very high cut resistance compared with natural and synthetic fibers. Without using composite fibers, cut resistance up to European standard EN388 level 3 or level 4 can be provided. Woven fabrics and knitwear give a very good protection in, for example, cut-resistant gloves, fencing suits and chain-saw pants. The multifilament HMPE fibers are extremely soft and kind to the skin, while the flexibility and the smoothness offers comfort and dexterity.

The thermal conductivity and effusivity of HMPE fibers are very high compared with other traditional materials. It results in a quick dispersal of body heat to the outside of the fabric, which is experienced as cool and dry hands when wearing gloves all day. The actual hand temperature stays very close to normal body temperature, while gloves with other fabrics, such as cotton, leather or aramids, cause an increase of hand temperature of several degrees above body temperature.

Standard chemicals typically used in industrial laundering, such as detergents, ammonium/sodium hydroxides and hydrochloric acid, do not adversely affect the performance of HMPE fiber, which results in high durability in the wash-and-wear cycles of protective clothing.

Cut resistance

Most gloves are knitted using yarns formed from a combination of HMPE and other fibers either to improve the cut resistance (stainless steel and glass), or to improve the fit or add color (polyamide, polyester, elastane and cotton). Owing to the wide variety of engineered yarns and spun yarns, gloves can be designed for different protection level (up to the highest levels) while maintaining a high level of comfort. In cut resistance the best protection is achieved when HMPE fibers are combined with stainless steel or glass fibers. The high abrasion resistance of HMPE fiber contributes to the consistency of the cut protection over longer periods of use, compared to gloves of other materials.

HMPE knitted into gloves or woven into fabrics for apparel components such as sleeves and aprons for work wear are used in demanding manufacturing and industrial environments as automotive, glass, paper, household equipment, steel, construction and emergency services. Another application is protective sporting apparel such as fencing suits.

Puncture resistance

Puncture resistance depends on both the fiber properties and the resistance of the fabric construction against penetration between the yarns. A normal knitted HMPE fabric can easily stand the test for fencing suits against penetration by the blunted weapon, but an ice pick will easily penetrate such a fabric.

Other protective applications

The cut and puncture resistance property of HMPE also makes it suitable for use in woven fabric for air cargo container components resistant to tears, cuts, impact and chemicals. The strong but extremely soft and flexible parts made with HMPE fiber do not damage the aircraft.

13.6.6 Medical applications

UHMW-PE is one of the best-known biomaterials within the medical community and is currently being used in many orthopedic implants in hip, knee and shoulder surgery. The biocompatibility of the raw material, combined with its toughness and abrasion resistance, makes it one of the most frequently used materials for bearing surfaces in orthopedic implants.

The high strength of HMPE fiber, made from UHMW-PE, contributes to the trend of miniaturization of devices and use of arthroscopic and endoscopic techniques within the medical industry lead by the increased focus on reducing invasiveness for the patient and on reducing costs at the same time. Dyneema Purity®, an HMPE fiber type especially developed for medical applications, meets ISO standards for genotoxicity, cytotoxicity, sensitization, hemocompatibility and mutagenicity and its production is ISO 13485 certified. Compared with traditional polyester, an HMPE braid of similar strength will be almost twice as thin, and will promote better tissue formation in orthopedic suture applications. This faster healing supports quicker patient recovery, shorter hospitalization time, and can promote better outcomes, which benefit the comfort of the patient and lead to a lower total cost of care. The small filament diameter, chemical inertness and an extremely smooth surface of this HMPE type contribute to these results.

Sutures and other orthopedic applications

HMPE fiber provides a stronger, more pliable suture material for arthroscopic and open repairs of ligaments and tendons. It is generally used in fixation of soft tissues; in rotator cuff repair, the high strength sutures made with Dyneema Purity® are the gold standard. The smoothness of the fiber material improves the sliding of sutures through both tissue and anchors, and its

abrasion resistance offers higher resistance to fraying. Knot strength is important for these applications. A flat-braid suture structure improves the knot slippage and knot strength, while smaller knots have the potential to reduce patient's discomfort.

Cardiovascular applications

For devices in endovascular applications, having a lower profile enables catheter-based therapies, to better navigate tortuous anatomy and cross difficult lesions through a reduction in the French size of the catheter. By offering higher strength per volume compared to other medical grade high performance yarns, HMPE fiber could be ideally suitable for these applications.

13.6.7 Composite applications

In composite applications, the weight-saving HMPE fiber combines a very high energy absorption capability with a non-brittle failure behavior. It can be found in a large variety of composite applications despite its limitations regarding creep, low melting temperature, low adhesion, low compression strength, low shear and low transverse strength.

Examples (Peijs *et al.*, 2000) are speaker cones, because of the combination of low weight, high sound speed and sufficient internal damping; radomes for low speed aircraft and helicopters, because of its low dielectric constant, negligible absorption of radar energy, no water uptake, and high impact and penetration resistance; sonar domes, because of the high transmission of sound waves, low reflection and impact properties and its suitability in a marine environment; bobbins for superconducting magnet coils, because of the high strength, electrical insulation, low coefficient of friction, toughness at very low temperatures and the negative axial expansion coefficient and motor helmets, for its weight saving down to 40% of the original shell weight.

HMPE in combination with glass or carbon fibers are found in boat hulls, surfboards, snowboards and crash boxes for racing cars where the HMPE fiber contributes to the penetration resistance and damage tolerance and glass or carbon fiber to the structural performance (Peijs *et al.*, 2000). Even in combination with wood laminates for, for example, boat hulls HMPE fibers can strongly improve impact resistance.

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Tensile failure of polyacrylonitrile fibers

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Abstract: The chapter discusses methods of producing acrylonitrile polymer using different procedures for polymerization and extruding the acrylic fibers utilizing dry and wet spinning techniques. It also includes an in-depth discussion of the fine structure, the mechanical properties and the mechanisms accounting for the tensile and fatigue failures of the fibers. The unique tensile and many physical properties found result from the strong interactions present among the chains due to the presence of polar acrylonitrile groups. Unlike most natural and manufactured fibers, the acrylic fibers do not give evidence of a well-defined two-phase fine structure; however, they do clearly show the presence of fibrillar morphology with reasonably strong cohesion between the fibrils. Tensile rupture usually supports granular breaks but fatigue failure leads to shearing of the bundles of fibrils and their separating along the weakest planes, resulting in split fiber at the broken ends. Although, acrylic fiber production has seen a decline, owing to the increased awareness lately of the environmental concerns and the high cost of recovery of the solvents, the fiber continues to be the primary precursor for the development of high quality carbon fibers.

Key words: acrylonitrile polymer, acrylic fibers, tensile fracture, fatigue failure.

14.1 Introduction

Acrylic fibers are spun from polymers that are made from monomers containing a minimum of 85% by mass acrylonitrile in the chain [1]. Acrylonitrile and polyacrylonitrile were first synthesized in 1893–1894 by the French chemist Moreau, but the fibers based on polyacrylonitrile (PAN) were not produced until 1938 [2, 3]. This delay in the industrial exploitation of PAN polymers until shortly before World War II was due to the fact that the polymer could not be melted without degradation, and the solvents to allow solution processing were unknown [4, 5]. Early interest in the acrylonitrile polymers was based on their projected use in developing synthetic rubber. The acrylonitrile–butadiene rubber, and the polyblends of acrylonitrile–butadiene with acrylonitrile–styrene copolymers, were developed by the American Cyanamide and the United States Rubber companies, respectively. Once a number of suitable polar solvents, such as dimethylformamide, dimethylacetamide, aqueous sodium thiocyanate, aqueous zinc chloride, dimethyl sulfoxide, nitric acid,

and ethylene carbonate [4], capable of disrupting hydrogen bonds between hydrogen atoms and nitrile groups, and dipole bonds between pairs of nitrile groups had been discovered, which happened in the late 1930s and early 1940s, the commercial development of acrylic fibers began with rapid growth. DuPont introduced the first commercial acrylic fiber under the trade name of Orlon in 1944 [3]. The acrylic fiber industry experienced a spectacular growth in the 1950s with at least 18 additional companies, including Hoechst and Bayer in Germany, Courtaulds in England, Montefibre and Snia-Viscosa in Italy, and Rhone-Poulenc in France, manufacturing the fiber. Acrylic fibers possess a property that made it possible, in the late 1950s and early 1960s, for them to find immediate acceptance in the knitted sweater field, until then dominated by wool [6]. When the fibers are heated in the form of a tow, stretched and cooled under tension, and then immersed in hot water after spinning them into yarn using a woolen system, they develop bulk resembling woolen yarn.

A second category of acrylonitrile-based fibers are known as 'modacrylic fibers'. A modacrylic is defined as a material containing at least 35% but not over 85% by mass of acrylonitrile. The comonomers used are almost all based on halogenated ethylenically unsaturated molecules that impart excellent flame-retardant properties to the polymer. The most commonly used comonomers are vinylidene chloride, vinyl bromide, and vinyl chloride. The first two modacrylic fibers ever introduced in the United States were Dynel (by Union Carbide) in 1949 and Verel (by Tennessee Eastman) in 1956. The former was a copolymer of 60% vinyl chloride and 40% acrylonitrile, and the latter was said to be a 50–50 copolymer of vinylidene chloride and acrylonitrile with perhaps a third component graft-copolymerized onto the primary material to secure dyeability. SEF[®], and its version for wigs, Elura[®], were introduced by Monsanto Fibers in 1972. Some foreign manufacturers are involved in producing modacrylic fibers, but the only modacrylic fiber being produced in the United States currently is SEF[®] [6].

Modacrylic fibers, like acrylic, require stretching and heat stabilization after spinning in order to develop the necessary properties. Unlike acrylic, the modacrylic fibers, such as Vinyon, have not become successful as general-purpose fibers. They can be dyed satisfactorily, as needed for normal textile applications, but their non-flammability tends to place them for uses in products where that property is critical. Blended with other fibers, they are used in carpets; but their largest market is in deep pile products, such as 'fake furs', or in doll hair, where a fire hazard cannot be tolerated [6].

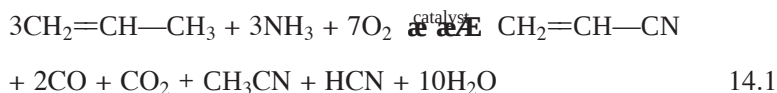
Because of the environmental concerns in the late 1980s and 1990s, however, the production of acrylic fibers greatly declined. By the year 1991 Monsanto and Cytec had remained as the only major US producers. Similar changes took place in the Western Europe and Japan, where growth slowed or

stopped. New production capacity in apparel markets continued to be added, but this happened largely in the developing countries [7]. The developed nations concentrated on restructuring their products mix, targeting new and non-traditional markets [3]. In view of the environmental concerns associated with manufacturing of fiber on one hand and the fiber's outstanding potential for use in range of products, including its efficient carbonization potential into high quality fibers, on the other hand, the scientists have sought over the years a method that could render the high acrylics melt-spinnable. Such a method will not only be economical and environmentally friendly but will also lead to engineering of fibers with a broader range of morphologies and properties. In 1997, British Petroleum patented a polymerization process in which the two components, usually used in developing spinnable acrylic copolymer, were redistributed to allow the resulting material to be melt processable [8–10]. Preliminary findings show that the polymer can be melt-spun into reasonably fine denier fibers with mechanical properties comparable to those found in the solution-spun material [10].

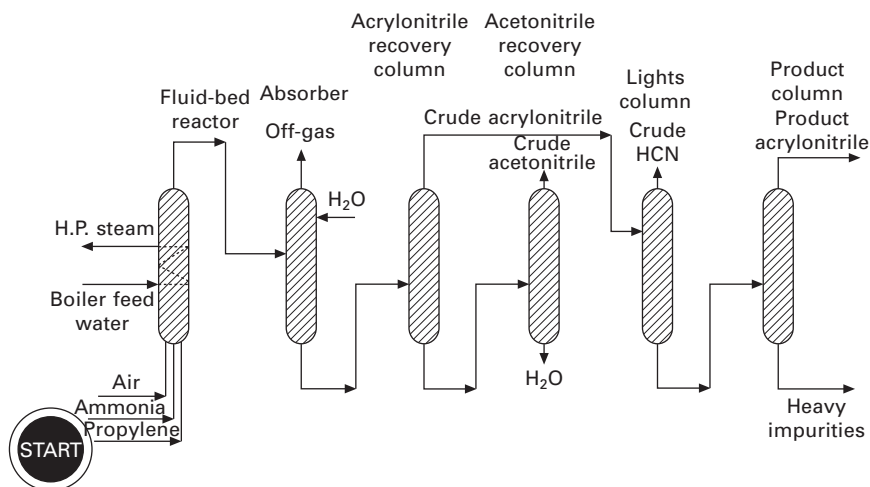
This chapter provides details relating to the manufacture of the acrylonitrile polymer, the extrusion of the polymer into fiber, and the structure, the morphology, and the physical and mechanical properties, including rupture, obtained in the resulting fiber. A section is also devoted to the carbonization behavior of the fiber.

14.2 Preparation of acrylonitrile

Acrylonitrile can be manufactured from propylene, acetylene, and ethylene; however, the currently used practice is to manufacture it from propylene using the Sohio process [11]. This is a heterogeneous vapor-phase catalytic process that uses selective oxidation of propylene and ammonia, commonly referred to as the propylene ammoxidation process:



The Sohio process (Fig. 14.1) uses a fluid-bed reactor in which propylene, ammonia, and air contact a solid catalyst at 400–510 °C and 50–200 kPa pressure. A useful by-product of the process is hydrogen cyanide, which is used in the manufacture of methyl methacrylate (one of the comonomers for the manufacture of acrylic fibers) and acetonitrile. Improvements in this popular process have been introduced as new and more efficient catalysts have been found. These catalysts are multicomponent mixed oxides, mostly based on bismuth–molybdenum oxide or antimony–iron oxide.



14.1 Process flow diagram of the commercial propylene ammoxidation process for acrylonitrile–Sohio process [12], reprinted by permission of John Wiley & Sons Inc.

14.3 Polymerization of acrylonitrile polymer

The commercial processes used to manufacture acrylic fibers are all based on free radical techniques. These are the solution polymerization and the aqueous dispersion or slurry polymerization. The polymers produced by these techniques are distinctly different. Another method available, i.e. the bulk polymerization process, is restricted by the autocatalytic nature of the process. The other method practiced is the emulsion polymerization, which is used primarily for forming modacrylic polymer where a high level of a water-insoluble monomer is used or where the monomer mixture used is relatively slow to react [4].

The typical commercial acrylic polymers for textile applications have number average molecular weights of 40 000–70 000 g/mol and weight average molecular weight of 90 000–170 000 g/mol with a polydispersity index of 1.5–3. High molecular weight polymers are used for high strength and modulus fibers for cement reinforcement and as carbon fiber precursors. The solubility and rheological properties of polymer are affected by the type and the concentration of comonomer, the molecular weight, and the type of solvent used.

Acrylic fibers have a slight tendency to yellow due to side chain reactions between adjacent cyano groups. The addition of fluorescent compounds, removal of as many impurities as possible, and the use of high monomer concentration, help to maintain required fiber whiteness. Fiber dyeability is critically dependent on the molecular weight distribution (sulfonate and

sulfate initiator fragments are at the polymer chain ends); particularly, it is very sensitive to the fraction of low molecular weight component. Because a balance between the molecular weight distribution required for good rheological properties and for good fiber dyeability cannot usually be achieved, it is the usual practice to incorporate one of the sulfonated monomers as a means of achieving the required fiber dyeability [3, 4].

14.3.1 Solution polymerization

This technique is widely used in commercial processes and offers cost advantages in as much as the polymer does not need to be isolated, washed, and dissolved. The process takes place in a homogeneous medium in which the polymer is formed in a suitable solvent for the polymer. The polar solvents such as dimethyl formamide (DMF), dimethylsulfoxide (DMSO), and aqueous sodium thiocyanate (45–55% solution), are commonly used.

Despite the advantage of ending up with a spinnable dope directly, after the monomers are removed, the process has some disadvantages:

- It is difficult to achieve high molecular weights because the chain transfer constant (C_s) is very high for DMF (e.g. $C_s = 2.8 \times 10^{-4}$ at 50 °C) and the termination of the chain growth occurs quite frequently.
- It is difficult to remove the unreacted non-volatile monomers, such as the ionic dye-site monomers and the low solubility monomers.
- The monomers such as vinyl acetate and vinyl chloride cannot easily be incorporated due to their slow reaction rates.

The kinetic of solution polymerization is straightforward with only a single phase reaction. A typical reaction scheme would be:

- (a) Radical formation (I = azo or peroxide initiator; $R^\bullet$ = free radical):



- (b) Chain initiation (AN = acrylonitrile; $P1^\bullet$ = chain with degree of AN polymerization, $DP = 1$):



- (c) Chain propagation ($P_n^\bullet$ = chain with $DP = n$; n includes 1):



- (d) Radical transfer to monomer, solvent, additives:



(e) Termination by radical recombination:



(f) Termination by radical disproportionation:



(g) Termination by metal ion (such as ferric):



The rate of polymerization, R_p , is:

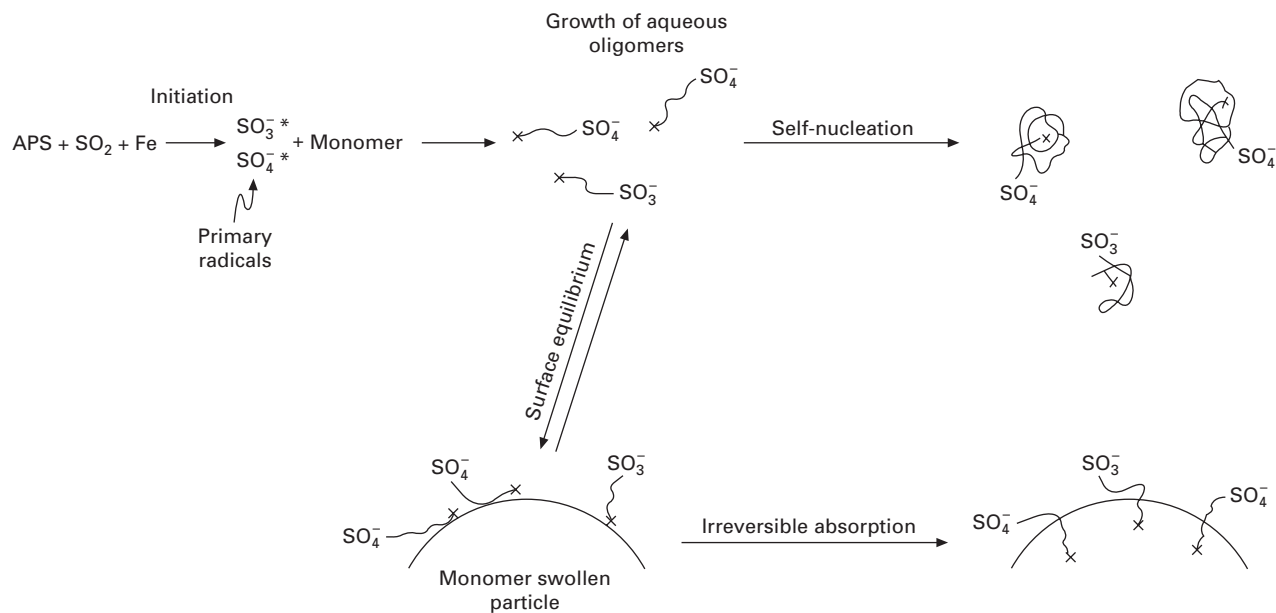
$$R_p = k_p[AN]^x \frac{f k_d [I]^{1/2}}{k_{ct}} \quad 14.8$$

where f is the initiator efficiency, k_d is the radical formation rate constant, and x and y are the exponential factors that characterize the rate dependence of the process on the monomer and initiator concentrations, respectively.

At monomer concentrations above 2–2.5 M, the reaction orders with respect to monomer and initiator have been found to be 1 and 0.5, respectively [13]. At higher monomer concentration, the monomer has the effect of adding a non-solvent to the reaction mixture and the reaction order with respect to the initiator and monomer can deviate from that expected. Vidotto *et al.* [13] found that the reaction became heterogeneous at monomer concentration above 4 M in DMF. Chain transfer is an important consideration in solution polymerization. Chain transfer to solvent may reduce the rate of polymerization as well as the molecular weight. Other chain transfer reactions may introduce dye sites, branching, chromophoric groups, and structural defects that reduce thermal stability. Between methyl acrylate and vinyl acetate as the polymer's most common comonomers, methyl acrylate is the least active in chain transfer. Vinyl acetate is also known to participate in the chain transfer-to-polymer reaction. This occurs primarily at high conversion rate, where the concentration of polymer is high and monomer is scarce [14].

14.3.2 Aqueous dispersion polymerization

In aqueous dispersion polymerization, up to three phases, important to the reaction, may be present: (1) a continuous aqueous phase, (2) a phase consisting of polymer particles swollen at the surface with non-water soluble monomer, and (3) a monomer droplet phase, i.e. the case in which the amount of monomer exceeds that which will dissolve in water or adsorb on polymer. In aqueous dispersion polymerization, the initiation and radical growth steps occur mainly in the aqueous phase. The aqueous phase polymer radicals may follow either of the two routes shown schematically in Fig. 14.2. Chain



14.2 Schematic depiction of particle nucleation and radical absorption in dispersion polymerization of acrylonitrile (APS = ammonium persulfate) [7], reprinted by permission of Marcel Dekker Inc.

growth, however, is limited in the aqueous phase, because the monomer concentration is normally very low and the polymer is insoluble in water. Nucleation occurs when aqueous chains aggregate or collapse after reaching a threshold molecular weight. If many polymer particles are present, as is the case in commercial continuous polymerization, the aqueous radicals are likely to be captured on the particle surface by a sorption mechanism. The particle surface is swollen with monomer. Therefore, the polymerization continues in the swollen layer and the sorption becomes irreversible as the chain ends grow into the particle.

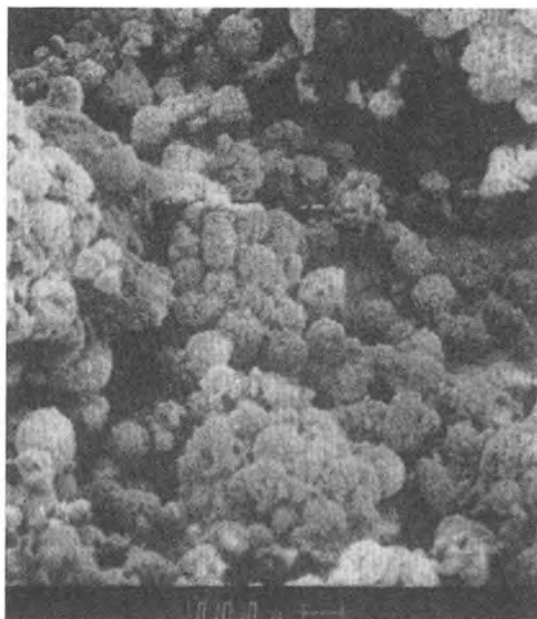
Lowering the water to the monomer ratio in the aqueous dispersion polymerization has the effect of producing denser, more spherical, particles because it favors polymer growth within particles instead of agglomeration (Fig. 14.3). Reactor agitation also has a great effect on the mean agglomerate particle size and the breadth of particle size distribution. Generally, medium-to-high shear mixing is required in aqueous dispersion polymerization of acrylic polymers as the viscosity of the slurry is moderately high (20–120 cP).

The use of an aqueous medium for the polymerization is the most widely used technique because water acts as a convenient heat transfer and cooling medium, and filtration or centrifugation easily recovers the polymers formed. The most commonly used type of reactor at present is the continuous stirred tank employing a steady state system, shown in Fig. 14.4. This system has replaced the semi-batch polymerization process due to the advantages it provides which are better control on molecular weight, on dye site levels, and on polymer compositions.

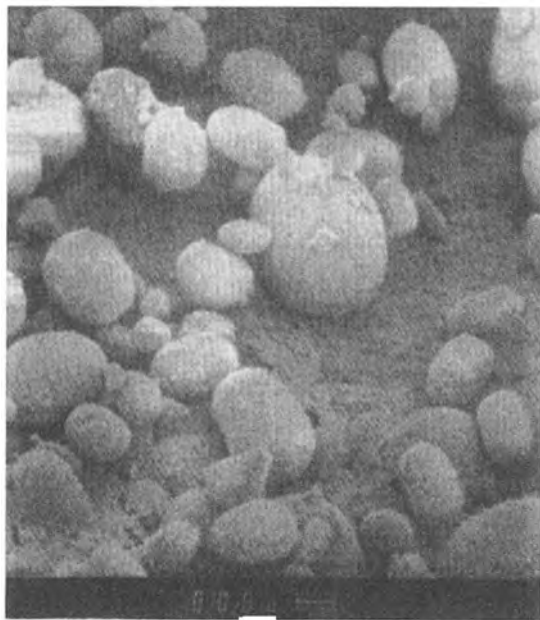
14.3.3 Emulsion polymerization

This technique involves stirring the monomers in water along with a suitable emulsifier and a radical initiator and is not widely used commercially for acrylic fiber polymer production. It has been shown that the emulsifier disperses a small portion of the monomer in aggregates of 50–100 molecules. These micelles have a diameter of about 5 nm. The majority of the monomer, however, stays suspended in droplet form with a diameter of 1000 nm. Radical formation occurs in the aqueous phase as described in Section 14.3.2. These radicals are rapidly absorbed into the monomer micelles. Polymerization proceeds rapidly, with the micelles converted into a polymer particle nucleus. The latter continues to grow in size, being assisted by the monomer diffused from the droplets. The size of the particles so produced is often less than 1 μm (Fig. 14.5), which is smaller than those formed from the bulk (20 μm) and aqueous dispersion polymerization methods (50 μm) [7].

The chain growth begins when the first radical enters the particle by absorption and ends when a second radical enters. Only half of the particles contain a growing radical, so this method allows high rates of polymerization and very high molecular weight polymers to be formed [4].

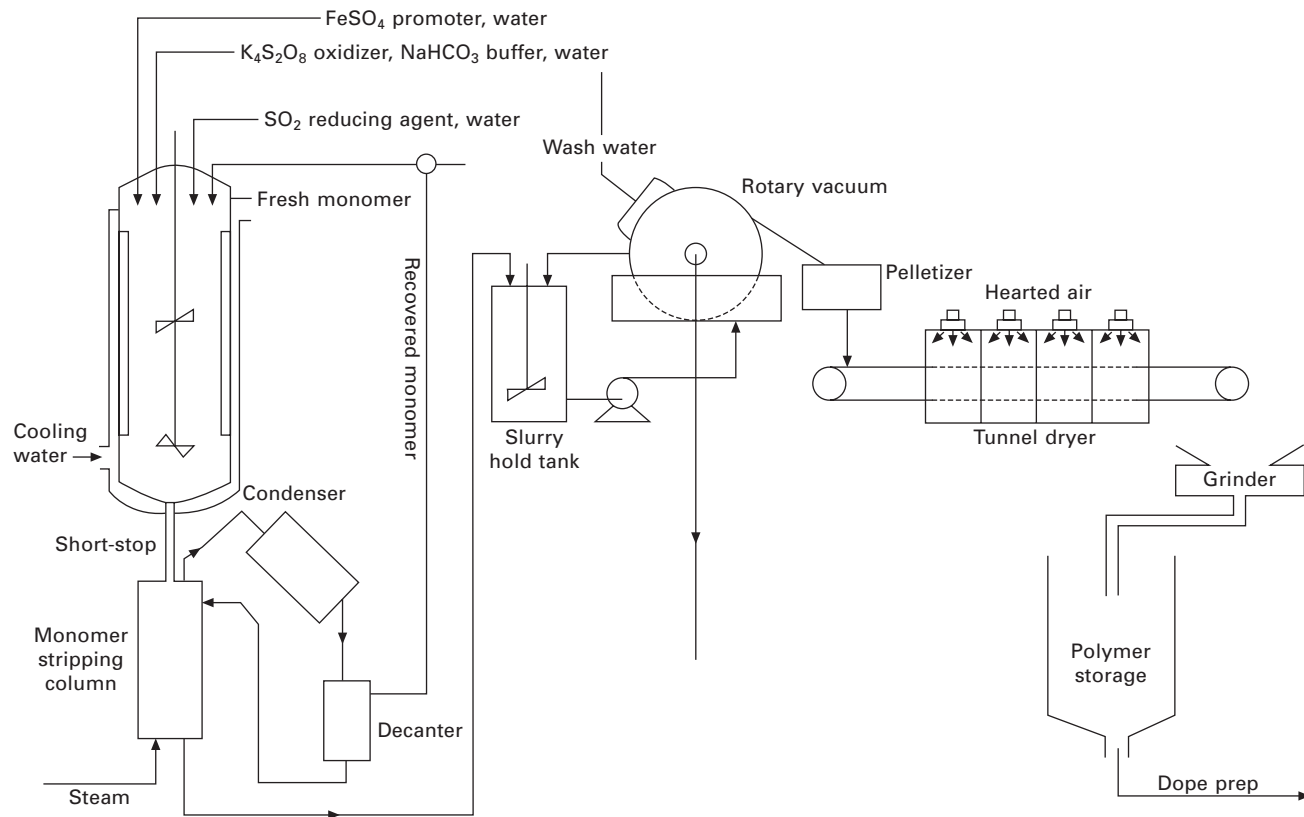


(a)

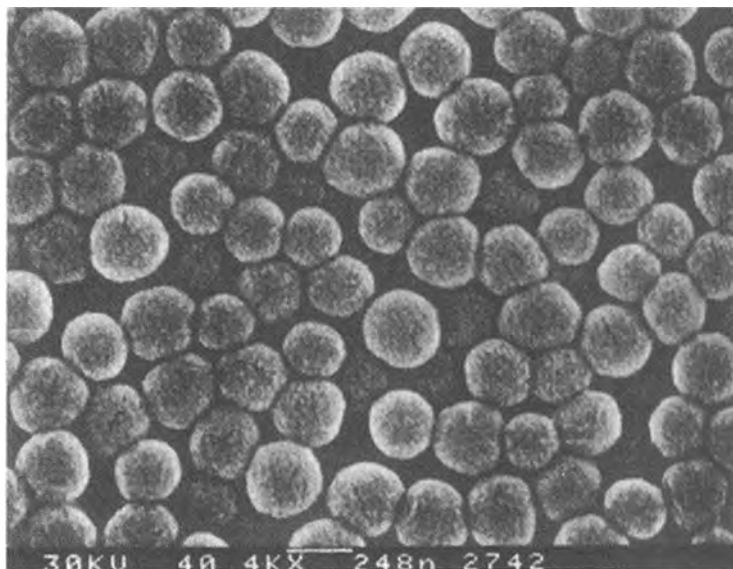


(b)

14.3 Scanning electron micrograph of acrylonitrile–vinylacetate polymer particle prepared by aqueous dispersion polymerization (a) at 3.5 water-to-monomer ratio and (b) at 2 water-to-monomer ratio [7], reprinted by permission of Marcel Dekker Inc.



14.4 An aqueous dispersion polymerization process used in the manufacture of acrylic and modacrylic fibers [12], reprinted by permission of John Wiley & Sons.

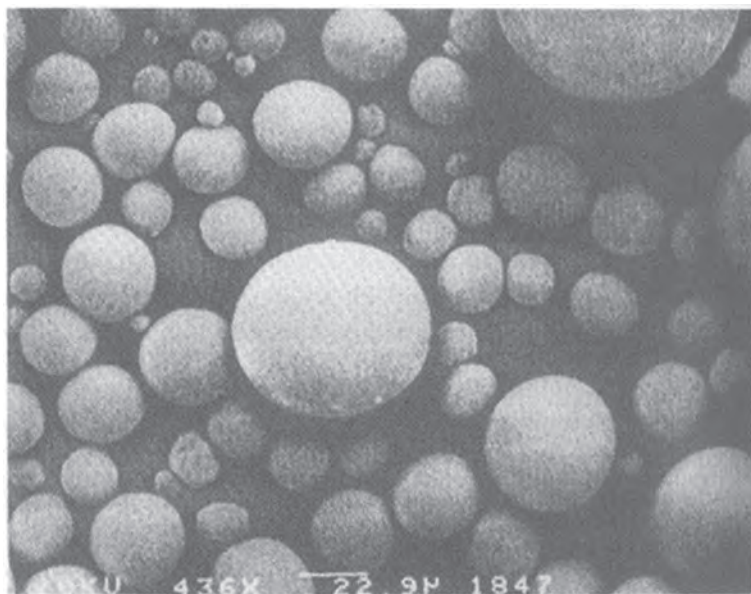


14.5 Scanning electron micrograph of acrylonitrile–vinylacetate polymer particle prepared by emulsion polymerization [7], reprinted by permission of Marcel Dekker Inc.

14.3.4 Bulk polymerization

The bulk polymerization of acrylonitrile is very complex and rarely used commercially because of the autocatalytic nature of the reaction and the very high viscosity obtained at relatively low conversion (40–50%). The rate of addition of free radical initiators with high decomposition rate constants controls the rate of polymerization. The polymer particles precipitate from the reaction medium due to insolubility of acrylic polymer (high polarity and pseudocrystalline structure) in its monomer. Figure 14.6 shows a much broader range of particle sizes obtained from the bulk than other polymerization processes, which is a result of the differences in the nucleation and agglomeration processes between the two polymerization techniques.

The polymerization is autocatalytic even under isothermal conditions. Three simultaneous propagation reactions (chain growth in the continuous monomer phase, chain growth of radicals that have precipitated from the solution onto the particle surface, and chain growth of radicals within the polymer particles) have been shown to account for the autoacceleration [15–17]. The polymerization of radicals within the core of the polymer particles is very slow owing to the limited diffusion of monomer from the particle surface to the poorly swollen core. Polymerization in the continuous



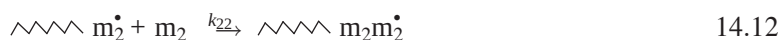
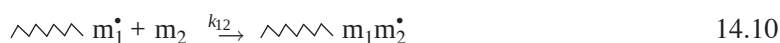
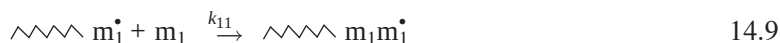
14.6 Scanning electron micrograph of acrylonitrile-vinylacetate polymer particle prepared by bulk polymerization [7], reprinted by permission of Marcel Dekker Inc.

monomer phase is also limited because the polymer precipitates at a very low degree of polymerization.

14.3.5 Copolymerization

Acrylic fiber producers need to be able to predict the overall polymer compositions and the sequencing of the various monomers used and the compositional heterogeneity (within a polymer chain and from chain to chain). So, one needs to know the reactivity of the various monomer pairs. Table 14.1 lists the reactivity ratios for the most commonly used combinations.

In the copolymerizations of monomers 1 and 2, four possible rate constants exist as follows:



A value of r_1 greater than 1 indicates a tendency for the monomer 1 to lead

Table 14.1 Reactivity ratios for acrylonitrile copolymerizations [18], reprinted by permission from Interscience

Monomer pair	$r_1 = k_{11}/k_{12}$	$r_2 = k_{22}/k_{21}$	Temperature (°C)
Vinyl acetate	4.05	0.06	60
Methyl acrylate	1.5	0.84	50
Vinyl chloride	3.6	0.05	50
Vinylidene chloride	0.91	0.37	60
Methyl methacrylate	0.15	1.2	60
Sodium styrene sulfonate	0.05	1.5	40
Acrylamide	0.87	1.35	30
Styrene	0.05	0.37	50

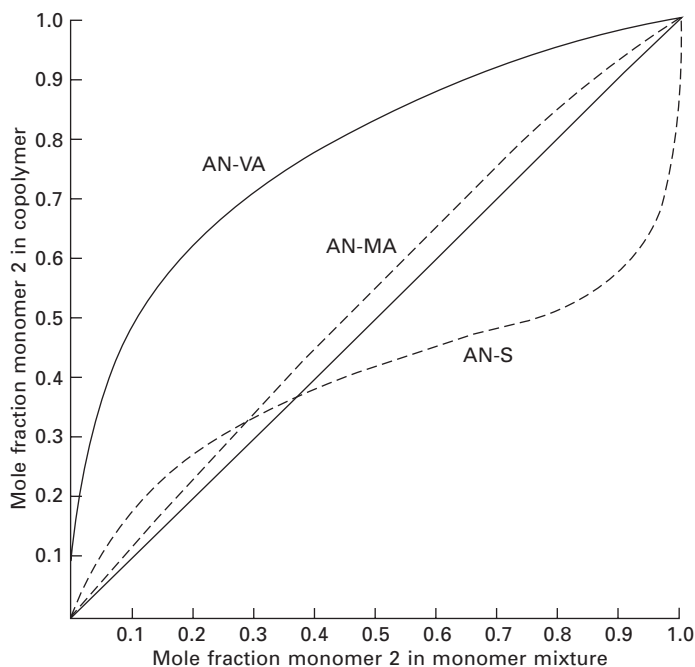
to blocks, whereas a value of r_1 less than 1 indicates a tendency for monomer 1 to alternate with monomer 2 along the chain. If r_1 and r_2 are both less than 1, then there is a tendency for the monomers to tend to be incorporated in an alternating sequence. Three typical copolymer compositions curves are given in Fig. 14.7.

14.4 Stereoregularity and chain conformation of polyacrylonitrile

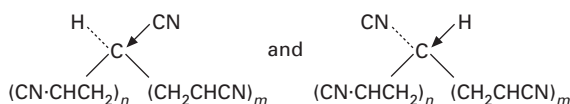
Acrylonitrile is an asymmetric monomer. Following polymerization, every tertiary C atom can be considered as a chiral center, as the adjacent chain fragments have different lengths. There are two possible configurations obtained when the positions of the hydrogen and nitrile groups are reversed (Fig. 14.8). These two types of configurations can be theoretically distributed in several ways along the chain, i.e. isotactic (three consecutive monomer units have the same configuration), syndiotactic (monomer groups have alternating configurations), and atactic (monomer units have completely randomly distributed configurations). The percentages of isotactic and syndiotactic structures are expected to be higher than the percentage of a purely random distribution.

The stereoregularity of a vinyl polymer influences its crystallinity. In contrast to some atactic polymers, such as polymethylmethacrylate and polystyrene, polyacrylonitrile is not truly amorphous and therefore possesses some crystallinity due to the presence of nitrile groups. Free radical polymerization generally produces polymers with little or no stereoregularity, which is confirmed for acrylic by nuclear magnetic resonance (NMR). Schaefer [19] showed concentrations of the hetero, syndio, and isotactic triads to be as 5:2:3, and, therefore, concluded that the stereoregularity was low.

The nitrile group in the polymer has very large dipole moment (3.9 D), compared with methyl group in polypropylene which has little or no dipole moment, however the two groups have similar volumes (27.2 cm³/mol for the nitrile and 32.3 cm³/mol for methyl). The glass transition temperatures



14.7 Three typical copolymer composition curves: acrylonitrile–vinyl acetate ($r_1/r_2 = 4.05/0.06$); acrylonitrile–methylacrylate (AN-MA, $r_1/r_2 = 1.5/0.84$); and acrylonitrile–styrene (AN-S, $r_1/r_2 = 0.05/0.37$) [3], reprinted by permission of Taylor and Francis Groups, CRC Press.

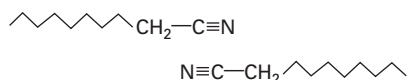


14.8 Configurations of acrylonitrile.

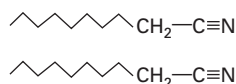
(T_g) of acrylic and polypropylene are 95 and -20°C , respectively [20]. The differences in T_g can be expected to be arising from the differences in the solubility parameters of polypropylene and polyacrylonitrile which are 16.6 and $31.5 (\text{J}/\text{cm}^3)^{0.5}$, respectively [21].

The dipole interactions between two nitrile groups can be either attractive or repulsive, depending on the spatial orientation of the nitriles (Fig. 14.9), while the magnitude of the interactions depends on the distances between the groups [22]. In a helical conformation, the chain potential energy will be lower and all of the nitrile groups will be pointing away from the axis of the helix.

Antiparallel orientation (maximum attraction) $E = -\mu^2/r^3$



Parallel orientation (maximum repulsion) $E = +\mu^2/r^3$



Parallel end-to-end orientation $E = -2\mu^2/r^3$



14.9 Types of dipolar interactions between nitrile groups: (E) dipolar interaction; (μ) dipole moment; and (r) vector dipoles [22].

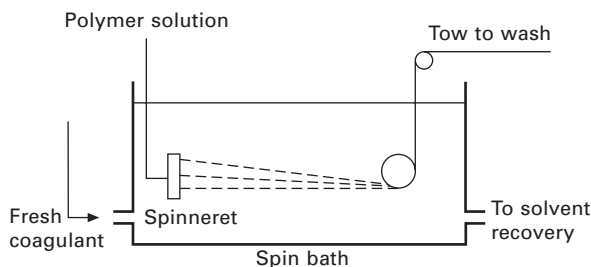
14.5 Acrylic fiber manufacturing

Commercial manufacturing of acrylic fiber includes both wet and dry spinnings. In the former, fiber is formed by a diffusion process in which solvent is exchanged for non-solvent. In the latter, fiber is formed by removal of the solvent by hot air. The major difference between the two is the absence of precipitation in the dry spinning. Some special fibers can be spun by melt spinning from plasticized melts. The decomposition of acrylic polymer before melting is used with advantage in converting the fiber into carbon fiber through slow decomposition at elevated temperatures.

We have mentioned in Section 14.3.1 that solution polymerization results in a polymer solution ready for fiber spinning, while the slurry polymerization technique requires the isolated polymer to be dissolved in an appropriate solvent. In order to form gel-free dopes, it is necessary that the polymer is dispersed in cold solvent (typically at 5°C) and then dissolved by the application of heat and shear. Owing to the difficulty involved in dissolving the polymer and the high pressure required on account of the high viscosity to pump the dope through the spinnerets, the concentration and fiber extrusion rates used are necessarily low. The polymer dope should be filtered and de-aerated in order to remove impurities and air bubbles before fiber spinning. Additives such as TiO_2 as delustrant and carbon black as pigment are introduced at an appropriate point during the process.

14.5.1 Wet spinning

In the wet spinning process, shown in Fig. 14.10, polymer comes out of the solution into the bath and forms a gel-state solid, or coagulates, after exchange takes place between the polymer solvent and the non-solvent.



14.10 The schematic of an acrylic fiber wet-spinning bath [7].

Two conceptually distinct phase transitions are thought to occur during coagulation: gelation and phase separation (precipitation). If coagulation happens without gelation, then the strength of filament is low owing to the lack of interconnectivity between chains. Polymer microcrystallites form during gelation that serves as physical crosslinks between chains. When the gel undergoes phase separation and the solid filament is formed, the crosslinks provide the internal cohesion needed for the drawing step. In the gel state, the hydrogen bonds and the dipole bonds present between the polymer and the solvent make the structure highly elastic [23].

The spinnerets are usually made of precious metal alloys, with the hole diameters ranging from 0.05 to 0.38 mm and hole numbers varying from few thousand up to 360 000. The ratio of hole diameter/hole length (aspect ratio) is critical in fiber formation as it governs the quality of spinning and the resulting tensile properties.

The material emerging from the coagulation bath is a highly swollen gel, containing both solvent and non-solvent. The fibers are slightly stretched (jet stretch = 1.5–2) by the first godet (driven roller) running at a higher velocity than the velocity of polymer extrudate through the spinneret. Then the fibers are washed to remove the remaining solvent, stretched in hot water or steam to develop the tensile properties, dried to remove the water, and finally crimped. The sequence of the steps varies among different companies. A spin finish that modifies properties, including friction and conductivity, is also given to the crimped fibers at some point during the process.

The relative rates of diffusion of solvent and non-solvent in the coagulation bath control the fiber structure. The independent variables for wet spinning are the rate of extrusion, the concentration, and the temperature. It has been shown that by increasing the concentration of the polymer solution, the diffusion of solvent and the non-solvent through the boundary layer is slowed down, and the relative rate of the diffusion of the solvent out to that of the non-solvent in is increased. As expected, as the temperature of the polymer dope and coagulant is decreased, the diffusion rates of solvent and non-solvent also decrease; these cause a denser and finer structure to form. However, the rate at which solvent diffuses out changes more than the rate

at which non-solvent diffuses in [7]. The other factor is the rate at which the fresh non-solvent is introduced to the coagulation bath. Many researchers have derived mathematical models for the diffusion process in wet spinning [24, 25]. Table 14.2 summarizes the effects of coagulation variables on structure and physical properties of the acrylic fibers [26].

Two important features of the morphology of the fibers are the shape of cross-section and the presence of macrovoids. If there is less volume of non-solvent diffusing in than solvent diffusing out, the shape will become non-circular and tend towards a kidney-bean shape as noted at lower temperatures in Fig. 14.11. The cross-section of dry spun fibers is dog-bone in shape and it has a lower bending stiffness than that of the round or kidney-bean shaped fiber. The rupture of skin, followed by penetration of the non-solvent into the interior, is responsible for developing macrovoids, which act as internal flaws and adversely affect the lateral strength of fibers [3]. In wet spinning of polyacrylonitrile with DMSO/H₂O coagulant, Chen *et al.* [28] also found that the nascent fibers became denser, with fewer inner defects, as coagulation time increased, but transverse stripes, fish tail, and inner microvoids continued to be present as some of the defects in the fiber.

A variation of wet spinning that has been developed by some companies is dry-jet wet spinning. The fiber is extruded into air and then enters the

Table 14.2 Summary of responses to coagulation variables [26], reprinted by permission from SAGE

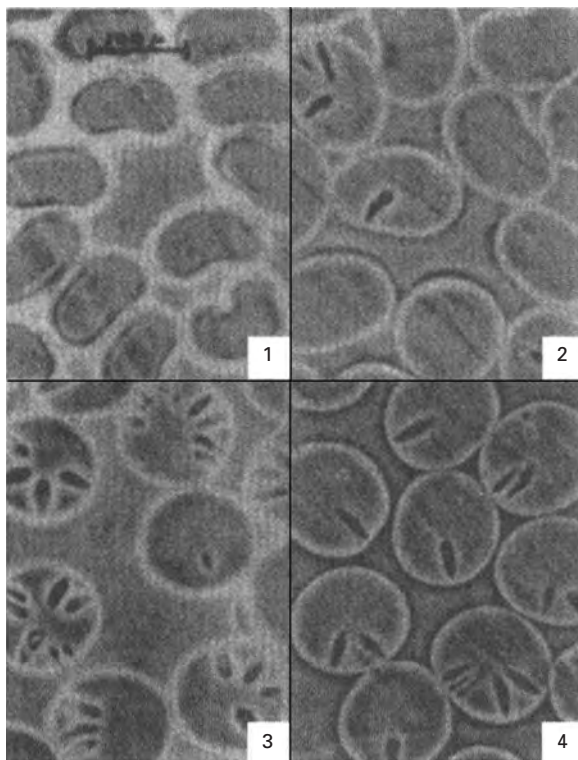
(a) Protofiber structure parameters

Variable	Protofiber density	Protofiber surface area	Cross-sectional shape	Homogeneity
Dope solids	(+)	0	0	++
DMAC	(+)	(+)	0	+
concentration of spin bath				
Spin bath temperature	--	--	-	-
Jet stretch	0	(-)	0	-

(b) Finished fiber properties

Variable	Tenacity	Elongation	Initial modulus	Abrasion resistance
Dope solids	+	0	0	+
DMAC	0	0	0	-
concentration of spin bath				
Spin bath temperature	-	+	-	-

(+) slight positive response; + strong positive response; ++ very strong positive response; 0 no effect; (-) slight negative response; - strong negative response; -- very strong negative response.



14.11 Cross-sections of acrylic fibers taken under a light microscope in the uncollapsed and unoriented state. Coagulation bath temperature: (1) 10 °C, (2) 40 °C, (3) 55 °C, (4) 70 °C [27], reprinted by permission from SAGE.

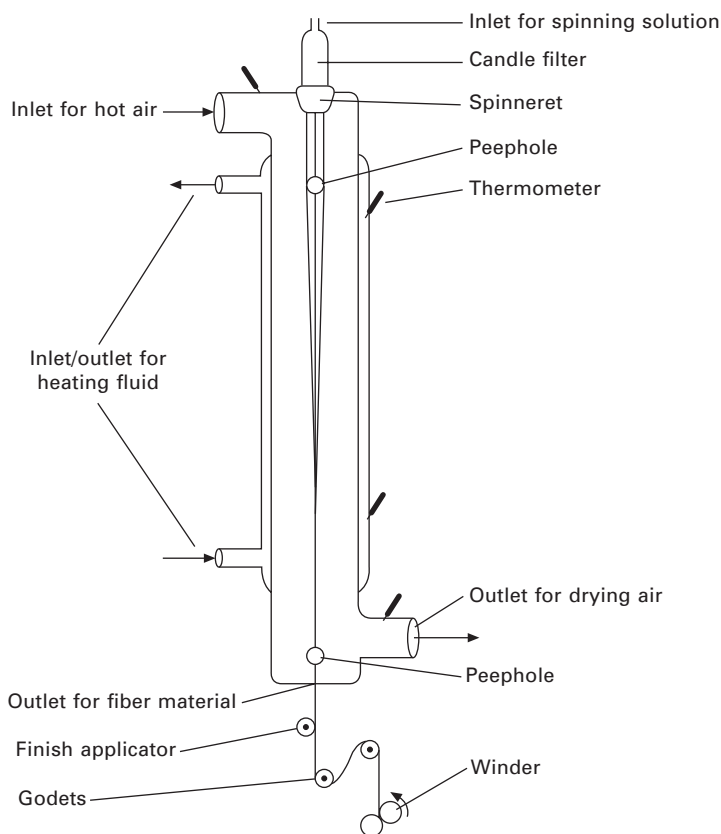
normal solvent/non-solvent coagulation bath, which has significant effects on diffusion rate of solvent and non-solvent, and consequently on fiber surface morphology, internal structure, and physical properties. Bajaj and coworkers [29] have studied structure development during dry-jet wet spinning in three copolymers, poly(acrylonitrile/methyl acrylate), poly(acrylonitrile/methacrylic acid), and poly(acrylonitrile/itaconic acid). The study shows that with the dry-jet wet technique, higher polymer concentration, higher spinning speed, and smaller jets can be used but it is necessary that the spaces between the holes are larger.

14.5.2 Dry spinning

Dry spinning of acrylic fibers was the first technology developed and used commercially by DuPont and by Bayer. Dimethyl formamide and dimethyl acetamide have been used effectively as the solvents for the dry spinning

process. Figure 14.12 shows a typical design for the dry spinning process.

The spinning dope is carried forward towards the spinning tube, it goes through a number of filtration steps and is heated to 90 to 130–140 °C. The spinneret used in dry spinning is made from stainless steel and contains up to 2800 holes with the diameter lying in the 0.1–0.3 mm range. The preferred hot gas to dry the extrudate is air mixed with nitrogen, the latter for reducing the fiber's tendency to yellow as well as to increase the explosion threshold. The resulting fibers are taken up by a godet and given a finish prior to their collection in spin cans, if tow, or winding up at high speed, if filament yarn. The second step in the case of tow is drawing in hot water bath at 98 °C. Draw ratios used range from 2 to 10 $\times$. After washing, the drawn fibers are dried at 120–170 °C, which can affect shrinkage, dyeability, and crimping potential of fibers. The final stage in staple fiber production is fiber crimping and cutting [4].

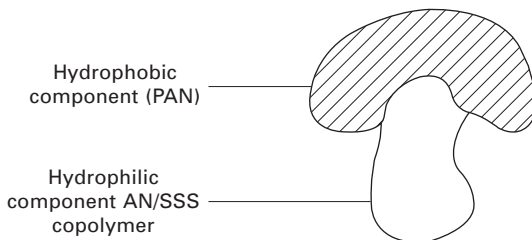


14.12 Spinning tube for dry spinning process [7].

When acrylic fibers, normally in the form of a heavy tow, are hot-stretched (e.g. by being drawn over a hot plate and then cooled under tension), they are converted to a labile state. Upon immersion in hot water, such fibers contract considerably, but not to their prior unstretched length. In practice, this characteristic is used to produce a bulky yarn resembling the woolen yarns long accepted for use in sweaters. The process is described briefly below [6].

Using 'stretch-break' process, the stretched labile fibers are further cold-stretched to the breaking point so that the fibers break at different points, leading to a distribution of lengths, similar to the lengths found in wool. These are crimped by a crimping process and then mixed with thermally stable stretched and relaxed acrylic fibers. The blend is converted to a spun yarn by the long staple process, and knitted into sweaters and other woolen type products. When such garments are dyed in hot water, the labile fibers in the blend contract lengthwise, carrying the stable ones by friction. Because the latter do not change their overall lengths, the yarn as a whole decreases in length and becomes more voluminous or 'hi-bulk' structure [6]. The other method for making enhanced bulk yarns is the use of side-by-side bicomponent acrylic fibers containing two polymers with different shrinkage potentials. In addition to using a bilateral symmetrical structure for producing high bulk yarns, another ingenious arrangement of pre-dividers of the two streams is used to produce from the full complement of holes in the spinneret the fibers wherein the amount and the position of each of the two components are randomly distributed in the cross-sections (Courtelles Lc). It follows, thus, that curls of uniform or random geometries can be produced to meet the required bulk characteristics [4,6].

The Orlon 21 bicomponent fibers produced by DuPont have water reversible crimp. The two polymers in Orlon 21 had a large difference in hydrophilicities. The acrylonitrile was hydrophobic while the acrylonitrile/sodium styrene sulfonate was relatively hydrophilic. The fiber ended up having a mushroom-type shape (Fig. 14.13) due to the different responses the two polymers had to the evaporation of the solvent [4].

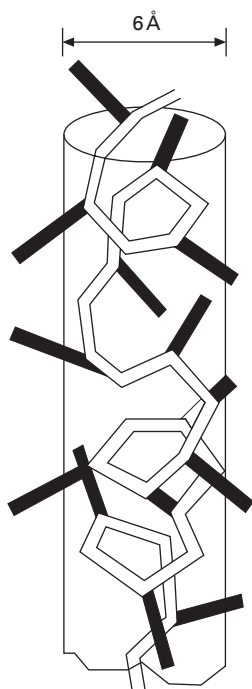


14.13 Cross-section of Orlon 21 fiber, reprinted by permission of Marcel Dekker Inc. [7].

14.6 Structure of acrylic fibers

One of the dominant features of an individual polyacrylonitrile chain is the presence of highly polar nitrile groups, attached to alternate C atoms, thus allowing the chain to be able to interact fairly strongly. Interaction between adjacent nitrile groups on the same chain, however, causes some repulsion to occur. This is due to the fact that the nitrile groups cannot adopt an antiparallel arrangement because the bond angles do not allow this. This tends to twist the chain into an irregular helical form. The X-ray diffraction patterns of acrylic fibers show only the presence of equatorial reflections. The equatorial reflections could be indexed; these support a two-dimensional hexagonal lattice. This is best imagined as a twisted chain backbone fitting within a cylinder, approximately 6 Å in diameter, with the nitrile groups pointing out from the chain at various angles. This structure is supposed to be partly responsible for the lack of a clear melting point in polyacrylonitrile. Figure 14.14 shows a simple model of the structure that has been proposed by Henrici-Olive and Olive [22].

Colvin and Storr [30] reported finding three-dimensional crystals in very highly oriented polyacrylonitrile fibers (drawn 10%) spun from an aqueous

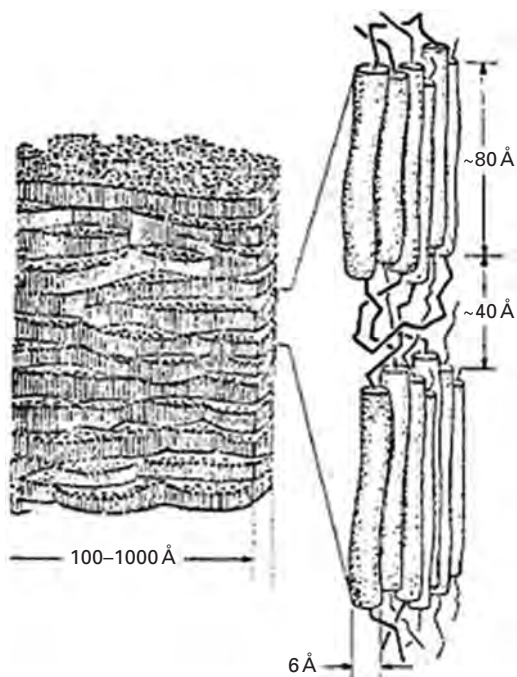


14.14 Model of helical conformation of polyacrylonitrile chain [22], reprinted by permission of Springer.

solution of sodium thiocyanate. The equatorial reflections could be indexed to support an orthorhombic unit cell ($a = 21.48 \pm 0.02 \text{ \AA}$, $b = 11.55 \pm 0.03 \text{ \AA}$, and $c = 7.096 \pm 0.03 \text{ \AA}$) for the material.

The debate relating to the presence of two-phase morphology in acrylic copolymers is still continuing and is not resolved. Bohn *et al.* [31] suggested that the structure is laterally bonded crystalline throughout the fiber (single phase with defects) with little evidence for the presence of a clear amorphous phase, a result concluded from the absence of halo scattering in the fiber X-ray diffraction patterns. The authors [31] compared the polymer volumetric expansion coefficient with temperature with the temperature dependence of the $5.2 \text{ \AA}$ Bragg spacing and observed an increase in both of these at 85°C . This result contradicts the classical two-phase model as the glass transition of the amorphous phase should have little effect on the chain packing within the crystalline phase. These observations are taken in support of a hybrid single-phase morphology that has both crystalline and amorphous polymer properties. Lindenmeyer and Hoseman [32] applied the theory of paracrystallinity to the acrylic fiber and concluded that the diffused scattering noted could arise as a result of the structure having different conformations distributed along the chain. Liu and Ruland [33] analyzed two-dimensional X-ray diffraction patterns of acrylic fibers and concluded that the predominant chain configuration was the planar zigzag. Numerous researchers have attempted to determine a degree of crystallinity for acrylic fibers from X-ray diffraction patterns, despite the fact that the structure strongly supported a single-phase model [34–37]. Warner *et al.* [38] proposed a two-phase model for fibers, as shown in Fig. 14.15. In this model, fiber is composed of fibrillar subunits that contained distinct regions of amorphous and partially ordered phases. The small angle X-ray diffraction of the fibers indicated that the oriented rows of lamellae at an angle to the fiber axis could be formed [39]. The addition of comonomer could be considered to reduce the crystallinity and crystalline perfection [40–43]. The difference in order between the two phases in acrylic fibers is much less than normally found in conventional melt-spun fibers. The maximum theoretical modulus of an atactic acrylic has been calculated to be about 55 GPa [3]. Sawai and coworkers [44] reported tensile strength of 1.8 GPa and modulus of 35 GPa in drawn ultra-high molecular weight polyacrylonitrile (UHMW-PAN) fibers ($M_v = 2.3 \times 10^6 \text{ g/mol}$). In the work reported, the UHMW-PAN fibers spun from a dilute solution (1 wt%) into methanol coagulation bath at different temperatures were uniaxially drawn by a two stage drawing procedure to total draw ratio of ~ 80 . The high tensile properties of drawn fibers were ascribed to the conformational change of crystalline chains from the 3/1 helix to planar-zigzag.

Kulshreshtha *et al.* [45] studied the effect of the fraction of comonomer (methyl acrylate) and annealing on morphology of acrylic fibers. Introduction of a small amount of methyl acrylate resulted in a reduction of crystallinity.



14.15 Schematic diagram of molecular structure of highly oriented acrylic fiber [38], reprinted by permission of Springer.

An increase in the amount of comonomer caused a shift in the exothermic peak toward higher temperature. Annealing of acrylic copolymers caused the onset of an intramolecular cyclization, as well as an increase in the segmental mobility; both leading to an increase in crystallinity and crystallite size. Therefore, the presence of methyl acrylate in copolymer led to a decrease in the efficiency of carbon fiber production due to low yield of cyclization, and also a decrease in crystallinity and in crystal size gave a decrease in tensile strength and initial modulus in carbon fiber [46–50].

14.7 Physical properties of acrylic fibers

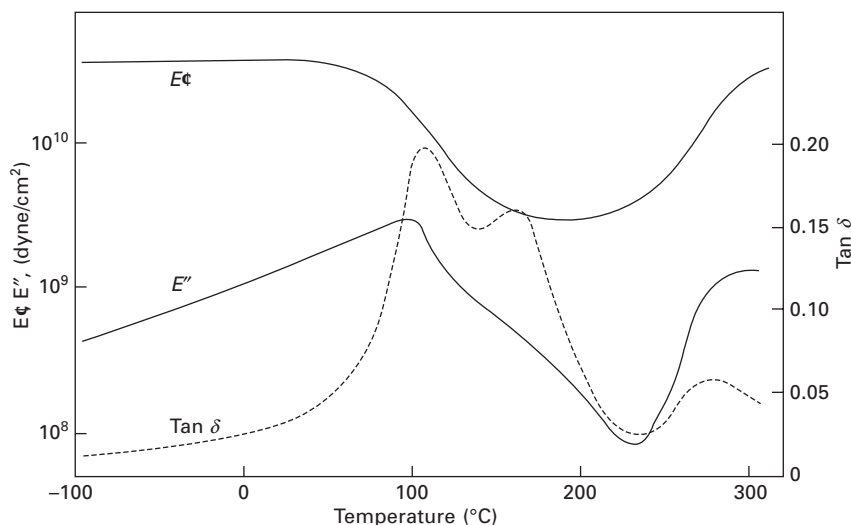
Acrylic and modacrylic fibers are sold predominantly as tow and staple products with only a small quantity of continuous filament sold as special product. Fiber linear densities between 0.84 and 17 dtex are produced, with the most common values being 1.7 for staple and 3.3–5 for tow to top conversion. Typical values of some of the physical properties of acrylic and modacrylic fibers are given in Table 14.3. The tensile strengths are considerably lower than those found in the polyester and polyamide fibers, but similar to that of cotton and higher than that of wool. The physical

Table 14.3 The physical properties of acrylic and modacrylic fibers [4], reprinted by permission of Woodhead Publishing limited

Property	Acrylic	Modacrylic
Specific gravity	1.14–1.19	1.28–1.37
Tenacity (N/tex)		
Dry	0.09–0.33	0.13–0.25
Wet	0.14–0.24	0.11–0.23
Loop/knot tenacity	0.09–0.3	0.11–0.19
Breaking elongation (%)		
Dry	25–45	25–45
Wet	29–61	
Initial modulus (N/tex)		
Dry	3.5–4.9	2.6–3.5
Wet	3.1–4.9	
Elastic recovery (%)		
2%	99	95–100
10%		70–95
20%		
Electric resistance	High	High
Static build-up	Moderate	Moderate
Flammability	Moderate	Low
Limiting oxygen index	0.18	0.27
Char/melt	Melts	Melts
Resistance to sunlight	Excellent	Excellent
Resistance to chemical attack	Excellent	Excellent
Abrasion resistance	Moderate	Moderate
Index of birefringence	0.1	
Moisture regain (%)	1.5–2.5	1.5–3.5

characteristics that distinguish acrylic fibers from other common textile fibers are the results of the fiber's dipolar interactions between nitrile groups. These are: high electrical resistance, moderate flammability, and excellent resistance to sunlight, chemical, and microbiological attacks. Because of the polarity, the fibers have a reasonable value of moisture regain which is 2–3%. The presence of water gives the fiber a relatively low value of T_g , which is about 70°C [3, 4].

The dynamic-mechanical properties of acrylic fibers have been studied by a number of researchers [51–54]. Figure 14.16 shows the dynamic-mechanical performance of acrylic fiber obtained by Minami [52]. The real modulus is approximately 4×10^9 MPa at room temperature. The modulus begins to decrease near 75°C and drops to 2×10^8 MPa. The $\tan \delta$ showed two distinct transitions, one at near 110°C and the other at 160°C. Some researchers have considered these two peaks as giving an evidence of two glass transitions [51, 54–56], arising from the structure having two amorphous phases with different levels of intermolecular bonding. Padhye and Karandikar [54] reported that the aromatic solvents (phenol, aniline, and resorcinol) caused the lower transition temperature (β 110°C) to disappear



14.16 The dynamic mechanical properties of undrawn polyacrylonitrile fiber at 110 Hz [52], reprinted with permission of Wiley Interscience.

and the higher transition temperature (α 160°C) to decrease, whereas non-aromatic solvents (methanol, amyl amine, dimethyl amine, ethylene glycol, and acetonitrile) caused the lower temperature transition to shift to lower value and the higher temperature transition to move to even higher values. Minami [52] associated the β value to an unspecified motion within the laterally bonded crystalline phase and α to the Brownian motion in the amorphous phase. They observed that the magnitude of α decreased upon stretching and increased upon relaxation, but there was little change in the value of β during these procedures.

Sawai *et al.* [57] studied the dynamic mechanical properties of isotactic polyacrylonitriles drawn to different ratios. They observed four kinds of relaxations: α and α_c relaxations at $\sim 150^\circ\text{C}$ (in amorphous phase), β_c relaxation at $\sim 100^\circ\text{C}$ (in paracrystalline phase), and γ relaxation at $\sim 25^\circ\text{C}$. The magnitude of the loss modulus (E'') and $\tan \delta$ peaks were sensitive to the isotacticity, the draw ratio, and the thermal history of the samples. They reported that based on wide angle X-ray diffraction, β_c and γ relaxations could be predominantly ascribed to the segmental motions of the helical and the planar zigzag sequences, in paracrystalline phase, respectively. They noted that there was a sharp $\tan \delta$ peak, around 150°C (α_c relaxation), in the ultradrawn atactic-PAN fiber (DR = 60) that was associated with a sudden decrease in the storage modulus (E') and in the differential scanning calorimetry (DSC) endothermic peak. Based on the results, they concluded

that the molecular motions in both the amorphous regions (α relaxation) and the paracrystalline regions (α_c relaxation) contributed to the relaxation at around 150°C.

14.8 Carbon fiber precursor

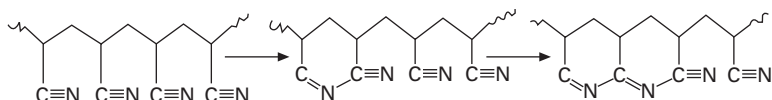
The acrylic fibers are the major fiber types used as precursors for carbon fiber production. The key factor in producing good carbon fibers from acrylic is the production of oxidized ladder type polymer parallel to the fiber axis by the cyclization of the pendant nitrile groups and the incorporation of oxygen. The stabilization process is a highly exothermic reaction that begins at ~ 200 – 230°C and peaks at 300 – 320°C . The stabilization is achieved by allowing the fiber to form a ladder-type polymer in the early stages of the carbonization process. In PAN, the ladder polymer is formed by the neighboring nitrile groups associating with each other, initiated by a free radical or ionic mechanism as shown in Fig. 14.17 [4].

The carbonization process involved is as follows [4]:

1. Oxidation process: the continuous fiber tow is held to length while it is heated for several hours at around 220°C in air. The fibers incorporate about 8% oxygen into their structure during this process.
2. Carbonization (high temperature phase): the stabilized fibers are passed through zones of increasing temperature to around 1500°C in an inert atmosphere, usually nitrogen. This is the first step in which the carbon fiber structure and associated properties are developed.
3. Graphitization: in this step, the fiber is heated to temperatures of up to and beyond 2500°C . High modulus carbon fibers are obtained by hot stretching during which the carbon chains are oriented and registered into better packed structures. Greater details about the carbonization process can be found in Chapter 16.

There is a direct relationship between the precursor fiber strength and modulus and the resulting carbon fiber strength and modulus. Therefore, it is desirable to use acrylic polymers that have high molecular weight and fibers that are made with high stretch ratios as precursors for carbon fibers [58].

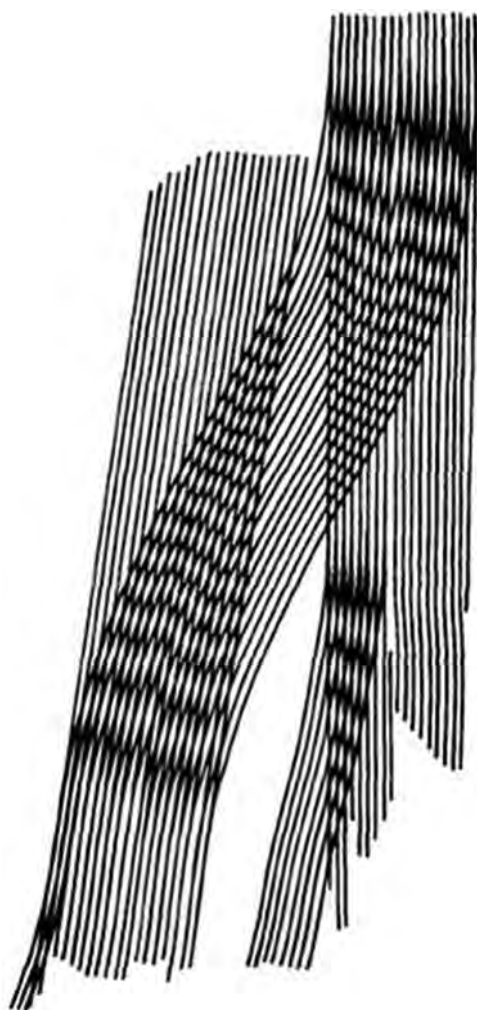
Some of the earliest TEM studies of carbon fibers were assumed to indicate the presence of a fibrillar structure; subsequent studies, however,



14.17 Initiation and formation of ladder polymer.

showed that the type of fibrils noted in the fibers such as cotton and wool, were not observed in carbon fibers. Fourdeux *et al.* [59] proposed the early model in which curvilinear layer planes were packed side by side, enclosing voids approximating needle shapes. Studies of the complex nature of the lattice-fringe images found in longitudinal sections led to a somewhat more realistic model of structure that involved a three-dimensional interlinking of the turbostratic layer planes, shown in Fig. 14.18 [60, 61].

Lattice-fringe images of transverse sections reveal a very complex structure which, at the surface and in the region close to the surface, shows that



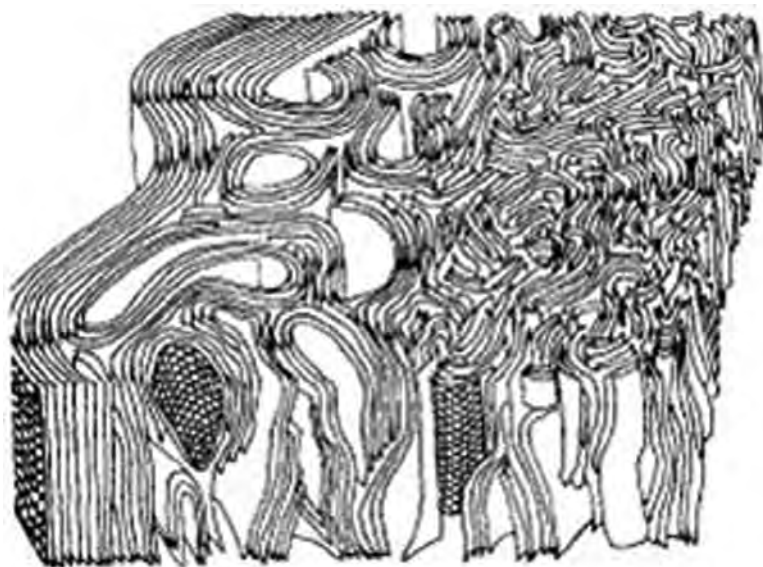
14.18 Model of longitudinal structure of PAN-based carbon fiber [60], reprinted by permission of Elsevier.

the layer planes are essentially parallel to the surface; some layer planes, however, are seen to fold through angles of up to 180° in a 'hairpin' fashion. In terms of a model for the structure of carbon fiber, formed from PAN, a detailed study of the lattice-fringe images from both the transverse and the longitudinal sections led to the structure as shown in the schematic of Fig. 14.19. This structure has been widely accepted as embodying most of the features of microstructure found in various studies conducted on the high modulus PAN-based carbon fibers.

14.9 Failure mechanisms of acrylic fibers

14.9.1 Tensile fracture

Fracture morphology of synthetic fibers depends on the fibers' manufacturing history. Hearle and Bunsell and coworkers [63–65], in their pioneering work, advocated the use of fiber fractography as an important diagnostic tool for both understanding the failure phenomenon and improving fiber properties. The manufacturing conditions exert a profound influence on fiber's morphology, mechanical properties, and deformation behavior [66, 67]. As a consequence, various kinds of internal stresses build up during the process. Kulshreshtha and coworkers [68] found that the acrylic fibers removed from the early and the final stages of manufacture show different failure mechanisms.

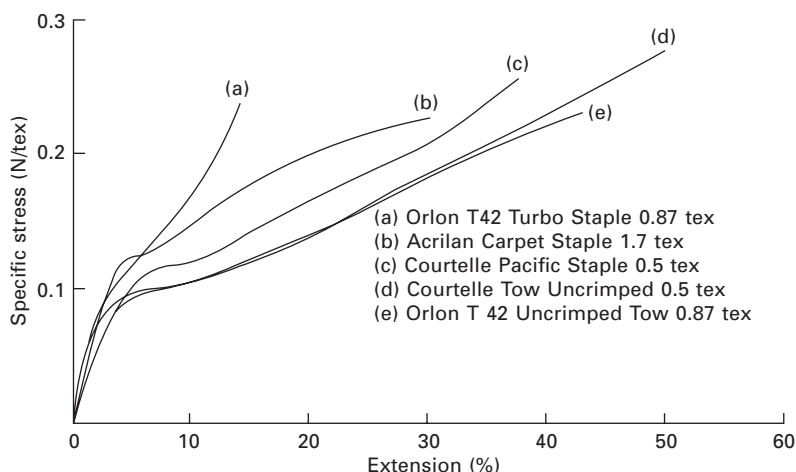


14.19 Model of transverse structure of PAN-based carbon fiber [62], reprinted by permission of Society of Chemical Industry.

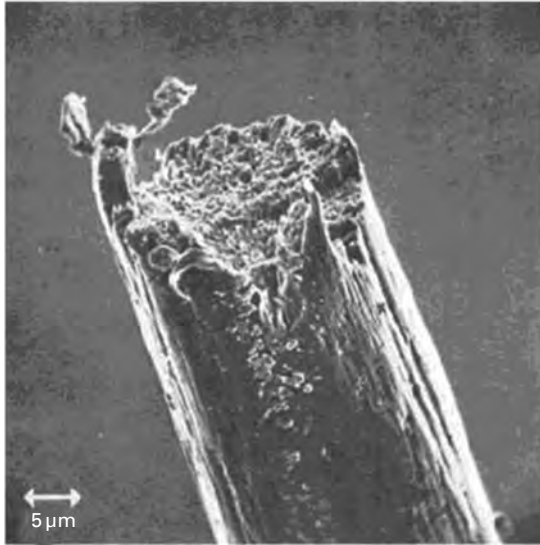
Bunsell *et al.* [65] studied the tensile fracture morphology of the uncrimped, 0.5–0.7 tex fiber (Courtauld's acrylic fiber). Figure 14.20 shows the stress–strain curves of a number of acrylic fibers. The tensile fracture is usually found to be straight across the fiber (Fig. 14.21a) with only moderate surface roughness and little evidence of crack development. Sometimes, as noted in Fig. 14.21(b), one may see some evidence of both the crack propagation and the catastrophic failure accounting for rupture. At some places, the bundles of fibrils are seen to project above the main fracture surface (Fig. 14.21a). The Courtele fiber fracture, thus, appears to fit into the category of a break material that is characterized by moderate cohesion between the individual axially aligned fibrous elements.

Monego and Backer [69] proposed a model for the fracture of acrylic yarn containing low twist. The model, shown in Fig. 14.22, cannot be taken as a realistic model for the fracture of Courtele fiber. It is expected that well-defined crack propagation across the specimen will be found in the material that has very high cohesion within the structure.

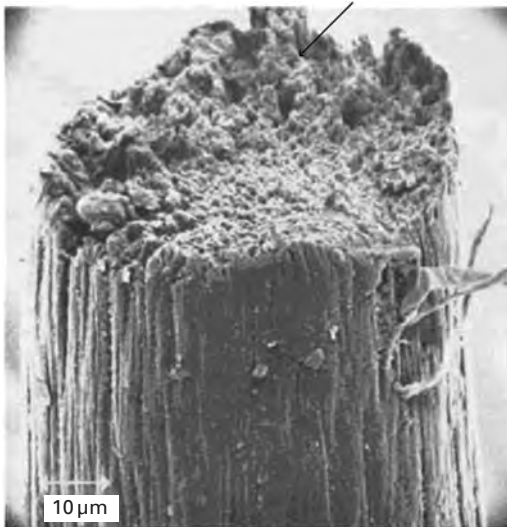
Figure 14.23 shows an idealized model for granular breaks of acrylic fibers. When the tension reaches a certain level, elements will begin to break (Fig. 4.23b), but the discontinuity prevents the occurrence of a large enough stress concentration to cause the crack to continue to propagate across the fiber. However, because some cohesion does exist between elements, the excess stress can be expected to be transferred to neighboring elements causing them to break at nearby positions. Eventually, the failure becomes cumulative over a cross-section (Fig. 14.23c), and leads to a granular break (Fig. 14.23d) [70].



14.20 The stress–strain curves of acrylic fibers [65], reprinted by permission of Wiley Interscience.



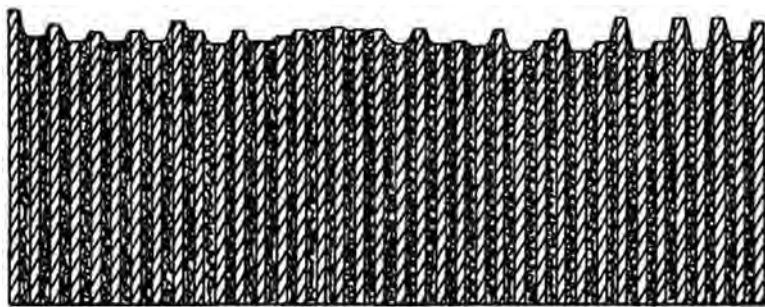
(a)



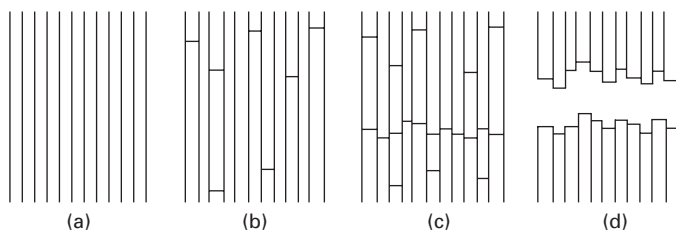
(b)

14.21 Tensile fracture of Courtelle unrimped tow [65]: (a) 0.5 tex, (b) 1.7 tex, reprinted by permission of Wiley-Interscience.

In tensile fracture of melt spun fibers such as polyamides, polyesters, or polypropylene, the break almost invariably starts at the surface, and then proceeds across by crack propagation. In examining the breaks of Courtelle, it has usually not been found possible to identify the point at which break starts, but it seems possible that it is internal [65].



14.22 Schematic representation of acrylic fiber fracture, based on fracture studies of yarn [69], reprinted by permission of SAGE.

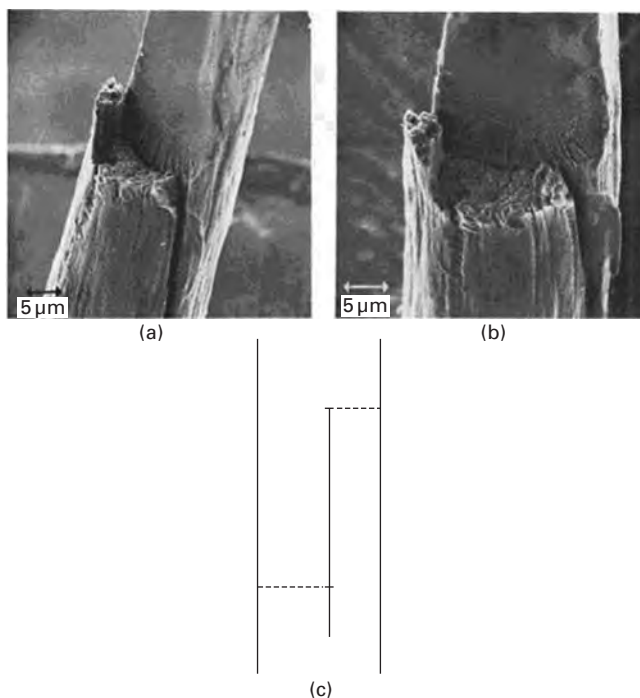


14.23 (a) Structure of separate elements; (b) under tension, elements start to break; (c) stress transfer causes cumulative break over a cross-section; (d) granular break [70], reprinted by permission of Woodhead Publishing Limited.

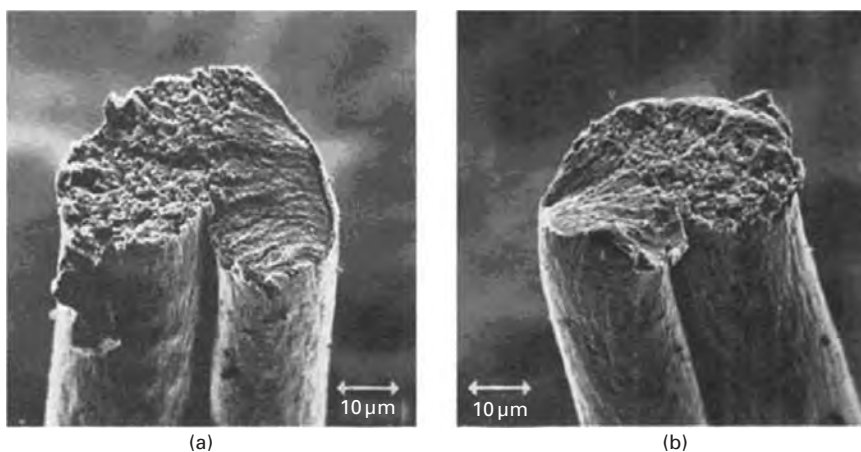
In some instances, the fracture is divided into two distinctly separated regions, marked by a split, as shown in Fig. 14.24(a,b). Presumably, this arises from two different fracture regions linked by a low shear interface between the two (Fig. 14.24c).

The 1.7 tex Acrilan (Monsanto's acrylic fiber) carpet staple, in contrast to the other results noted so far, shows a well-developed crack region (V notch) as seen in Fig. 14.25. This result is similar to those found in nylon and polyester fibers. In this case, most probably, the spacing and cohesion between fibrillar units was such that break was initiated at or very near the surface and then transmitted from one fibrillar unit to the next, thus leading to a crack formation.

Orlon type 42 (DuPont's acrylic fiber), which is a dry spun material, commonly shows, in contrast to the wet spun acrylic fibers, a fracture which is usually distributed over lengths of the order of a fiber diameter (Fig. 14.26a,b). Sometimes, the fiber is seen to split on breaking (Fig. 14.26c). As found with the breaks of some of the Courtele, the inner surfaces of the splits are relatively smooth (Fig. 14.26d). The fracture noted in some of the Orlon fibers is essentially perpendicular to the axis of the fiber



14.24 Tensile fracture of Courttelle, 0.5 Tex, uncrimped tow; (a, b) micrographs showing tip and base of split; (c) schematic of the weak shear interface linking the two fracture regions [65], reprinted by permission of Wiley-Interscience.



14.25 Opposite ends of Acrylan 1.7 tex carpet staple, broken in tension [65], reprinted by permission of Wiley-Interscience.

(Fig. 14.26e). Under high resolution, the Orlon fractured surface usually shows a granular appearance as found in other acrylic fibers (Fig. 14.26f).

The bicomponent Orlon Sayelle 21 and 23 behave in a manner similar to that noted in Orlon 42 on fracturing. Figure 14.27a shows a split break in Orlon Sayelle 21, and Fig. 14.27b, a perpendicular break in Sayelle 23.

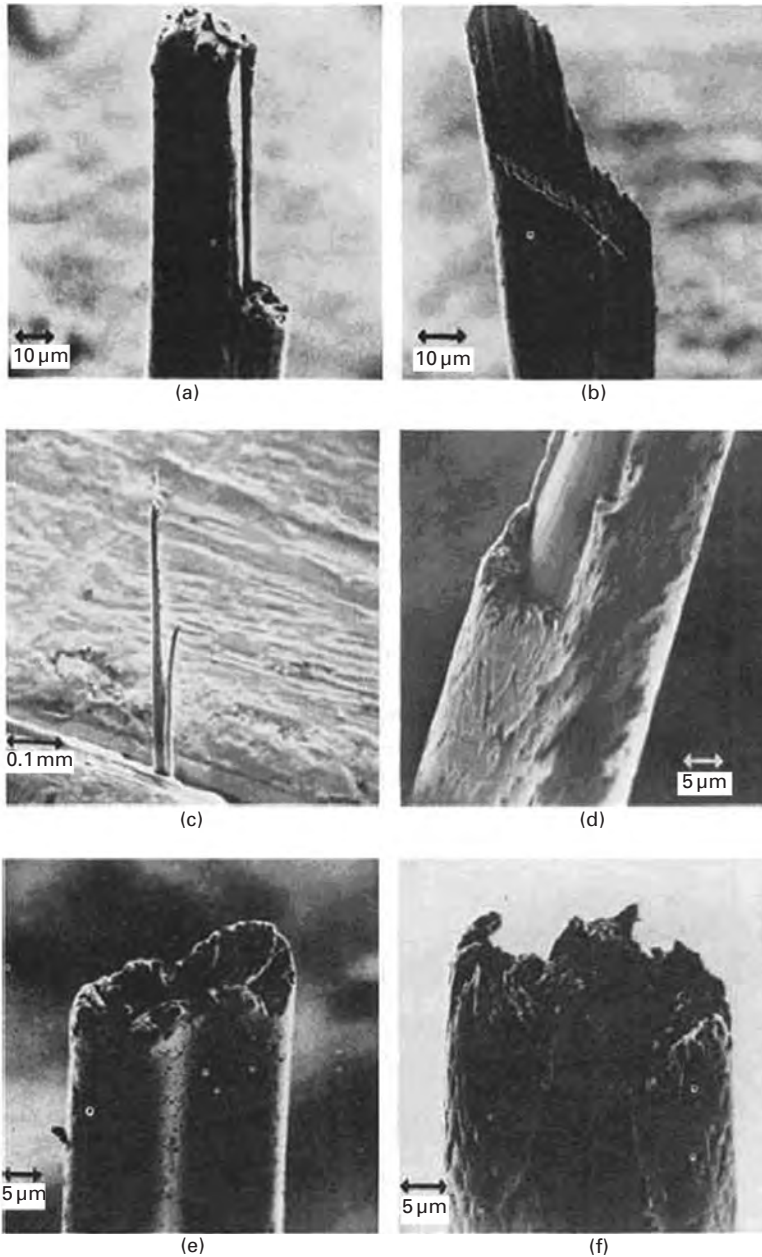
Kulshreshtha and coworkers [68] investigated the failure mechanism of three types of wet spun acrylonitrile methyl acrylate copolymer fibers which were: (1) partially drawn, (2) fully drawn, dried and crimped, and (3) fully drawn, dried, crimped and heat set materials. The properties obtained in the third sample were not intelligible or explained by the authors but those of the first two are in accordance with the expectations and are presented in Table 14.4.

14.9.2 Fatigue failure of acrylic fibers

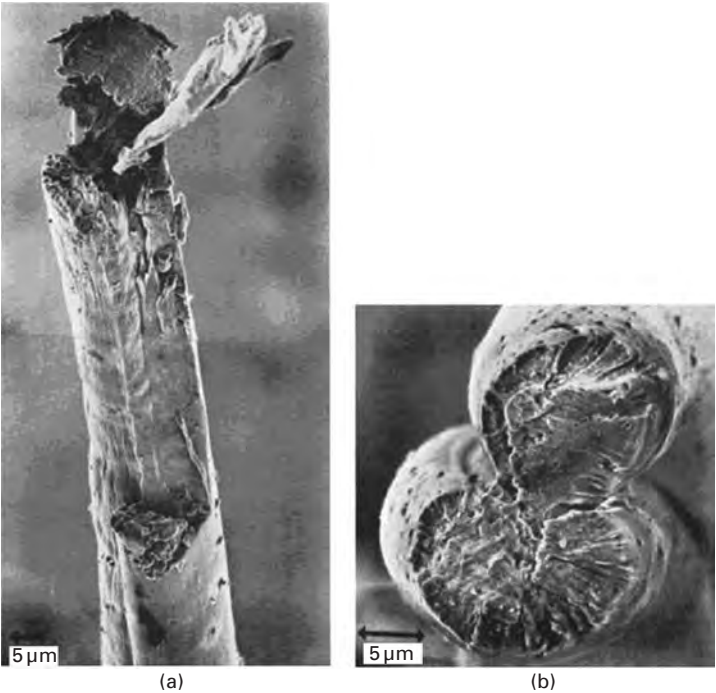
Bunsell and coworkers [65, 71] studied the tensile fatigue properties of acrylic fibers (Courtelle). Under cycling loading conditions, the Courtelle fibers tended to fail at a lower load, i.e. at load as low as about 65% of the tensile strength. This is because under oscillatory load conditions, the fiber tended to split axially and become weaker (Fig. 14.28). There is no evidence that the failure started on the surface; and indeed the cracks may be wholly internal.

Figure 14.29 shows a schematic representing the hypothetical axial splitting in fatigue test of acrylic fibers. The whole load on the fiber has to be taken by a reduced cross section represented by widths A–B and C–D. Eventually, when the crack has extended to Q and R, the stress will be sufficient to cause tensile failure over the reduced area given by widths P–Q and R–S. The fatigue life will thus be determined by the relation between the rate of crack propagation, the deviation of crack propagation from the axis in each cycle, and the extent of area reduction needed to cause the stress resulting from the applied load to reach the tensile strength of the fiber. Any non-uniformity at a local defect or void, e.g. X (Fig. 14.29), a fibril end, a fibril branch, or even a slight variation in fibril or matrix dimensions or structure, can lead to shear stress in the matrix between fibrils. A cyclic shear stress, which necessarily implies tension–compression cycling, is a form of deformation which seems particularly likely to cause fatigue failure through initial split among the fibrillar elements. When the split has started, the shear stress will be located at the ends of the split and, therefore, should be greater, and so the fatigue splitting will accelerate. The slight deviation of the split from the axial direction can be caused by the local structure variation. The split can be very long, extending over many fiber diameters, and these long breaks may tend to curl, as seen in Fig. 14.30.

The fibrillation of acrylic fibers is in contrast to that found in the carbon



14.26 Tensile fracture of 0.7 tex Orlon 42: (a) high bulk staple, showing split break; (b) crimped tow, showing split break; (c) turbo process staple, showing split break; (d) turbo process staple showing smooth surface in split region; (e) turbo process staple, showing a break perpendicular to fiber axis; (f) turbo process staple, showing granular appearance of fracture surface [65], reprinted by permission of Wiley-Interscience.

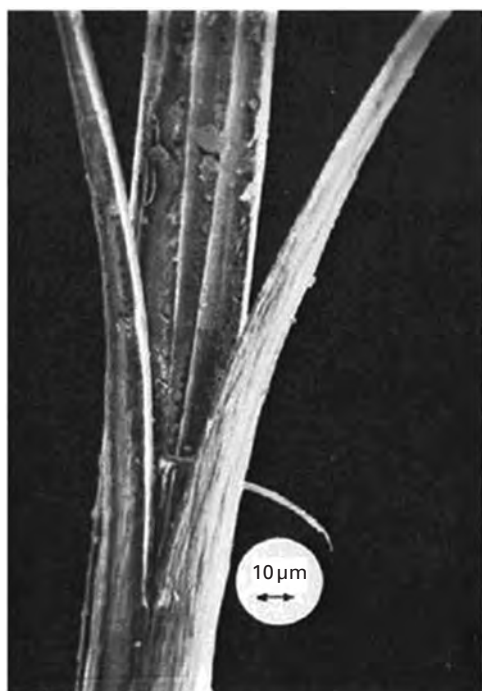


14.27 Tensile fracture of bicomponent acrylic fibers: (a) Orlon Sayelle 21, 0.7 tex; (b) Orlon Sayelle 23, 0.7 tex [65], reprinted by permission of Wiley-Interscience.

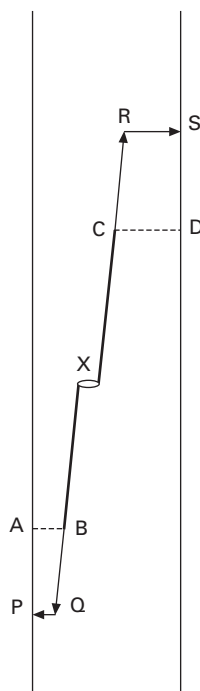
Table 14.4 Influence of manufacturing history on structure and property development in acrylic fibers [68], reprinted by permission of SAGE

Particulars	Sample A	Sample B
Sample history	Partially drawn	Fully drawn, dried, and crimped
Degree of crystallinity (%)	20	44
Tenacity (gm/tex)	28.5	41
Elongation to break (%)	49.5	26
Features of stress-strain curve	Yielding, ductile, high initial modulus	No yielding, brittle, reduced initial modulus
Tensile fracture morphology	Crazing, no axial splitting or necking, clean transverse fracture	Failure by axial splitting, no crazing
Fiber morphology	Slightly oriented amorphous structure	Highly oriented microfibrilar structure

fibers, which do not show splits, probably because of the three-dimensional crosslinking induced during the manufacture. The carbon fibers usually broke straight across radial planes under both the simple tensile and the cyclic loading conditions [71].



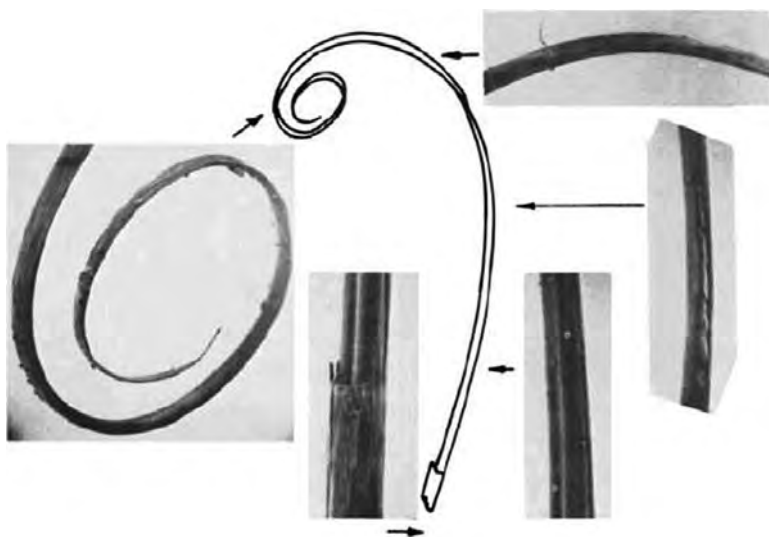
14.28 Fatigue failure showing splitting of a Courttelle fiber induced under cyclic loading conditions [71], reprinted by permission of Wiley-Interscience.



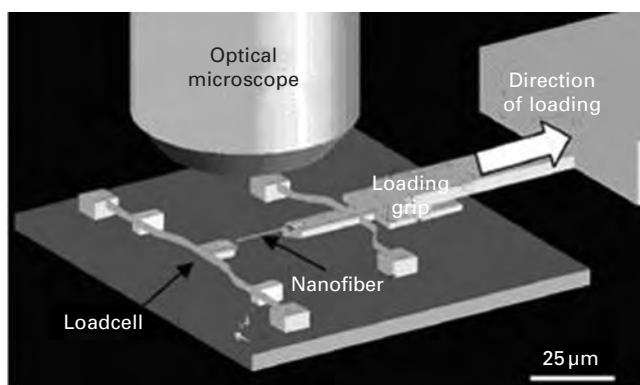
14.29 Schematic representation of the nature of axial splitting during fatigue [65], reprinted by permission of Wiley-Interscience.

14.9.3 Tensile fracture of electrospun polyacrylonitrile nanofibers

The mechanical behavior of electrospun polymeric nanofibers is expected to differ from that of the normal textile denier and microdenier fibers due to their differences in both the fabrication processes and the surface-to-volume ratios. Determining the mechanical properties of nanofibers is a challenge because of the fiber's very small dimensions and fragile nature. Naraghi *et al.* [72] investigated the mechanical behavior of polyacrylonitrile electrospun nanofibers by microscale tension experiments at different strain rates (2.5×10^{-2} , 2.5×10^{-3} , and $2.5 \times 10^{-4} \text{ s}^{-1}$). The test platform employed was a surface micromachine device with an on-chip leaf-spring load cell and grips for sample mounting (Fig. 14.31). The test device was transformed by a piezoelectric actuator to allow high draw ratios. Nanofibers were mounted on the grips by a micromanipulator and attached with epoxy resin. The



14.30 Courttelle, 1.7 tex, uncrimped tow, failed in tensile fatigue. Inserts illustrate various sections of the long split region [65], reprinted by permission of Wiley-Interscience.

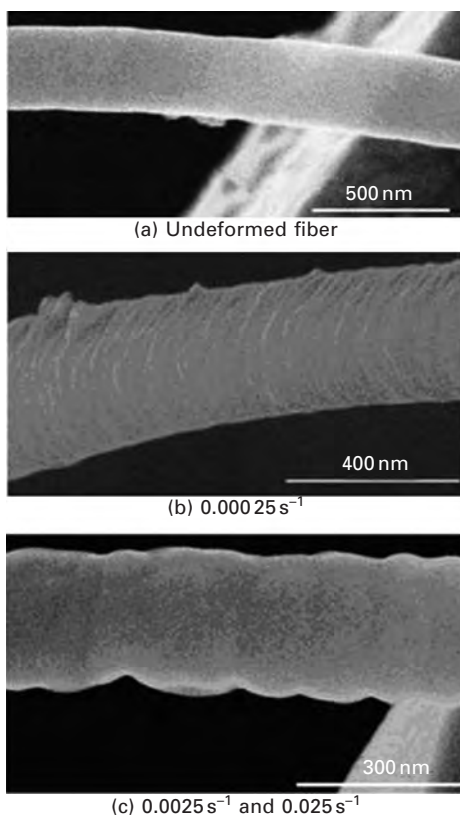


14.31 Schematic and operation of test platform for nanofiber tension experiments [72], reprinted by permission of American Institute of Physics.

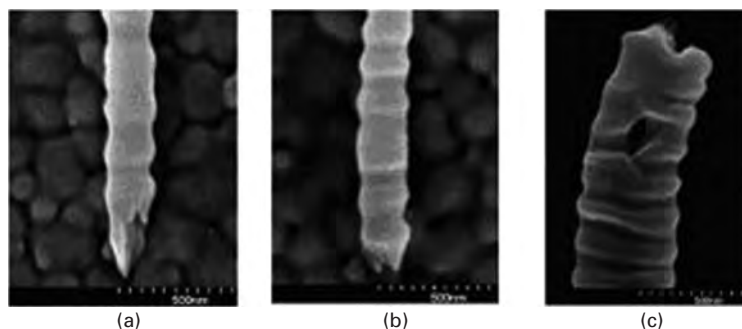
actual behavior during the test was observed with an optical microscope at 500 $\times$ magnification.

The results showed that the elongation at break of fibers was 60–130%, and the value monotonically decreased with increase in strain rate. The fiber strength was found to lie in the range 30–130 MPa and the modulus was about 7.5 ± 1.5 MPa.

The undeformed nanofibers had uniform cross-sections and smooth surfaces (Fig. 14.32a), but even at the lowest value of strain rate used densely packed fine transverse ridges or ripples formed on the surface during axial attenuation (Fig. 14.32b). The depth of these ripples was 20–40 nm and distance between them about 50 nm. The failure modes of the nanofibers clearly demonstrated necking. Contrary to the generally expected neck propagation to failure by reduction in its diameter, however, the fracture of several PAN nanofibers were owed to the extrusion of a nearly 45° cone (wedge) from the thick section of a neck (Fig. 14.33a,b). Also despite the very small diameter of the fiber, the fracture in some cases was noted to be due to the formation of nanopores in the fiber (Fig. 14.33c).



14.32 (a) Undeformed PAN nanofiber; (b) surface morphology of deformed nanofibers at the slowest (nearly homogeneous drawing); (c) at faster (formation of necks) strain rates [72], reprinted by permission of American Institute of Physics.



14.33 (a, b) Matching surfaces of a fractured PAN nanofiber. Final fiber failure was due to the spinning of a 45° cone (wedge) (a) from the thick section of a neck (b). (c) Fiber failure due to formation of voids [72], reprinted by permission of American Institute of Physics.

14.10 Conclusions

Acrylic fibers are unique materials with several unique properties. Most of these result from the polymer chain having acrylonitrile groups that are highly polar and lead to strong interactions among the chains. Thus, the fiber has high resistance to UV degradation, and to damage from mould, mildew and micro-organisms. The structure allows the acrylic fibers to develop wool-like bulk and resiliency; accordingly, some of the major applications of the fiber in its early history of commercial success were in the production of sweaters, knits, hosiery, coats, active wear, and blankets, the applications in which wool was normally utilized. The polymer tended to degrade before melting, it has, therefore, been traditionally extruded into fiber using a wet or dry spinning method. Because of the increased awareness later of the environmental concerns and the high cost of recovery of the solvents, acrylic fiber production has seen a decline. The fiber, however, continues to be the primary precursor for the development of high quality carbon fibers. There is a direct link between the mechanical properties obtained in the carbon fiber with those present in the precursor polymer. Accordingly, it has been of general interest to examine the fiber's fine structure and correlate it with its failure behavior, both in simple tensile and cyclic loadings. Although the fiber does not give the evidence of a well-defined two-phase fine structure, it does clearly show the presence of fibrillar morphology with reasonably strong cohesion between the fibrils. Tensile rupture usually supports granular breaks but fatigue failure leads to shearing of the bundles of fibrils and their separating along the weakest planes, resulting in split fiber at the broken ends.

14.11 References

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Structure and properties of glass fibres

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Abstract: This chapter describes the structure and properties of the variety of glass fibres manufactured principally for use as reinforcements for composites. We give a brief history of the glass fibre industry before describing the fundamental thermodynamic and atomistic concepts of glass formation. Sufficient detail is given to enable the manufacture, structure and properties to be described. The role of the different oxide compositions is reviewed, and there is a detailed discussion of the strength of fibres. The phenomenon of static fatigue is also considered. For completeness, the role of sizing technologies on protecting glass fibres from damage and for functionalising the surface for compatibility with polymers and resins in composite manufacture is also given. Recent ideas about the structure of silane coupling agents (adhesion promoters) deposited on glass fibres, is also reviewed.

Key words: glass fibres, manufacture, structure, strength, static fatigue, sizing technologies, structure of silane coupling agents, interphase formation in composites.

15.1 Introduction

On a weight basis, more than 99% glass fibres (also known as synthetic vitreous fibres or SVCs) in use today are spun from silicate glasses. Therefore, this discussion of glass fibres will be limited to silicate (containing at least 50% SiO_2 on a molar basis) glass fibres. We will not discuss fibres made from chalcogenide glasses which are mainly used in infrared optics. Thus, we will discuss neither fibres made from $\approx 100\%$ silica glass nor chalcogenide glasses which are mainly used for optical fibres. Fibres made from glassy metals will also not be discussed.

15.2 Historical perspective

Glass fibres have been known for centuries but there were few utilitarian uses for them until the middle of the 19th century. At that time, methods were devised for melting naturally occurring basaltic rocks and producing fine fibres from them. This rock wool (also known as mineral wool or basalt wool) was used as a thermal insulation material. This wool material had a large range of fibre diameters (from 1 to more than 15 μm). It also contained

a significant amount of shot or partially melted input raw material. The composition of rock wool varies depending upon the geographic source of the basaltic material. This material is still used in many applications as a high temperature thermal insulation material throughout the world. However, there are now health concerns associated with its use because of the number of very small ($< 3\text{ }\mu\text{m}$) diameter fibres it contains. These fibres have the potential of being inhaled into the deep lung. Since they are not readily soluble in lung fluids, they may cause health issues because they could be a long-term irritant in the lung (European Directive 97/69/EC).

One of the more unusual examples of the early use of glass fibres was in a dress worn by an actress of the day at the Columbian Exposition in Chicago in 1893 to draw attention to a cut glass exhibition (1)*. The first actual significant commercial use of glass fibres made from 'standard' glass making raw materials where the composition was closely controlled in a glass melting furnace would appear to be as a substitute for steel fibres in air filters. These were produced in the 1920s from a furnace used for making milk bottles in Newark, Ohio, USA (2).

It was recognised by a number of different people in the early part of the 20th century that fine glass fibres made with a controlled glass composition could be a very effective material for thermal insulation. However, it was not until the 1930s that a commercially viable process was developed which could compete with the rock wool processes of the day. The breakthrough occurred in 1932 when a recently graduated engineer, Dale Kliet, working at Owens-Illinois attempted to seal architectural glass blocks together using a metal layer gun. The compressed air metal layer gun was popular at that time in applying a thin layer of bronze to objects. In place of a bronze rod, the researcher used a glass rod in the device. Instead of a smooth layer of molten glass being laid down on the blocks, fine fibres came out of the gun in a manner totally unacceptable for sealing glass blocks together. An associate researcher, Jack Thomas, involved in the use of fibreglass for air filters saw the fibres and immediately recognised that this could be a method of making fibreglass for thermal insulation applications. Compressed air was replaced with steam and the first commercial fibreglass thermal insulation based on this concept, identified in the 'failed' sealing experiment, was installed in October of 1933. Work continued on a commercial process at both Owens-Illinois Glass Company and Corning Glass Works and at St. Gobain in France. In 1935, Owens-Illinois and Corning decided to pool their technical resources and, in 1938, formed a joint venture known as Owens Corning whose main product was fibreglass produced in the former glass milk bottle factory. That factory is still a major producer of fibreglass for thermal insulation applications.

*The glass fibre wedding dress and accessories worn by Professor W.E.S. Turner's bride in 1943 are on exhibition in the Turner Museum, University of Sheffield, UK.

In 1933, the same Owens-Illinois research group utilised a refractory ‘bushing’ to produce continuous glass filaments. Experiments were performed using these continuous filaments in textile machines, substituting the glass fibres for natural fibres such as cotton. In 1935, the first polymer–glass fibre composites were produced. That same year, a commercial process for the manufacture of continuous glass fibres was made operational in the same plant in Newark, Ohio, USA, that was now being utilised to produce the glass wool used for thermal insulation and air filters. The first plant dedicated exclusively to the manufacture of continuous filament glass fibres was commissioned in 1941 at Ashton, Rhode Island, USA. This plant showed that it was commercially feasible to produce continuous filament fibreglass for use as a reinforcement material in literally thousands of composite applications.

The three people most responsible for the development of the modern fibreglass business, Dale Kleist, Jack Thomas and Games Slayter, were inducted into the (USA) National Inventors Hall of Fame in 2006 for their pioneering efforts in this now global industry.

15.2.1 Fibreglass for insulation and filtration

The first significant commercial application was in air filtration, especially in forced air furnace systems for buildings. Fibreglass dominated the market for several decades. Although in the last decade, lower cost organic polymer fibres have replaced fibreglass in most air filtration systems for home and commercial applications, the market for thermal insulation has continued to grow, driven by the desire to provide more energy-efficient buildings. This market is, in fact, the largest (by mass) user of fibreglass of all types. The energy required to produce thermal insulation products from fibreglass compares very favourably with the energy which can be saved in space heating/cooling applications over a few years. This makes fibreglass wool one of the most energy-efficient commodity products on the market today. This is especially important where, in the USA, 40% of the total energy usage is in residential and commercial buildings.

15.2.2 Fibreglass for reinforcement

The second largest market (by mass) for fibreglass is in composite materials, where the fibreglass is used as reinforcement for a polymer. The tensile strength and elastic modulus of fibreglass reinforcement are much higher than those for the matrix polymer. However, the glass fibre can serve as a reinforcement only when stress transfer to the polymer matrix can occur. Otherwise, the glass filaments would simply act as a filler reducing the overall cost of the composite. To achieve this, the fibres are coated within milliseconds of exiting the spinneret or bushing with a dilute (typically

aqueous) mixture or emulsion of organic molecules called the sizing. The sizing system effectively acts as an adhesive which bonds the polymer to individual glass filaments. The mechanism by which the sizing system functions is discussed in Section 15.5.5.

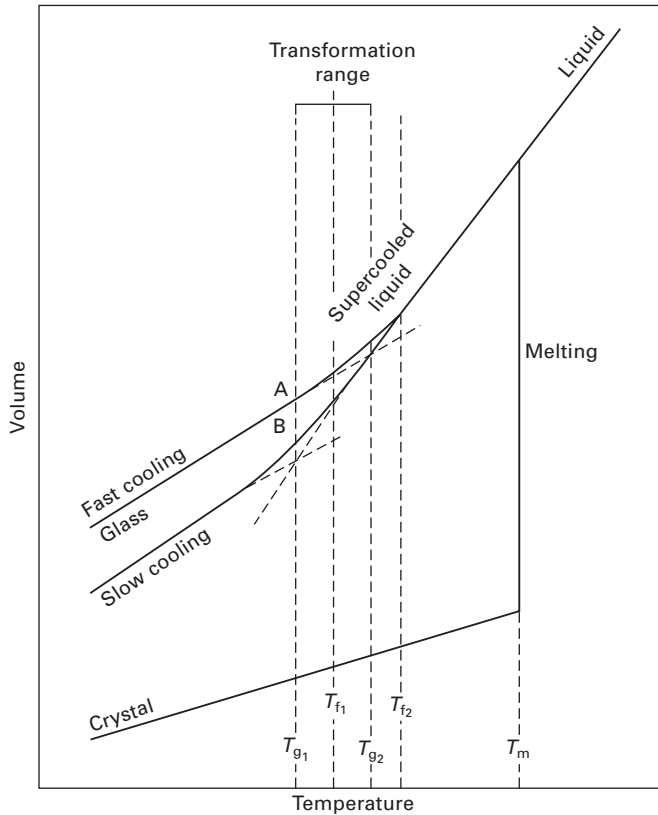
15.2.3 Other glass fibres

Fibres used for optical communications are an order of magnitude larger in diameter ($>100\text{ }\mu\text{m}$) than typical insulation and reinforcement fibres ($5\text{--}30\text{ }\mu\text{m}$). Furthermore, the manufacturing process is very different. A chemical vapour or particulate deposition process is used to produce 'preforms' weighing up to a few kg which are used in the optical fibre drawing process. This is to be compared with the tonnes of raw materials which are charged into a fossil fuel fired or electric furnace to produce fibreglass wool or continuous filament fibreglass for the reinforcement market. The chemical composition is also very different. For optical communication, extremely high purity silica with precisely controlled concentrations of doping ions to adjust the refractive index are utilised. In contrast, a mixture of several oxides with a range of impurities is used for drawing continuous filaments. Furthermore, there is a range of glass-ceramic fibres available commercially but these are not considered here. There are also limited uses for non-oxide glasses whose structure will not be discussed here.

15.3 The nature of glass

15.3.1 A thermodynamic viewpoint

In the absence of long range order within the atomic structure of a glass, the material solidifies in an amorphous arrangement. The polymeric nature of the chain molecules in organic polymers and inorganic silicates means that on cooling the viscous 'melt' there is insufficient time for crystallisation to occur and a random structure occurs. This leads to the concept of the glass transition (3). This concept of a non-equilibrium structure being 'frozen in' implies that the particular structure which is frozen in is a function of the kinetics of the relaxation process. Because of the rapid change in viscosity of glass-forming liquids (especially silicate glasses) with temperature, the structure which is frozen in is dependent upon the cooling rate. Thus, there is a range of temperatures over which the transition from a true liquid to the glassy state occurs. This is called the glass transition temperature (T_g) range. One can define T_g based upon measurements of specific properties of the material. For example, Fig. 15.1 shows how a T_g can be defined by monitoring the change in volume of the material (or thermal expansion coefficient) as it is cooled. Because of the change in heat capacity of the



15.1 Volume–temperature relationships for glasses, liquids, supercooled liquids and crystals. On fast cooling the supercooled liquid curve follows path A and on slow cooling path B. The temperature at which the structure of the supercooled liquid is ‘frozen in’ is referred to as T_f or the fictive temperature. The glass transition temperature, T_g can be defined by extrapolating the linear expansion curves above and below the transformation range (adapted from Hutchins and Harrington (3)).

material in the glass transition region, one can also define the T_g through calorimetric methods. Again, the value of T_g obtained is dependent upon the measurement conditions and the glass cooling rate.

The concept of the ‘fictive temperature’ as represented in Fig. 15.1 is an attempt to characterise uniquely the structure of the glass. The fictive temperature itself is dependent upon the cooling rate which the material undergoes. However, Agarwal *et al.* (4) have utilised IR measurements in an attempt to measure the fictive temperature of glasses where the measurement technique itself is performed at a constant temperature.

Thermodynamically, there is a difference in heat capacity between the

glass and its liquid. It is also seen that the glass which was prepared after fast cooling has a higher T_g (T_{g_2} in Fig 15.1) and occupies more volume and therefore has a lower density. After slow cooling, the glass which forms has a T_g at T_{g_1} and a higher density. Thus, the entropy of the glass formed at T_{g_2} must be higher than that of T_{g_1} . As a result, it can be considered that the configurational structure of the glass differs across the transformation range of $(T_{g_2} - T_{g_1})$. Therefore, the glass cannot be considered to be a supercooled liquid. The temperature at which the liquid becomes supercooled is referred to as the fictive or configurational temperature T_f in Fig 15.1 (5). In Fig 15.1, a fast-cooled glass will also have a higher fictive temperature than that prepared after slow cooling. Studies on polymer glasses have attempted to examine whether the glass transition is a thermodynamic quantity. A second order transition is represented by a discontinuity in a second order thermodynamic property.

According to the well-known thermodynamics of Ehrenfest, for a glass to exhibit a second order transition of temperature, T_2 , the following relationships need to be applicable:

$$\frac{dT_2}{dP} = \frac{\partial \Delta V / \partial T}{\partial \Delta S / \partial T} = \frac{V \Delta \alpha T_2}{\Delta C_p} \quad 15.1$$

$$\frac{\partial T_2}{\partial P} = \frac{\partial \Delta V / \partial p}{\partial \Delta S / \partial p} = \frac{\Delta k}{\Delta \alpha} \quad 15.2$$

where P is pressure, ΔV is the change in volume at the transition, ΔS the change in entropy, ΔC_p is the change in heat capacity. $\Delta \alpha$ is the difference between the linear thermal expansion coefficients above and, below T_2 , Δk is the compressibility. The second order temperature dependence of Gibbs free energy, G , is given by equation 15.3, pressure dependence by equations 15.4 and 15.5.

$$\frac{\partial^2 G}{\partial T^2} \bigg|_P = - \frac{C_p}{T} \quad 15.3$$

$$\frac{\partial^2 G}{\partial P^2} \bigg|_T = kV \quad 15.4$$

$$\frac{\partial}{\partial T} \left[\frac{\partial G}{\partial P} \bigg|_T \right]_P = \alpha V \quad 15.5$$

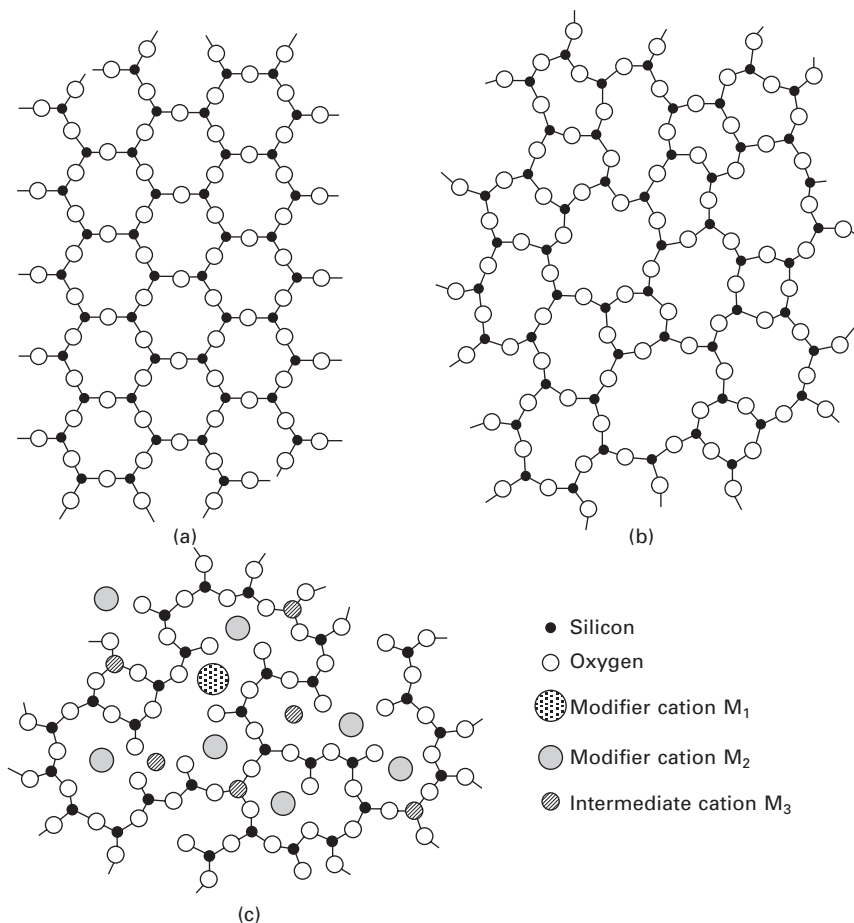
For a detailed discussion of the thermodynamics of second order transitions, the reader is referred to the review by Haward and Young (6). Gibbs and

DiMarzio (7) have argued that T_2 is effectively the lowest value of T_g which can be achieved. At this temperature, the configurational entropy is considered to be zero and that no further reorganisation of the molecular glass structure occurs at temperatures below T_2 . Thus, this model has been applied to inorganic glasses (8) with some success to explain the structure and formation of glasses. In practice, equation 15.1 holds but equation 15.2 does not, so a glass has both kinetic and thermodynamic characteristics. If neither equation 15.1 nor 15.2 held, the glass would be considered to be a supercooled liquid. Thus T_2 can be considered the lowest value of T_g which would be achieved by cooling the glass infinitely slowly.

15.3.2 An atomistic viewpoint

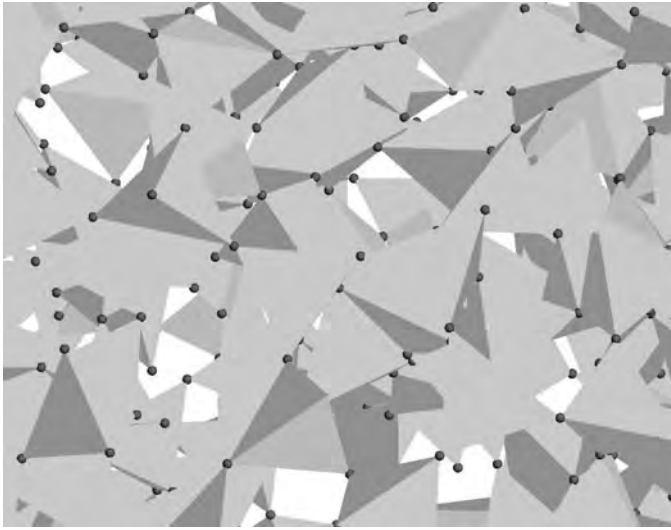
The structure of glass on an atomistic level has been the subject of much theoretical speculation and experimental work for nearly a century. Still, however, we do not have a clear atomic level concept of glass structure. This difficulty comes from the lack of a high degree of long-range (greater than 1 nm) atomic level order present in the glass structure. Attempts to explain the short-range order but long-range disorder of glasses have revolved mainly around two theories. One explanation proposed by Lebedev (9) postulated the presence of 'crystallites' in glasses. These crystallites were essentially assumed to be very 'small' regions consisting of dozens of atoms which were arranged in a crystalline order in the glass. These 'crystallites' were joined together in a somewhat random manner. There were a number of variations on this theme proposed from the 1920s for the next 50 or so years. As the sensitivity of experimental techniques have improved the maximum possible size of these 'crystallites' has decreased to the point where there is little to distinguish them from the 1 to 2 nearest neighbour order assumed by Zachariasen (10) in his random network model. Zachariasen's model suggested that vitreous silica was composed of a random network of SiO_4 tetrahedra. Early X-ray diffraction work (11, 12) supported Zachariasen's general picture of short-range order present in silica (<0.3 nm) but little long-range order (>3 nm). Early two dimensional representations of the differences between (a) a crystal, (b) a SiO_2 glass, and (c) a glass with 'modifier cations' are presented in Fig. 15.2. The short-range order and lack of long-range order in Fig. 15.2(b) result from SiO_4 tetrahedra being the basic building block of amorphous silica but the orientation of the tetrahedra with each other possess some random character. The O atoms at the corners of the tetrahedra are shared between two tetrahedra. Thus, the overall chemical composition is that of SiO_2 .

Molecular dynamics (MD) modelling of silica glass using a variety of force fields (13) indicates that the basic building block is a 4-coordinated Si atom surrounded by four oxygen atoms as suggested by Zachariasen (10). MD

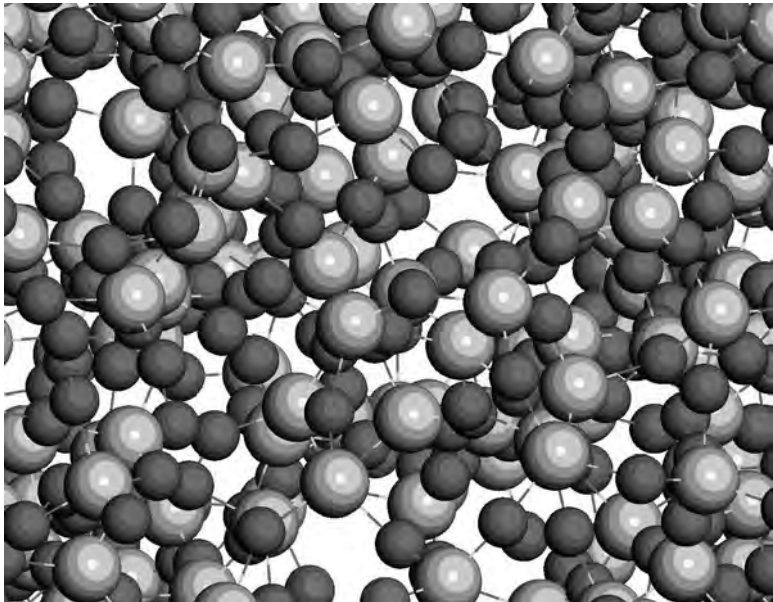


15.2 Two-dimensional schematic representation of (a) a crystalline structure; (b) a simple glass; and (c) a multicomponent glass.

simulations suggest that the O—Si—O bond angle distribution is centred at about 108° with the bond angle distribution at half the maximum amplitude (full width half maximum or fwhm) of the distribution being about 15° . This implies that the O atoms assume a four-fold tetrahedral arrangement around the Si atoms. Calculations on the MD structure indicate that about 99% of the Si atoms are four-fold coordinated. Thus, some disorder is introduced even at the nearest neighbour interatomic distance. These same calculations indicate that there is a much wider distribution of angles between tetrahedra (represented by the Si—O—Si bond angle). The tetrahedron-to-tetrahedron bond angle is about 155° while the fwhm is about 35° . With this wide variation in bond angles, the resulting structure is a 3-dimensional joining of the tetrahedra. This is represented in Fig. 15.3(a).



(a)



(b)

15.3 Two different representations of a molecular dynamics generated structure of silica glass. (a) Emphasis on the tetrahedral configurations of O atoms around Si atoms at the centre of the tetrahedrons. (b) A CPK representation of the same atomic arrangement in (a). In this representation, the spheres are proportional to the van der Waals radii of the atoms.

The tetrahedra tend to form non-planar ring structures. The most common ring size contains six Si and six O atoms. (In the inorganic glass community, the size of these rings is commonly referred to by the number of Si atoms contained in the ring. Thus, a ring containing six Si and six O atoms would be called a six-member ring.) The large variation in the Si—O—Si bond angles is consistent with a 3-dimensional structure where there is a rather large distribution of ring sizes, varying from three Si member rings to ten Si member rings. Smaller rings will produce structures with somewhat strained Si—O bonds. When these are located at the surface of the glass, they are expected to be more reactive than other regions containing six-membered rings. Molecular dynamics and density functional *ab initio* calculations support this view (14).

Because of the irregular distribution of strained bonds, these reaction sites will likely be randomly located on the glass surface. This, of course, greatly complicates our ability to study how the coatings (e.g. sizing systems) on a glass surface are assembled at the molecular level. This, in turn, makes the study of the interphase region between the glass surface and an organic polymer matrix a very complex subject (see Section 15.5.5).

Because of the somewhat random relative orientation of SiO₄ tetrahedra, significant variation in the density of the glass can occur over distances of 1–2 nm. MD calculations suggest that the density of several hundred atom regions can vary by as much as 5%. This is supported by experimental scattering measurements (15).

From a thermodynamic standpoint, this random nature of glass structure suggests that there are many atomic configurations that silica glass can assume which are very nearly of the same energy. The energy barriers between local minima are relatively low. This is consistent with the concept of fictive temperature discussed by Tool (16) that results from the inability of the glass structure to transition from one configuration to another of lower energy because the rate at which the silica can move over an energy barrier to a lower energy configuration becomes slower and slower as the thermal energy in the glass (represented by the average glass temperature) is reduced. Moynihan *et al.* (17) and others have expressed the change in fictive temperature as a function of the rate of change in cooling of the glass and a structural relaxation activation energy which is approximated by the shear viscosity activation energy. Again this type of model is consistent with the idea that there are many atomic configurations of nearly the same energy which are separated by low energy barriers.

15.3.3 Glass forming systems and composition

The discussion above has focused upon amorphous silica. Commercial glasses, including fibreglasses, contain significant amounts of elements other than

Si. In fact, most large tonnage glasses typically contains between 55 and 75% SiO_2 on a molar basis. Elements in the first column (e.g. Na, K) and second column (e.g. Mg, Ca, Sr, Ba) of the periodic table typically make up a significant fraction of the compositions used for most fibres. These exist as cations and are generally referred to as network modifiers, which disrupt the corner bonding of tetrahedral SiO_4 units. This results in significant changes in the physical properties of glasses. The thermal expansion and density increase, while viscosity decreases. This leads to a decrease in hardness, tensile strength and electrical resistivity (especially for the alkali metal atoms) at a given temperature. Other properties, such as refractive index, can either increase or decrease on addition of network modifiers to the silica glass. Chemical durability can either increase or decrease depending upon the environment. For example, the addition of alkali metals to silica will decrease the chemical durability of the glass in acidic solutions. However, it will tend to increase the chemical durability in alkaline solutions.

Atoms in the third column of the periodic table (e.g. B, Al) can participate in the network structure by assuming either three-fold or four-fold coordination with the O atoms. This type of coordination is dependent upon the network modifiers present in the glass. Boron plays a significant role in the thermal conductivity properties of fibreglass used for thermal insulation. Aluminium is a significant component of various types of fibreglass used for reinforcement of organic polymer materials. Boron is also present in many reinforcement fibreglasses (18, 19) but its use is decreasing in order to reduce batch costs and pollution control equipment required in the melting and forming process.

Although pure silica glasses appear to mostly have random arrangements of atoms beyond the nearest neighbours, when network modifiers (e.g. Na, Ca) and alternate network formers (e.g. B and Al) are introduced, some of the randomness of the structure is compromised. For example, in a sodium silicate glass, molecular dynamics simulations indicate that there are regions of relatively higher and lower concentrations of sodium atoms. This sort of phenomenon can result in phase separation in some glasses where, in essence, there are two types of glass compositions present in a glass body. The two phases can separate in either a spinodal manner where one phase can form channels through the other phase, or in a droplet manner where one phase separates typically into droplets within the other phase.

The existence of glass lasers also implies that order beyond just the nearest neighbours of the atoms do exist in modified silicate glasses. For example, the phenomenon responsible for laser properties of some glasses implies that there is order in more than just the nearest neighbours of the lasing ions (e.g. Nd^{+3}) in silicate glasses.

15.3.4 Fibreglass compositions

Table 15.1 illustrates the range of glass compositions which have been used in fibre spinning operations (18, 19). The applications and some characteristics of these are described below.

'A'-glass

Fibreglasses designated as 'A'-glasses are essentially a sodalime-silica glass very similar to the type of glass used to produce bottles and flat glass. Such a glass has lower batch costs than the glasses typically used for thermal insulation and reinforcements for plastics. 'A'-glasses typically have lower tensile strengths and lower chemical durability, especially in acidic media, than glasses normally used in thermal insulation and reinforcement applications.

AF (wool) glass

AF-glasses are typically used in producing fibreglass used as thermal insulators and for sound absorbers in buildings. The name AF (all fibre) was coined to differentiate it from basalt glass wool insulation which contains significant amounts of non-fibrous materials (shot). The composition of AF-glasses is similar to glass container and flat glasses (basically a sodalime-silica glass). The main difference is the inclusion of 2–10% B_2O_3 . The addition of boron to the glass batch does significantly increase the batch cost. It also significantly impacts the melting characteristics of the glass, its chemical durability and the effective thermal conduction properties of the glass in its fibrous form.

AR-glass

AR (alkali-resistant) glass fibres were developed as a reinforcement fibre which could be used in alkaline environments. Specifically, AR-glass is mainly used as a reinforcement in concrete. It is considered as a speciality glass but it is produced in furnaces using standard fibreglass melting techniques.

Basalt glass

Historically, basalt glasses have been used in thermal insulation applications (often called mineral wool). The method of producing these wool glasses is quite different from the glass melting tank and spinners used in the production of AF-glasses used for insulation.

Because of the production techniques, the wool pack contains particles of non-fibre materials call shot. As the name implies, basalt glass is produced

Table 15.1 Compositions (in weight %) of typical glasses for fibres (18, 19)

Constituent	E	ECR	Advantex® (20)	C	A	S-2®	R	Cemfil (21)	AR1 (22)	AR ₂	D
SiO ₂	55.2	58.4	59–62	65	71.8	65.0	60	71	60.7	61.0	75.5
Al ₂ O ₃	14.8	11.0	12–15	4	1.0	25.0	25	1	–	0.5	0.5
B ₂ O ₃	7.3	0.09	–	5	–	–	–	–	–	–	20.0
ZrO ₂	–	–	–	–	–	–	–	16	21.5	13.0	–
MgO	3.3	2.2	1–4	3	3.8	10.0	6	–	–	0.05	0.5
CaO	18.7	22.0	20–24	14	8.8	–	9	–	–	5.0	0.5
ZnO	–	3.0	–	–	–	–	–	–	–	–	–
TiO ₂	–	2.1	<1	–	–	–	–	–	–	5.5	–
Na ₂ O	0.3	–	0.1–2	8.5	13.6	–	–	11	14.5	–	} 3.0
K ₂ O	0.2	0.9	<2	–	0.6	–	–	–	2.0	14.0	
Li ₂ O	–	–	–	–	–	–	–	–	1.3	–	
Fe ₂ O ₃	0.3	0.26	<0.5	0.3	0.5	Trace	–	Trace	Trace	–	–
F ₂	0.3	–	<0.5	–	–	0	–	–	–	–	–

using naturally occurring basalt rocks as the main batch ingredient. As a result, the composition of basalt glass varies significantly from one geographical region to another. Recently, there have been some efforts to add other batch materials to basalt rocks in an attempt to have a more consistent glass composition and to alter its chemical durability so that it will dissolve in the lungs and thus not have any long-term health effects if very fine fibres are inhaled into the deep lung. (Fibres need to be less than about 3 μm in diameter to be inhaled into the deep lung.)

Some basalt compositions have also been used in the production of continuous roving for use in reinforcement applications. Because of the high content of FeO in basalt rock and the relatively high tendency of these compositions to form crystals, the production of continuous basalt roving has been limited to rather low throughput and thus labour intensive production methods. (The presence of relatively large amounts of FeO in these compositions greatly reduces the radiative thermal conductivity of these glasses in melting and forming operations which results in glass with poor thermal homogeneity. This greatly reduces the efficiency of melting and forming operations.) Up to the present time, this has severely limited the use of continuous basalt fibreglass in reinforcement applications.

E-glass

Table 15.2 illustrates the composition of a range of E-glass fibres (18, 19). Glasses broadly classified as E-glass are primarily used as reinforcements in a wide variety of organic polymers (plastics). The term E-glass came from its early use as a reinforcement in electrical applications. At room temperature, E-glasses have very high electrical resistivity. Thus they are well suited as reinforcement in such applications as printed circuit boards. E-glasses have higher viscosity at a given temperature than most other high tonnage fibreglasses or glass compositions used in container and flat glass applications. The chemical durability of these glasses in acidic solutions is very good, exceeding the resistance of most stainless steels to acids containing chloride ions. The main oxides used in these glasses are silica, calcia and alumina. Most E-type glasses used to contain boron. However, E-type glasses without boron or fluorine are now gaining wide acceptance in the fibreglass industry because of lower batch costs and lower emissions during the melting and forming operations. These glasses have even higher chemical durability to acidic solutions than the boron-containing type of E-glasses but also higher melt viscosities (and thus melting temperatures). Because of the excellent chemical durability, especially in acidic solutions, they belong to the subclass of E-glasses called ECR (chemically resistant) E-glasses.

Table 15.2 E-glass compositions 1940–2008 (weight %)

	Original E-glass (23)	Improved E-glass (24)	621 glass (25)	MgO -free glass	816 glass (26)	F-free glass (27)	B & F-free glass (28)	Advantex®	Low n_D glass (29)
SiO ₂	60	54.3	54.0	54.3	58.0	55.3	59	60	55.8
Al ₂ O ₃	9	14.0	14.0	15.1	11.0	13.9	12.1	13.5	14.8
B ₂ O ₃	–	10.0	10.0	7.4	–	6.8	–	–	5.2
TiO ₂	–	–	–	–	2.4	0.2	1.5	–	–
MgO	4	4.5	–	0.1	2.6	1.8	3.4	3.0	–
CaO	27	17.5	22.0	22.1	22.5	21.4	22.6	22.5	21.0
ZnO	–	–	–	–	2.6	–	–	–	–
Na ₂ O/ K ₂ O	–	1.0	1.0	0.1	1.0	0.4	0.9	1.0	1.4
Fe ₂ O ₂	–	Trace	Trace	0.2	0.1	0.2	0.2	–	n.d
F ₂	–	0.5	0.5	0.6	0.01	–	–	–	0.5

High strength glass (R- and S-glasses)

High strength glasses typically have relatively higher amounts of SiO_2 than the other types of fibreglass (Table 15.1). Because of this, these glasses have higher melting temperatures than the conventional E-glasses. There are a number of designations of these types of glasses with various degrees of improved tensile strength. In Europe this glass is referred to as R-glass but the highest tensile strength glass sold in relatively large tonnages is called S-2^{®1} glass. This magnesia–alumina–silica glass has a tensile strength which is about 50% higher than that of standard E-glasses (Table 15.3). It is melted in special small volume and very high temperature melters. As a result, it is relatively expensive and is used only in speciality applications where very high thermal durability and strength retention are required. Recently, a magnesia–alumina–silicate glass with significantly higher tensile strength than E-glass has been developed which can be melted in modified conventional E-glass melters. Because of the relatively high throughput achievable for this glass, it holds the potential for greatly increasing the use of glass as a reinforcement material in such applications as ballistics, wind turbine blades and compressed gas tanks. The term high performance glass has been used to characterize these fibre glasses.

D-glass

For the specific requirements of fast-response electronic circuit boards, dielectric glass with low dielectric constant is available as shown in Table 15.1 where a typical D-glass composition is given.

15.4 Fibre manufacture

The manufacture of glass and glass fibres is described in detail by Mohr and Rowe (32) and Loewenstein (18) and only a brief description is given here.

15.4.1 Wool process

The main process used today to produce fibreglass wool for thermal insulation purposes involves draining a stream of molten glass into a spinner (bowl-shaped base metal container with holes in the walls). The spinner operating temperature is typically 900–1100 °C. The spinner typically rotates at 2000 to more than 3000 RPM, ejecting fine streams of glass through the holes in the spinner sidewalls. These streams of glass coming out of the sidewalls

¹ AGY Holding Corp.

Table 15.3 Some typical properties of glass fibres (18, 19, 30, 31)

Property	E	ECR	Advantex® C	A	S-2®	R	Cemfil (21)	AR1	AR2	D
Liquidus temp ^a (°C)	1140	–	–	–	1010	–	–	1201	1172	–
Fiberising temp ^b (°C)	1200	–	1250	–	1280	–	–	1470	1290	–
Single fibre tensile strength at 25°C, (GPa)	3.7	3.4	3.8	3.4	3.1	4.7	4.5	2.9	3.24	2.5
Single fibre tensile modulus (GPa)	76.0	73.0	–	–	72.0	85.0	85.0	–	73.0	80
Density (g/cm ³)	2.53	2.6	2.62	2.49	2.46	2.48	2.55	–	2.74	2.74
Refractive index	1.550	1.58	1.56	–	1.541	1.523	–	–	1.562	1.561
Coefficient of linear thermal expansion (10 ⁻⁶ K ⁻¹)	5.4	5.9	–	7.1	9	2.85	4.10	–	6.5	–
Volume resistivity (Wcm)	10 ¹⁵	–	–	–	10 ¹⁰	10 ¹⁶	–	–	–	–
Dielectric constant at 25°C and 10 ⁶ Hz	6.6	6.9	–	6.9	6.2	5.3	6.2 ^c	–	8.1	–
Dielectric constant at 25°C and 10 ¹⁰ Hz	6.11	7.0	–	–	–	5.2	–	5.21	–	–
Loss tangent at 25°C and 10 ¹⁰ Hz (10 ⁻³)	3.9	–	–	–	–	–	1.5 ^c	6.8	–	–

^aThe liquidus temperature is the highest temperature at which a glass, if held there sufficiently long, will develop crystals. The greater the difference between this and fiberising temperature, the more stable the fibre-forming process with respect to process interruptions caused by crystals forming in the glass.

^bIndicates temperature at which the viscosity of the glass is 10³P.

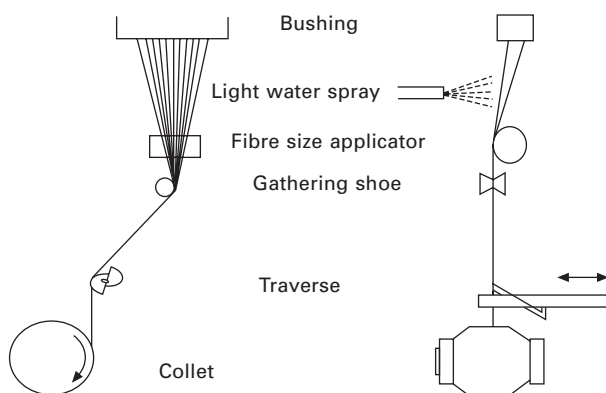
^cMeasured at 10⁶ Hz.

are attenuated by high velocity air and combustion gases or steam into fine (<10 mm diameter) fibres which are several centimetres in length. A binder is applied to the glass fibres just below the spinner and the discontinuous filaments move through the 'forming hood' and are collected on a moving chain belt. The function of the forming hood is to distribute the fibres evenly and in a random alignment across the width and length of the moving chain. The chain continues through an oven which dries and cures the binder. The wool mat is then cut into appropriate lengths and widths and packaged. Because the fibres are thermally quenched at high rates, the density of the glass is less than the density of the same composition which had been cooled slowly (annealed).

15.4.2 Continuous filament process

While the wool manufacturing process produces fibres of varying length and diameter, the process used to produce filaments for reinforcement purposes produces fibres with small diameter (most reinforcement fibres have diameters between 9 and 25 μm) with a relatively narrow diameter distribution (e.g., one standard deviation of the fibre diameter is normally less than 8% of the mean diameter). In addition, the fibres are typically produced in packages with strand lengths up to 10 km. (A strand is a collection of typically a hundred to several thousand fibres.)

Figure 15.4 shows a schematic representation of a typical continuous filament fibreglass production process. The continuous fibres are produced using bushings (sometimes called spinarets) which have a few hundred to several thousand small tubes (or tips) in the bottom (a flat plate) of the



15.4 Schematic of a typical continuous filament fibreglass production process. The left side of the figure represents the view from the front of the bushing. The right side of the figure represents the view from the end of the bushing.

bushing. One fibre is produced from each tip. The temperature of the glass exiting the tip is typically in the range of 1150–1300 °C, depending upon the composition of the glass. The bushings are typically made from an alloy of platinum and rhodium. The rhodium improves the high temperature mechanical properties of the bushing. Attempts to utilise ceramic oxides to coat or strengthen the bushing have not been commercially successful for continuous filament large tonnage fibreglass compositions.

The glass will normally flow out of the bushing under the force of gravity into fibres on the order of 1 mm diameter. The final diameter of the glass fibre is a strong function of the tension applied to the fibre as it is being drawn. Tension increases with lower glass temperatures (higher glass viscosity) and with higher pull speeds. Both temperature and pull speeds are process variables that are adjusted to obtain the desired fibre diameter. Typically, lower pull speeds are utilised for large diameter fibres and high pull speeds are utilised with small diameter fibres. In commercial production operations, the pull speed of the fibre is produced by winding the fibres around a rotating tube (collet) placed 1–4 m below the bushing. In addition to collecting long lengths of the strands of fibreglass, the rotation of the tube applies stress to the fibre and stretches the fibres to their final diameter. This force on the fibres also results in the glass moving through the tips at a higher velocity than is attained from gravity only. The linear pull speeds typically range from a few m/s to more than 30 m/s. This results in the glass fibre velocity increasing from a few mm/s through the bushing tip to as high as 30 m/s (108 km/h) over a distance of a few centimetres.

In some processes, the continuous filaments are not collected on a tube but instead are chopped into short lengths (a few millimetres to a few centimetres in length). In this process, a large wheel serves the same function (pulling the filaments) as the collet in Fig. 15.4. The fibres are cut into the short lengths while the strand is in contact with the wheel by a smaller rotating wheel which has a series of blades. These blades cut (or more precisely break) the continuous filaments into bundles of the appropriate length.

Clean air and water (a fine mist) are introduced into the area just below the bushing to help remove the heat from the vicinity of the bushing and cool the individual fibres. The thermal quench rates which the fibres undergo are the highest quench rate of any high volume commercial process. These quench rates are typically in the range of 500 000–1 000 000 K s⁻¹.

Because of the high quench rates and acceleration of the fibres, the structure of the glass fibres is of a more open nature (lower density) than if the fibres had been cooled slowly. Fine fibres are cooled more quickly than more coarse fibres. As a result, as-formed large diameter fibres will typically have a higher density than small diameter fibres of the same glass composition.

The marble process

In the early days of continuous fibre operations, the glass was made into marbles. The marbles were produced by a machine similar to a bottle making machine in that the glass stream coming out of the forehearth was cut into individual 'gobs'. These gobs dropped into a marble machine which rolled the gob into a sphere. These marbles would be cooled and shipped to a facility where the marbles were remelted in specially designed bushings and drawn into continuous filaments. Originally, the marble process could produce higher glass quality (good chemical homogeneity, low bubble populations, etc.). Now comparable glass quality can be obtained with large continuous melt furnaces so the marble process is being phased out. Because of the remelt process, the energy required to produce continuous fibres from marbles is higher. However, the continuous filament process described above involves a huge furnace and tank in which the mineral batch is continuously melted, refined and homogenised as it flows into the tank immediately above the bushing. However, for smaller specialist fibre drawing, the marble process is still used. One advantage of remelting on a smaller scale is that the fibres exiting the bushing can be quenched rapidly without the need for water spray. More details are given by Mohr and Rowe (32).

15.5 Strength of glass fibres

Table 15.3 gives the typical properties of a range of glass fibres. The modulus of E-glass is very much a function of the chemical forces operating within the amorphous network. As the number and strength of the chemical bonds in the three-dimensional network decrease and/or become weaker, the modulus of the glass will decrease. Thus, the introduction of network modifiers such as alkali or alkaline earth oxides will decrease the moduli of the various glasses. Typical glass formulations used for continuous filament applications will have Young's moduli in the order of 70–80 GPa. Similarly, the tensile strength of the fibres will vary with the composition of the glass. For typical E-type glasses, the tensile strength of filaments collected without contacting other filaments will have tensile strengths around 3.5 GPa. Pure silica glass filaments collected in the same way will exhibit tensile strengths up to about 7 GPa. The introduction of alkali network modifiers can reduce the tensile strength of the fibres to around 2.5 to 3 GPa. Borate glasses, phosphate glasses and lead silicate glasses typically have strengths of approximately 1–2 GPa.

While tensile strength as typically determined is a function of composition, it is not a fundamental material property because it depends heavily on the presence of defects and flaws within the structure. Although the actual flaw responsible for the strength of a glass is still uncertain, molecular dynamics

simulations are starting to give us insights into the mechanism of brittle fracture (33).

15.5.1 Griffith theory of strength

It has been established by Griffith (34) that the strength of glass is a strong function of the presence of flaws or defects in the material. He used the spinning of glass fibres to validate the theory of strength. Equation 15.6 defines the critical stress before fracture where γ is the surface-free energy of the solid, E is the modulus, c is the crack length. If we assume that a micro-crack exists at the surface, we can substitute half the depth of the micro-crack for the crack length c in equation 15.6 to obtain the maximum technical strength (σ_m) of the glass (eqn 15.7).

$$\sigma_k = 2 \sqrt{\frac{\gamma E}{c\pi}} \quad 15.6$$

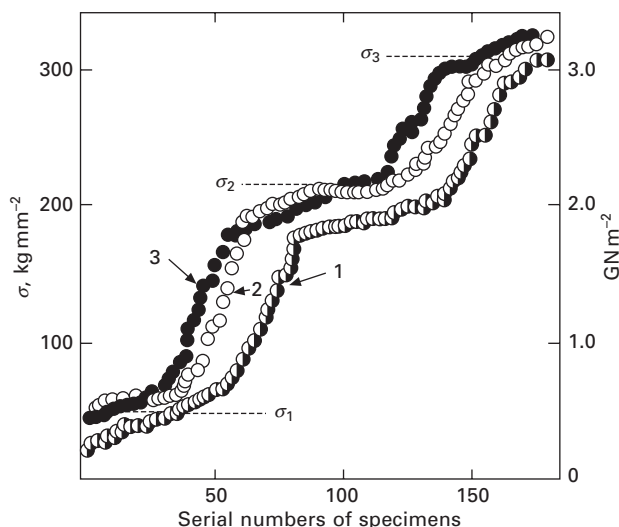
$$\sigma_m = \sqrt{\frac{2\gamma E}{\pi\ell}} \quad 15.7$$

where ℓ is the depth of a surface crack which is half that of an inner flaw.

Thus the strength is a function of the surface free energy created when the crack propagates. The surface free energy of glass changes from 122 erg/cm² to 290 erg/cm² in the presence of water which is the explanation for the observation of static fatigue. Thus, in the presence of flaws the theoretical strength of approximately $E/10$ is reduced further. Thus a glass with a Young's modulus of 70 GPa would have a theoretical strength of 7 GPa, but its practical strength could be as low as 0.07 GPa (35) for bulk glass. Converting bulk glass into fibres reduces the probability of the presence of a strength reducing flaw enabling the actual strength to be nearer to the theoretical. However, to reduce the development of surface flaws, methods have been developed to coat the fibre with a polymer or otherwise hermetically seal the fibre to protect it from damage and attack by moisture. Fibre strengths approaching the theoretical $E/10$ value can be obtained with such processes.

15.5.2 Theories of fibre strength and structure

The explanation for the distribution of fibre strength is dominated by the ideas of Metcalfe and Schmitz (36) and Bartenev (37). Figure 15.5 illustrates the observation of three strength levels in fibre population (38, 39).



15.5 Distribution of strength values for three series of industrial glass fibre specimens 10 μm in diameter in order of serial number. (1) Average strength 1.48 GPa, specimen length 40 mm ($\bigcirc$). (2) 1.76 GPa and 25 mm ($\bigcirc$). (3) 1.89 GPa and 25 mm ($\bullet$) (after Bartenev and Izmailova (37, 41). Reproduced from McCrum (38) with permission of the Controller, Her Majesty's Stationery Office, London.

Concepts of Metcalfe and Schmitz (36)

These authors used a statistical analysis to conclude that the fibres had a distribution of flaws of different severity, which gave rise to the differing populations of strength. The fibres of average strength of 3 GPa could be attributed to severe surface flaws of 20 mm spacing.

The population of average strength of 4.5 GPa could be attributed to flaws of 0.1 mm spacing. The population of average strength of 5 GPa could be attributed to internal defects of 10^{-4} mm spacing, characteristic of a defect-free filament with an uninterrupted surface layer.

Hand and Seddon (40) have attempted to identify the Griffith flaws responsible for the strength of a glass network and have associated these defects within the random structure of the glass network.

Concepts of Bartenev (37)

Figure 15.5 shows the distribution of strengths in 175 specimens of industrial alkaline-free aluminium boro-silicate glass fibre of diameter 10 mm, with gauge lengths of 25 and 40 mm. As with Metcalfe and Schmitz (36), three levels of strength are apparent in the distribution: σ_1 is the lowest strength, σ_2 the intermediate strength and σ_3 the maximum strength. The population

of highest strength, at 3 GPa, is considered to be determined by the presence of a tempered surface layer of 10 nm thickness, because after treatment with hydrogen fluoride, to remove a 10 nm surface layer, the strength decreased to the σ_2 level of 2.0 GPa. σ_2 was considered characteristic of a flawless glass where the strength was determined by structural heterogeneities within the glass. This was confirmed because heat-treated fibres required 60 nm etching before the strength returned to the magnitude of σ_2 .

Furthermore, industrial glass fibres, after prolonged storage, required the removal by etching of 40 nm before the strength returned σ_2 . They also demonstrated that heat treated fibres have a lower level of strength, to σ_0 of 0.821 GPa. In summary, Bartenev and coworkers (37, 38, 39) identified six strength levels within inorganic glasses, ranging from 0.05 to 3 GPa. The maximum strength observed was 10–20 GPa. They also pointed out that the data in Fig. 15.5 would move to the right after heat treatment, indicating a higher population of fibres of σ_1 and σ_2 strengths. Thus, the strength of these glass fibres was attributed to a tempered surface layer of 10 nm thick arising from the cooling of the polymeric inorganic glass and viscoelastic deformation. The tempered layer was considered either to exhibit a compressive thermal stress or to have a more uniform molecular structure.

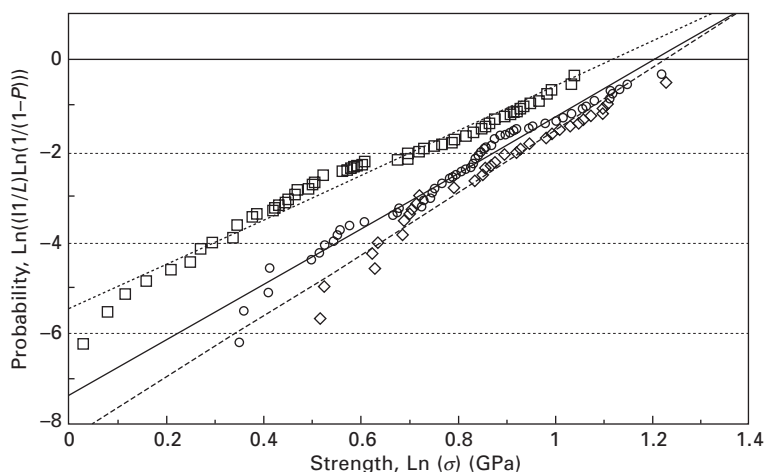
Fibre strength-summary

As described above, the theories of fibre strength discuss the population and size of strength reducing flaws. The role of a tempered surface layer is not generally accepted because for a 10 μm fibre the temperature gradient across the fibre is calculated to be less than 5 K which would be insufficient to set up a tempered layer. Therefore, the drawing of fibres under clean conditions with a very low concentration of surface flaws, is probably more important. This can also explain the diameter-dependence of strength (41). Low tensile strength can be attributed to significant flaws, such as partially melted batch material.

15.5.3 Weibull statistics of strength

It is clear from Fig. 15.5 (36, 37) that the distribution of strengths within one continuous fibre or within a bundle of glass fibres can be characterised by a statistical method. The Weibull statistical method is commonly used to describe the distribution of strengths. This can be used to enable the strengths of fibres at different lengths to be analysed. First, the strength is strongly dependent on the gauge length of the fibre under test, and this can lead to uncertainty about the correct value of strength to be used in any predictive analyses of mechanical properties.

Figure 15.6 shows the typical Weibull plot for the strength of glass fibres



15.6 Weibull plots for three laboratory coated E-glass fibres showing differing protective abilities. $\square$ = Pure γ -APS (Sigma Chemicals); $\circ$ = commercial γ -APS (A1100); $\times$ = polydimethyl siloxane. The values of the Weibull parameter m and the characteristic strength σ_0 are, respectively 4.88, 3.1 GPa; 6.1, 3.4 GPa; 6.7, 3.4 GPa. L = gauge length of fibres tested (= 6.35 mm); P = probability of failure (19).

with different treatments (19), Marks and Jones (43) have also studied the effect of plasma polymer coatings on the statistics of strengths of glass fibres, and these are summarised in Table 15.4. The role of surface defects on fibre strengths again comes to the fore since manipulating the fibres for plasma polymer coating reduced the fibre strength from 1.46 to 1.35 GPa and the Weibull modulus (m) from 3.10 to 1.65. The latter shows that the distribution of fibre strength was also much broader. It confirms the benefit of polymer coatings in protecting strength. Note that the relatively low strengths arise from the fact that as-received fibres were water-sized and not coated with a polymeric size on manufacture.

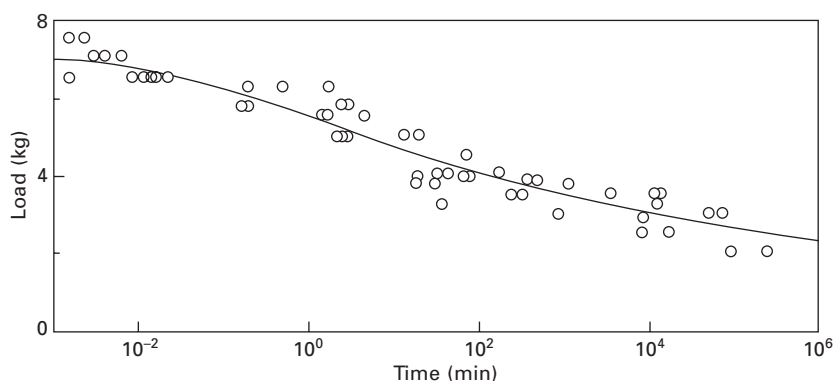
15.5.4 Static fatigue of glass fibre

Glass fibres suffer from time-dependent fracture under load. This is referred to as static fatigue (44, 45). This differs from the conventional use of the word, fatigue, in so far that the load is constant. Static fatigue of glass fibres is illustrated in Fig. 15.7 (44, 45). This shows the time dependence of fibre strength as a function of time at a constant temperature in distilled water. This illustrates that the static fatigue phenomenon is, in effect, a stress corrosion phenomenon. Water is the effective reagent and only in high vacuum is the time dependence of strength absent. It is worse in alkali glasses because the sodium ion, Na^+ , acts as a catalyst for the hydrolysis of the silica network the degradation of the silica network as shown below.

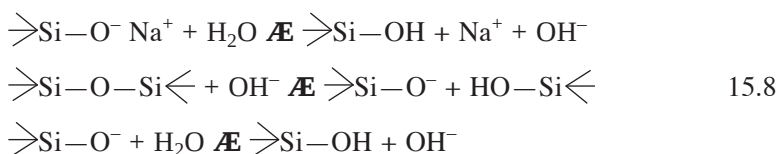
Table 15.4 Single filament strength of plasma polymer coated E-glass fibres (43)

Fibre type/plasma copolymer	Average failure stress (GPa)	Weibull modulus
90% Acrylic acid/10% 1,7-octadiene	1.33 ± 0.56	3.94
0% Acrylic acid/100% 1,7-octadiene	1.58 ± 0.64	3.58
Unsize (as-received fibres)	1.46 ± 0.8	3.10
Unsize (after spreading tow, and travelling through the uncharged reactor)	1.35 ± 0.7	1.65

Note: The unsize fibres were water sized and stored before use.



15.7 Static fatigue of E-glass strands in distilled water. A load of 2 kg caused an applied strain of 0.5%. Redrawn from Aveston *et al.* (44) and Jones (45).



Static fatigue occurs in three stages, giving rise to differing time dependence, depending on the load applied. In stage one, where the fracture behaviour is largely dominated by the mechanics of crack growth, the static fatigue phenomenon is considered to be sodium ion diffusion rate determining. In stage two, which is the stress corrosion region, a synergism exists between the applied load and the environment because the rate of crack growth is equal to the rate of corrosion. Thus, the crack always remains sharp and propagates into the weakened material.

Stage three occurs through stress-assisted corrosion, where the effect of stress on the failure time is much less significant. This is because the rate of hydrolysis of the silica network is higher than the rate of crack growth. According to the theory of Charles (46), the crack tip is blunted by corrosion so that the stress concentration at the crack tip is reduced. The rounding

results in a reduction in the radius (ρ) of the propagating crack so that in accordance with equation 15.9 a higher load is required for the crack to propagate at the same rate:

$$s_{\max} = 2s_a \left(\frac{E_x}{E_r} \right)^{1/2} \quad 15.9$$

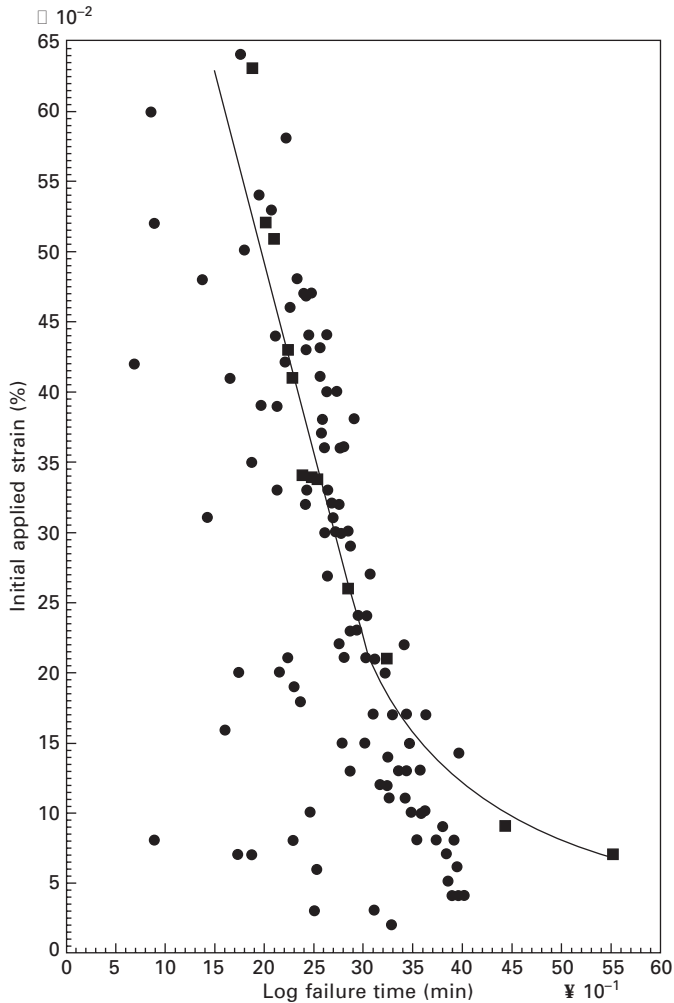
where x is the crack length.

Ghosh (47) has studied sub-critical crack growth in E glass and measured the static fatigue limit of threshold stress intensity factor (K_{th}) which had a value of $0.15 \pm 0.04 \text{ MN m}^{-2/3}$ which compares to the critical stress intensity factor (K_{Ic}) of $0.93 \pm 0.03 \text{ MN m}^{-3/2}$ for monotonic mode I loading. In order to predict the time-to-failure of a filament, the stress corrosion exponent to K_{th} is required, for the calculation crack growth rate. This can be estimated from the strain rate dependence of fibre strength. For a bundle of fibres (as a model for a composite) this needs to be combined with Weibull statistics (48).

The static fatigue of glass fibres will determine the maximum life of any structural material based on glass fibres. In a composite material, where resin is used to bind the fibres together, the rate of moisture diffusion will be a controlling factor and, as such, the protection given by a well-bonded resin matrix can extend the life of the structure significantly. Under these circumstances diffusion of moisture through the resin becomes an important predictive parameter for the life of the structure. It is also important to ensure that the interfacial bond between the glass fibre and any matrix is maintained in the presence of moisture, otherwise the capillary reaction associated with a poor interface would dominate the failure process. While interfacial failure may not necessarily lead to a brittle fracture, it can reduce the strength of a composite material significantly.

Environmental stress corrosion

In the presence of moisture, E-glass fibres have a reduced lifetime under load as indicated by the static fatigue described above. However, in the presence of more severe degrading environments, usually of low pH, brittle fracture can be initiated (Fig 15.8). This is referred to as environmental stress corrosion cracking (ESCC). Also included in Fig 15.8 are comparative failure times for composite materials showing the direct link between time-dependent fracture of glass fibres and the failure of an epoxy composite. As with static fatigue, there is a synergism between the stress and the chemistry as described above for stage 2. Clearly with a more corrosive environment, the load at which the crack propagates at the same rate as the corrosion leads to a brittle fracture at a lower load than for water alone. In alkaline environments the rate of



15.8 The stress corrosion failure times of single E glass filaments (●) and their epoxy resin composites (■) in 0.5M aqueous sulphuric acid. An error of $\pm 10\%$ in applied strain for $10\mu\text{m}$ single filaments (redrawn from Jones *et al.*) (49).

corrosion is relatively slow so that the phenomenon observed is mostly that of stress-assisted corrosion, rather than environmental stress cracking. In acidic environments corrosion of the glass is highly pH dependent and at acidities at which the glass modifiers can be readily dissolved then the fracture of the glass can occur at strains as low as 0.1%. The network modifiers which are involved in the corrosion process are those associated with Ca^{2+} , Al^{3+} , Mg^{2+} , Na^+ and K^+ . This means that glasses which have reduced aluminium concentration and alkali concentration can have more

resistance to environmental stress cracking. ECR glass, or chemical resistant E-glass, is an example of these phenomena. High strength glasses, such as S2[®] glass, also exhibit good resistance to stress corrosion cracking.

Owens Corning has recently introduced to the market Advantex^{®2} glass fibres. These are based on boron-free, fluorine-free E-glass compositions (Table 15.2). As such, they tend to be closer in structure to the ECR glass and have brought a higher chemical resistance to the commercial 'E-glass fibres'.

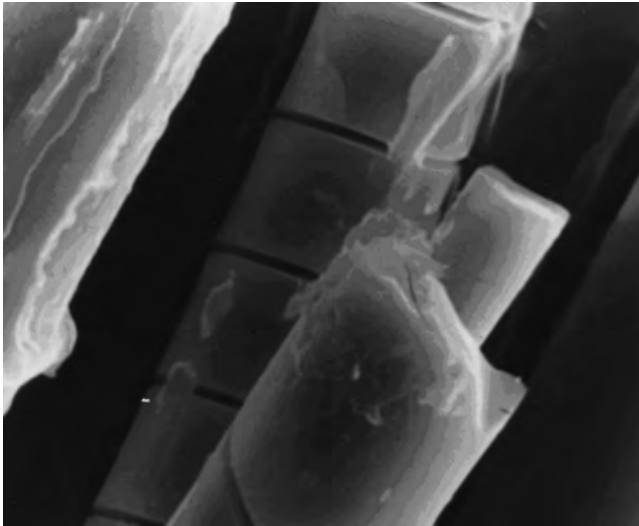
Of particular relevance to the structure of glass fibres is the phenomenon that the extractions of alkali and other network modifiers from the glass fibre can lead to spiral cracking of unstressed fibres (50) after storage in aqueous acid (Fig 15.9). While it is not clear whether the formation of the spiral crack is the result of drying during electron microscopic examination, one could assume that the formation of a weakened sheath on the fibre surface implies that the structure of the glass is not homogeneous. This is consistent with the Bartenev model (Section 15.5.2). However, there are only limited studies on the effect of annealing on this phenomenon. However, slight inhomogeneities within the glass fibre structure certainly contribute to the static fatigue and ESCC phenomena.

Figure 15.10 demonstrates how the retained strength of unloaded E-glass fibres is affected by the pH of the environment (51). E-glass fibres have the least durability in an acidic pH of 0.5. This can be explained by the thermodynamics of the interaction of aqueous solutions with the glass. Figure 15.11 shows how the solubility of the different glass modifiers varies with pH (45, 52). It can be seen that below pH 9, aluminium is soluble and similarly above a pH of about 10.5, calcium is insoluble. As a result, in mildly alkaline environments the network modifiers become mobile in the aqueous environment, but can be precipitated at higher pH. At pH above 10, the silica network becomes hydrolysable and the ions then become soluble as various silicate salts. In this way, the corrosion rate in alkali is increased.

Effect of composition

Following the discussions above, the strength of a glass fibre is generally a function of chemical composition and microstructural features. The microstructural features which are responsible can be induced through the drawing conditions, thermal history, environmental effects and those which can introduce surface defects. Experimental studies show that the highest strength is achieved in melted quartz and S glass which has a composition near to MgO, Al₂O₃, SiO₂ eutectic (53, 54).

²OCA intellectual Capital LLC.



(a)

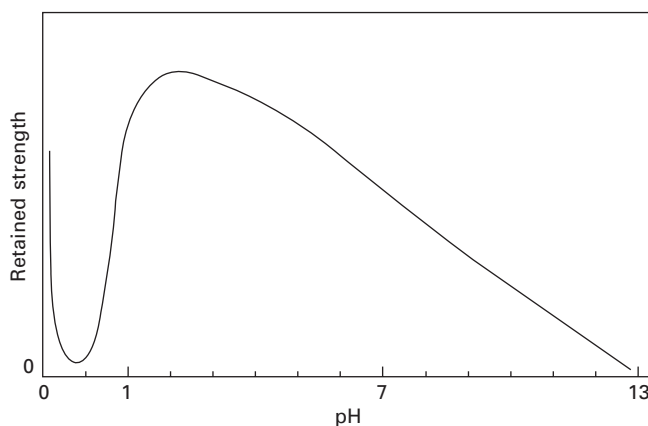


(b)

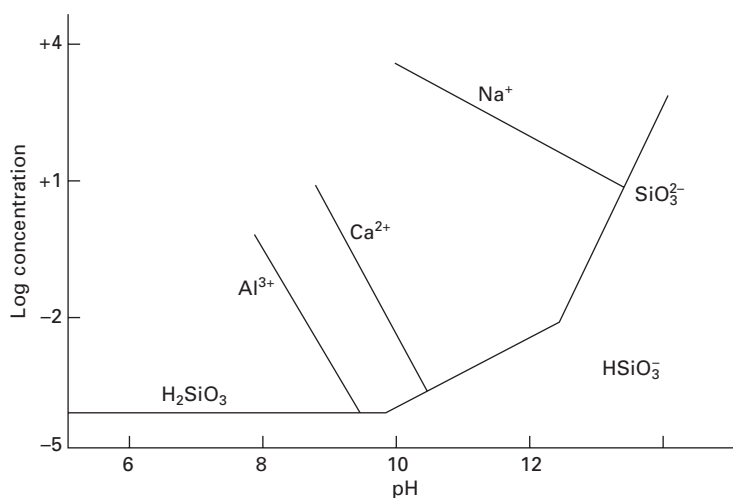
15.9 (a) E-glass fibres showing 'spiral cracking' after immersion in 0.5M aqueous sulphuric acid. (b) Stress-corroded fracture surface of an E-glass fibre showing core sheath structure (50).

Khazanov (53) and Aslanova (55, 56) have classified glass fibres into three groups:

- Fibres of high strength (5–7 GPa) from quartz or S-2[®] glass composition.
- Fibres of intermediate strength (2.5–3 GPa) of aluminosilicate composition.
- Fibres of low strength (1–2 GPa) borate, phosphate and multi-alkali glasses.

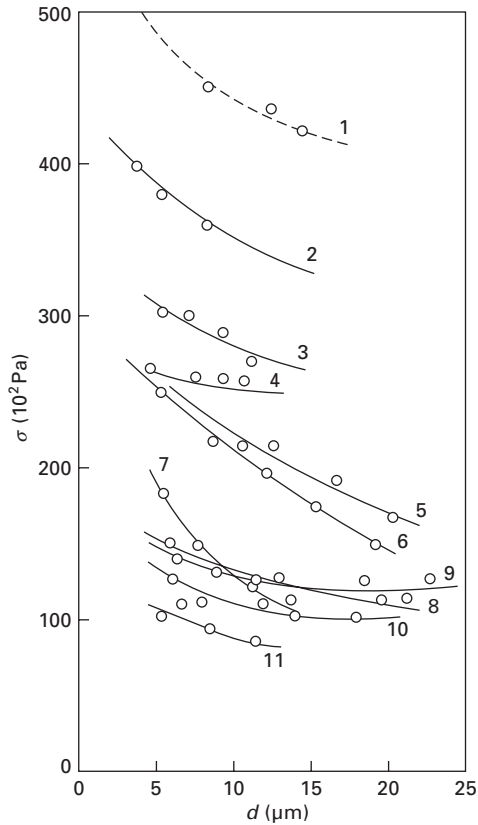


15.10 Schematic of the retained strength of unloaded E-glass fibres in environments of differing acidity and alkalinity (redrawn from Jones (45) and Cockram (51)).



15.11 Thermodynamic calculations of the aqueous solubility of differing glass components at differing pH (after Jones (45) and Fox (52)).

Figure 15.12 shows the range of strengths for a variety of glasses as a function of diameter. The filaments were captured between the bushing and before the fibres were wound-up from high temperature, low viscosity melts, structural non-uniform (e.g. borosilicates) and low chemical resistance (e.g. sodium silicate or high boron oxide) glasses had a weak dependence on diameter. Thus, high performance glass fibres tend to come from compositions where there is a strong diameter effect which demonstrates that introduced

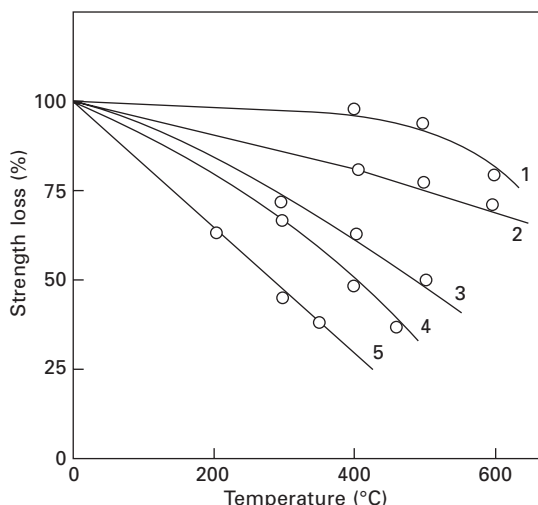


15.12 Dependence of strength of the glass fibres of various chemical compositions on diameter. 1, 2, magnesium aluminosilicate containing 10 and 20 wt% respectively of MgO; 3, zinc titanium magnesium of aluminosilicate; 4, sodium calcium aluminosilicate; 5, E type aluminoborosilicate; 6, copper aluminoborosilicate; 7, sodium calcium aluminosilicate; 8, borate; 9, lead; 10, phosphate; 11, sodium silicate (redrawn from 53).

flaws and defects were important. These glasses were mainly those with strong structural bonding and, hence, higher moduli. In the seminal work of Thomas (42), it was demonstrated that under careful control of the fibre drawing process, the strength-diameter phenomenon was absent for E-glass. Thus, with these glasses fibre drawing conditions are critical to the production of high strength fibres (54, 56).

Thermal effects

After heat treatment, glass fibres exhibit a reduced strength. Figure 15.13 shows how fibres of differing composition respond to heat treatment. Quartz



15.13 Influence of chemical composition of glass on glass fibre strength after heat treatment: 1, quartz; 2, silica; 3, alkali-free aluminoborosilicate; 4, sodium calcium silicate; 5, borate (redrawn from 53).

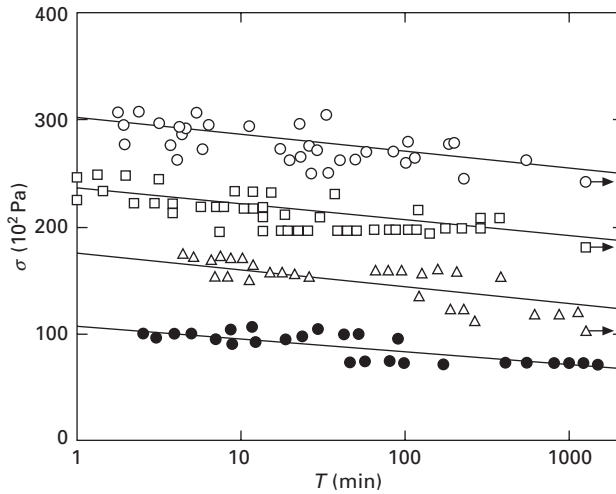
fibres are the most resistant only showing an effect above 600 °C, whereas borate glasses appear to show a linear degradation in strength even at temperatures < 200 °C. A heating–cooling cycle can induce a reduction in strength through the following mechanisms:

- network hydrolysis (see Section 15.5.4);
- annealing of compressive tempered layers;
- devitrification of the glass.

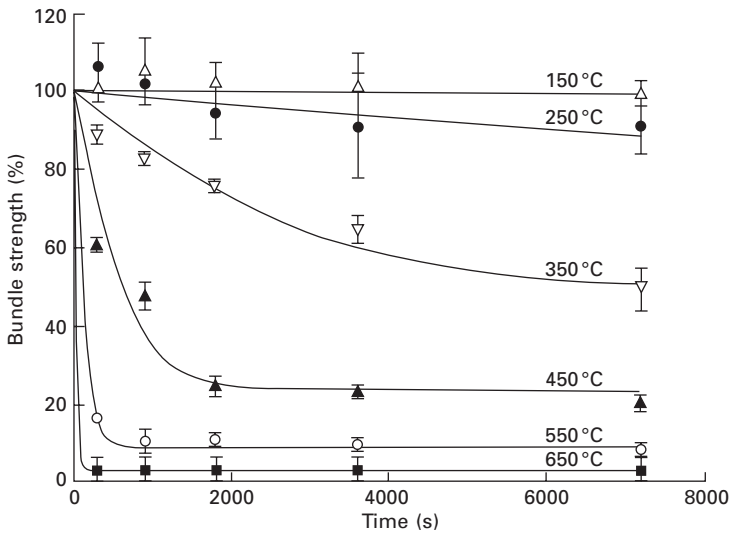
The time dependence of glass fibre strength (static fatigue) is independent of temperature as shown in Fig. 15.14, demonstrating that the dominating mechanism is one of network hydrolysis. Nishioka and Schramke (57) have shown how water is lost from the surface at temperatures near 300 °C and from the bulk at higher temperatures.

Thus, commercial fibre glasses tend to exhibit degradation in strength as a result of interactions with water. Equation 15.8 shows that alkaline ions such as sodium or potassium are catalysts for hydrolysis so that more recent commercialised glass fibres which are closer in composition to S-2 glass can be expected to have reduced strength sensitivity at high temperatures.

Most recently, Feih *et al.* (58) have re-examined the temperature dependence of commercial E-glass in the context of residual strength of glass fibre composites in fire. Figure 15.15 shows the temperature dependence of sized E-glass bundles of 300 tex. The most important observation is that temperatures in excess of 250 °C have a major effect on fibre strength. This data further



15.14 Time dependence of E-type glass fibre strength at various temperatures: ○, 124°C; □, 400°C; △, 500°C; ●, 600°C (redrawn from 53).



15.15 Effect of time and temperature on E-glass fibre bundle strength (58).

supports the silica network hydrolysis mechanism. Below $\approx 300^\circ\text{C}$ surface silanol groups will tend to condense to siloxane bonds, whereas above this temperature hydrolysis will dominate.



The clear switch from strength stability below 300 °C can be attributed to the thermodynamics of the above reaction. As with any chemical reaction, the rate of hydrolysis is a function of the presence of catalysts. Since the alkali metal glass modifiers (sodium/potassium) catalyse hydrolysis, alkali metal-free glasses are expected to show more resistance to high temperature excursions.

15.5.5 Protection of fibres for strength retention

Sizings and binders

In production, commercial glass fibres are immediately coated at the bushing with a polymeric sizing. An aqueous-based emulsion is generally used for coating the fibres in contact with a rubber or graphite roller. There are many designs of sizing applicators, but usually they involve the fibres touching a roller which is in contact with the aqueous-based size. One role of the sizing is to provide the fibre surface with protection during handling and transport for the manufacture of artefacts such as woven textiles, preforms or composite materials. In addition, the sizing is chosen to provide strength protection and compatibility with the matrix into which the fibres will be incorporated. The sizing is also chosen to suit the manufacturing process for the composite material. For example, where the maintenance of strand integrity or slow wet out is needed in certain manufacturing processes, hard-sized fibres with reduced sizing solubility are used. Where preforms or fibre mats are employed, a secondary binder is used to hold the fibres together during manufacture. Therefore, the finish, which is applied to a glass fibre, typically consists of (a) an adhesion promoter which is often a silane coupling agent, (b) a protective polymeric film former, (c) lubricants of different composition to aid the flow of the fibres through machinery without damage, (d) differing surfactants used in the emulsification of the polymeric film former and (e) an optional polymeric binder. A typical emulsion applied to the glass fibre will have a solid content of approximately 10% of which 0.3–0.6% will be the silane coupling agent. The film former will be an appropriate compatible polymer which can be either emulsified or synthesised as a polymer emulsion. A lubricant is usually present in the emulsion at a concentration of 0–0.3%. A surfactant is often added at a level of 0–0.5%, while an antistatic agent may also be used at a loading of 0–0.3%.

The term ‘sizing’ may refer to the film former polymer, as well as the compounded finish, sometimes independently of the silane coupling agent, which is used as an adhesion promoter. The generic term ‘finish’ universally refers to the deposited solids on the glass fibre and will include any optional binder in the case of fibre mats and textiles. The film former is used to impart good handleability and control wet out kinetics for the manufacture of composite materials and is therefore chosen for compatibility with the matrix

as well as the choice of fabrication process. For specialist applications such as those requiring environmental resistance, the chemical nature of the film former and/or the binder should be chosen to have excellent compatibility with the resin matrix, otherwise the interface can fail during service, giving rise to a low durability composite.

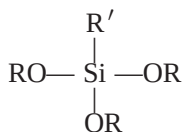
The film former needs to satisfy a number of criteria: (a) compatibility with coupling agents and other components of size, (b) a stable emulsion during application at the bushing, (c) good handling characteristics of the roving after the drying of the package, (d) for textile rovings and similar structures the sizing needs to allow the fibres to be unwound for repackaging, (e) the wet out rate in the resin matrix and (f) to achieve good hot/wet properties for the composite materials.

Since emulsion technology is used in the preparation of the coating on the fibres, the sizing deposited onto a typical glass fibre has a very complex chemistry. Typical surfactants are polyoxyethylene monophenyl ethers. Typical lubricants are fatty acid amides which are protonated in the presence of the acetic acid used to adjust the pH of the sizing emulsion. The cationic quaternary ammonium sites have an affinity to the negatively charged glass surface providing the glass with the lubricated structure. The build up of static electricity during the use of glass fibre rovings can also lead to degradation of the structure of the rovings and other phenomena associated with fabrication breakdown. Therefore, anti-static agents such as the alkyltrimethyl ammonium chloride are used to impart surface conductivity to the roving (18, 19).

Silane coupling agents and the structure of hydrolysed silanes on glass surface

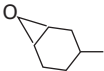
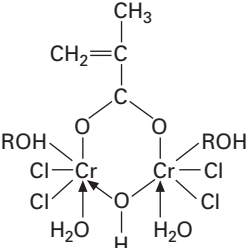
Adhesion promoters are added to the sizing emulsion to provide the glass with compatibility and chemical reactivity to the appropriate matrix. The silane needs to displace adsorbed water from the glass surface to create a hydrophobic surface with the correct thermodynamic characteristics for complete wetting by the matrix resin. This aids in developing a strong interfacial bond between the fibre and the polymeric resin.

Table 15.5 gives details of typical silane coupling agents (19, 59) which are used to promote adhesion between polymers and the glass fibres. The majority of them are trialkoxy organo silanes with a generic structure as given below:

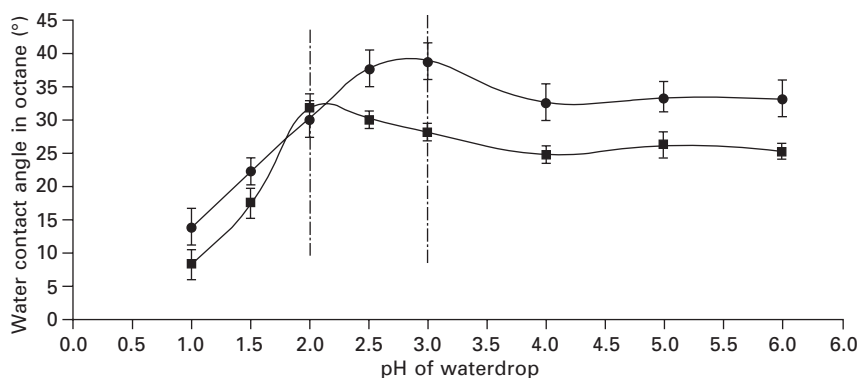


where R' is a polymer-compatible or reactable organic group. R is either ethyl or methyl.

Table 15.5 Typical coupling agents for glass fibre–resin adhesion (19, 59)

Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$
Epoxy	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \\ \\ \text{CH}_3 \end{array}$
Methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Primary amine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Mercapto	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Cationic styryl	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3\text{HCl}$
Cationic methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{COOCH}_2\text{CH}_2-\text{N}(\text{Me}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \\ \text{Cl}^- \\ + \end{array}$
Cycloaliphatic epoxide	 $\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
Titanate	$[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}]_3\text{TiOCH}(\text{CH}_3)_2$
Chrome complex	

In the aqueous emulsion, the alkoxy groups are hydrolysed into hydroxyl groups. Depending on the pH of the emulsion, the rate of hydrolysis can vary. The pH is often chosen to be slightly acidic at a pH of 4. Under these conditions, the rates of hydrolysis and polycondensation are such that oligomeric siloxane polymers are formed which are deposited together with oligomers and monomers onto the glass fibre surface. As shown in Fig. 15.16, the deposit on glass fibre is a complex crosslinked polymer containing oligomers of varying degrees of polymerisation which depends on the relative rate constants for silanol polycondensation and alkoxy hydrolysis. The polycondensation of the alkoxy groups is an equilibrium polymerisation whose floor concentration is of the order of 0.1%. This means that above this concentration, silanol polymers form in the aqueous solution, whereas below it monomeric trihydroxysilanes are more stable. Therefore, for monomeric-type silane deposits the concentration of silanol in the sizing solution has to be very low. Typically, the concentration of silane in the sizing emulsion is $\approx 0.5\%$, so that there will always be a mixture of oligomeric silanols of differing degrees of polycondensation. Since the floor concentrations of the



15.17 The effect of pH of water on the contact angle of E-glass ($39 \pm 3^\circ$) ($\blacklozenge$), boron-free E-glass ($\blacksquare$) ($32 \pm 2^\circ$). It is calculated that E-glass surface has $2.29 \pm 0.04 \text{ nm}^{-2}$ and boron-free E-glass surface has $2.38 \pm 0.03 \text{ OH nm}^{-2}$ (61).

remaining crosslinked component can then accept the penetration of the matrix resin to form an interpenetrating network.

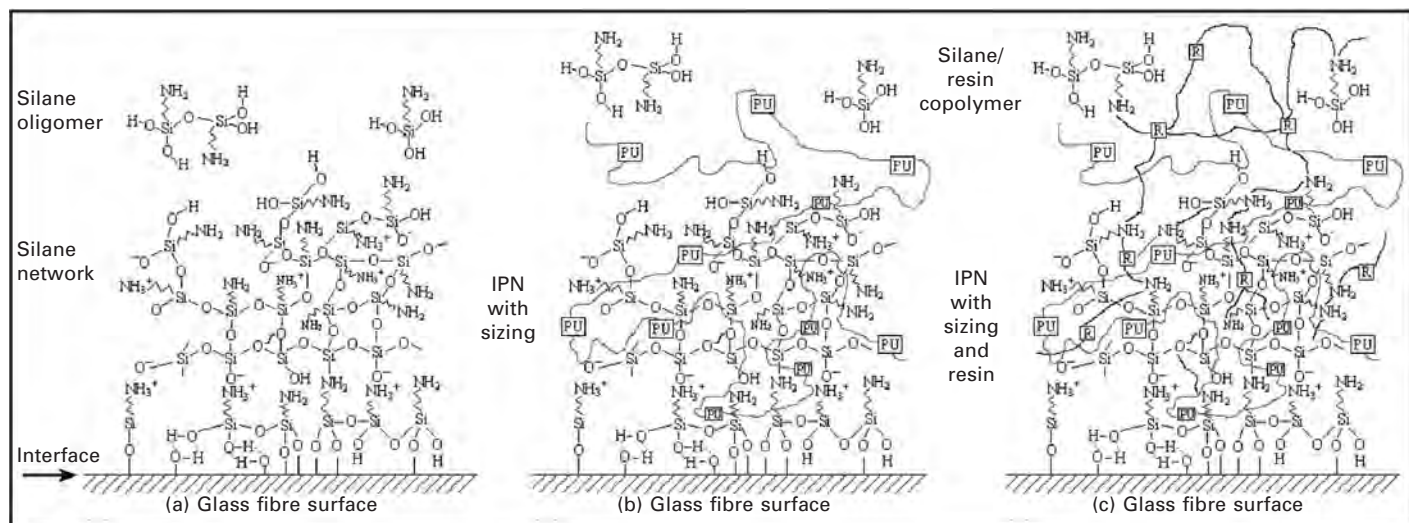
The silane sizing/matrix interphase

Because of the presence of other matrix-soluble components (65) within the sizing, the interphase region which forms will consist of a semi-interpenetrating network between the silane and the resin, together with dissolved surfactants and monomeric and oligomeric silanols which have diffused over a longer length scale. The interphase region, therefore, has a dimension determined not just by the thickness of the silanol deposit, but also on the diffusional length scale of the other additives, which includes the film former. Figure 15.18 illustrates schematically the structure of the interphase which forms in a composite (66).

A further complication arises because of the sensitivity of the E-glass to the aqueous environment of the sizing emulsion. It is reported (67, 68) that certain elements of the glass structure are solubilised in the presence of an alkaline or acidic pH. As a result, it is possible to observe the presence of glass elements within the surface coatings on glass fibres. It has been shown by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF SIMS) analysis that the silanised glass fibre surface has an enriched concentration of aluminium. It appears that aluminium can be extracted from the surface of the E-glass and become copolymerised into the silane deposit. A further consequence of this is that the glass surface becomes denuded of these ions, enabling penetration of the silane into the surface of the glass fibre. Therefore, the interphase region within a glass fibre composite can extend into the subsurface of the glass fibre. The structure of a silanised

Table 15.6 The maximum water contact angle (CA_{max}) and calculated concentrations of hydroxyl groups on a variety of E-glass and boron-free E-glass surfaces (61)

	E-glass	Boron-free E-glass	Dehydrolysed E-glass	Dehydrolysed boron-free E-glass	Rehydrolysed E-glass	Rehydrolysed boron-free E-glass
CA_{max}	39 ± 3	32 ± 2	71 ± 2	61 ± 2	52 ± 3	47 ± 5
pH	3	2	3	2	3	2
$n_{\text{OH}}(\text{nm}^{-2})$	2.29 ± 0.04	2.38 ± 0.03	1.71 ± 0.03	1.91 ± 0.03	2.08 ± 0.05	2.16 ± 0.08



15.18 Schematic of the structure of (a) the silane deposit, (b) sizing structure and (c) interphase in a composite (66).

glass fibre after silanisation with γ -aminopropyltriethoxysilane, shown in Fig 15.18(a), should be modified by the incorporation of $-\text{O}-\text{Al}-\text{O}-$ bonds in the deposit at the fibre surface. In a previous publication, a revised structure was given (19, 69).

Silanes – their role in strength retention

It can be seen in Fig. 15.6 that the silane deposit has a major impact on the strength distributions of individual coated glass fibres. Both the Weibull parameter, which represents the distribution of strengths, and the average strength of the fibres are clear functions of the coating. It is noticed here that the purity of the silane used for the silanisation also has a major impact. The reasons for this are unclear. However, it demonstrates the need for careful sizing of glass fibres and the choice of appropriate conditions for the silanisation.

Silanes – selection for adhesion promotion

Several mechanisms of adhesion have been identified (19). The most common mechanism is that of chemical bonding which is referred to as chemical coupling. In this mechanism it is assumed that monolayer silane deposits are adhered to the glass fibre surface and that the resin compatible group is reacted directly to the polymer during the curing mechanism. This gives a strong chemical bond between the two components in the formation of an interface. However, as shown above, it is more likely that an interphasal region is formed in which an interpenetrating network has been created. Therefore, the deformable layer hypothesis of adhesion can also be invoked as this can explain many of the phenomena associated with the micromechanics of adhesion of fibres to resins. It has to be recognised that many of the adhesion test methods used for fibre composites measure the stress transfer efficiency between the two components. Since the stress transfer is also a function of the properties of the interphase region, it is clear that the deformable layer hypothesis merely represents this concept. It also explains why the sizing formulations on glass fibres have to be finely tuned to the matrix into which the fibres will be introduced. This is because interphase formation can have a major impact on the micromechanics. It has been shown by finite element analysis and together with experimental validation that for optimum performance the interphase region should have a yield strength which is slightly below that of the matrix so that the shear stresses at the interface can be accommodated by deformation rather than debonding (70). Ideally, the modulus of the two components should be similar so that the shear stress is confined to the interphase region and the stress transfer efficiency maximised. This observation also explains why the reversible hydrolytic

bonding mechanism of Plueddemann (59) may not be applicable. Reversible recovery of dry properties after immersion in water can be accounted for by local reversible plasticisation of the interphase region so that the concept of reversible hydrolysis of the siloxane bonds is not required.

Adhesion of unsilanised and unsized glass fibres

It is also observed that under dry conditions, E-glass fibres form an apparently strong bond to epoxy resins (71). It is known that this interfacial bond is lost after immersion in water or humid environments. Therefore, this interfacial response can be attributed to hydrogen bonding between the cured epoxy resins and the glass fibre surface, and radial thermal residual stresses which form on cooling after curing at elevated temperatures. It should be emphasised that silane coupling agents are still essential for durable composites because, in service, residual matrix stresses will relax and interfacial hydrogen bonding lost on moisture absorption.

Plasma polymers as functional sizing for adhesion and protection

Plasma polymerisation is a technique for depositing molecularly thin conformal polymeric layers onto surfaces. By choosing appropriate conditions, the functional group within the deposit can be retained at a high level. Therefore, this approach is a good sizing technique for achieving a functional adhesive coating at the same time as providing strength protection to the fibres. Table 15.4 shows the strength retention after plasma polymer coating of E-glass fibres. Liu *et al.* (71) have shown that the interlaminar shear strength of the composites can be increased to above that of the matrix through the formation of an interphase between the plasma polymer and the epoxy resin.

This demonstrates how the interphasal properties of the composite can be optimised for performance. An interphase of thickness 5 nm appeared to provide an optimum mechanical performance of the composite. Plasma polymerisation represents, therefore, an efficient environmentally friendly technique for creating a functional coating on reinforcing fibres and at the same time producing the appropriate protection that the sizing polymer needs to give to the fibres for use in manufacturing techniques. Swait *et al.* (72) have demonstrated that the combination of controlled interphase and fibre strength retention can change the micromechanics to benefit energy absorption.

15.6 Conclusions

The structure and properties of glass fibres have been discussed. The requirements for fibre drawing have been identified and used to explain their

properties. The chemical structure of the glass has been related to the strength properties of drawn filaments. The need for the coating of glass immediately after forming has been addressed. Further, the role of these coatings on the formation of a strong fibre and a durable composite is discussed.

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Abstract: Carbon fibers are reviewed and discussed from the points of view of different categories of carbon fiber, their history, characteristics, performances, applications, environmental effects and future trends. Emphasis is given to polyacrylonitrile (PAN)-based carbon fiber, which is the most widely used form of carbon fiber. Cellulose and pitch-based carbon fibers are also discussed and compared with PAN-based carbon fibers.

Key words: carbon fibres, PAN polyacrylonitrile, pyrolysis, pitch based carbon fibres, cellulose based carbon fibres, structure, properties markets

16.1 Introduction

Carbon filaments were first produced in the 19th century by the pyrolysis of cellulosic fibers and they were used as experimental filaments for the first trials of electric light bulbs. Towards the end of the 19th century vacuum techniques had progressed sufficiently for light bulbs to become a possibility and Edison obtained a patent for the commercial exploitation of carbon filaments made from bamboo in 1901. For several years electric light bulbs were produced with carbon filaments made in this way but they were replaced around 1904 by tungsten wire. Continuous regenerated cellulose fibers began to be developed around the same time and were used in the 1950s by researchers in the USA to produce the first continuous carbon fibers. The incentive for this research was the requirement of light and stiff materials for the aerospace industry. The carbon–carbon bond is the strongest in nature and it was expected that such fibers would provide a valuable structural material. This would be the case but not with the carbon fibers made from cellulose as the atomic structures of the fibers were poorly organized and the fiber moduli were disappointingly low. This was due to there being only approximately 24% by weight of carbon available in cellulose from which fibers could be formed. The removal of the other elements left a fiber with poor atomic organization. Nevertheless these fibers are still produced because the poor order at the atomic level means that they have useful heat transfer properties and they find use in carbon–carbon composite applications for which the low coefficient of heat transfer is an advantage.

The commercial production of carbon fibers made from polyacrylonitrile (PAN) began in the 1960s. These have become the most widely used form of carbon fiber. In the intervening period effort has been put into the improvement of performance and productivity of the carbon fibers by the manufacturers. Along with the progress in the performance and productivity of the fibers, many applications have been developed in the fields of sporting goods, aerospace and industrial applications for the carbon fibers.

The first industrial uses for PAN-based carbon fibers were in the aerospace and sports goods fields. Today black golf shafts made with carbon fibers are very popular and are widely used so as to obtain high club-head speed and to increase comfort of the player throughout the game. Fishing rods made with carbon fibers are also very popular, since the rods are very light, easy to handle and sensitive to the touch of fish. The aerospace industry has adopted carbon fiber composites as a major structural material. The latest generation of planes, such as the Airbus A380 and Boeing 787, use around 35 tonnes of carbon fiber reinforced plastics (CFRP) for each airplane to reduce weight, to get better mileage and to improve passenger comfort.

Carbon fiber also has a very important role in reducing greenhouse gases. Huge windmills of around 100 meters in diameter are being installed thanks to the light weight and very rigid blade spars made with CFRP, providing more effective and clean power generation. Reducing the weight of airplanes, automobiles, trains and all transportation vehicles is crucial in reducing CO₂ emissions during the service life of these vehicles. Carbon fiber is one of the best materials to replace conventional metals and to get better mileage, resulting in the reduction of CO₂ emissions from the vehicles. Carbon fibers have moved from being specialty products to being used in an ever-increasing number of applications.

High strength and modulus along with the low specific gravity of carbon fibers are the key characteristics which make the carbon fiber an outstanding material compared with conventional materials. In this chapter all aspects of carbon fibers, including their history and tensile failure mechanisms, are reviewed and future development discussed.

16.2 Carbon fibers

Carbon fibers can be categorized into two groups: as carbon fibers made by carbonizing precursor fibers and carbon fibers synthesized directly from a hydrocarbon gas, such as methane. The former fibers can be continuous in length and are finding increasing numbers of applications.

Carbon fibers made by carbonizing precursor fibers are categorized according to the type of precursor fibers used, such as PAN-based carbon fibers, pitch-based carbon fibers and rayon-based carbon fibers. Of these carbon fibers, PAN-based carbon fibers have become the most widely used

form of carbon fiber. More than 90% of commercial carbon fibers produced globally are made from PAN precursor fibers. The reason for the popularity of PAN-based carbon fibers is their superiority in balancing performance and cost in the production of fibers of high strength and reasonably high modulus, which can easily be transformed into intermediate products that can be readily processed to make CFRP. Carbon fibers made from pitch, which is a residue of the oil refining industry and also the coking process in the steel industry are also finding use. Pitch-based carbon fibers are superior to PAN-based carbon fibers in balancing tensile modulus and cost in producing ultra-high modulus carbon fibers. Rayon-based carbon fibers find few applications in the commercial market due to their low performance and productivity; however, they are the fiber of choice for carbon-carbon applications, which normally exploit their low heat transmission properties.

Carbon fibers synthesized in the gas phase have been made in the form of carbon whiskers, with diameters in the range of 0.5–1.5 μm . Finer carbon nanotubes can be categorized as one of the gas phase grown carbon fibers. The performance of carbon fibers is mainly determined by the structure of graphite crystallites in their microstructures. The carbon nanotube, which has perfect graphite crystallites, is the ideal material for obtaining high performance as a single reinforcing element. However, mass production or mass application, such as in airplanes or satellites made from carbon fiber, is still a very difficult target for carbon nanotubes. PAN and pitch-based fibers are currently the only carbon fibers to be used to make such large structures.

Carbon fibers are also categorized by performance according to their tensile moduli, into low modulus carbon fibers (lower than 200 GPa), standard modulus carbon fibers, of around 230 GPa, intermediate modulus carbon fibers, of around 300 GPa, and high modulus carbon fibers (higher than 350 GPa). High modulus carbon fibers, (>600 GPa) are sometimes called ultra-high modulus carbon fibers. High modulus or ultra-high modulus carbon fibers are also known as graphite fibers. Depending on the application of the carbon fibers, the fiber type is chosen so as to obtain the best balance between performance and cost.

Carbon fibers are also categorized according to their tow size. Historically, tows of 3000 or 6000 filaments were standard. However, in order to reduce the cost of carbon fibers, the standard tow size has been increased to 12000 filaments but 24000 filaments are also available with the same level of performance as 12000 filaments. Tows of 24000 or fewer are called regular tows. Recently a move to large tow production with a fiber count of 50000 fibers or more has gained success in reducing the cost of fibers for non-aerospace applications. The characteristics of the large tow carbon fibers are somewhat lower than those of regular tow carbon fibers, not only in performance but also in variability. In the future, filaments of 48000

filaments carbon fibers may come to be considered as a regular tows for the development of carbon fibers for industrial applications. Table 16.1 shows the production of PAN-based carbon fibers in the world.

16.3 Carbon fibers produced from polyacrylonitrile (PAN) precursors

The production process for making carbon fibers from PAN precursor fibers consists of three main steps, namely a polymerization process to produce PAN polymers from acrylonitrile monomer, a spinning process to produce PAN precursor fibers and a carbonization process to carbonize the PAN precursor fibers. Throughout the processing of the PAN precursors to make carbon fibers, it is vital that the fibers are held under tension. If not, the alignment of the molecular structure, induced in the PAN precursor by drawing, is lost and the carbon fibers have low moduli, as with carbon fibers made from cellulose and from isotropic pitch, as will be explained below. Performance and cost of PAN-based carbon fibers are dominated by all three processes. Therefore all the processes are designed and optimized to improve both performance and cost of carbon fibers.

Since the requirements for PAN precursors are different from those for PAN fibers of textile applications, the details of the polymer makeup are also

Table 16.1 Production estimate (tonnes/year) of PAN-based carbon fibers in the world

		2004	2006	2008
Regular tow				
Toray Group	Toray	4 400	4 400	6 600
	SOFICAR	2 600	2 600	3 400
	CFA	1 800	3 600	3 600
	Sum	8 800	10 600	13 600
Toho Group	Toho-Tenax	3 700	3 700	6 400
	TTE	1 900	3 400	3 400
	TTA		700	700
	Sum	5 600	7 800	10 500
Mitsubishi Rayon Group	Mitsubishi Rayon	3 200	3 200	5 400
	Grafil	1 500	2 000	2 000
	SGL		500	500
	Sum	4 700	5 700	7 900
Hexcel, Cytec, Taiwan-Plastic		5 900	7 800	7 800
	Sum	25 000	31 900	39 800
Large tow				
Fortafil Æ TTA		2 100	1 300	1 300
Zoltek		2 500	4 000	6 000
SGL		1 000	500	500
Aldila		1 000	1 000	1 000
Toray		300	300	300
	Sum	6 900	7 100	9 100
	Total	31 900	39 000	48 900

different. Namely PAN polymers for carbon fibers are designed to improve productivity, both of the spinning and the carbonization process, so as to improve graphite crystallinity and to reduce defects in the carbon fiber.

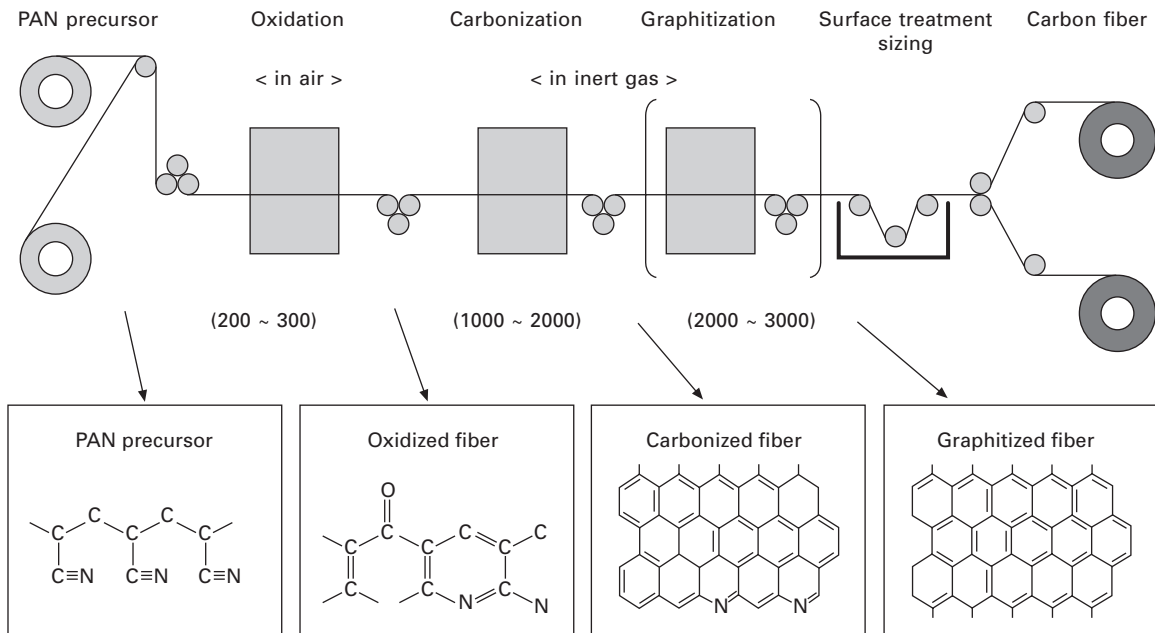
The spinning process is crucial in determining the performance and cost of carbon fibers. Therefore very careful, minute design and optimization are very important. PAN does not melt under elevated temperatures so melt spinning cannot be applied for the production of PAN fibers. Solution wet spinning is normally used. One of the reasons why the carbon fiber share of three Japanese companies is around 70% in the world, as shown in Table 16.1, is that those three companies, namely Toray, Toho-Tenax and Mitsubishi Rayon, were originally producers of regenerated cellulose fibers, as their original names showed and rayon is also spun from solution. This, together with their experience of spinning textile fibers, prepared them well spinning technology used for making carbon fibers.

Figure 16.1 shows a schematic representation of the PAN carbonization process. This consists of an oxidation step during which precursor fibers are heat treated in an oxidative atmosphere, such as air, in the temperature range from 200 to 300 °C, followed by a carbonization process, during which the oxidized fibers are heat treated in a non-oxidizing atmosphere, such as nitrogen, at temperatures higher than 1000 °C. The oxidation process is necessary in order to make PAN precursor fibers heat resistant for carbonization process by a crosslinking process involving the closing of nitrile functions, so making ring structures.

PAN consists of around 67% by weight of carbon. This value is obtained from the ratio of the atomic weight of the three carbon atoms in the pure monomer to the sum of the atomic weights of all the species in the pure PAN monomer ($3C/CH_2=CHCN$). The other species are nitrogen and hydrogen. In the carbonization process, those species and oxygen, which was introduced during the oxidation process, are removed from the fibers, and carbon fibers, literally fibers made of carbon, are produced.

Standard modulus carbon fibers consist of 90% or higher of carbon by weight. High modulus carbon fibers are normally produced by heat-treating carbon fibers at temperatures higher than 2000 °C after the carbonization process. This process is often called, misleadingly, the graphitization process, although the structures of PAN-based carbon fibers do not contain graphite, which is a specific crystalline form of carbon. The atomic structure tends towards a graphite structure as higher temperatures are used but perfect crystallization is not achieved. Strength passes through a maximum around 1500 to 1600 °C and thereafter decreases, although Young's modulus continues to increase with temperature. This enables a family of carbon fibers to be produced from the same precursor fibers. High modulus carbon fibers consist of almost 100% carbon.

The translucent PAN precursor fibers change to black oxidized fibers



16.1 Carbonization process of PAN-based carbon fibers.

through the oxidization process due to ring formation in the chemical structure. However, oxidized fibers are still organic fibers and change to inorganic fibers through the carbonization process. It can therefore be understood that the carbonization process is a drastic step making a dramatic change in the fiber structure. Weight reduction during the carbonization process is roughly 50%, so that half of the oxidized fibers are removed through carbonization. Therefore the carbonization process dominates carbon fiber performance and controls tensile modulus, although all three processes during the conversion of PAN to carbon fiber need to be designed and optimized as a totally integrated process.

The carbon fiber surface, just after the carbonization process, consists of planar graphite microcrystallites aligned parallel to the fiber surface and along fiber axis direction. There are no pendant bonds available so that these crystals are quite inert. Carbon fibers are therefore surface treated using an oxidation process or other methods to make the fiber surface more reactive so as to improve adhesion between the fiber surface and matrix resin. After the surface treatment, carbon fibers are normally coated with a sizing agent to improve processability in the proceeding fabrication process.

Carbon fibers are normally used as reinforcements in composite materials with various kinds of resins as matrix materials. Therefore surface treatment and the nature of the sizing agent are very important in controlling the ultimate performance of CFRP and the processability of CFRP during the fabrication process. For this reason the surface treatment and sizing agents are designed and optimized according to the fibers' end uses and fabrication processes.

These production processes are basic ones. Since the beginning of commercial production many kinds of technology developments have been introduced so as to improve the design and control capability of the product and process. It can be expected that further improvements will occur in the future.

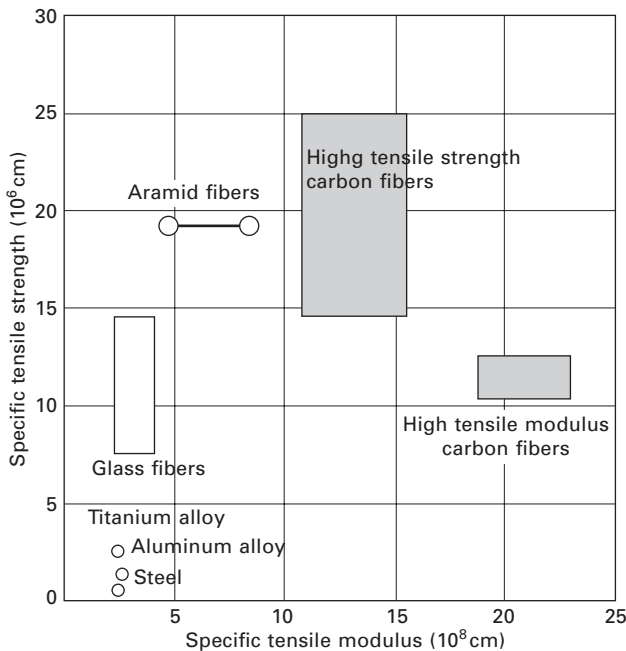
The specific gravity of a perfect graphite crystallite is 2.26. Since PAN carbon fibers are made of fine graphite crystallites, the sizes of which are around 10 nm or smaller and the structure of the fibers is not perfect, so that some porosity occurs and the specific gravities of standard and intermediate modulus carbon fibers are around 1.8, and that of high modulus carbon fibers is around 2.0. This value for the specific gravity at around 2.0 or lower is distinctively lower than that of steel, 7.8, and lower than that of aluminum, 2.7, or glass fiber, 2.5.

In addition to the low specific gravity, high tensile strength and modulus and fineness, with diameters of 5 to 7 μm are other big advantages of carbon fibers made from PAN precursors. Thanks to these characteristics, their specific tensile strength and specific tensile modulus, which are calculated by dividing tensile strength and modulus by the specific gravity or density,

are much higher than those of conventional metals and other reinforcements, such as glass fibers and aramid fibers, as shown in Fig. 16.2. The values of the specific properties can be expressed in GPa or cm, depending on whether the dimensionless specific gravity or the density which has units of mass per volume is used.

The high specific tensile strength and modulus are the main characteristics which make carbon fibers materials of choice to replace conventional materials and to reduce the weight of sporting goods, aerospace and industrial products. In particular, their high specific tensile moduli are the reason why the material has been adopted by the aircraft industry so that planes such as the Boeing 787 containing carbon fibers of more than 50% by weight are being produced.

Another characteristic of carbon fibers is their elasticity, which is determined by the covalent bonds linking the carbon atoms. In the case of conventional metals, elastic deformation ends at a low yield stress with plastic deformation, due to dislocation movement occurring, under further loading. That is why fatigue damage in metals occurs under repeated loading–unloading cycles in the case of conventional metals. In contrast, carbon fibers are perfectly elastic and fatigue deformation does not occur by loading–unloading (Somer and Bunsell, 1992). This means that carbon fibers are very reliable in terms of fatigue, at least in tensile loading in the axial direction, although large cyclic



16.2 Specific tensile strength and modulus of carbon fibers.

loading of CFRP can induce damage by provoking failure in the matrix or at the fiber–matrix interface (Meziere *et al.*, 2005).

In terms of physical characteristics, another benefit of carbon fibers is its low coefficient of thermal expansion (CTE). The CTE of carbon fiber is as low as 1×10^{-6} per °C, which is one order lower than that of metals. Therefore the effect of temperature on structural dimensional stability of CFRP is one-tenth of that of metal structures. It is very beneficial in reliability for space and other structural applications which are subjected to varying temperatures.

Other beneficial characteristics of carbon fibers are chemical and thermal stability, X-ray transparency, high electrical and thermal conductivity. CFRP does not rust like metals. Practically, resin performances sometimes limit the performance of CFRP rather than that of carbon fibers, since normally thermal and chemical stability of resins are lower than those of carbon fibers.

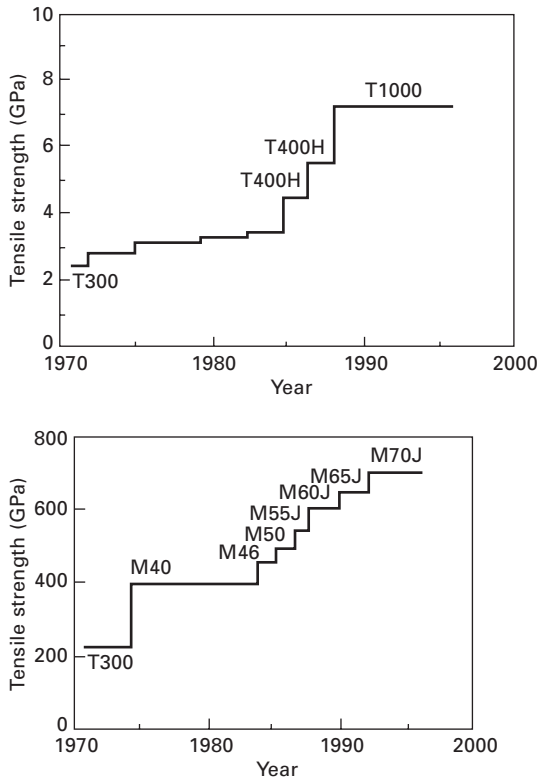
Amongst the characteristics mentioned above, tensile strength and modulus are the most important properties of carbon fibers. Tensile strength and modulus are dominated by the perfection of the graphite crystallites, known as basic structural units (Oberlin and Guigon, 1988), and of the overall fiber structure.

Tensile modulus is a parameter mainly dominated by the size and alignment of the basic structural units, with respect to the fiber axis. Technical developments have resulted in improved tensile modulus by increasing crystallite size and aligning their orientation along the fiber direction. Figure 16.3 shows the historical trend of high modulus carbon fiber development.

The highest tensile modulus of PAN-based carbon fibers is 700 GPa. In the case of pitch-based carbon fibers, ultra-high modulus carbon fibers above 900 GPa have been developed due to the possibility of obtaining a true graphite structure. The structure of pitch used to make carbon fibers contains ring structures and the raw material can be converted to a mesophase or liquid crystal phase which permits perfect alignment of the atomic structure. Therefore graphite crystallites can grow easily during the carbonizing or graphitizing process. In contrast, the PAN polymer is linear and needs much more energy to grow graphite crystallites compared with pitch-based carbon fibers.

Tensile strength is mainly dominated by defects. A carbon fiber is an elastic material and tensile failure is initiated at a defect. If a defect is big, tensile failure occurs at a low stress level. Therefore decreasing the size and number of defects is the key in order to improve tensile strength. As shown in Fig. 16.4, tensile strength can be improved by decreasing the size of voids in a fiber and defects at the fiber surface (Noguchi, 1984).

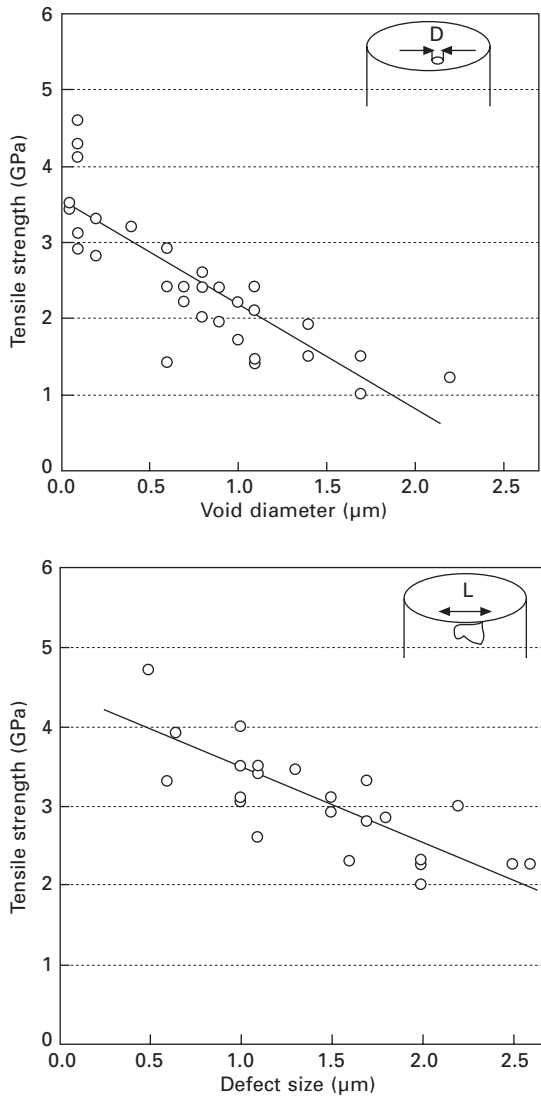
Normally the tensile modulus of the surface layer in the carbon fiber is higher than that of the inner region of the fiber. This is due to the carbon crystallites being parallel to the surface and also as oxidation of the precursor,



16.3 Historical improvement in tensile strength and modulus of carbon fibers.

during the oxidation process, progresses from the surface. The tensile stress applied throughout the carbon fiber production process tends to concentrate defects in the surface region of the fiber during the oxidation and carbonization processes. Additional defects also tend to be generated in the fiber surface during the production process. Therefore the control of surface defects is very important in improving the tensile strengths of carbon fibers.

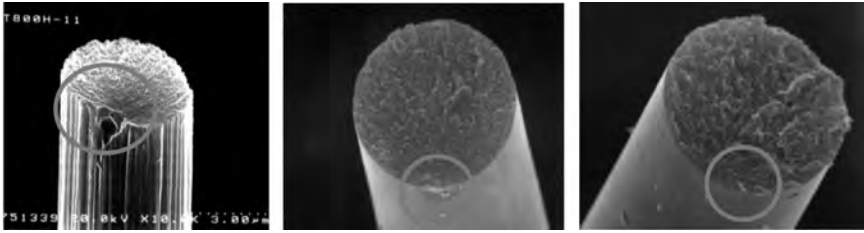
Therefore the historical improvement in tensile strength has been achieved through decreasing the size and number of defects by designing and optimizing all the carbon fiber manufacturing processes. In the early stage of production there were some voids in the carbon fibers. Purifying polymers and all the utilities, such as water, steam and atmosphere, was found to be very important in preventing contamination with other species, such as metals, and to reduce voids from the carbon fiber. Surface defects can be generated by abrasion or adhesion between filaments during the spinning or carbonization process. Preventing adhesion among filaments is very important, especially when the fiber surface is very smooth. An important consideration is the fiber diameter



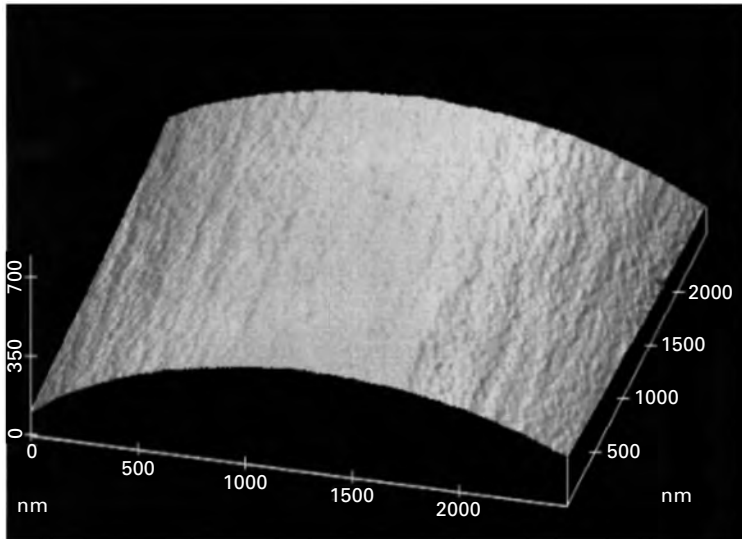
16.4 Effects of void diameter and defect size on tensile strength (Noguchi, 1984).

and the reduction from 7 mm for the diameter of the earlier fibers to 5 mm has been significant in increasing strength (see Chapter 1 for the Weibull statistical analysis of fiber strength).

As shown in Fig. 16.3, tensile strength reaches 7 GPa. This was achieved by the reduction of the size and number of defects in the fibers, as shown in Fig. 16.5. Figure 16.6 shows a fiber surface of ‘Torayca’ T700S carbon fiber, which, at present, is the most widely used carbon fiber, observed with



Micron size defect $\leftrightarrow$ Sub-micron size defect $\leftrightarrow$ Nano size defect
16.5 Decrease in defect size on carbon fiber surface.

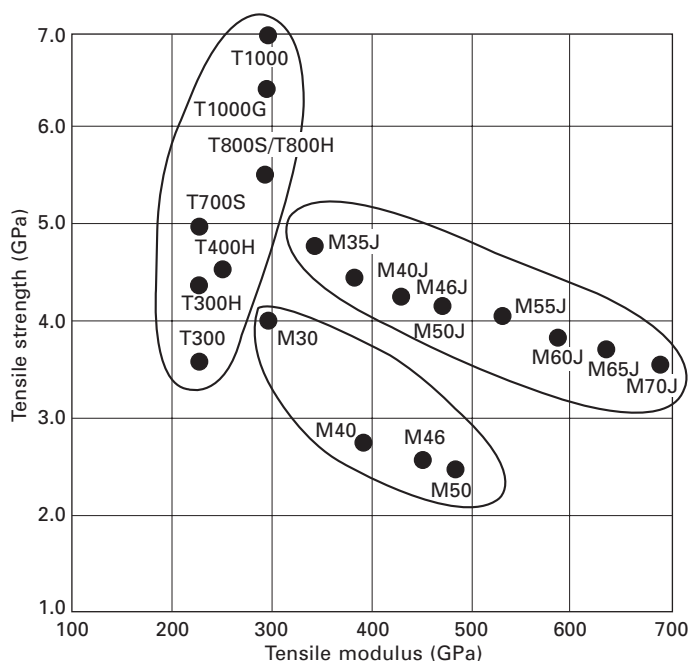


16.6 Surface of 'Torayca' T700S (atomic force microscope).

an atomic force microscopy, at the full scale of 2 mm. The fiber surface is very smooth and free from defects, which is the result of the continuous efforts to decrease defects in the fibers.

Through the improvements in tensile strength and modulus, many products with different characteristics have been generated, as shown in Fig. 16.7. As the modulus of carbon fibers increases, their tensile strength tends to decrease. The reason for the decrease in tensile strength is considered to be due to micro-defects among graphite crystallites, which tend to grow among graphite crystallites growing randomly in the transverse direction in the fibers.

Based on the improvements in tensile strength, mentioned above, the tensile strengths of the most widely used standard modulus fibers improved from 3 GPa in the 1970s and 1980s to 5 GPa at present. This means that the tensile strain at failure improved from around 1.3% to around 2.0%.



16.7 Product line-up of PAN-based carbon fibers ('Torayca').

The result has been that carbon fibers have become more resistant in bending and to wear during the composite fabrication process and easier to handle.

For airplane applications, intermediate modulus fibers, which have both higher strengths and moduli than standard modulus carbon fibers, are mainly used and contribute to the reduction of the weight of airplanes. High modulus fibers are mainly used for space application, such as satellites, and high performance sporting goods, such as golf shafts and fishing rods.

Historically, improvements in tensile strength and modulus of commercial PAN-based carbon fibers reached the highest levels around 1990, and have remained steady since. A main reason for this is the change in market requirements. At first markets sought champion materials to make champion products. After reaching satisfactory levels in product performance, markets then sought better cost performance and reliability, including of supply.

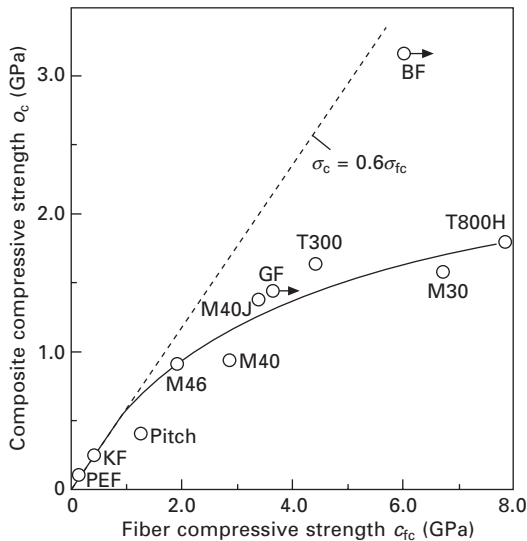
In order to meet the market requirements, the main development targets moved to high cost performance fiber with more efficient and stable processing. As a result, stable mass production of high cost performance and reliable fibers was achieved. All these improvements in performance, cost-performance and reliability resulted in CFRP becoming the dominant material in the most recent generation of commercial jet airplanes.

16.3.1 Compressive strength

In the case of pressure vessel applications made by the filament winding process, tensile strength and modulus are the dominant parameters for determining end product performance. However, in other applications, such as laminate shape structures, flexural stress is the most common stress in service. In the flexural mode, failure occurs in the tensile or compressive mode depending on which strength is lowest. Therefore compressive strength is also as important as tensile strength for flexural mode stresses.

Measuring compressive strengths of single filaments is more difficult than tensile strengths due to buckling of single filaments under compressive stress. Therefore the loop method or recoil test is applied for measuring compressive strength of single filament (see Chapter 2).

The dominant factor or failure mechanism for compressive strength is more complex than that for tensile strength. Together with the improvement in tensile strength, the compressive strength of carbon fiber has also improved, as shown in Fig. 16.8 (Norita *et al.*, 1988). Therefore the presence of defects is also an important factor for the compressive strength. Another important factor for compressive strength of single filament is crystallite size. Large crystallites tend to shear failure under compressive stress. That is why compressive strength of pitch-based carbon fibers is much lower than that of PAN-based carbon fibers. Crystallite size in pitch-based carbon fibers is around 10 nm or greater and this can be contrasted with the crystallite size of PAN-based fibers which is in the region of 1–5 nm. Even in PAN-based



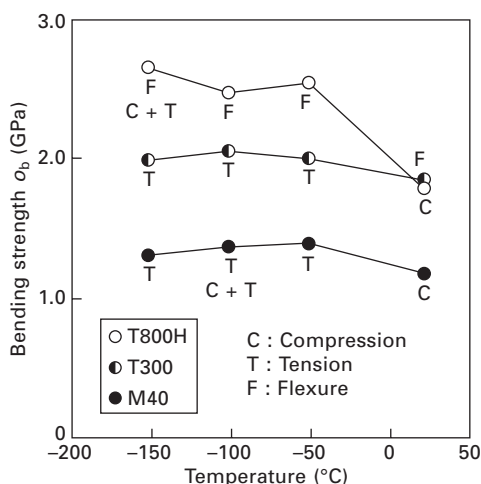
16.8 Relationship between fiber compressive strength and CFRP compressive strength (Norita, *et al.*, 1988).

fibers, high modulus carbon fibers which have larger crystallite size have lower compressive strengths than intermediate or standard modulus carbon fibers.

Another factor controlling the compressive strength of CFRP is buckling of fibers. As shown in Fig. 16.8, even with a high compressive strength of single carbon fibers the compressive strength of CFRP is limited. This is due to the buckling of carbon fibers in CFRP. It is not a matter of alignment of carbon fibers but the support of carbon fibers by the matrix resin. As shown in Fig. 16.9, lowering the test temperature increases the flexural strength of CFRP and the failure mode changes from the compressive mode to flexural or tensile mode failure. This is due to the higher compressive strength with greater support strength with the more rigid resin at lower temperatures, although material and alignment are exactly the same among under all the test temperatures.

Therefore the dominant factor for compressive strength of CFRP with standard and intermediate modulus-based carbon fibers is fiber buckling, which is mainly determined by the rigidity of the matrix resin. In the case of high modulus carbon fibers, the dominant factor for compressive strength of CFRP is fiber compressive strength, which is mainly determined by crystallite size in the fiber itself.

Therefore reducing crystallite size and keeping crystallite alignment is effective in improving the compressive strength of high modulus carbon fibers. As an example, ion implantation was found effective in improving the compressive strength of high modulus carbon fibers, although the method is not yet applicable in mass production (Matsuhisa and Washiyama, 1992).



16.9 Effect of test temperature on bending strength of CFRP and its failure mode (Norita, *et al.*, 1988).

16.3.2 Other characteristics of CFRP

Carbon fibers are normally used as CFRP in which they are incorporated into a matrix resin. The adhesion between fiber and resin is very important in determining the performance of CFRP. As mentioned above, compressive strength is affected by the fiber support by the matrix resins. Adhesion between fiber and matrix resin is important in transferring the compressive strength of single filaments to that of the CFRP even at the same test temperature.

Transverse tensile, or shear strength, of CFRP is more directly dominated by adhesion between the fibers and the matrix resin. Better adhesion leads directly to higher transverse and shear strength of the composite.

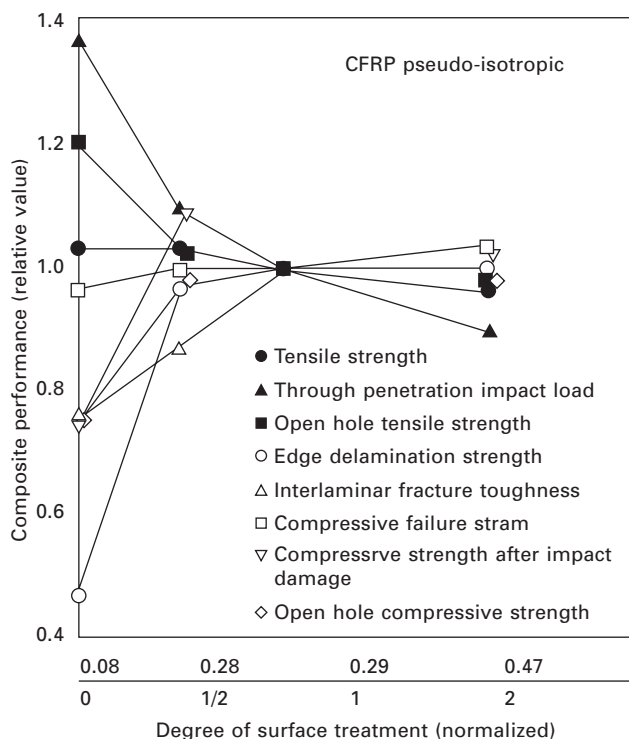
In the case of tensile strength, better adhesion between fiber and matrix resin results in a lower tensile strength of the CFRP. Tensile strength of CFRP is determined by how much energy can be absorbed during the tensile failure. Tensile failure can initiate from the tensile failure of a single filament which has the lowest strength amongst all the filaments in the composite. If adhesion between fiber and matrix resin is too high, the crack, initiated from the single filament failure, propagates in the transverse direction without hindrance and without being hindered by the interface between fibers and matrix. Such failure causes catastrophic failure with a flat failure surface at a low stress level. A similar mechanism is important for impact performance. Penetrating energy produced by an impact is lower with higher adhesion between fiber and matrix.

Therefore the adhesion between fiber and matrix needs to be optimized so as to achieve the best overall performance of CFRP. Figure 16.10 shows an example of the effect of surface treatment on the performance of CFRP (Norita *et al.* 1986). As mentioned above, tensile and through penetration impact performances decrease with higher levels of surface treatment. Compressive and adhesion performances, such as edge delamination strength and interlaminar fracture toughness, increase with greater surface treatment. Surface treatment must therefore be optimized to satisfy all the performances required of composite applications.

As a result of the increasing numbers of applications, various matrix resins have been developed for the different applications. For example, for marine applications vinyl ester resin is more popular than epoxy resin, as it shows greater resistance to humidity. Therefore a sizing agent for vinyl ester resin has been developed for marine applications. Such efforts are important so as to allow different applications of composites to be successfully developed and allow better performance with various matrix resin systems.

16.3.3 Applications of PAN-based carbon fibers

Commercial production of PAN-based carbon fibers started in the UK around 1967 and in Japan in the early 1970s. The initial development of PAN-based



16.10 Effect of surface treatment of carbon fibers on CFRP properties (Norita *et al.*, 1986).

carbon fibers in the UK was for aerospace applications but their potential for improving sports goods was rapidly recognized, particularly in Japan. Such sporting goods were golf club shafts, fishing rods, tennis rackets, vaulting poles, archery equipment, skis, racing cars, yachts and many more. The development of lightweight composite sporting goods allowed records to be broken and results to be attained which would not have been possible with conventional materials.

In space, satellites were another application for which, from the beginning of the commercial production of carbon fibers, were composed largely of carbon fiber composites; about 80% of the weight of a satellite can be attributed to the use of this composite. Space applications are the most effective use for low weight and high modulus carbon fibers even with their very high cost. Low weight, high modulus and low CTE are very beneficial for space applications.

After becoming very popular for sporting goods and spacecraft, the next big market to develop was for the airplane. The use of CFRP in airplanes is the most effective application for low weight and high modulus carbon fibers, next to aerospace applications. At the beginning of aerospace applications,

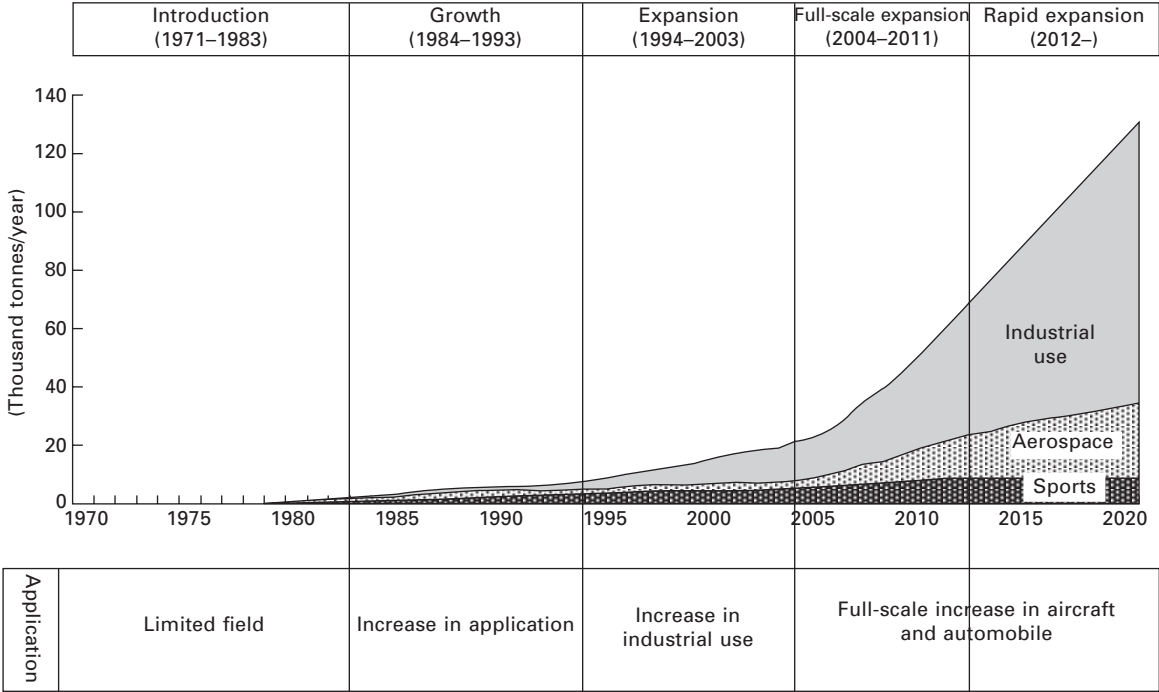
carbon fibers were used for secondary structures, such as rudders, spoilers and so on. After accumulating experience and demonstrating the reliability of carbon fibers with these secondary structures, carbon fibers were then used for main structures, such as the empennage and floor beams. Nowadays the fuselage, main wing, empennage and other main structures of Boeing 787 are made with carbon fibers.

Historically the next large market was for industrial applications, which cover pressure vessels, automobiles, marine, wind-generators, off-shore oil applications, rollers for paper making, robot arms, support bars, X-ray cassettes, centrifuges, flywheels, PC cases, IC trays, battery electrodes, C/C brakes, rubber belting, automobile tires, and so on.

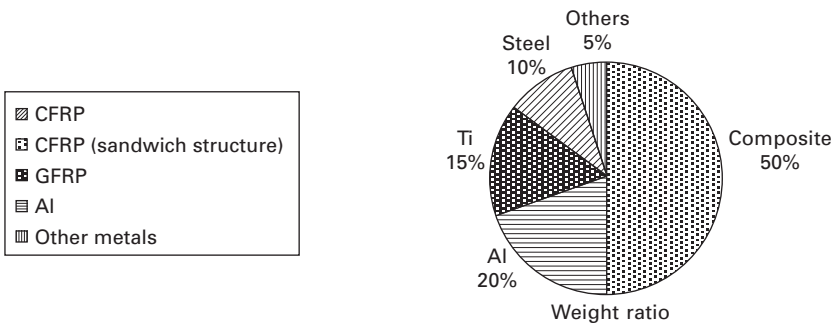
Pressure vessels, such as CNG (compressed natural gas) tanks for automobiles, SCBA (self-contained breathing apparatus) tanks for fire-fighters and medical usage, and CHG (compressed hydrogen gas) tanks for fuel cell automobiles, are big volume applications. Another big application are wind-generators. Because of the large size of wind-generator blades, which are now as long as 50 m or more, CFRP is the only feasible material which can be used. Another growing application is in the automobile. Because of increasing fuel costs, the lightweight automobile is becoming very important. CFRP is an ideal material for automobile structures in determining performance. Although the automobile is one of the most cost-sensitive applications, because of the benefit of carbon fibers for the applications and progress in cost performance of carbon fibers and fabrication process, carbon fibers are becoming a very popular material in automobile applications.

Nowadays half of all applications in volume are industrial applications, as shown in Fig. 16.11. These applications are growing rapidly and this expansion will continue or become more accelerated in near future.

Environmental consideration is another area of interest in developing new applications for CFRP. Carbon fibers need high temperature in the production process as mentioned above. Therefore carbon fibers need much energy for the production. In other words the environmental impact of the production of carbon fiber is larger than that for conventional metals, such as iron. However if the life cycle of the products with carbon fibers is considered, carbon fibers are a very environmentally friendly material. An LCA (life cycle assessment) analysis shows that 395 000 tonnes of CO₂ are generated by the manufacture and flight of a conventional aluminum-made airplane. This is reduced by 7%, by the incorporation of CFRP for the Boeing 767 type mid-size jet airplane, even if only a 10-year lifespan is considered (Fig. 16.12). If carbon fibers are used for 50% of the structure of the airplane, such as in the Boeing 787, one tonne of carbon fibers allows 1400 tonnes of CO₂ to be reduced during the lifetime of the airplane. CO₂ emission for the production of carbon fibers is around 20 tonnes per one tonne of carbon fibers, including oil production and all the processes involved in making



16.11 Carbon fiber demand in the world.



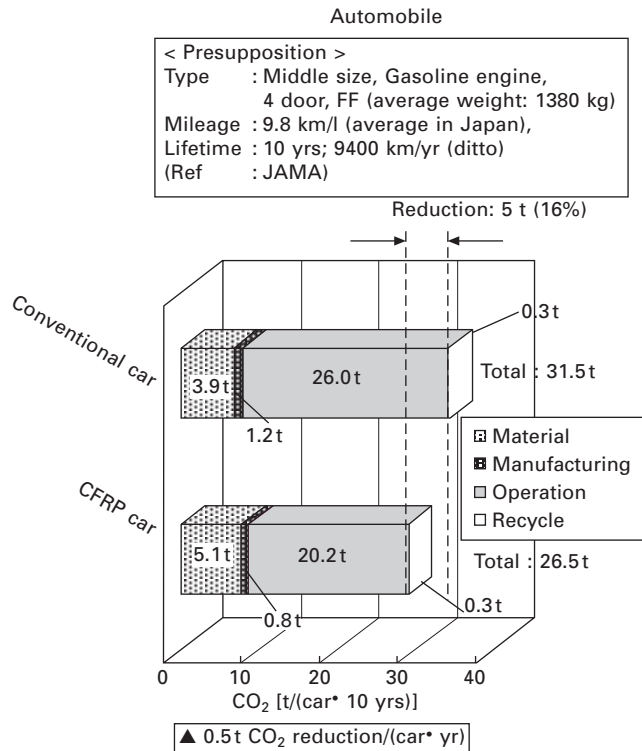
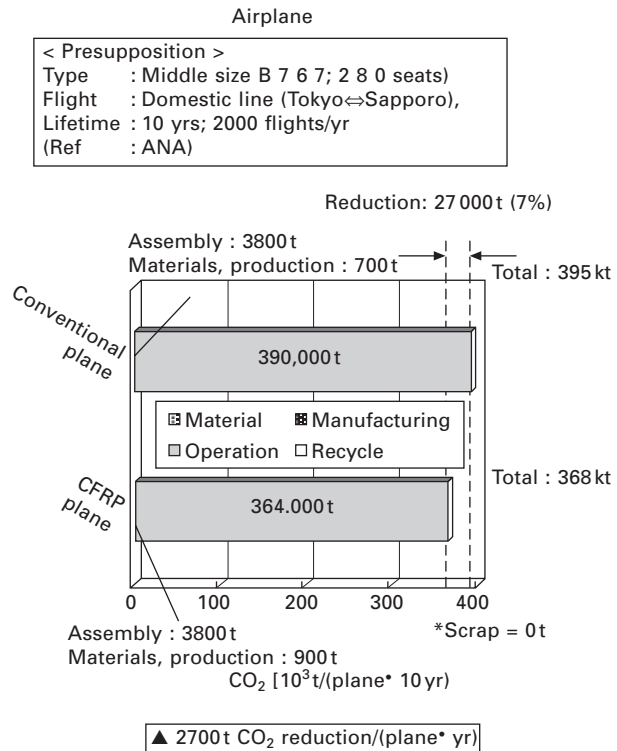
16.12 Carbon fiber usage in Boeing 787.

carbon fibers. Therefore carbon fibers are very effective in reducing CO_2 emissions from airplanes. This model considers domestic flights in Japan. Considering intercontinental flights the effects will become much larger owing to longer flight distance and larger annual consumption of oil.

In the case of automobiles, CFRP can be used around 17% in weight of the body of automobile. Considering the life cycle of the average passenger car in Japan including oil production to recycling, 5 tonnes of CO_2 and 17% of CO_2 emissions of the conventional steel-made car can be reduced over a 10-year period. In terms of the effect of one tonne of carbon fibers, 50 tonnes of CO_2 emission can be reduced over a 10-year life of the car.

Since CO_2 emissions from airplanes and private cars accounts for around 10% of total CO_2 emission in Japan, the effect of CO_2 reduction due to CFRP usage in those applications is very important. Figure 16.13 summarizes the effects of CO_2 reduction through the application of carbon fibers to automobiles and airplanes.

The effects in Europe or the USA of CO_2 reduction effects should be larger than those in Japan, since automobiles and airplanes are used for longer periods and for greater mileages, which increase the CO_2 reduction effects due to lightweight bodies.

16.13 CO₂ reduction effects with CFRP ('Toray LCA Model').

16.4 Carbon fibers produced from pitch precursors

Pitch is the residue of the oil refining process or the coking process from coal tar produced as a by-product of the steel industry. Large quantities of raw material are available and are of very little value. Indeed pitch is of such little value that it is mainly converted into bitumen and used in surfacing roads. Pitch is composed of between 80 and 90% carbon. For these reasons there has been interest in using pitch as the precursor material for carbon fibers since the 1960s (Lavin, 2000).

The cheapest form of carbon fibers made from petroleum pitch involves producing short fibers from isotropic pitch. This type of production began in the 1960s. This type of fiber, produced by Kureha in Japan, is finding an increasing market, particularly in reinforcement of cement, exhaust gas filters for diesel cars and also for reinforcing some plastics. Pitch is a natural product and shows considerable variability. Isotropic pitches can soften over a wide range of temperatures from 40 to 200 °C and at a higher temperature, typically around 280 °C, it has a sufficiently low viscosity for fibers to be drawn from it. Two methods are used for producing isotropic pitch fibers, centrifugal spinning and blowing. The former process involves the molten pitch being dropped onto a spinning plate with holes at the circumference. Centrifugal force throws the pitch against the edges of the plate and through the holes. Blowing involves extruding the pitch into a high velocity stream of gas, which draws the pitch out into an elongated form. Both techniques produce short fibers, which, depending on the application, can be milled to lengths from 0.1–1 mm or chopped to lengths from 3 to 200 mm. Typical properties of these fibers are given in Table 16.2.

The random arrangements of the atomic structures of carbon fibers made from isotropic pitch results in low elastic moduli and strengths. However, these fibers are attracting attention because of their low cost and inertness in aggressive environments such as cement.

In the early 1970s, Union Carbide, in the USA developed mesophase pitch-based high performance carbon fibers (Volk, 1975). In this method the pitch is treated so that the molecular structure is ordered to give a nematic (one-dimensional) liquid crystal structure. Mesophase pitch melts around 300 °C and is then processed around 400 °C. The polymerized pitch molecules are made up of chains of aromatic hexagonal units consisting each of six

Table 16.2 Typical characteristics of isotropic pitch-based carbon fibers

	Standard carbon grade	Graphite grade
Tensile modulus (GPa)	35	35
Tensile strength (GPa)	0.75	0.8
Failure strain (%)	2.2	2.3
Specific gravity	1.63	1.6

atoms of carbon. When the polymerization is sufficiently advanced, the molecules form spheres which grow until a phase inversion occurs, at which point the previous situation with the discrete spheres being embedded in the isotropic medium reverses and the molecules become the medium consisting of a continuous nematic liquid crystalline phase, called a mesophase (Fitzer and Heine, 1988). The precursor pitch fibers are then usually spun from the melt.

The processes of refinement of the pitch and subsequent preparation of the mesophase are costly. This has done much to undermine the ambitions of the original fiber producers, which was to produce a cheap route to carbon fiber manufacture. After production of the precursor fibers the production processes of pitch-based carbon fibers are fundamentally the same as those of PAN-based carbon fibers. The stabilization process is quite similar to the oxidation process of PAN-based carbon fibers. However, owing to the brittle, weak and thermally melt pitch spun fibers the stabilization process of pitch-based carbon fiber is more difficult and this also significantly increases production costs.

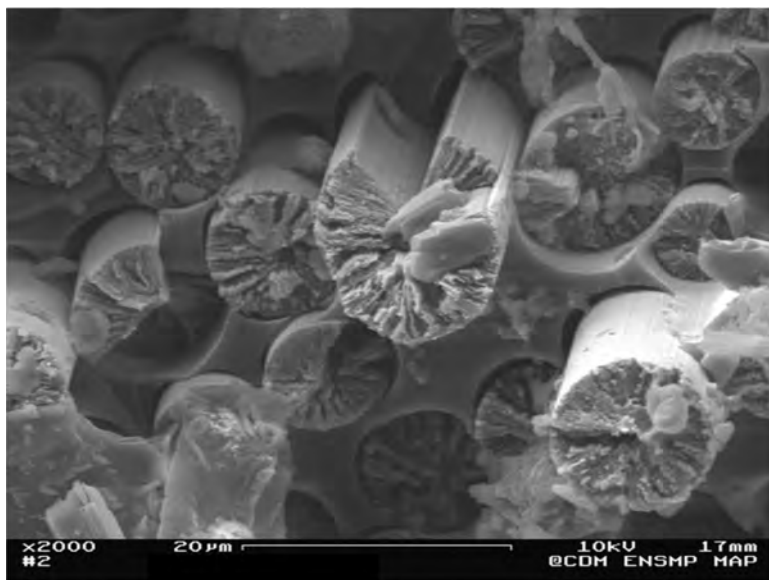
The arrangement of the atomic structures of the carbon fibers produced from pitch can be more regular than that obtained from PAN precursors and the result is the possibility of obtaining much higher moduli and at lower temperatures. The maximum tensile modulus of a carbon fiber is limited to that of a graphite single crystal which is 1050 GPa. Today, carbon fibers made from coal tar pitch are commercially available with moduli of 935 GPa, which is more than 40% higher than that of the stiffest PAN-based fibers. The regularity of the arrangements of the carbon atoms means that the basic structural units of the carbon are larger than in PAN-based fibers and this results in lower strengths. Strengths do not vary with pyrolysis temperature as is the case in producing carbon fibers from PAN so that the strengths of very high modulus fibers are similar to those of fibers with much lower moduli, as can be seen from Table 16.3. The production of high strength fibers, for which the biggest market exists, at a reasonable cost, has so far been difficult. The compressive strengths of pitch-based carbon fibers are also considerably lower than those of PAN-based fibers. The diameters of most pitch-based carbon fibers have been around 10 mm but, as with PAN-based fibers, manufacturers of carbon fibers from pitch are reducing the diameter of their fibers which, as can be seen from the explanation of Weibull statistics in Chapter 1 results in increasing fiber strengths. Pitch-based carbon fibers are now being produced with diameters of 7 mm. However, the large crystallites of basic structural units sometimes cause transverse failure of the carbon fiber under transverse tensile stress, which does not occur with PAN-based carbon fibers. However, owing also to their large crystallites, pitch-based carbon fibers are superior in thermal and electrical conductivities when compared with PAN-based carbon fibers

Table 16.3 Typical characteristics of pitch-based carbon fibers

Manufacturer	Fiber type	Diameter (mm)	Young's modulus (GPa)	Tensile failure stress (GPa)	Strain to failure (%)	Specific gravity
Nippon Graphite	YS-95A	7	900	3.53	0.3	2.19
	YS-80A	7	785	3.63	0.5	2.17
	YSH-70A	7	720	3.63	0.5	2.14
	YSH-60	7	630	3.90	0.6	0.60
	CH-90	10	860	3.43	0.4	2.19
	CH-60	10	620	3.43	0.6	2.12
Mitsubishi Chemicals	Dialead	11	935	3.7	0.4	2.20
	K13 D2U					
	Dialead K63710	11	640	2.6	0.4	2.12

When Union Carbide began to produce high performance pitch-based carbon fibers, a great concern was that apparently segments of the fiber were lost during processing so that instead of a circular cross-section the fibers had a section with a segment missing. These fibers have become known as Pacman carbon fibers, after the video game. It was later determined that the missing segment was created by shrinkage of the fiber during processing. Unlike PAN-based fibers, carbon fibers made from pitch can be produced with organized cross-sections so that fibers with circumferential or radial arrangements can be made as well as more random textures. Varying the textures can alter ultimate mechanical properties. Figure 16.14 shows the fracture surface of a pitch-based carbon fiber composite revealing the radial texture of the fibers and also the Pacman failure of the fiber in the center.

In the early 1970s when Union Carbide developed the first high performance pitch-based carbon fibers, the worldwide production capacity for carbon fibers was around 10 tonnes and it was not clear how the commercial development of the fibers would evolve. Now it is clear that the biggest market is for high strength carbon fibers and unfortunately the pitch route has been found to be more easily adapted to producing high modulus fibers, which were difficult to process because of their brittle nature. Union Carbide ceded their production to Amoco-BP which then ceded it to Cytec, which produces high modulus fibers finding a market in space and some sporting goods applications. From the early 1980s there was a big effort in Japan to use the pitch route to produce carbon fibers, no doubt with the aim, initially, of reducing the cost of carbon fibers and therefore encouraging new markets. The cost of purifying the naturally occurring pitch precursor product was found to be high but today two major Japanese producers, Mitsubishi Chemicals and Nippon Graphite Fibers, are finding increasing markets, such as in satellites, industrial rollers and robot arms for which the ultra-high moduli of pitch based carbon fibers



16.14 Fracture surface of pitch-based carbon fiber composite broken in compression revealing the Pacman structure of some of the fibers.

can be exploited. Typical characteristics of high performance pitch-based carbon fibers are shown in Table 16.3.

There are certain applications and markets for which pitch-based carbon fibers are particularly suited and this means that the production of these fibers will continue and grow as these markets develop. However, owing to their low tensile and compressive strengths, pitch-based carbon fiber cannot replace PAN-based carbon fiber applications and markets for these latter fibers are predicted to grow more rapidly than those of pitch-based carbon fibers.

16.5 Carbon fibers produced from regenerated cellulose

The first carbon fibers were made by carbonizing filaments of bamboo in an inert atmosphere, and in the late 1950s and early 1960s, considerable effort in the USA was given to producing carbon fibers from regenerated cellulose, rayon, obtained mainly from wood (Kaverov *et al.*, 1995). There are sound environmental reasons why this route could be attractive as the primary source of cellulose, wood, is a renewable product which is widely available. However, the production of rayon in Western Europe and North America has declined dramatically because of competition from synthetic fibers. There are in any case differences between textile rayon fibers and

those used as precursors for carbon fibers. Union Carbide in the USA was the first company to produce rayon-based carbon fibers with their first fiber called Thornel 25 (Bacon, 1973). Many aerospace applications use rayon fabric to produce structures with high thermal resistance but relatively low strength. In contrast to textile rayon fibers, those regenerated cellulose fibers which are best suited for producing carbon fibers destined for mechanical applications, have a smooth surface and circular cross-section coupled with a fine microcrystalline microstructure. These characteristics, as we have seen above, are found to be desirable in other types of carbon fibers. The reasons are straightforward as the smaller crystal size and the smooth surface results in fewer defects introducing stress concentrations into the fiber and hence lowering its strength. The precursor fibers are spun from a purified solution of cellulose containing a catalyst (frequently a phosphorus compound) and subjected to heat treatment around 100 °C to dehydrate the cellulose structure. Other compounds, such as NH_4Cl , are added which facilitate crosslinking around 250 °C and render the fiber infusible. Alternatively organo-silicon products can also be used to aid the pyrolysis process. At temperatures over 500 °C ordering of the carbon occurs. Pyrolysis, under a non-oxidizing atmosphere, typically takes place at around 1200 °C (Palaisantin *et al.*, 2006). Higher heat treatment, up to and beyond 2200 °C, increases carbon basic structural unit size and the degree of orientation is enhanced.

The greatest problem for obtaining high performance carbon fibers from a cellulose-based solution is that cellulose contains only 24%wt of carbon which can be used in making the fiber. This means that three-quarters of the mass of the starting material has to be removed during pyrolysis. The result is that any orientation introduced into the precursor fiber is lost during pyrolysis and this leads inevitably to low mechanical properties. This can be partially compensated by stretching the fibers during pyrolysis, at temperatures which can be up to and above 2600 °C. Pyrolysis typically takes place at around 1200 °C (Palaisantin *et al.*, 2006). The moduli of the fibers are not very high. Although results from laboratory produced fibers show that moduli can be much higher than those of such fibers usually produced, this is misleading as typically the values of moduli range from 35 to 60 GPa with strengths no greater than 1.5 GPa, as can be seen from Table 16.4.

The main interest for cellulose-based carbon fibers is for their heat transmission characteristics. The poor organization of their microstructures

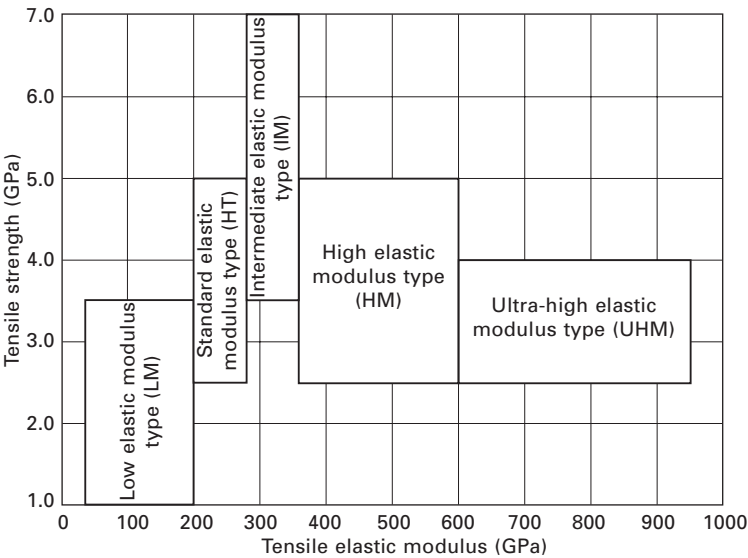
Table 16.4 Characteristics of rayon-based carbon fibers

Tensile modulus (GPa)	35–60
Failure stress (GPa)	0.5–1.5
Specific gravity	1.4–1.5
Diameter (mm)	6–10
Carbon content (%)	99–99.9

leads to relatively low coefficients of heat transmission compared with other types of carbon fibers. This makes cellulose-based carbon fibers particularly attractive for use in carbon–carbon composites, used in ablative heat shields and also in brake linings. These markets are, however, very limited in size and cellulose-based carbon fibers have been largely eclipsed by the PAN and pitch-based fibers described above. The fibers find use also as activated carbon products for absorption of noxious gases.

16.6 Conclusions

Carbon fibers exist in a large variety of types, as can be seen in Fig. 16.15, published by the Japan Carbon Fiber Manufacturers Association. PAN-based fibers find the biggest market; however, other types of carbon fibers find applications due to their unique properties. The stiffness of the carbon fibers depends on the regularity and alignment of the fibres’ atomic structures and this allows carbon fibers with a very wide range of elastic moduli to be produced. Some carbon fibers have elastic moduli about half that of glass whilst others can be as stiff as graphite or four and a half times as stiff as steel with a quarter of its density. Carbon fibers established their reputation as the most effective lightweight material to replace conventional metals for structures of airplanes, satellite, automobile, windmill, pressure vessel and other many applications. Now growing awareness of the consequences of global warming, carbon fibers are finding an increasingly central role



16.15 Carbon fibers: product types by mechanical performance
(Japan carbon Fiber Manufacturers Association).

in the reduction of CO₂ emissions because of its light weight and high performance.

In the carbon fiber market, PAN-based carbon fibers are strengthening their status along with rapidly expanding applications in many fields to promote safety, energy and environment throughout the world. Pitch-based carbon fibers are also expanding in the region of ultra-high modulus applications.

In terms of mechanism, tensile strength of carbon fibers is mainly dominated by defects. For the tensile strength of CFRP, not only fiber tensile strength but also alignment and adhesion between fiber and matrix resin are important. The tensile moduli of carbon fibers are mainly dominated by the graphite crystallite structure in terms of size and orientation. Compressive strength is dominated, not only defects, but also by crystallite size. PAN-based carbon fibers are superior on the whole amongst those characteristics and performances. Pitch-based carbon fibers have too large graphite crystallites, and it gives ultra-high modulus performance but at the same time low tensile and compressive strength.

The development of higher performance carbon fibers is a never-ending target and theme for carbon fiber manufacturers. However, according to market and technology trends, high cost performance carbon fibers are finding greater markets rather than at the very high performance fibers, obtained with high cost. It has become clear that cost performance is the key word for the development of carbon fibers and their applications.

Applications of carbon fibers are rapidly expanding. Matrix resin systems, application environment, targets of performance and cost are encouraging more varieties of carbon fibers to be produced. To support those applications new carbon fibers are necessary to be developed. For larger and more established markets, the development of cost competitive fabrication processes is also becoming very important. Carbon fibers need to be optimized according to new fabrication processes. The spiral of the developments from various viewpoints will move forward more dramatically and quickly in future. In many ways, carbon fibers are still new and evolutionary materials which are finding increasing numbers of applications and improving the lives of the people all over the world.

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The mechanical behaviour of small diameter silicon carbide fibres

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Abstract: Continuous ceramic fibres based on silicon carbide, with diameters of 15 μm or less, have been produced since the early 1980s. They offer the possibility of reinforcement for composite materials destined to be used at temperatures above 1000 °C. They have undergone considerable changes in their manufacture and characteristics since their initial development. The manufacture, compositions, microstructures and properties of the various generations of silicon carbide (SiC) fibres which have been developed are described, together with discussions on their limitations.

Key words: silicon carbide, manufacture, structure, properties, limitations.

17.1 Introduction

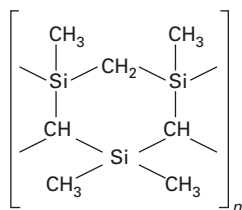
Silicon carbide (SiC) is a ceramic which can be stable in air, in bulk form, up to 1600 °C. This has prompted the development of several types of SiC fibres including fibres with diameters usually greater than 100 μm made by chemical vapour deposition (CVD) onto a core filament and also monocrystalline short filaments, known as whiskers, with diameters of the order of 1 μm (Akiyama, 1988; Wawner, 1988). The CVD fibre, first produced in the 1960s, is finding interest as a reinforcement for titanium but its diameter of more than 100 μm makes it unsuitable for weaving and other types of fibre handling processes, which are commonly used with finer fibres found in the majority of composite materials. The SiC whiskers also present serious handling difficulties together with worries about health-related problems.

This industrial production of SiC fibres with diameters of around 15 μm was the direct result of research started in the 1970s and carried out by Professor Yajima and his team at the Tohoku University in Japan. Commercial production began in 1982 by Nippon Carbon. The starting polymer was polycarbosilane (PCS), which contains both carbon and silicon atoms arranged in a cyclic form consisting of six atoms, suggesting their arrangement in β -SiC. The synthesis of the PCS used dimethyldichlorosilane $(\text{CH}_3)_2\text{SiCl}_2$ which was converted into polydimethylsilane $[(\text{CH}_3)_2\text{Si}]_n$, by dechlorination with metal sodium and which in turn was converted into a polycarbosilane polymer by heating in an inert atmosphere at 400 °C (Yajima *et al.*, 1975). The chemical

composition of PCS can be simplified as $-\text{[SiCH}_3\text{H—CH}_2\text{]}_n-$. PCS can be melt spun to give continuous weak fibres. Stabilisation was initially by crosslinking of the polymer by heating in air. This was followed by heating in vacuum at around 1200°C to produce the first generation of small-diameter SiC fibres. The availability of these SiC fibres brought rapid interest from the aerospace and aero-engine industries as they offered the possibility of producing ceramic fibre reinforced carbon and ceramic matrix composite materials, capable of being used as structural materials to higher temperatures than those attainable with the best nickel-based super-alloys and which were less sensitive to oxidation than carbon–carbon. The attraction of silicon carbide is that it is a ceramic, which in bulk form has a Young's modulus twice that of steel for less than half the density and can be used up to 1600°C . Although oxidised at high temperature, bulk SiC undergoes surface passive oxidation which protects the bulk of the specimen. However, it was found that the characteristics of these first generation fibres were not those of bulk SiC. The first generation of fibres possessed a Young's modulus less than half that expected. The fibres crept at 1000°C and above and degraded above 1250°C . Better understanding of the mechanisms involved has led to the development of three generations of fibres, the latest of which has properties approaching the limits of what is physically possible with silicon carbide.

17.2 First generation fine silicon carbide (SiC) fibres

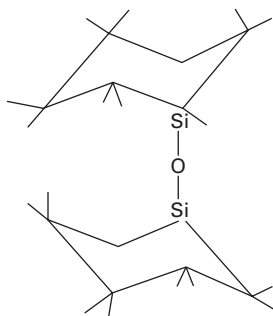
The production of SiC-based fibres having diameters in the range of 10–20 μm offered the possibility of reinforcements capable of operating in an oxidising atmosphere at over 1000°C , above the limits of nickel-based alloys (Yajima *et al.*, 1976a,b). Yajima and his colleagues explored several routes to produce precursors for the ceramic fibre (Emsley, 1999). The decomposition of polydimethylsilane (PDS) which was heated in an autoclave at 470°C for 14 hours, was eventually chosen as the route for the production of PCS as it gave a precursor which, although difficult to spin, could be spun from the melt and converted into a ceramic fibre. The repeat element in the chemical structure of polycarbosilane (PCS) is given in Fig. 17.1. A steric view of



17.1 Repeat unit of polycarbosilane (PCS).

this molecule shows that the cycle of carbon and silicon atoms, with some bonds removed, is arranged in the form of a chair configuration (Bunsell and Piant, 2006). This is similar to the arrangement seen in β -SiC. Molecular weights of around 1500 were used for commercial production. The precursor filaments were then spun from the melt in a nitrogen atmosphere at around 300 °C and crosslinked. The PCS precursor was made infusible, in the first generation of fibres, by crosslinking in air, in the temperature range from 145 to 200 °C, which introduced oxygen into the polymer, as shown in Fig. 17.2. The crosslinked PCS fibres were insoluble in all solvents. Heating the crosslinked precursor up to 550 °C induced the evaporation of low molecular weight components in the carbosilanes, which led to a considerable weight loss but resulted in an increase in molecular weight. Above this temperature and up to around 800 °C, hydrogen and methane were lost from the methyl groups (CH_3), leaving behind free carbon and crosslinking was enhanced. At 1050 °C hydrogen was again given off and the excess carbon reduced and the X-ray diffraction (XRD) patterns became sharper, indicating greater regularity in the structure. At and above 1300 °C the remaining free carbon reacted with the Si—O group with the evolution of CO gas and the formation of Si—C bonds. The nascent β -SiC grains, formed at slightly lower temperatures, increased in size and the amorphous structure evolved into a semicrystalline structure consisting of nanometre-sized β -SiC grains surrounded by a much less ordered phase made up of silicon, carbon and oxygen. Heating to 1500 °C produced large grain growth, the evolution of carbon monoxide and the disintegration of the fibre.

The first fibres of this first generation, produced by Nippon Carbon around 1982, were the Nicalon 100 series but were replaced after about four years by the Nicalon 200 series which became the standard grade for much of the ceramic matrix composite studies subsequently undertaken. These fibres have diameters of around 15 μm and show variability in diameter along their



17.2 The first generation of fine SiC fibres were made by crosslinking the precursor PCS with oxygen.

length because of the difficulties of spinning the precursor fibres. Table 17.1 shows the approximate chemical composition of these fibres.

Yajima and his colleagues had considered several routes for making SiC fibres including the addition of titanium to the PCS so as to give polytitanocarbosilane (PTC) (Yajima *et al.*, 1981). This precursor was obtained by the grafting of titanium alkoxide, $\text{Ti}(\text{OR})_4$, in which $\text{R} = \text{C}_n\text{H}_{2n+1}$, onto the PCS chains. This linked the polymer chains together, increasing molecular weight and its spinability. In 1987, another Japanese company, Ube Industries began producing Tyranno fibres made from PTC precursors and reported that they had better thermal and chemical stability compared with the then existing Nicalon fibres and they could be made with smaller diameters (Yamamura *et al.*, 1988). The precursors of these first Tyranno fibres were also crosslinked in air. The Tyranno LOX-M, contained approximately 13% by weight of oxygen, which explains the letter M, which is the 13th letter in the alphabet.

By the end of the 1980s the two Japanese companies were producing first generation fine diameter SiC fibres and their compositions, Young's moduli and densities are shown in Table 17.2. As can be seen, the details of the composition and the nomenclature used to describe the fibres have changed slightly since their initial introduction. Bulk SiC is, however, the second hardest material known and is crystalline, it possesses a Young's modulus of around 400 GPa and a density of 3.15 g/cm^3 and can be used in air up to 1600°C . At this temperature passive oxidation of the surface to SiO_2

Table 17.1 Compositions of early varieties of first generation SiC fibres produced by Nippon Carbon

	Elemental composition %wt			Chemical composition %wt		
Fibre type	Si	C	O	SiC	SiO_2	C
NLP-101	60	27	13	69	24	7
NLP-202	54	37	9	66	17	17

Table 17.2 Compositions, Young's moduli and densities of first generation commercialised SiC fibres

Producer	Nippon Carbon	Ube Industries
Fibre name	Nicalon 200	Tyranno LOX-M
Precursor	PCS	PTC
Cured by	Oxidation	Oxidation
Si (wt%)	56.6	54
C (wt%)	31.7	31.6
O (wt%)	11.7	12.4
Ti (wt%)	0	2.0
C/Si	1.31	1.36
Density (g/cm^3)	2.55	2.37
Young's modulus (GPa)	200	185

protects it from further degradation. Table 17.2 reveals that the properties of the first generation of fine SiC fibres were not those of the bulk material. This has been shown to be due to the non-stoichiometric composition of the first generation of fibres, which are rich in carbon and contain oxygen. This results in an amorphous phase in which SiC grains of around 2 nm are embedded.

17.2.1 Mechanical behaviour of first generation SiC fibres

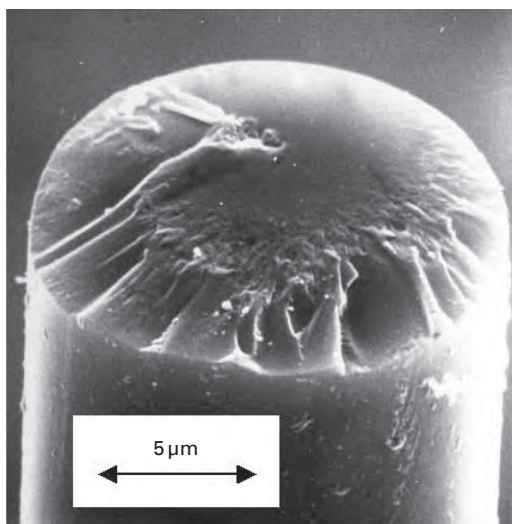
At room temperature, the fibres are linearly elastic in tension. The variation in fibre diameter along individual fibres makes the measurement of stress and modulus inherently difficult, which explains some discrepancies in the published data for these fibres that in any case have been improved since their introduction. Some typical property data for first generation SiC fibres can be found in Tables 17.2 and 17.3. Figure 17.3 shows the fracture morphology of a first generation Nicalon fibre broken in tension (Simon and Bunsell, 1984a). The fracture suggests a glassy structure of the fibre.

The tensile behaviour of the first generation fibres remains linearly elastic up to 1250 °C but short-term strength falls from 1000 °C. When tested in air and in argon, there is an earlier onset of strength reduction observed when the fibres are tested in air, indicating a higher sensitivity to carbon oxidation of the surfaces. However, the oxidation of the Nicalon 100 series fibres could be beneficial particularly under long-term loading conditions as it slowed internal decomposition of the fibres (Simon and Bunsell, 1984b). Growth of silica is observed on the surfaces of the fibres when they are heated in air at 1200 °C and above. This layer can have an irregular thickness along the fibre and pores are formed at the silica/SiC fibre interface and pores can be formed at 1450 °C which induce local decohesion of the silica layer from the fibre. These pores are produced by the outgassing of carbon monoxide from the interior of the fibre. Failure surfaces remain brittle at high temperature but new types of defects are seen compared with those found at room temperature. Local chemical inhomogeneities at the fibres' surfaces such as carbon-rich zones are preferentially decomposed or oxidized, giving rise to porous weak regions.

The fibres were seen to creep from around 1000 °C (Simon and Bunsell, 1984b) but, when not loaded or under low loads, shrank on heating above this temperature. This behaviour could be attributed to β -SiC grain growth in the fibres which stabilised with grain sizes around 3 nm. The period of grain growth depended on the temperature but corresponded to primary creep observed at higher loads. It was observed that it was possible to measure an initial shrinkage followed by positive creep, showing that two mechanisms were in competition. The variation of steady state creep rate with temperature, T , and applied stress, σ , can often be modelled by:

Table 17.3 Details of manufacture, elemental composition and approximate cost of all three generations of fibres

	Trade mark	Manufacturer	Crosslinking method	Approximate maximum production temperature (°C)	Elemental composition (wt%)	Density (g/cm ³)	Average diameter (mm)	Cost (US \$/kg)
First generation	Nicalon 200	Nippon Carbon	Oxygen	1200	56Si + 32C + 12O	2.55	14	2000
	Tyranno LOX-M	Ube Ind.	Oxygen	1200	54Si + 32C + 12O + 2Ti	2.48	11	1250
Second generation	Hi-Nicalon	Nippon Carbon	Electron irradiation	1300	62.5Si + 37C + 0.5O	2.74	12	8000
Third generation	Tyranno ZM	Ube Ind.	Oxygen	1300	57Si + 34.5C + 7.5O + 1Zr	2.48	11	1500
	Tyranno SA 1	Ube Ind.	Oxygen	>1700	68Si + 32C + 0.6Al	3.02	11	N/A
	Tyranno SA 3	Ube Ind.	Oxygen	>1700	68Si + 32C + 0.6Al	3.1	7.5	5000
	Sylramic	COI Ceramics	Oxygen	>1700	67Si + 29C + 0.8O + 2.3B + 0.4N + 2.1Ti	3.05	10	10 000
	Sylramic iBN	COI Ceramics	Oxygen	>1700	N/A	3.05	10	>10 000
	Hi-Nicalon Type-S	Nippon Carbon	Electron irradiation	>1500	69Si + 31C + 0.2O	3.05	12	13 000



17.3 Fracture morphology of a first generation Nicalon fibre.

$$\dot{\epsilon} = A s^n \exp \left(\frac{\hat{E} - Q}{RT} \right)$$

in which A is a constant depending on the material. The stress exponent, n , and the activation energy for creep, Q , can be deduced from creep experiments and their values can suggest the processes involved. Below 1200 °C, Newtonian creep dominates in Nicalon 200 fibres, most probably caused by grain boundary sliding and controlled by the oxygen-rich intergranular phase. Above 1200 °C, the stress component increases from 1 to 2 as the intergranular phase decomposes and grain sliding becomes more difficult. The two competing mechanisms were grain growth and perfection and grain boundary sliding. The creep activation energy was found to be around 250 kJ/mol.

As the applied stress was increased, at a given temperature, the period during which shrinkage was observed decreased until a stress was reached at which only positive creep was measured.

17.2.2 Compositions and microstructures of first generation fibres

Figure 17.3 shows a typical failure surface of a first generation SiC fibre. The fibre appears to be glassy and possibly amorphous, as was originally concluded. However, wide angle XRD studies and later examination by transmission electron microscopy (TEM) showed that the first generation fibres contained β -SiC grains of less than 2 nm (Simon and Bunsell, 1984b; Le Coustumer *et al.*, 1993).

The compositions by weight percentages and densities of the fibres are given in Table 17.2, together with the carbon-to-silicon atomic weight ratios. The first generation fibres were far from stoichiometric SiC and contained an excess of oxygen and carbon. The oxygen, used to crosslink and render infusible the precursors, remains after pyrolysis of the PCS and PTC fibres. The excess carbon in the SiC fibres came from the methyl groups present in the PCS and PTC polymers. The presence of oxygen in the precursor fibres induced the out-gassing of carbon oxides between 400 and 600 °C at the beginning of the pyrolysis, so reducing the final carbon content of the ceramic fibre. The oxygen also produced an amorphous phase in which the small SiC grains and the free carbon aggregates were embedded.

It was shown that the oxygen was in the form of a ternary phase SiO_xC_y (Porte and Sartre, 1989). With such a model for the microstructure of the fibre, a porosity level of more than 2% was calculated (Le Coustumer *et al.*, 1993).

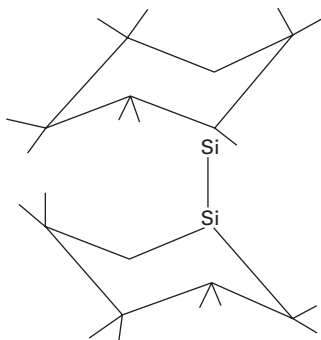
The presence of the amorphous intergranular phase was clearly due to the oxygen which remained in the fibres after pyrolysis, making an Si—O—C phase. The low fraction of a granular SiC phase accounted for the Young's modulus of the fibres being only half that of bulk SiC. The amorphous phase also explained why the fibres began to lose strength and creep at temperatures around 1000 °C (Mah *et al.*, 1984).

The rate of strength loss of first generation fibres was seen to be lower in oxidizing atmospheres than in an inert argon atmosphere due to the production of a silica coating which hindered outgassing of the products of the decomposition of the Si—O—C phase (Shimoo *et al.*, 2002).

17.3 Second generation small diameter silicon carbide (SiC) fibres

The need for oxygen in the crosslinking of the precursor fibres was removed by using electron irradiation which could interact with the precursor polymers to produce free radicals and gaseous products by the scission of the chemical bonds of Si—CH₃, Si—H and C—H. This allowed Si—Si and Si—C bonds to be formed. This technique was developed jointly by both fibre producers working in collaboration with the Japanese Atomic Energy Research Institute. The crosslinking step was followed by heat treatment at 327 °C for a short time to eliminate the remaining free radicals which were trapped in the irradiated precursor fibre. The hydrogen atom, bonded to the silicon atom, in the PCS, is removed by electron bombardment, so as to allow direct bonding between the two silicon atoms in neighbouring molecules, as is shown in Fig. 17.4 (Taki *et al.*, 1988).

Below 550 °C crosslinking between main chains dominates and is induced by the dehydrogenation condensation of the Si—H groups. From 550 to



17.4 Direct crosslinking of the PCS precursor polymer by irradiation curing.

800 °C, the side chains on the crosslinked polymer begin to decompose and CH_4 and H_2 are given off, producing an inorganic fibre. Above 800 °C and up to 1000 °C, hydrogen is given off, most probably associated with the decomposition of C—H bonds remaining in the PCS. Above 1000 °C, β -SiC grains, free carbon aggregates and a poorly organised intergranular phase comprising silicon and carbon atoms are formed (Yajima *et al.*, 1979). The presence of the free carbon aggregates hinders grain growth so allowing the SiC grains to remain small during fibre production which takes place at around 1300 °C as indicated in Table 17.3.

The radiation crosslinking process, although costly, was successful in reducing the oxygen content of fibres produced from PCS precursors to 0.5 wt% and gave rise to the Hi-Nicalon fibre produced by Nippon Carbon (Takeda *et al.*, 1993).

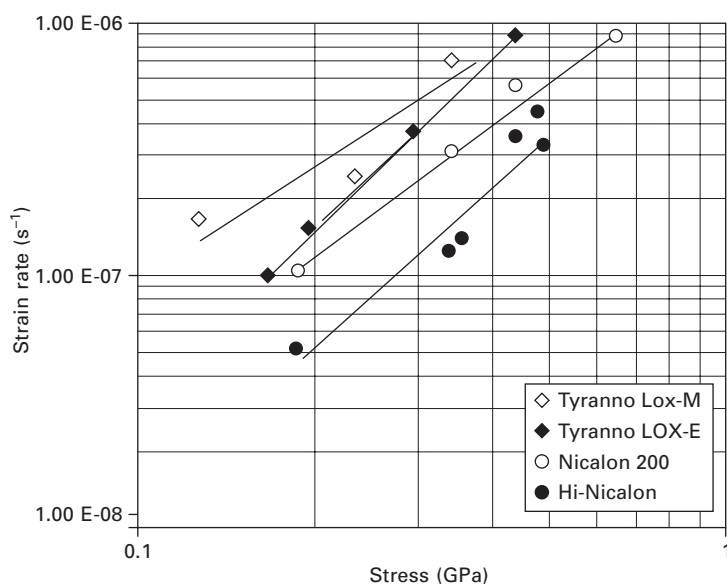
However, this process, applied to PCT precursors, only reduced the oxygen content to around 5wt%. This was due to the addition of the alkoxide, $\text{Ti}(\text{OR})_4$, to the PCS, so as to introduce titanium. This added oxygen by another route than that of oxygen crosslinking. Ube Industries did not commercially produce the Tyranno LOX-E fibre as the irradiation process was expensive and the improvement in properties not sufficiently adequate. The company produced other fibres with the intention of reducing the oxygen content by changing the metal added to the PCS polymer and the titanium was replaced by zirconium. This substitution reduced the oxygen concentration as the compound used to graft the zirconium onto the PCS polymer contained less oxygen than was the case with titanium alkoxide (Kumagawa *et al.*, 1997). The Tyranno ZM fibre was cured by oxidation and was commercially produced. The stability of the intergranular phase which contained zirconium was said to be improved, compared with the titanium-containing intergranular phase, as weight loss began at 1600 °C for the Tyranno ZM fibre which was 200 °C higher than for the Tyranno LOX-M. The Tyranno ZM fibre found a market, for some time, in filters for engines running on sulphur-rich diesel.

17.3.1 Mechanical behaviour of second generation SiC fibres

The only second generation fibre produced commercially is the Hi-Nicalon fibre which is approximately 35% stiffer than the first generation fibres. There was no change in appearance of the fracture surfaces between the first and second generation fibres which remained devoid of any obvious signs of an ordered microstructure, as seen in the scanning electron microscope.

Strength retention at high temperatures of the Hi-Nicalon fibre was improved, when compared to the first generation fibres (Hochet *et al.*, 1997). These fibres remained linearly elastic up to 1350 °C which was 100 °C higher than the first generation fibres and room strength was retained up to around 1200 °C in both argon and air. Sensitivity to oxidation is seen in the Hi-Nicalon fibres. Growth of a silica layer was observed on the surfaces of the fibres when heated in air at 1200 °C and pores at the silica and SiC fibre interface were observed at 1450 °C induced by the decomposition products of the fibre.

The Hi-Nicalon fibre was found not to creep below 1000 °C. The strain rates of the fibres, under an applied stress of 1 GPa at 1050 °C, were 10^{-10} s^{-1} compared with $2 \times 10^{-8} \text{ s}^{-1}$ for the Nicalon 200 fibre. The creep rates of all the first and second generation fibres were very similar at 1400 °C, at around $5 \times 10^{-7} \text{ s}^{-1}$ under a stress of 0.3 GPa, as can be seen from Fig. 17.5. The activation energy for the creep of Hi-Nicalon fibres was around 360 kJ/



17.5 Creep rates at 1400 °C for the first and second generation fibres.

mol and could be explained by grain boundary sliding accommodated by interface-controlled diffusion mechanisms. The carbon layers, between the grains facilitate this sliding. Ultimate failure in creep of the fibres was found not to be due to a lack of accommodation, as is the case for bulk ceramics, but related to surface defects, such as cavities or porous zones growing from local chemical heterogeneities.

The mechanical properties of the second generation Hi-Nicalon fibres are given in Table 17.4.

17.3.2 Compositions and microstructures of second generation fibres

The removal of oxygen from the crosslinking process used to make the Hi-Nicalon fibres, made from electron-irradiated PCS precursors, resulted in an increase in size of the β -SiC grains which were observed by transmission electron microscopy to be in the range of 5–10 nm (Berger *et al.*, 1995). This accounts for the higher thermal conductivity of these fibres compared to the first generation fibres, as can be seen in Table 17.4. The microstructure consists of areas of well-ordered SiC surrounded by Si and C atoms which are not completely crystallized into β -SiC grains. The Hi-Nicalon fibre contained a higher ratio of carbon atoms to silicon atoms than in the first generation fibres as the absence of oxygen did not allow the excess carbon to be oxidized. The free carbon was composed of 4 to 10 distorted layers with some aggregates measuring up to 5 nm. The small amount of oxygen in these fibres was presumed to be present at the SiC/SiC boundaries. The Hi-Nicalon fibre would be composed by weight of 85% SiC, 11% C and 4% of $\text{SiC}_{0.86}\text{O}_{0.29}$ if the oxycarbide phase is taken to be composed of $\text{SiO}_x\text{C}_{1-x/2}$ with three carbon atoms to every one oxygen atom. It was calculated that the non-crystallized SiC in the Hi-Nicalon fibre represented around 26% by weight of the fibre (Berger *et al.*, 1999). The absence of a significant amount of oxygen removed the amorphous phase present in the first generation fibres and allowed larger SiC grains to form at the higher manufacturing temperature used. Their size, however, was limited by the excess free carbon in the fibre. This microstructure explains the observed increase in Young's modulus of these fibres when compared with first generation fibres, as can be seen from Table 17.4.

The microstructure of the Tyranno LOX-E fibres was very similar to that of the first generation Tyranno LOX-M fibres. No Ti compounds were found, indicating that the grains were separated by a Si—C—Ti—O phase.

The oxygen content was clearly the key factor in controlling the microstructures and ultimately the mechanical properties of the polymer-derived SiC fibres. The oxygen cured, first generation fibres, the Nicalon 200 and Tyranno LOX-M fibres, possessed similar grain sizes, of about

Table 17.4 Details of mechanical and thermal properties of all three generations of fibres

	Trade mark	Manufacturer	Thermal expansion coefficient, ppm/°C ($\geq 1000^\circ\text{C}$) (DiCarlo and Yun, 2005)	Room temperature axial thermal conductivity (W/m K) (DiCarlo and Yun, 2005)	Room temperature strength (GPa)	Room temperature Young's modulus (GPa)
First Generation	Nicalon 200	Nippon Carbon	3.2	3	3	200
	Tyranno LOX-M	Ube Ind.	3.1	1.5	3.3	185
Second Generation	Hi-Nicalon	Nippon Carbon	3.5	8	2.8	270
	Tyranno ZM	Ube Ind.	NA	2.5	3.4	200
Third Generation	Tyranno SA1	Ube Ind.	NA	65	2.8	375
	Tyranno SA3	Ube Ind.	NA	65	2.9	375
	Sylramic	COI Ceramics	5.4	46	3.2	400
	Sylramic iBN	COI Ceramics	5.4	>46	3.5	400
	Hi-Nicalon Type-S	Nippon Carbon	NA	18	2.5	400

2 nm, and properties. However the Hi-Nicalon and Tyranno LOX-E fibres had distinctly different microstructures and showed different behaviours. The reduction in oxygen content to 5 wt% in the Tyranno LOX-E fibre did not produce a significant change when compared with the first generation fibres; however, the Hi-Nicalon with only 0.5 wt% can be seen to be a very different fibre.

Although bulk SiC can be used to 1600 °C, the oxygen-rich SiC fibres became too brittle to be handled when heated above 1500 °C and were reduced to a powder at 1800 °C by the degradation of the silicon oxycarbide intergranular phase (Takeda *et al.*, 1994). The absence of an oxycarbide intergranular phase in the Hi-Nicalon fibre clearly helped its high temperature stability and the larger percentage of crystalline SiC accounted for its higher Young's modulus when compared to the first generation fibres and the still oxygen rich Tyranno LOX-E fibre.

Heating Hi-Nicalon fibres in air above 800 °C produces a weight gain indicating oxidation of the fibre (Chollon *et al.*, 1997) and from 1200 °C a double layer consisting of crystallised silica and amorphous silica covered the surface of the fibre. At this temperature, the amorphous silica nearest the fibre surface was devitrified and converted to cristobalite. At 1400 °C, the layer was completely devitrified and was cracked when observed at room temperature due to shrinkage associated with a phase change in the cristobalite at 270 °C. The pores, mentioned earlier, between the silica coating and the fibre were due to bubble formation which is observed with SiC polycrystals, which contain carbon inclusions, during oxidation in air. The growth of the silica layer is more rapid with the Hi-Nicalon fibre than that seen with bulk SiC but the layer does play a passive role in inducing a parabolic rate law up to 1400 °C. Above this temperature, the oxide layer no longer provides a protective sheath. When heated for five hours to 1500 °C in flowing argon, the Hi-Nicalon fibres lost all tensile strength but room temperature strength was retained after ten hours under the same heating conditions but under flowing CO (Shimoo *et al.*, 2003). This was due to the suppression by the CO atmosphere on the thermal decomposition of the SiC_xO_y phase.

The microstructure of the Hi-Nicalon fibre could be made to evolve further by heat treatment. Grain growth was seen to begin at 1300 °C which, as Table 17.3 shows, was the approximate temperature during fibre manufacture. At 1400 °C, the grains ranged in size from 10 to 40 nm and from 10 to 70 nm at 1500 °C. The grain growth was not impeded in this fibre by a non-stoichiometric oxygen-rich phase, as in the other fibres considered so far. This permitted the grains to grow and develop facets by consuming the less well-ordered regions which surrounded the grains. The free carbon became organised parallel to the SiC grain facets forming cages around the grains and eventually limiting their growth.

The consequence of these changes was that the fibre became stiffer, with

Young's moduli being measured up to 295 GPa and the fibre showed lower creep rates. The stress exponent for the creep of Hi-Nicalon fibres was between 2 and 3 between 1000 and 1450 °C (Pysher *et al.*, 1991).

17.4 Third generation small diameter silicon carbide (SiC) fibres

A major driving force for the development of the small diameter SiC fibres has been the need of the gas turbine generator industry for materials able to withstand higher temperatures than nickel-based alloys, which are limited to a maximum temperature of 1150 °C. The development of ceramic matrix composites based on the small diameter SiC fibres embedded in a SiC matrix held out this promise from the early 1980s; however, those composites based on first generation fibres did not meet all the high temperature requirements. Improvements in the high temperature stability of the fibres were therefore desired and calls were made from the mid-1980s for the development of more stoichiometric fibres which would be stable in air up to 1400 °C. The fibres needed to be based on truly sintered SiC. The approach taken by the two Japanese fibre manufacturers to meet this challenge has been to extend their technology based on an understanding of the processes controlling the behaviour of the first and second generation fibres.

Ube Industries further developed their control of the chemistry of the precursor polymer and grafted another metal, aluminium, by reaction of aluminium acetylacetonate with PCS. The role of the aluminium is to help in crosslinking the precursor fibres and also play the part of a sintering agent (Ishikawa *et al.*, 1998; Ichikawa and Ishikawa, 2000). The fibre contains up to 2 wt% of aluminium. The precursor fibre is cured by oxidation and then pyrolysed in two steps, first to allow oxide phases to decompose and to allow the outgassing of CO during heating above 1200 °C and then, in the second step, the aluminium sintering aid allows the SiC grains to sinter at temperatures up to 1800 °C. These fibres are designated Tyranno SA fibres and two versions have been made available: Tyranno SA1 and Tyranno SA3.

The American company Dow Corning, which had long been studying the production of small diameter ceramic fibres, extended the approach adopted by Ube Industries in making the Tyranno LOX-M fibre. Using such fibres made from PTC they diffused boron into them as a sintering aid (Lipowitz and Rabe, 1997). In this way degradation of the oxycarbide phase at high temperature is controlled and catastrophic grain growth and associated porosity, as occurred with the previous oxygen-rich fibres, is avoided. The precursor fibre can then be heated to around 1400 °C so that the excess carbon and oxygen are lost as volatile species and then sintered at a higher temperature, as for the Tyranno SA fibre, to yield a polycrystalline, near-stoichiometric,

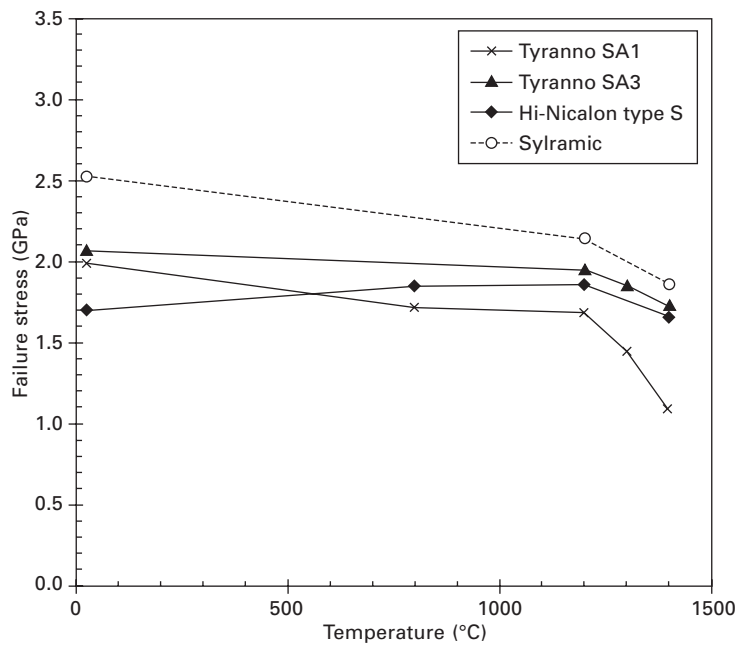
SiC fibre called Sylramic fibre. This fibre is now produced by a company called ATK COI Ceramics, which, in collaboration with researchers at NASA Glenn, has improved on the original Sylramic fibre by removing the boron from the fibre surface by further heating in a nitrogen-containing gas (Yun and Di Carlo, 1999). This latter fibre is called Sylramic-iBN and it is claimed that it shows reduced creep and increased oxidation resistance together with a BN-rich surface (DiCarlo and Yun, 2005).

Nippon Carbon saw that to achieve near stoichiometry the excess carbon in the Hi-Nicalon fibre had to be reduced. The radiation cured precursor route taken by Nippon Carbon to make the Hi-Nicalon fibre was used as an intermediary step to producing a near stoichiometric SiC fibre without the use of sintering aids. The Hi-Nicalon fibre was further heated to above 1500 °C in a hydrogen-rich atmosphere to reduce the excess carbon from a C/Si ratio of 1.39 to 1.05 for the near stoichiometric fibre, which was called Hi-Nicalon-Type-S (Ichikawa *et al.*, 1995).

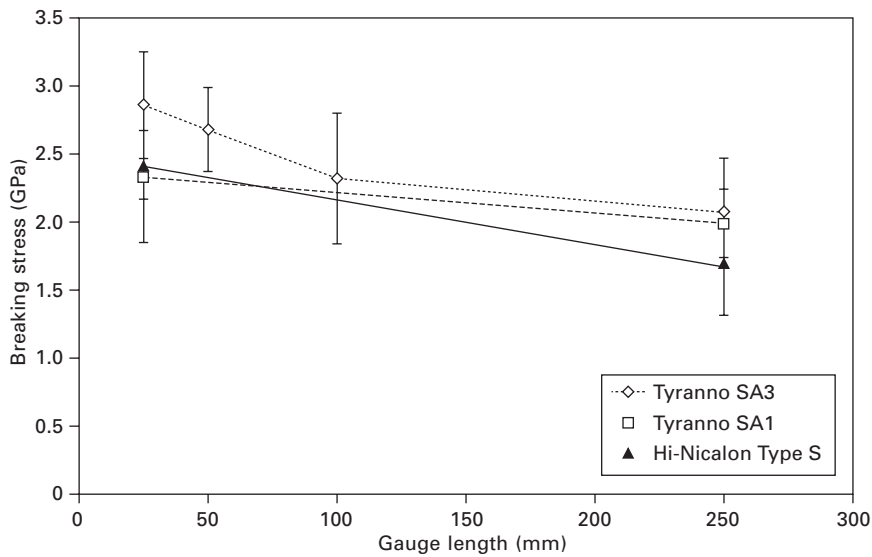
Some details of manufacture and the elemental composition of these third generation fibres are given in Table 17.3.

17.4.1 Mechanical behaviour of third generation SiC fibres

The third generation fibres exhibit properties which are much closer to those of bulk SiC than either of the two earlier generations. In particular their Young's moduli and thermal conductivities are considerably increased, as can be seen from Table 17.4, for which some data has been quoted from DiCarlo and Yun (2005) which summarises the properties of fibres of all three generations. The third generation fibres retain their strengths and moduli up to at least 1300 °C, as shown in Fig. 17.6 for the Tyranno SA3 fibre. The strength and modulus of the Hi-Nicalon-Type-S fibre remain steady up to 1400 °C. The values of breaking stresses, shown in Fig. 17.6, should not be taken as absolute as they depend on the testing method and gauge lengths used (250 mm in this case as compared with 25 mm for the results given in Table 17.4) but rather Fig. 17.6 should be seen as showing relative values of fibre strengths at the different temperatures. Figure 17.7 illustrates this last point as the strength of these fibres is very gauge-length dependent. The tests at high temperature are often carried out with grips outside the furnace which means that the fibre specimen is much longer than the 25 mm which is usually used for tests at room temperature. As there is a greater probability of a large defect occurring, with increasing lengths, the mean strength of the fibres falls. This is clearly shown in Fig. 17.7 for three types of third generation fibre but is also seen with the earlier produced fibres. Comparable data have not been published for the Sylramic family of fibres. The improved stability of the Tyranno SA3 fibre compared with the Tyranno SA1 can be clearly seen. Improvements have also been reported



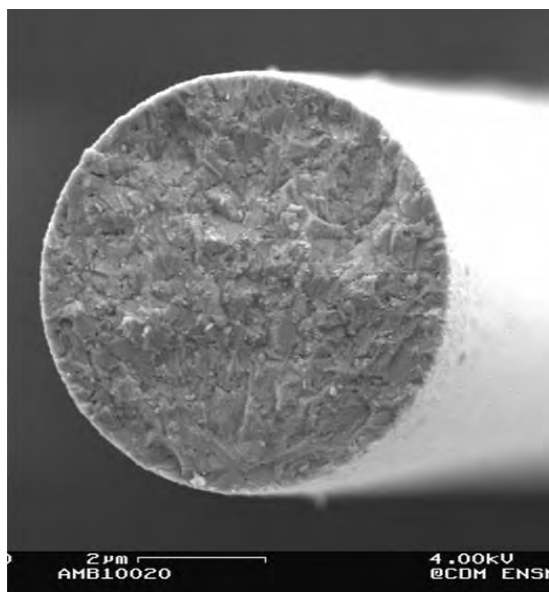
17.6 Strength as a function of temperature for third generation fibres.



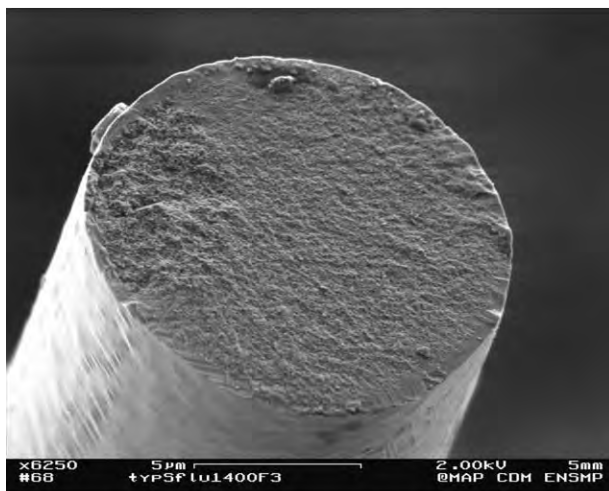
17.7 Length dependence of the strength of third generation SiC fibres.

for the Sylramic fibre in, what the present authors take to be an early form of the Sylramic-iBN fibre. This latter fibre is said to retain its strength, after exposure to high temperatures and then tested at room temperature, better than the Hi-Nicalon-Type-S (DiCarlo and Yun, 1999).

The latest generation of fibres which are described as being near stoichiometric show a marked change in fracture morphology when compared to earlier generations. Figure 17.8 shows the fracture morphology of a Tyranno SA1 fibre. The fibre had a diameter of 10 μm . The fracture surface can be seen to be markedly granular, in sharp contrast to the earlier fibres. The SiC grains in the Tyranno SA1 fibre were around 200 nm in size. Despite the claim of near stoichiometry, there was free carbon in the fibre and its concentration increased near the centre of the fibre, indicating incomplete removal during sintering. The Sylramic fibre also showed a granular fracture surface with SiC grains of around 100 nm with smaller grains of TiB_2 at triple points, identified by TEM studies (Berger *et al.*, 1999). The Hi-Nicalon-Type-S fibre had a fracture surface which was noticeably less granular in appearance than the other two near stoichiometric fibres due to a smaller average grain size of around 50 nm, as shown in Fig. 17.9. An elastic fracture mechanics analysis of fibre failure, using the Griffith criterion, shows that grain sizes have to be greater than 100 nm to control failure stress but below this size the strength is limited to a maximum of 3 GPa due to processing defects but also because the carbon-rich surface blunts the effects of surface flaws. If the carbon is removed the strength falls up to 20% (DiCarlo and Yun, 2005).



17.8 Fracture morphology of a Tyranno SA1 fibre.

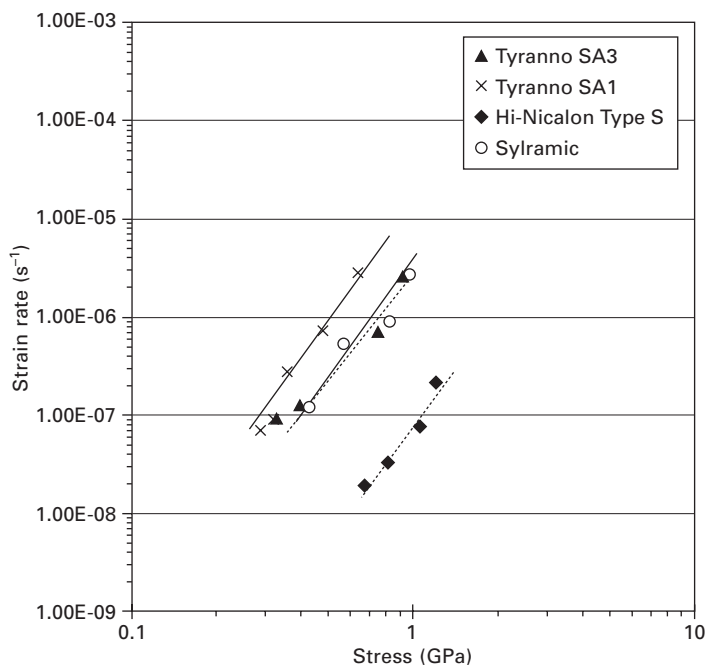


17.9 Fracture morphology of a Hi-Nicalon Type-S fibre broken at 1400°C.

The differences in grain size are attributable to differences in manufacturing temperatures, as can be seen in Table 17.3. Creep behaviour of the third generation fibres also shows considerable improvements when compared with the earlier generations. Figures 17.10 and 17.11 show the strain rates of third generation fibres tested at 1300 and 1400 °C respectively. The fibres showed creep rates of the order of 10^{-8} s^{-1} at 1400 °C (Berger, 2003). The creep resistance of the Hi-Nicalon-Type-S fibre can be seen to be greater than the Tyranno SA3 and Sylramic fibres. The smaller grain size in the Hi-Nicalon-Type-S fibre could, however, be expected to increase sensitivity to creep. This is further discussed below.

These results show that the Hi-Nicalon-Type-S fibre crept at a lower rate than those fibres which contained a sintering aid by one order of magnitude. Creep rates are reduced in Sylramic after heating (annealing) near to their production temperatures. No increase in grain size is observed, in this latter fibre, but the behaviour is thought to be due to the elimination of boron from grain boundaries.

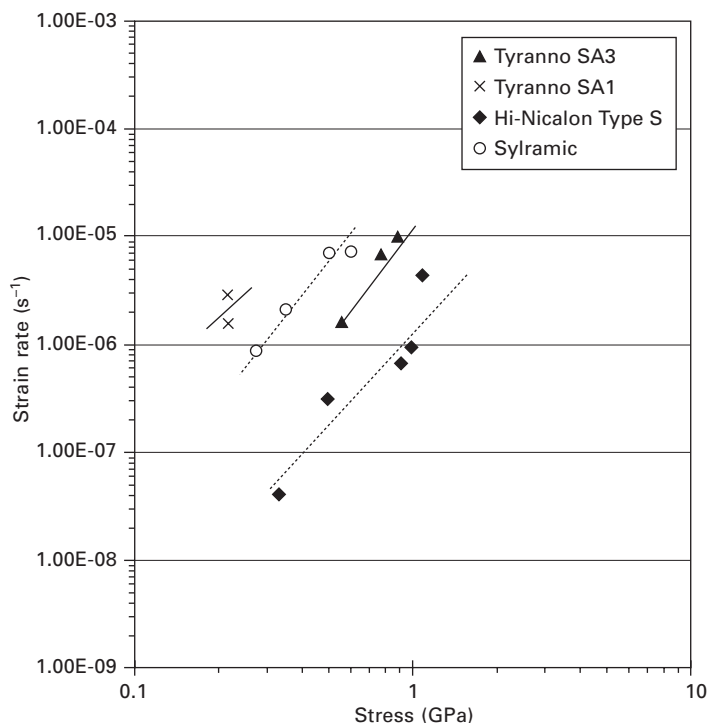
It is claimed that an early form of the Sylramic-iBN fibre, denoted as Sylramic (1, 2) crept at an even lower rate. These latter results have been extracted from a NASA document (Yun and Di Carlo, 1999) for purposes of comparison but no independent data seems to be available in the literature.



17.10 Strain rates of four third-generation fibres at 1300 °C.

17.4.2 Compositions and microstructures of third generation fibres

The Hi-Nicalon-Type-S fibre shows the greatest strength and modulus retention at high temperatures of those fibres tested and reported in the open literature, although the makers of the Sylramic-iBN fibre claim greatest strength retention when tested at room temperature after over one thousand hours at high temperatures (DiCarlo and Yun, 2005). The presence of the a small amount of free carbon in the Hi-Nicalon Type-S fibre is said, by Nippon Carbon, to be deliberate as it serves to limit grain growth and explains why the size of SiC grains in this fibre is limited to around 50 nm. This may help explain the good strength retention of the fibres tested at room temperature after exposure in argon for ten hours at temperatures up to 1600 °C (Tanaka *et al.*, 2003). The absence of a grain growth limiting mechanism, as in a pure stoichiometric polycrystalline SiC fibre, could lead to an explosive growth of the grains and a catastrophic fall in strength. The presence of sintering aids in the Tyranno SA and Sylramic fibres may explain why, even with larger grain sizes than those in the Hi-Nicalon-Type-S fibre, they creep at faster rates. The aluminium and boron in these fibres may explain their slightly earlier fall in strength and faster creep rates at temperatures of 1300 °C and above. The removal of the boron from the surface of the Sylramic fibre is



17.11 Strain rates of four third-generation fibres at 1400°C.

said to improve its creep properties which suggests that those elements used to favour sintering also favour creep at high temperatures. This implies that the removal of the aluminium from the SA fibres would increase their thermal stability. The results shown in Fig. 17.11 suggesting that the Sylramic-iBN fibre creeps at a lower rate, if corroborated, indicate that the larger grain sizes in this fibre compared to the Hi-Nicalon-Type-S fibre, due to a higher manufacturing temperature, may be responsible. This leaves open the possibility of improving the creep behaviour of the Hi-Nicalon-Type-S fibre by further heat treatment. An alternative explanation would be that an intergranular phase, so far undetected, in the fibre increases the creep rate of the fibre over what could be achieved.

The first type of third generation fibre produced by Ube Industries seems to have suffered from incomplete elimination of the Si—O—C amorphous phase created by the crosslinking by oxygen of the precursor used. The Tyranno SA3 is of a smaller diameter, which generally is a means of increasing fibre strength but in this case allows more complete pyrolysis of the fibre. The results are improved thermal resistance and a lowered creep rate of the fibre when compared to its earlier version. It would seem to be the least costly route for obtaining third generation SiC fibres.

Although the electron-irradiated fibres from Nippon Carbon show the greatest retention of strength at high temperature, of those fibres for which data are published, it must be recognized that the process is costly. The oxygen crosslinking process used to make the first generation of fibres has been shown to be a viable and less costly method for producing near stoichiometric fibres by the addition of sintering aids.

Data for ceramic matrix composites based on Sylramic-iBN fibres indicate that their creep rates are similar to those found for similar composite specimens reinforced with the Hi-Nicalon-Type-S fibres. This can be taken as an indication that the Sylramic-iBN fibres possess similar or even better creep characteristics than the Hi-Nicalon-Type-S, as is hinted at in Fig. 17.11 and the producers clearly believe that further progress can be made (Yun *et al.*, 2003).

The most stable form of silicon carbide fibres will, however, be ultimately limited by oxidation; however, observations suggest that all the third generation fibres show considerable resistance to degradation by this process even at 1300°C in air.

17.5 Conclusions

The development of silicon carbide fibres with diameters of 15 μm , or less, was stimulated by end users' needs for fibres which show the characteristics of stoichiometric silicon carbide at high temperatures. The requirement was for fibres which would remain stable up to 1400°C in air. The first generation of fibres showed that filaments based on silicon carbide could be produced but these first generation fibres were limited to maximum temperatures of around 1000°C above which the fibres crept and ultimately decomposed. It was only when the vital role of oxygen in the fibre, which allowed an amorphous phase to be created, was understood, that the step towards making a second generation of fibres could be made. The use of electron irradiation for crosslinking the precursor fibres enabled the oxygen content to be controlled but only in those fibres which did not contain other species which contained oxygen.

The third generation fibres to be produced are nearly stoichiometric in composition with the microstructure of granular silicon carbide and Young's moduli close to that of bulk silicon carbide. The creep and strength retention at high temperatures of the third generation of fibres approach those of bulk silicon carbide.

17.6 Acknowledgements

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The structure and tensile properties of continuous oxide fibers

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Abstract: This chapter will focus on polycrystalline oxide fibers based on alumina, especially sol/gel fibers. Themes of the chapter will include manufacturing methods, fiber properties as a function of chemical composition and microstructure, tensile testing methodology and results, high temperature tensile properties including creep and tensile strength, failure processes and fractography. The chapter includes perspectives on current oxide fiber temperature capability and strength improvements as related to application requirements, with prospects for future improvements.

Key words: sol/gel, α -Al₂O₃ fibers, alumina fiber, polycrystalline fiber, fractography, high temperature creep.

18.1 Introduction

Continuous oxide fibers can be defined as having effectively an infinite length and a microstructure that consists of partially or fully polycrystalline ceramic grains. Commercial polycrystalline ceramic oxide fibers are characterized by high alumina content compared with glass and melt-spun refractory fibers and an ultra-fine or even nanoscale microstructure. These properties provide good strength and flexibility which is maintained up to 1200 °C and above in oxidizing atmospheres. Most commercial applications for these fibers are for thermal insulation, where load-bearing capability is not a major concern. More recently, fibers designed specifically for the reinforcement of metal and ceramic matrix composites have been developed.

Continuous oxide fibers are produced by the sol/gel process. Fibers are spun into continuous tows or rovings typically consisting of 400–1000 filaments, each having a diameter of 9–17 μm . Fiber tows are flexible and easily handled, which allows them to be woven into fabrics and other complex-shaped refractory articles. Major uses, as shown in Fig. 18.1, include high temperature thermal and electrical insulation for applications requiring flexibility and light weight, such as sleeves for pipes and electrical cables, high temperature shielding, belts, blankets and gaskets. A related family of discontinuous or staple high-alumina fibers such as SaffilTM and SaffimaxTM are also produced by the sol/gel process^{1,2}. These fibers have



18.1 Continuous rovings, fabrics and braided sleeving of ceramic oxide fibers.

similar microstructure and thermal stability as continuous fibers, but have very different applications and will not be discussed here.

Reinforcement of metals, polymers and ceramics is a growing application area. Nextel™ Ceramic Fibers 610 have been used to fabricate aluminum matrix composites with specific strength and modulus much higher than steel³. An example is high strength, lightweight high voltage power conductors as shown in Fig. 18.2. These conductors, which are reinforced by light-weight fiber-reinforced aluminum composite wires, are now produced in commercial amounts (hundreds of miles). High temperature oxide-matrix composites with good strength at 1200 °C for use in aerospace applications and turbine engine components is another area of growing interest⁴⁻⁷.

The advantages of ceramic oxide fibers compared with other fibers include stability in air and oxidizing environments at high temperatures, resistance to chemical attack, compatibility with molten metals such as aluminum, high compressive strength, high elastic modulus, and high electrical resistivity. Disadvantages include low strength and comparatively high density (3.2–4.0 g/cm³) compared with fiberglass and carbon fibers.

18.2 Sol/gel processing and technology

Continuous oxide fibers are produced by sol/gel technology. In the sol/gel process, a high viscosity (>30 000 cps) sol is extruded through a multiple-



18.2 Reinforcement of high voltage power conductors with Nextel™ 610 Ceramic Fiber-reinforced aluminum wires.

orifice spinneret and solidified or gelled to form a multi-filament bundle. After spinning, the green fibers are conveyed into a furnace for heat treatment. Heat treatment removes volatile components of the sol that enabled fiber forming and causes the fiber to crystallize into a thermally stable microstructure.

The goal of heat treatment is to develop a ceramic microstructure with both high strength and good high temperature properties (i.e., resistance to thermal degradation via grain growth, creep resistance). To achieve high fiber strength at room temperature, a small grain size is required. In practice, grain size below $0.1\text{ }\mu\text{m}$ is preferable. Achieving these very small crystallite sizes requires an in-depth understanding of the effect of sol precursor on the structures produced during thermal treatment. Achieving mixing of sol components on the nanometer level is a minimum prerequisite to good microstructural development.

In addition, during fiber manufacture, extreme care must be taken in all process stages to prevent the formation of defects and flaws that reduce fiber strength. Heat treatment must be performed with care to gently decompose the green fiber to the oxide form without forming defects or flaws. Too-rapid evolution of gases can cause the formation of porosity and/or macro-defects such as blisters, voids, and cracks, all of which reduce fiber strength.

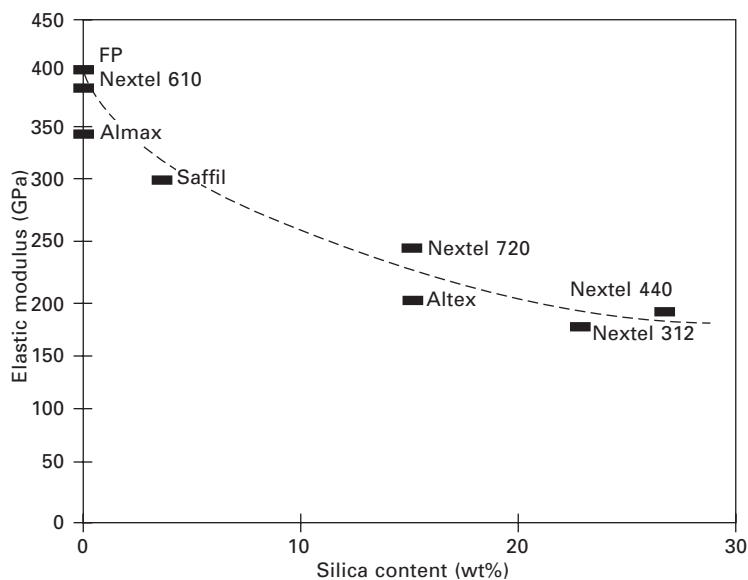
18.3 Heat treatment and fiber microstructure

High alumina content provides a number of advantages for a reinforcing fiber, including increased chemical stability, high melting point, high modulus, and

good strength up to 1200 °C. A number of alumina precursors suitable for forming fibers are available. The aqueous chemistry of aluminum allows for the formation of viscous basic aluminum salt solutions which can be made into fibers by dry-spinning⁸. More recently, polymeric aluminoxane precursors have also been used to as a route to commercial alumina-based fibers⁹.

Most commercial oxide fibers also contain SiO₂, in amounts from 0% to 30%. The addition of silica to alumina fibers reduces the inherent modulus of the fibers as shown in Fig. 18.3. The Young's modulus of alumina is ~400 GPa and that of silica approximately 70 GPa. The modulus of the fibers scales directly with silica content, with modulus reduced to only 200 GPa at ~20 wt% silica.

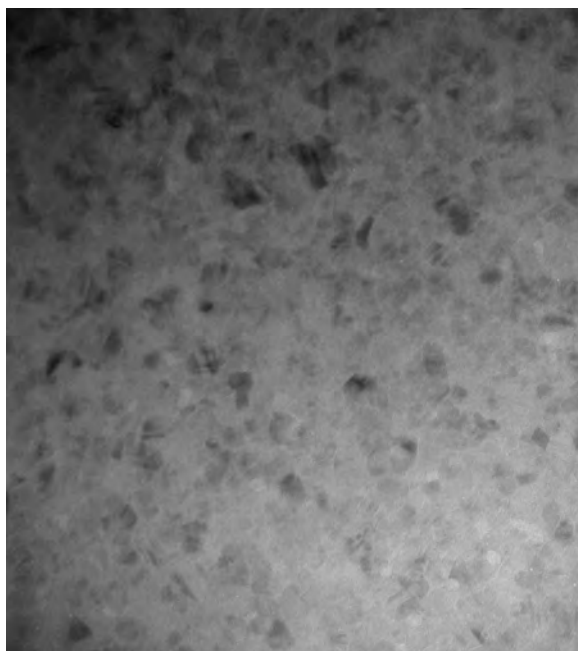
Microstructures in alumina-based fibers must be viewed through an understanding of crystalline transformation sequences in alumina, and the effect of silica on microstructure and transformation kinetics. As shown in Table 18.1, all commercial oxide ceramic fibers are based on alumina with varying amounts of silica. The stable phases for alumina–silica fibers with $\leq 28\%$ SiO₂ at all temperatures are α -Al₂O₃ and mullite. However, a series of cubic alumina spinels commonly called transition aluminas form in the temperature range 800–1200 °C during heat treatment of alumina and alumina–silica precursors. Depending on the sol precursor used, the first phase to crystallize is either η -Al₂O₃ (cubic) or γ -Al₂O₃ (tetragonal), which form in the range 800–900 °C. In many systems, δ -Al₂O₃ and θ -Al₂O₃ are formed



18.3 Variation of Young's modulus as a function of silica content for a number of alumina-based fibers.

with additional heating in the range 1000–1150 °C. These polymorphs are similar to γ -Al₂O₃ but have a higher degree of ordering on the cation lattice. The transformation to α -Al₂O₃ (a hexagonal crystal structure) occurs above 1200 °C; mullite (3Al₂O₃·2SiO₂) also may crystallize above 1280 °C.

For alumina and alumina–silica fibers, the crystallization of new phases such as mullite and α -Al₂O₃ often result in large grains, causing the fibers to become brittle and weak. A low volumetric nucleation density, which leads to large grain sizes, is typical of both alumina and mullite. For instance, crystallization of α -Al₂O₃ in high alumina fibers causes the formation of large, porous, spherulitic grains several micrometers in size¹⁰. These large grains cause the fibers to become brittle and weak. To avoid this problem, most commercial fibers are stabilized as transition alumina by the addition of SiO₂. The addition of SiO₂ to alumina fibers increases the temperature of the α -Al₂O₃ transformation by as much as several hundred degrees, to 1200 °C and above. This allows the preservation of the submicrometer transition alumina microstructure (and therefore strength and flexibility) for extended periods above 1100 °C. Figure 18.4 shows a transmission electron microscopy (TEM) micrograph of the microstructure of AltexTM fibers (85% Al₂O₃–15% SiO₂). Altex microstructure consists of small γ -alumina grains of a few tens of nanometers intimately dispersed in an amorphous silica phase.



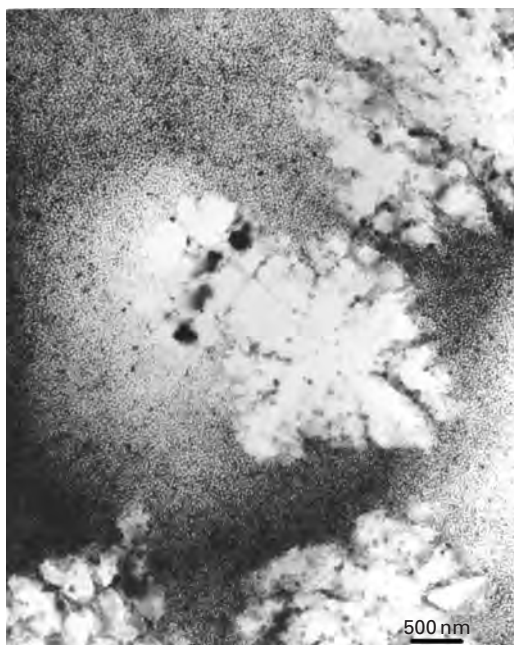
18.4 Transmission electron micrograph of AltexTM fibers (85% Al₂O₃–15% SiO₂) showing 20 nm γ -alumina grains intimately dispersed in an amorphous silica phase.

At high silica contents, mullite will crystallize. Figure 18.5 shows large mullite crystals growing in Altex fibers after heat treatment at 1127°C.

High strength fibers consisting mainly or entirely of crystalline α -Al₂O₃ have been developed in recent decades. Crystalline fibers containing high amounts of α -Al₂O₃ that are free of glassy phases are very chemically stable. High chemical stability leads to good environmental stability in corrosive atmospheres, low reactivity with respect to metal matrixes such as aluminum, and less interaction with a variety of ceramic matrices. In these fibers, the crystallization to alpha alumina is managed by a nucleation process. Several nucleating agents have been used to manage the crystallization process and facilitate the transformation to fine-grained, high density microstructure, including α -Al₂O₃, γ -Al₂O₃, and Fe₂O₃.

18.4 Comparative properties of oxide fibers

Tables 18.1 and 18.2 compare the density, strength, and elastic moduli of commercial ceramic oxide fibers. Commercial fibers can be divided into two classes: (1) alumina–silica fibers, which are those consisting of a mixture of transition alumina and amorphous silica and (2) crystalline α -Al₂O₃ fibers. Alumina–silica fibers have their largest applications as high temperature



18.5 Large mullite crystals growing in Altex fibers after heat treatment at 1127°C (reprinted with permission, Marcel Dekker, Inc.).

Table 18.1 Composition and properties: alumina-silica fibers

Fiber	Manufacturer	Composition Al ₂ O ₃ -SiO ₂	Density	Crystal phase	Tensile strength, GPa	CTE 10 ⁻⁶ /°C	Elastic modulus, GPa
Nextel TM 312	3M	62-24 (+ 14% B ₂ O ₃)	2.7	9Al ₂ O ₃ 2B ₂ O ₃ + am. SiO ₂	1.7	3 (25-500 °C)	150
Nexcel TM 440	3M	70-28 (+ 2% B ₂ O ₃)	3.05	η -Al ₂ O ₃ + am. SiO ₂	2.0	5.3	190
Nexcel TM 550	3M	73-27	3.03	η -Al ₂ O ₃ + am. SiO ₂	2.0	5.3	193
Altex TM	Sumitomo	85-15	3.2	γ -Al ₂ O ₃ + am. SiO ₂	2.0	6	193
Alcen TM	Nitivy	70-30	3.1	γ -Al ₂ O ₃ + am. SiO ₂	1.6	~5	160

Table 18.2 Composition and properties: crystalline α -Al₂O₃ fibers

Fiber	Manufacturer	Composition Al ₂ O ₃ -SiO ₂	Density	Crystal phase	Tensile strength, GPa	CTE 10 ⁻⁶ /°C	Elastic modulus, GPa
Nextel TM 610	3M	100-0	3.9	α -Al ₂ O ₃	3.1	8 (100-1100 °C)	373
Nextel TM 720	3M	85-15	3.4	α -Al ₂ O ₃ + mullite	2.1	6 (100-1100 °C)	260
Almax	Mitsui	100-0	3.6	α -Al ₂ O ₃	1.8	7	330

textiles for insulation, while crystalline α -Al₂O₃ fibers are used for composite reinforcement.

Alumina–silica fibers have densities between 2.7 and 3.2 and elastic moduli between 150 and 200 GPa. α -Al₂O₃ fibers have much higher elastic modulus (380 GPa) as well as higher density (3.6–4.2 g/cm³). In addition, α -Al₂O₃ fibers have superior chemical and thermal stability than the silica-containing fibers, and are therefore less reactive with potential oxide matrices during fabrication and are more stable in corrosive service environments. Disadvantages of the high α -Al₂O₃ fibers are higher density, and higher elastic modulus, which lowers strain to failure and flexibility during handling. Most fibers have tensile strengths in the range of 1.7–2.1 GPa. An exception is NextelTM Fiber 610, which has a strength of 3.1 GPa.

18.4.1 Continuous alumina–silica fibers

The AltexTM fiber is an 85% Al₂O₃–15% SiO₂ fiber produced by Sumitomo Chemicals. The fiber is 17 μ m in diameter, circular in cross-section and has a smooth surface. Altex fiber is obtained by the chemical conversion of a polymeric precursor fiber, made from a polyaluminumoxane dissolved in an organic solvent to give a viscous product with an alkyl silicate added to provide silica⁹.

3M produces a range of ceramic fibers under the trade name NextelTM Ceramic Fibers. NextelTM Ceramic Fibers 312, 440, and 550 represent a series of fibers all composed of 3 moles of alumina for 2 moles of silica with various amounts of boria to restrict crystal growth. These textile-grade NextelTM Ceramic Fibers have smooth surfaces and oval cross-sections with the major diameter up to twice the minor diameter. NextelTM 312 Ceramic Fiber, which first appeared in 1974, is composed of 62% wt Al₂O₃, 24% SiO₂ and 14% B₂O₃ and appears mainly amorphous by TEM. Small crystals of aluminum borate have also been reported. Instead of γ -Al₂O₃, NextelTM 312 Fiber crystallizes to 9Al₂O₃·2B₂O₃, which gradually transforms to mullite via exchange of Si and B ions in the crystal lattice during further heat treatment above 1000 °C¹¹. The high B₂O₃ content provides several advantages, including low density, low thermal expansion, and low elastic modulus (and therefore higher flexibility and strain to failure) than the other fibers. NextelTM 312 Fiber has the lowest cost of the three fibers and is widely used but is limited in applications to temperatures below 1200 °C as boria compounds volatilize.

NextelTM 440 Fibers have the composition 70% Al₂O₃, 28% SiO₂ and 2% B₂O₃. NextelTM 440 Fiber is formed in the main of small γ -alumina in amorphous silica. The lower B₂O₃ level greatly improves thermal stability, enabling the conversion of the transition alumina fiber to fine-grained, high strength mullite. NextelTM 440 Fiber is suitable for continuous use

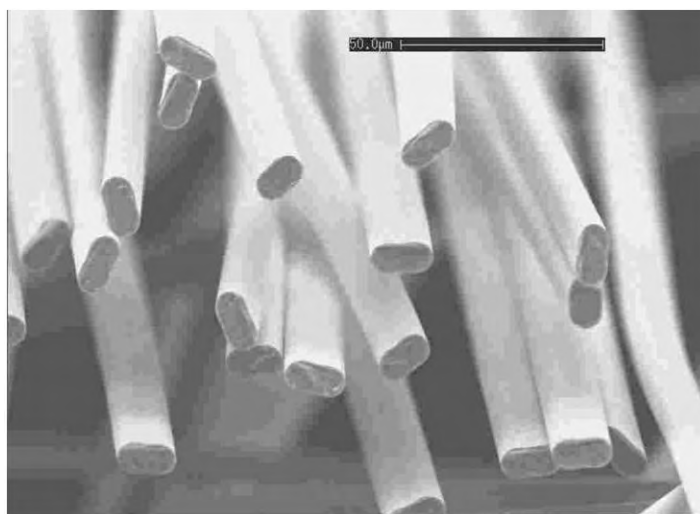
at temperatures as high as 1400 °C. Nextel™ 550 Fibers are similar to Nextel™ 440, but are free of B_2O_3 . The lower B_2O_3 level has advantages in applications requiring high purity, but Nextel™ 550 Fiber has 100 °C lower thermal stability relative to Nextel™ 440 Fiber since large mullite grains form at 1200 °C and above.

Nitivy produces a fiber with the composition 70% Al_2O_3 –30% SiO_2 fiber. Properties and thermal stability are similar to Nextel™ 550 Fiber, though modulus and strength are slightly lower.

18.4.2 Crystalline alpha alumina fibers

Two alpha alumina fibers with >99% alumina are commercially available. Because of their crystalline structure and high alumina content, α - Al_2O_3 fibers are intended for composite reinforcement. These fibers have high stiffness, low reactivity with metal and ceramic matrices and potentially the highest strength.

The most widely available α - Al_2O_3 fiber is Nextel™ 610 Ceramic Fiber. This fiber (Fig. 18.6) has by far the highest tensile strength at 3.1 GPa of any commercial oxide fiber. The high strength results from a very fine grain size of <0.1 μm and low defect population, as discussed below. Other physical properties are as would be expected from its α - Al_2O_3 structure. Fiber density is 3.9 g/cm³, near theoretical for alumina, and modulus of Nextel 610 is very high at 380 GPa, and thermal expansion is $8 \times 10^{-6}/^{\circ}C$. The surface of



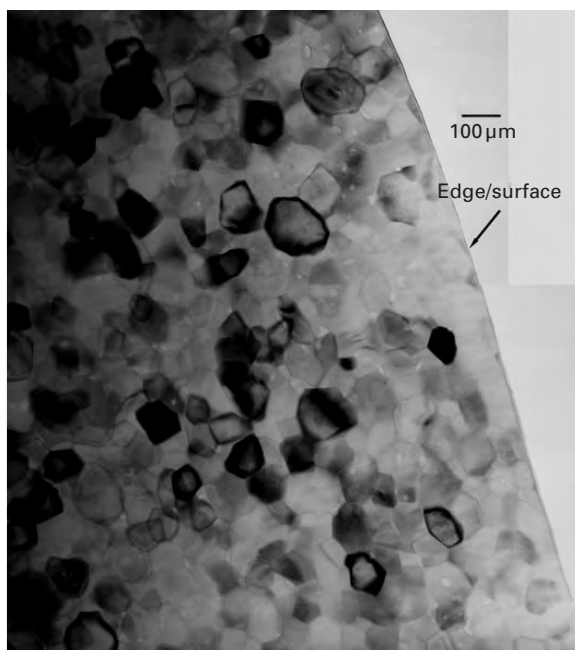
18.6 Low magnification micrograph of Nextel™ 610 Ceramic Fiber showing oval cross section and uniform filament cross-sections.

Nextel™ 610 is smooth, which facilitates textile handling and composite fabrication.

Figure 18.7 is TEM micrograph of Nextel™ 610. The grains are ~ 80 nm in size, and only a small amount of very small porosity is present. This ultra-fine grain size is produced via a nucleation process and contributes to the relatively high strength of this fiber.

Mitsui Mining produces the Almax fiber. This fiber is composed of almost pure alpha alumina and but exhibits a fairly large grain size ($\sim 0.5 \mu\text{m}$), a rough surface, and a large amount ($\sim 9\%$) of porosity. Because of these factors, the Almax fiber has relatively low strength (1.8 GPa) and also has lower modulus than Nextel™ 610.

The literature contains many references to Fiber FP, a $>99\%$ alpha alumina fiber from DuPont. Fiber FP had a grain size of $0.5 \mu\text{m}$ and mediocre tensile strength of 1.4 GPa. This fiber was the standard for composite fibers in the 1980s and had superior tensile properties to Almax, but has not been manufactured since 1985. Both 3M and DuPont also previously manufactured $\alpha\text{-Al}_2\text{O}_3$ fibers containing ZrO_2 , Nextel™ 650 and PRD-166, respectively. The ZrO_2 provided slightly superior high temperature properties to $\alpha\text{-Al}_2\text{O}_3$ fibers (e.g., resistance to grain growth) but neither has been commercially available for some time. Note that transformation toughening provided by



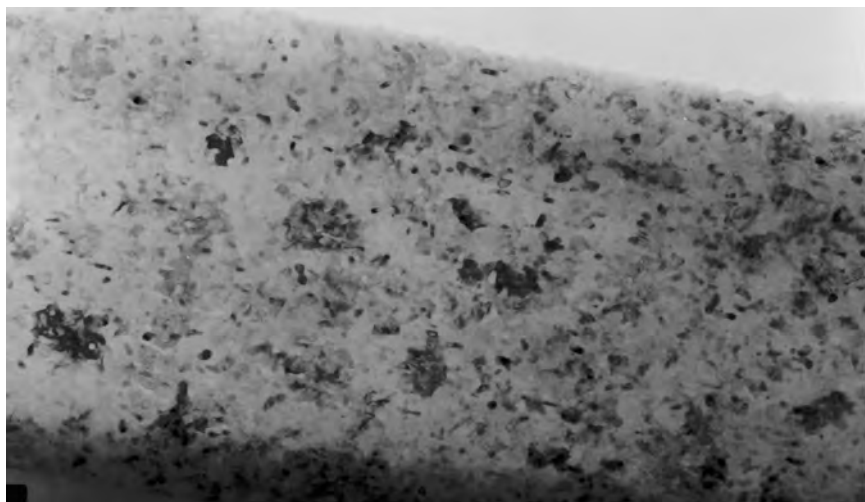
18.7 Transition electron microscope micrograph of Nextel™ 610 Ceramic Fiber.

ZrO₂ in bulk ceramics is not likely to improve the strength of fibers - the nanometer scale of the ZrO₂ will reduce the chemical driving force for transformation, and the small scale of the fibers will reduce the effectiveness of crack-blunting mechanisms.

18.4.3 Crystalline, composite-grade alumina-silica fibers

Another fully crystalline fiber is NextelTM 720 Ceramic Fiber. The fiber has a circular cross-section and a diameter of 12 μm , and has a smooth surface like the other NextelTM fibers. As expected from its relatively high alumina content, the modulus, density, and thermal expansion of this fiber are intermediate between commercial alumina-silica fibers and the crystalline α -Al₂O₃ fibers.

NextelTM 720 contains the same alumina to silica ratio as in the Altex fiber – 85% wt Al₂O₃ and 15% wt SiO₂ – but has a very different microstructure. NextelTM 720 Fiber consists of a two-phase, fully crystalline microstructure consisting of ~45% α -Al₂O₃ and 55% mullite (3Al₂O₃·2SiO₂). Fiber microstructure is quite complex; as shown in Fig. 18.8, it is composed of a mosaic of mullite grains of around 0.5 μm in size in which elongated α -alumina grains are found; each mosaic grain consisting of several slightly mutually misoriented sub grains^{12,13}. The large grains of mullite promote good creep resistance, while the interpenetrating structure resists grain growth as well as deformation under load.



18.8 Microstructure of NextelTM 720 Ceramic Fiber revealing mullite aggregates and elongated α -Al₂O₃ grains.

18.5 Fiber strength and properties

The strength of ceramic oxide fibers is their most critical property. High fiber strength provides flexibility and handleability in textile applications and load-bearing capability and toughness in composites. Single filament strength testing is the best technique for developing an understanding the fundamentals of fiber tensile behavior and variability, provides important insight into comparative fiber properties, and provides information for composite designers. However, single filament strength testing is somewhat difficult because handling of small diameter, high modulus fibers and measuring small loads and small filament diameters require special care to avoid errors that can compromise the accuracy of the test.

The variability of strength within a sample of fibers is very important. Models indicate that strength of composites is not determined only by the mean tensile strength of the reinforcing fiber, but also the distribution of strength of fibers. This occurs since the failure of a few weak fibers within the composite at low loads can lead to failure of the entire composite. Weibull statistics are commonly used to predict strength at different tested volumes (gauge length, area), to predict the strength of bundles of fibers and, ultimately, to predict the strength of fiber-reinforced composites.

18.5.1 Single filament strength testing: procedural issues

Continuous ceramic oxide fibers behave as brittle, elastic solids, i.e., fibers exhibit a linear stress–strain curve. Thus, strength is defined as the load at failure divided by the cross-sectional area of the fiber. Measurement techniques for both breaking load and fiber diameter must be well understood if accurate data are to be obtained.

Breaking load measurement is performed by mounting a single filament on a paper tab with an open slot in the center corresponding to the gauge length, typically 25 mm. A suitable adhesive is strong enough to prevent the fiber from pulling out during testing but not so stiff that fibers break at the edges of the adhesive. High modulus fibers should be mounted with as perfect alignment as possible to prevent bending stresses which cause premature failure at the edge of the adhesive. The ends of the tabs are gripped in a testing machine, the sides of the tab are carefully cut or burned away, and the fiber is tested to failure at a constant strain rate. Direct gripping using rubber-faced grips has also been used for testing of small diameter filaments¹³.

The second part of single filament testing is determining the cross-sectional area of the fiber. The measurement of fiber area, although conceptually simple, is not straightforward. A round-robin test undertaken by a joint government-industry task group has identified a number of shortcomings and concerns with the current standard test method, ASTM 3379-75¹⁴. This study found

that the measurement of filament diameter is the major source of error in fiber strength determinations.

The small size of fibers makes an accurate determination of fiber cross-section difficult. A very small error in diameter measurement can have a large effect on calculated fiber strength. For instance, for a 12 μm diameter fiber, a measurement error of only 0.6 μm in diameter will change calculated strength by 10%. If calibrated, scanning electron microscopy (SEM) can produce very accurate diameter measurements, but SEM is too time-consuming and costly for routine testing. Optical microscopes, often in combination with video image analysis systems, are frequently used for diameter measurement but are limited by their ultimate resolution of $\sim 0.5 \mu\text{m}$. Laser diffraction patterns from opaque fibers can also be used for diameter measurement.

Additional complications in diameter measurement also exist. During testing, high modulus fibers almost always shatter owing to the release of stored strain energy at fracture, causing the original fracture location to be lost. The diameter of fibers can vary slightly down their length, so this effect can make it impossible to determine the actual fiber diameter at the point of fracture. A further complication is that fibers may not be round but oval or irregular in cross-section. In this case, it is critical to measure fiber cross-section end-on rather than longitudinally.

In many cases, for instance to assess lot-to-lot variability or to measure degradation of properties after exposure to certain process conditions, it is appropriate to use average strength. ASTM 3379-75 calls for the measurement of a 'representative' number of filament diameters from sample cross-sections of composites to determine a mean filament diameter. The mean diameter is used to calculate the individual fiber breaking stresses. The use of mean diameter is sufficient for the determination of *average* fiber strength; however, the use of mean diameter rather than individual fiber diameters means that individual fiber strength values will not be strictly accurate. This effect must be taken into account during statistical analysis of the strength data.

18.5.2 Statistics of fiber fracture: Weibull theory

The strength of oxide fibers is controlled by 'weakest link' statistics, i.e., fracture occurs at the largest flaw present in the sample¹⁵. This type of behavior is described by Weibull statistics. In Weibull theory, the probability of failure of a material is given by:

$$P = 1 - \exp [-V/V_0(\sigma/\sigma_0)^m] \quad 18.1$$

where m = Weibull modulus, V = tested volume, σ = failure strength and V_0 and σ_0 = scaling constants. Reinforcing fibers typically have broad strength distributions and therefore low Weibull modulus values, between 4 and 15. Weibull failure data is commonly presented using the form:

$$\ln[\ln(1/1-P)] = m \cdot \ln \sigma + k \quad 18.2$$

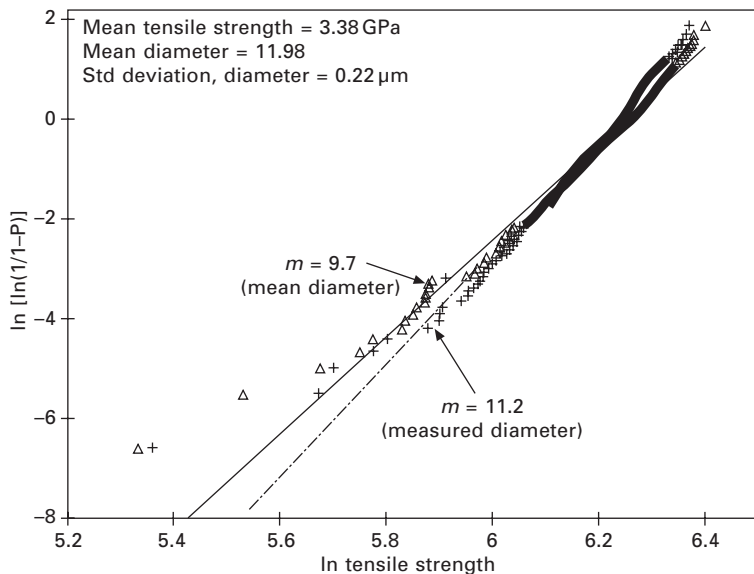
where k is a constant. The Weibull modulus, m , is then determined graphically as the slope of the 'Weibull plot' of $\ln [\ln(1/1-P)]$ against $\ln \sigma$.

Figure 18.9 shows a Weibull plot for Nextel™ 610 Fiber. The data is presented two ways, using both individually measured fiber diameter and also using the average diameter. The Weibull modulus was ~10% higher using individually measured fiber diameters. For this fiber, which has a relatively narrow fiber diameter distribution, the two values are nearly indistinguishable.

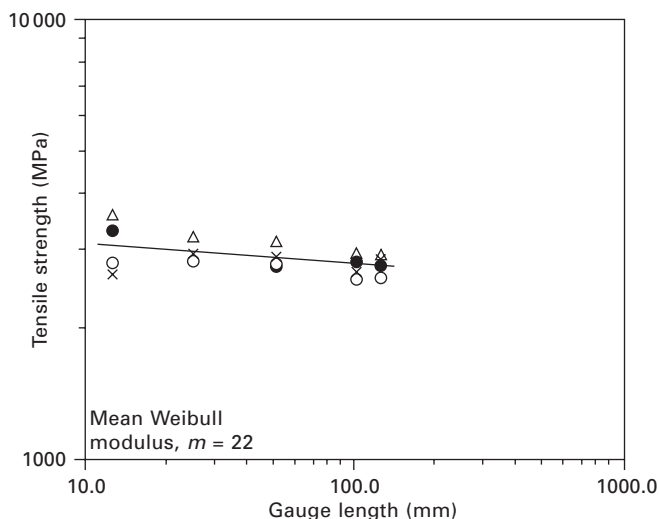
Another method of determining Weibull modulus is to measure fiber strength as a function of gauge length. With increasing gauge length, the chance of finding a large flaw increases, so fiber strength decreases. Equation 18.1 can be reduced to:

$$\sigma_1/\sigma_2 = (V_2/V_1)^{1/m} = (L_2/L_1)^{1/m} \quad 18.3$$

where the strengths at tested volumes V_1 and V_2 are σ_1 and σ_2 , respectively. For fibers, it is commonly assumed that the tested volume is proportional to gauge length, so gauge length L can be substituted for volume V . Using this approach, the Weibull modulus m can be determined by plotting the log of mean strength as a function of log of gauge length. The slope of the log-log gauge length plot is equal to $-1/m$. Figure 18.10 shows a log-log



18.9 Weibull Plot of Nextel™ 610 Ceramic Fiber using measured and average filament diameter.



18.10 Tensile strength of four lots of Nextel™ 610 Ceramic Fiber at five different gauge lengths. The line is the least squares fit of the mean strength of all four lots ($m = 22$).

plot of tensile strength as a function of gauge length for Nextel™ 610 fiber. The Weibull modulus as calculated from Fig. 18.10 is 22.

Recent work has illuminated some issues with the classic Weibull analysis given in Equations 18.2 and 18.3 as applied to fibers. The Weibull modulus of fibers as measured by the strength distribution technique (Eq. 18.2) is usually lower than with the gauge length technique (Eq. 18.3)^{16,17}. Several reasons for the discrepancy have been proposed. One potential cause is the effect of natural variations in fiber diameter on tested volume. Since, for given gauge length, larger diameter fibers have larger tested volumes than smaller fibers, equation 18.3 is not strictly accurate. Since large diameter fibers would be expected to have lower strength than smaller fibers, this will also broaden the distribution of strengths at a single gauge length but not the distribution at different gauge lengths. Secondly, the assumption that flaws are distributed randomly with volume is most likely not accurate. Specifically, as discussed below, fibers commonly fracture owing to surface flaws rather than flaws distributed through the volume of the fiber. Thus, fiber strength may scale not with fiber cross-sectional areas, i.e., diameter squared, but with surface area (e.g., proportional to diameter). Thirdly, issues related to processing normally cause larger diameter fibers to be even weaker than smaller fibers than one would expect. In the sol/gel fiber process, removal of volatiles during pyrolysis is more difficult the larger the fiber diameter. Thus, larger diameter fibers have larger flaws than would be expected from their larger volume.

The result of these factors is that it is rarely possible to extrapolate predictions of strength at various tested volumes in real systems. Extensive testing in the specific geometries and conditions is almost always required to assess fiber characteristics. Nevertheless, single filament testing statistics remain a powerful method for understanding fiber strength characteristics.

18.5.3 Microstructure-strength relationships in fibers

Fractographic examination reveals defects or flaws that limit fiber strength. As such, fractography is an indispensable method for the developer of improved fibers. Eliminating defects by modification of precursors and processing is the key to superior fiber strength. Fractography reveals the exact modes of failure, which can reveal the origin or cause of the defect, promotes understanding of which type microstructural flaw is most severe, and provide insight into long-term rupture behavior.

Fractography for brittle oxide fibers is carried out in a damping medium such as grease to avoid secondary fracture and loss of the origin of fracture. After cleaning, the defects can be characterized via SEM observation.

Flaws in oxide fibers are generally classified in two categories: (1) surface defects and (2) internal defects. Examples of Nextel™ 610 Fibers with typical defects are shown below. The fracture origin can be located by the presence the classic ‘mirror-hackle’ morphology. Within 1–2 μm of the fracture origin, the fracture surface is smooth, and farther away, striations in the more textured fracture surface lead directly away from the fracture origin. Figure 18.11(a) shows an internal flaw caused by a particulate inclusion in the sol used to spin the fiber. During sintering, the shrinkage of the fiber opened up porosity immediately adjacent to the inclusion. Figure 18.11(b) shows a second internal round pore or void. This was most likely caused by the presence of a bubble in the sol. Figure 18.11(c) shows a fiber that fractured at a linear surface defect. This defect was caused by inter-filament welding during heat treatment. Figure 18.11(d) is a different type of surface flaw, most likely caused by abrasion, impacted particles or other damage during processing.

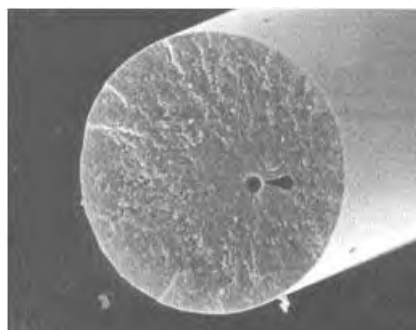
As brittle ceramics, the strength of Al_2O_3 fibers is controlled by the Griffith fracture criterion:

$$\sigma = K_{\text{Ic}}/m(\pi c)^{1/2} \quad 18.4$$

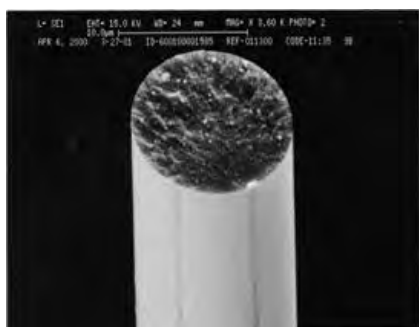
where c is flaw size and m is a geometrical factor. Fracture toughness of fibers is no higher than bulk materials; the high strength of fibers is created by very small flaw or defect sizes. The Griffith equation predicts that a material with a fracture toughness of 3 (as expected for Al_2O_3) can achieve a fracture strength of 3 GPa only when the critical flaw size is below 0.5 μm . Thus, not only must defect sizes be kept low by careful fiber processing, but high



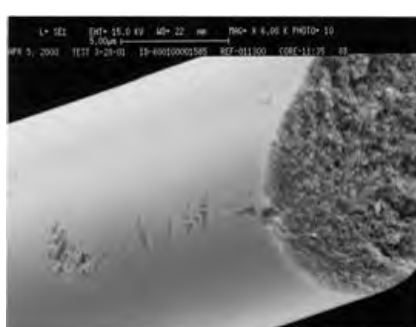
(a)



(b)



(c)

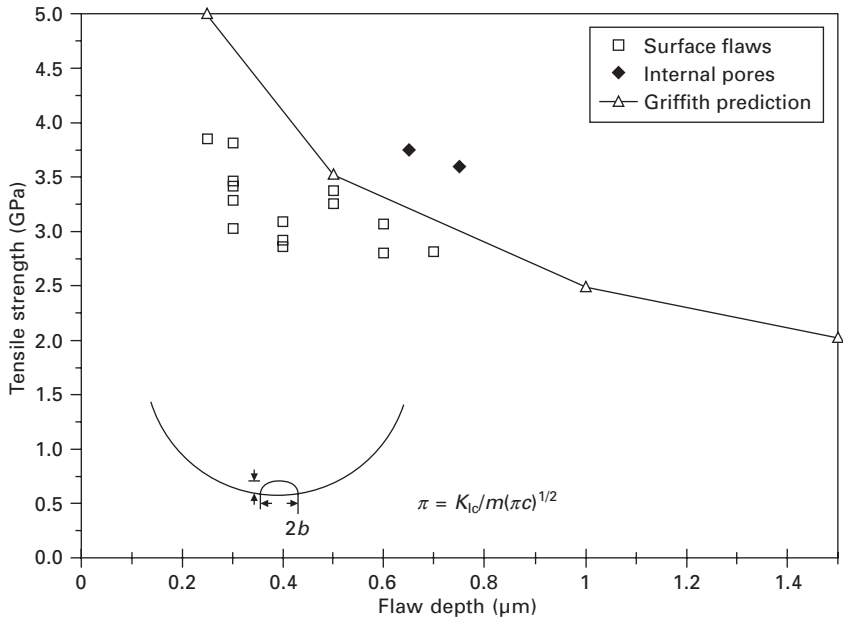


(d)

18.11 Typical surface and internal defects in Nextel™ 610 Ceramic Fibers (a) Internal particulate inclusion; (b) internal bubble; (c) weld lines; (d) surface damage.

fiber strength requires a very small grain size. The grain size of commercial fibers is usually below 0.1 μm .

Fractographic examination of Nextel™ 610 indicates that most fracture origins are at the fiber surface. Figure 18.12 compares the Griffith strength prediction for Al_2O_3 as a function of flaw size to measured defect size in Nextel™ 610 Fibers using the assumption of a semicircular surface flaw ($m = \pi/2$). As predicted by the Griffith equation, larger defects correlated with lower fiber strength. The Griffith equation also predicted Nextel™ 610 fiber strength relatively accurately, within 20%. Two data points had higher strength than expected (Fig. 18.12). These specific fibers fractured at round, internal pores. The cause of the higher strength for these two fibers is that the smooth, round internal surface of these pores do not act as sharp flaws, i.e., a round pore has a lower stress concentration relative to other types of defects.



18.12 Tensile strength of Nextel™ 610 Ceramic Fibers as a function of flaw size.

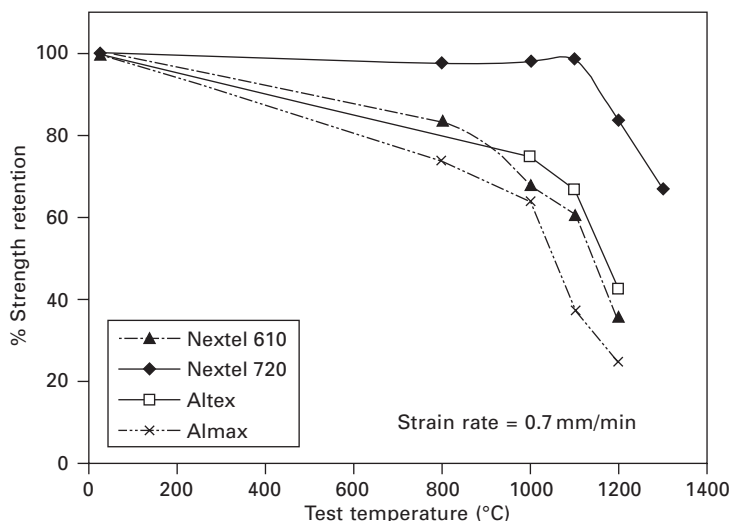
18.6 High temperature fiber properties

Since the application of most oxide fibers is at high temperatures, high temperature testing is required to predict behaviour in intended service environments. This is especially true for applications as composite reinforcement, where the fiber will carry significant load during service. The most critical properties are high temperature strength and resistance to creep.

Creep-rupture can provide useful insight into high temperature behaviour, but extremely minor impurities in testing environments can lead to fiber degradation via chemical reaction. Extrapolating fiber creep rupture data to composites can underestimate the rupture life of composites. High temperature fiber strength and creep tests provide an upper bound for properties, so in this way are predictive of composite behavior.

18.6.1 High temperature strength

For oxide fibers, high temperature testing is normally carried out in air. This allows the fiber to be fixtured in the test frame using ‘cold’ grips outside of the heated zone, which is typically ~100 mm in length. Figure 18.13 compares the ‘hot’ strength of several commercial fibers as a function of



18.13 Percentage retained strength as a function of test temperature for commercial fibers^{18, 19}.

testing temperature. Data is given as a function of initial room temperature strength to eliminate gauge length effects and to highlight comparative strength decrease with temperature. Three fibers, Altex, Almax and NextelTM 610, all show a significant reduction in strength at elevated temperatures. These three fibers retained ~70% or room temperature (RT) strength at 1000°C. By 1200°C, fiber strength was reduced to 30–40% of RT values. A reduction in high temperature strength is expected at temperatures where inelastic deformation mechanisms (i.e., creep) are active, leading to the extension of existing critical flaws and to the formation of new cracks and other flaws. In fact, the relative high temperature strengths of these fibers correlated well with relative creep rates (see below). Single filament testing is normally carried out at a relatively slow rate ($\ll 1\%/min$) so that creep mechanisms become active. Stress–strain plots start to show significant deviation from linearity by 1100°C for most fibers, such as NextelTM 610 and Altex. Extrapolation of the creep data for NextelTM 610 fiber at 1100°C indicates that the expected creep rate at 2 GPa stress is greater than the strain rate for single filament tensile testing ($4 \times 10^{-5}/s$). At very high strain rates, fibers have been reported to retain their strength up to 200°C higher than at low strain rates¹⁸.

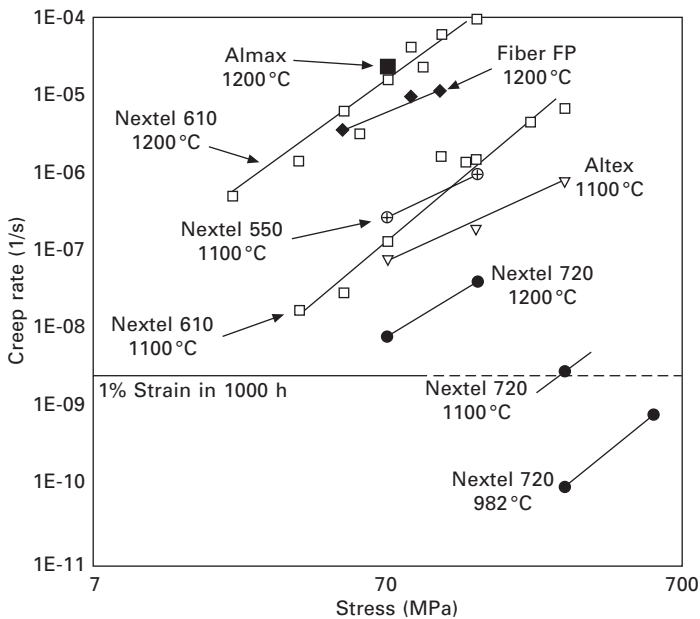
As would be expected from its high creep resistance (Section 18.6.2), NextelTM 720 Fiber has the best hot strength of any commercially available fiber. NextelTM 720 retains 70% of its room temperature strength at test temperatures up to 1300°C. Oxide–matrix composites reinforced by NextelTM 720 Fibers that retain 100% of RT strength at 1200°C have been reported⁵.

18.6.2 Comparative creep rates

Figure 18.14 compares the creep rate of commercially available fibers at 1100 and 1200 °C^{18,19}. The creep rate of Nextel™ 720 Fiber at 982 °C is also shown. For reference, a total strain of 1% in 1000 h (2.7×10^{-9} /s) is also given. With the exception of Nextel™ 720, the commercial fibers all had creep rates within approximately one order of magnitude of each other. The creep rate increased in the following order: Altex @Fiber FP < Nextel™ 610 @Nextel™ 550 < Almax. Fiber FP, Nextel™ 610 and Almax fibers are polycrystalline α -Al₂O₃ fibers, and Nextel™ 550 Fiber and Altex consist of transition alumina and amorphous silica.

The creep rate for Nextel™ 720 Fiber was approximately three orders of magnitude less than any of the commercially available polycrystalline alumina fibers. The superior high temperature creep performance of Nextel™ 720 Fiber results from a high content of mullite, which has much better creep resistance than alumina. Additionally, Nextel™ 720 Fiber consists of 0.5 μ m globular grains of mullite; thus, grain size is five times larger than grains in Nextel™ 610 Fiber. Lastly, the presence of acicular and globular grains of mullite and alumina reduces grain boundary sliding.

The temperature and stress dependence of the steady-state creep rate of alumina and other crystalline ceramics can be described by the following equation:



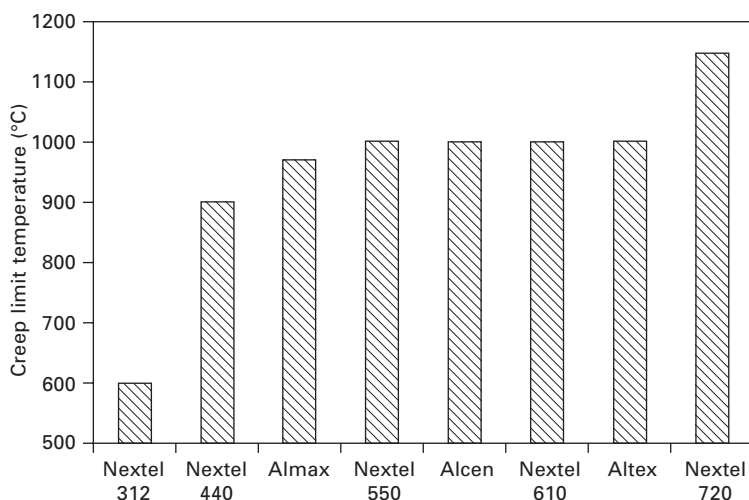
18.14 Strain rate vs. stress for polycrystalline oxide fibers at 1100 and 1200 °C.

$$\dot{\epsilon} = A [\exp(-E_a/RT)] (1/d)^p (\sigma/G)^n \quad 18.5$$

where $\dot{\epsilon}$ is the steady-state creep rate, A is a constant, G is the shear modulus, E_a is the activation energy, σ is the applied stress, d is the grain size, p is the grain size exponent, and n is the stress exponent. Since all oxide fibers have extremely fine polycrystalline grains, on a scale in the tens of nanometers, diffusion deformation will be dominated by grain boundary properties. In bulk ceramics, diffusion within grains is rate-controlling, and stress exponents are near 1. The stress exponent, n , for all fibers tested was 2–3; high stress exponents are consistent with results for superplastic deformation of fine-grained ($< 0.5\mu\text{m}$) ceramics, including Al_2O_3 .²⁰ High stress exponents are associated with grain boundary phenomena such as interface reaction rate-controlled creep, grain boundary sliding, and grain rotation. High stress exponents in oxide fibers are technically important because they lead to very large increases in strain rate as stress is increased. Doubling stress increases for fibers with a stress exponent of 3 increases creep rate by almost an order of magnitude.

The grain size exponent, p , appears to be near 1 for most alumina-based fibers. For instance, Fiber FP, with a grain size 5 times larger than NextelTM 610 Fiber, has a creep rate 3–5 times lower. Also, the large mullite grains contribute to superior creep resistance in NextelTM 720. However, note that the large grains represent a tradeoff with respect to strength. Owing in part to its larger grain size, the strength of NextelTM 720 Fiber is 2.1 GPa, two-thirds of that of NextelTM 610 Fiber.

Figure 18.15 compares the temperature capability of commercial fibers as composite reinforcement, as measured by creep rate limit. A reasonable



18.15 Temperature limit of load-bearing capacity of commercial fibers (criterion: 1% strain in 1000 h at 70 MPa).

creep rate limit criterion for a materials designer might be total strain of 1% over 1000 hours. Most high temperature applications of composites are at relatively low stress, so the creep rate limit is defined using an applied stress of 70 MPa. Depending on application stress and required service life, temperature capability will differ, but this rating provides a relative guide to fiber temperature capability.

NextelTM 312 Ceramic Fiber has the lowest temperature capability as a composite reinforcement with a creep limit is only 600 °C. This results from the low Al₂O₃ content (62%) and the presence of 14% B₂O₃, which will reduce the viscosity of the SiO₂ phase in the fiber. NextelTM 440 Fiber, which has a 72% Al₂O₃ content and B₂O₃ content of only 2%, has 300 °C higher temperature capability than NextelTM 312 Fiber.

Three alumina–silica fibers have similar creep limits near 1000 °C. These are Alcen, Nextel 550 Fiber, and Altex. The Altex fiber, with higher Al₂O₃ content at 85%, has slightly superior properties. However, it is somewhat surprising that a reduction in SiO₂ content from 28% for NextelTM 550 Fiber to 15% for Altex has only a minor effect on high temperature creep rate. Another observation of interest is that the fully crystalline α -Al₂O₃ fibers such as NextelTM 610 Fiber and Almax have similar creep performance to the alumina–silica fibers. The good performance of the alumina–silica fibers is actually somewhat surprising given their grain size of <20 nm and presence of significant silica phase. The relatively large amount of silica (>30 vol%) might be expected to promote rapid deformation via viscous flow in the silica phase. But this does not seem to be the case. It may be that the nano-scale of the interpenetrating alumina and silica phases prevents the operation of bulk viscous flow behavior in the silica phase. Changes in mechanical and flow behavior are often seen with this type of nano-scale microstructure, but are not fully understood in the case of oxide fibers.

The creep limit temperature for NextelTM 720 Fiber at 70 MPa is 1150 °C. This is 150 °C higher projected use temperature than the other commercial fibers. Microstructural origins for the low creep rate of NextelTM 720 Fiber relative to polycrystalline alumina and other fibers have been discussed.

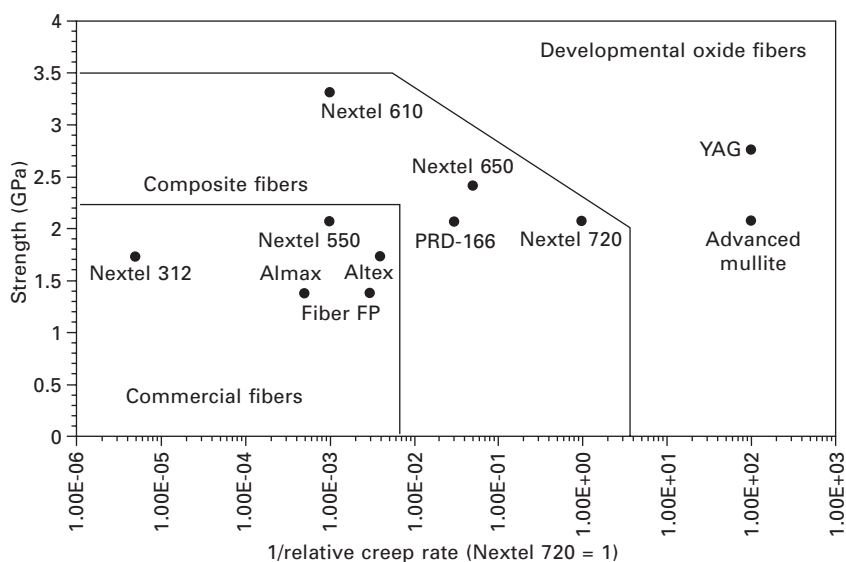
18.7 Conclusions and future trends

The advantages of flexibility/weavability and stability in high temperature oxidizing environments will continue to provide incentive for further improvements in high temperature properties of oxide fibers. Fiber manufacturers are examining new and improved processing approaches which attempt to eliminate or minimize microstructural sources for high temperature strength degradation and creep. One fertile area for research is the development of fine-grained, fully crystalline fibers of multi-component oxides such as yttrium–aluminum garnet (YAG) and mullite that resist

degradation via grain growth, and also have superior creep properties compared with alumina. The complex crystalline lattice structures of both YAG and mullite provide both very slow grain growth kinetics at high temperature and much superior creep resistance compared with Al_2O_3 , suggesting that these fibers would provide a temperature advantage of 100 °C or more. YAG has superior chemical stability (e.g., with respect to corrosion by alkalis), whereas mullite has the advantage of lower density, lower thermal expansion, and more flexible synthetic routes. In fact, both polycrystalline YAG and mullite sol/gel fibers have been developed at several laboratories^{18,21} that have exhibited even better creep resistance than NextelTM 720 fibers but have not been commercialized.

The use of dopants (e.g., Y^{3+} in NextelTM 650 Fibers¹⁸) has also been shown to provide another promising route to improved high temperature capability in oxide fibers. Grain growth inhibitors will probably also be required for oxide fibers to keep grain sizes small and to pin grain boundary motion for additional improvement in fiber creep resistance.

Figure 18.16 maps comparative room temperature strength and creep resistance of commercial, composite-grade, and developmental fibers. The properties of most commercial fibers are bounded by a box with strength up to 2.1 GPa and a creep rate 1000 times inferior to NextelTM 720 Fiber. The composite-grade fibers, which include the two commercial, textile-grade NextelTM fibers as well as two $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ fibers, NextelTM 650 Fiber and PRD-166, which have superior high temperature and strength characteristics



18.16 Map of comparative room temperature strength and creep resistance of commercial, composite-grade and developmental fibers.

based on the second-phase doping. Nextel™ 610 has the highest strength of any fiber, and is thus suited for high strength metal and polymer composites, whereas Nextel™ 720 has superior creep resistance and is targeted at high temperature ceramic composite applications. Based on published reports, developmental mullite and YAG fibers have the potential for 100 times lower creep rates than Nextel™ 720 Fiber while maintaining good tensile strength.

18.8 Sources of further information and advice

One of the most complete studies of ceramic fiber structure and properties is *Fine Ceramic Fibers*, edited by A. R. Bunsell and M.-H. Berger (Marcel Dekker, 1999). Other recommended books that discuss fiber properties and applications include *Ceramic Matrix Composites* by K. K. Chawla (Chapman & Hall, 1993) and *Fiber and Whisker Reinforced Ceramics for Structural Applications* by D. Belitskus ((Marcel Dekker, 1999). Proceedings from the International Conference on Advanced Ceramics and Composites, held annually in Cocoa Beach, FL, have been published by the American Ceramic Society. An excellent summary of the processing and properties of ceramic fibers in the late 1990s with recommendations and needs is given in *Ceramic Fibers and Coatings, Advanced Materials for the Twenty-first Century*, a report from the National Materials Advisory Board, published by National Academy Press in 1998.

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