

High-performance fibres

Edited by
J W S Hearle



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Chapter 1: Introduction

Professor John Hearle, The Old Vicarage, Church Road,
Mellor, Stockport SK6 5LX, UK
Tel: 0161 427 1149 Fax: 0161 427 8527
e-mail: *johnhearle@compuserve.com*

Chapter 2: Aramids

Dr Serge Rebouillat, DuPont de Nemours Int. SA, 2,
Chemin du Pavillon, PO Box 50, CH-1218 Le Grand-
Saconnex, Geneva, Switzerland
e-mail: *serge.rebouillat@che.dupont.com*

Chapter 3: Gel-spun high-performance polyethylene fibres

Dr Jan L J van Dingenen, DSM High Performance Fibres,
Eisterweg 3, 6422, PN Heerlen, The Netherlands
Tel: +31 45 54 36 856 Fax: +31 45 54 36 778
e-mail: *jan.dingenen-van@dsm-group.com*

Chapter 4: Other high modulus-high tenacity (HM-HT) polymer fibres

Dr David Beers, 8115 Prince George Road, Charlotte,
NC 28210, USA
Tel: 001 704 552 2201
e-mail: *dbeers22@bellsouth.net*

Professor Robert Young and C L So, Materials Science
Centre, UMIST, Manchester M60 1QD, UK
e-mail: *robert.young@UMIST.ac.uk*

Professor Dr Doetze Sikkema, Magellan Systems
International
PO Box 9300, 6800 SB Arnhem, The Netherlands
Tel: +31 26 366 3459 Fax: +31 26 366 5175
e-mail: *Doetze.Sikkema@msfiber.com*

Professor Kirill Perepelkin, Materials Science Department,
St Petersburg State University of Technology and Design,
Bkl'shaya Morskaya Str., 18, Saint-Petersburg 191186,
Russia

Fax: +7(812) 31512-10 and 315 1456

e-mail: *msd@sutd.ru*

Mr Gene Weedon, 4919 Waycrest Terrace, Richmond,
Virginia 23234, USA

Tel. and Fax: 804 271 0259

e-mail: *Gweedon@erols.com*

Chapter 5: Carbon fibres

Dr J G Lavin, Carbon Nanotechnologies Inc,
16200 Park Row, Houston, TX 77084, USA

e-mail: *lavin@cnanotech.com*

Chapter 6: Glass fibres

Professor F R Jones, Department of Engineering
Materials, University of Sheffield, Sir Robert Hadfield
Building, Mappin Street, Sheffield S1 3JD, UK

e-mail: *F.R.Jones@shef.ac.uk*

Chapter 7: Ceramic fibres

Professor Anthony Bunsell and **Dr M-H Berger**, Ecole des
Mines de Paris, Centre des Materiaux, BP 87, Evry, Cedex
91003, France

Fax: 01-60-76-31-50

e-mail: *Anthony.Bunsell@mat.ensmp.fr*

Chapter 8: Chemically resistant fibres

Professor A R Horrocks, Director of Research, Bolton
Institute, Deane Road, Bolton BL3 5AB, UK

e-mail: *arh1@bolton.ac.uk*

Mr Bruce McIntosh, Zyex Ltd., Stonedale Road, Oldend
Lane Industrial Estate, Stonehouse, Gloucestershire
GL10 3RQ, UK

e-mail: *bmm@zyex.com*

Chapter 9: Thermally resistant fibres

Professor A R Horrocks, Director of Research, Bolton
Institute, Deane Road, Bolton BL3 5AB, UK

Dr H Eichhorn, BASF Aktiengesellschaft, KF – E100,
67056 Ludswighafen, Germany

Tel: +49 621 60 47160 Fax: +49 621 60 20275

e-mail: *hans-dieter.eichhorn@basf-ag.de*

Mr Hasso Schwaenke, Kynol Europa GmbH, Hochallee 11,
20149 Hamburg, Germany

Tel: +49-40-458403 Fax: +49-40-459602

e-mail: *Schwaenke@kynol.de*

Mr Neil Saville, N and M A Saville Associates, 40, Penn
Drive, Liversedge, West Yorks WF15 8DB, UK

Tel: 01274 853220 Fax: 01924 401099

Mr Charles Thomas, Celanese Acetate, PO Box 32414,
Charlotte, NC 28232-4500, USA

e-mail: *Charles.Thomas@CelaneseAcetate.com*

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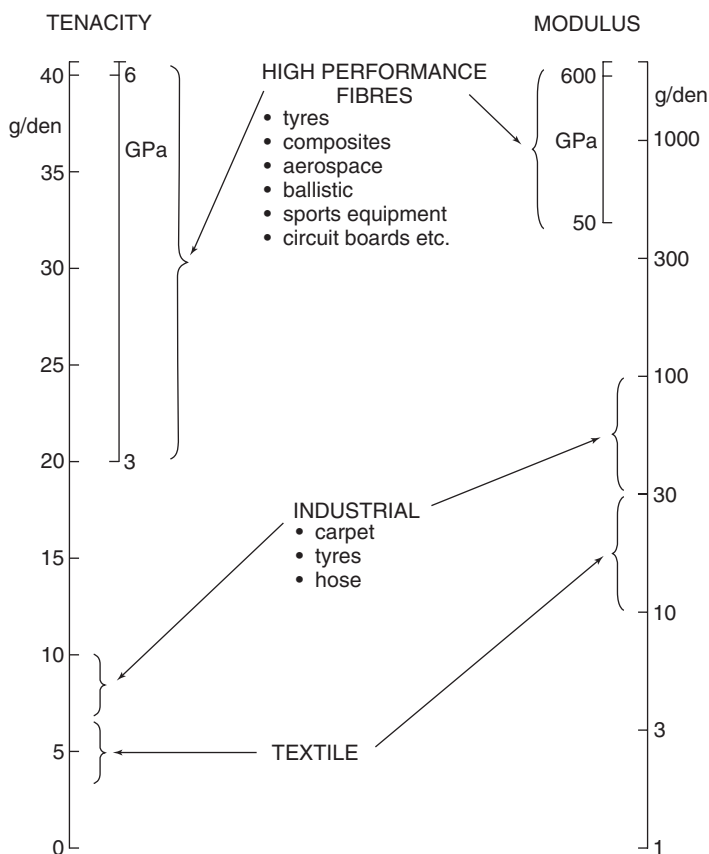
1.1 A new generation of fibres

1.1.1 'High-performance' defined

In a sense, all fibres except the cheapest commodity fibres are high-performance fibres. The natural fibres (cotton, wool, silk . . .) have a high aesthetic appeal in fashion fabrics (clothing, upholstery, carpets . . .): Until 100 years ago, they were also the fibres used in engineering applications – what are called *technical* or *industrial textiles*. With the introduction of manufactured fibres (rayon, acetate, nylon, polyester . . .) in the first half of the twentieth century, not only were new high-performance qualities available for fashion fabrics, but they also offered superior technical properties. For example, the reinforcement in automobile tyres moved from cotton cords in 1900, to a sequence of improved rayons from 1935 to 1955, and then to nylon, polyester and steel, which dominate the market now. A similar replacement of natural and regenerated fibres by synthetic fibres occurred in most technical textiles.

The maximum strengths of commercial nylon and polyester fibres approach 10 g/den (~ 1 N/tex) or 1 GPa*, with break extensions of more than 10%. The combination of moderately high strength and moderately high extension gives a very high energy to break, or *work of rupture*. Good recovery properties mean that they can stand repeated high-energy shocks. In this respect, nylon and polyester fibres are unchallenged as high-performance fibres, though their increase in stiffness with rate of loading reduces their performance in ballistic applications. It is notable that polyester has proved to be the fibre of choice for high-performance ropes with typical break loads of 1500 tonnes, used to moor oil-rigs in depths of 1000–2000 m. The high-stretch characteristics of elastomeric fibres, such as *Lycra*, have an undeveloped potential for specialised technical applica-

* See Appendix for a note on units.



1.1 The step change in strength and stiffness from first generation to second generation manufactured fibres. (After Mukhopadhyay¹)

tions. However, because of their large-scale use in general textiles, these fibres are dealt with in another book in this series.

In the last quarter of the twentieth century, a second generation of manufactured fibres became available. As shown in Fig. 1.1, these *high-performance fibres* showed a step change in strength and stiffness. They are *high-modulus, high-tenacity (HM-HT) fibres*. This is the characteristic feature of the polymeric and inorganic fibres described in Chapters 2 to 7. The other members of the new generation, which are described in Chapters 8 and 9, are fibres with high thermal or chemical resistance. A negative definition might be that none of the fibres included in this book find a market in clothing, furnishings and other household uses, except where some technical requirement, such as protection from bullets or fire, takes precedence over comfort and fashion.

Glass fibres, which have an ancient history, but became important commercially through advances in the 1930s, belong to the first generation of manufactured fibres. However, because of their properties and uses, they are appropriately included in this book.

There is a third generation of fibres, which is appearing as the twentieth century leads to the twenty-first. These are the smart fibres with some special physical or chemical properties, which give a new dimension to the use of textiles.² A typical example is *Softswitch* – fibres that become electrically conducting under pressure. However, these fibres go beyond the scope of this book and are not yet ready for a definitive treatment.

1.1.2 Strength and stiffness

Pre-industrial fibres, such as cotton, wool and silk, typically had tenacities in the range of 0.1–0.4 N/tex and initial moduli from 2 to 5 N/tex, though fibres such as flax and ramie could go higher in strength and stiffness. Apart from silk, which was the fibre used in some demanding applications such as parachute fabric, they were all short fibres, so that the conversion efficiency to yarn and fabric strength was low. The earliest regenerated cellulose fibres, such as viscose rayon and acetate, had strengths below 0.2 N/tex. There was a challenge to achieve higher strengths in cellulose fibres.³ Continuous-filament rayon yarns such as *Tenasco*, with a strength of 0.4 N/tex, were introduced for use in tyre cords. By 1960, strengths had increased to 0.6 N/tex, with a break extension of 13%. Other approaches led to fibres with higher stiffness. The most notable was *Fortisan*, which was made by highly stretching acetate yarns and then converting them to cellulose. This gave a tenacity of 0.6 N/tex and a modulus of 16 N/tex, but it failed to retain a place in the market for long after its 1939–45 wartime usage. Now the story has come full circle. Building on the experience of the aramid fibres, a new cellulose fibre, *Bocell*, has been produced in Akzo-Nobel laboratories by spinning from a liquid-crystal solution in phosphoric acid.^{3,4} Development samples of Fibre B had strengths of 1.1 N/tex and moduli of 30 N/tex, but increases, particularly in strength, would be expected with improved control if, as expected, this fibre is commercialised by Acordis, or Newco, the cellulose spin-off of Acordis, which was itself the fibre spin-off of Akzo Nobel. The polymer cost would be much less than for aramids and similar high-performance fibres, though the spinning costs would probably be similar.

Meanwhile, nylon had come on the market in 1938 and found wartime technical uses. Tenacity was about 0.5 N/tex and modulus 2.5 N/tex. Textile grades of the polyester fibre polyethylene terephthalate, which followed, had a similar tenacity but a higher modulus of about 10 N/tex. Development for industrial uses, such as tyre cords and ropes, has taken nylon and polyester to tenacities over 0.8 N/tex and moduli of 9 N/tex for nylon and

12N/tex for polyester. Higher values have been reported in patents, but there is still a challenge for commercialisation.

Two advances in the 1960s brought a step change, which is the major theme of this book. As described in Chapter 2, DuPont researchers spun para-aramid fibres from liquid-crystal solutions. High orientation led to tenacities of over 2N/tex and moduli up to 80N/tex. Other polymer fibres have now reached tenacities over 3.5N/tex and moduli over 150N/tex. At the Royal Aircraft Establishment (RAE) in UK, Watt and his colleagues produced the first high-strength carbon fibres by high-temperature processing of acrylic fibres under tension. As described in Chapter 5, this has taken tenacities up to over 5 GPa (3N/tex) and moduli over 800 GPa (400N/tex).

The polymer fibres are all organic chemicals, and carbon fibres may be described as quasi-organic, because they result from organic chemistry. The other group of high-performance fibres described in this book are the inorganic fibres. Glass achieved widespread use as a stiff reinforcement for composites. Strengths of glass fibres reach 4 GPa (1.6N/tex) and moduli 90 GPa (35N/tex), which, on a weight basis, are less than those of aramids. Ceramic fibres were developed primarily for their high-temperature performance in metal and ceramic matrix composites for use in engines. Because of their structure they naturally have high moduli, up to 400 GPa (100N/tex), but strengths up to 3 GPa (1 N/tex) are not particularly high on a weight basis.

1.1.3 Molecular stability

Many of the high-modulus, high-tenacity fibres also have good chemical or thermal stability. However, due to their inextensibility, they lack the textile qualities that make for comfortable clothing and furnishings. This need has been met by another group of second generation manufactured fibres, which are described in detail in Chapters 8 and 9. Other fibres in this group can be used for industrial purposes where environments are severe but mechanical forces are not. These polymer fibres mostly have strength, stiffness and break extensions comparable to general textile fibres. They differ in the stability of their chemical and physical constitution. Strong intermolecular bonding gives thermal resistance and inert molecular groups give chemical resistance.

1.2 Molecular dimensionality

1.2.1 Three forms

The high-modulus, high-tenacity fibres naturally fall into three groups: the polymer fibres of Chapters 2 to 4, carbon fibres in Chapter 5 and inorganic

fibres in Chapters 6 and 7. In a sense, they are all polymers in that the chemical bonding extends over large molecules. The difference is in the dimensionality of the bonding. The similarity is that the axial bonding is always strong and continuous. There are no rubbery amorphous regions, as in nylon and polyester, and none of the special features found in fibres like cotton and wool that lead to low stiffness.

1.2.2 Linear polymers

The first group are one-dimensional. In the simplest case, polyethylene, a linear string of carbon atoms merely has hydrogen atoms in the transverse direction. In others, the chain has a more complicated transverse structure of rings of atoms and side-groups, but always the aspect ratio of the molecule is extremely high. High molecular weights, or equivalently high degrees of polymerisation, are needed. In the 1930s, Staudinger⁵ drew a diagram, Fig. 1.2, which shows the ideal form for a linear-polymer fibre with high strength and stiffness; and at a Faraday Society Discussion in 1936, attended by the pioneers of polymer science, theoretical moduli of $11\,000\text{ kg/mm}^2$ were calculated in the direction of primary bonds, but only 45 kg/mm^2 ($\sim 0.5\text{ GPa}$ or N/tex) when controlled by van der Waals bonds.⁶ In order to achieve strength and stiffness, the molecules must be fully extended and well oriented. Chain folding, whether regular or irregular, and off-axis orientation of molecular segments must be avoided; both occurred in the first ways in which synthetic polymers were processed. New inventions were needed to achieve the necessary structure. Paradoxically, these came from two extremes of molecular characteristics: stiff, interactive molecules and flexible, inert molecules.

In solution or in the molten state, molecules which act as rigid rods will tend to associate in blocks of parallel chains, liquid crystals, particularly if there are strong intermolecular forces. The molecules are naturally fully extended because folding is difficult. If a fine stream of material is stretched as it moves to solidification, all the blocks are pulled into orientation along the fibre axis. The first to be commercialised, by DuPont as



1.2 A diagram drawn by Staudinger,⁵ which is the ideal form for a linear-polymer fibre with high strength and stiffness.

Kevlar, was the para-aramid, polyphenylene terephthalamide (PPTA), with an alternation of benzene rings and amide groups. The rings provide stiffness and phenylene interactions; the—CO.NH—groups provide hydrogen bonding. An intense effort by US Air Force research groups studied even stiffer chains. Molecules containing groups with the triple form of six-membered benzene rings flanked by five-membered rings led, after government-funded applications studies by DuPont and Dow, to the commercialisation by Toyobo of the last fibre of the twentieth century, *Zylon*, composed of polybenzoxazole (PBO), which is described in Sections 4.2 and 9.6.

There are other variants of the rigid-rod approach to high-strength fibres. In the golden age of the synthetic industry, when large profits funded research, scientists at Chemstrand Research Center, part of Monsanto, experimented with polyamide hydrazides, which contained two amide groups between each benzene ring in the chain, and polyoxadiazole-amides, with an alternation of five-membered rings and benzene rings. Although these polymers gave high-modulus, high-tenacity fibres, they did not prove competitive with *Kevlar*. However, the research led to the first book on the subject, *High-modulus wholly aromatic fibers*, edited by Black and Preston.⁷ Like Hamlet without the Prince of Denmark, the para-aramids are barely mentioned. Successful developments were the aramid copolymer *Technora*, from Teijin, described in Chapter 2, the melt-spun fully aromatic polyester *Vectran*, from Celanese (see Section 4.1) and the Russian fibres (see Section 4.4). Section 4.3 describes a new fibre, PIPD or M5, which is expected to be commercialised by Magellan. The chain geometry of M5 is similar to PBO, but hydrogen bonds in both transverse directions, in contrast to the planar sheets of PPTA, give higher shear and transverse moduli and higher axial compressive yield stress.

The other route to HM-HT fibres results from the ease with which flexible, inert chain-molecules can be pulled out into a fully-extended, oriented state. This is like combing hair or processing short-staple fibres into spun yarns. The problem is how to do this on a molecular scale. As shown by Ward and his colleagues at the University of Leeds,⁸ melt-spun polyethylene can be super-drawn at draw ratios up to 40x. Fibres made by this route were commercialised by Snia in Italy and Celanese in USA, as *Certran*, but, although cheaper to produce, their properties were inferior to other high-modulus polyethylene (HMPE or HPPE) fibres, and production ceased. Chapter 3 describes the method that has achieved commercial success: gel-spinning of *Dyneema* by DSM and Toyobo and of *Spectra* by Allied Fibers (now Honeywell). Extrusion of a concentrated solution leads to a gel, which has the solidity to hold together during drawing but the freedom for folds to be pulled out of the molecules. Because of the weak intermolecular forces, it is necessary to use ultra-high molecular weight polyethylene for

HMPE fibres. An alternative method of solid-state processing is described in Section 4.5.

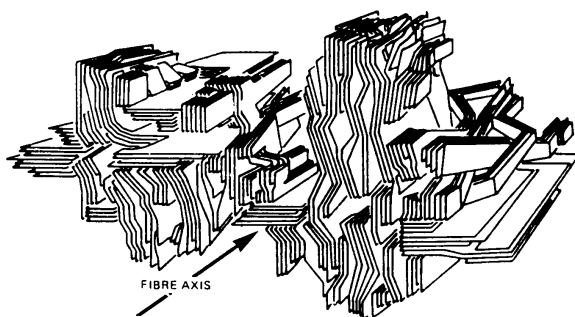
Both routes to HM-HT fibres have drawbacks. Except for the copolyesters, the rigid rod polymers are difficult to process, because they decompose chemically before they melt and require strong acid solvents. The HMPE fibres have a low melting-point, which limits their utility. Unfortunately, no way has been found to produce highly oriented, chain-extended fibres of the polyamides and polyesters, which are easily available and have intermediate melting-points. Recent research has shown that drag-line spider silk, which is a protein fibre, is among the strongest of known fibres, with a higher breaking extension than the HM-HT fibres. Genetic engineering makes it possible to achieve production of the right proteins by other organisms; but the problem remains of controlling the molecular packing in fibre spinning in order to make a high-strength structure.

In connection with the thermal and chemical resistance discussed in Chapters 8 and 9, it can be noted that increased chain aromaticity, stiffness and packing efficiency give rise to reduced accessibility by aggressive chemicals and enhanced thermal stability. These properties result from the increased intermolecular force efficiency and main chain bond scission energies, and reduced hydrogen (and hence 'fuel') content.

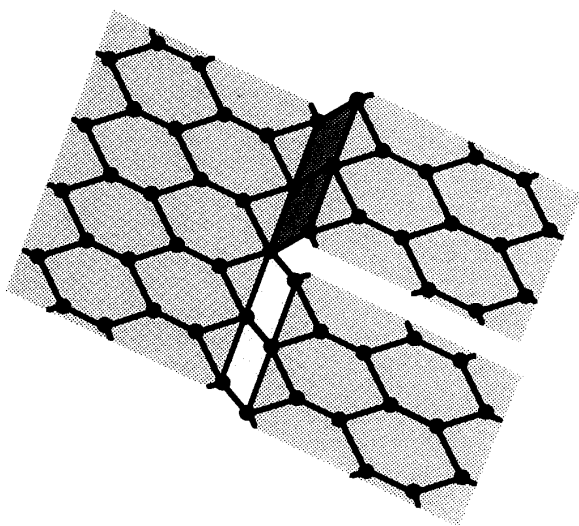
1.2.3 Graphitic sheets

Large two-dimensional (2D) molecules are not common. Mono-functional reagents give small molecules; bi-functional give linear polymers; and tri-functional or higher will normally lead to three-dimensional (3D) networks. Only a specific geometry for bond directions will give molecular sheets. Graphite, with a hexagonal planar network of carbon atoms, is the prime example. As described in Chapter 5, high-temperature processing of organic fibres under tension gives strong and stiff carbon fibres, in which graphitic sheets are oriented parallel to the fibre axis.

Paradoxically, although perfect orientation of graphite crystals would give the highest axial strength and stiffness, such a form would be useless as a fibre. The transverse properties would be so poor that sheets would rub off as they do in graphite pencils or lubricants. Fortunately, some disorder is inevitable and this provides the cohesion to hold the fibres together. The literature shows many different models of the form of disorder. An early example is shown in Fig. 1.3; another in Fig. 5.11. The real forms will vary with processing conditions, which give fibres optimised for different applications, depending on whether high strength, high stiffness, good electrical properties, economics or other factors are most important. The sheets, which are mostly packed in the turbo-stratic form, without the lateral register of graphite, are preferentially oriented in the axial direction; but transversely



1.3 A 1971 view of disorder in carbon fibres. (Johnson *et al.*⁹)

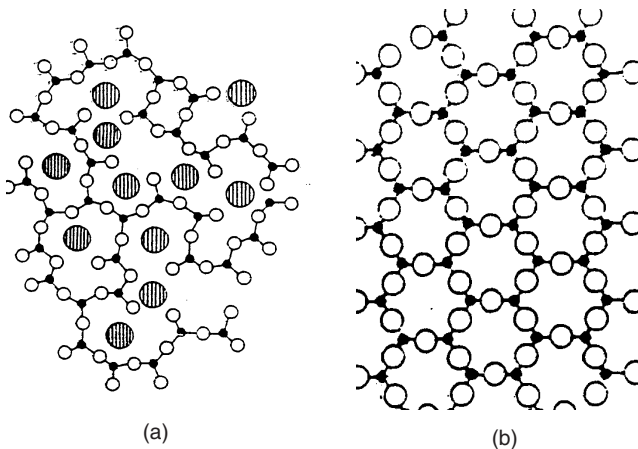


1.4 Possible interconnection between graphite planes. (Hearle¹⁰)

they are bent and folded in an interlaced pattern. It is also likely that the sheets are not perfect, but may contain some residual chemical bonds linking one sheet to another, or locations in which one sheet divides into two at a molecular discontinuity, as shown in Fig. 1.4.

1.2.4 Three-dimensional networks

Polymeric 3D networks are well known as thermoset resins. As described in Section 9.2, these can be produced in fibre form. Although stiff, the load sharing is not sufficient to give high strength. Their application is based on



1.5 Schematic views of networks, which must be converted in the viewer's mind from 2D on paper to 3D in reality. (a) An amorphous network as in glass; (b) a crystalline network in a ceramic fibre.

thermal resistance. However, inorganic 3D networks provide both stiffness and strength, as well as high-temperature performance.

Schematic views of amorphous and crystalline inorganic networks are shown in Fig. 1.5, though these are two-dimensional analogues of the three-dimensional reality. Such networks are found in the glass fibres described in Chapter 6 and the ceramic fibres in Chapter 7. Mostly, these are oxides or carbides of silicon and various metals.

1.3 Contrasting mechanical properties

1.3.1 Directional bonding

The structural division of HM-HT fibres into three groups is reflected in major differences in mechanical properties, which result from the different strengths of bonds in different directions. Along the fibres of all three types, there is continuity of covalent bonding, so that axial stiffness will be high, and so will strength unless there is poor load sharing in amorphous 3D networks or excessive defects causing brittle fracture. The differences are in the transverse properties. Linear polymer fibres will have low transverse and shear moduli, whereas fibres with 3D networks will have high values. These small-strain effects are a direct consequence of the high force-deformation constants of covalent bonds compared to the low values for van der Waal's bonds or the somewhat stronger forces from hydrogen bonds and others with a substantial electronic interaction. The differences in failure effects are more complicated.

1.3.2 Compressive yield and bending behaviour

As Euler showed quantitatively, columns easily buckle under compressive loads. Timoshenko treated the buckling of rods on an elastic foundation, and more recently Hobbs showed the influence of axial slippage in the buckling of pipelines on the seabed. The treatment has been extended to the axial kinking of fibres within a rope by Hobbs *et al.*¹¹ The same phenomena occur at the molecular level for oriented polymer molecules within fibres. As a result, the linear polymer HM-HT fibres have compressive yield stresses, and hence compressive strengths, that are at least an order of magnitude less than their tensile strengths.

In order to provide greater resistance to buckling in structures, engineers insert cross-members. At the molecular level, this is what happens in 3D networks. Consequently, glass and ceramic fibres do not yield in compression, but follow Hooke's Law up to the point at which the structure fails in some other way, such as rupture on diagonal planes. Because there is no crack opening in compression, compressive strengths may be higher than tensile strengths.

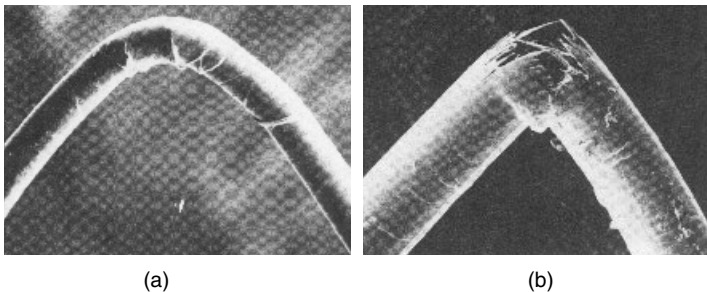
Carbon fibres tend to be closer to the 3D model, though their compressive properties are weaker than their tensile properties.

A secondary consequence of the difference in compression behaviour is the behaviour in bending. The 3D bonded fibres follow the classical analysis of bending. The outside of the bend is in tension and the inside is in compression. Because these are equally balanced, a neutral plane of zero strain remains at the centre of the fibre. The maximum strain at the farthest point from the neutral plane is $\pm(r/R)$, where r is the fibre radius and R is the radius of curvature of the fibre bend. Flexural rupture occurs when the axial strain, usually on the tension side, equals the tensile breaking strain. Schoppee and Skelton¹² measured the maximum curvature of fibres before they fractured. Table 1.1 shows that glass and carbon fibres failed at low bending strains, slightly higher than measured tensile strains because the effective length in bending failure is smaller than in tensile tests.

In linear polymer fibres, the low compressive yield strength changes the behaviour. Compression on the inside of the bend is easier than extension on the outside. Consequently, in order to minimise the energy of deformation, the neutral plane moves out, which keeps the strain low on the outside of the bend and higher where there is compressive yielding on the inside of the bend. As shown in Table 1.1, this means that fibres such as Kevlar, as well as common textile fibres, can be bent right back on themselves with a nominal bending strain, (r/R) , of 100%. The outside remains below the tensile break strain, and, although there is structural disturbance on the inside of the bend, there is not rupture. Most of the disturbance can be pulled out by tension, but multiple bending leads to cracking and flex

Table 1.1 Rupture in bending¹²

Fibre	Break strain in tensile test (%)	Nominal break strain in bending (%)
Glass	6.2	7.3
Carbon HM-S	0.8	1.4
HT-S	1.4	2.8
<i>Kevlar 49</i>	3.0	100
<i>X-500</i>	2.6	4.3
Steel, annealed	11.2	100
Boron, 92 μm	0.7	0.9
Polyester	7.0	100



1.6 Bent fibres observed by Schoppee and Skelton.¹² (a) *Kevlar 49*, showing kink bands coming out of the fibre on the inside of the bend as compressive plastic yielding occurs. (b) An experimental high-modulus fibre from Monsanto, *X-500*, which failed in tension on the outside of the bend.

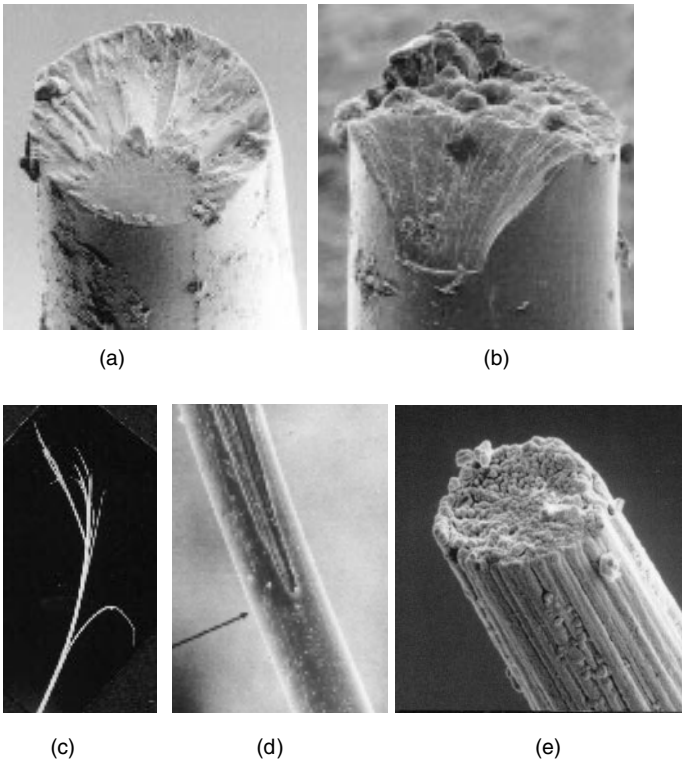
fatigue failures. In tension–tension cycling of ropes, it is possible for a component to go into compression, due to uneven loading or rope twisting, which causes the fibres as a whole to buckle into sharp kinks – and in turn to kink bands at the molecular level inside the fibres. For this reason, it is recommended¹³ that deepwater mooring ropes made of para-aramid yarns should not be allowed to go below 10% of break load for more than 2000 cycles, HMPE ropes below 10% for 40 000 cycles and polyester ropes, which are less sensitive to axial compression fatigue, below 5% for 100 000 cycles.

Figure 1.6 shows an interesting comparison of deformation in bending. The aramid fibre suffers kink bands, but there is no rupture, whereas the experimental Monsanto fibre, which was not commercialised, breaks by axial splitting on the tension side.

Both high and low compressive yield stresses have advantages and disadvantages. Easy compressive yielding is a problem when composites go into compression, but the ease of bending makes the fibres easier to handle in processing. Sharp bends do not lead to failure. In contrast to this, fibres that do not yield in compression are brittle and easily broken by bending. They must be treated more carefully in processing, but, once in a composite, they resist compressive loading well.

1.3.3 Tensile fracture

Another way in which the different types of fibre show a different behaviour is in their fracture morphology,¹⁴ which reflects a different balance of internal bonding. Figure 1.7(a) shows that a glass fibre breaks in the classic brittle-fracture form: from an initial surface defect, the stress concentration, which depends on the depth of the crack, causes a crack to grow over a



1.7 (a) Brittle fracture in glass. (b) Ductile fracture in nylon. (c) Axial splits in Kevlar. (d) Start of axial split. (e) Granular fracture in a carbon fibre.

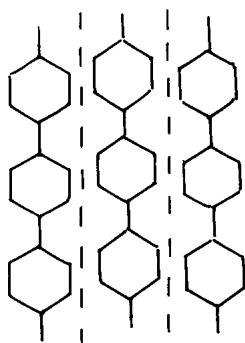
mirror region until multiple new crack initiation forms the final hackled region. This contrasts with ductile crack propagation in common melt-spun fibres, such as nylon and polyester, where a slow ductile crack propagation causes a V-notch to open up, with extensive plastic yielding on the other side of the fibre, until final catastrophic break occurs, Fig. 1.7(b).

The HM-HT polymer fibres are different again. The common form, shown in Fig. 1.7(c) for *Kevlar*, is break by axial splitting over a length of around 100 fibre diameters. As shown in Fig. 1.8, any discontinuity, usually a surface flaw, leads to an axial shear stress. Because, as indicated in Fig. 1.9, the covalent bonding is much stronger than the intermolecular bonding, a crack grows axially due to the shear stress, instead of transversely due to the tensile stress. Figure 1.7(d) shows a typical start of axial cracking at a surface flaw. If the crack growth is slightly off-axis, it eventually crosses the fibre and completes the break. Branching of the crack leads to ends with multiple splits, as in Fig. 1.7(c), but the geometry of splitting, which is shown in Fig. 1.10, explains the common observation that one end of a break has a single split and the other has multiple splits.

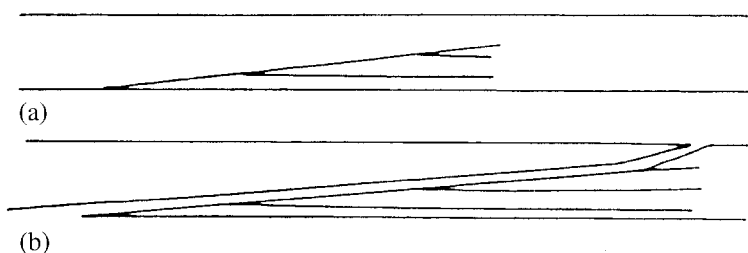
Yang,¹⁵ in his classic text on *Kevlar*, refers to three basic forms of fracture: 'type (a), pointed break: type (b) fibrillated break: type (c) kink band break'. Type (a) corresponds to the single split and type (b) to the multiple split, which may be opposite sides of the same break. The kink-band breaks, which extend over a length approximately equal to a fibre diameter, can be



1.8 Shear stress at a discontinuity in a fibre under tensile stress.



1.9 Contrast between strong axial covalent bonds and weak transverse intermolecular bonding.



1.10 (a) Bifurcation of a crack. (b) Resulting failure shows a single split on one end and multiple splits on the other end.

attributed to fibres that have been weakened by axial compression, as described above. Other models of aramid fibre breakage, such as the one shown in Fig. 2.10, combine axial splitting with regions of transverse rupture. However, in undamaged fibres, the full axial splits are most commonly found. Yang¹⁵ points out that the diameter at the final break point is about 2–4 μm , compared to 12 μm for the whole fibre: ‘Thus the true fiber strength based on the fiber cross-sectional area at break is very high.’ If the final break is due to axial tensile failure, when the reduction in aspect ratio means that tensile rupture is easier than shear cracking, this implies an ultimate molecular tensile strength of 30 to 100 GPa.

The third type of break in HM-HT fibres is the granular break shown in Fig. 1.7(e). This is commonly found in textile fibres spun from solution. It is a consequence of initial coagulation into a spongy structure containing voids. After drying, the surface of the voids remain as areas of weakness. The granular surface is similar to a low-magnification view of a fibre-reinforced composite. The mechanics of failure are similar. At a critical stress, a fibrillar element breaks. The crack does not propagate directly across the weak discontinuity, but, due to stress transfer, triggers rupture of a neighbouring fibre element in a position close to, but not exactly continuous with, the existing crack. Figure 1.7(e) is the break of a carbon fibre and the granular form reflects the void structure of the polyacrylonitrile precursor.

The overall picture of the occurrence of different forms of fracture is as follows. Glass fibres show brittle fracture, though sometimes the crack follows the angled line of maximum shear stress instead of the perpendicular line of maximum tensile stress. Ceramic fibres and carbon fibres show either smooth brittle fractures, if there is strong lateral bonding, or granular fractures, if there are voids or other lateral weaknesses. The highly oriented linear polymer fibres, including HMPE as well as liquid-crystal fibres, break by axial splitting, with partial transverse cracking if there are

lateral discontinuities, either in the original structure or, more likely, due to subsequent damage.

1.3.4 Practical consequences of failure modes

Brittle fracture causes a sudden failure. In contrast to this, long axial splits take longer to grow and absorb more energy. As a result, the consequences in a practical failure situation are less catastrophic. Furthermore, although long splits across a fibre cause the load to drop to zero in a tensile test on a single fibre, in an assembly of fibres the fibrillar elements will continue to carry load, provided there is some transverse interaction due to bonding or friction.

None of the HM-HT fibres show the type of fatigue experienced by metals. The inorganic fibres do not have the yield regions in which fatigue cracks develop. In tension-tension cycling of *Kevlar*,¹⁶ it was found that failure only occurred when the peak load was in the same range as the scatter of peak load in tensile tests. However, the axial splits were much longer. In a fibre cycled to over 90% of break load, which lasted for 285 000 cycles, the fracture extended over a length of 6 mm, which was 485 times the fibre diameter. In order to record the break, it was necessary to make a montage of SEM pictures that was about 3 m long. A variety of forms of splitting were observed, such as splits that terminated at both ends without breaks and peeling of a layer from the surface.

In most HM-HT fibres, creep rupture (static fatigue) is not a problem, unless it is accompanied by stress corrosion as in glass fibres. Aramid fibres show creep, but this is a tightening of the structure under low stresses and does not lead to creep rupture. HMPE fibres are the one important exception. Crystal defects, as described by Reneker and Mazur,¹⁷ allow polyethylene molecules to move past one another. Above a certain load for any HMPE fibre, creep continues at a constant rate, the plateau creep rate, which increases with tension and temperature. Creep rupture is a factor that must be taken into account when HMPE fibres are used under high tensions for long periods of time, especially at higher temperatures. Typically, the plateau creep rate is 100 times greater at 50 °C than at 20 °C.¹³

The first HMPE fibre to appear on the market, *Spectra 900*, had a very high creep rate, and creep rupture occurred in a rather short time even at moderate loads. *Spectra 1000*, which was introduced in 1985, had improved creep properties. Other HMPE fibres, produced in slightly different ways, show lower creep. In one set of tests,¹³ under 15% of break load *Spectra 900* crept by 13% between 10 and 100 days, whereas the values for *Spectra 1000* and *Dyneema SK60* were 6.3 and 0.47% respectively. At 30% of break load, *Spectra 900* broke in 4 days, but *Spectra 1000* and *Dyneema SK60* lasted for 28 and 123 days, respectively.

The effects of compression and bending have been discussed above. Brittle fibres will break when even a low curvature is applied; oriented linear polymers can be severely bent, but will fail in flex fatigue if subject to repeated sever kinking. Due to the weakness of the transverse bonding, surface abrasion, which leads to peeling away of layers from the fibre surface, is a greater problem in the oriented linear polymer fibres than in three-dimensionally bonded fibres.

1.4 Economics

1.4.1 Fibre markets

In the 1950s, nylon and polyester were the new miracle fibres. They were sold at prices several times higher than cotton and wool in a rapidly growing market. This enabled fibre producers to cover their earlier research and development (R&D) costs and continue to show a large profit, much of which was fed into more fibre research, including the development of the second generation of high-performance manufactured fibres. Now polyester is cheaper than cotton and has become the general purpose commodity fibre. Both nylon and polyester are made in large quantities by many companies, so that their pricing reflects the real costs of production, and, in bad times, the marginal costs. There is a wealth of production and marketing data, both in publications such as *Fiber Organon* and in proprietary reports of consultants. The situation is more difficult for the high-performance fibres, both in reality and in obtaining economic information.

When DuPont and other companies started on the research that eventually led to *Kevlar*, their eye was on the large tyre-cord market. By 1960, this had moved from cotton to rayon, and then to nylon competing with rayon, as the available fibre strengths increased, and polyester was beginning to mount another challenge. Each increase of strength led to a proportionate reduction in the amount of fibre needed in a tyre. Unfortunately, this did not continue when the strength became double that of nylon. Reducing the amount of fibre in the tyre means that the yarns become thinner and more widely spaced. Eventually this becomes the limiting factor and not the strength. Consequently, *Kevlar* and similar fibres never penetrated the market for tyres for passenger cars and most commercial vehicles. Steel cords also became a competitor at this time. High-performance fibres have only been used for special purposes, such as racing cars and heavy-duty off-road machines.

With one exception, all the high-performance fibres are produced in comparatively small quantities by a limited number of manufacturers of each type of fibre – and they have had to find specialised markets where their superior properties justify a high price. Their applications are described in

various sections of this book. The one exception is glass. E-glass is produced in large quantities as the fibre used for the large market for GFRP (glass fibre reinforced plastics), as distinct from ‘advanced composites’, which use expensive carbon fibres, HM-HT polymer fibres and ceramic fibres. Even within glass, as mentioned in Section 6.2.1, S- and R-glass are expensive to manufacture and their use is limited to the fairly small market for advanced composites.

1.4.2 Production

Nylon and polyester are made by easy polymerisation processes from readily available intermediate chemicals, and are spun by the easy melt-spinning process at speeds that may be as high as 5000m/min. The large producers use continuous polymerisation that feeds directly into melt-spinning, but polymer chips are available on the market for smaller producers. Even apart from the consequences of low-volume production, all the high-performance fibres, save for melt-drawn E-glass, involve higher costs in one way or another, than fibres such as nylon and polyester.

Almost all the polymers used in the fibres described in this book, whether as HM-HT fibres or thermally or chemically resistant fibres, are more complicated, more expensive to make, and are not available on the market. Sometimes, other applications help: *Vectran* and *PEEK* would probably not be made as fibres if there was not also a market for the polymer in plastics. One exception, which uses a low-cost polymer, is HMPE: ultra-high molecular weight polyethylene is readily available on the market. Most current carbon fibres start with polyacronitrile (PAN) fibres: textile grades of PAN cost more than nylon and polyester and more expensive, special grades are needed for carbon fibre production. Pitch may offer economies as raw material, but freshly spun pitch fibre is difficult to process. The ceramic fibres require both costly inorganic materials and a polymer solution to spin the precursor fibres.

Wet-spinning, which is the route to the ceramic precursors and to many of the chemically and thermally resistant fibres, is slower and costs more than melt-spinning. When the solvent is sulphuric or phosphoric acid, as for the aramids and similar fibres, the costs are still higher. Gel-spinning necessarily involves solvent recovery processes. It is also a slow process: a patent¹⁸ refers to speeds of less than 50m/min for the production of a fibre such as *Spectra 900*.

Frequently, further processing is necessary. Hot treatments under tension are needed to give higher modulus forms of aramid and similar fibres. The cost advantage of making *Vectran* by melt-spinning is off-set by the subsequent slow heating needed to build up the molecular weight by solid-state polymerisation. The gel-spinning patent¹⁸ describes a further heat treatment

under tension at a temperature close to the melting-point at less than 20 m/min, in order to produce an improved fibre such as *Spectra 1000*. The carbon fibre process involves two steps of heat treatment, the second at temperatures approaching or even above 2000°C, and residence times are quoted in hours in the literature. Similarly, the precursor ceramic fibres have to undergo slow heating at high temperature.

The scale of production is obviously an important factor in production costs and high-performance fibres are different to a general purpose fibre such as polyester. Some of the fibres are still being produced on pilot plants in R&D facilities, because companies do not have the confidence in market growth to build substantial production plants. Where large-scale industrial

Table 1.2 Fibre prices (from various sources). Except where otherwise indicated, values given are typical starting prices for coarse yarns or rovings; finer deniers and special grades will be more expensive

Fibre	US\$/kg
<i>Polyester</i>	3
<i>High-modulus polymer fibres</i>	
para-aramid	25
meta-aramid	20
HMPE	25
Vectran	47
Zylon (PBO)	130
Tensylon (SSPE)	22–70
<i>Carbon</i>	
PAN based	14–17
pitch based – general purpose	15
– highest modulus	2 200
oxidised acrylic	10
<i>Glass</i>	3
E-glass	15
S-2 glass	
<i>Ceramics</i>	
SiC types: Nicalon NI, Tyranno Lox-M, ZM	1 000–1 100
near stoichiometric types	5 000–10 000
alumina types	200–1 000
boron	1070
<i>Thermally and chemically resistant fibres</i>	
PEEK	100–200
thermoset: Basofil	16
Kynol	15–18
PBI	180
PTFE	50

production is in place, the cost of increasing capacity affects decision making. Production may be giving a profitable return on the operating expenses of an existing plant whose costs were incurred in earlier years, but might not yield profit on investment in a new plant. In this respect, HMPE is in a more favourable position because the polymer is readily available and individual production units are comparatively small. Aramids require a larger investment in polymerisation and in the size of economic production units. Finally, there is the difficult decision as to whether it is better to limit production and command a high price in specialised markets or go for a larger volume use at a lower price.

1.4.3 Prices and production

Production costs are naturally the proprietary information of manufacturers. Prices must be disclosed to customers, but, even so, it is difficult to find generally available information. In addition to the fact that different deniers of fibre and yarn and different grades of a generic type will be priced differently, prices will be lowered when a manufacturer is keen to develop a particular market and will be higher when demand outstrips manufacturing capacity. Sources for most of the fibre types are limited, so that there is no open competitive market. This leads to reports of a wide range of prices: one source quotes prices for carbon fibres from 18 US\$/kg for low grade heavy tow to 1000 US\$/kg for high grade fine tow.

Table 1.2, which contains information from a variety of sources, gives a general indication of the relative prices of high-performance fibres.

Accurate estimates of the production of high-performance fibres are difficult to obtain. The general purpose polyester fibre for textile and technical uses has global production in tens of millions of tonnes per year. Glass fibre is also produced in large volume with world capacity approaching three million tonnes per year. The other more widely used high-performance fibres will reach only tens of thousands of tonnes per year, and the newer or more specialised fibres, hundreds of tonnes per year or less.

1.4.4 Economic returns and the future

Economic returns for advanced technologies can be based on the costs incurred at the following levels:

- 1 basic scientific and engineering research, publicly funded or otherwise
- 2 directed scientific and engineering research, e.g. by defence agencies
- 3 specific technological R&D, by pioneering companies
- 4 capital cost of plant and commercial infrastructure
- 5 operating costs.

In first generation synthetic fibres, particularly polyester and nylon, there is little doubt of the value of the economic return when costs at all levels are taken into account. By the 1960s, the three top levels will have been matched by the profits of fibre companies and, even though the market became much more competitive by the end of the century, the fibres continued to be valuable source of revenue to many companies. Very few companies who entered this industry, even if they later dropped out, will have made a loss on their investment.

For the second generation high-performance fibres, the situation is different. The top two levels of public funding do not enter commercial calculations. The basic science can be regarded as part of the public good and has many associated benefits, such as the link to higher education. The defence spending is justified on other grounds, and has led to major expenditure on advanced fibres for lightweight composites used in aerospace applications. This expenditure overlaps with the third category of company research, for example in the contracted research carried out by DuPont and Dow to develop PBO fibres following the basic research in US Air Force laboratories. Commercial accounting, which relates to value to shareholders, concerns only the expenditure of company funds in Categories 3–5. It is clear that many companies have not had a return on their investment, because they have never commercialised their products or have dropped out of the market. It may be invidious to name names, because there are many fibres and many companies in this position, but to illustrate the situation, we can mention Monsanto with their aromatic polymers, Celanese with *Certran* melt-spun and drawn PE (polyethylene), Courtaulds with carbon fibres, and DuPont with FP alumina. Where companies are continuing in production and marketing, it is doubtful if the returns on high-performance fibres have matched the development costs. Production on existing plants will certainly continue to supply the specialist markets. The more important questions for the future are whether the predicted return on investment is sufficient to justify the building of new plants – and whether there is sufficient confidence in the future demand for high performance and in the technical advances that might be made to justify research expenditure.

Techno-economic questions remain open. Will high-performance fibres be limited to small-volume, high-price applications? If the use of a fibre will save or enhance life in a medical device, will help to win a major sporting event or serves military capability, price is almost irrelevant. Or will some large-volume uses be found where, despite a high price, there is cost-benefit when a total system is costed? For example, it is estimated that every 100kg of weight saved in an aircraft reduces fuel costs by \$20000 per year and increases the range by 100km.¹⁹ Or will routes be found to lower-cost production that compete with fibres for the large-volume market for tech-

nical textiles? Here the strength, moderately high stiffness and low cost of polyester are a challenge, although it has weaknesses, especially for applications such as severe loading in high performance tyres, or use in adverse conditions.

Aside from the prospects for this particular industry, there is the general question of the attitude to risk. Many companies carry out detailed calculations of potential costs of R&D for particular projects and rate these against potential returns. But the input data is uncertain and can be given an optimistic or a pessimistic gloss. A more robust attitude is given in a comment by Soichiro Honda, founder of the Japanese car firm: 'To me success can only be achieved through repeated failure and introspection. In fact, success results from the 1 per cent of your work which results only from the 99 per cent that is called failure.'

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2.1 Introduction

Aromatic polyamides became breakthrough materials in commercial applications as early as the 1960s, with the market launch of the meta-aramid fibre *Nomex*® (*Nomex*® is a DuPont Registered Trademark), which opened up new horizons in the field of thermal and electrical insulation. A much higher tenacity and modulus fibre was developed and commercialised, also by DuPont, under the trade name *Kevlar*® (*Kevlar*® is a DuPont Registered Trademark) in 1971. Scientists in the fields of liquid crystals, polymers, rheology and fibre processing, as well as process and system engineers, spent several years prior and during the early stage of its market introduction establishing the basics and fundamental understanding necessary to take full advantage of this new class of high-performance materials. Their outstanding potential derived mostly from the anisotropy of their superimposed substructures presenting pleated, crystalline, fibrillar and skin-core characteristics. This achievement is due in part to DuPont science and technology excellence brought into this field by Kwolek,¹⁻⁴ Blades,^{5,6} Tanner and co-workers,⁷⁻⁹ Gabara and co-workers,¹⁰ Yang,^{11,12} and many others who took an active part in this enterprise, starting with the inception of the aramids. Among a rather scattered literature on the matter, paramount contributions appeared relatively early in four books entitled *High modulus wholly aromatic fibers*, Black and Preston¹³ (1973), *The strength and stiffness of polymers*, Schaefer¹⁴ (1983), *High performance aramid fibers*, Jones and Jaffe¹⁵ (1985), and *Aromatic high-strength fibers*, Yang¹¹ (1989).

Another para-aramid, *Twaron*® (*Twaron*® is a registered product of Teijin), similar to *Kevlar*®, and an aromatic copolyamide, appeared on the market towards the end of the 1980s. The aromatic copolyamide derived from a good fundamental understanding of the earlier work done with rather stiff para-aramid chains and the new space created for more flexible, high tenacity fibres. Teijin, after a remarkable scientific interpretation of the prior art by Ozawa and Matsuda,¹⁶ who pioneered the develop-

ment of the aromatic copolyamide fibre, commercialised the *Technora*® (Technora® is a registered product of Teijin) fibre.

In the last 15 years, tremendous scientific contributions have been made towards establishing the structure–property relationships. Dobb and co-workers,^{17,18} Morgan *et al.*,¹⁹ Termonia,^{20,21} Roche *et al.*,²² Northolt and co-workers^{23–26} and Jackson *et al.*,²⁷ were part of the scientific community who brought analytical, theoretical and modelling tools to approach these rather complex relationships revealing important characteristics which go beyond the traditional mechanical and chemical interpretations – such as the role which the micro-morphology plays in the biological accessibility of the internal structures.

For the sake of completeness, in the 1970s, based on an aromatic polyamide–hydrazine composition, Monsanto developed an aromatic copolyamide fibre under the code *X500* which almost reached the market.

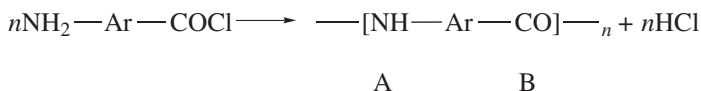
In this chapter we will focus on the synthesis, fibre processing, structure–property relationships and applications of the commercial aramids. We will use the word para-aramid for both the *Kevlar*® and the *Twaron*® fibres.

2.2 Polymer preparation

2.2.1 Basic synthesis

The following designation was adopted in 1974 by the United States Federal Trade Commission to describe aromatic polyamide-based fibres under the generic term aramid: ‘a manufactured fibre in which the fibre-forming substance is a long chain synthetic polyamide in which at least 85% of the amide (—CO—NH—) linkages are attached directly to two aromatic rings’.

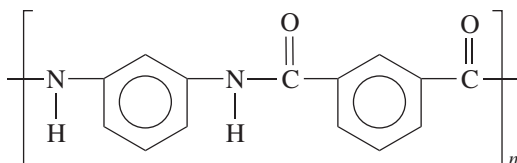
Aramids are prepared by the generic reaction between an amine group and a carboxylic acid halide group. Simple AB homopolymers may be synthesised according to the scheme below:



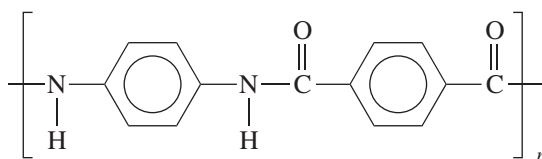
A similar reaction scheme also yields AABB homopolymers. For these reactions several methods^{28–30} of preparation can be used, such as interfacial polymerisation and low-temperature polycondensation, which remains the most frequently encountered synthesis. Melt or vapour-phase polymerisation reactions should also be mentioned.

AABB aromatic polyamides are prepared from various aromatic diamines and diacids or diacid chlorides. This facilitates the generation of

aromatic polyamides with extensive variations in molecular structure. The early AABB polymers contained predominantly meta-orientated linkages. The earliest representative of this class is poly-*m*-phenyleneisophthalamide, which was commercialised by DuPont in 1967 as *Nomex*® aramid fibre. Its chemical formula is:



The discovery in 1965 of high modulus, high tenacity (HM-HT) fibres from liquid crystalline solutions of synthetic para-aromatic polyamides led to the commercial production of *Kevlar*® aramid fibre by DuPont in 1971;¹ the corresponding chemical formula is given below:



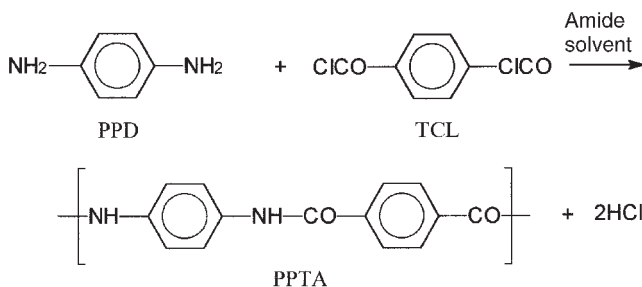
Kevlar® fibres are poly (*p*-phenylene terephthalamide) (PPTA),³¹ the simplest form of AABB para-orientated polyamide.

2.2.2 The aromatic polyamide polymerisation process

Many examples of low-temperature polymerisation for aromatic polyamides and copolyamides can be found in seminal work by Kwolek.² Morgan³² pointed out several pertinent factors affecting polymer characteristics in low-temperature polycondensation reactions. The most critical ones are:

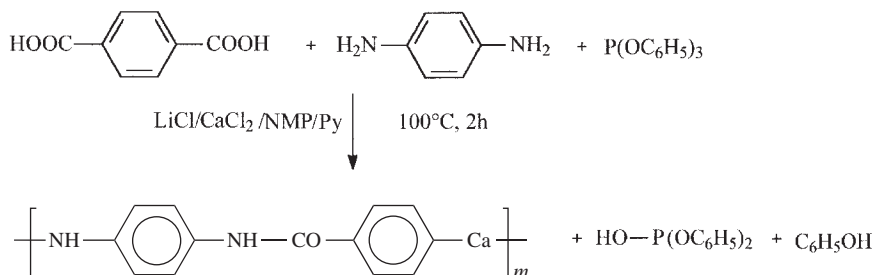
- the solubility–concentration–temperature relationships, which make the choice of solvent critical, and
- the salt concentration at constant polymer concentration, which partly governs the degree of polymerisation and polymer inherent viscosity (η_{inh}).

Rather than detailing generic, mostly empirical, rules governing the polycondensation to achieve the optimum and narrowest molecular weight distribution, we propose below a more specific description of a process based on patent examples and related literature.

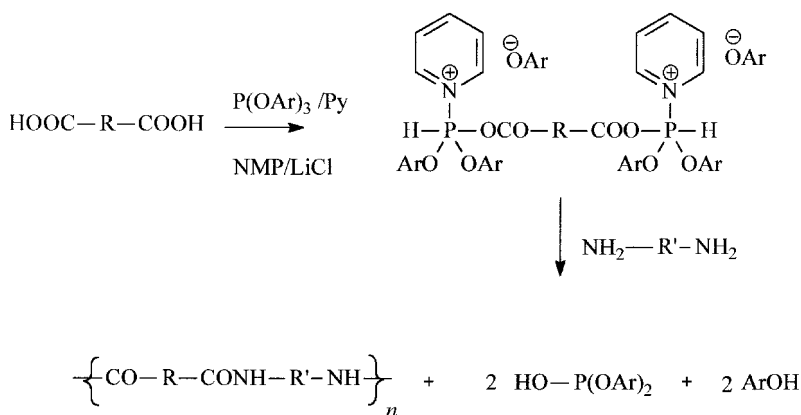


2.1 PPTA synthesised by low-temperature polycondensation of *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCL).

Aromatic polyamides of the PPTA type are usually synthesised via a low-temperature polycondensation reaction based on *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCL), according to Fig. 2.1. The specifics of the process have been reported by Bair and Morgan,^{33,34} Kwolek² and Blades.^{5,6} One methodology involves the dissolution of appropriate quantities of PPD in a mixture of hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone (NMP), cooling in an ice/acetone bath to 258 K (−15 °C) in a nitrogen atmosphere, and then adding TCL accompanied by rapid stirring. The resulting product is a thick, paste-like gel. Stirring is discontinued and the reaction mixture is allowed to stand overnight with gradual warming to room temperature. Work-up of the reaction mixture is accomplished by agitating it with water in a blender to wash away solvent and HCl. The polymer is collected by filtration. The stoichiometry of the solvent and reactant mixture is important in determining the molar mass of the final product. For instance, Bair and Morgan^{33,34} report that a 2:1 ratio by volume of HMPA: NMP produced PPTA product with the highest inherent viscosity (and hence largest molar mass). An optimum reactant (PPD and TCL) concentration was *ca* 0.25 M. The inherent viscosity was shown to decrease quite rapidly if reactant concentrations less than 0.25 M. were used. A similar behaviour was observed for reactant concentrations greater than 0.3 M, although the fall-off in inherent viscosity was observed to be more gradual in this case. The viscosity fall-off at low reactant concentrations can be ascribed to the occurrence of competitive side-reactions of the type described by Herlinger *et al.*,³⁵ who examined the solution polymerisation of aromatic diamines and aromatic dicarboxylic acid chlorides in *N,N*-dimethylacetamide (DMAc). The drop-off in inherent viscosity at higher values of the reactant concentration could well be ascribed to a decrease in reactant mobility due to the onset of gelation before a high value of inherent viscosity could be attained. Of course, the polymerisation reaction is exothermic and a greater quantity of heat will be generated if higher



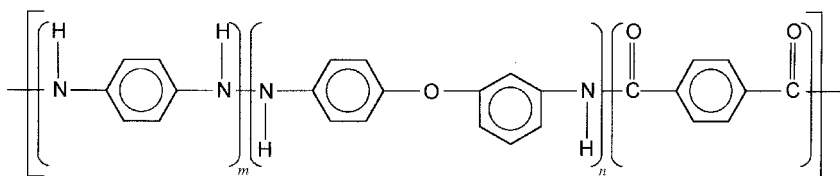
2.2 The Higashi synthesis: polycondensation of terephthalic acid and *p*-phenylene diamine.¹¹



2.3 The Higashi triaryl phosphite reaction: note the generation of the *N*-phosphonium salt of pyridine, which subsequently undergoes aminolysis.

reactant concentrations are used. This could lead to an increased rate in side-reactions, which would also depress the value of inherent viscosity attainable.

Alternative synthetic pathways have been reported. In particular, reactions between aromatic dicarboxylic acids and diamines have been investigated since the diacids are reasonably cheap starting materials. The work of Higashi and co-workers is of note in this respect.^{36–38} Solvent mixture/salt systems are utilised. In the Higashi approach³⁷ PPTA of high molecular mass was obtained when the polycondensation of terephthalic acid (TPA) and PPD was carried out in NMP which contained dissolved CaCl_2 and LiCl in the presence of pyridine. The synthetic strategy is illustrated in Fig. 2.2.



2.4 Polymer chemical structure of *Technora*®.⁴³

In earlier work, Higashi *et al.*³⁶ explored the direct polycondensation reactions of aromatic dicarboxylic acids and diamines by using diphenyl and triaryl phosphates in NMP/pyridine solvent mixtures containing LiCl. The reaction with triaryl phosphates was assumed to proceed via a mechanism outlined in Fig. 2.3. This development arose from earlier work of a fundamental organic chemistry nature reported by Yamazaki and Higashi.^{39,40}

The work of Preston and Hofferbert^{41,42} is also relevant to the synthetic strategy under discussion. However the latter strategy was unsuccessful when terephthalic acid and diamines were used as polycondensation reagents, since high molar mass aromatic polyamide product was not obtained. This difficulty was subsequently overcome by substituting poly(4-vinylpyridine) in lieu of pyridine.

2.2.3 Copolyamides

The search for aramid copolymers was largely driven by scientific observations made early on by Ozawa and Matsuda.¹⁶ In the pursuit of an ideal synthetic fibre with improved processability, it was recognised that the incorporation of diamines with wider distances between the two amino groups would be favourable to a lower spatial density of hydrogen bonding and rate of crystallisation. Furthermore, the incorporation of comonomers in which two phenylene groups are connected with a single atom unit generally improves the fibre drawability.

The resultant species, prepared via the copolymerization of several aromatic diamines and diacid halides, are referred to as copolymers. The use of copolymers in fibre production is a common technique with aromatic polyamides. These wholly or partially aromatic copolyamides contain alkyl-aryl groups, and other cyclic and heterocyclic groups. Some also contain pivotal substitutions and some pendent groups.

Teijin has commercialised an aromatic copolyamide, *Technora*®, Fig. 2.4, which exhibits high tensile stress properties as well as high resistance to hydrolysis. The manufacturing process of *Technora*®^{43,44} reacts PPD and 3,4'-diaminodiphenylether (3,4'-ODA) (each at 25 mole %) with terephthaloyl chloride, in an amide solvent such as *N*-methyl-2-pyrrolidone/CaCl₂

(10% concentration), to complete the polycondensation. The reaction mixture is neutralised and subjected to spinning into an aqueous coagulation bath. The as-spun fibre is then brought to extraction of solvent, superdrawn at high temperature, and passed through finishing to give the final product. The whole process is very simple and straightforward since only a single solvent is used throughout. This greatly simplifies the solvent recovery process and also makes *Technora*® completely free of residual acid, which avoids later difficulties in the spinning process. Unlike the stiff chain *Kevlar*® aramid that is spun from a liquid crystalline solution directly to orientated HM-HT fibres, *Technora*® is spun from an isotropic solution. Its fibres have tensile stress properties similar to *Kevlar*® 29. This semi-stiff chain copolymer has a homogeneous morphology, which leads to very good hydrolytic stability, while its greater molecular flexibility results in limited modulus.

2.2.4 Other aromatic polyamides

There are many aromatic polyamides not mentioned in this brief overview. They are extensively covered in the monograph by Yang.¹¹

2.3 Spinning

2.3.1 Solution properties

Rigid chain macromolecules such as the aromatic polyaramids exhibit low solubility in many common solvent systems utilised in polymer technology. This is due to the fact that the entropy term in the Gibbs energy of solvation makes a very small contribution because of the rigidity. Consequently, the dissolution of such polymer materials is attained because of an extensive interaction of the polymer chains with solvent molecules, which is manifest in the enthalpy contribution to the solvation free energy.

The conformation adopted by macromolecules in solution is a well-established area of macromolecular science, but a somewhat general discussion of the possible states adopted by macromolecules in solution may be presented at this stage with some profit. A number of common scenarios may be envisaged. A common situation is that of randomly coiled polymer chains. The statistical analysis of such ensembles is well established.⁴⁵ However, if the chains are relatively stiff and are linked to extend the chain in one direction, then they are ideally described in terms of a random distribution of rods. Of course, association with the solvent may contribute to rigidity and also to the volume occupied by each polymer molecule. Now, as the concentration of rod-like macromolecules is increased and the saturation level for a random array of rods is attained, the system

will simply become a saturated solution with excess polymer; or more interestingly, if the solvent/polymer relationships are right, additional polymer may be dissolved by forming regions in which the solvated polymer chains approach a parallel arrangement. These ordered regions define a mesomorphic or liquid crystalline state and form a phase incompatible with the isotropic phase. Continued addition and dissolution of polymer forces more polymer into the ordered state. If the rod-like chains are arranged in an approximately parallel array but are not otherwise organised, then the ordered phase is termed 'nematic'. Usually, a polymer sample will be poly-disperse and the ordered phase will be organised in microscopic domains of varying size and direction of orientation. Aromatic polyamides form liquid crystal solutions on account of their extended chain structure.

It is clear that orientational order appears in solutions of rigid chain polymers because a random arrangement of the macromolecule assembly will be possible only up to a certain solution concentration. To retain a minimal volume, and indeed a minimal free energy, above a certain critical concentration, asymmetric macromolecules must acquire an ordered mutual arrangement that corresponds to a transition to the state typical for liquid crystals. In this case the solution becomes anisotropic. The degree of this anisotropy will be less than the strict three-dimensional ordering typical of a crystalline system, but at the same time it will differ significantly from an isotropic state characteristic of amorphous systems. The concentration threshold defining the transition to the liquid crystalline state will depend on the degree of shape asymmetry of the macromolecules, which will be determined as the ratio of their equilibrium length to their diameter, termed the 'axial ratio'. It should also be noted that liquid crystallinity can arise from anisotropy of intermolecular forces. But the latter are usually prominent in liquid crystal materials of low molar mass, although they could also be important in polymers that contain groups such as *p*-phenylene, whose polarizabilities are highly anisotropic.

Flory and co-workers⁴⁶⁻⁴⁹ have described theoretically the behaviour of 'hard' rod-like polymers in solution and considered, in particular, the conditions under which the latter macromolecules would produce anisotropic phases. The Flory approach utilised a lattice model. This work followed on from the initial models developed by Onsager⁵⁰ and Ishihara,⁵¹ which were relatively complex. These approaches rely on analysis of the second virial coefficient for very long, rod-like particles. Indeed, the Onsager paper⁵⁰ was the first to show that a solution of hard, asymmetric particles should separate into two phases above a threshold concentration that depends on the axial ratio of the particles. The paper also indicated that the phase separation was due to shape asymmetry alone, and that recourse to intermolecular attractive forces was not necessary. However, an approach based on the

virial expansion suffers from the difficulty of evaluating higher virial coefficients for highly shape-asymmetric particles and, indeed, from the non-convergence of the virial series at the concentration required for the formation of a stable, anisotropic, liquid crystalline phase. The simple Flory lattice theory has been extended to consider polydisperse systems,⁵² mixtures of rod-like particles with random coils,⁵³ and three-component systems consisting of a solvent and two solutes, the latter consisting of rod-like molecules with different axial ratios.⁵⁴ The problem of biphasic equilibria involving rod-like macromolecules has also been described.⁵⁵ Finally, the statistical mechanical analysis has been extended to mixtures of rod-like particles in which flexible joints connect the rods.⁵⁶

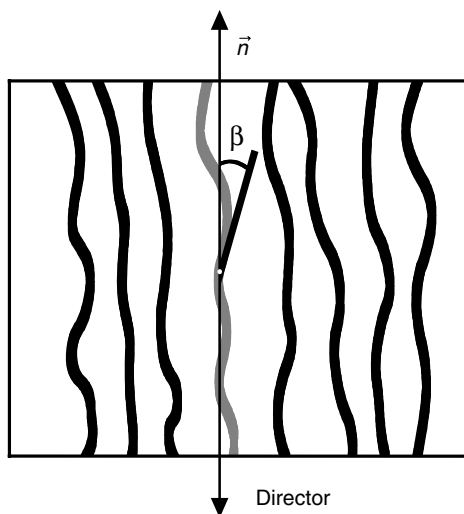
The behaviour of para-aromatic polyamides in solution has attracted considerable attention, especially with respect to their liquid crystalline behaviour. Both poly(*p*-benzamide) and poly(*p*-phenylene terephthalamide) have received particular attention in this respect. Papkov⁵⁷ has provided a useful review of this area. The topic has been discussed in a general way by Morgan.³² The latter macromolecules are characterised by a stable *trans* configuration of the amide bond and by a high barrier to rotation around the stable aryl carbon bond.

Bair *et al.*⁵⁸ examined the behaviour of poly(1,4-phenyleneterephthalamide), PPTA, in solutions of HMPA/NMP. A strong dependence between the inherent viscosity attained by the polymer solution and the reactant concentration used was found. When dissolved in high strength sulphuric acid or HMPA/NMP/LiCl solvents, PPTA was found to form an interesting liquid crystalline solution composed of liquid isotropic and anisotropic (mesomorphic) phases at some critical concentration. The effect of polymer intrinsic viscosity on the critical concentration needed to form the anisotropic phase was determined. In the same paper it was shown that liquid crystalline solutions were formed from poly(chloro-1,4-phenyleneterephthalamide) (Cl-PPTA) in DMAc/LiCl solvents. In the latter case, the liquid crystalline solutions were readily separated into the component isotropic and anisotropic phases. Analysis of the polymer distribution in the respective phases indicated that the distribution depended on polymer concentration, polymer intrinsic viscosity and LiCl content. It was shown that the anisotropic phase always contained a greater amount of polymer than the isotropic phase. Furthermore, the intrinsic viscosity of the polymer present in the anisotropic phase was greater than that found in the isotropic phase. Hence, one could conclude that formation of an anisotropic phase occurred by the highest molar mass polymer chains packing into the ordered more dense fluid. It was also noted that by proper selection of polymer and solvent variables, the extent of anisotropic phase relative to isotropic phase could be varied from zero to essentially 100%.

2.3.2 Spinning of fibres

Production of fibres initially involves heating the spinning solution up to a suitable processing temperature, which is of the order of 80°C for the highly concentrated solutions in 100% (water-free)⁸⁷ sulphuric acid. At this temperature, above a polymer concentration of about 10 wt% the solution state corresponds to a nematic liquid crystalline phase. The concentration limit for the polymer in spinning solution is 20 wt%. If concentrations above this critical limit are used, spinnability is affected due to undissolved material; therefore the resulting fibre has inferior mechanical properties. Because these rod-like polymers are rigid, they orientate themselves with respect to each other, forming a nematic phase as illustrated in Fig. 2.5 which shows the orientation angle β with respect to the director \vec{n} . This phase is dominated by liquid crystalline domains that contain aligned polymer chains. The degree of orientation of these polymer chains depends on solution temperature and polymer concentration.

Polymer spinning solutions are extruded through spinning holes and are subjected to elongational stretch across a small air gap, as illustrated in Fig. 2.6. The spinning holes fulfil an important function. Under shear, the crystal domains become elongated and orientated in the direction of the deformation.^{3,32,58} Once in the air gap, elongational stretching takes place. This is effected by making the velocity of the fibre as it leaves the coagulating bath higher than the velocity of the polymer as it emerges from the spinning

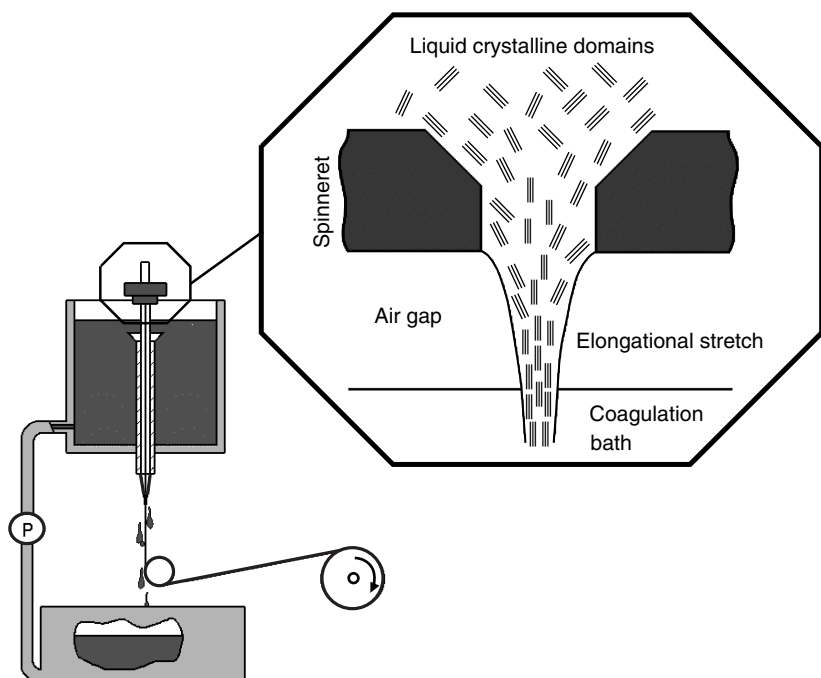


PPTA molecules are indicated by the thick lines

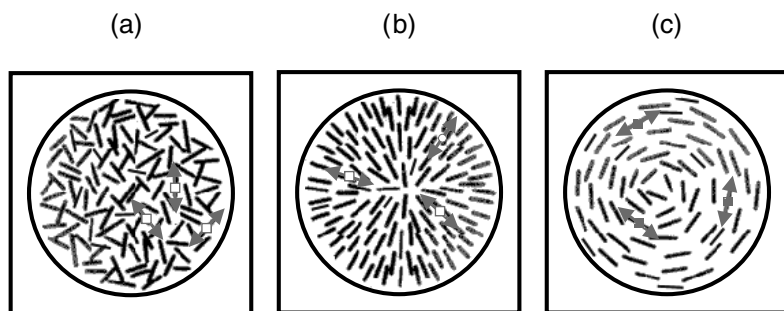
2.5 Schematic representation of the liquid crystalline solution.

holes. This ratio is often referred to as the 'draw ratio' and can be fine-tuned to obtain higher tenacities and moduli with lower elongations and denier. The resulting stretch in the air gap further perfects the respective alignment of the liquid crystal domains. Overall, a higher polymer orientation in the coagulation medium corresponds to higher mechanical properties of the fibre. Because of the slower relaxation time of these liquid crystal systems, the high as-spun fibre orientation can be attained and retained via coagulation with cold water.⁴ Essentially, the crystallinity and orientation of the solution are translated to the fibre. These factors allow the production of high strength, high modulus, as-spun fibres. Fibres can exhibit three possible lateral or transverse crystalline arrangements and these are illustrated in Fig. 2.7. Figure 2.7(a) represents a fibre with random crystal orientation, Fig. 2.7(b) radial crystal orientation and Fig. 2.7(c) tangential crystal orientation. Interestingly, the radial crystalline orientation can only be brought about using the dry-jet wet-spinning process used for para-aramid fibres. This had never been observed before in a synthetic organic fibre.

Present para-aramid products have need of a very high molecular



2.6 Schematic representation of the extrusion of the liquid crystalline solution in the dry-jet wet-spinning process.



2.7 Crystal orientation of para-aramid fibre: (a) random; (b) radial; (c) tangential.

orientation (less than 12°), which has an almost directly proportional relationship to fibre modulus. The tenacity of a particular fibre material is also, but not only, governed by this molecular orientation angle. The modulus of the as-spun yarn can be greatly affected by the drying conditions, temperature and tension. Additional orientation inside the solid phase occurs during drying.

Fibres prepared by a dry-jet wet-spun process have a noteworthy response to very brief heat treatment (seconds) under tension.⁵⁹ These fibres will not undergo drawing in the conventional sense, showing an extension of less than 5% even at temperatures above 500°C , but the crystalline orientation and fibre modulus is increased by this short-term heating under tension. As-spun fibre has an orientation angle of $12\text{--}15^\circ$; this decreases to about 9° or less after heat treatment, with the fibre modulus increasing from 64 GPa to over 150 GPa. The applications of these principles led to development of rigid polymer systems forming lyotropic liquids.⁶⁰ Molecular orientation, structure, and spinning method all affect how aramid fibres respond to this heat treatment. A recent study⁶¹ of the mechanical change during heat treatment provides a comprehensive set of data regarding the relationships between the annealing time, the final crystallite size, the orientation angle, and the tensile modulus. Thermally induced changes in para-aramid fibre surface were evidenced by inverse gas chromatography. Rebouillat and co-workers^{62–64} reported quite extensively on the use of this technique for fibre surface characterisation.

In order to circumvent the insolubility of rigid molecules in most solvent media, a significant amount of research has gone into semi-rigid molecules and their use in fibre production. For example, Black and Preston¹³ worked on polymers based on aromatic polyamide hydrazine structures. The best-known semi-rigid rod aramid copolymer fibre in use is *Technora*®, developed from the work of Ozawa.⁶⁵ The copolymer is soluble in its polymerisation solvent, allowing the reaction mixture to be wet- or dry-jet

wet-spun from an isotropic solution directly into filaments. The presence of solvent in a reasonably concentrated solution and the inherent rigidity of the molecules avoid molecular entanglement. The spun filaments are washed, neutralised, drawn at a high ratio (10 at 490°C), and dried. As before, the hot drawing process helps to develop their strength further and to give them their high properties. The fibres have moderate crystallinity, with a random distribution of amorphous regions through their fine structure, with their high strength and modulus attributed to their extended chain structure.

Ozawa and Matsuda¹⁶ provide more details regarding the effect of draw ratio and the associated mechanism in the case of aramid copolymer processing. They refer to three modes of drawing. An ordinary draw mechanism would prevail in the case of a low draw ratio (below 2 for *Technora*®), which is characterised by improved crystal size and uniformity, and better orientation of the chains. An intermediate draw mechanism, for a medium draw ratio (2 to 14 for *Technora*® fibre), is dominated by shearing, which yields to chain slips, reduction of the imperfections and therewith higher tenacity, elongation, and modulus (TEM) properties. Finally, an excessive draw mechanism (above 15 in the case of *Technora*®), is associated with the formation of microvoids and microfibrils, and therefore the beginning of decreasing TEM.

A fairly large coverage of spinning variants is proposed in the compilation on aromatic high-strength fibres written by Yang.¹¹

2.3.3 Aramid types

The properties of aramid fibres depend on the particular spinning and post-treating conditions. Table 2.1 lists the forms that are commercially available, together with their TEM properties.

Table 2.1 Aramid types*

Type	Tenacity (mN/tex)	Initial modulus (N/tex)	Elongation at break (%)
Kevlar® 29	2030	49	3.6
Kevlar® 49	2080	78	2.4
Kevlar® 149	1680	115	1.3
Nomex®	485	7.5	35
Twaron®	2100	60	3.6
Twaron® High Modulus	2100	75	2.5
Technora®	2200	50	4.4

* From the manufacturers' leaflets and references.^{3,15,87}

2.4 Structure and properties

2.4.1 Characteristics of aramid fibres

Aramid fibres have unique properties that set them apart from other fibres. Aramid fibre tensile strength and modulus are significantly higher than those of earlier organic fibres, and fibre elongation is lower. Aramid fibres can be woven on fabric looms more easily than brittle fibres such as glass, carbon or ceramic. They also exhibit inherent resistance to organic solvents, fuels, lubricants and exposure to flame.

Each type of aromatic polymer gives certain characteristic fibre properties because of its fibre and intrinsic polymer structure. Rather than going through an encyclopaedic description of the properties of the aromatic polyamides, we propose in the following section to review some of the predominant studies that we believe are important in order to understand the unique properties of this class of fibre materials. The superimposed structures, such as the crystallites, the fibrils and the skin-core boundaries, are definitely unique attributes that can be partially tailored through the fibre process engineering. This is worth examining in more detail. It is equally important to provide more insights into the pleated structure and the formation of the hydrogen bonds acting as zippers between the chains. Finally, the mechanical models and the related mathematical analysis are tremendous tools for both the scientist and the engineer to gain fundamental understanding through useful engineering parameters. We propose to focus on these aspects in the following sections.

2.4.2 Structure

It is a truism that the physical properties of macromolecules are determined by their structural characteristics at a molecular level. This is particularly cogent when aromatic polyamides are considered. For instance, as noted by Dobb and McIntyre,⁶⁸ the tensile modulus of a fibre will be largely determined by the details of the molecular orientation about the fibre axis, and the effective cross-sectional area occupied by single chains, which will, of course, be related to the degree of chain linearity. For instance, in poly(*p*-phenylene terephthalamide), the polymer chains are very stiff, brought about by bonding of rigid phenylene rings in the *para* position. In contrast, for *Nomex*® fibres, the phenylene and amide units are linked in the *meta* position, which results in an irregular chain conformation and a correspondingly lower tensile modulus. Also in PPTA, the presence of amide groups at regular intervals along the linear macromolecular backbone facilitates extensive hydrogen bonding in a lateral direction between adjacent chains. This, in turn, leads to efficient chain packing and high crystallinity.

A similar situation is encountered for non-aromatic polyamides such as nylon. In the latter material (nylon 6.6 for example), the molecules present in the form of extended planar zigzags joined together in hydrogen bonded sheets.

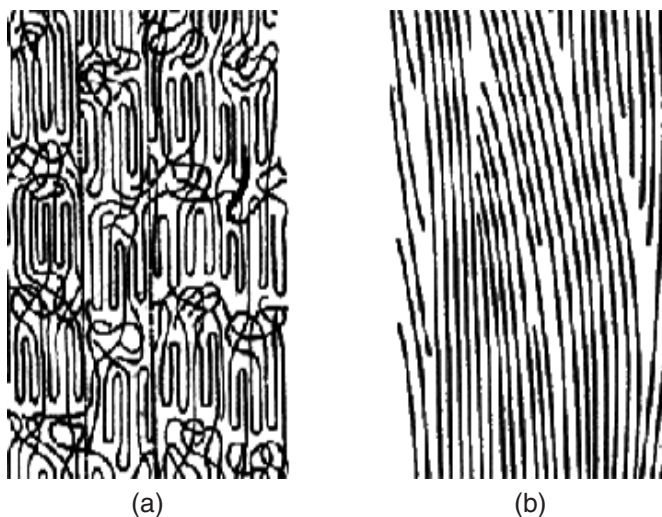
Structural studies on PPTA fibres have been described by Northolt,²³ Haraguchi *et al.*⁶⁶ and Yabuki *et al.*⁶⁷ The supermolecular structure of the high-modulus aramid fibres which are essentially of the PPTA type have been reported by Dobb and co-workers.^{17,18} A useful review discussing the relationship between the microstructure and the mechanical properties of aramid fibres has been presented by Northolt and Chapoy.²⁴

Haraguchi *et al.*⁶⁶ have noted that two crystal modifications of PPTA are observed. Northolt and Chapoy²⁴ have reported on an X-ray diffraction analysis of PPTA fibres and proposed a model for the crystal and molecular structure of the PPTA. When the polymer is spun from a highly concentrated anisotropic solution, the chains form an essentially monoclinic²⁴ (pseudo-orthorhombic) unit cell with associated parameters $a = 0.787\text{ nm}$, $b = 0.518\text{ nm}$, c (defining the fibre axis) $= 1.29\text{ nm}$. There are two molecular chains per unit cell, one through the centre, the other through a corner, and two monomeric units in the axial repeat. Approximate values for the orientation angles between the phenylene planes and the amide planes are 38° for the *p*-phenylene diamine segment and -30° for the terephthalic segment. However, fibres formed from anisotropic solutions of lower concentration exhibit a different packing arrangement that is equivalent to a lateral displacement ($b/2$) of chains along alternate 200 planes. It should be noted that both crystallographic forms coexist in fibres spun from solutions of intermediate concentration. Northolt and Chapoy²⁴ proposed that hydrogen bonds are formed between adjacent chains lying in the 100 plane. They argued that the chain conformation is primarily governed by competitive intramolecular interactions between the conjugated groups in the chain. Similar interactions are also found for the conformation of benzamide, acetanilide and the terephthalamide molecules. These interactions arise from the operation of a resonance effect, which results from an attempt to stabilise coplanarity of the amide groups and the phenylene groups. A counteracting steric hindrance is also found between the oxygen and the ortho-hydrogen of the *p*-phenylene diamine segment, and between the amide hydrogen and the ortho-hydrogen of the terephthalic segment.

The regularly positioned amide segments allow reasonably strong hydrogen bonds, which facilitate a proper load transfer between the chains, as found, for example, in a zipper. The hydrogen bonded chains form sheets, which are stacked parallel into crystallites. Between adjacent hydrogen bonded planes, the interaction largely takes place by van der Waals' forces, with some pi-bond overlap of the phenylene segments. This causes the hydrogen bonded planes to function as slip-planes in a manner analogous

to close-packed planes in metals. Note also that bond rotation and hence molecular flexibility is inhibited by the presence both of the aromatic rings and the double bond nature of the amide group arising from resonance effects.

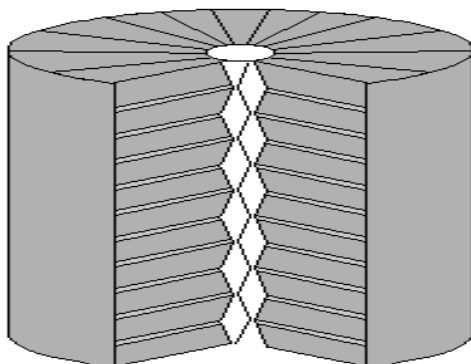
It should be appreciated that the microscopic chain structure and chain properties dictate the manner of fibre production. Northolt and Chapoy²⁴ have stated that the aromatic polyamides are manufactured in a wet-spinning process in which the chains are given a narrow orientation distribution around the filament axis. This optimises the tensile modulus. Dobb and McIntyre⁶⁸ have stated that no evidence has been found for small-angle two or four point meridional reflections, which would be traditionally associated with chain folding in polyamide and polyester fibres. The latter observation supports the proposal of an extended chain conformation. A schematic representation of the microstructure of (a) a semicrystalline polymer such as nylon 6 and (b) PPTA is outlined in Fig. 2.8. In each case the fibre axis is vertical. It should also be noted that PPTA fibres are generally characterised by intense but diffuse small-angle scattering features on the equator of the X-ray diffraction (XRD) patterns. This effect can be ascribed to the presence of microvoids. Electron microscopy and X-ray data indicate that the voids are rod shaped, with their long axis almost parallel to the fibre axis, having typical widths in the range 5–10 nm and length about 25 nm. The influence of microvoids in para-aramid fibres has been explored



2.8 Schematic representation of the microstructure of: (a) semi-crystalline polymers such as nylon 6 and (b) PPTA (fibre axis vertical).

by Dobb *et al.*,⁶⁹ using a test method originally described by Allen.⁷⁰ The surface microstructure of an aramid fibre was also observed directly by atomic force microscopy.^{71,72} The unit cell parameters b and c of the crystalline structures and the coplanar-like rotation of benzene rings are similar to the reported results but the registration angle is not constant. This discrepancy is explained as the difference between surface and bulk crystalline structure. At the surface of the polymer, chains tend to be arranged less perfectly and the surface crystalline structure can be influenced by several parameters such as the fibre manufacturing conditions and post treatment, adsorbed water, and even the possible friction of the atomic force microscopy (AFM) scanning tip.

The supermolecular structure of a high modulus polyaromatic material such as *Kevlar® 49* has been reported by Dobb *et al.*⁶⁹ In this work, a combination of electron diffraction and electron microscope dark field image techniques was utilised. The dark field images derived using selected meridional or off-meridional reflections from longitudinal sections, exhibited banding of two main types having periodicities of 500 and 250 nm. The former periodic band spacing is associated with the off-meridional reflections whereas the latter is assigned to meridional reflections. Detailed analysis conducted by the authors led to the assignment that there was a uniform distribution of ordered crystalline material throughout the fibre and that the dark field banding observed was a manifestation of changes in crystalline orientation and not of crystalline order. The results reported by Dobb *et al.*⁶⁹ provide strong evidence for a regular pleated structure with the alternating components of each sheet arranged at approximately equal but opposite angles to the plane of the section, as illustrated in Fig. 2.9.



2.9 Radial pleated structure model of PPTA fibre.

Experimental measurements indicate that the angle between adjacent components of the pleat is about 170° .

2.4.3 Analysis of mechanical properties

The mechanical properties of aramid materials underlie their significant commercial utilisation in many areas. For instance, the as-spun *Kevlar*® aramid fibre exhibits over twice the tenacity and nine times the modulus of high strength nylon.⁷³ On a weight basis it is stronger than steel wire and stiffer than glass. Both creep and the linear coefficient of thermal expansion are low and the thermal stability is high. The latter properties resemble those of inorganic fibres and, of course, can be attributed to the extended chain morphology, high molar mass and excellent orientation in a thermally stable structure that does not melt. Para-aramid fibres have utility due to a combination of superior properties allied with features usually associated with organic fibres such as low density, easy processibility and rather good fatigue and abrasion resistance.

The macroscopic mechanical properties of a polymer are determined by the molecular structure of the chain. Northolt²³ has described a polymer chain as a one-dimensional load-bearing conformation. He notes that a material such as polyethylene can be processed to exhibit a high tensile modulus and tensile strength (gel spinning followed by hot drawing of polyethylene afforded a fibre of tensile strength 3 GPa and modulus 200 GPa). The downside is that extremely long chains are required to ensure optimum load transfer between adjacent polymer chains due to the fact that intermolecular adhesion in the fibre arises only due to van der Waals' forces. Also, polyethylene has a very low melting point, which limits practical application. The latter disadvantages are removed if stiff polymer chains linked by hydrogen bonds are used. As previously noted in this chapter, chain stiffness is achieved when free rotation around interatomic bonds is not allowed and, by necessity, the chain will adopt the linearly extended conformation. Of course, the latter idea is manifested in the aromatic aramid materials. As noted by Northolt,²³ regularly positioned amide segments in the latter materials allow for medium to strong intermolecular hydrogen bonds that ensure a proper load transfer between the chains as, indeed, is found in a zipper. However, the chain properties exhibited by aromatic polyaramids are mainly due to the alignment of chains in one direction, which limits the macroscopic shape of the material to filaments and films. The aromatic polyamides are manufactured in a dry-jet wet-spinning process in which the chains are given a narrow orientation distribution around the filament axis. This procedure leads to an initial modulus of *ca* 70 GPa, which is subsequently increased by short-term heating under tension to *ca* 140 GPa. Typically, the filament strength for a gauge length of 2.5 cm is 4 GPa,

with an elongation at break of about 4% and a fracture energy of *ca* 80 MJ/m³.

An excellent theoretical approach by Termonia^{20,21} led to the calculation, based on the molecular weight of commercial para-aramid fibres, of the ultimate tensile strength of PPTA filaments being 10 GPa. Another estimation can be calculated from the weakest chemical bond of the PPTA chain divided by the surface area of a cross-section of the chain in the crystal lattice. In the later case, a tensile strength of 29 GPa is found. These calculations, for a hypothetical ideal molecular structure and molecular alignment, take into account the weakest bond dissociation energy of the polymer molecule in its most elongated conformation, which, as we have emphasised in a previous section, is a difficult target to attain in view of the solution properties and the spinning conditions. Mechanical modelling further helps to appreciate the attainable improvement from the observable tenacity.

A detailed mathematical model to adequately describe the mechanical properties of an aromatic polyamide fibre such as PPTA has been developed by Northolt and van Aartsen²⁵ and by Northolt.²⁶ This model was based on knowledge gained of the polymer microstructure, and the analysis rests on the adoption of a single-phase paracrystalline model of the latter. The analysis is based on earlier work reported by Bartenev and Valishin⁷⁴ in which a theory describing the orientational dependence of the compliance for completely crystalline fibres was developed. The model adopted by Northolt is in good accord with XRD studies. On the basis of the mathematical model developed, and if we assume a uniform stress distribution along the fibre, it is possible to show^{25,26} that the elastic extension of the aramid fibre is governed by the following expression:

$$S_{33} = \frac{1}{e_3} + A \langle \sin^2 \phi \rangle \quad [2.1]$$

In this expression, S_{33} denotes the fibre compliance, e_3 is the modulus of elasticity of the chain parallel to its axis of symmetry, and the factor $\langle \sin^2 \phi \rangle$ represents the orientation distribution parameter of the crystallites with respect to the fibre axis. The latter quantity will be zero if the orientation is perfect and $\frac{2}{3}$ if the orientation is random. The factor A represents a measure of the mechanical anisotropy of the crystallite and is given by:

$$A = \frac{1}{2g} - \frac{2(1 + \nu_{13})}{e_3} \quad [2.2]$$

where g denotes the shear modulus in the plane containing the chain axis and ν_{13} represents the Poisson ratio for a stress along this axis. Equation [2.1] has been confirmed experimentally by Northolt²⁶ for PPTA fibres using

dynamic moduli and crystallite orientation measurements. He has shown that the dynamic compliance S_{33} ($S_{33} = 1/E$, where E represents the dynamic tensile modulus) varies linearly with $\langle \sin^2 \phi \rangle$ for three different fibre samples. Very little scatter is obtained over the entire measurement range. Indeed, the expression is valid up to rupture. From least squares analysis of the data, $A = 0.26 \pm 0.01 \text{ m}^2/\text{GN}$. Typically, $e_3 = 240 \text{ GPa}$ and $g = 2 \text{ GPa}$. It was determined that, up to a stress of *ca* 1.5 GPa, the extension of the fibre (the strain) is brought about mainly by elastic rotation, by some retarded as well as plastic rotation of the crystallites towards the fibre axis, and by elastic extension of the polymer chain itself.

Northolt also derived a relation between the stress σ and the orientation parameter as follows:

$$\langle \sin^2 \phi \rangle = \langle \sin^2 \phi \rangle_0 \exp[-(2A + \lambda)\sigma] \quad [2.3]$$

where the parameter λ represents both the permanent and the retarded elastic rotation of the crystallites and $\langle \sin^2 \phi \rangle_0$ denotes the initial value of the orientation parameter. The relation expressed in Equation [2.3] has been confirmed experimentally. Typical values for λ lie in the range 0.15 to $0.28 \text{ m}^2/\text{GN}$ for the aramid fibres examined (four samples). It was noted that λ values tend to be larger for less oriented fibres.

Northolt also determined that, for $\sigma > 1.5 \text{ GPa}$, the fibre extension increases by axial flow that would, in principle, be caused by slip between adjacent chains. The work of Northolt²⁶ resulted in the generation of an approximate analytical expression for the tensile curve of a fibre, which consists of a linear arrangements of crystallites that have a narrow orientation distribution $\langle \sin^2 \phi \rangle_0$ with respect to the fibril axis. The stress(σ)/strain(ϵ) relation is given by:

$$\epsilon = \frac{\sigma}{e_3} + \frac{\langle \sin^2 \phi \rangle_0}{2} [1 - \exp(-C\sigma)] \quad [2.4]$$

where $C = 2A + \lambda$. Hence we can conclude that the ductility of the fibres is primarily determined by the initial orientation distribution of the crystallites and by the ability of the crystallites to rotate their symmetry axis towards the stress direction as a result of the relatively low value of the shear modulus g . During fibre extension, the latter distribution contracts and at near rupture the chains are oriented almost parallel to the stress direction.

Northolt²⁶ has also noted that because of the crystallite orienting mechanism governing the entire tensile deformation process, the presence of structural irregularities may hamper the alignment of the crystallites along the stress direction. This could give rise to premature rupture of the fibre. However, local slip of hydrogen bonded planes may serve to mitigate the effect of the presence of inhomogeneities.

2.4.4 Some useful comparisons between aromatic polyamides and copolyamides

The levels of tensile properties and thermal stability of *Technora*® are comparable to those of highly crystalline para-aramid fibres over standard practical temperature ranges. *Technora*® has a comparatively high fatigue resistance, which is the direct result of the flexibility of the copolymer chain and loose crystal structure in the copolymer; this has been confirmed using wide-angle X-ray studies.³

Most of the differences between these two families, the para-aramid and the meta/para copolymers, seem to have been anticipated at the design stage as described by Ozawa and Matsuda¹⁶ in Table 2.2.

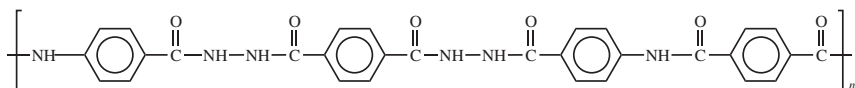
Although mainly derived from hypotheses partly validated through analytical methods, there are several mechanical failure modes, morphology characteristics and chemical accessibility properties which have been proposed by Morgan *et al.*,¹⁹ Panar *et al.*,⁷⁵ Jackson *et al.*,²⁷ Lee *et al.*,⁶¹ Li *et al.*,⁷⁶ Fukuda *et al.*,⁷⁷ Roche *et al.*,⁷⁸ Rao and Farris,⁷⁹ Young,⁸⁰ and Mooney and MacElroy.⁸¹

Regarding, more specifically, fibre failure modes and related morphologies, the atlas of fracture, fatigue and durability compiled and commented on by Hearle *et al.*,⁸² constitutes a unique piece of literature in which a comparative series of scanning electron microscopy (SEM) pictures speak for themselves. Supplemented by the necessary information on how breaks occurred, this outstanding collection of data provides quite relevant information that sets the aramids apart from most man-made fibres owing to the

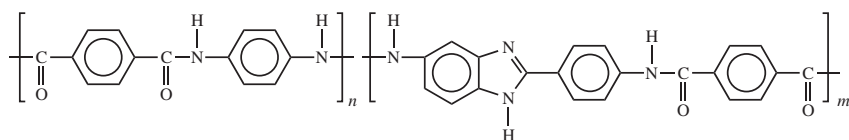
Table 2.2 Molecular requirements for improved characteristics of HM-HT aromatic fibres¹⁶

Improvement	Polymeric composition
Thermal resistance	Wholly aromatic polyamide Absence of unstable linkage (urethane, urea, alkylene, etc.)
Solubility	Copolymer with dissymmetrical units Inclusion of —O—, —CO—, —SO ₂ —, etc. Amides rather than esters
Drawing potential	High molecular weight Enhanced chain flexibility by incorporating —O—, —CO—, —SO ₂ —, etc. into polymer chain
Dimensional stability	Rigid molecular chain Crystallinity

multiple and long axial splits in the filaments, observable when the material is fractured by tensile testing. This mode of failure, which is also observed in the case of high-modulus polyethylene (HMPE) fibres, is easily distinguishable from the brittle tensile fracture of glass, ceramic, carbon and elastomeric fibres, the ductile tensile fracture of nylon, polyester and polypropylene fibres, and the granular fracture typical of polybenzimidazole (PBI) or alumina fibres for example. Finally, the fibrillar failure of cotton may, to a certain extent, show some similarities with the aramids owing to the microfibril assembly found in this type of natural fibres, although the very high strength nature of the para-aramids largely limits this kind of analogy. Hearle and Wong⁸³ also provide more insight into the flex fatigue and abrasion resistance of high modulus fibres. Although never commercialised, the experimental *X500* series of aromatic copolyamide fibres developed by Monsanto has been subject to detailed research work, the major findings of which have been disclosed in the extensive technical compilation done by Black and Preston¹³ in 1973. The chemical formula of *X500*,¹³ which is provided below, underlines the larger number of amide functions which shall increase significantly the amount of intermolecular chain bonding. This material remains very attractive as a comparative research model to help the understanding of the rather complex behaviours of para-aramids.



A more recent initiative from a Russian research organisation⁸⁴ (see also 4.4) led to the experimental development of the fibre *Armos®* (*p*-phenylene-benzimidazole-terephthalamide – co-*p*-phenylene-terephthalamide), based on a copolyamide consisting of para-substituted phenylene and benzimidazole whose fibre shows encouraging mechanical properties. Its chemical formula⁸⁴ is:

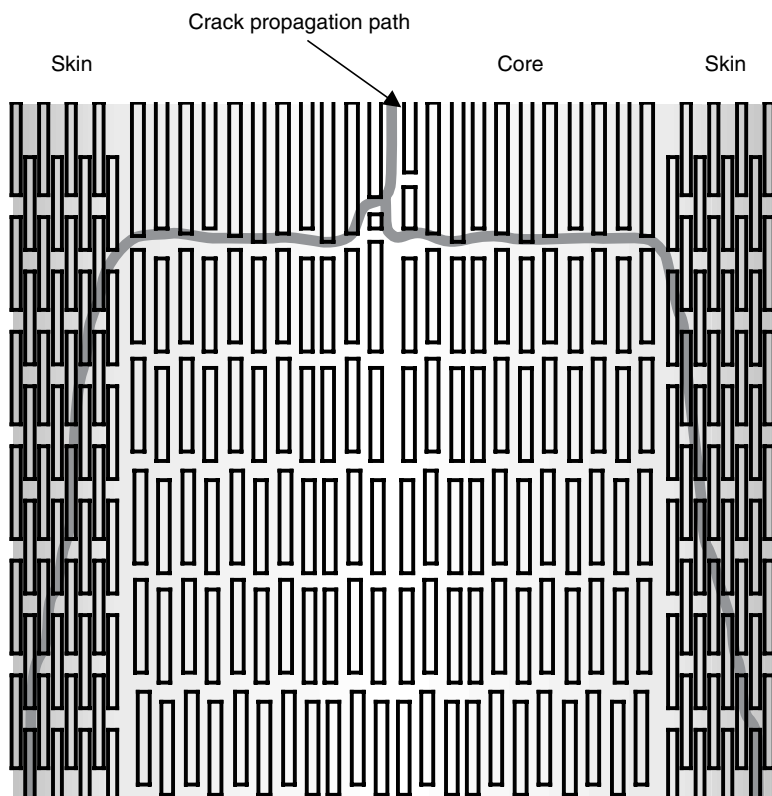


The comparative analysis⁸⁴ of the structure and the mechanical behaviour of regular para-aramid and the *Armos®* (*Armos®* is a registered product) remains a unique research work, outlining the analogies between these two materials although they differ significantly in terms of crystallinity. It is hoped that more studies will confirm the surprising presence

of smectic structure as well as nematic mesophase in the non-crystalline phase of the copolyamide.

Although not always being unanimously accepted, the conclusions presented in these studies offer tremendous opportunities to gain fundamental understanding of structure–property relationships associated with fibre formation and consolidation, as well as fibre usage and biological accessibility and degradation.

The skin–core supermolecular structure of the PPTA fibre is probably the most broadly accepted feature. The difference in orientation and alignment of the skin chains versus the core microfibrils, which are substructured by crystallites, has been often used to support the hypothetical fracture model shown in Fig. 2.10. An explanation of this type of propagation can be associated with the fact that the nematic-like structure observable in the spinning solution is rearranged under a relaxation effect into a smectic-like structure during the fibre coagulation. The smectic alignment is parallel and



2.10 Schematic representation of a fracture model of PPTA fibre.

stratified like a two-dimensional order, with a very limited number of liaisons across the transverse boundaries like the ones depicted in the central part of Fig. 2.10, while the nematic order corresponds to molecules showing a parallel one-dimensional order with overlaps which resemble the skin representation of Fig. 2.10. The type of periodic alignment observed in the core part is promoted by the concentration of chain ends in transverse connecting zones, which are mechanically and chemically vulnerable.

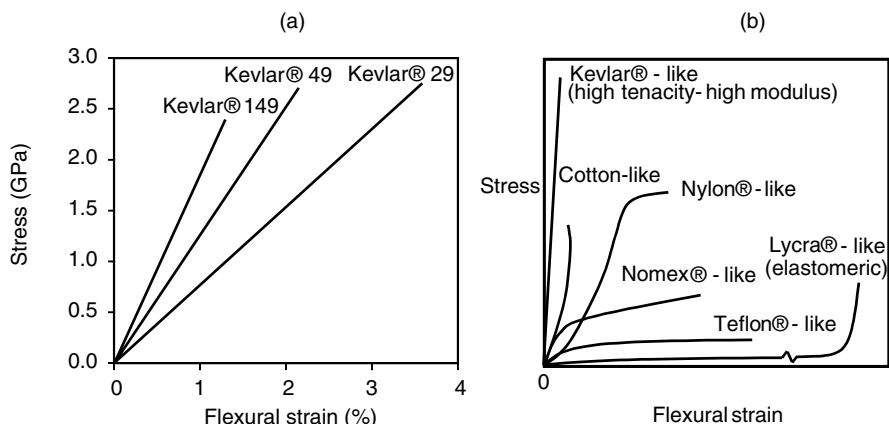
Ozawa and Matsuda¹⁶ suggest that aromatic copolyamides are less susceptible to the formation of smectic structures, therefore offering different mechanical and chemical properties. In the case of *Technora*® fibres, they attribute this tendency to the fact that the chains are much more flexible than PPTA chains and the crystallites are looser; furthermore, the process allows more stress dissipation to occur. SEM and X-ray analysis support this position.

There are rather significant differences between PPTA fibres and the aromatic copolyamide *Technora*® in terms of moisture absorption, permeability of small entities and the related mechanisms. The moisture absorption relative to the unit weight of fibre is about half for the latter (2% vs 4–6% for para-aramids), which Ozawa and Matsuda¹⁶ explain by the density of the hydrophilic amide groups at the surface and the degree of crystallinity. This further supports the observed difference in terms of chemical resistance and higher fatigue performance of the copolyamide fibre, whose level of chain extension and orientation caused by the super-drawing tends to retard the migration of small molecules, contributing to a higher apparent chemical resistance. Additional studies regarding the moisture transport phenomena and aqueous accessibility of PPTA crystallites are available.^{27,85} These all tend to support and complement, using different approaches, the structure and mechanical properties described previously.

The stiffness of the PPTA chain is partly associated with the limited rotation of the carbon–nitrogen bond, itself due to the resonance-conjugation existing between the amide and the aromatic groups. This situation does not exist in the case of the meta configuration of the *Nomex*® fibre; therefore the fibre is white in contrast to the golden yellow colour of the para-aramid. The *Technora*® copolyamide, with a meta and a para molecular configuration, presents a golden brown coloration. The conjugated patterns provide a predominantly double bond character to the carbon–nitrogen liaison in the para-configuration, whose rotational energy is approximately ten fold greater than for a single bond.

2.4.5 A selection of observed mechanical properties

Typical stress–strain curves of different *Kevlar*® fibres are provided in Fig. 2.11(a), which clearly outlines the modulus increase from *Kevlar*® 29 to



2.11 Typical stress-strain curves of: (a) *Kevlar* fibres; (b) other commercially representative industrial yarns.

Kevlar® 149. The respective moduli, brought by various spinning conditions and post-treatments performed on para-aramid precursors, are generally considered as intermediate between those of graphite, boron and glass fibres. The typical linear stress-strain behaviour of para-aramids is typical compared to most man-made fibres, whose tensile behaviours are depicted in Fig. 2.11(b).

Creep is measured either by the length variation under tension or by the stress decrease at constant gauge length. Para-aramids, which exhibit little creep, differ significantly from other highly oriented polymeric fibres, such as HMPE fibres, which can break after several days under intermediate load due to their high creep properties associated with a stress slip of molecules (compared to a structure-tightening in the case of para-aramids). Creep is affected by the temperature, the load relative to the fibre ultimate strength, the water content and other parameters. There are differences between *Kevlar® 49* and *Kevlar® 29*. The latter tends to show no dependency of the creep amplitude as a function of temperature and load if the load is below 50% of the fibre breaking strength.

Compressive and shear properties tend to relate very well with the degree of axial orientation and radial intermolecular bonding. It is therefore not too surprising to find that HMPE fibres have been reported⁷⁰ to exhibit lower compressive yield stresses than para-aramids. Sikkema⁸⁶ gave a compressive strength of 0.6 GPa for the *Twaron®* fibres, which is about one-fifth of the tensile strength mentioned by Yang.¹¹ Greater than those of conventional man-made fibres, the shear moduli of para-aramids are lower than

Table 2.3 Properties of commercially representative reinforcement fibres*

Material	Density (g/m ³)	Decomposition melt (°C)	Tenacity (mN/tex)	Initial modulus (N/tex)
Para-aramid standard	1.44	550	2065	55
Para-aramid high-modulus	1.45	550	2090	77
Nomex®	1.46	415	485	7.5
Technora®	1.39	500	2200	50.3
PA 66	1.14	255	830	5
Steel cord	7.85	1600	330	20
Carbon HT	1.78	3700	1910	134
Carbon HM	1.83	3700	1230	256
E-Glass	2.58	825	780	28

* From the manufacturers' leaflets and references.^{3,15,16,87}

their compressive moduli, which to a certain extent is due to the degree of anisotropy of their radial structure.

Like other polymers, aromatic polyamides are sensitive to radiations,^{11,87} especially in the range between about 300 (nm) and 450 (nm). For outdoor applications proper protection from these radiations is necessary to maintain good mechanical properties.

The preceding discussions of structural and mechanical relationships provide a more precise and complete picture of the properties of the related polymers. Of the very large number of reports on the subject, general tendencies are broadly, although not unanimously, accepted amongst scientists. This situation is largely favourable to fruitful scientific debates, which support the uniqueness of the aromatic polyamides. One may see an opportunity, as a future direction, for translating this immense knowledge into end-use science that could help the fundamental understanding of the design parameters and the properties of items manufactured from these polymers in various forms. In order to offer comparative basic data, some of the most frequently encountered materials used in advanced technologies are compared in Table 2.3.

2.5 Applications

2.5.1 Systems engineering

The previous section of this chapter illustrated the role of molecular chain extension, orientation and structure in the fibre characteristics. The transition from the chemical structure to a physical structure, such as a polymer, can be considered as being part of *molecular engineering* as described by

Tanner *et al.*⁷ A further step is the transition from the given physical structure to a product form, such as a fibre, and can be defined as part of *process engineering*. A later step encompasses the integration of the product, such as the aramid fibre, into an advanced structure or an advanced technology, which according to the definition of Tanner *et al.*⁷ is part of *system engineering*.

The present section takes into consideration a selected, mostly commercially dominant, range of applications of the aramids with an attempt to emphasize some of the system engineering aspects. This approach may provide not only a better understanding of the major reasons for these fibres contributing to the best balanced performance of the system, but also may stimulate new ideas in the way these fibres are used in the considered system or how they could be used in a new one. As an example, the understanding of how a para-aramid fibre can be shaped into an optimised fabric pattern to resist a fragment impact, can provoke new ideas regarding the engineering of these fibres to offer cut and heat protection in other sectors, where the kinetics may be much closer to static conditions.

This is a system approach, which forces clarity of rationale to utilise the advantageous properties of the fibre. These can be used to minimise the effect of some features of the fibre, as well as finding possible synergistic combinations of properties of the other system components. Such approaches have led to the development of some of the aramid fibre applications to be outlined in this section, illustrated in Table 2.4.⁸⁷

2.5.2 Ballistic and life protection

The dynamic mechanical properties of the aromatic polyamide fibres, as well as their viscoelastic behaviour, which can be tailored via suitable resin reinforcement, are perfectly adapted to their use in impact-resistant systems for low or high velocities. As early as the 1970s, this opportunity was rapidly recognised and translated into concrete applications such as protecting the lives of military personnel and then of civilians, and the protection of vital strategic equipment.

This type of application implies the use of a fairly large variety of materials, reinforced or not, in various forms, exposed to a fairly wide range of threats with different geometrical shapes being directed at the target, with variable dynamic impact profiles in terms of energy and velocity.

The diversity of components and parameters renders the task of the scientists, the designers and the engineers extremely complex and furthermore, multidisciplinary. Rather than giving descriptive detail regarding how aramids are used in this area, we want to pursue a more scientific approach, favouring the comprehension of some selected physical phenomena related to the fibre structure–property relationships and the dynamics involved. Therefore, our approach does not pretend to be exhaustive but should

Table 2.4 Aramid market segments and key attributes⁸⁷

End-use	End-use systems	Key attributes
Composites	Fabrics for aircraft & containers Pressure vessels Ship building Sport goods Plastics additive Civil engineering	Light weight High strength High modulus Good impact strength Wear resistance
Protective apparels	Heat resistance workwear Fire blankets Flame retardant textiles Cut protective gloves Cut protective seat cover layers	Heat resistance Flame retardation Cut resistance
Tyres	Truck and aircraft tyres High speed tyres Motorcycle tyres Bicycle tyres	Low density Weight saving High tenacity Dimensional stability Low shrinkage Puncture resistance
Mechanical rubber goods	Conveyor belts Transmission belts Hoses for automotive Hydraulic hoses Hoses in off-shore Umbilicals	High strength High modulus Dimensional stability Thermal resistance Chemical resistance
Friction products and gaskets	Brake linings Clutch facings Gaskets Thixotropic additive Industrial paper	Fibre fibrillation Heat resistance Chemical resistance Low flammability Mechanical performance
Ropes and cables	Aerial optical fibre cable Traditional optical fibre cable Electrocable Mechanical construction cable Mooring ropes	High strength High modulus Dimensional stability Low density Corrosion resistance Good dielectric properties Heat resistance
Life protection	Bullet proof vests Helmets Property protection panels Vehicle protection Strategic equipment shielding	High tenacity High energy dissipation Low density and weight reduction Comfort

stimulate a reflection mode rather than an empirical guessing methodology. One needs nonetheless, to remain humble in front of the enormous challenge, which is yet to be faced to enhance further the ever-evolving life protection requirements and associated fundamental understanding.

Armour systems are generally classified in two groups, that is, soft and quite rigid composite structures. For the sake of conciseness, associated with the risk of possibly oversimplifying, we propose a single approach to summarise the rather complex dynamics of ballistic impact and relevant fibre property relationships. The absorption of the kinetic energy of the projectile is related to the wave propagation, transversely and longitudinally, and the penetration stress/strain profile which largely depends on the frictional energy dissipation.

Although there exist separate basic concepts and approaches for fibre and textile fabrics, and their interpretation in the case of embedded textile and/or fibres, it is generally admitted that the crossover tightness for the textile, the delaminating effect obtainable by adhesion-tailoring in the composite armour, and the looseness of the yarn ends at the boundaries are key elements in terms of the wave propagation, both longitudinally and transversely. A simplified physical explanation relates to the reflection of the wave at the boundaries, which, if they are too tight or compact, tend to promote a series of multiple reverberations back to the impact region, amplifying the local stresses and further helping the projectile penetration.

For the textile designer and engineer there are some practical consequences that can be deduced from the above. As long as the reverberation effect can be optimised by means of uniform tension, fabric density and crossover compactness, one can consider that the number of overlapping entangled zones and the number of yarns are the key variables affecting the ballistic performance of the textile structure. As a point of reference, it is generally accepted that up to 50% of the impact energy can be absorbed through wave propagation in the secondary yarn networks, which are the ones neighbouring the fibre bundles directly impacted by the projectile.

Regarding the fibre, a dominating selection parameter lies with the fact that the velocity of the wave propagation is directly proportional to the square root of the modulus and inversely proportional to the square root of the fibre density. This, of course, is quite favourable to the aramid fibres in general since, as an example, the velocity of propagation in the para-aramids is about 8000 m/s, that is four folds higher than for nylon.⁸⁸ This relates directly to the volume of matter that can participate in the wave propagation and energy dissipation. In this example, up to four times the volume of para-aramid can be involved in this process compared to nylon. One can easily conceive that the trivial approach of energy potential, based on the stress-strain curve integral, is far underpredictive of such phenomena, especially in the case of nylon, which would be superior to the para-aramid if such

a limited approach was used. This is, today, not even a matter of comparison since the aramids are predominantly used in ballistic protection.

Transverse and longitudinal wave propagations have common physics, although the former more directly affects the local deformation and penetration of the matter being impacted at the ballistic strain rate. A debate still prevails within the community of ballistic experts, associated physicists, mathematicians and more and more rheologists and tribologists. This debate lies in the necessity to associate a rate-dependent or independent effect in the analysis of the impact effectiveness. By rate-independent effect one has to understand that the fibrous structure would deform and respond to the impact variable rate of stress and strain as if the governing parameters were the ones corresponding to their static properties. One can easily agree with the fact that all materials, including fibres, exhibit rate-dependent properties. Then, should the dynamic viscoelastic properties of the fibre, and of its direct neighbouring environment, be taken into account? Undoubtedly, yes. To what extent? Attempts⁸⁹ have been reported and reveal extreme complexities in their interpretations. In this discussion, which may generate opportunities for fundamental understanding of end-use science programmes, it appears clear that high modulus fibres with oriented molecular structures, in which internal process stresses have been dissipated by relaxation and/or drawing with the minimum boundary stress gradients, are by far the ones least affected by variable strain rate. Nylons are known to have tensile properties that are highly dependent on strain rate. On the other side, a superior dynamic modulus, which may contribute to a higher wave propagation speed, is not by itself always the answer. The brittleness of carbon fibres is detrimental to their ballistic performance.

Finally, once the maximum energy allowable by a given structure has been extracted from the incoming projectile, there are still numerous aspects to be considered to assess the probability of total penetration. Among these, the deformation mode and the frictional characteristics of both the matter and the projectile itself have attracted the most attention. Beyond and during the initial contact, the protective layers deform, depending in part on their respective shapes and geometry. Here again, scenarios are multiple and one should not oversimplify. For example, the well-known deformation cones are rarely conical but pyramidal in the case of woven fabrics. This anisotropy has to be integrated right away at the design level and on assembly blueprints of the armour structure being developed. Similarly, idealised projectiles, mostly seen as blunt curve shapes, by definition, are too ideal and may be misleading in view of the more complex multifaceted shapes encountered.⁹⁰ Self-explanatory fracture descriptions, such as brittle, radial, fragmenting or spalling, plugging and petaling or the blends of, correspond to given modes of penetration, whose descriptions are

beyond the scope of this study. In these later cases, more semi-empirical analyses based on fractals coupled with finite element computing are probably the most predictive and are of reasonable help in detecting the impact characteristics and their relationships with the armour system's strengths and weaknesses.

Prior to the eventual penetration of the impacting threat, and after the cone has been extended to its maximum strain, which is dictated by the fibre elongation and/or the fabric distortion and/or eventually the fibre-reinforced matrix delamination, the projectile further loses energy in order to surpass the boundary frictional forces at the fabric-projectile interface. Many components are to be considered in the frictional force balance, such as the impacting velocity and the morphology of the penetrating fragment or bullet, the fabric pattern and its volume density, the fibre surface characteristics, and the tribological properties of all these elements. Once the maximum energy dissipation has occurred, either the projectile energy has been overcome and the threat is stopped, or the projectile reaches the target if the residual kinetic energy is still sufficient. Of course, during this ballistic event considerable heat has been generated at the impact zone. In this case para-aramids are more suitable, owing to their intrinsic thermal resistance compared to fusible polymers such as nylon and polyethylene. Furthermore, the formation of a glassy layer associated with the polymer melting can facilitate penetration at lower speeds. Such aspects may put into the spotlight the advantages of certain categories of fibres that offer tremendous frictional resistance, such as the para-aramids, compared to others that may present better potential for wave propagation than for frictional dissipation, such as nylons.

For obvious reasons, the theoretical physics of a ballistic event can only be simplistic, regardless of the degree of mathematical sophistication brought into the modelling steps. Reality checks against well-designed experiments are more than recommended in view of the ever-growing complexity and changing nature of the ballistic threats and related dynamics. The rather well-known V50 ballistic velocity limit is accepted as the performance parameter. V50 is defined as the statistical minimum velocity at which 50% of the projectiles will pass through the tested structure while the other 50% will be stopped by this ballistic barrier. Three books⁹¹⁻⁹³ should be mentioned, to cover in more detail impact dynamics and penetration mechanics.

In concluding this section, one should note that para-aramids are quite suitable in this domain of application where, for a number of years, multi-layered jackets have been produced and successfully used, saving numerous lives. Helmets, tank panels and other military devices are reinforced with para-aramids, which have also been the fibres of choice in these applications for several decades.

2.5.3 Protective clothing with a focus on fire protection

It is well established that aramid polymers, particularly meta-aramids, exhibit high temperature resistance and stability. This gave a strong incentive to develop these materials for specific industrial heat-resistant applications. Poly-m-phenyleneisophthalamide (*Nomex*®) was the first aramid fibre developed with good thermal stability at exposure temperatures as high as 500°C, and long-term stability in environmental temperatures as high as 220°C.

One of the attributes among these that has further promoted this type of application is associated with a peculiar physical behaviour initially described by Tanner *et al.*⁷ as follows. When meta-aramid fabrics are rapidly heated in a flash fire, the vaporised moisture and degradation gases expand the 'softened' polymer. This expanded material forms a carbonaceous insulating foam up to ten times the thickness of the original layer. When the flame is removed from the fibre, it self-extinguishes. Initially, these fibres seemed ideal for use in clothing, which can benefit from this intumescence. However, extensive studies showed that the fibre would shrink when heated to temperatures above its glass-transition threshold, causing tearing. This would expose the wearer to direct flames, leading to serious injuries. Further work led to the development of a material using intimate staple blends of the meta-aramid fibre *Nomex*® with the para-aramid *Kevlar*®. The para-aramid fibre maintains a strong structural integrity while the meta-aramid provides the insulating, foam-like barrier, which also contributes to the stress translation of the reinforcing network.

A specific piece of equipment, the *Thermoman*® (Thermoman is a DuPont Registered Trademark), initially developed for this very purpose and now more widely used for protective clothing flame-resistance testing, has been and remains very instrumental to the evaluation of newly engineered blends and designs. The corresponding instrumented *Thermoman*® manikin is equipped with a large number of thermo-sensors (>100) connected to a computer that delivers a comprehensive mapping of the burn level profiles, outlining the sensitive zones which can then be further engineered to meet more and more stringent specifications. This type of technology has found uses for *Nomex*®, *Kevlar*® and 'spunnized' yarns of *Technora*® in protective garments such as flight and industrial coveralls, fire fighters' turnout coats, and welders and race car drivers' apparel.

Hand injuries count heavily in the safety statistics. Metal-sheet forming, glass manufacturing and handling, and food processing are but a few areas where hand protection is a standard. Formerly made of cotton, synthetic commodity fibres, metal and other basic materials, gloves are now more and more manufactured from aramids, mostly para-aramid, either alone or in blends. The advantages are several, including the cut and puncture resis-

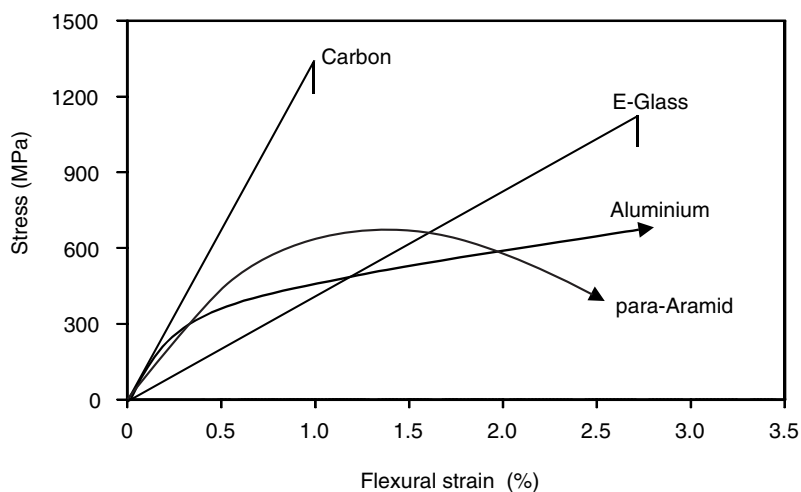
tance through adequate coating, the abrasion resistance, the inherent thermal and insulating properties against heat and cold, and the tremendous weight saving which is part of better comfort properties. In this application area, the synergism gain from the association of various materials is a typical system engineering approach where the benefits are highly visible. A mitt designed for high-temperature protection is made of multiple layers, such as a para-aramid in knitted or woven form as a framework, an aluminium reflective foil and a meta-aramid or fibreglass woven or felt. The best balance of performance offered by the intrinsic properties of the aramids, as described in the more fundamental sections, can be reached without major compromise and most of the time with added comfort, associated with light weight and breathability of fibre structures, and dexterity.

2.5.4 Advanced composites

Advanced composites reinforced with aramid fibres have found significant applications in areas where the strength-to-weight and stiffness-to-weight ratio of these composites makes them more attractive for use than conventional materials such as aluminium and steel. This has been particularly evident where systems engineering has been used to incorporate fibres with high properties into structural components of aircraft. Not only must these components sustain the full spectrum of stresses and strains incurred in flight and remain structurally sound, they must also survive a catastrophic impact. Carbon fibres are not perfectly suitable since they are unyielding and undergo brittle fracture, despite their stiffness and compressive strength. This brittle behaviour is attributed to their rigid coplanar ring structure.

The usually expected significant reduction in composite compressive strength with the increase of the modulus has not been observed in para-aramid fibres.⁹⁴ Such fibres in a resin mix have structural features that provide excellent damage tolerance. Under compressive strain (0.5%), para-aramid molecules tend to buckle rather than fracture. This is, in part, due to the molecular rotation of the amide carbon-to-nitrogen bonds, which allows configurational changes without resulting in bond cleavage.^{8,9} Consequently, although damaged, the structure will continue to sustain a load and the material collapses accordion-like upon stress. This material ductility compared to carbon fibre materials can be illustrated by the flexural stress-strain behaviour of unidirectional epoxy material composites and of aluminium; this is illustrated in Fig. 2.12.

These considerations have brought about the development of hybrid composites of para-aramid and carbon fibre that are used in commercial airliners and helicopters today. The more favourable strength-to-weight

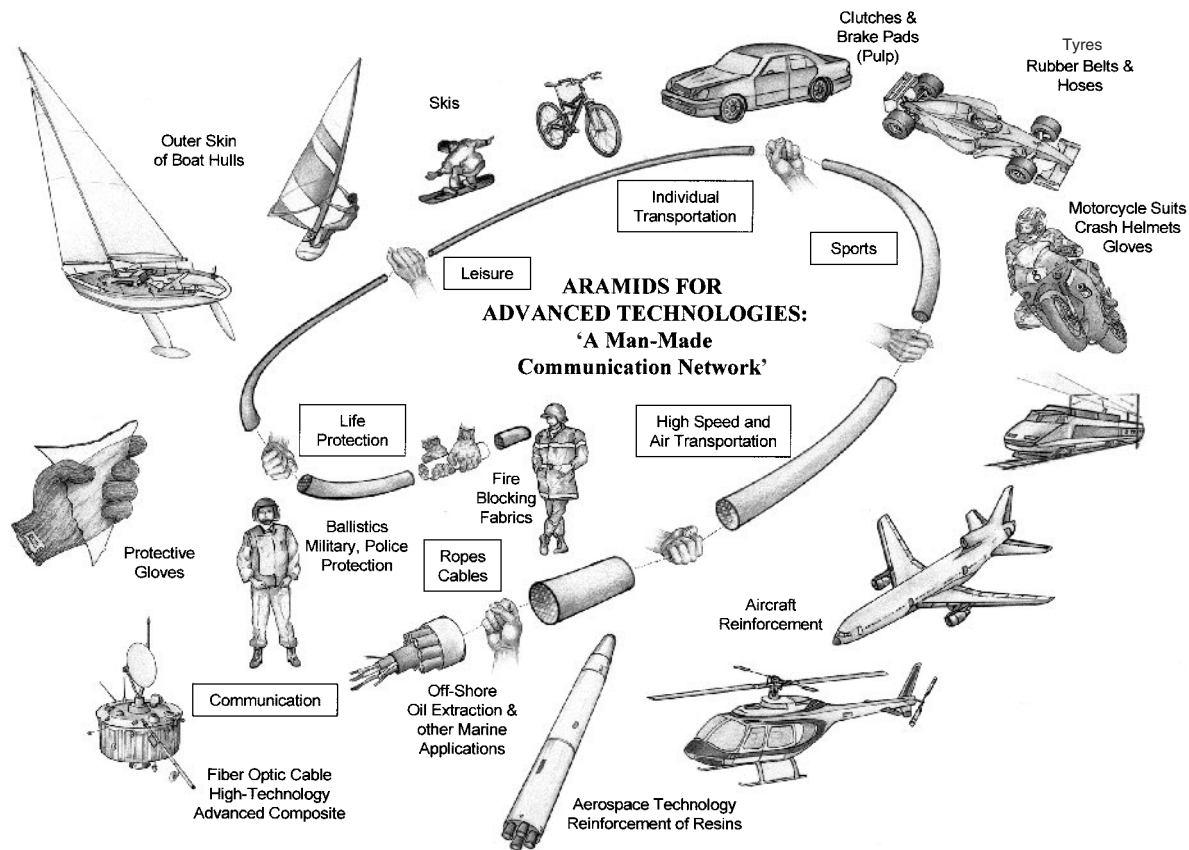


2.12 Stress-strain behaviour for unidirectional reinforced epoxy matrix composites.

ratio of *Kevlar® 49*/epoxy composite is the key reason for their use in floorings, doors fairings and radomes for airliners. Filament-wound pressure vessels developed using *Kevlar® 49* have been used to successfully contain high-pressure gases in space ships and aircraft. The flammability resistance is also of great obvious advantage for these applications.

2.5.5 Other important applications and future directions

There are several other end-use technologies where aramids have provided significant benefits. These are listed in Table 2.4,⁸⁷ which categorises most applications in seven classes outlining the key benefits for each. For the sake of uniformity we have adopted, after minor modifications, the well accepted classification described in the recent literature.⁸⁷ Notice that each specific advantageous property can be almost seamlessly related to the polymer or the fibre attributes that have been described before in other sections of this chapter. The system engineering approach, which we have attempted to illustrate with the selected end-use segments described earlier in this section, has been adopted in most cases given in Table 2.4 and can be revisited in the literature.^{7,10,95} *Technora®* copolyamide fibre, to a lesser extent, is used in several applications listed in this table. The associated Fig. 2.13 provides a concrete illustration of the ‘man-made’ dynamic network established since the inception of the aramids. This network outlines the dynamic integration of aramids in advanced and modern technologies, with constant adaptation to the new challenges associated with various



2.13 Applications of para-aramid fibres.

generations of product. There are end-use market segments that have been rethought because of the aramids, such as the replacement of asbestos by para-aramid pulps. There are other areas that will continue to evolve because of the ever-growing stringent requirements for energy saving in transportation for example. The aramid contribution in this sector is outstanding. Clearly, communications, including transportation as well as transmission, leisure and sports, life protection, and health and safety in general, have been tremendously improved and adapted to modern technologies in part because of the aramids. The present chapter has brought, hopefully, a refreshing scientific description of state-of-the-art knowledge, with an effort to stimulate the desire to go beyond the knowledge and applications of today. There are properties of the aramids that can still be optimised via the system approach. These materials have the potential to participate in the solutions of tomorrow.

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Gel-spun high-performance polyethylene fibres

JAN L J VAN DINGENEN

3.1 Introduction

Gel-spun polyethylene fibres are ultra-strong, high-modulus fibres that are based on the simple and flexible polyethylene molecule. They are called high-performance polyethylene (HPPE) fibres, high-modulus polyethylene (HMPE) fibres or sometimes extended chain polyethylene (ECPE) fibres. The gel-spinning process uses physical processes to make available the high potential mechanical properties of the molecule. This has been quite successful but there is still ample room for improvement.

Owing to 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 fibre and this can both be positive and a limitation: abrasion, flexlife, etc. are very high but the melting point is sometimes too low for certain applications.

3.2 Manufacture

3.2.1 Molecular character

Gel-spun high-performance polyethylene fibres are produced from polyethylene with a very high molecular weight (UHMW-PE). This material is chemically identical to normal high-density polyethylene (HDPE), but the molecular weight is higher than the commonly used PE grades. It is in the range that is used in abrasion-resistant engineering plastics.

Different from all other high-performance fibres, the molecules in high-performance polyethylene fibres are not 'preformed' to form high tenacity and modulus fibres. In aramids and comparable fibres, the molecules tend to form rod-like structures and these need only be oriented in one direction to form a strong fibre. Polyethylene has much longer and flexible molecules and only by physical treatments can the molecules be forced to

assume the straight (extended) conformation and orientation in the direction of the fibre.

All the physical and chemical properties of polyethylene remain in the fibres. The differences result from the high chain extension (stretching), the high orientation and the high crystallinity.

The gel-spun fibres have properties that are superior to those made by solid-state processes.

3.2.2 Gel-spinning

High performance polyethylene fibres are commercially produced under the trade names *Dyneema* by DSM High Performance Fibers in the Netherlands and by the Toyobo/DSM joint venture in Japan, and *Spectra* by Honeywell (formerly Allied Signal or Allied Fibers) in the USA. The basic theory about what a super-strong polyethylene fibre should look like was already available in the 1930s from the ideas of Carothers, but it took almost half a century to produce HPPE fibres.¹

The basic theory of how to produce a super-strong fibre from a polymer such as polyethylene is easy to understand. In normal polyethylene the molecules are not orientated and are easily torn apart. To make strong fibres, the molecular chains must be stretched, oriented and crystallised in the direction of the fibre. Furthermore, the molecular chains must be long to have sufficient interaction and for this reason polyethylene with an ultra-high molecular weight (UHMW-PE) is used as the starting material. Usually extension and orientation are realised by drawing. The problem is that spinning these fibres from the melt is almost impossible due to the extremely high melt viscosity. Furthermore, the drawing of a melt-processed UHMW-PE is only possible 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 (superdrawn). As the fibre is superdrawn, a very high level of macromolecular orientation is attained (see Fig. 3.1) resulting in a fibre with a very high tenacity and modulus. In the processes used by DSM and Honeywell, high-molecular weight polyethylene is spun using relatively low concentrations. In the 1980s, Mitsui Petrochemical used the gel-spinning process to produce a relatively strong fibre based on a lower molecular weight PE and a higher concentration. This process is now not in commercial use.

In 1979 DSM invented and patented the fibre and the gel-spinning process to produce it (Smith and Lemstra.)² Several further patents

High-performance
polyethylene

Orientation >95%
Crystallinity up to 85%

Regular
polyethylene

Orientation low
Crystallinity <60%

3.1 Macromolecular orientation of HPPE and normal PE.

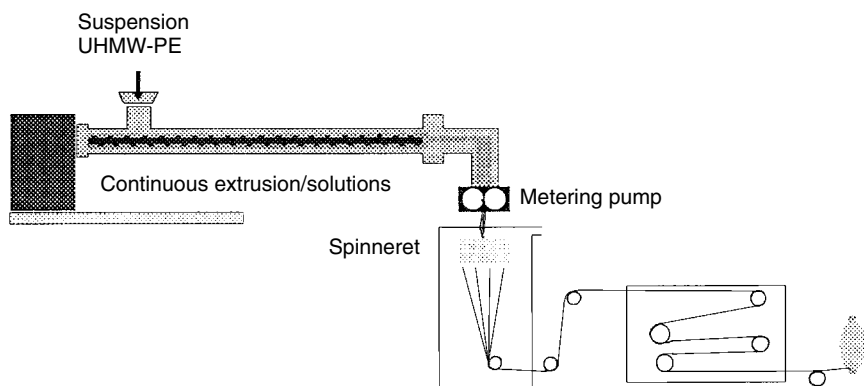
concerning this process have been filed in later years. *Dyneema* fibres have been in commercial production since 1990 at a plant at Heerlen, The Netherlands. The production of *Dyneema* fibres demands relatively little energy and uses no aggressive chemicals. The product can easily be recycled so environmental pollution from product and process is minimal.

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* fibre at Petersburg (Va).

Since the start of commercial production, the performance of the *Dyneema* and *Spectra* fibres has been improved considerably. New grades have been introduced and a significant potential for further improvements is still present. Gel-spinning of HPPE fibres is a process that hinges on mechanical and physical parameters, not on chemistry. This makes it relatively easy to produce a wide range of fibre grades. The gel-spun fibres are characterized by a high degree of chain extension, parallel orientation greater than 95% and a high level of crystallinity (up to 85%). This gives the fibres their unique properties.

3.2.2.1 Gel-spinning process

Figure 3.2 shows a diagram of the gel-spinning process.³



3.2 Gel-spinning process.

The main steps in the process are:

- The continuous extrusion of a solution of ultra high-molecular weight polyethylene (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.
- Superdrawing and removal of the remaining solvent gives the fibre its final properties but the other steps are essential in the production of a fibre with good characteristics.

In the gel-spinning process, not only do all the starting parameters have an influence on the final properties of the fibre, the different process steps also influence all the following stages in the production of the fibre. So, starting from the same principles, *Dyneema* and *Spectra* may use very different equipment to produce comparable fibres.⁴

3.2.2.2 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 fibres, ultra-long chains with a high overlap lengths are required. The starting material for the high-performance polyethylene fibres is polyethylene with an average molecular weight of one million or more. The higher the molecular weight, the higher the strength that can be obtained. Improvements 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; short chains are less effective in the transmission of the load in the final fibre. Branches on the chains also interfere with the drawing; however, it has been shown that a limited number of branches gives a better performance.

3.2.2.3 *Spinning solution*

With long-chain, flexible polymers the high orientation required can be obtained by drawing 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 cross-overs determined by the concentration and the length of the molecules. The flexible molecules assume 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 more elongated form. This is the first step in the orientation process and the geometry of the spinneret has been thoroughly studied in DSM's research into improvements to the properties of the *Dyneema* fibre.

For maximum fibre 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 optimisation of these parameters is an essential part of the process.

3.2.2.4 *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 fibre 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 fibres can be derived from that of these polyethylene crystals.

The spatial structure of the polyethylene molecules at the moment of crystallization is critical for obtaining good drawability. 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 drawability.

Between a single crystal and a fibre there is quite a long way to go. Lamellar crystals with folded chains do not form suitable building blocks for a strong fibre. Long, thread-like crystals (fibrils) with extended chains are much better suited for this purpose. After the removal of the solvent, the fibres 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 fibre.

3.2.2.5 *Drawing*

The final properties of the fibre in the gel-spinning process are achieved in the superdrawing 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, due to insufficient molecular overlap.

The explanation for this drawing behaviour 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 fibre will break. The elasticity is then too low and the forces in the spinning process cannot be passed on over a great length. The fibre will break before it is drawn. A very low concentration is, of course, not interesting 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.

Gel-spinning a high performance polyethylene fibre has proven to be a highly interrelated process. At each step, not only the starting parameters and local conditions determine the result, but also all the preceding process steps are an important part of the polymer's history. Polyethylene as a polymer has a very long relaxation time – a long memory.

3.2.3 Other gel-spun fibres

The gel spinning process can also be used for other polymers. To obtain a strong fibre it is necessary that the gel fibre can be drawn to get a high orientation of the molecules, so only a limited number of polymers are suitable. Most polymers have too many side chains or possess chains with a strong interaction and so resist drawing below the melting temperature. Polymers such as PECO (a copolymer from ethylene and carbon monoxide) and PAN (polyacrylonitrile) have been tested, but only gel spun PVA (polyvinyl alcohol) is commercially available. Kuraray from Japan uses a gel-spinning process to produce a PVA fibre. The main characteristics of this fibre, however, are not its high mechanical properties, but its easy solubility in water.

3.3 Fibre characteristics

3.3.1 Fibre form

Dyneema and *Spectra* are produced as a multifilament yarn. The titre of the monofilaments varies from about 0.3 denier per filament (dpf) (0.44 dtex) to almost 10 dpf (11 dtex). Tenacity of one filament may well be over 5 N/tex, and the modulus can be over 120 N/tex.

Staple fibre is not produced as such. Stretch broken and cut fibres are used by specialised companies.

Most fibre grades have a more or less circular cross-section. The fibre skin is smooth.

3.3.2 Structure and morphology

The fibre is highly crystalline; the crystallinity is typically >80%. The crystal domains, mainly orthorhombic with a small contribution of monoclinic, are highly extended in the fibre direction. The crystal domains are organised 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 characterised by a high density, a high orientation and restricted mobility of the molecular chains.

3.3.3 Commercially available fibres

The product portfolio for *Dyneema* and *Spectra* at the end of 2000 is shown in Table 3.1. The reported physical properties are representative of published information from the fibre manufacturers. These values are influenced by testing methods and hence the direct comparison of properties is not always correct.

Table 3.1 Commercially available HPPE filament yarns

	Density (kg/m ³)	den/fil (dpf)*	Tenacity (N/tex)	Modulus (N/tex)	Elongation to break (%)
DSM HPF					
<i>Dyneema SK60</i>	970	1	2.8	91	3.5
<i>Dyneema SK65</i>	970	1	3.1	97	3.6
<i>Dyneema SK75</i>	970	2	3.5	110	3.8
<i>Dyneema SK76</i>	970	2	3.7	120	3.8
Toyobo					
<i>Dyneema SK60</i>	970	1	2.8	91	3.5
<i>Dyneema SK71</i>	970	1	3.5	122	3.7
Honeywell					
<i>Spectra 900</i>	970	10	2.6	75	3.6
<i>Spectra 1000</i>	970	5	3.2	110	3.3
<i>Spectra 2000</i>	970	3.5	3.4	120	2.9

* dtex values are 10% larger than dpf.

3.4 Properties

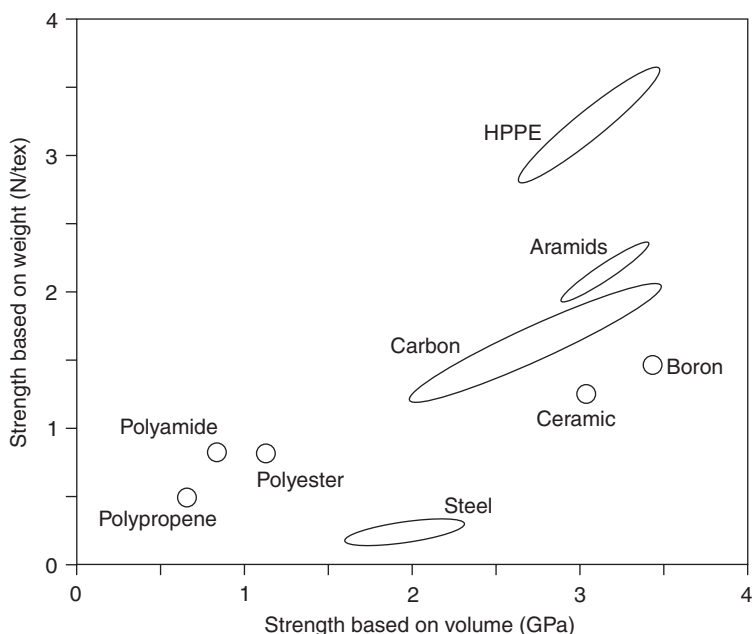
3.4.1 Density

HPPE fibres have a density of 970 to 980 kg/m³, typical for highly crystalline linear polyethylene.

3.4.2 Tensile properties

The primary properties of the *Dyneema* and *Spectra* fibres are high strength and high modulus in combination with the low density. HPPE fibres have a density slightly less than one, so the fibre floats 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 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 fibre grades and high modulus PBO. Elongation at break is relatively low, as for other high-performance fibres, but owing to the high tenacity, the energy to break is high.

Figure 3.3 gives fibre strength in textile units (N/tex) and in engineering units (GPa). Textile units relate the strength to the weight of the fibre whilst engineering units refer to the cross-section and the volume of a fibre. It is clear from this diagram that the combination of low density and high strength makes *Dyneema* and *Spectra* unique products. The diagram also



3.3 Strength based on weight vs strength based on volume of various fibres.

shows that HPPE fibres are not only first choice in weight saving, but that their use can also give volume saving.

In Table 3.2, the theoretical maximum values for tenacity and modulus are shown for a number of polymer fibres (Yasuda *et al.*).⁵ It is clear that for HPPE substantial improvements in properties are still possible.

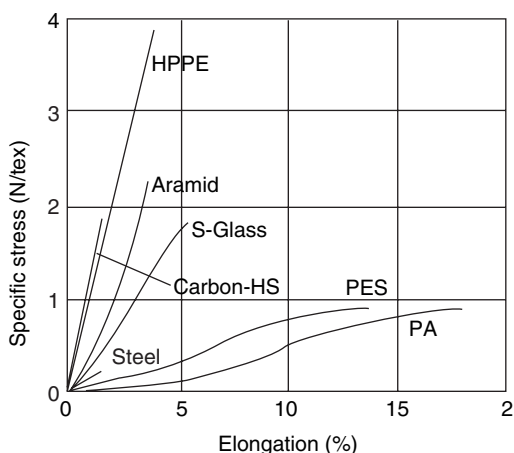
In Fig. 3.4 the specific stress and the elongation of various fibres are shown. The areas below the curves are the energy-absorbing capacities of the fibres.

The strength of a fibre can also be expressed as the free breaking length. The free breaking length is the theoretical length of a fibre, yarn or rope at which it breaks under its own weight when hanging freely. This free breaking length is material related and corresponds to the tenacity. Free breaking length is independent of the thickness of the fibre or the rope. Figure 3.5 is an artist's impression of the free breaking length of different fibres. *Dyneema* and *Spectra* would in theory reach to a satellite's orbit.

Figure 3.6 shows the specific strength versus the specific modulus and illustrates why HPPE fibres give veritable high performance. The high specific modulus is also relevant in ballistic protection. The sonic velocity in the fibre determines the speed of spreading energy on ballistic impact and the sonic velocity is calculated as the square root of the specific modulus.

Table 3.2 Theoretical and achieved properties of fibres

Polymer	Strength, theoretical		Strength, commercial		Modulus, theoretical		Modulus, commercial	
	GPa	N/tex	GPa	N/tex	GPa	N/tex	GPa	N/tex
PE	32	33	3.6	3.7	240	247	116	120
Aramid	30	21	3.3	2.3	183	127	120	83
PA-6	32	23	0.9	0.8	142	125	6	5
PES	28	20	1.1	0.8	125	90	14	10
PP	18	20	0.6	0.6	34	38	6	6



3.4 Fibre stress–strain curves. PES = polyester, PA = polyamides, HS = high strength.

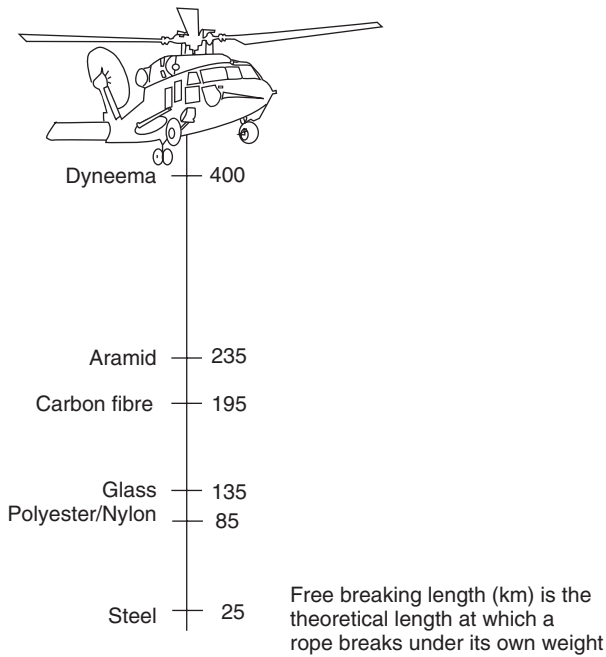
In contrast to the high tensile strength, the gel-spun fibre has a low compressive yield strength, approximately 0.1 N/tex.

3.4.3 Mechanical properties in the transverse direction

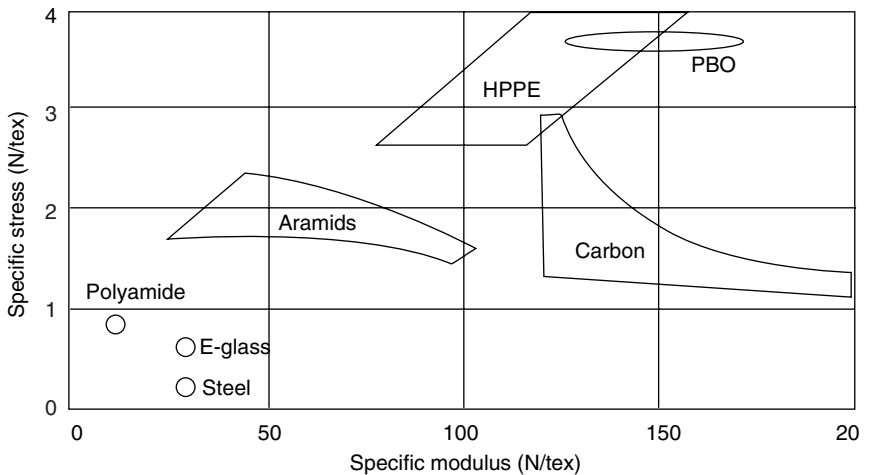
As all the chains in the fibre are aligned in the fibre direction, the mechanical properties are highly anisotropic. In the transverse direction the modulus and strength are much lower than that in the fibre direction. Table 3.3 gives estimated values.

3.4.4 Viscoelasticity

Polyethylene is a viscoelastic material, that is, the properties depend significantly on such variables as temperature and loading history.



3.5 Free breaking length of various fibres.



3.6 Specific strength vs specific modulus for various fibres.

Table 3.3 Transverse properties of HPPE fibres

Transverse elastic modulus	3 GPa
Transverse compressive yield stress	0.05 GPa
Transverse tensile strength	0.03 GPa

One feature is that the mechanical properties of HPPE fibres 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 alternatively at low temperatures, both modulus and strength are significantly higher than the values given in the tables before. This is important in ballistic protection.

Another feature is that the fibre is prone to creep; the deformation increases with loading time, resulting both in a lower modulus and a higher strain at rupture. Creep is important, for instance, when ropes are under relatively high loads over a long period of time.

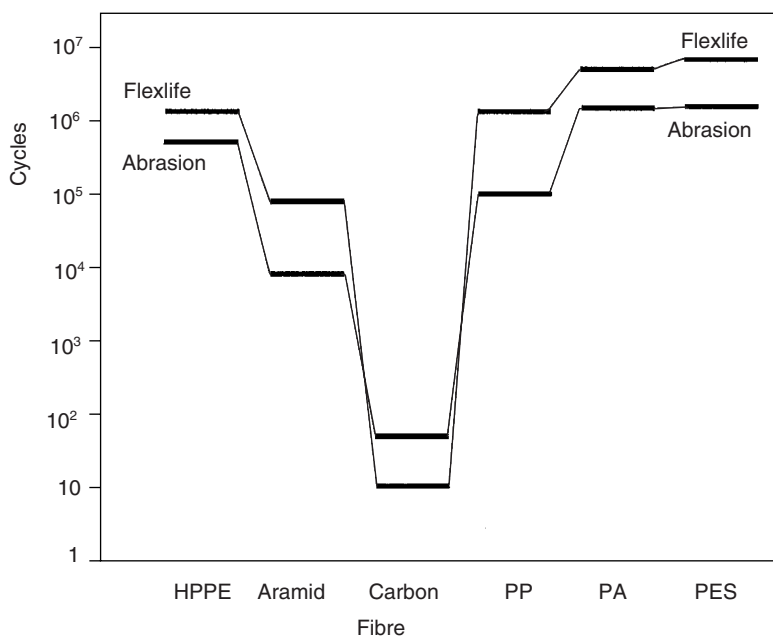
Creep values are not the same in all HPPE fibres but depend on choices made in the production process. Creep is not an important and controlled property in all the HPPE fibre types so it should not necessarily be constant in value in, for example ballistic fibre grades. For the *Dyneema* fibre grades that are used in ropes and comparable applications, there is a computer model that predicts creep in rope constructions (Smeets *et al.*¹²).

3.4.5 Energy absorption

Dyneema and *Spectra* fibres can absorb extremely high amounts of energy. This property is utilized in products for ballistic protection. But it makes the fibre equally suited for products such as cut-resistant gloves and motor helmets. The fibres can also be used to improve the impact strength of carbon or glass fibre-based composites. In these applications, not only the high tenacity is used but also the high energy absorption.

3.4.6 Fatigue

Fatigue is very important in, for example, rope applications. HPPE fibres are the first high-performance fibres that not only have a high tenacity but that also have tension and bending fatigue properties comparable with the commonly used polyamide and polyester grades in ropes. Carbon fibres and glass fibres have a high modulus and a brittle breaking mode, but HPPE fibres demonstrate that this is not an obvious combination. *Dyneema* and *Spectra* fibres have a high modulus but still are flexible and have a long flex



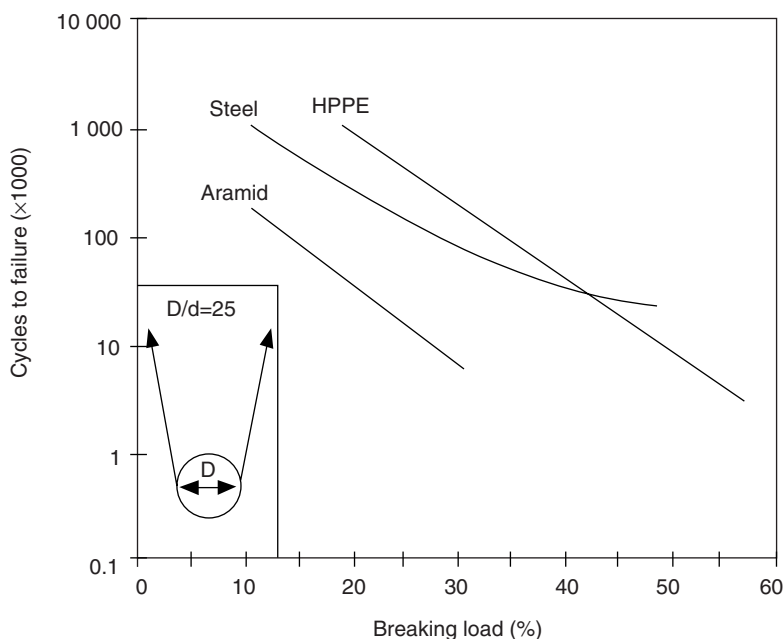
3.7 Abrasion and flex life of various fibres.

life (see Fig. 3.7). The good flexural fatigue resistance is related to the low compressive yield stress.

In tension fatigue testing, a rope is repeatedly loaded in tension. A typical example is loading to, for example 50% of its breaking load followed by relaxation to about 5%. The high strength polyethylene fibre 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.

The relatively low melting temperature makes the fibre sensitive to warming-up due to hysteresis losses. This process causes warming of the rope and the balance of energy creation and 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 a thick rope immersed in water may stand the test without any difficulty, as has been shown in, for example, offshore mooring.

In bending fatigue or flex-life testing, a loaded rope is moving over two or three sheaves. In the test with three sheaves, two sheaves bend the rope clockwise, and the middle one counter-clockwise. In this test the fibres and the strands move relative to each other and cause internal abrasion. It is clear that the rope construction has a great influence on the results



3.8 Bending fatigue of various fibres: cycling over sheave at increasing percentage of break load.

of this test, but as HPPE fibres have a very high abrasion resistance the test results are comparable with those from commonly used synthetic fibre ropes and far higher than aramids and carbon fibres. See Figures 3.7 and 3.8.

3.4.7 Abrasion resistance

Abrasion resistance is very important in ropes, also in gloves. In many of applications it is at least one of the factors that determines wear and tear and so the service life. The high molecular weight polyethylene used for HPPE fibres 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 HPPE fibres also have good abrasion resistance.

3.4.8 Effects of water

Polyethylene is not hygroscopic and does not absorb water. The fibres have a very low porosity, therefore water absorption in the fibre is negligible. However, multifilament yarns used as strands in a rope or in a fabric,

Table 3.4 Resistance of fibres to various chemicals: 6 months immersed at ambient temperature

	HPPE	Aramid
Distilled water	***	***
Sea water	***	***
10% detergent	***	***
Hydrochloric acid (pH = 0)	***	*
Nitric acid (pH = 1)	***	*
Glacial acetic acid	***	***
Ammonium hydroxide	***	**
Sodium hydroxide (pH > 14)	**	*
Petrol	***	***
Kerosene	***	***
Toluene	***	**
Trichloromethane	***	***

*** Unaffected ** slightly affected * seriously affected.

typically have 40% void. Therefore, water can be absorbed between the fibres. If that is not acceptable, water repellent additives should be used.

Polyethylene fibres do not swell, hydrolyse or otherwise degrade in water, seawater or moisture.

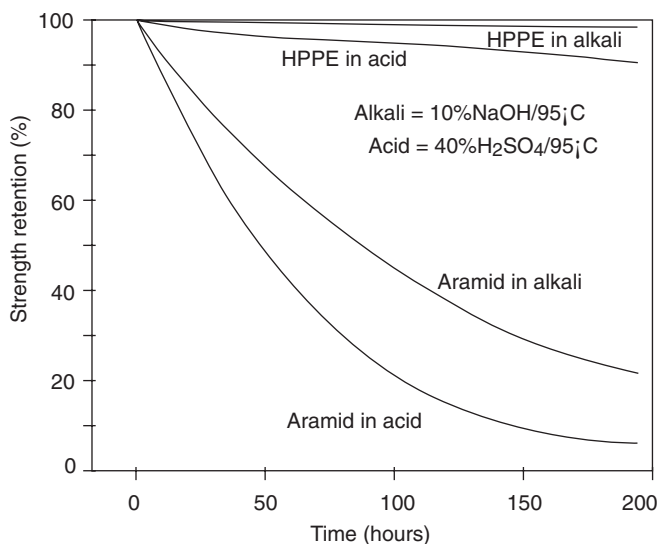
3.4.9 Chemical resistance

HPPE fibres 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 against chemicals. Table 3.4 gives examples of the effect of chemicals on HPPE fibres, in comparison with aramids. The resistance to acids and alkalis is also very good, see Fig. 3.9.

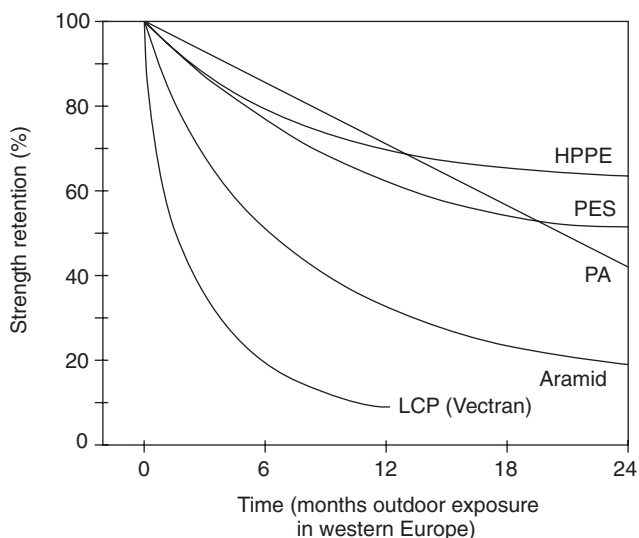
Dyneema and *Spectra* fibres, being of a polyolefinic nature, are sensitive to oxidizing media. In strongly oxidizing media, fibres will lose strength very fast. In normal air the fibre is stable for many years.

3.4.10 Resistance to light and other radiation

Figure 3.10 shows the resistance of HPPE to ultraviolet (UV) light. It is clear that special precautions are not 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.



3.9 Resistance to acids and alkalis: HPPE vs aramid.



3.10 UV resistance of high performance fibres.

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 100kGy; however, the fibres retain a useful tenacity up to a dose of 3MGy.

3.4.11 Electrical properties

Polyethylene is an insulator and has no groups with dipole character. The fibre is characterised by a high resistivity (volume resistivity $>10^{14} \Omega\text{m}$), low dielectric constant (2.2) and a very low dielectric loss factor (2×10^{-4}). As-spun yarns contain a small fraction of spin oil of a hydrophilic nature. So, for applications where the electrical properties are important, the spin finish should be removed.

3.4.12 Acoustic properties

As with all mechanical properties, the acoustic properties are strongly anisotropic. In the fibre direction, the sound speed is much higher ($10\text{--}12 \times 10^3 \text{m/s}$) than in the transverse direction ($2 \times 10^3 \text{m/s}$). The acoustic impedance, the product of density and transverse sound speed, is near that of water. Mechanical damping losses are significant in both the longitudinal as well in the transverse direction.

3.4.13 Biological resistance

The biological resistance of the fibre is that of high-density polyethylene. The fibre is not sensitive to attack by micro-organisms.

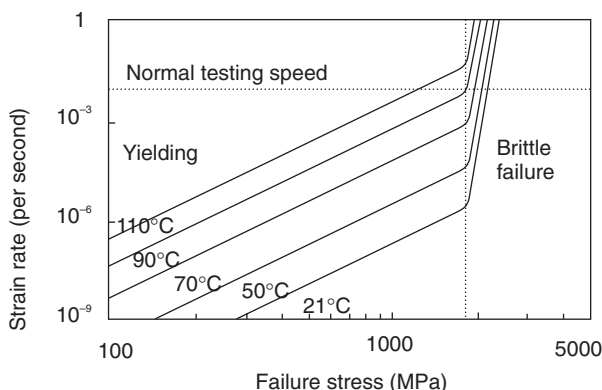
3.4.14 Toxicity

Polyethylene is regarded as biologically inert.

3.4.15 Thermal resistance

Dyneema has a melting point between 144 and 155°C , depending on the conditions, the higher temperature being measured if the fibre is constrained. The tenacity and modulus decrease at higher temperatures but increase at sub-ambient temperatures. There is no brittle point down to 4K (-269°C), so the fibre can be used from cryogenic conditions up to a temperature of 80 to 100°C . Brief exposure to higher temperatures, but below the melting temperature, will not cause any serious loss of properties.

The mechanical properties are influenced by the temperature and the main reason is thought to be chain slippage, that is polyethylene chains that move relative to each other in the direction of the fibre (Peys *et al.*⁶) (see Fig. 3.11). Normally the testing of tenacity and modulus is done around 1% per second, so below about 100°C breakage will always be in the brittle failure range.



3.11 Effect of temperature on the failure stress of *Dyneema*.

3.4.16 Fire properties

HPPE fibres and products have been tested to establish the performance in heat and fire. The results are that ignition of HPPE fibres is normal and acceptable under most conditions. The emission of toxic gases in fire was studied and, as polyethylene contains only carbon and hydrogen and no nitrogen or other hazardous chemical elements, toxicity of the gases is relatively low.

Fire properties are far more complicated than indicated by just the LOI (limiting oxygen index). Like most polymeric and organic materials, *Dyneema* and *Spectra* fibres have a LOI index lower than 20, which simply means that they can burn in atmospheric conditions. A number of tests were conducted to specify the fire properties.

- Flammability test, Federal Motor Vehicle Safety Standard (FMVSS 302).⁷
A US standard that is used in the automobile industry. This test on a horizontal sample qualifies it as being self-extinguishing.
- Flammability test, Federal Aviation Regulation (FAR) 25.853 b.⁸
Also a US standard and in use with the aviation industry. In this test the specimen is mounted vertically. As in the preceding test, the fabric shrinks away from the flame and no ignition occurs. No dripping was recorded.
- DIN 4102, 'Behaviour of building materials and components in fire'.⁹
A German standard that was first designed to establish the fire properties of building products but that is now more generally used. Also here, no dripping of material occurred. The samples passed the DIN 4102 B2 test.

All polymeric materials are combustible and their behaviour when exposed to heat and fire differs less than it often seems to do. Thermoplastics normally melt first, then decompose, and 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 gases are usually in the same range as for thermoplastic polymers. HPPE fibres are polyethylene, a thermoplastic material that melts at about 150°C and decomposes over 300°C . Aramid fibres are thermosets, there is no melting point and gas emission starts at about 400°C .

The toxicity of the gases in a fire depends on:

- The composition of the substrate; if the material contains nitrogen, sulphur 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.
- Given the composition, 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.

3.4.17 Shrinkage

The fibre is characterised by high molecular extension of the molecules. 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°C and 140°C . If the fibre is constrained, it will develop significant shrinkage forces (up to approximately 0.1 N/tex).

3.4.18 Properties summary

Table 3.5 gives an overview of the chemical and physical properties of HPPE.

3.5 Yarn and fabric processing

3.5.1 General precautions

Processing of *Dyneema* and *Spectra* yarns is not difficult, but to keep tenacity and modulus as high as possible some precautions should be taken:

- The use of ceramic guides, preferably rolling, is advised. Contact points should have a durable matt surface (so-called orange skin). This can be secured through the use of ceramic materials or by inchromising metal contact points. Contact points should be without burrs or grooves.
- Sharp angles and high tensions during processing should be avoided.

Table 3.5 Overview of chemical and physical properties of HPPE

<i>Water and chemicals</i>	
Moisture regain	zero
Attack by water	none
Resistance to acids	excellent
Resistance to alkalis	excellent
Resistance to most chemicals	excellent
Resistance to UV light	very good
<i>Thermal</i>	
Melting point	144–155 °C
Boiling water shrinkage	<1%
Thermal conductivity (along fibre axis)	20 W/mK
Thermal expansion coefficient	-12×10^{-6} per K
<i>Electrical</i>	
Resistance	$>10^{14}$ Ohm
Dielectric strength	900 kV/cm
Dielectric constant (22 °C, 10 GHz)	2.25
Loss tangent	2×10^{-4}
<i>Mechanical</i>	
Axial tensile strength	3 GPa
Axial tensile modulus	100 GPa
Creep (22 °C, 20% load)	1×10^{-2} % per day
Axial compressive strength	0.1 GPa
Axial compressive modulus	100 GPa
Transverse tensile strength	0.03 GPa
Transverse modulus	3 GPa

3.5.2 Yarn processing, blends and fusing

All the HPPE fibres are produced as filament yarn and by the far largest part is used as such. Twisting and twining can be done using standard machinery. Table 3.6 shows the influence of twist on the tenacity. The k -factor is highly independent of the yarn titre and is calculated as:

$$k = (\text{dtex/density})^{1/2} \cdot (\text{turns/meter})/3025$$

HPPE fibres can be cut to long or short staple or can be stretch broken. Short staple fibre can be processed using open-end and ring spinning, the latter producing spun yarn with superior properties. Long staple fibre and stretch broken fibres can be spun on wool spinning equipment (three cylinder spinning). Both short and long fibres can be combined with other fibres to form blended yarns.

A large number of fibre blends has been produced for different applications but most for cut protection. Both filament yarns and long and short staple can be used.

Table 3.6 The *k*-factor and tenacity

<i>k</i> -factor	Tenacity (%)
0	100
0.57	104
0.85	104
1.13	96
1.70	85
2.83	65

A unique property of high-strength polyethylene fibres is the ability to be fused into monofilaments or tapes. Both *Dyneema* and *Spectra* have been used to fuse the multifilament yarn to a monofilament. These monofilaments are in use in sport fishing lines and are under test in filter cloth.

3.5.3 Dyeing

Owing to their chemical inertness and high crystallinity, dyeing high-strength polyethylene fibres is extremely difficult. A limited success has been demonstrated by using advanced technology, for example dyeing in subcritical carbon dioxide.

3.5.4 Weaving

When weaving *Spectra* and *Dyneema* yarns, the main concern is to minimize the loss of tenacity and modulus. The areal density and the construction of the fabric influence the performance of the final product. In Table 3.7, a first indication is given of the yarns and fabrics used in a number of applications.

3.5.5 Knitting

Knitting of HPPE yarns does not require any special equipment. Filament yarns can be used in all available grades and deniers. HPPE filament yarn has been used as such for 100% *Dyneema* or *Spectra* fabric. The filament yarn is also knitted in combination with cotton to improve wearing comfort or to diminish the performance where 100% would give better-than-needed results.

In cut-resistant clothing, 100% HPPE filament yarns are used and combinations of HPPE filament with other (filament) yarns. *Dyneema* filament yarns are stretch broken and then spun with a great range of other fibres to obtain an 'engineered' yarn with well-defined properties.

Table 3.7 Woven fabric styles and applications

Ballistic vests

*Dyneema SK76

*Spectra 1000 and 2000

*very tight fabrics

Composite ballistic armour

*Dyneema SK76

*Spectra 1000

*pliable fabrics (satins)

Protective clothing

*Dyneema SK60, SK65 or SK75

*Spectra 900 or 1000

*knitted or woven fabrics

Composite reinforcement

*Dyneema SK60, SK65 or SK75

*Spectra 1000

*corona or plasma-treated yarn or fabric

*open fabrics

*hybrids with glass or carbon fibres

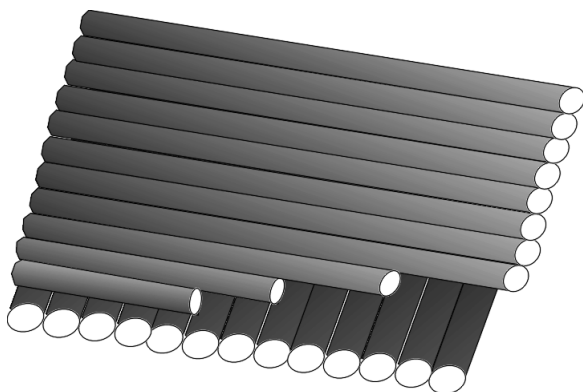
3.5.6 Ropemaking

In ropemaking, whatever the rope construction, the key to good performance is to keep the HPPE fibres under constant tension and to avoid differences in path length during processing. The contact points are very important: these should be hard, preferably rolling and certainly not worn-out. These requirements have to do with the high tenacity and the low elongation. The fibre as such, however, is flexible and very easy to process.

Double braids with HPPE or polyester in the outer layer are in common use. HPPE ropes can be heatset to remove the extra elongation that is introduced during the production of the ropes and to increase the strength. This action results in an improved orientation of the HPPE fibres in the ropes. Heatsetting HPPE ropes or twines must always be done under tension.

With HPPE, the double-braided rope construction is mostly used for flexible, dynamic loaded ropes up to 16 mm diameter. The 4×2 plaited and 12×1 braided ropes are used in far higher diameters and breaking strengths.

Laid ropes have a higher breaking strength but are less flexible. In highly dynamic loaded applications (much bending, changing tension loads, much handling) braided or plaited constructions are often preferred. There are no special problems with HPPE fibres in this application. The ropes are often produced with a braided cover to prevent damage to the load bearing strands.



3.12 Construction of *Dyneema UD* and *Spectra Shield*.

3.5.7 Netting

Normally fishing nets, safety nets, etc. are made by knotting braided HPPE twines to form net panels that are used to build, for example, a trawl net. Single knots in HPPE nets may lead to knot slippage owing to the slippery nature of the fibres so double knots are advised. In knotless nets (Raschel and Nichimo), the panels are produced directly from the yarn and twines are not made first. Heatsetting is common practice with HPPE nets for the same reasons as with ropes, but also to improve fixation of the knots.

3.5.8 Nonwovens

Dyneema UD and *Spectra Shield* are non-wovens, but not of the conventional types. They are made of unidirectional layers, in which the yarns are not woven but lie parallel to each other and are bonded by various thermoplastic matrices, Fig. 3.12. This construction is used in ballistic protection against bullets (police vests, lightweight armour panels) as this gives a far better protection at the same weight than fabrics. This system is patented and *Dyneema UD* and *Spectra Shield* are only produced by licensed companies.

Dyneema Fraglight is a needle felt non-woven, produced from staple fibre, that is used, for example in military vest, for the protection against fragments from exploding grenades and bombs.

3.5.9 Composites and laminates

In non-ballistic composites, HPPE fibres are mainly used to improve the impact resistance and the energy absorption of glass or carbon fibre rein-

forced products. Woven fabrics or hybrid fabrics with glass or carbon can be used and the fibre or the fabric can be corona or plasma treated to improve the adhesion of the matrix to the fibre. The matrix material is normally an epoxy or a polyester resin. The only basic limitation here is that the curing temperature should not exceed 140°C.

In composites used for ballistic protection, such as helmets and lightweight armour panels, only the ballistic fibre types are used. Both fabrics and the unidirectional products are used with thermoset and thermoplastic matrix systems. The fibre content is normally far higher than with non-ballistic composites.

Dyneema and *Spectra* are well suited for use in flexible composites or laminates. Most common use is in laminated sails using a scrim or an open fabric and polyester film.

3.6 Applications

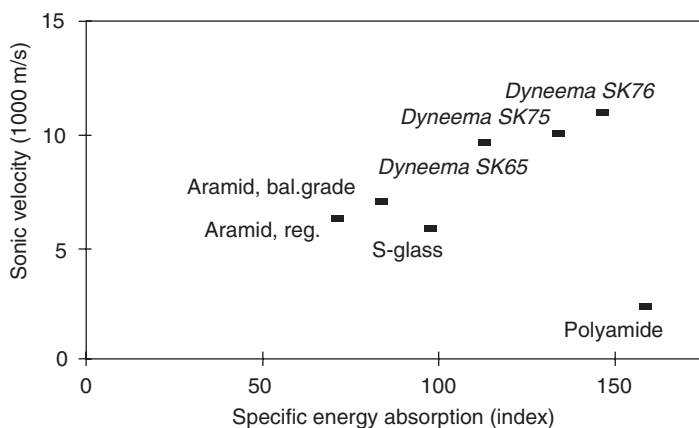
3.6.1 Ballistic protection

HPPE fibres have a high energy absorption at break and, owing to the low weight, the specific energy absorption is also very high. This opens up opportunities for these fibres in applications that need a combination of low weight and protection against mechanical threats.

Most important in ballistic protection are the mechanisms of energy absorption at ballistic speeds. The tenacity and elongation to break determine the amount of energy that can be absorbed by an amount of fibres. The specific modulus determines the sonic velocity in the fibre and that indicates the area of the fabric that is involved in stopping the projectile. Figure 3.13 shows the specific energy absorption and the sonic velocity of fibres: the primary factors that determine the weight needed to stop a projectile.

Against most ballistic threats, unidirectional layered HPPE constructions *Dyneema UD* and *Spectra Shield* give the best protection: this means protection at the lowest weight. The theory behind the unidirectional layer construction is that at ballistic impact of a fabric, the spread of energy in the fibres is hindered by reflections of the shock waves at the crossover points of the yarns. In the unidirectional construction, this is far less and a larger part of the sheet is involved in the absorption of energy.

HPPE fibres are used both in 'soft' and 'hard' ballistic protection. Soft ballistic protection is used in flexible vests for the police and military, and protects against handgun ammunition. In police vests the unidirectional form is used as such or in combinations with woven fabric from low titre HPPE or other fibres. Helmets and lightweight panels are hard armour. The military helmets protect against fragments from bombs and grenades; the armour panels can also protect against highly penetrating military rifle



3.13 Energy absorption and sonic velocity in ballistic fibres.

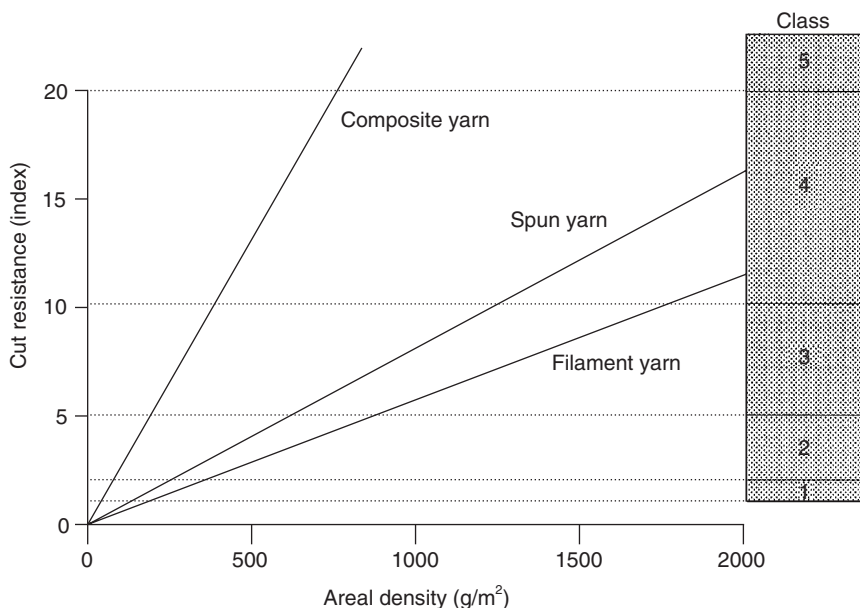
ammunition and can be incorporated in vests and also in civil cars and light-weight (military) vehicles.

3.6.2 Cut and puncture resistance

The protecting properties of HPPE fibres can be exploited not only in ballistic applications, but also in protection against cuts and puncture. Woven fabrics and knitwear give a very good protection in, for example cut-resistant gloves, fencing suits and chain-saw hoses. In cut resistance the best protection is achieved when high-performance fibres are combined with stainless steel or glass fibres. Theory does not give a full explanation of this effect but in practice most gloves are knitted using yarns formed from a combination of HPPE and other fibres: so-called engineered yarns. In engineered yarns, HPPE filament or staple fibre and various other yarns such as stainless steel, glass, polyamide, polyester and cotton are combined, partly to improve the cut resistance, partly to improve, for example, wearing comfort. Figure 3.14 shows the cut-resistance according to the European standard EN 388 (1994).¹⁰ Dyneema engineered yarns meet the requirements of the highest Class 5.

Puncture resistance depends on both the fibre properties and the resistance of the fabric construction against penetration between the yarns. A normal knitted HPPE 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.

The low moisture sensitivity and good chemical resistance of HPPE fibres guarantee high durability in the wash-and-wear cycles of protective clothing.



3.14 Cut-resistance according to European Standard EN 388.

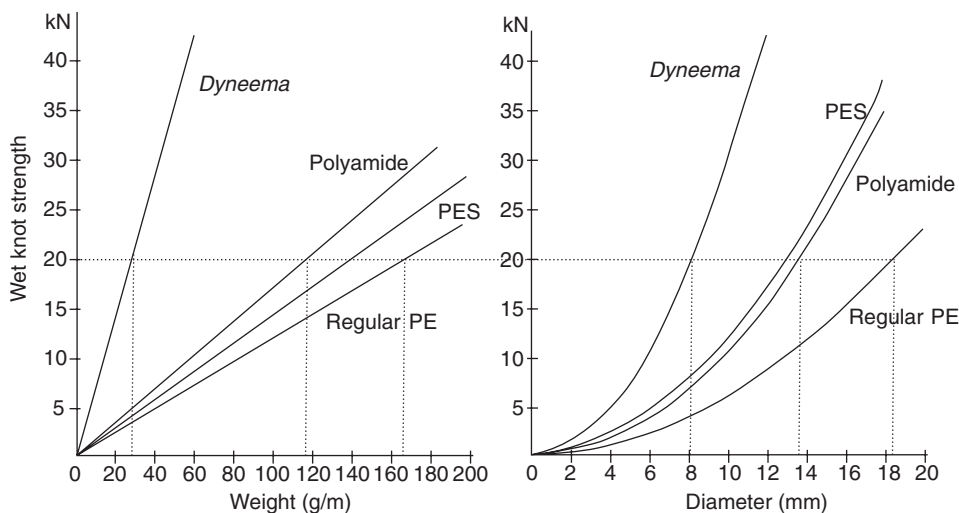
3.6.3 Low-speed impact

In composites, HPPE fibres can absorb the impact energy that would otherwise destroy the brittle reinforcing glass or carbon fibres. In addition, the use of HPPE affords great weight savings. In motor helmets, for instance, a weight saving of 300–400 g has been realized, down to 40% of the original shell weight. Even in combinations with wood laminates for boat hulls for instance, HPPE fibres can strongly improve impact resistance.

3.6.4 Twines and nets

An HPPE fibre is an ideal material for use in a marine environment. Its density is slightly less than 1, so it is virtually weightless in water and floats. The fibre is strong and does not lose its tenacity in water, it does not rot and is not affected by UV light or seawater. So it is not surprising that ropes, twines and nets were among the first products to be made of these fibres.

Most important applications of smaller cords are in halyards, twines for nets and the very thin lines used for angling. Halyards normally have a double braid construction with a braided load-bearing core and a coloured polyester cover. On a weight basis, the halyards with a HPPE core are by far the strongest on the market. Elongation is only slightly higher than that



3.15 Wet knot strength of various twines in fishing nets.

of wire rope so that HPPE halyards guarantee accurate and stable positioning of the sails. In long-distance sailing contests, it was confirmed that the ropes are reliable and durable, and HPPE halyards are now the standard in these contests.

Very thin, ultra-strong braided HPPE angling lines were a major change in sport fishing after many years of polyamide monofilament. The braided line was followed by a fused HPPE line with monofilament characteristics. Not only is a HPPE line far stronger than polyamide at the same diameter but owing to the low elongation the angler has far more 'contact' with the fish.

The reduction in weight and diameter of ropes and twines in trawl nets opens up new opportunities for the design of more efficient nets. The drag resistance of the net in water can be reduced by as much as 40% per square metre net opening. This benefit can be utilized to save energy on trawling or to use larger nets with a larger mouth opening for the same ship with the same horsepower. Fishing efficiency can be increased by 80% in this way. Figure 3.15 shows the wet knot strength of braided twines that are used in fishing nets. The wet knot strength is the lowest strength in netting and is taken as the design criterion in nets.

Of course, the weight of fishing gear can also be reduced by using HPPE in the wing lines, jompers and gilson lines, etc. Alternatively, using the same rope diameter but with a rope made from HPPE in the construction of the net or in the cod-end, the risk of breakage, and so the loss of the catch, can be reduced.

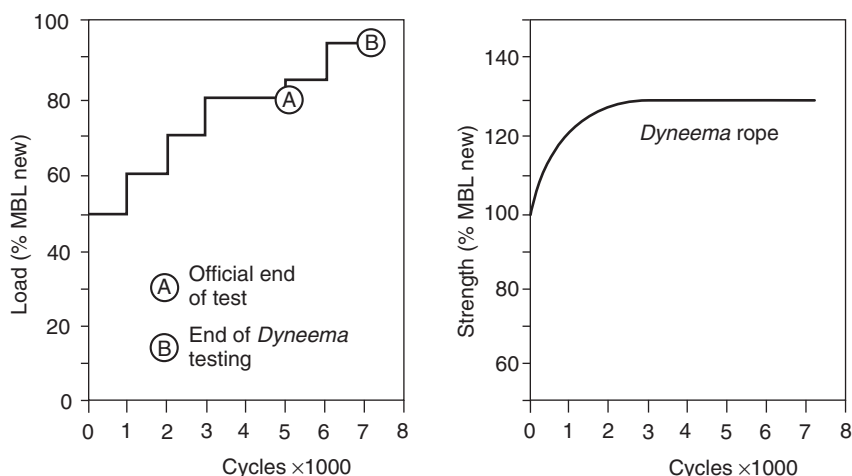
3.6.5 Ropes

The low weight and high strength of HPPE fibres make it possible to produce heavy-duty ropes with very special characteristics. HPPE ropes float on water, are flexible and have a low elongation. Thus, they are very easy to handle. Abrasion resistance and fatigue are good to any standard, which is why HPPE ropes last much longer than other ropes. In a matrix in Table 3.8, the different ropes constructions and different types of loading are shown with an indication of the use of HPPE fibres.

Dyneema ropes were tested as to their suitability for offshore applications according to the thousand cycles load level (TCLL) test of the Oil Companies International Marine Forum (OCIMF).¹¹ The TCLL test is an accelerated fatigue test in which the rope is loaded and unloaded 1000 times with loads of 50%, 60%, etc. of the breaking load. The residual strength is determined after testing at 80% if the rope did not break during testing. In tests carried out on the *Dyneema* ropes, the increasing strength of these ropes frustrated the testing procedure. The testing was continued to 95% of the breaking load and then the residual strength was determined at 130% of the initial breaking load (see Fig. 3.16.).

Figures 3.17 and 3.18 show the strength of a number of ropes versus diameter and weight. The low weight and low elongation of a HPPE rope can be used to reduce the effects of backlash on breakage. In some applications it is advantageous that, at the same strength, a HPPR rope and a wire rope

Test according to Oil Companies International Marine Forum - 1987

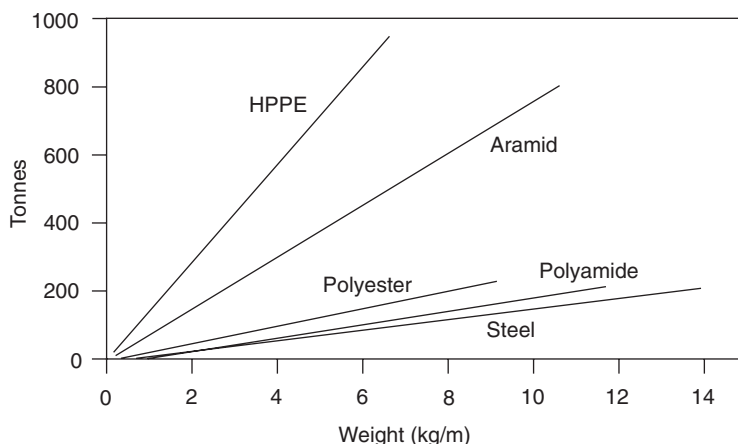


3.16 The thousand cycles load level (TCLL) test. MBL = minimum breaking load.

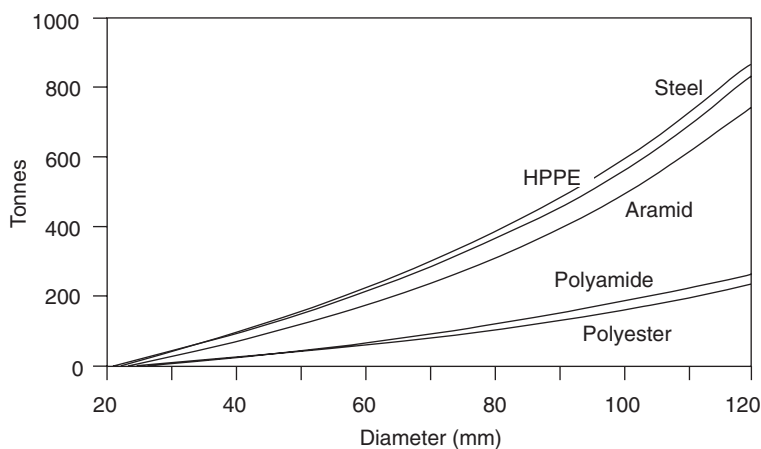
Table 3.8 Constructions and applications of HPPE ropes

Demand	Static loading		Slowly increased loading				Shock loading		Load in bending	
Application	guys	fasten	mooring	tug	fishnet rope	nets	safety	mountaineer	changing hoisting	static stretch
Construction										
Laid, 3 strand			++	+	++				+	
Laid, 4 strand			+						+	
Braided		+	+		++	++			++	
Double braid		+	+	++	+				++	
12 strand braided				++						
Parallel	+									+

+ in common use, ++ recommended.



3.17 Breaking strength vs weight of various laid ropes.



3.18 Breaking strength vs diameter of various laid ropes.

have about the same diameter. Heavy-duty HPPE ropes are used on tug-boats for towing, on ferries and other sea-going vessels for mooring, for mooring offshore platforms and for a large number of auxiliary applications in the offshore industry.

3.6.6 Other applications

Low-stretch sails that last a long time and that can be used and stored repeatedly without loss of properties are now possible by using HPPE

fibres. Excellent class sails are now available not only for the professionals, but also for recreational sailors who want their sails to last longer than one season. HPPE sails are mainly used for the main sail and foresails. Low weight and high strength are very important in these applications.

Both *Dyneema* and *Spectra* have been used to reinforce laminates that are used in balloons for stratospheric exploration and in balloons used for load-bearing applications at lower altitudes.

Hoisting slings can be made from a rope, from narrow fabric or can be laid from yarns or twines. HPPE is used in all types. Weight saving is normally not the first reason to choose this material, service life is more important.

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Other high modulus-high tenacity (HM-HT) fibres from linear polymers

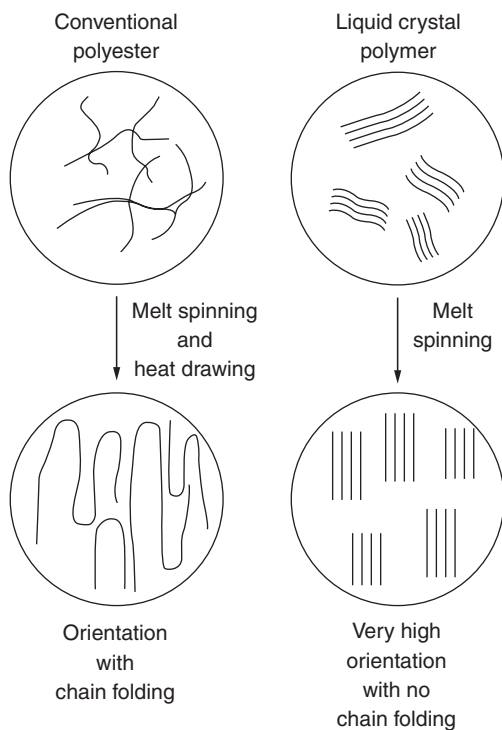
DAVID BEERS (4.1),
ROBERT J YOUNG, C L SO (4.2),
DOETZE J SIKKEMA (4.3),
KIRILL E PEREPELKIN (4.4),
AND GENE WEEDON (4.5)

4.1 Melt-spun wholly aromatic polyester (DB)

4.1.1 Thermotropic liquid crystal polymers

Research into liquid crystal polymers dates back to the 1970s. This research has resulted in a commercially available melt-spun wholly aromatic polyester fibre called *Vectran*[®]. This high-performance fibre is used in numerous applications around the world that require its unique properties. Because of its relatively high cost, it remains a niche-market product driven by cost–performance benefits. Nevertheless, it significantly improves end-product performance when used properly. Much has been written about liquid crystal polymers (LCP) generally. This section focuses on the commercial fibre produced from thermotropic liquid crystal polymer (TLCP).

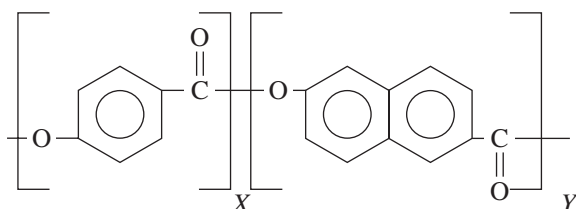
‘Liquid crystal’ is a term given to an organic polymer that exhibits order similar to an ordinary solid crystal. When viewed in the molten state on a hot stage microscope through polarising lenses, this polymer is called a ‘thermotropic liquid crystal polymer’. The temperature range over which this phenomenon is observed depends on the chemical composition of the TLCP. These polymers consist of very rigid, chain-like molecules that position themselves into randomly oriented domains. When these domains are extruded through very small holes, the flow and accompanying shear aligns the domains parallel to each other in the direction of flow (Fig. 4.1). When cooled down, the extruded fibre has a highly oriented structure with high tensile strength and modulus. Because of this high orientation, drawing after spinning is not necessary. What is needed for high strength is to increase chain length. Solid-state polymerisation of the spun fibre, which raises the molecular weight, results in fibres with very high strength and modulus.



4.1 Schematic of molecular chain structure of fibres.

4.1.2 Vectra and Vectran

The commercially available TLCP fibre, *Vectran*, is produced from *Vectra LCP* polymer. This polymer is made by the acetylation polymerisation of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic (Fig. 4.2). It is one of a family of naphthalene-based thermotropic liquid crystal polymers developed by Celanese Corporation in the 1970s and discussed by Calundann *et al.*¹ No classical glass transition temperature is clearly observed in the polymer, although molecular transitions do occur with increasing temperatures. Research and development for the polymers and fibres were focused on tyre cord, to compete with para-aramids. When a cost advantage with these TLCP polymers could not be realised in tyre cord, emphasis shifted towards resin development for electronics parts. The excellent dielectric properties of the polymer and tight tolerances allowed during injection molding resulted in commercial success with the polymer and the start-up of the first commercial liquid crystal polymer manufacturing plant in 1989.



4.2 Vectran fibre chemical structure.

Celanese licensed its TLCP fibre technology to the Kuraray Company. Since the mid 1980s, both companies have pursued process and market development with a focus towards cost performance in niche markets. Kuraray produces significant volumes of TLCP fibre in Saijo, Japan. Celanese produces specialty products in the US for the US and European markets.

4.1.3 Fibre production

TLCP fibre is melt spun using conventional polyester extrusion practices. Attention to uniform polymer flow is essential. Wind-up speed is much lower, as is draw down, compared with PET processes. Some form of lubrication, either finish or water, is necessary for ease of processing, owing to the fibrillar nature of the fibre surface. Typical physical properties for the spun product are 10g/denier tenacity (0.9N/tex), 2% elongation, and 425g/denier initial modulus (40N/tex). This product represents a small percentage of the total TLCP fibre sales.

High strength, 23–28g/denier tenacity (2–2.5N/tex), is achieved in TLCP fibres by heat treating in an inert atmosphere. Again, some type of lubricant, normally water, is initially applied to ease processing. However, care must be taken to remove the water before the final heat-treatment temperatures are reached, to preserve the inert atmosphere required and thus achieve maximum physical properties. The fibre is produced as a continuous filament. Typical properties are given in Table 4.1. There are no significant environmental issues in the production of TLCP fibres.

TLCP fibres have been produced from polymers with varying chemical compositions to achieve an initial modulus in the range of 850–1000g/denier (80–90N/tex; 105–124GPa). However, these fibres were not commercialised because of their lower tensile strength and flex fatigue when compared with commercial TLCP fibre products.

Long and short cut length TLCP fibres are produced by combining high denier continuous filament thread lines for cutting. The traditional economics of producing staple fibre from high denier tow are not realised with

Table 4.1 Properties for high-strength thermotropic LCP fibres

Physical forms:	
Yarn denier (continuous filament)	50–3750
Filament denier	5
diameter, μm	23
Density, gm/cm^3	1.4
Moisture regain, %	<0.1
Extractables (MeCl_2), %	<0.1
Mechanical properties*:	
Tenacity, g/denier	23–28
M/Pa	2850–3470
Elongation, %	≥ 3.3
Initial modulus, g/denier	525–700
GPa	65–87
Thermal properties:	
Melting point, $^{\circ}\text{C}$	330
Boiling water shrinkage, %	≤ 0.5
Hot air shrinkage (177°C), %	≤ 0.5
Limiting oxygen index	30
Coeff. of axial thermal expansion,	-4.8 (20 – 145°C)
$\text{m/m}^{\circ}\text{C} \times 10^{-6}$	-14.8 (145 – 200°C)
	-26.7 (200 – 290°C)

* Test conditions – 25cm gauge length, 10% strain rate, 98tpm twist.
5 breaks/sample, ASTM D885 for I.M.

TLCP fibres because the high cut resistance of the material necessitates the use of low tow deniers. Paper products are also produced from short-cut fibre and pulp made from TLCP fibre.

4.1.4 Fibre properties

Essentially all high-performance fibres have high strength and modulus as well as low elongation, and these properties are very important for most TLCP fibre markets. However, the commercial applications for TLCP fibres also take advantage of one or more of the other unique properties of the fibre as well as high strength and low elongation.

Fibre-to-fibre abrasion resistance: A low level, generally <0.8% oil-on-yarn (OOY), weaving finish is applied to facilitate fibre processing during twisting, braiding, weaving, or knitting and for use in composite applications. This finish can be scoured off or removed with methanol. Processors topcoat over this finish with special coatings for improved UV resistance or to add colour, since TLCP fibre cannot be dyed. For dynamic applications requiring fibre-to-fibre abrasion resistance, silicone finishes are applied

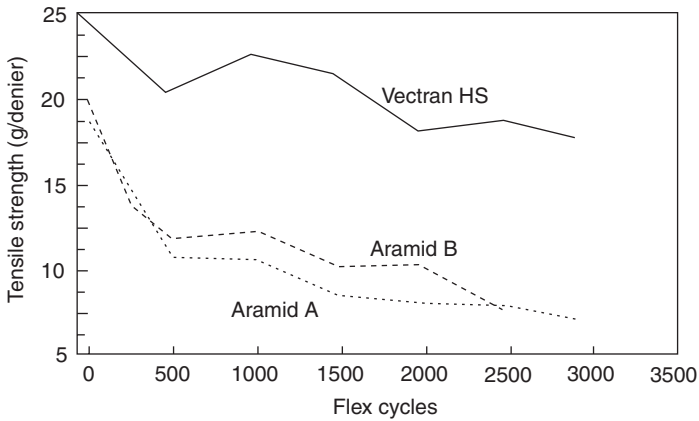
Table 4.2 Comparison of fibre-to-fibre abrasion resistance

Fibre	Average cycles-to-failure (CTF)	
	Dry	Wet
TLCP	16 672	21 924
Aramid (lowest CTF dry)	718	258
Aramid (highest CTF dry)	1 773	758
UHMW-PE (lowest CTF dry)	8 518	23 619
UHMW-PE (highest CTF dry)	17 761	78 369

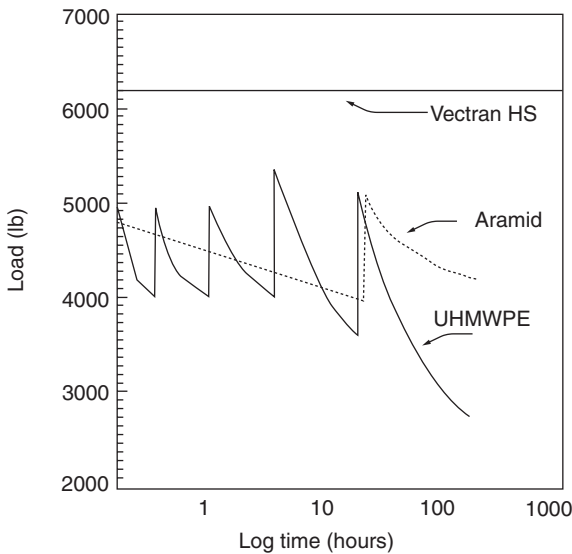
at a higher level, generally >4.0% OOY. These silicone finishes can be removed with hexane. TLCP fibre exhibits excellent fibre-to-fibre abrasion resistance when compared with other fibres in thread-line dynamic abrasion testing (Table 4.2). These relative values of abrasion resistance for the fibres listed are confirmed in tests of braided ropes. Wax or a combination of wax/silicone top-coated onto the fibre is also used to improve fibre-to-fibre abrasion resistance.

Bending properties: The high strength and modulus of both TLCP and aramid fibres are attributed to their highly oriented structure, although they are made by different processes and from different polymers. However, the flex fold characteristics of these fibres are very different. During flex fold testing, failure generally occurs by strain localization or energy absorption via the formation of kink bands, and also by fibrillation. Kink band formation has been studied by Dobb and McIntyre,² and Sawyer and co-workers.³⁻⁵ The kink bands are believed to be dislocations caused by buckling and breaking of the stiff polymer chains. TLCP and aramid fibres both show kink band formation with increased flex cycles. However, more energy is absorbed in kink-band formation in TLCP than in aramid, and it is believed that this results in the significantly increased resistance to failure in flex folding of TLCP fibres compared with aramids (Fig. 4.3). This is further demonstrated in fabric testing. Specifically, in one test a heavy roller was passed over the crease of a folded strip of sample fabric and the specimen was folded back upon itself in the opposite direction and rolled again (the total constituting one cycle). After 100 cycles, the tensile strength of the TLCP fabric sample was reduced by 0.8% as compared to 22% tensile strength loss for an aramid fabric sample.

Creep: Tests at ambient temperature show that TLCP fibres in thread-line form exhibit no creep when loaded at <50% of the breaking strength. Stress relaxation studies on a nominal 13 mm diameter wire rope construction confirmed the lack of change in TLCP fibres under tension (Fig. 4.4). When tested at 80°C, TLCP fibres exhibited some creep (0.8% after four days),



4.3 Tensile strength vs flexural fatigue of *Vectran HS* and aramids. Flex: Tinius Olsen/MIT, Modified ASTM D2176.



4.4 TLCP parallel strand rope stress relaxation. Whitehill Manufacturing Corporation WMCJETS/JETSTRAN 1-A VEC 1/2" Rope.

but less than the aramid tested (1.2%) and significantly less than the ultra high molecular weight polyethylene (UHMW-PE) tested (>25%).

Thermal effects: TLCP fibres retain their strength for short periods at elevated temperatures, but gradually decrease in strength over extended time

at elevated temperatures. For example, no strength loss was observed when the TLCP fibre was tested at ambient temperature following exposure to 195°C for 30 eight-hour cycles. Aramid fibre tested simultaneously exhibited considerable strength loss. However, when exposed continuously to 195°C for 30 days and subsequently tested at ambient temperature, TLCP fibre showed a 24% strength loss. TLCP fibres lose tensile strength when tested at elevated temperature. For example, when tested at 100°C, the tenacity of these fibres is reduced by 35%. At the other end of the spectrum, tests on the polymer from which the fibre is produced indicate no tensile strength reduction after exposure to -196°C (77°K).

Cut resistance: TLCP fibres generally demonstrate excellent cut resistance, although this can be dependent upon the test used. Early tests measured the load necessary for a 5 cm diameter blade to begin cutting a tensioned knitted fabric. The relative cut resistance ranking using this test was:

High-strength TLCP	3.4
Aramid	1.1
UHMW-PE	1.0

Other test methods give different fibre rankings depending on the cutting method (slice or chop), test load and speed.

Chemical resistance: Tests have shown that the polymer from which commercial TLCP is produced is hydrolytically stable, resistant to organic solvents, and stable to acids at <90% concentration and bases at <30% concentration depending upon time and temperature of exposure.

Adhesion: Tests with an adhesive activated development finish resulted in very good TLCP fibre adhesion to rubber, provided the fibre is processed properly downstream. TLCP fibres are used in solid composites and in polyurethane systems.

Ultraviolet radiation (UV): Similar to other highly oriented fibres, TLCP fibres exhibit poor resistance to UV. The fibres must be protected when exposed to UV over extended periods of time. This protection can be a jacket over a TLCP fibre rope or a protective film over a fabric. UV inhibitors are not added to the TLCP polymers used for fibre because of the potential for reducing fibre strength.

4.1.4 Applications

A summary of commercial markets for TLCP fibres is given in Table 4.3. Ropes and cables for dynamic applications requiring fibre-to-fibre abrasion resistance and good bend-over-sheave is the largest single market for TLCP fibres. End-products include towed arrays/streamers for off-shore exploration, halyards for racing yachts, restraint lines for race cars, and long lines

Table 4.3 Commercial uses for TLCP fibres

Market	Examples	Reasons for using TLCP fibre
Ropes and cables	Yacht ropes Towed arrays Control cables Fishing gear	Abrasion resistance, flex/bend-over-sheave, no creep, small terminations possible in eye-splice, cut resistance
Protective materials	Gloves	Cut resistance, abrasion resistance, resistance to bleach and dryer heat
Industrial fabrics	Sailcloth Inflatable structures	Flex/fold, dimensional stability, tear strength
Sports	Bow strings Hockey sticks Bicycle forks Tennis rackets/strings	No creep, abrasion resistance, vibration damping, impact resistance
Medical	Catheters Control cables	Abrasion resistance, no creep, gamma sterilisation
Paper/non-wovens	Insulating papers Speaker cones	Dielectric properties, vibration damping, low moisture absorption, tear strength

for tuna fishing. Small TLCP braids (e.g. ~1.5 mm diameter) are terminated in an eye-splice with a pin diameter:braid diameter ratio down to 1:1, important for applications where space is critical, such as in ships or aircraft, and adding to the uniqueness of TLCP fibres.

TLCP fibres are used with other high-performance fibres in the sophisticated sail designs for the America's Cup sailboats. The relatively high cost of the fibre generally prevents it from being used by the weekend sailor. The air bags used to land the Jet Propulsion Laboratory Pathfinder on Mars in 1997 were produced with TLCP fibre because of the flex/fold characteristics and tear strength of composite fabrics made from the fibre. These properties are being utilized in a broad range of inflatable structures. In addition, TLCP fibres have thermal vacuum stability for space applications.

High-performance fibres are broadly used in composites for tensile strength reinforcement. TLCP fibre is used in composites when its additional properties provide unique performance or solutions to specific problems. For example, it improves vibration damping for bicycle forks, hockey sticks and tennis racket handles. Its low moisture absorption results in greatly reduced stress cracking when used as a sewing thread in an epoxy/fibre composite.

TLCP fibres are used in non-implant medical applications such as

catheters and surgical device control cables. The material withstands gamma ray sterilization and is supplied in very low deniers for many of these applications. While there are no known health and safety issues related to the use of TLCP fibres, concern over the potential for litigation has prevented development of TLCP fibres for human implants. Nevertheless, its inertness, non-toxicity and bio-inactivity may bring significant potential for veterinary implants.

Recent developments in cutting and pulping technology allow the use of TLCP fibres for specialty insulating papers which take advantage of the excellent dielectric properties and low moisture absorption of the material for use in motors and printed circuit boards.

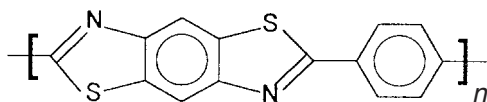
The market for TLCP fibres is growing in an expanding variety of specialty applications owing to the clear performance advantages achieved in end-use products because of the broad range of properties inherent in these fibres.

4.2 PBO and related polymers (RTY and CLS)

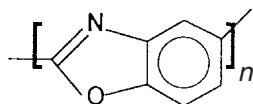
4.2.1 Introduction

Research at the Wright Research and Development Centre, Wright Patterson Air Force Base was directed in late 1960s and early 1970s toward the synthesis of highly fused aromatic heterocyclic polymers for high-temperature applications.⁶ The initial polymers synthesised under this programme were the ladder polymers BBB and BBL, but difficulties in processing prevented further progress as has been reviewed by Arnold and Arnold.⁷ In the 1970s, DuPont reported that extended chain, all para-aromatic polyamides ('aramids') gave high strength, high modulus fibres when processed from liquid crystalline solutions.⁸ The ability greatly to increase the order in the liquid crystalline state, compared to conventional polymer solutions, offered an excellent opportunity to design and process new para-ordered polymer systems for fibre-reinforced composites. The synthetic effort at Wright laboratories began to focus on aromatic heterocyclic systems, other than ladder polymers, with a para-ordered geometry. One class of heterocyclic polymer system that could meet all the harsh requirements for advanced aircraft and aerospace applications and could be obtained in the form of fibres was the benzobisazole materials,⁶ which have five-membered rings on either side of benzene rings. Poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBT) have received the most attention.

The molecules of PBO and related polymers are characterised by high rigidity and form highly ordered structures. The discovery of this highly ordered structure led to the term 'ordered polymers' for the aromatic



(a)



(b)

4.5 Chemical repeat units of related ordered polymers (a) PBT (b) ABPBO.

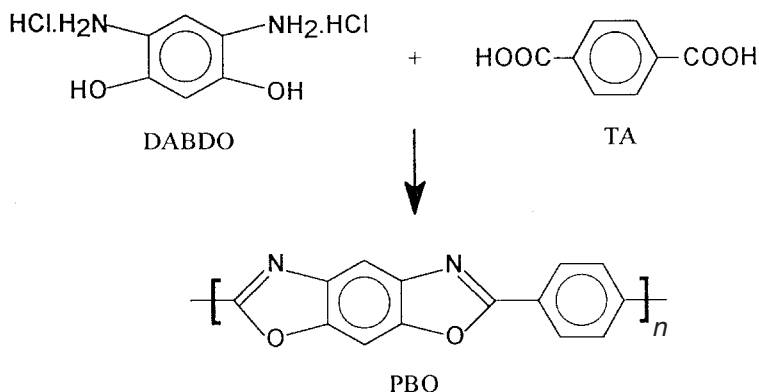
heterocyclic rigid rod polymers such as PBO and PBT. The term also includes some semi-rigid polymers such as poly(2,5(6)-benzoxazole) (ABPBO) and there have been a number of detailed reviews in the area of ordered polymer fibres.^{6,7,9-12}

PBT is a rigid-rod polymer, shown in Fig. 4.5(a), in which sulphur replaces the oxygen in PBO, and its fibre manufacture is similar to that of PBO, as described below. PBT is synthesized by the polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TA), in a poly(phosphoric) acid (PPA) solution^{6,7} and then spun into fibres via the dry-jet wet-spinning process. PBT fibre has excellent mechanical properties similar to those of PBO although not quite as good; this is mainly due to the slight differences in synthesis and processing. The high cost of manufacturing PBT has allowed the PBO fibre production to become more dominant.

ABPBO is a semi-rigid ordered polymer with high thermal stability, but the chain stiffness is much lower compared with PBT and PBO¹⁰ owing to the presence of kinks in the main chain, Fig. 4.5(b), and thus it does not have the stiffness required for use as a reinforcing fibre. It does, however, have good thermal properties.

4.2.2 Manufacture of PBO fibres

PBO is manufactured via the monomer synthesis of 4,6-diamino-1,3-benzenediol dihydrochloride (DABDO), developed by Wolfe,⁶ and a simplified synthetic route to PBO is shown in Fig. 4.6. This involves the condensation polymerisation of DABDO with terephthalic acid (TA) carried out in poly(phosphoric) acid (PPA). Stoichiometric amounts of amine and



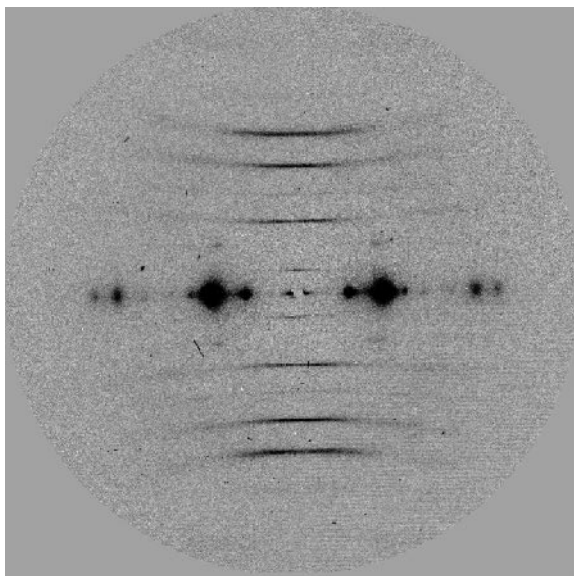
4.6 Simplified schematic of PBO polymerisation.

TA are heated in 77% PPA at 60–80°C for the dehydrochlorination of the amine monomer. The temperature is lowered to 50°C and P_2O_5 is added to obtain the high degree of polymerisation (between 82–84%) that is favoured for the dehydration of PPA and drives the polycondensation to completion.⁶ A relatively more economic synthesis route for PBO monomer using 4,6-diaminoresorcinol has been produced at the Dow Chemical Company.⁹

Rigid rod polymers decompose at high temperatures without melting and can be dissolved in very few solvent systems owing to their aromatic structure and to their rigid molecular backbone. Conventional melt-spinning and solution-spinning technologies cannot therefore be used. These fibres, however, can be spun from solutions in PPA via the dry-jet wet-spinning technique,⁹ as described in Chapter 2. This involves extrusion of polymer solution (liquid crystalline phase) under heat and pressure through an air gap into a coagulating bath (generally water at room temperature), followed by washing, drying, and finally heat treatment. Heat treatment is usually carried out in the 500–700°C range under tension, in nitrogen, for between a few seconds and a few minutes. The structure formed during coagulation shows a network of oriented microfibrils. This network serves as a basis for the structure and properties of the final material.

4.2.3 Structure of PBO fibres

The degree of molecular alignment present in PBO fibres can be determined using wide-angle X-ray scattering (WAXS). Figure 4.7 shows a WAXS pattern obtained from a single PBO fibre using synchrotron radiation.¹³ The sharp equatorial peaks indicate that the crystallites are well

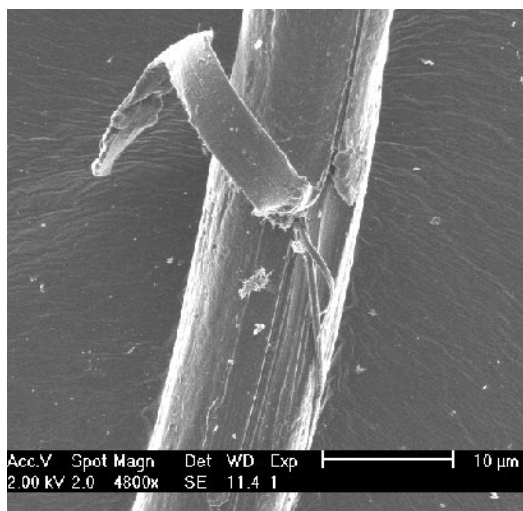


4.7 Wide-angle X-ray diffraction pattern of a single PBO fibre, showing the high degree of molecular orientation characteristic of rigid-rod polymer fibres. (The fibre axis is vertical).

aligned parallel to the fibre axis, whereas the streaks up the meridian are a result of scattering from the highly aligned PBO molecules.

A hierarchical microstructure for high-performance polymer fibres has been proposed by Sawyer *et al.*¹⁴ A fibre is envisioned to comprise macrofibrils, fibrils, and microfibrils, with typical diameters of 5, 0.5 and 0.05 μm , respectively. The microfibrils consist of crystallites in combination with amorphous or disordered regions. Figure 4.8 shows a scanning electron micrograph (SEM) from a damaged PBO fibre revealing the underlying fibrillar structure. Although a fibril structure is the common feature of high-performance polymer fibres, the dimensions cannot always be discerned from the ratios indicated in this model, i.e. different high-performance polymer fibres have different fibril structures owing to the various molecular structures and processing conditions.³ Kitagawa *et al.*¹⁵ have proposed a similar structure for as-spun PBO fibre, where the microfibrils run parallel to the fibre axis with inherent voids between them. The fibrils consist of highly oriented PBO molecules parallel to the fibre axis, with the *a*-axes of the crystals aligned radially across the fibre.

Additionally, heat treatment results in fibres that have improvements in their overall axial orientation, crystal perfection and lateral order, leading to improved mechanical properties. The existence and magnitude of the



4.8 Scanning electron micrograph of a damaged PBO fibre, showing the surface skin and fibrillar structure.

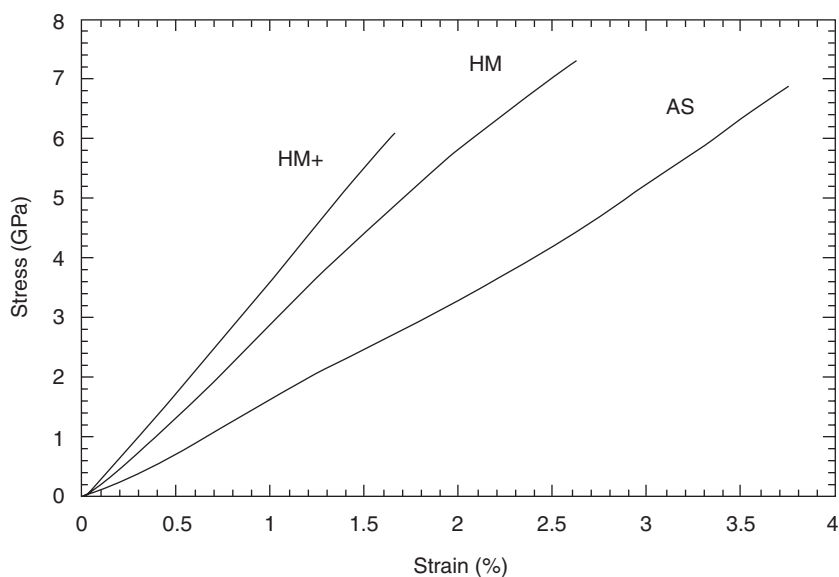
skin/core differences (Fig. 4.8) are believed to be the result of processing conditions, such as solvent diffusion and fibre coagulation.

4.2.4 Properties of PBO fibres

The excellent mechanical properties of PBO fibres compared with other high-performance fibres (Table 4.4) are accompanied by equally impressive thermal properties (Chapter 9). PBO fibres exhibit very high flame resistance and have exceptionally high thermal stability (onset of thermal

Table 4.4 Mechanical properties of a range of high-performance fibres^{8-11,16,17}

Fibre	Density (g/cm ³)	Tensile modulus (GPa)	Tensile strength (GPa)	Compressive strength (GPa)
PBO	1.56	280	5.8	0.20
PBT	1.58	325	4.1	0.26–0.41
'M5'	1.70	330	4.0	1.00
<i>Kevlar 49</i>	1.45	125	3.5	0.35–0.45
Twaron HM	1.45	115	3.2	0.45
P100	2.15	725	2.2	0.48
T300	1.80	230	3.2	2.70–3.20
Alumina	3.70	350	1.7	6.90
E-glass	2.58	76	3.4	4.20



4.9 Stress–strain curves for different PBO fibres. (After Kitagawa *et al.*²⁰)

degradation in the 600–700 °C range). PBO fibres also have very good resistance to creep, chemicals and abrasion. However, the poor compressive strength of these fibres restricts their use in composites (Table 4.4). Under compression, the failure of polymeric fibres is via kinking.¹⁸ Unlike carbon and inorganic fibres, polymeric fibres do not exhibit a catastrophic failure in compression. The kinks in polymeric fibres develop at the yield point in compression. Attempts have been made to improve the compressive strength of ordered polymeric fibres via processing variation (fast and slow coagulation), crosslinking and structural disruption. None of these approaches has resulted in significant improvements in compressive strength.

Toyobo have recently succeeded in improving PBO fibres further in laboratory experiments by adopting a non-aqueous coagulation system and a new heat-treatment method.¹⁹ It is important to implement a slow coagulation process during fibre production because the prestructure of the fibre induced before heat-treatment determines both the final fibre structure and its mechanical properties. The modulus of the improved PBO fibre thus obtained can be as high as 360 GPa. Figure 4.9 shows a series of single-fibre stress–strain curves for different PBO fibres.²⁰ The as-spun (AS) fibre has the lowest Young's modulus, which is improved by heat treatment in the HM fibre. The HM+ fibre produced using the non-aqueous coagulation

system has the highest Young's modulus. It should also be noted from Fig. 4.9 that individual fibres can have very high values of strength, in excess of 7 GPa, although lower average values are normally quoted (Table 4.4).

The HM+ fibres also show an absence of the four-point small-angle X-ray scattering pattern that is characteristic of the morphology of heat-treated PBO fibre obtained using the normal (aqueous) coagulation process.¹⁹ The apparent crystal size measured is almost the same as for the HM fibre and the molecular orientation is slightly higher for the improved HM+ fibre. This implies that factors other than just molecular orientation are concerned with improving moduli.

4.2.5 Applications of PBO fibres

The applications of PBO fibres are vast²¹ owing to the excellent properties mentioned previously. Current PBO fibre composites, however, appear to be limited mainly to secondary structures and non-structural uses where axial compressive loading is minimised. Therefore, significant improvement in the compressive properties of PBO would be a major breakthrough.¹⁰ Secondary structures that benefit from the excellent mechanical properties are found in such diverse areas as athletic equipment and high-fidelity speaker cones, in which good dielectric properties are important. Non-structural applications may take the form of woven fabrics and cables. PBO fabrics are light and flexible, providing improved comfort and mobility, and are ideal for heat and flame resistant work-wear such as for fire fighters. Motorcycle suits have particular areas, such as the knee and elbow regions, reinforced with PBO fabric, providing the required excellent heat, flame and abrasion resistance. As with aramids, PBO is ideal for ballistic-protection fabrics and panels owing to its high energy absorption and rapid dissipation of impact by the fibrillar morphology. Another application utilising the excellent thermal properties is heat-resistant felt, which is now being used by glass manufacturers as mats on which the hot, shaped-glass fabrications are placed for cooling. General applications for reinforcement include those for tyres, belts, cords, etc., as well as for optical fibre cables.

4.2.6 Conclusions

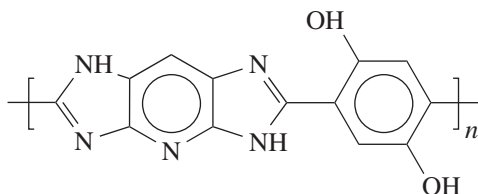
PBO fibres are the successful result of a research programme aimed at designing, synthesising and processing rigid-rod molecules into ordered polymer fibres with exceptional mechanical properties. The fibres are now being commercialised by Toyobo Co. Ltd of Japan under the trade name *Zylon*®. They are finding use in a number of applications where they have benefited somewhat from the development of a market for such materials through the exploitation of aramid fibres. PBO fibres have specific (per unit

weight) values of strength and stiffness in excess of all other materials and their future appears to be very promising indeed.

4.3 PIPD or 'M5' rigid-rod polymer (DJS)

4.3.1 A new HM-HT fibre

As a result of research in Akzo-Nobel laboratories a new high-performance fibre, known as 'M5', has been produced. The polymer is poly{2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene} or PIPD, with the formula:



Two methods have proved effective in preparing high modulus, high tenacity (HM-HT) polymer fibres:

- perfecting the drawing technique of precursor fibres to attain draw ratios far above ten, as in the well-known polyethylene *Dyneema* and *Spectra* yarns²² described in Chapter 3.
- manipulating rigid rod-like molecules into fibres that are already very highly oriented in the as-spun state, as in PPTA fibres,²³ described in Chapter 2.

Work has been directed at much stiffer rigid rod-like materials, culminating in the PBO fibre (Section 4.2) that is now becoming commercially available from Toyobo after much development at Wright-Patterson AFB, at SRI International and at Dow Chemical.^{23a,24} Although PBO shows very impressive tensile properties, its performance under compression has been disappointing, and much work has been done in various ways to correct the problem, without making much headway. Various schemes have been tried to increase lateral strength in PBO after fibre formation,²⁵ often by crosslinking. One attempt at introducing hydrogen bonds in such a polymer did not afford the improved compression performance hoped for; its lack of success in attaining improved compression properties was attributed to the hydrogen bonds being formed intra- rather than inter-molecularly.²⁶

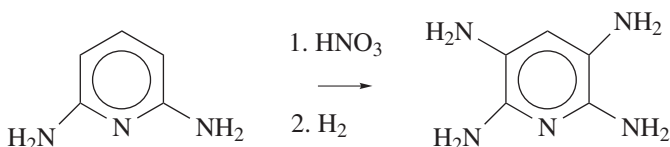
It has been the ambition of this author to create polymers as *rigid rod-like* as PBO, with *strong intermolecular hydrogen bonds*.

After much experimentation, some of which has been reported,²⁷ we turned our attention to the well-proven (albeit experimentally challenging, see

Ref. 25) polymerisation of one-ring aromatic tetrafunctional nucleophiles. An example of high merit appeared to be 2,3,5,6-tetraaminopyridine: 2,6-pyridinediamine, a commercial product, fairly simply accessible by Chichibabin amination,²⁸ and, importantly, nitration was expected to be highly selective to produce the 3,5-dinitro isomer. Literature reports existed on this nitration, albeit with low yield after purification,²⁹ as well as on polymerisation of the tetraamine HCl salt (along the USAF-SRI (US Air Force-Stanford Research Institute) lines²⁵ for PBO), with isophthalic acid to prepare a thermally stable polymer.³⁰

4.3.2 Monomer selection and syntheses

Synthesis of 2,3,5,6-tetraaminopyridine (TAP) along the lines of Gerber,³⁰ with low yield after nitration, and including reduction with tin/hydrochloric acid, afforded our early samples of TAP.

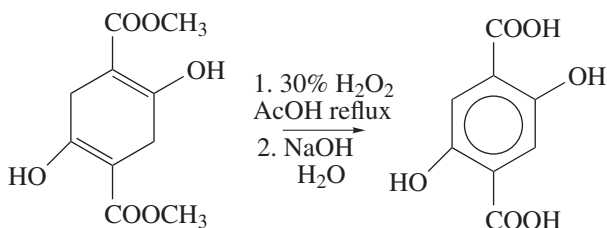


In early work, we isolated TAP as the hydrochloride salt and used it in the polymerisation, see Ref. 25. The nitration problems were soon corrected by modifying the nitration medium – changing from concentrated sulphuric acid²⁹ to oleum.³¹ Thus, we could isolate high-purity products at 90–95% from the nitration and 85% yield of polymer grade purity crystal (TAP.3HCl.1H₂O) from the reduction with hydrogen. Having a sufficient supply of TAP in hand, we tackled the polymerisation. Reaction according to the method developed in Ref. 25 with terephthalic acid produced almost instantaneous precipitation of very low molecular weight (MW) oligomer.

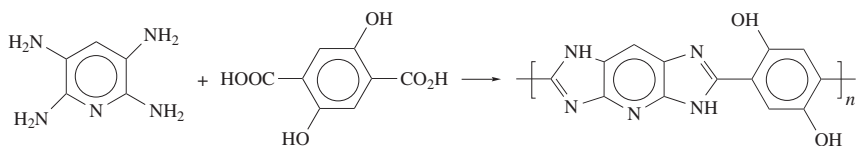
Polymerisation with 2,5-dihydroxyterephthalic acid seemed desirable in itself because the hydroxyl groups could³² contribute to the hydrogen bond network envisioned; the reaction led to high molecular weight products, in contrast to the results with unsubstituted terephthalic acid. Thus, not only an enhanced-polarity polymer proved accessible, in fact the analogue with fewer active protons could not be prepared in a usable form. Concentrations of almost 20 wt.% of polymer in solution in PPA could be attained. By contrast, 1,2,4,5-tetraaminobenzene³³ (which likewise gives insoluble, very low MW material with terephthalic acid)³⁴ proved to have a solubility limit in its high-MW polymer with 2,5-dihydroxyterephthalic acid of about 8.5%, in related work in our laboratory.³⁵

2,5-Dihydroxyterephthalic acid (DHTA) is described in the literature as the product of bromine/sulphuric acid mediated aromatisation³⁶ of diethyl

succinoylsuccinate, a commercial product, followed by hydrolysis. The aromatisation can also be effected with sulphur,³⁷ or with sulphur and a Pd/C catalyst.²⁷ We found a convenient and non-noxious procedure in aromatising the succinoylsuccinate in acetic acid at reflux with 30% aqueous hydrogen peroxide and a sodium iodide catalyst. After hydrolysis, >90% of polymer grade DHTA³⁸ from succinoylsuccinate can be isolated upon acidification. Alternatively, the sodium salt of DHTA can be crystallised from the hydrolysis reaction mixture in high purity and somewhat lower yield (*ca* 87%).



4.3.3 Polymerisation



Right from the outset of our work with TAP hydrochloride and DHTA, we avoided the experimental difficulties inherent in the traditional²⁴ method of adding most of the phosphorus pentoxide and the organic diacid only after driving off the hydrochloric acid by heating in 'weak' polyphosphoric acid (PPA). When working at a small scale at least, we could add all ingredients at the outset of a heating cycle that involved (see Ref. 24) many hours of heating at about 100 °C while evacuating, to eliminate the hydrochloric acid. An important improvement was found in isolating TAP as its phosphoric acid salt, resulting not only in a much faster polymerisation cycle, but also eliminating the corrosion-type difficulties implicit in the earlier route. A much greater step forward was achieved by the synthesis of the TAP-DHTA 1:1 complex, or TD salt. This complex is significantly more stable against oxidation than TAP phosphate and it precipitates in a high yield from the combination of aqueous solutions of TAP HCl salt and DHTA Na or K salt. A fast polymerisation cycle (typically 4–5 h, rather than >24 h according to Ref. 24) now yields high MW polymer much more consistently than in the case where amine and acid components are weighed separately: relative

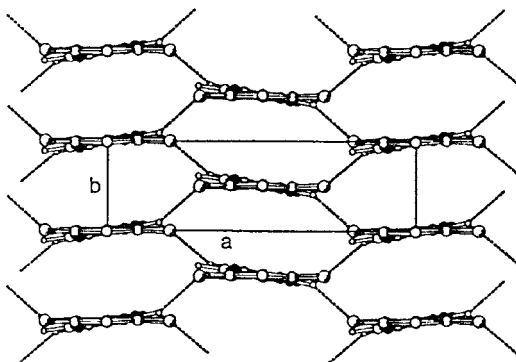
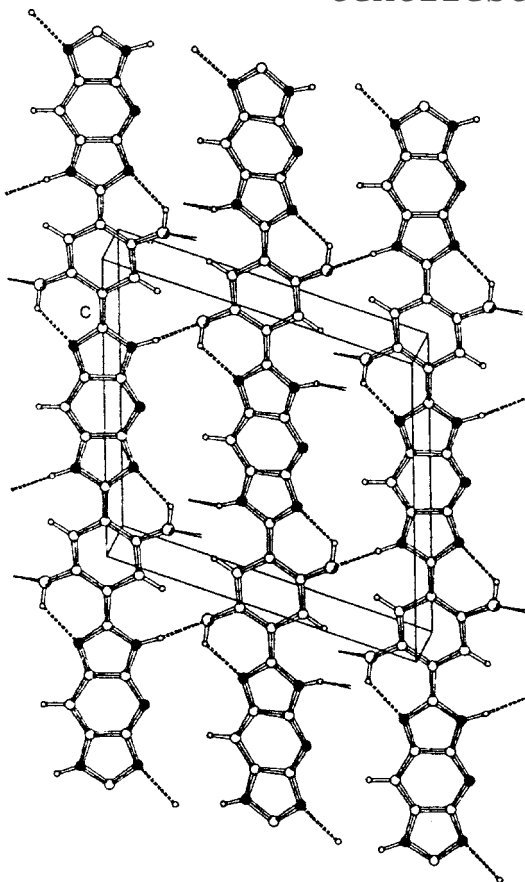
viscosities (0.25 g/dl in methane sulphonic acid) of 50 and above could be reached routinely. We did not succeed in preparing the terephthalic acid salt of TAP, which we attribute to the weaker acidity of terephthalic acid.³⁹ Thus, copolymers employing both DHTA and terephthalic acid (TPA) necessitated use of TAP phosphate and TPA next to TD salt. Such copolymers showed lower relative viscosities when more TPA was used as a comonomer, and became insoluble in the polymerisation medium when more than 50% of DHTA was substituted by TPA.

The polymerisation of homopolymer consists of taking TD salt, polyphosphoric acid and P_2O_5 with a trace of tin powder into the reactor, displacing air by nitrogen and raising the reaction temperature to 140°C. Mixing for at least 1.5 h at that temperature before taking the mixture to 180°C and stirring for another 1–2 h yields the spinning solution. The solution becomes liquid crystalline about 1 h after it reaches 140°C. Work on the mechanism of PBO polymerisation has been reported.⁴⁰

The P_2O_5 content of the solvent system controls the final molecular weight, and obviously only the highest purity TD salt will deliver the highest MW polymers. The solubility limit of high MW homopolymer in 80.5–83% PPA (i.e., a PPA consisting of 80.5–83% of P_2O_5 , the balance being water) is 19 wt.%. At 180°C, the solution (18 wt.% of polymer) is a nematic solution with long relaxation times of orientation; upon cooling, it crystallises at about 110°C; the crystallised solution melts at about 140°C. A further thermal transformation can be seen at about 80°C by DMA (dynamic mechanical analysis). Crystallosolvate fibres of astoundingly high and perfect crystallinity could be prepared under special conditions.⁴¹

4.3.4 Spinning and fibre properties

Conventional air gap wet-spinning of the as-polymerised solutions of polymers with M_w 60 000–150 000 (Twaron aramid calibration SEC (size exclusion chromatography) in methane sulphonic acid) at 180°C into a water or dilute phosphoric acid bath, proceeded readily; spin-draw ratios attainable depend on spinning orifice diameter and the result normally delivers filaments with a diameter of about 10 μ m, which are further washed to a low phosphorus content and drawn (by a few percent at most) at high temperature (>400°C) to produce the final, high modulus product. It is unclear whether the crystal solvate can form in this process characterised by very fast cooling. The coagulated and washed fibre is isolated as a crystal hydrate and the hot drawing process transforms this into the final high modulus 'M5' crystal structure.⁴¹ The as-spun fibre already shows attractive mechanical properties, comparable to para-aramid fibres, although the modulus is higher (about 150 GPa). The as-spun fibre excels in fire resistance.⁴² The crystal-to-crystal transformation during the hot drawing leads to a much



4.10 The crystal structure of M5-HT seen along the chain axis. Note the bidirectional hydrogen bonded network between the chains resembling a honeycomb and reinforcing the lateral chain-chain interaction. This leads to a high shear modulus and shear strength and thus to good compressive properties of the M5 fibre. We speculate that this honeycomb-like structure may be involved in the explanation of the impact and damage tolerance properties of M5 products.

higher modulus, owing to a more slender effective chain and much stronger interchain bonding, coupled with an improvement of the orientation.⁴¹ Note that the fibre modulus depends on the shear modulus through non-perfect orientation of the molecules.⁴³

Evolution of fibre structure and morphology, and its properties, during the manufacturing process is discussed in detail by Lammers *et al.*⁴¹ The final crystal structure is analysed by Klop and Lammers⁴⁴ and illustrated in Fig. 4.10. The rod-like polymer molecules feature internal hydrogen bonds between –O–H groups and imidazole N atoms, and a *network in both directions perpendicular to the rod-like chains* between imidazole N–H atoms and the –O–H groups.⁴⁴ For the determination of this hydrogen-bond structure, it was not sufficient to ascertain the precise arrangement of the heavier atoms, but further measurements were needed. The fact that over a very large temperature range, both directions perpendicular to the polymer chain direction showed the same thermal expansion was the final lock on the proof of the three-dimensional (3D) network character of the hydrogen-bond system (as opposed to a sheet-like character),⁴⁴ as an independent observation in addition to the very high shear modulus determined from the relation⁴³ between molecular orientation and fibre properties.⁴¹

Even though much optimization remains to be done, we soon achieved promising mechanical properties and structure data in our new ‘M5’ fibres, even from bench scale operations using improvised machinery. Moduli well over 300 GPa, tenacities of over 2.3 N/tex (4 GPa), elongations at or above 1.5% and compressive strengths of 1.7 GPa (onset of plastic deformation) were recorded – the highest compressive yield strength by far shown by any polymer fibre.⁴¹ Tensile and compressive deformation were investigated by micro-Raman spectroscopy, with qualitatively the same conclusions.⁴⁵ The good compressive properties are coupled to a very high internal shear modulus of 7 GPa.⁴¹ The first composite test bars that were tested for longitudinal compressive strength confirmed the high compressive properties of the new fibre in composite form.⁴⁶ Three-point bending tests of composite bars pointed to a compressive yield stress of 1.75 GPa in the fibre.⁴⁶

Ab initio calculations were performed on the M5 molecule and crystal.⁴⁷ A chain modulus of 553–578 GPa was concluded (depending upon details in the unit cell), in good agreement with the experimental chain modulus from WAXS measurements of 510 GPa.⁴¹ The internal hydrogen bond contributes to this particularly high value.

Work is proceeding to spin fibres with properties exceeding the values given in Table 4.5 for early experimental samples of the new⁴⁸ fibre. Details of convenient laboratory-scale procedures for preparing the monomers and the polymer have been published;⁴⁹ alternative routes intended for scaling up were worked out also.^{28,31,38}

Table 4.5 Provisional characterisation of M5 fibre, *spun at bench scale*, compared with commercial fibres

	Twaron HM	Carbon HS	PBO ^b	M5 experimental
Filament averages, except carbon HS ^a				
Tenacity, GPa	3.2	3.5	5.5	5
Elongation, %	2.9	1.5	2.5	1.5
E-modulus, GPa	115	230	280	330
Compr. str., GPa ^c	0.58	2.1	0.4	1.6
Compr. strain, % ^c	0.5	0.9	0.15	0.5
Density, g/ml	1.45	1.8	1.56	1.7
Water regain, %	3.5	0	0.6	2
LOI, % O ₂	29		68	>50
Onset of thermal degradn, air, °C	450	800	550	530
Electr. conduction	–	++	–	–
Impact resistance	++	--	++	++
Damage tolerance	+	--		++
Weaving props	+	–	+	+
Knot strength	+	--	0	0

^aMechanical properties of carbon are evaluated in resin-impregnated strands to protect the material against premature brittle failure in the tensile testing machine. (The organic fibres are tested as such: filament averages at 10 cm gauge length are presented.)

^bToyobo data.

^cMeasured in UD composite test bars, three-point bending test, onset of deflection for the organic fibre-reinforced composites; catastrophic failure for the carbon composites. M5 composites proved to be able to carry much higher loads than the load at onset of deflection in these tests, and to absorb much energy at high strains in a mode analogous to the ductile behaviour of steel structures being overloaded.

4.3.5 Applications and outlook

The mechanical properties of the new fibre make it competitive with carbon fibre in most applications – in light, slender, load-bearing *stiff* advanced composite components and structures. Very promising indications were obtained pointing to a *ductile* failure mode of (bending and compression) test pieces, notwithstanding the high stiffness. Similarly, such very stiff composite test pieces showed outstanding *impact* properties in scouting experiments. This suggests the possibility of designing, for instance, vehicle parts substantially lighter than can now be done on the basis of *brittle* reinforcing fibres. The ductile (as opposed to brittle) properties of the fibre under (bending; compression) overload conditions also explain the easy *processability* of the new fibre in textile-type operations (weaving, knitting, braid-

ing, and so on). Exploratory evaluation of the *UV stability* of M5 indicated excellent performance in that field, unsurprising in view of its chemical similarity to existing commercial UV stabilisers. The high *electrical resistance* of the new fibre would enable it to perform in areas where carbon fibre presents problems (corrosion in metal contacts) or is unsuitable, such as in electrical and electronic contexts. The high polarity of M5 aids in easy *adhesion* to a variety of matrix materials, judging by bundle pull-out tests performed with various epoxy, unsaturated polyester and vinyl ester resins. These gratifying results were obtained without any optimisation, suggesting further possibilities of even higher or (if needed) specifically tailored adhesion levels, depending on the application.

Stepping up from the bench scale to semi-technical, and later technical scale manufacture of this fibre is being addressed by Magellan Systems International, with special emphasis on further optimisation of its properties.

4.3.6 Acknowledgements

In addition to my colleagues, then at Akzo Nobel Central Research, whose names are in the references to this paper, special thanks are due to Antoine Duindam for his indefatigable efforts in improving our syntheses and polymerisation procedures, and to Henk ter Maat, and Bert-Jan Lommerts for their pioneering work in spinning the new polymer. The expertise and professionalism of many further colleagues, especially Leo Busscher and Bart Janssen, made it possible for this study to progress from a laboratory-scale curiosity to a multigram venture producing fibre samples on a sufficient scale for a first and successful evaluation in filament winding and pultrusion. The invaluable help of Noor van Andel to make this project survive in the corporate environment is also gratefully acknowledged.

4.4 Russian aromatic fibres (KEP)

4.4.1 Monomers and polymers

The search for aromatic fibres with high strength and stiffness began in Russia (by Prof. Georgy I. Kudryavtsev, All-Russia Research Institute of Polymeric Fibres) in the 1970s. The research generated an extensive literature,^{50–183} which is not well known by much of the world. The investigations concentrated on:

- polymers based on poly-(*p*-phenylene terephthalamide) (PPTA) and related copolymers
- heterocyclic para-polyamides and para-copolyamides – para-heteroarylenes (PHA), mainly poly-para-amidobenzimidazole, which

is used here as a contraction for poly(terephthaloyl-2-*p*-aminophenyl-5-aminobenzimidazole)

- other heterocyclic aromatic polymers – polyimides, polyoxazoles, separate semi-ladder polymers, etc.

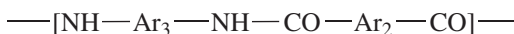
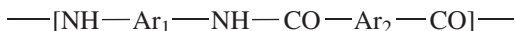
The main reactants that were investigated are presented in Fig. 4.11 (indicated by their residues). This list includes raw materials for polymers of regular and irregular molecular structure and statistical copolymers.

The research led to the production of the following fibres:^{50,51,60,61,67,68}

- *Terlon*® – PPTA copolymer including diamines selected from the left column of Fig. 4.11.
- *SVM*® (formerly *Vnivlon*®) – aromatic heterocyclic polyamide of principal chemical constitution:



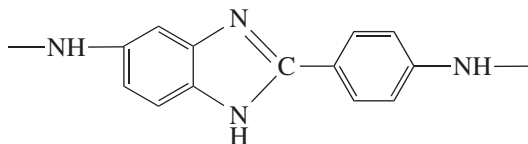
- *Armos*® – aromatic heterocyclic copolyamide of principal chemical constitution:



Terlon is an aramid copolymer fibre, based on PPTA with up to 10–15% comonomer content. Its manufacture, structure and properties are similar to other aramid fibres, which are described in Chapter 2, although the *Terlon* copolymer is not the same as the copolymer in *Technora*. This section concentrates on the *SVM* and *Armos* fibres.

The aromatic groups that are shown in the above heterocyclic polyamide formulae are as follows:^{68,168,169}

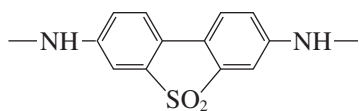
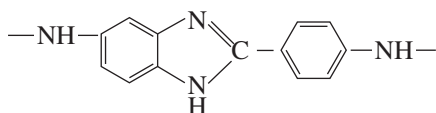
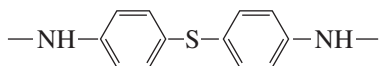
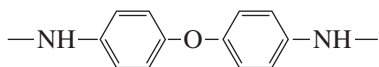
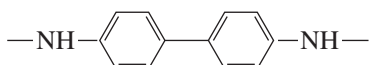
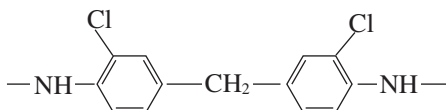
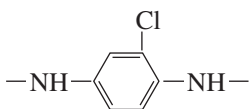
- $\text{—[NH—Ar}_1\text{—NH]—}$ is the heterocyclic diamine:



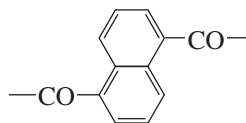
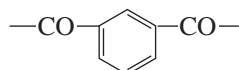
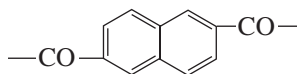
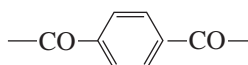
- $\text{—[CO—Ar}_2\text{—CO]—}$ is the residue of terephthalic acid shown at the top of the right column in Fig. 4.11
- $\text{—[NH—Ar}_3\text{—NH]—}$ is the residue of *p*-phenylenediamine shown at the top of the left column in Fig. 4.11

The first publication about the PHA fibre *Vnivlon*, now *SVM*, was written in the middle of 1969. *Armos* is a higher tenacity fibre and yarn that retains the high thermal and fire-resistant properties of *SVM*. Creation of *Armos* was the principal step after the elaboration of *SVM* fibres. This achievement

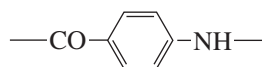
Diamines



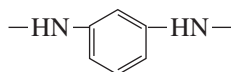
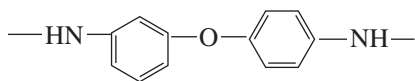
Dicarboxylic acids



Aminoacid



Diamines



4.11 Structural units derived from reactants investigated in Russian HM-HT fibre research.

is the result of joint work (investigations and production) by the All-Russian Research Institute of Polymeric Fibres and the 'Tverchimvolokno' Joint-Stock Company.⁵⁴⁻⁶¹

PPTA and the copolymer in *Terlon* form liquid crystals in solution, which are oriented in spinning. However, our view is that it is not necessary to have a liquid crystalline state as the initial state in the dope for making super-high tenacity fibres. The non-crystalline solutions of poly-*p*-heteroarylenes give higher tenacity fibres, but do not have the ability to

crystallise in solutions or in the solid state. There is an opinion that PHA polymers transform to a liquid crystalline or quasi-crystalline state during the structure building process, but this transformation is not proven.

The high thermal properties of aramids are the result of their wholly aromatic structure, but heterocyclic units, such as those in PHA polymers, lead to increased thermal and fire resistance.

4.4.2 Polymer solutions and fibre formation

Heterocyclic para-polyamides and para-copolyamides (PHA) are soluble in highly polar aprotic amide solvents with addition of lyophilic salts (in particular dimethylacetamide with the addition of lithium chloride or calcium chloride).^{50,58–60,62,74–76} They do not create a liquid crystalline state, owing to their irregular molecular chain structure. Their solutions are isotropic and therefore have high viscosity. For a suitable spinning viscosity, the dope concentration must be limited: 5–6% concentration gives a viscosity of 50–70 Pa s.^{50,67,73–76} These solutions are structured and their rheological properties are classical for non-crystalline high polymers solutions of this type.

The spinning solutions are directly obtained from the synthesis of PHA polymers. They contain hydrogen chloride, which is ionically connected to tertiary nitrogen atoms.^{73,83,84} The role of this complex is important both in viscosity regulation and in orienting effects during fibre formation, owing to neutralisation (discharging) of polar tertiary nitrogen groups and therefore increase of molecular chain rigidity. Both these effects lead to more ordered packing in structure building during fibre formation. It is interesting to note the same effects in the case of other rigid polymer solutions (for example, xanthogen groups neutralised by sodium hydroxide in viscose) and the pH dependence in concentrated protein solutions. Variation of the electrically charged ionised group leads to changes in molecular chain rigidity and therefore influences the process of fibre formation.

PHA fibres are produced by a normal wet-spinning process from solution into an organic or water bath. This method is used for the organic solvent solutions of heterocyclic para-polyamides (poly-*p*-amidobenzimidazole) and heterocyclic copolyamides. This process is carried out at low speed (12–25 m/min) with a long fibre-forming time. The fibre structure is thus built up by a ‘soft’ spinning bath action, which allows for simultaneous solidification over the whole cross-section. Coagulation is followed by wet drawing at a higher take-up speed. Fibre formation in a tube which has a spinning bath stream allows for an increased spinning velocity and leads to more uniform fibre bundle (yarn) formation. The molecular orientation of as-spun fibres results from the transverse velocity gradient flow in the spinneret orifices, which is due to the high ratio of orifice length to diameter,

and after that from stretching the extruded fibres in a plasticised state. The formed fibres are washed to remove solvent and dried. Simultaneous structure building in the cross-section of fibres is necessary to create a homogenous macrostructure. The as-spun fibres have a gel structure that includes a large amount of immobilised solvent. Cross-section contraction during fibre drying leads to additional structure orientation.^{94,95} After drying, the fibres from this wet method of formation have a deformation modulus of 50–70 GPa and a tenacity of 0.8–2.0 GPa. The fibre-formation process has been extensively researched.^{50,62,67,75,76,86,88–95}

Thermal treatment is the next stage of processing. This occurs in a temperature range approximately 100 °C higher than the glass transition temperature, and leads to spontaneous structure ordering in the fibres.^{50,62,67,75} The thermal treatment at 350–450 °C may be either uninterrupted or interrupted, with or without a small loading. The additional drawing (2.5–5.0% only) is applied in order to increase mechanical properties.^{50,96} The self-ordering, orientation and number of stress-holding molecular chains increase, and hence there is an improvement in mechanical properties into the range for dynamic modulus of 130–160 GPa and for tenacity of 4.0–5.5 GPa.

The conventional view, which applies to the aramid fibres described in Chapter 2 of this book and to the Russian fibre *Terlon* produced in a similar way, is that in order to obtain the right structure, it is necessary to start with a liquid crystalline state in the polymer solution. This is right, but is not the only possibility. Limited aggregation in solution also gives the possibility of high orientation and chain extension. This may be a thermodynamically more advantageous state of 3D order for homopolymers in conflict with kinetic peculiarities for creation of maximal high-ordered fibre structure. The new polymers and copolymers with controlled molecular regularity and rigidity were optimal for improving fibre properties. Our experience shows that better results will be obtained if the initial solution is not liquid-crystalline, but is isotropic, and the transition to a liquid crystalline state is during the time of structure building by fibre formation. The rapid crystallisation of para-aramids prevents attainment of high orientation order, owing to reduced molecular mobility during the stages of fibre structure formation by spinning and of thermal treatment.⁶⁷ The progression from *Terlon* (PPTA copolymer, liquid crystalline in solution) to *SVM* and *Armos* (hetero-aromatic polymer and copolymer fibres, non-crystalline in solution) illustrates this situation.

4.4.3 Fibre production

The scheme for production of *Terlon* fibre is similar to that for other aramid fibres. PHA fibres and yarns, on the other hand, are produced from ‘direct’

solutions immediately after their formation during polymer synthesis. The principal scheme of this process is shown in Fig. 4.12.^{59,105,179,183} Homopolymer and copolymer synthesis (poly-*p*-benzimidazole type) is based on polycondensation in solution (dimethylacetamide with addition of lithium chloride) of terephthaloyl chloride with heterocyclic diamine and, for the copolymer, *p*-phenylenediamine. There is a possibility of either a one-stage or a two-stage polymer synthesis process, the first stage being oligomer synthesis and the second further polycondensation. The solutions are isotropic and their concentration is limited to 5–6% by viscosity value. Polymer solutions are made by a classical scheme: mixing, filtration and degassing. Of great importance for spinning dope is careful removal of impurities and gel particles by filtration. Therefore, there are two filtration operations, first of oligomer solution and then of polymer solution, before the stages of degassing and subsequent transport of the solution to fibre extrusion.^{58,59}

The fibre formation process is by a wet method into a water–organic spinning bath, or, in some cases, to an organic–organic spinning bath, such as dimethylacetamide plus isobutanol. The as-spun yarns then go to wet-drawing, washing to remove residual solvent, drying and winding. Countercurrent flow of water and yarn is important for controlling the increase of solvent concentration and aiding solvent recycling or waste purification. All these above-mentioned operations are carried out in a step-by-step uninterrupted process on equipment similar to that used for production of viscose or polyacrylonitrile yarns.^{175,176}

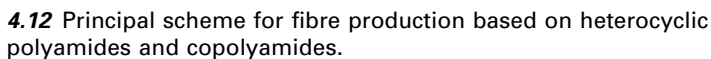
The spun yarns go to thermal treatment or to thermal treatment plus drawing, which may be either continuous or periodic (interrupted). At this stage there is a small self-elongation of the yarns and increased orientation. Owing to these phenomena, the modulus and strength are increased to their final values. The final operations are, for yarn production, winding, and for roving production, a combination of yarns and winding.

There is maximal recycling of chemicals and water for improved economics and waste elimination. Part of the washing water goes to spin bath dilution. The main part of the after-spinning bath and the washing water, which contain dimethylacetamide and lithium chloride, go to regeneration. The solvent is rectified, lithium chloride is crystallised, centrifugally separated and dried, and both are returned to the technological cycle.

4.4.4 Fibre structure

The fibre structures differ on all three levels (molecular, super-molecular and micro) from the usual fibre structure of flexible and semi-rigid polymers.^{50,63,76,106–112} The main structural features are shown in Table 4.6.

SVM and *Armos* fibres contain heterocyclic links and two kinds of polar



4.12 Principal scheme for fibre production based on heterocyclic polyamides and copolyamides.

Table 4.6 Para-aramid and PHA fibre structure features

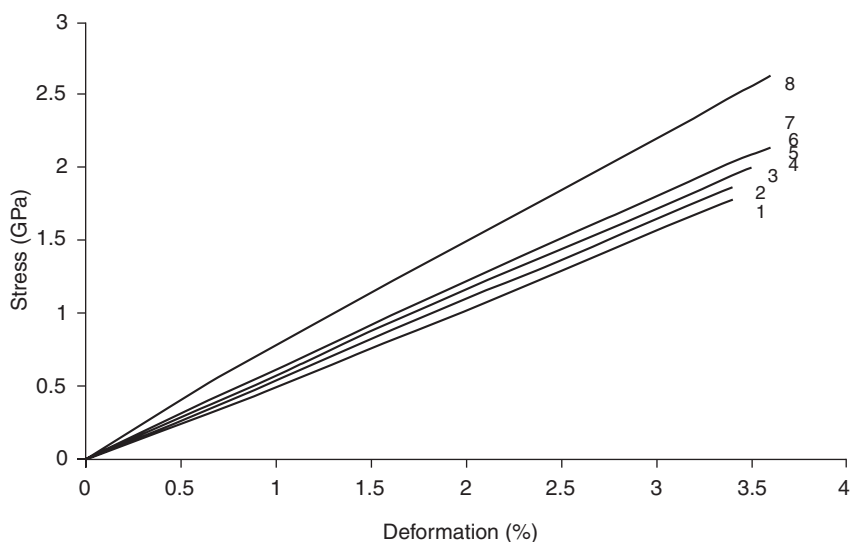
Structural levels	<i>Terlon</i>	<i>SVM</i>	<i>Armos</i>
Molecular level	PPTA and co-polymers; statistical segment 30–50 nm; main polar group: —CONH—	Heterocyclic para-aramid; statistical segment 20–40 nm; polar groups: —CONH—; =N—	Heterocyclic para-aramid copolymer; statistical segment 20–40 nm; polar groups: —CONH—; =N—
Super-molecular level	Extended chain 3D crystalline order; fibrillar; highly oriented.	Extended chain 1D crystalline order; fibrillar; highly oriented.	Extended chain non-crystalline; fibrillar; highly oriented.
Stress-holding molecular chains proportion 0.6–0.75			
Micro level (fibre)	Round cross-section, low heterogeneity		

group, amide links and tertiary nitrogen atoms. The structure of these polymers and copolymers is characterised by less regularity and less rigidity than PPTA. The absence of liquid crystalline domains in solution makes it possible to regulate structure building at the fibre forming and thermal treatment stages to give maximal orientation order. Owing to the lack of a plane of symmetry in the heterocyclic groups and to the mixed linking of monomers (head-to-head, tail-to-tail and head-to-tail), the extended chain conformations are irregular and lead to minimal crystalline order, with a consequent reduction in the possibility of axial movement. The less regular molecular chain structure leads to a higher proportion of stress-holding molecular chains and therefore to mechanical properties that are superior in *SVM* and especially in *Armos* fibre to those of aramid fibres such as *Terlon*, which is similar to *Kevlar* and *Twaron*.

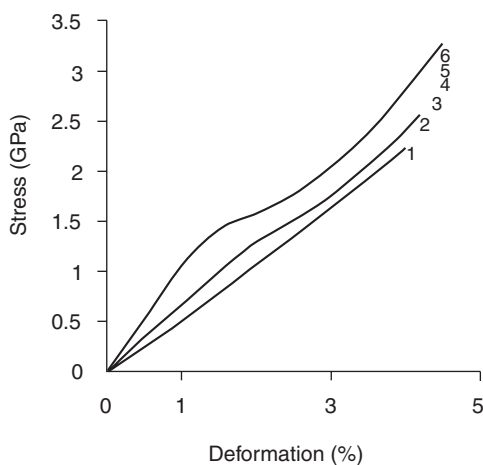
4.4.5 Mechanical properties

SVM and *Armos* fibres have mechanical properties superior to those of *Terlon* as shown by the data in Table 4.7. Stress-strain curves at different temperatures for *Terlon*, *SVM* and *Armos* yarns are presented in Figs. 4.13–4.15.¹⁷⁸ An interesting feature is that the high strength of *SVM* and *Armos* fibres is due to a higher breaking elongation, not to a higher modulus. The energy to break is therefore greater.

The data that are shown in Table 4.7 are determined by different

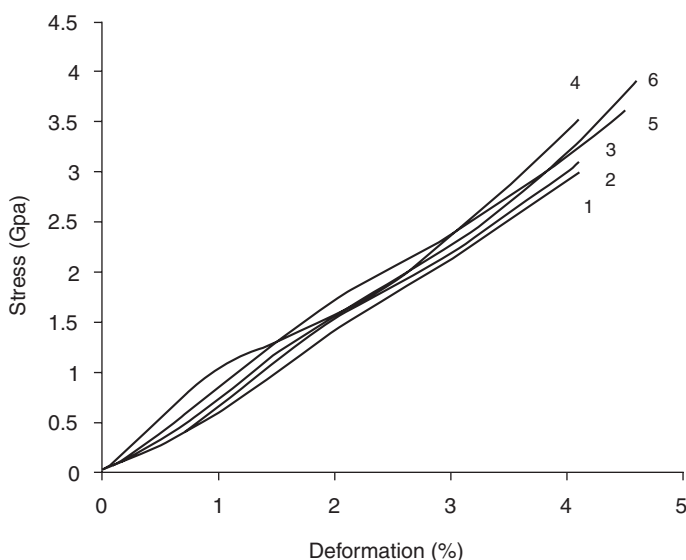


4.13 Stress-strain plots for *Terlon* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 80 °C; 6, 60 °C; 7, 40 °C; 8, 20 °C.



4.14 Stress-strain plots for *SVM* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 60 °C; 6, 20 °C.

methods. The deformation modulus is determined by three methods: mechanical (from the initial slope of the stretching diagram), dynamic and acoustic. Breaking characteristics are determined by single-fibre testing and a microplastic method; the results are approximately the same. There are differences in mechanical properties in literature data, resulting from



4.15 Stress-strain plots for *Armos* yarns: 1, 220 °C; 2, 180 °C; 3, 140 °C; 4, 100 °C; 5, 60 °C; 6, 20 °C.

Table 4.7 Fibre mechanical properties

Fibre (yarn) types	Density, g/cm ³	Deformation modulus, GPa*		Tenacity, GPa*	Elongation at break, %	Standard moisture content, %
		Dynamic	Static			
<i>Armos</i>	1.45–1.46	140–160	100–120	4.5–5.5	3.5–4	3–3.5
<i>SVM</i>	1.45–1.46	135–150	95–115	4–4.5	3–3.5	3.5–4.5
<i>Terlon</i> *	1.45–1.47	130–160	95–120	2.5–3.5	2.5–3	2–3

*The tenacity data are based on different testing methods for separate fibres or epoxide microplastic; modulus data for yarns.

different and often unrecorded testing methods, that make objective comparison difficult.

Fibre tenacity depends on moisture content owing to two influences – the plasticisation effect and the intermolecular interactions caused by hydrogen bond bridges, which are created by water molecules. These two influences lead to tenacity increasing to some extent with increasing moisture content up to a maximum value and then falling when wet to 90–95% of the dry value.

High orientational, structural and energy anisotropy of the fibres lead to

Table 4.8 Anisotropy of mechanical properties

Fibres	Modulus, GPa		Strength, GPa	
	Axial	Across	Axial	Across
<i>Terlon</i>	100–105	3.5–5.5	3.0–3.5	0.025–0.055
<i>SVM, Armos</i>	100–110	4.0–6.0	4.0–5.0	0.035–0.055

anisotropy of their mechanical properties.^{63,108,110} The moduli across the fibre axis were determined by two methods: fibre compression and calculation based on data from one-dimensional (1-D) composites. Tenacity across the fibre axis was determined for the first time by stretching of an epoxide film containing a single fibre.⁶⁰ The results of mechanical anisotropy determinations are presented in Table 4.8.

The calculated theoretical modulus, based on perfect crystals, for the PHA fibre is slightly less than for PPTA fibres, and the strength is about 30% less. The modulus realisation is between 60 and 70% for both types, but the strength realisation is about 15% for *Terlon* aramid fibre with higher values of 24% for *SVM* and 30% for *Armos*.

4.4.6 Thermal properties

All three para-aramide types are characterised by high glass transition temperatures, high thermal and thermal-oxidative resistance, high ignition and self-ignition temperatures, and high limiting oxygen indexes.^{50,55–57,108,114,120–125,180} All three, especially *SVM* and *Armos*, are dimensionally stable on long heating. The tendency to spontaneous elongation in technological heat treatment ('self-ordering effect') leads to the same effect in the first stage of heating – slight elongation or very small shrinkage with rise in temperature. The data show that change in dimensions is practically absent up to 300 °C. There is a small shrinkage of *SVM* and *Armos* yarns by 350 °C; the shrinkage at 400–450 °C is not more than 2–3%.

It is known theoretically and practically that thermo-oxidative degradation includes three main reactions – separation of substances with low molecular weight, molecular chain destruction by oxidation or hydrolysis, and intermolecular bridge creation. From this point of view, carbocyclic aromatic polyamides are more stable than heterocyclic ones.¹²³ If chain degradation leads to loss of mechanical properties, on the other hand, the intermolecular bridges lead to tenacity preservation. Therefore the resultant effect of all three kinds of reaction is indefinite in terms of change in mechanical properties.

Table 4.9 Effect of ageing on mechanical properties

Fibres	Ageing conditions		Properties retention, %	
	Temperature, °C	Time, hours	Tenacity	Elongation at break
<i>Terlon</i>	300	100	27	33
	250	325	47	45
	225	500	60.4	54.8
	200	1500	63.7	57.1
<i>Armos</i>	300	100	27.5	39.2
	250	325	60.6	80.4
	225	500	61.5	76.3
	200	1000	82.9	109.8*

*The result of relaxation processes

Table 4.10 Fire resistance and thermal characteristics

	<i>Terlon</i>	<i>SVM</i>	<i>Armos</i>
Ignition temperature, °C	450–500	500–600	500–600
Self-ignition temperature, °C	500–600	550–650	550–650
Limiting oxygen index, %	27–30	41–43	39–42
Glass transition temperature, °C	345–360	270–280	220–240
Exploitation temperature (limited), °C	200–250 (250–270)	250–270 (300–330)	250–270 (300–330)
Destruction temperature, °C	450–550	450–550	450–550

The comparative thermal-ageing characteristics of *Terlon* and *Armos* fibres at 200–300 °C are presented in Table 4.9.^{120–122} At higher temperatures, the loss of strength is greater. For *Armos*, the retention of tensile properties (strength and elongation at break) is slightly higher than for *Terlon*. These data give calculated activation energies of 52.5 kJ/mol for *Terlon* and 55 kJ/mol for *Armos*.

The high glass transition temperature and practically zero shrinkage for para-aromatic fibres give thermoresistant goods made from them important advantages in high temperature media, in comparison with meta-aramid fibres. *SVM* and *Armos* fibres are highly fire resistant and superior to PPTA fibres, owing to the nitrogen-containing heterocyclic structure and the presence of hydrogen chloride, which is a good fireproofing compound. The main thermal characteristics and fire resistance indices are shown in Table 4.10.

4.4.7 *Armos* fibres and applications

At present, *Armos* fibres and yarns have the highest mechanical properties among aramids and related fibres. *Armos* yarns are produced by the Tverchimvolokno Joint-Stock Company in Tver city, not far from Moscow. The linear density of yarns is in the range of 29.8–167 tex; and rovings of 600 tex or 1000 tex are made by combining 100 tex or 150 tex yarns.^{54,56–59,105,126,179,180,183} The main types of *Armos* yarns are:

- high-modulus reinforcement yarns and roving (*Armos HMR*)
- high-modulus yarns for technical textiles (*Armos HMT*)
- highly thermally stable yarns for textiles (*Armos HTS*).

The properties of these yarns are listed in Tables 4.11 and 4.12. All values were measured by Russian standard methods. The yarn tests were done on the base of State Standard 6611 at clamp length 250 mm, microplastic tests by State Standard 28007 at clamp length 100 mm. Dynamical elastic

Table 4.11 Properties of high-modulus reinforcement and technical yarns

Properties	<i>Armos HMR</i>		<i>Armos HMT</i>	
Linear density, tex	100	600	58.8	100
Load at break, N	208–221	>1225–1324	>116	>206
Elongation at break, %	—		3.5–4.5	
Dynamical elasticity modulus, GPa	>14 200		>14 200	
Breaking stress by microplastic method, MPa	>4905		>4412	
Yarn twist, twist/m	—		50 ± 15	
Oiling agent content	none		on agreement	

Table 4.12 Properties of highly thermally stable yarns

Properties	<i>Armos HTS</i>	
Linear density, tex	58	100
Specific tenacity, cN/tex	>127	160–170
Elongation at break, %		3.5–4.5
Yarn twist, twist/m	50 ± 15	50 ± 15 (or <15*)
Oiling agent content		on agreement

*To order.

modulus was determined by the impulse dynamical method of State Standard 28007 at clamp length 100 mm. Yarn moisture content was 3.5% under standard conditions.

4.4.8 Modified fibres

New chemically and physically modified fibres based on heterocyclic polymers and copolymers have been produced with properties depending on the modification method:

- use of different monomers for new polymer or copolymer synthesis at the stage of polycondensation (see Fig. 4.11)
- polymeric mixtures
- additives to polymer solution
- surface modification.

One way is to include meta-links or other non-para-links in polymeric chains. This leads to increased chain flexibility and therefore lower fibre modulus. These copolymers have better solubility and their solutions are isotropic. The principles of fibre formation are approximately the same as for traditional flexible chain polymer processing – wet-spinning, stretching for orientation, and additional thermal treatment to fix fibre structure. The fibre properties are characterised by modulus and tenacity, which are similar to general purpose fibres, of the type required for some kinds of technical textiles and reinforcement of rubber goods.

Changing up to 50% of the terephthalic links in the heterocyclic polymer to isophthalic links at the polycondensation stage leads to decrease of fibre rigidity and increase of elongation to normal textile values. This kind of fibre, named *Togilen*®, has good thermal and fire resistance (high oxygen index),^{73,129,130,172,173,183} but it has the disadvantage of water action on mechanical properties – the tenacity in the wet state is only 70% of that in the conditioned state.

Another possibility is to change up to 30% of heterocyclic diamine to *m*-phenylenediamine in the polycondensation stage. This polymer also gives fibres, named *Tverlana*®, with good thermal properties.^{169–171,183} The properties of these two fibres are presented in Table 4.13 in comparison with the ‘mother-fibres’ – *SVM* and *Armos*.

New analogues of *Armos* yarns have been produced on the basis of a copolymer with chlorinated aromatic links based on a chlorine-containing *p*-diamine – *Diamet-X* (chemical name 3,3'-dichloro-4,4'-diaminodiphenylmethane).^{67,127,131} The mechanical properties are approximately the same, but this way gives a simplified fibre production process owing to a change from organic solvent to sulphuric acid. Therefore the production technology of these fibres is similar to *Terlon* and other aramid fibres.^{87,132,133}

Table 4.13 Property comparison of heterocyclic polymer fibers – ‘mother fibres’ and modified fibres

Properties Composition	<i>SVM</i> Heterocyclic <i>p</i> -polyamide	<i>Armos</i> Heterocyclic <i>p</i> -copolyamide	<i>Togilen</i> <i>m</i> (25%)- <i>p</i> (75%)- copolyamide	<i>Tverlana</i> <i>m</i> (15%)- <i>p</i> (85%)- copolyamide
Assembly	Yarn, roving	Yarn, roving	Yarn, staple fibre	Yarn, staple fibre
Density, g/cm ³	1.45–1.46	1.45–1.46	1.43–1.44	1.40–1.41
Tenacity of yarn (fibre)	Yarn 3–3.5 GPa	Yarn 3.5–4 GPa	30–45 cN/tex	35–50 cN/tex
Deformation modulus, GPa		Dynamic 140–160 (Static 95–120)	Static 8–12	Static 10–14
Elongation at break, %	3–3.5	3.5–4	15–30	12–17
Yarn tenacity (as epoxide microplastic), kg/mm ²	400–450	450–550	—	—
Shrinkage onset temperature, °C		350–370	320–370	320–370
Boiling water shrinkage, %	—	—	2–2.5	2–2.5
Limiting oxygen Index, %	41–43	39–42	42–44	35–36
Moisture content (at standard climatic conditions), %	3.5–4	3–3.5	13–15	11–12

Modified aramid fibres, created by adding different polymers in the spinning solution,^{60,134–136} lead to new application possibilities. The best result was obtained by adding flexible-chain polymers to the solution of PPTA in sulphuric acid. A modified *Terlon* yarn with 10% addition of polycapromide (nylon 6) had improved adhesion to rubber in tyres or other elastomeric manufactured goods.^{50,137,138} At the same time this polymer addition led to an increase in mechanical properties. These practically important effects may be due to formation of intermolecular bonds and increase in super-molecular structural order. Addition of rigid-chain polymers did not have a positive effect.

The inclusion of disperse fillers in fibres may be useful in obtaining special physical properties. There is experimental research on the addition of different dispersed oxides and ceramic powders to the spinning solution.^{139–141} One aim of such additions is to make super-conducting fibres. The fibre mechanical properties are decreased by a small amount of additives.

Surface modification is useful for barrier creation against water and protection against external influences. Surface treatment of *SVM* and other fibres by silicon–organic substances as emulsions in water leads to higher moisture resistance.¹⁴² Surface grafting of polytetrafluorethylene decreases wettability and water sorption.¹⁴³

4.4.9 Conclusions

The fibres described in this section may be regarded as part of the ‘aramid family’, although they may not fall within the strict definition of aramids. They have a wide spectrum of characteristics and the raw materials, production processes, structure and properties are different for each member of this ‘family’.¹⁸⁰ All the fibres and yarns are thermal and fire resistant and they can be divided into two main groups:

- high mechanical properties (high tenacity and high modulus) plus thermal resistance
- normal mechanical properties with thermal resistance.

Comparative data have been given earlier, but it is informative also to review mechanical properties on a mass basis. These quantities are presented in Table 4.14 and show that the tenacity of *Armos* yarn is 20–50% higher than that of other aramid and related yarns and glass yarns. The thermal characteristics show the advantages of heterocyclic polymers (*SVM*, *Armos*, *Togilen*, *Tverlana*) in comparison with aramid fibres based on PPTA (*Terlon*, *Twaron*, *Kevlar*) and meta-aramid fibres (*Fenilon*, *Nomex*), especially to open fire resistance.

Table 4.14 Specific mechanical properties

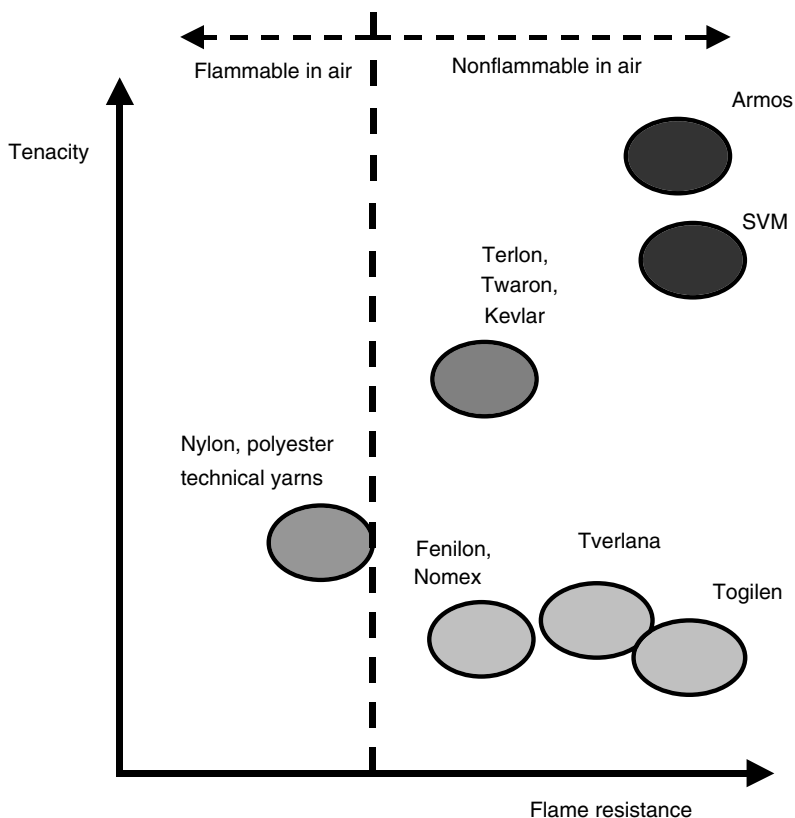
Yarns	Specific modulus, km	Specific strength, km
<i>Armos</i>	7600	350
<i>SVM</i>	7000	295
<i>Terlon</i>	7000	215
<i>Glass yarn S-type*</i>	3450	170

* Data for glass yarn S-type are following: density 2.52–2.55 g/cm³; elasticity modulus 85–90 GPa; tenacity 4–4.6 GPa.

It is important to compare fibres and yarns in terms of the two above mentioned characteristics – mechanical and thermal properties. The main peculiarities of different fibre types are presented in the scheme of Fig. 4.16.^{126,180–182} Properties of high-tenacity technical yarns (nylon and polyester) are shown on this diagram for comparison. *Armos* fibres and yarns are the best in two qualities simultaneously – tenacity and open fire resistance.

The applications found for the Russian aromatic HM-HT fibres are similar to those found elsewhere and reported for aramids in Chapter 2 – high-strength and high-stiffness technical textiles loaded in the axial direction. This includes high-strength composites, ropes, conveyor belts, hoses, protective clothing and a host of similar uses.^{144–167}

The creation of para-aramid and related fibres was an important step in the field of fibres and yarns for high-performance technical textiles and composites. The newer Russian aramid-related fibres – production principles, structure, properties, modification and application areas – are described in this chapter. The methods of fibre modification and property improvement for different applications are discussed. New super properties of heterocyclic PHA fibres (*SVM* and, even more, *Armos*) were found by the All-Russian Institute of Polymeric Fibres using advanced methods and these fibres are produced today with mechanical and thermal property values that exceed those of PPTA and other conventional aramid fibres. At present the Russian Tverchimvolokno joint-stock company is producing reinforcing *Armos* yarns with tencity as high as 5.0–5.5 GPa and dynamic deformation modulus more than 145 GPa. This yarn is highly thermo-resistant in conditions of use up to about 330 °C and flame resistant (oxygen index about 39–43% – see Tables 4.10 and Figure 4.16). There is a possibility of further advances in fibre properties by means of structure building and technology optimisation.



4.16 Comparison of tenacity and fire resistance of various aramid and other fibres.

4.5 Solid-state extrusion high-molecular weight polyethylene fibres (GW)

4.5.1 Background

As has been described in Chapter 3, ultra-high molecular weight polyethylene (UHMW-PE) is an ideal candidate for the production of fibres of exceptional strength. The molecular conformation and chemical structure lend themselves to the achievement of very high specific strength and moduli, provided that the molecule can be fully oriented. For ultra-high molecular weight polyethylene it was believed that the molecular chain needed to be in either the molten state or solution in order to facilitate orientation. In these situations, however, the process must be carefully controlled or the molecule can freely rotate and entangle, thus contravening the original purpose.

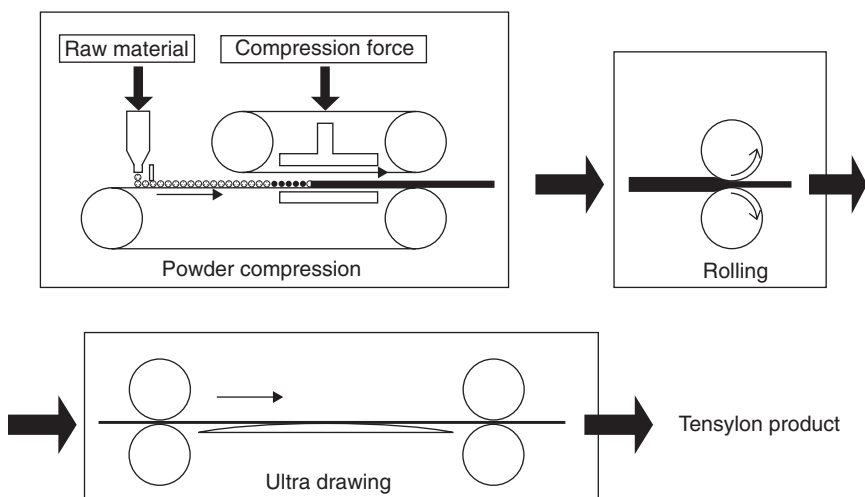
Several approaches have been developed to unfold these long chains or to draw the polymer in such a way that the entanglements are not exacerbated. The most notable commercial technologies for accomplishing this orientation are gel-spinning, solid-state extrusion (SSE), and special high-stress spinning and tensile drawing (using conventional molecular weight polyethylene).

The details of gel-spinning are described in Chapter 3, and the process and properties are repeated here only as comparisons arise. The special drawing technology developed by Ian Ward (Leeds) was licensed by the British Technology Group to Snia Fibre (Italy) and Hoechst-Celanese (USA).^{184,185} The commercially produced fibres were known as *Tenfor*TM and *Certran*TM, respectively. These fibres enjoyed only limited commercial success and both companies ceased production of these fibres in the 1990s.

In the late 1970s, A E Zachariades, T Kanamoto, and R S Porter reported that they had succeeded in orienting ultra-high molecular weight polyethylene powder by solid-state extrusion.¹⁸⁶ Subsequently, in 1986, the Nippon Oil Company (NOC), (now the Nippon Mitsubishi Oil Corporation – April 1999), began an extensive research project on developing the solid-state extrusion process for commercial applications. This process was envisioned as a low-cost alternative to gel-spinning for the production of high-modulus polyethylene fibres. NOC ultimately commercialised a pilot plant in Japan in 1994. For a limited period, they produced and sold the SSE fibre, *Milite*TM, through a subsidiary, the Nippon Petrochemicals Company (NPCC),¹⁸⁷ which was already a major manufacturer of low and high density polyethylene. In 1999, NOC licensed the solid state technology for fibre production in the USA¹⁸⁸ to Synthetic Industries (SI), who worked with Integrated Textile Systems (ITS). This product is being produced and sold in North America under the *Tensylon*TM trademark. Subsequently, Synthetic Industries withdrew and the enterprise is now run solely by ITS.

4.5.2 Process description

Like gel-spinning, the starting material for the solid-state extrusion (SSE) process begins with a conventional ultra-high molecular weight polyethylene (UHMW-PE) polymer having a molecular weight range of three to five million. Because of the nature of the solid-state process however, it is important that the starting UHMW-PE polymer has low inherent chain entanglements in the nascent powder. In this respect, polymers produced at low polymerisation temperatures are more desirable. It is also important that the powder is not exposed to melting temperatures prior to processing. Such exposure could cause an undesirable increase in chain entanglements. Polymer powder containing a high level of chain entanglement cannot be used for SSE.



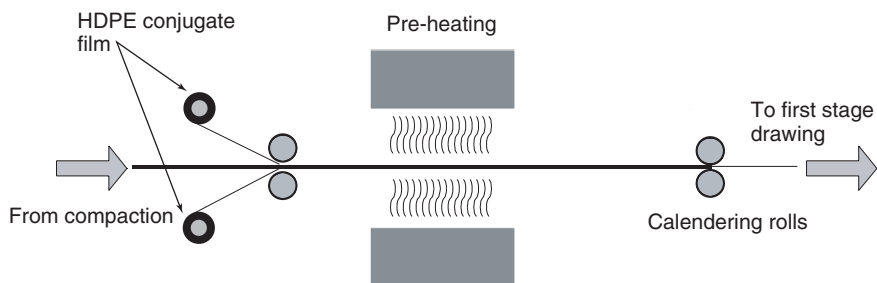
4.17 The SSE process. (Reproduced by courtesy of Synthetic Industries.)

Unlike gel-spinning, solid-state extrusion uses no solvents, processing aids, or adjuvants to facilitate processing of the powder into a drawn fibre. Additionally, all of the operations in the process are carried out below the melting point of the polymer. These rather remarkable features of the process give rise to an operation that avoids the high costs and environmental difficulties of handling large amounts of solvents common to many high-performance fibres. This process simplicity also significantly reduces the need for large support utilities.

The solid-state extrusion process consists of three basic unit operations: powder compression and compaction, rolling, and ultra-drawing (see Fig. 4.17). In the first step (compaction), the polymer powder is fed between two endless, heated, counter-rotating steel belts. A compression force is applied through each of the belts by a series of rollers which cause the powder to be compressed into a cohesive sheet capable of being handled and processed further. During this process, the density of the UHMW-PE powder is increased more than two-fold, from about 0.4 to 0.95 g/cm³. This precompression step is necessary because it is extremely difficult to calender (roll) the powder directly into a cohesive, oriented film in a single operation.

In the next step (rolling), the compressed sheet is fed into a pair of heated, counter-rotating rolls. The compressed sheet is calendered to about one-seventh of its original thickness, slit to the desired width and taken up on conventional low-speed winders.

In the final step (ultra-drawing), the tapes are drawn at a draw ratio of



4.18 Schematic view of conjugating process. (Reproduced by courtesy of Synthetic Industries.)

about 12 to 13 using very long hot plates. The temperature of the hot plates must be carefully controlled to maintain the temperatures below the melting point of the polymer. Long draw zones also are required in order to reduce the high drawing stress generated during solid-state drawing. If desired, split (fibrillated) yarns can be produced during the ultra-drawing step for products requiring a softer ‘hand.’

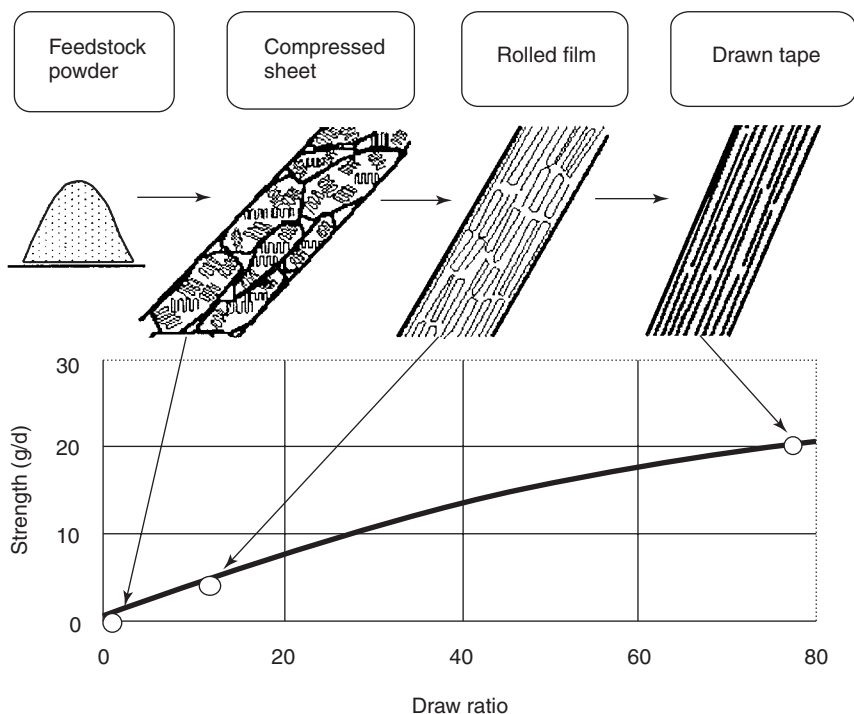
The total draw ratio (TDR) of the finished product is defined by the product of the rolling shear stress effect multiplied by the ultra-draw ratio, i.e. $TDR = (\text{rolling ratio}) \times (\text{ultra-draw ratio})$. A TDR of 85 to 100 is typical for the SSE process. A standard 720d drawn tape is about 2 mm wide and 45 μm thick.¹⁸⁹

The most important feature of the solid-state extrusion process, however, is the on-line capability to laminate coloured, heat stabilised, UV stabilised, adhesion promoting, or other modified films to the compacted sheet (Fig. 4.18). This ‘conjugating’ film technology allows the manufacturer to provide a wide variety of specialised products from the same production line without making any major alterations to the feedstock or the process.¹⁹⁰ For many applications, such as specialty ropes, fishing lines, and composites, this unique feature of the solid-state process is often the major determinant for its use versus gel-spun UHMW-PE yarns.

The fully drawn tapes and yarns from the SSE process have tensile strengths of ~1.9 GPa (18–20 g/denier; 1.6–1.8 N/tex), a Young’s modulus of ~120 GPa (1000–1400 g/denier; 90–130 N/tex) and an elongation of about 2.6%.

4.5.3 Structure

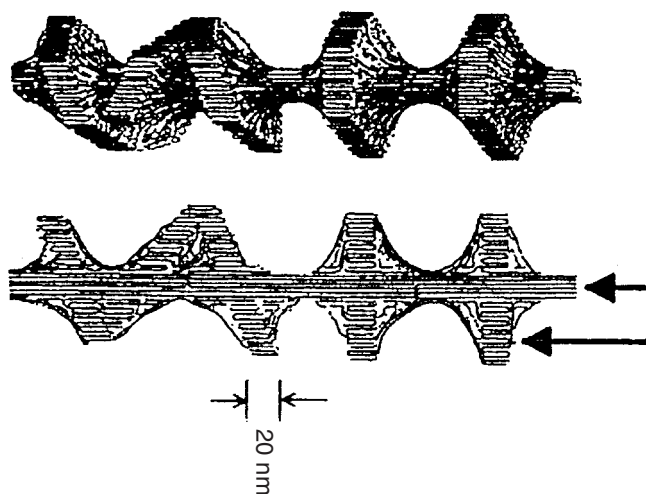
Generally, polyethylene is considered to consist of a crystalline phase, an amorphous phase in which the molecular chain is entangled and cannot grow into a crystal, and an intermediate phase. As noted earlier, in the solid-



4.19 Structural changes during SSE. (Reproduced by courtesy of Nippon Oil Co.)

state process it is imperative that the starting UHMW-PE powder has minimal chain entanglements in the amorphous phase. In practice, the suitability of a particular polymer can be determined by measuring the thermal characteristics of the material. Measurements of the melting point, heat of fusion, and crystallinity in the powder give an early indication of the suitability of a particular feedstock. It is these initial morphological properties that will control the ultimate performance of the particular UHMW-PE being used in the process. Obviously, other parameters such as particle size, particle size distribution, bulk density, and flow times are important to overall processing, but they have no direct effect on the ultimate tensile properties achieved.

The structural changes that occur in the UHMW-PE during compaction, rolling, and ultra-drawing are illustrated in Fig. 4.19. As heat and pressure are applied to the feed powder, the powder is compacted. As a result, the air between the particles is expelled and the polymer particles stick together. The internal crystal structure is not destroyed, however, because



4.20 Structure of the final solid-state extruded product.

the powder surface is only slightly melted. At this stage the compacted sheet still can be easily broken into powder. The process is similar in some respects to compressing snow to make a snowball. The material is cohesive, but still frangible.

As the shearing force is applied to the sheet in the rolling stage, the crystals are literally broken into pieces, increasing the number of terminal chains. In addition, because these crystals are oriented in the drawing direction by the shearing force, the crystals can be easily drawn. Moreover, because the folded molecular chains are slightly drawn during this process, the fragility of the compacted sheet decreases. At this stage, the film can be easily torn in the machine (longitudinal) direction, but not in the cross-machine orientation.

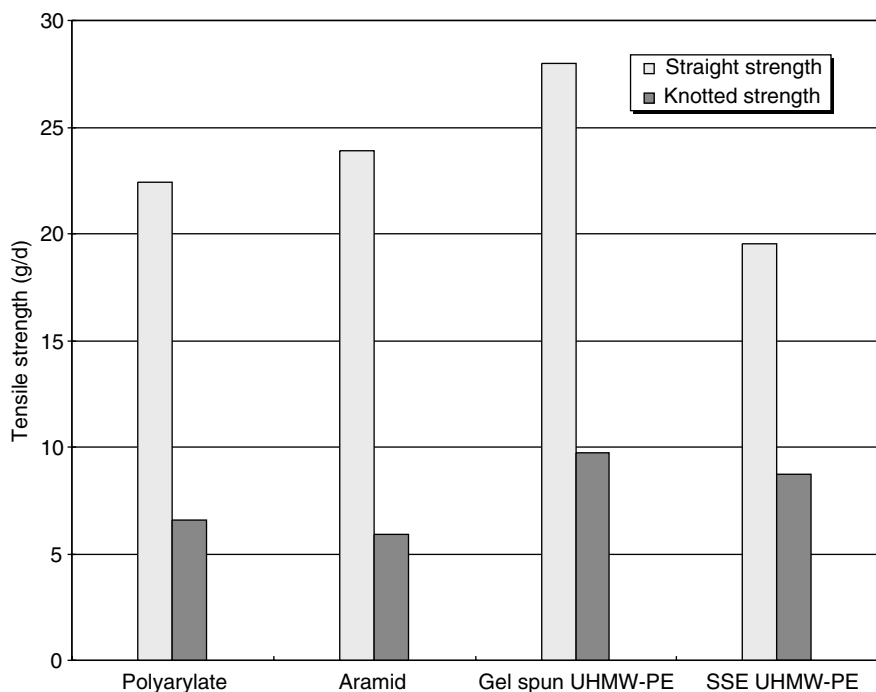
The changes in the internal organization of the material during processing also can be confirmed by X-ray diffraction patterns. As expected, the compacted sheet X-ray pattern is ring shaped, indicating no major orientation. As the processing proceeds to rolling and drawing, the X-ray pattern clearly transitions from a hemispherical pattern to the characteristic X-ray pinpoints of a highly oriented structure.

Although the molecular structure after SSE ultra-drawing is well ordered, the polymer chains are not as perfectly aligned as is the case with gel-spun fibre. SEM photomicrographs clearly show a 'shish-kebab' structure in the final SSE product. As illustrated in Fig. 4.20, there are a significant number of residual lamellae. For this reason, the tensile strength of fibres produced by SSE is lower than from gel-spinning.

4.5.4 Properties

Tapes and yarns produced from solid state extruded polyethylene, for example *Tensylon*TM, possess many of the same useful features as those from gel-spinning. Both have low shrinkage, high abrasion resistance, high strength and modulus, and excellent chemical resistance. The major property differences between the two technologies lie in creep resistance, translation efficiency, and ease of surface modification for improved adhesion, increased UV stability, or the addition of colour.

Yarn strength comparisons between *Tensylon*TM and other high strength yarns are shown in Fig. 4.21. In general, the breaking strength of polyethylene yarn from SSE is about 65%–75% of that achieved with gel-spinning. However, in practice, this differential is offset somewhat by the higher translational efficiency for the SSE product. As shown in Fig. 4.21, the knot strength for *Tensylon*TM is about 50% of the original yarn strength. For gel-spun yarns, the knot strength is about 35% of the original yarn. Therefore, the two yarn knot strengths are nearly equal. This phenomenon also is observed in some rope constructions and twisted yarn applications, in which



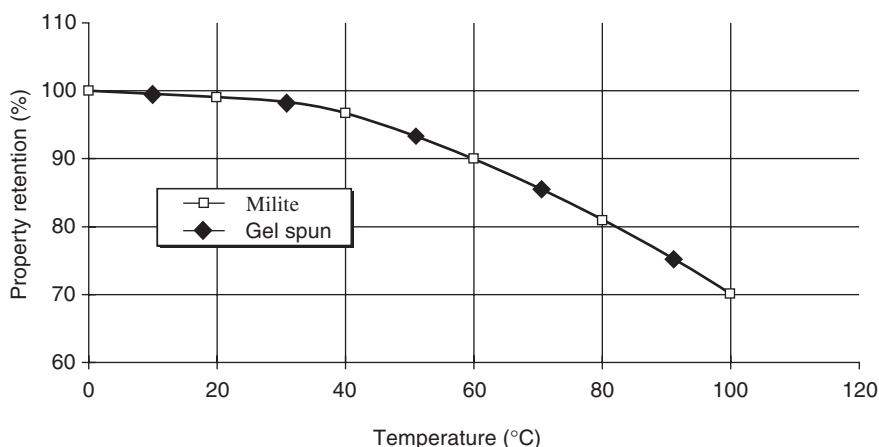
4.21 Strength comparison of various yarns. (Reproduced by courtesy of Nippon Oil Co.)

the finished products have comparable strengths in spite of the strength differences in the starting yarns. It is probable that the physical structure of the SSE yarn, that is, fibrillated tape versus multifilament, contributes to this effect.

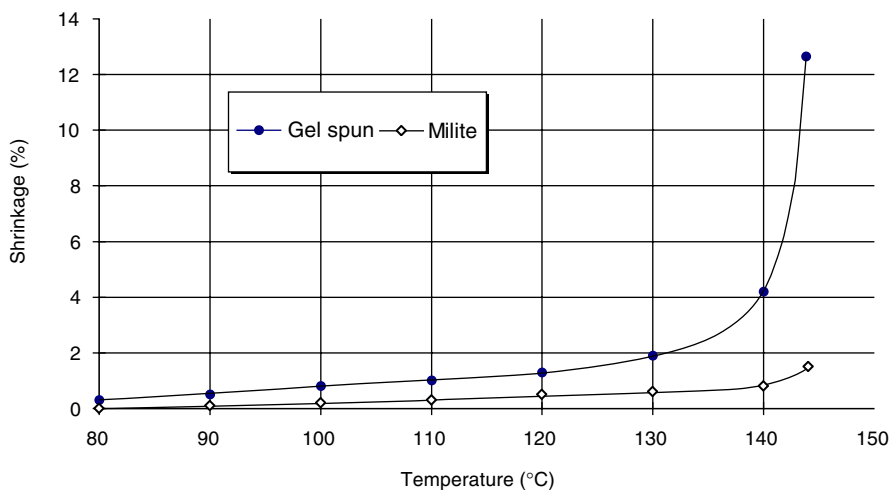
The effect of temperature on the strength and heat shrinkage of *Tensylon*TM versus gel-spun yarn is shown in Figures 4.22 and 4.23. As shown in the plot, the tensile responses of SSE and gel-spun yarns to temperature are identical. This is to be expected since the melting behaviour of both products is dependent primarily upon the physical nature of polyethylene. In the case of shrinkage, however, yarn subjected to solid-state processing exhibits substantially less shrinkage near its melting point. This response is somewhat unexpected because of the 'shish-kebab' structure of SSE yarn and the very high shearing forces in SSE.

Although both gel-spinning and SSE may start with similar molecular weight UHMW-PE polymers, the polymers in gel-spinning are necessarily subjected to a higher degree of thermal degradation during the process and, consequently, the final yarns have much lower molecular weights. Because SSE is carried out under relatively mild conditions, the molecular weight of the polymer is essentially unchanged during the process. As a result, there is a significant difference between the two yarns in terms of abrasion resistance and creep properties that can be attributed to the higher molecular weight of SSE yarn.

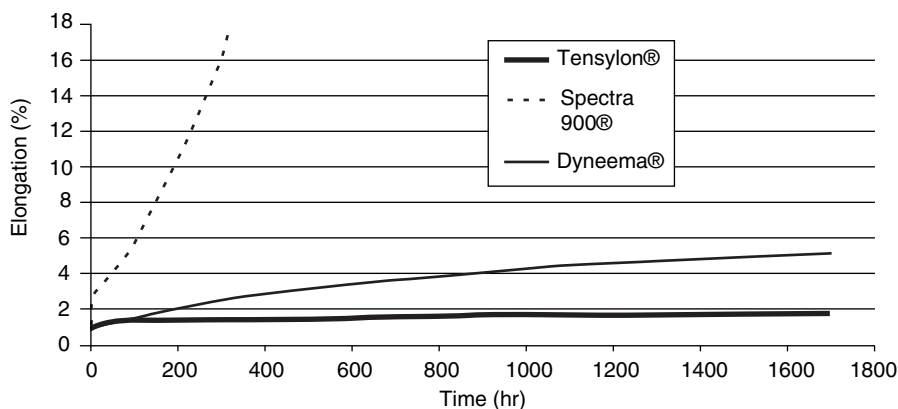
Although some of the improvements in the abrasion resistance of SSE yarn also can be attributed to its physical form (tape), the degree of improvement in this property is very dependent upon the construction of



4.22 Effect of temperature on thermal strength. (Reproduced by courtesy of Nippon Oil Co.)



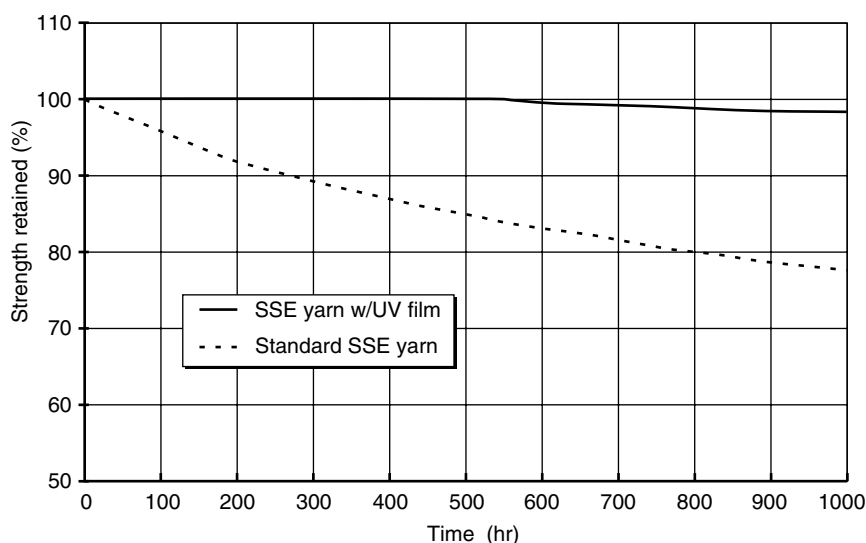
4.23 Effect of temperature on heat shrinkage. (Reproduced by courtesy of Nippon Oil Co.)



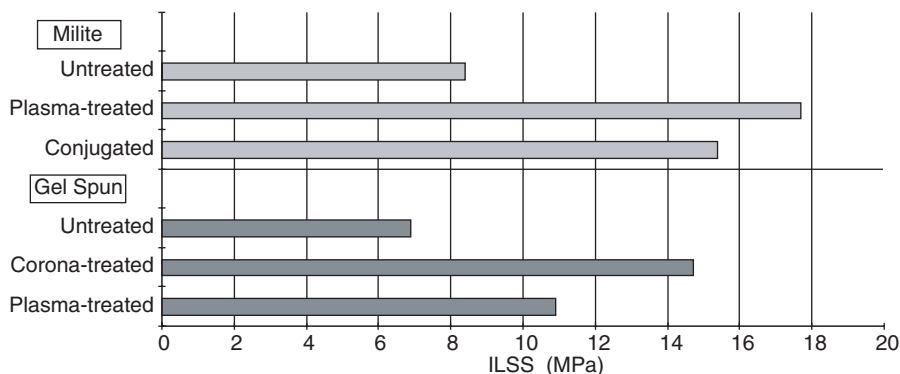
4.24 Creep elongation at 20% breaking load. (Reproduced by courtesy of Synthetic Industries.)

the fabricated article and the particular abrasion test being used. With respect to creep resistance, both the lack of residual solvent and the higher molecular weight of the polyethylene in SSE yarns probably contribute to its improved creep performance (See Fig. 4.24).

As mentioned earlier, it is possible to laminate coloured, stabilised, or adhesive films to the compressed sheet during processing. By using pigmented films it is possible to make coloured yarn for ropes and other applications where a colour is desired or needed. Since colouring of gel spun



4.25 UV-resistance (light and water exposure test based on JIS B 7754). (Reproduced by courtesy of Nippon Oil Co.)



4.26 Effect of surface treatments on interlaminar shear stress (ILSS). (Reproduced by courtesy of Nippon Oil Co.)

polyethylene yarns is usually very difficult, this is a distinct advantage for the SSE process.

The UV resistance of SSE yarns also can be improved by application of films containing UV stabilisers, as illustrated in Fig. 4.25. By using high density polyethylene copolymer films containing reactive groups it is also possible to create long-lived active bonding sites on the yarn to improve

adhesion in composites. This technique gives interlaminar shear strengths comparable to conventional corona and plasma treatment of gel-spun yarns (Fig. 4.26).

4.5.5 Applications

The fields of application for SSE yarns are the same as those for gel-spun polyethylene (see Chapter 3). As noted earlier, this is not surprising since yarns from both processes share many similarities. In applications where very high strength or stiffness, high flexibility, exceptional ballistic protection, or very small deniers are required, gel-spun yarn will have an advantage. In applications where low cost, low creep, colour, UV stability, or exceptional abrasion resistance is required, SSE yarn generally will have an advantage. Because the commercial production of *Tensylon*TM SSE fibre started only in August 1999, there were few announced commercial applications at the time this text was written.

Specialty ropes, cordage, and fishing line are the largest identified markets for SSE yarns. It is in these applications that all of the attributes of the SSE product are utilised: good translational efficiency (offsetting its lower initial strength), the ability to be coloured or UV stabilised, and significantly lower creep. It is the combination of these features that make the product a strong candidate in these areas.

Like gel-spun fibres, the toughness and low friction properties inherent in UHMW-PE also translate into the finished SSE yarn. Both properties are important in the production of cut-resistant gloves and aprons. The tape form of the SSE product enhances the high cut resistance because of the benefit of a monolithic form versus a multifilament, but this bulk also reduces fabric flexibility (hand). In most constructions, however, fibrillating the yarn mitigates the harsher hand. Since it is common to use high modulus yarns in combination with other materials, such as steel wire or glass fibres, to create very highly cut-resistant yarns, the tape form is advantageous because it facilitates complete encapsulation of the secondary component. The ability to colour SSE yarn also is an advantage in this market.

As announced by Synthetic Industries, the new markets being explored for SSE fibres are those of geotextiles and building materials for reinforcement, repair and retrofit.¹⁸⁸ The high specific strength, potentially low cost, and the ability to modify the fibres for increased UV stability and adhesion offer great promise in this area.

As the data in Fig. 4.26 suggests, it is possible to produce low cost, surface modified SSE yarns for composite applications. The low dielectric properties of polyethylene coupled with the improvements provided by an adhesive film would suggest that radar enclosures such as radomes are a natural area for SSE yarn development. Other composite structures where high

modulus, low cost, high impact resistance, and colour or UV stability are important also would be likely candidates.

The major area where SSE yarns currently do not compete with gel-spun polyethylene fibres is in the area of ballistic protection. Although SSE fibres have high moduli (1000–1400 g/d), a critical requirement for good ballistic protection, these moduli are significantly lower than those of gel-spun polyethylene. Nevertheless, preliminary ballistic tests have indicated that there is a strong potential for SSE yarns to compete in areas where less than maximum ballistic protection is required. However, because a high level of technology is involved in producing ballistic-resistant articles and the production of SSE yarns is only just beginning, it may be several years before there is any significant penetration of SSE yarn into this area.

There are several potential medical applications for SSE yarns, such as dental floss, sutures, and reinforcement for *in vitro* devices. These products tend to be low volume, specialty end-uses and, although evaluations are underway in several of these areas, no commercial applications have been announced.

4.5.6 Economics

The announced capacity for the *Tensylon*TM semi-works is 80–100 metric tons per year.¹⁸⁸ Therefore, it is difficult to compare the economics of this initial SSE process directly with the older, more established ones for gel-spinning. A general estimation of the relative production costs can be made, however, by examination of the general elements of the two processes.

Both processes use UHMW polyethylene as a feed stock, so raw material costs in this regard will be similar. Both processes involve relatively low-speed multiple-stage drawing equipment. Again, the capital and operating costs in this area should be similar. General staffing for labour and supervision for the yarn processing are probably equivalent. The major difference in production costs, therefore, lies in the costs for conversion of the powder into the intermediate yarn product (xerogel versus compressed sheet).

Regardless of the gel-spinning technology used, a large solvent recovery plant is needed to recover, purify, and recycle the spinning solvent(s). The capital costs for this recovery plant, the special spinning equipment, the associated labour and supporting utilities constitute a major additional cost for gel-spinning. By comparison, the SSE process requires only a compaction extruder and rolling unit.

On this basis, one would estimate that the production costs for SSE should be approximately 40–50% of those of gel-spinning. Long term, at similar production levels, one would expect the selling prices of SSE yarns also to be about half those of gel-spun yarns.

The future of SSE yarns will depend upon both the general price/performance factors as well as the market's need for the unique features that the solid-state process/products provide. Although the product features appear to offer clear benefits in several important high-performance fibre areas, it is much too early in the commercialisation process to predict the outcome. The initial predictions on markets and costs, however, have proved accurate. The sales have been in areas where colour and low creep are important: rope, fabric stabilisation (geotextiles), and luggage. Cut protection is currently the biggest market, in addition, the product line has been broadened to include 350 and 1000 denier yarn and unfibrillated full width tape (21 800 denier) with a breaking strength of 800 lb. The ITS pilot plant is now being run at its full design rate and there are plans for a larger (225 metric tons/year) unit.

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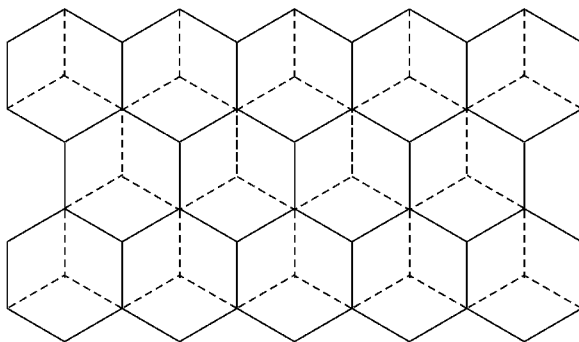
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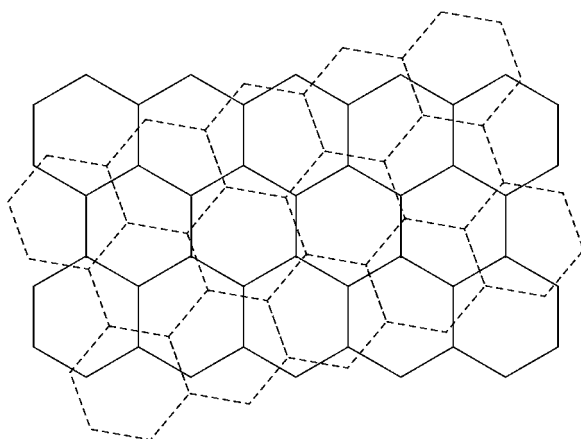
5.1 Introduction

Carbon fibres have been under continuous development for the last 50 years. There has been a progression of feedstocks, starting with rayon, proceeding to polyacrylonitrile (PAN), on to isotropic and mesophase pitches, to hydrocarbon gases, to ablated graphite and finally back to carbon-containing gases. Rayon-based carbon fibres are no longer in production, and so are of historical interest only; they will not be discussed in this chapter. PAN-based fibre technologies are well developed and currently account for most commercial production of carbon fibres. Pitch-based fibres satisfy the needs of niche markets, and show promise of reducing prices to make mass markets possible. Vapour-grown fibres are entering commercial production, and carbon nanotubes are full of promise for the future.

There are several excellent books on carbon fibres. Among them, Dresselhaus *et al.*¹ reviews physical properties in a comprehensive fashion, Donnet *et al.*² is an encyclopaedic treatment of carbon fibre technologies from the mid-1990s, and Peebles³ is an excellent review of the period 1980–1992, which was extremely rich in carbon fibre developments.



5.1 Regular stacking of aromatic sheets in graphite.



5.2 Irregular stacking of aromatic sheets; turbostratic carbon.

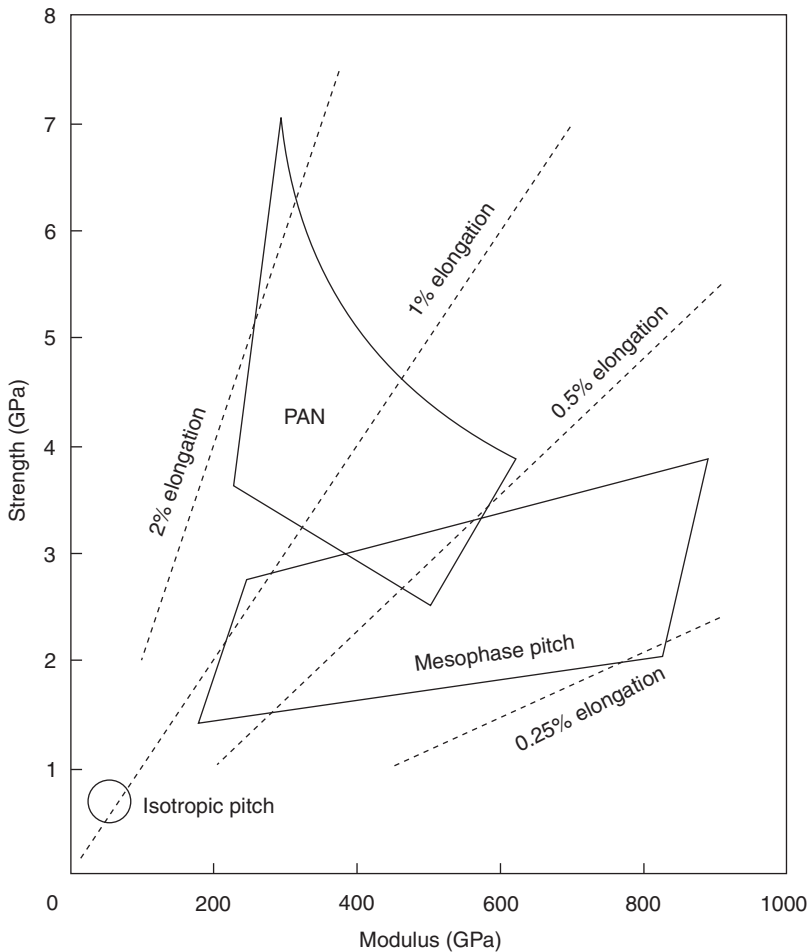
The word ‘graphite’ is much misused in carbon fibre literature. The word refers to a very specific structure, in which adjacent aromatic sheets overlap with one carbon atom at the centre of each hexagon, as shown in Fig. 5.1. This structure appears very rarely in carbon fibres, especially in PAN-based fibres, even though they are conventionally called graphite fibres. While high-performance fibres are made up of large aromatic sheets, these are randomly oriented to each other, and are described as ‘turbostratic’ (turbulent and stratified), as shown in Fig. 5.2. Many physical properties depend merely on the large aromatic sheets.

5.2 Physical properties

Because of the rich variety of carbon fibres available today, physical properties vary over a broad domain (Table 5.1). Figure 5.3 shows a plot of

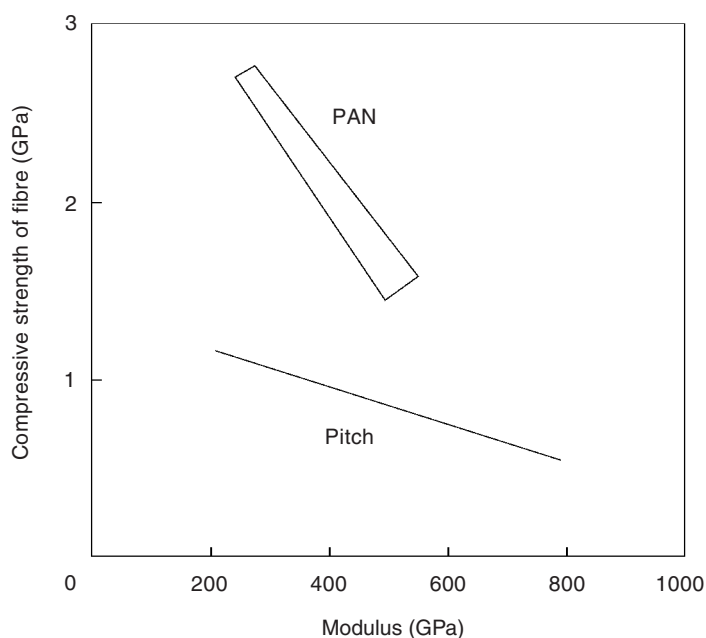
Table 5.1 Mechanical properties of selected carbon fibres

Type	Manufacturer	Product name	Tensile strength (GPa)	Young's modulus (GPa)	Strain to failure (%)
PAN	Toray	<i>T300</i>	3.53	230	1.5
		<i>T1000</i>	7.06	294	2.0
		<i>M55J</i>	3.92	540	0.7
	Hercules	<i>IM7</i>	5.30	276	1.8
GP-Pitch	Kureha	<i>KCF200</i>	0.85	42	2.1
HP-Pitch	BP-Amoco	<i>Thornel P25</i>	1.40	140	1.0
		<i>Thornel P75</i>	2.00	500	0.4
		<i>Thornel P120</i>	2.20	820	0.2

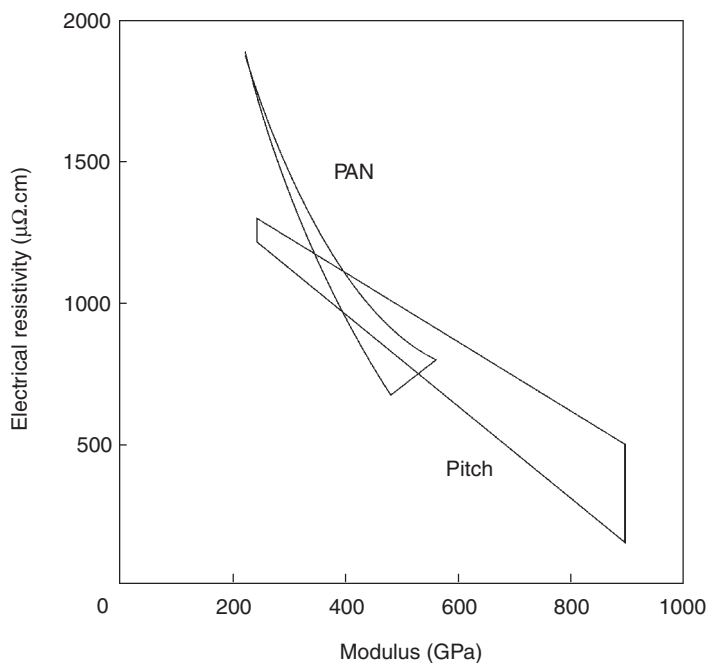


5.3 Tensile properties of carbon fibres.

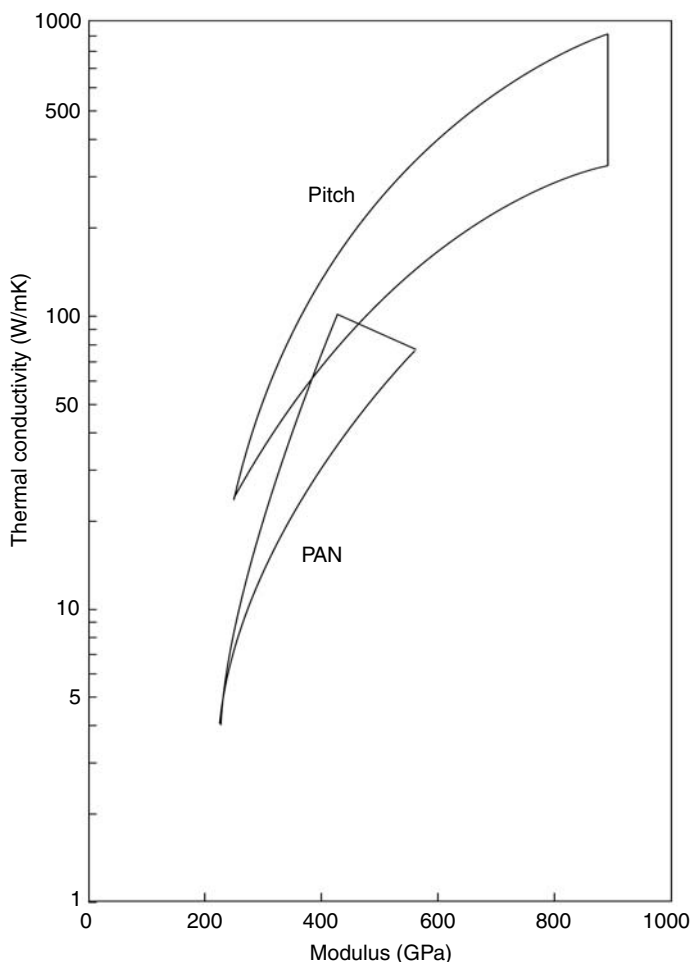
strength versus modulus. ‘General purpose’ fibres made from isotropic pitch have modest levels of strength and modulus. However, they are the least expensive pitch-based fibre, and are useful in enhancing modulus or conductivity in many applications. PAN-based fibres are the strongest available; however, when they are heat treated to increase modulus, the strength decreases. Mesophase pitch fibres may be heat treated to very high modulus values, approaching the in-plane modulus of graphite at 1 TPa. The Achilles heel of mesophase pitch-based fibres in composite applications is low compressive strength; this is illustrated in Fig. 5.4. Electrical and thermal conductivity are important in many applications, and these are illustrated in Fig. 5.5



5.4 Compressive properties of carbon fibres.



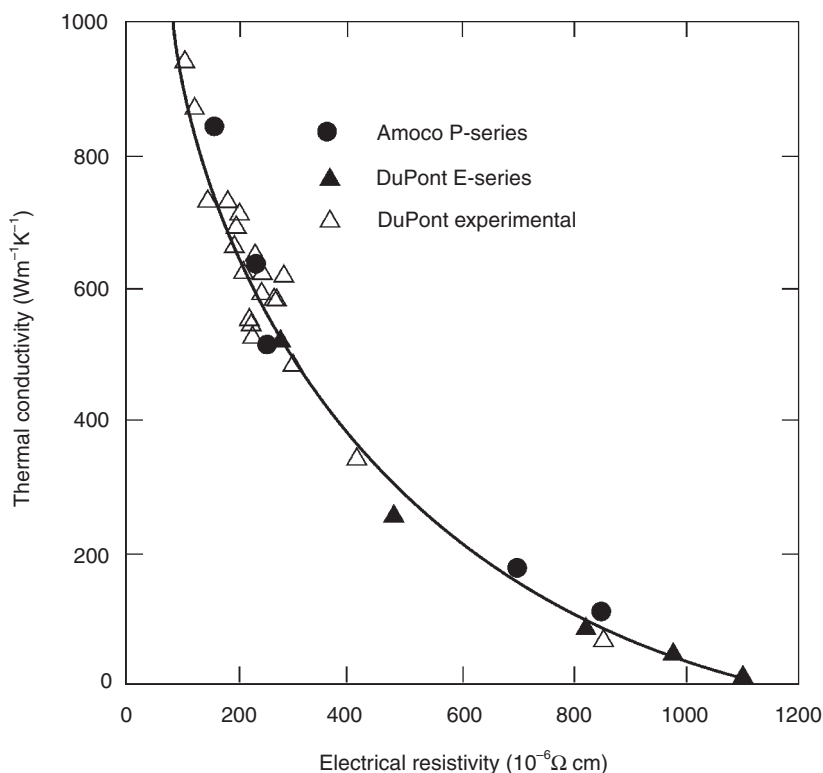
5.5 Electrical resistivity of carbon fibres.



5.6 Thermal conductivity of carbon fibres.

and 5.6, respectively. Mesophase pitch fibres have the highest conductivity and lowest resistivity.

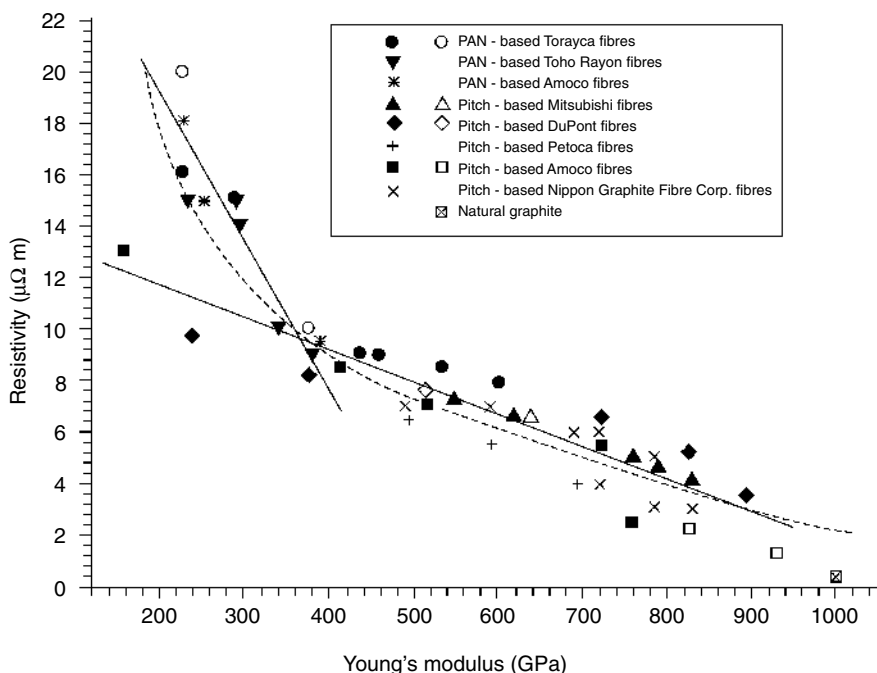
Finally, there is a property of high-performance carbon fibres, both PAN and mesophase pitch-based, which sets them apart from other materials. They are not subject to creep or fatigue failure. These are important characteristics for critical applications. In a comparison of materials for tension members of tension leg platforms for deep sea oil production, carbon fibre strand survived 2 000 000 stress cycles between 296 and 861 MPa. In comparison, steel pipe stressed between 21 and 220 MPa failed after 300 000



5.7 Relationship between electrical resistivity and thermal conductivity in pitch-based carbon fibres.⁷ (Copyright 1993, reproduced with permission from Elsevier Science.)

cycles.⁴ Creep studies on PAN and pitch-based carbon fibres were conducted at 2300°C and stresses of the order of 800 MPa .^{5,6} Projections of the data obtained to ambient temperatures indicates that creep deformations will be infinitesimally small.

There is a surprising degree of cross-correlation in the physical properties of carbon fibres. The mechanisms for conduction of heat and electricity are different in carbon fibres: heat is transmitted by lattice vibrations, and electricity by diffusion of electrons and holes. However, there is a strong correlation between the two, as illustrated in Fig. 5.7, which allows thermal conductivity to be estimated by measurement of the electrical resistance, a much simpler measurement.⁷ Young's modulus is also correlated with electrical resistance, as shown in Fig. 5.8.⁸

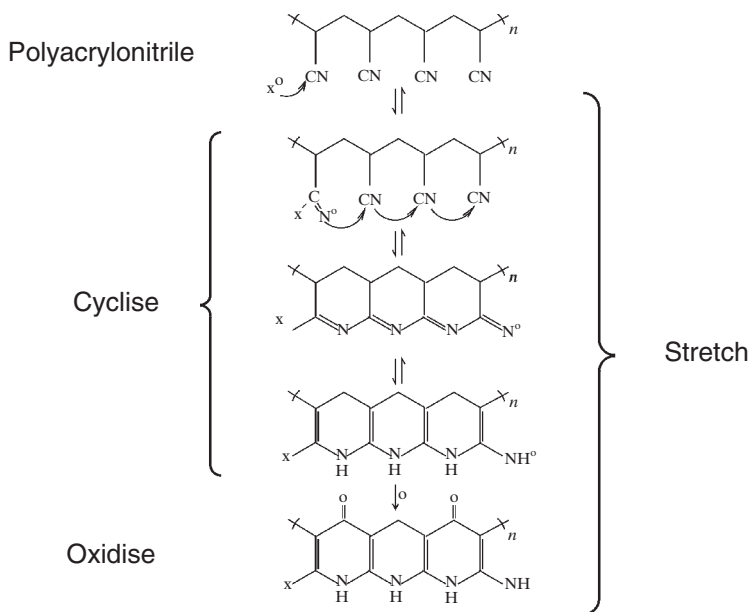


5.8 Relationship between Young's modulus and electrical resistivity in carbon fibres.⁸ (Copyright 1997, reproduced with permission from Elsevier Science.)

5.3 PAN-based carbon fibres

5.3.1 Principles of production

Polyacrylonitrile (PAN) fibres are made by a variety of methods. The polymer is made by free-radical polymerisation, either in solution or in a solvent–water suspension. The polymer is then dried and redissolved in another solvent for spinning, either by wet-spinning or dry-spinning. In the wet-spinning process, the spin dope is forced through a spinneret into a coagulating liquid and stretched, while in the dry-spinning process, the dope is spun into a hot gas chamber, and stretched. For high-strength carbon fibres, it is important to avoid the formation of voids within the fibre at this step. Dry-spun fibres are characterised by a ‘dog-bone’ cross-section, formed because the perimeter of the fibre is quenched before much of the solvent is removed. The preferred process for high-strength fibre today is wet-spinning. Processes for melt-spinning PAN plasticised with water or polyethylene glycol have been developed, but are not practised commercially. A significant improvement in carbon fibre strength was obtained by

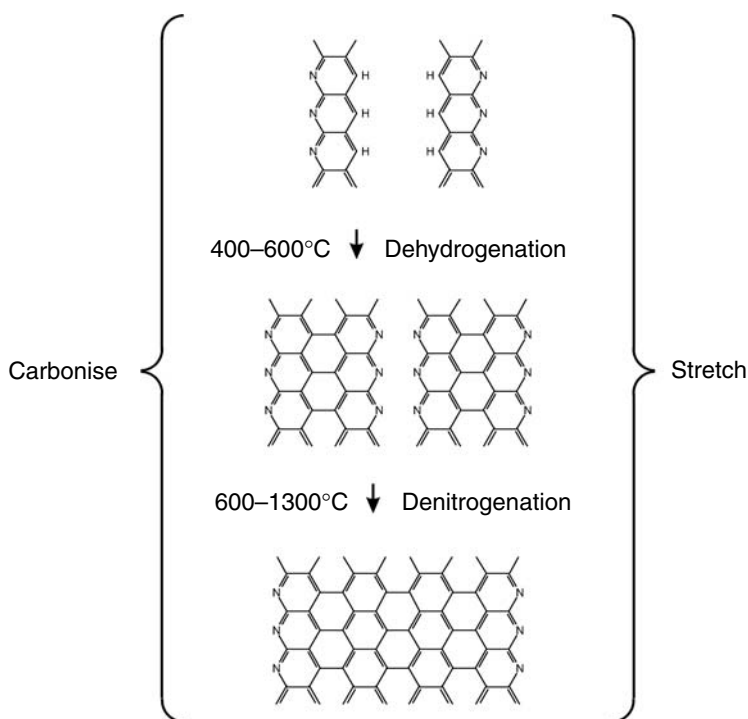


5.9 PAN-based carbon fibre chemistry: cyclization and oxidation.

spinning the PAN precursor under clean room conditions.⁹ The strength of fibers spun in this way and subsequently heat treated was found to improve by >80% over conventionally spun fibres. The mechanism is presumed to be removal of small impurities which can act as crack initiators. This technology is believed to be critical for production of high strength fibres such as Toray's *T800* and *T1000*.

Initially, commercial PAN-based carbon fibres were made from the polymers developed for textile applications. However, these fibres were neither very stiff nor strong. Development efforts over the 1960s and 1970s focused on increasing molecular weight, introducing co-monomers to assist processing, and eliminating impurities that limited mechanical strength. The chemistry of conversion of PAN to carbon is quite complex, and the interested reader is referred to an excellent treatment in Peebles.³ The critical steps are outlined as follows.

The first critical step in making carbon fibre from PAN fibre is causing the pendant nitrile groups to cyclise, as illustrated in Fig. 5.9. This process is thermally activated and is highly exothermic. The activation temperature is influenced by the type and amount of co-monomer used. It is also important to keep the fibre under tension in this process, and indeed, during the whole conversion process. The next step is to make the fibre infusible: this is accomplished by adding oxygen atoms to the polymer, again by heating in air (for a fuller discussion of stabilisation chemistry, see Section 5.4.8).



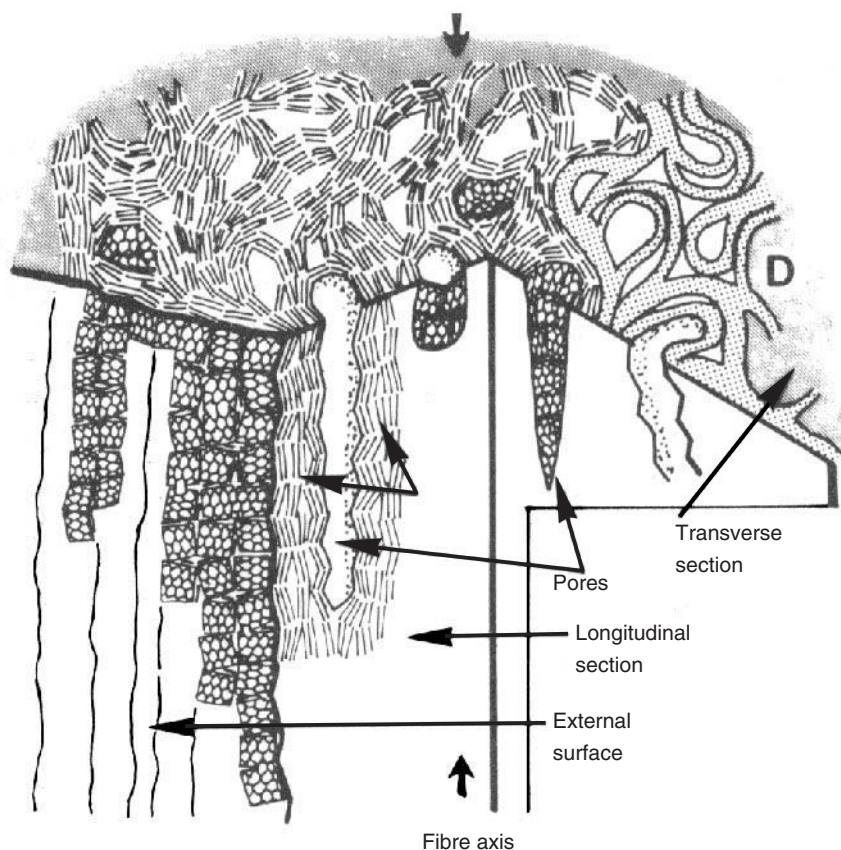
5.10 PAN-based carbon fibre chemistry: carbonisation.

The reaction is diffusion limited, requiring exposure times of tens of minutes. When about 8% oxygen by weight has been added, the fibre can be heated above 600°C without melting. At such temperatures, the processes of decyanisation and dehydrogenation take place, and above 1000°C large aromatic sheets start to form, as illustrated in Fig. 5.10.

The weight loss experienced in the production of carbon fibres from PAN precursor is approximately 50%. This leads to a structure containing many longitudinal voids, as illustrated in the view of the structure shown in Fig. 5.11,⁹ and a density of ~1.8g/cm³, compared with 2.28g/cm³ for pure graphite, and 2.1g/m³ for pitch-based carbon fibres. The polymeric nature of the fibre is evident from the fracture surface shown on Fig. 5.12.¹⁰ The fibrils are evident on the wall of the fibre. An enlargement of the fracture surface in Fig. 5.13 shows fibrils at the nanometer scale.

5.3.2 Manufacturing technology

Most details of the manufacturing processes for carbon fibres are the proprietary information of producers. A general impression of the operation is



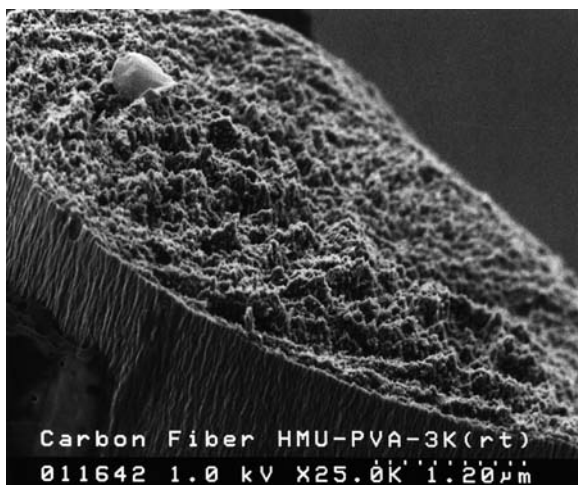
5.11 Model of microtexture of high tensile strength PAN-based carbon fibre.⁹ (Copyright 1984, reproduced with permission from Elsevier Science.)

illustrated in Fig. 5.14 which is a diagram of machinery sold by RK Textiles in the 1980s for the production of carbon fibres. The upper diagram is the oxidising stage and the lower is the carbonising stage. The long residence-times needed for the reactions to occur and for volatile by-products to exit from the interior of the fibre mean that: (a) very large ovens are needed; (b) process speeds are slow.

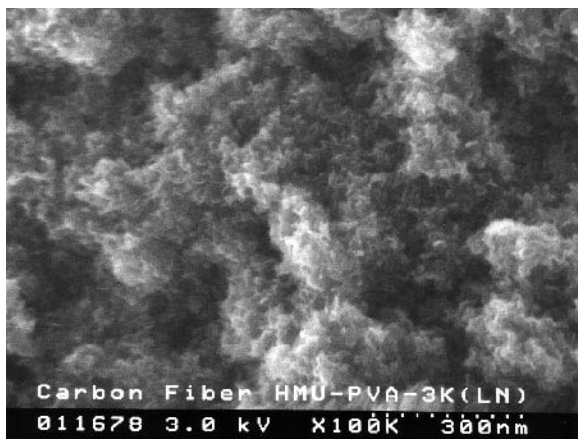
5.4 Pitch-based carbon fibres

5.4.1 General purpose pitch-based carbon fibre

The low-strength fibres, which are shown at bottom left of Fig. 5.3, are sometimes referred to as 'isotropic' carbon fibres, since they are made from



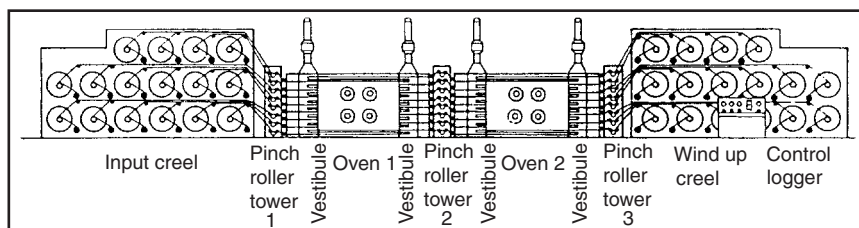
5.12 PAN-based carbon fibre fracture surface.¹⁰



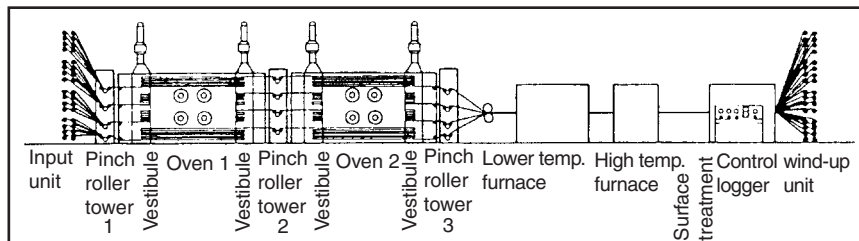
5.13 Enlargement of fibrils in PAN-based carbon fibre fracture surface.

isotropic pitch. These pitches are prepared from high-boiling fractions of petroleum feedstocks, usually heavy slurry oils produced in catalytic cracking of crude oil. A typical commercial pitch is Ashland *Aerocarb 70*, which has a softening temperature of 208°C and a viscosity of 1 Pas at 278°C. Pitches may be subjected to additional treatments to reduce low molecular weight components selectively.¹¹

General purpose fibres are prepared by two different spinning methods, centrifugal spinning and melt blowing.



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CARBONISING LINE

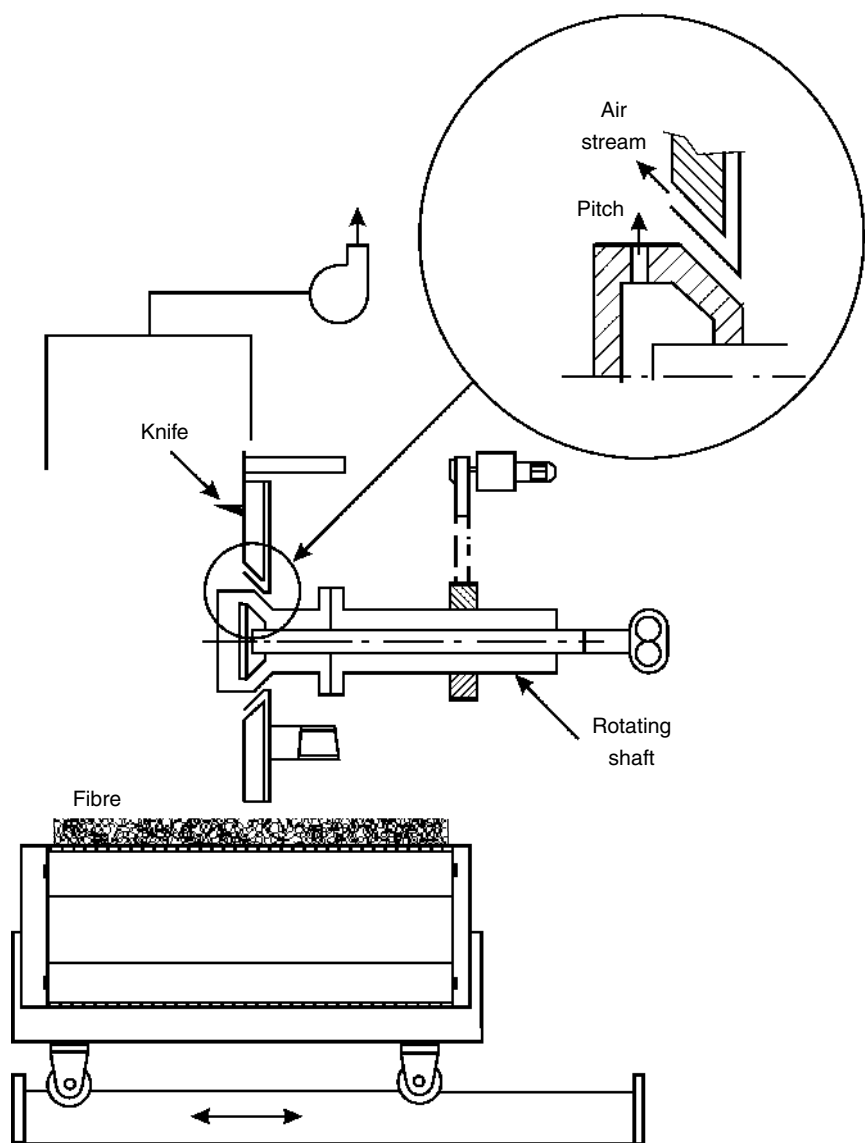
5.14 Schematic diagram of machinery for production of carbon fibres. (Reproduced from *Fiber Reinforcements for Composite Materials*, ed. A R Bunsell, Elsevier 1988, p. 103.)

Centrifugal spinning is practised commercially in the production of glass fibres. It was adapted for carbon fibre production by the Kureha Company in Japan in the 1970s.^{12,13} In this process, molten pitch is forced through small holes in a rotating bowl. The pitch stream is attenuated into a fibre by centrifugal forces, and is directed against a cutter by a stream of air (see Fig. 5.15). The spun fibres may be cut into shorter lengths by a judiciously positioned knife. The fibres are then processed in the form of a tow or a mat.

Melt blowing was originally developed for the manufacture of fibres from polypropylene, but was adapted for pitch by Ashland Oil Co in the 1970s. It is a very high productivity process, giving production rates per spinneret hole of the order of 10 times conventional melt spinning. In this process, a molten stream of pitch is extruded into a high velocity stream of forward-ing gas, which rapidly attenuates the fibre. A commercial die is illustrated in Fig. 5.16. The physics and mechanics of the process are well articulated.^{14,15}

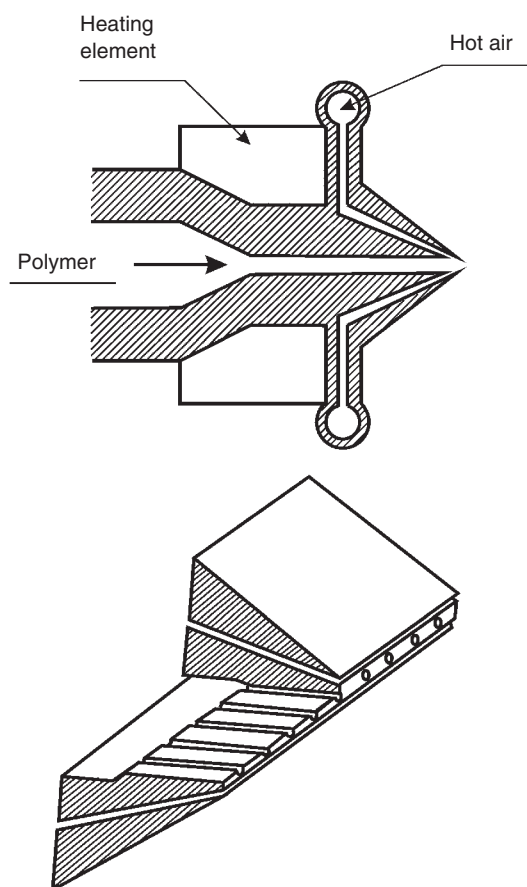
5.4.2 High-performance pitch-based carbon fibres

High-performance fibres are made from mesophase pitch, which is a discotic liquid crystalline material. While mesophase pitches can be made from many starting materials, there are only a few that are of commercial interest. These are dealt with in the sections which follow. These fibres are typically melt spun, and spinning technology is the same for all pitch types.

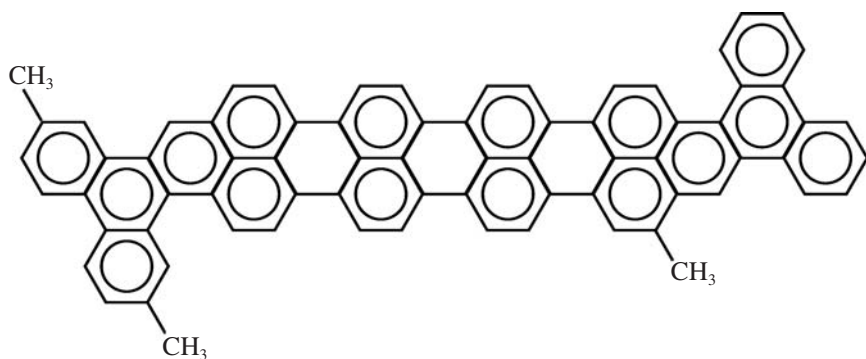


5.15 Centrifugal spinning apparatus.

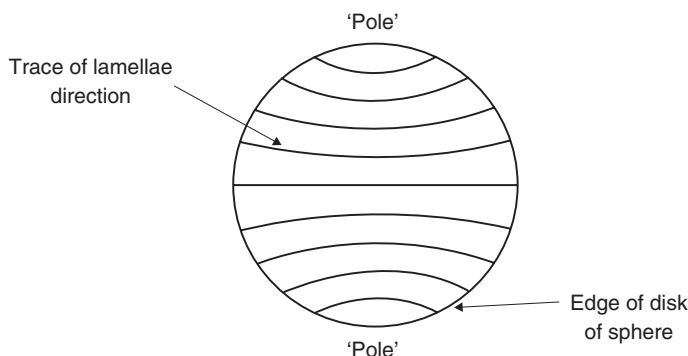
There are three common elements in pitch preparation: first, a highly aromatic feedstock; second, a process for polymerising the molecules; third, a process for separating out the unreacted feed molecules. The feedstock is typically a decant oil from cat cracker bottoms. When polymerised, the pitch molecule will have characteristics similar to the molecule shown in Fig. 5.17.



5.16 Melt-blowing apparatus.¹⁴ (Copyright 1988, the American Chemical Society. Reproduced with permission of R L Shambaugh.)



5.17 Typical pitch molecule.

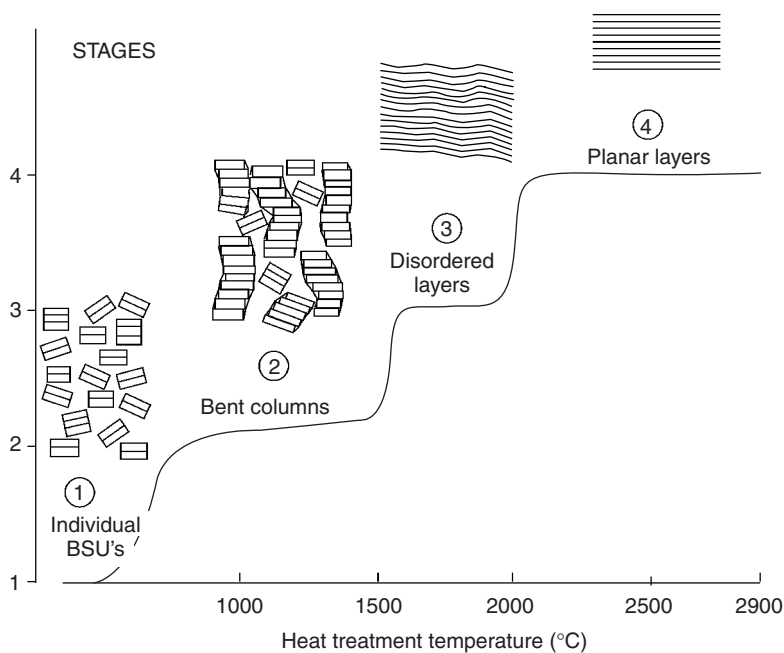


5.18 Brooks and Taylor sphere.

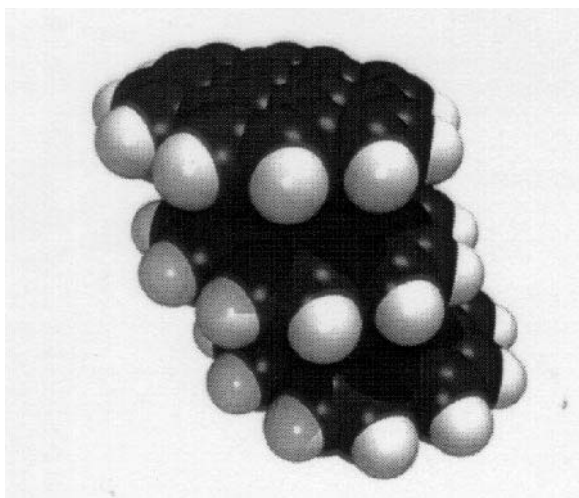
When they get sufficiently large, the pitch molecules aggregate will form 'Brooks and Taylor' spheres,¹⁶ as shown in Fig. 5.18. These in turn coagulate to form larger spheres and then, as polymerisation continues, there is a phase inversion and a continuous nematic liquid crystalline phase, typically called mesophase (Greek for changing phase) is formed. In a classic treatise showing the various structural changes as the pitch progresses to graphite, Oberlin¹⁷ shows the mesophase as consisting of molecules consisting of two or three aromatic molecules that are stacked face to face in a slight overlapping pattern, as shown in Fig. 5.19. These are called basic structural units (BSU's). This arrangement was confirmed by Vorpagel and Lavin,¹⁸ via molecular dynamics calculations on model compounds. Figure 5.20 shows the lowest energy configuration for three coronene atoms, in which each molecule is slightly shifted compared to its neighbour, and Fig. 5.21 shows that the lowest energy configuration for a fourth molecule (in this case ovalene) is parallel to the slanted face.

Pitches are characterised by their fractional solubility in increasingly powerful solvents; for example toluene, pyridine, quinoline. The highest molecular weight fractions are not soluble in any known solvent. It is believed that the smaller molecules in the pitch are solvents for the larger ones, and allow the pitch to flow at elevated temperatures.

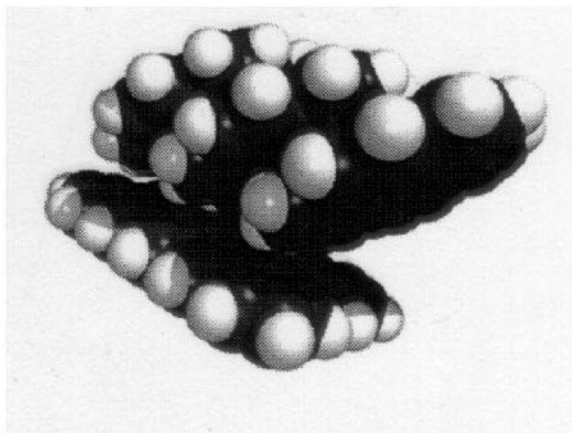
Petroleum-based pitches are typically made from the same slurry or decant oils used to make isotropic pitches. The earliest processes for making mesophase pitches used a long heat soak (typically about 30 hours at 400 °C) under an inert atmosphere, while a gas sparge was used to take away volatile compounds.¹⁹ Such pitches might typically have a molecular weight of about 1000 Daltons (Da), and melt at about 300 °C. They would also be characterised by high quinoline insolubles.



5.19 Stages in graphitisation of a pitch-based fibre.¹⁷ (Copyright 1984, reproduced with permission from Elsevier Science.)



5.20 Lowest energy state for three coronene molecules.¹⁸ (Copyright 1992, reproduced with permission from Elsevier Science.)



5.21 Lowest energy state for three coronene molecules and one ovalene molecule.¹⁸ (Copyright 1992, reproduced with permission from Elsevier Science.)

Coal-tar pitches are a by-product of coke ovens associated with steel-making operations. They differ from petroleum pitches in their rheological properties; for a given molecular weight, the flow viscosity is much higher. Coal-tar pitches also have fewer aliphatic groups on the molecules, which gives longer stabilisation cycles. A breakthrough in preparation of coal-tar pitches came when the Japanese Agency of Industrial Science and Technology developed a process for hydrogenating them,²⁰ significantly reducing viscosity and reducing quinoline insolubles to zero. The physical properties of fibres from coal-tar pitches are generally competitive with fibres from petroleum pitches, except that they are not capable of making the highest modulus products (800 GPa and higher).

5.4.3 A paradox

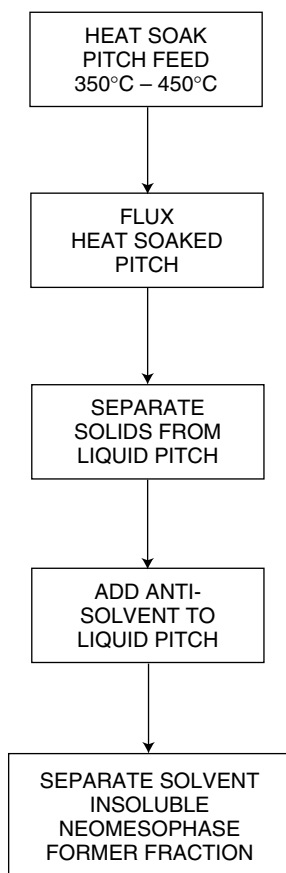
The requirements for a strong polymer fibre are well known. They start with extremely pure ingredients, which are polymerised to very high molecular weights. Once spun, the crystallites are oriented parallel to the fibre axis by stretching. In the case of pitch-based carbon fibres, the situation is very different. The ingredients come from a waste stream of unknown and variable composition. Since the molecular weight of a pitch is positively correlated with its melting point, molecular weight must be kept down, so that fibre can be spun below about 300 °C. Above this temperature, seals are unreliable and equipment becomes very expensive. Finally, the as-spun pitch-based carbon fibre is too weak to stretch. These failings are compensated by the wonderful self-organising properties of aromatic carbon, particularly

its ability to orient crystallites along the fibre axis by heat treatment in the relaxed state.

5.4.4 Pitches via solvent extraction

Diefendorf and Riggs²¹ observed that isotropic pitch contains a separable fraction, capable of forming mesophase pitch. They also found that the isotropic pitch developed an anisotropic phase on heating, which could be concentrated by a solvent extraction process. This approach was extended by Greenwood to obtain a 'heart cut' pitch,²² as shown in Fig. 5.22. First, the slurry oil would be heat soaked for a moderate period of time, say 10 or 12 hours. Then the product would be dissolved in a solvent, such as benzene

U.S. Patent Jul. 7, 1981 Sheet 1 of 2 4,277,324



5.22 Process for preparation of mesophase pitch.

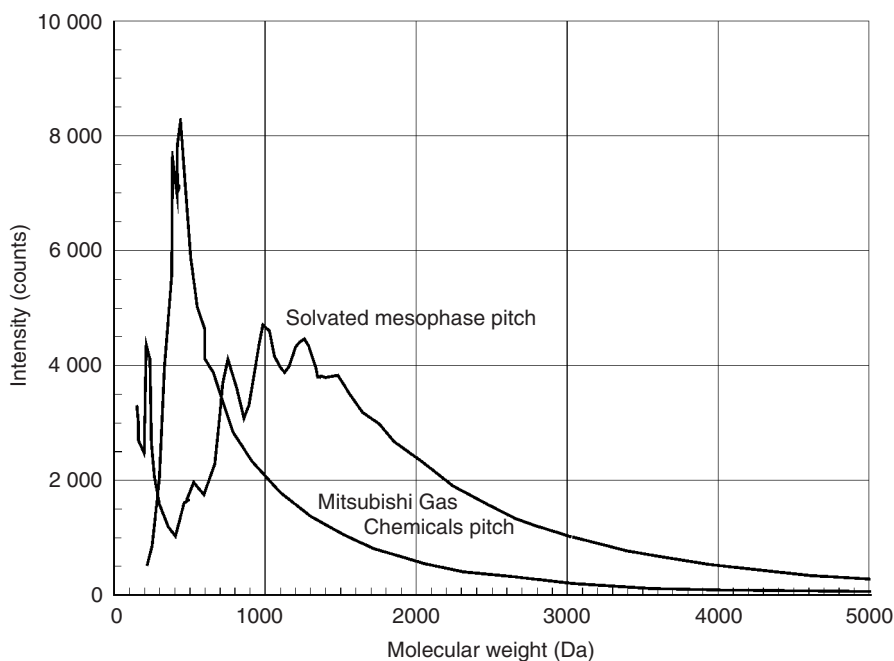
or toluene, and the insoluble fraction (high molecular weight material) rejected. Next, a poor solvent was added to the solution, causing precipitation of the higher molecular weight material remaining. The lowest molecular weight material remained in solution and was rejected. The precipitate was then dried and prepared for spinning. Such pitches typically had negligible quinoline-insoluble content. This was a particularly effective route to making very high strength and modulus fibres but is no longer used.²³

5.4.5 'Polymeric' pitch

Polymerisation of aromatic molecules is known to be promoted by 'Lewis acid' catalysts such as AlCl_3 . However, large ratios of acid to oil are needed, and it has proven difficult to remove all of the catalyst from the finished pitch. Mochida *et al.*²⁴ realized that a strong Lewis acid combination, HF/BF_3 , is both a solvent for aromatic molecules and an effective catalyst for their polymerisation into mesophase pitch. Since HF/BF_3 is a gas at atmospheric pressure, it can be removed completely from the product. Mochida showed that pitches yielding excellent fibres could be made from starting materials such as naphthalene²⁴ or methylnaphthalene.²⁵ The latter ingredient gives the resulting pitch a large number of aliphatic groups, and speeds the stabilisation process. This process has been commercialised by Mitsubishi Gas Chemicals, Inc., and the pitch is offered for sale on the merchant market. In this process, the pitch is made from pure ingredients akin to a polymer.

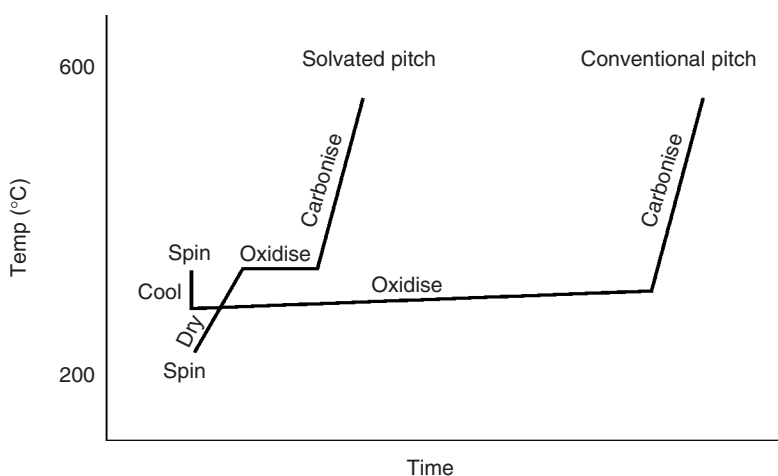
5.4.6 Solvated mesophase pitch

A technological advance which holds great promise for reducing fibre costs is the development of solvated mesophase pitch. This material consists of a heavy aromatic pitch fraction, and a volatile solvent fraction.²⁶ The solvent fraction is rich in materials with more than one aromatic ring. These act as plasticisers and allow the spinning of very high molecular weight pitches. The high molecular weight mesophase fraction melts at temperatures above 350°C , and may even be unmeltable. Measurement of molecular weight in pitches has been both difficult and unreliable. However, Southard *et al.*²⁷ showed that useful information could be obtained via matrix-assisted laser desorption ionization mass spectroscopy (MALDI) and the distinguishing characteristics of the solvated mesophase pitch are shown in a MALDI plot in Fig. 5.23. Note the peak at 230 Da, representing the solvent, and additional peaks at multiples of this level, representing polymerisation. In comparison, the Mitsubishi Gas Chemicals pitch peaks at 400 Da, and then decreases monotonically. Once the solvent is removed, the fibre can be thermoset rapidly at high temperatures,²⁸ as illustrated in Fig. 5.24. The pitch may be processed by melt blowing into fibres, using the process described



Positive ion spectra

5.23 Matrix assisted laser desorption ion (MALDI) spectra for mesophase pitches.



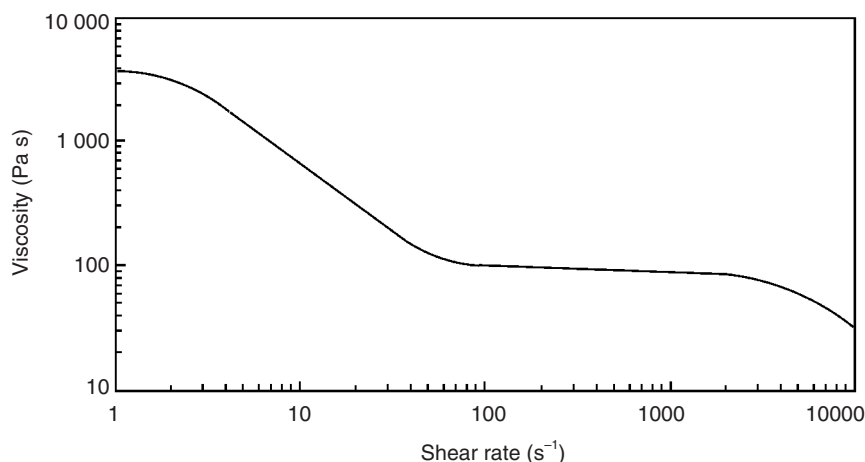
5.24 Comparative thermosetting of solvated and conventional mesophase pitch fibres.

in Section 5.4.1. Typically, melt-blown carbon fibres are curved and low in strength. However, advances in this technology²⁹ have led to straight fibres that, when made from solvated mesophase pitch, have strengths in the same range as melt-spun fibres.

5.4.7 Fibre formation

Preparation of high-performance pitch-based carbon fibres requires critical understanding of the rheology of mesophase pitches (a discotic liquid crystalline material). The molecules are aromatic structures which, through interaction, are associated to form optically ordered liquid crystals, which are either liquid or solid depending on temperature. This ordering, or lack thereof, affects processing and more importantly product responses.³⁰ The response of mesophase pitch in shear flow is dependent upon composition but, similar to that seen in shear-thinning materials with several Newtonian plateaus (Fig. 5.25). However, steady-state behaviour of this nature is generally not experienced in the fibre formation process. This necessitates careful consideration of the molecular state in the various flow regimes. Not only the relaxation condition but the orientation relative to flow field must be considered. Temperature sensitivity, or flow activation energy of mesophase pitch, is also high.³¹ All these elements must be properly balanced and controlled to produce uniform filaments from commercial spinning processes and subsequent downstream treatments.

Melt-spinning of mesophase pitches is the preferred method of obtaining high-performance fibres.³² The controlled drawing process provides the most uniform continuous filament products, while the wound product form



5.25 Rheological characteristics of mesophase pitches.

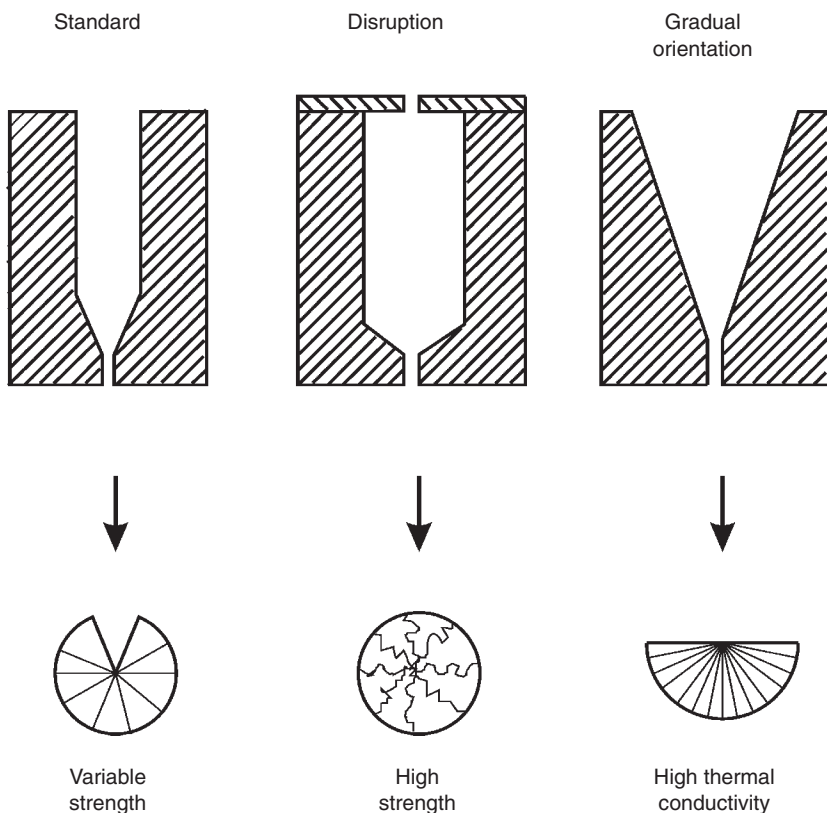
necessitates uniform treatment of bundles of fibres in downstream processing. However, processing rates are generally low and greatly depend upon the quality of the pitch feedstock. Pitch rheology and the arrangement of the discotic liquid crystal determines mesophase pitch structure³³ and resultant product responses. This structure can be defined on a macroscopic scale by scanning electron microscopy (SEM), whereas microscopic structure on the atomic scale requires use of other techniques such as transmission electron microscopy (TEM). Several researchers have effectively used these techniques to determine the structure of pitch fibres.^{33,34} The orientation of discs relative to one another and the fibre axis is an important element of control in the filament formation step.^{35,36}

By utilising filament formation geometry to establish preferred flow profiles and spin conditions that complement them, structure can be manipulated and controlled. Example geometries, when coupled with appropriate feedstocks and operating conditions, conducive to structure control and resultant product responses, are shown in Fig. 5.26. Fibre cross-sectional structures, as defined by SEM, are schematically represented while product categorisations of physical and thermal properties are noted. The typical fibre structures illustrated here have been labelled by several researchers as ‘pacman’ radial, wavy radial and severe ‘pacman’. Other structures such as random, onion-skin and ‘Pan Am’ have also been produced and categorised. The fibres with ‘pacman’ cross-sections have longitudinal splits which may adversely affect physical properties. Downstream processing, within limits, appears to have minimal influence in changing the general ‘structure’ established in the filament-formation step. Subsequent heat treatment densifies the initial structure, i.e. increases the packing to increase tensile and thermal properties and modulus.

The use of non-round pitch carbon fibre cross-section provides an alternate approach to modify ‘structure’, with potential enhancement of fibre adhesion to matrices or improved surface characteristics. This forced filament geometry is routinely practiced with several polymeric systems in melt spinning to control product response. Ribbon and C-shaped carbon fibres have been provided to accomplish this.^{37,38} However, the stiffness aspects of modified fibre cross-section could be adversely affected while thermal and adhesion responses may be improved. Packing densities of individual fibres in fibre assemblages may also be changed. Processing continuity and part fabrication costs could be critical aspects influencing adoption of this technology to modify product responses.

5.4.8 Stabilisation and carbonisation

When pitch-based carbon fibres are spun, they must be prepared to undergo the ‘coking’ reaction, in which much of the hydrogen in the fibre is removed

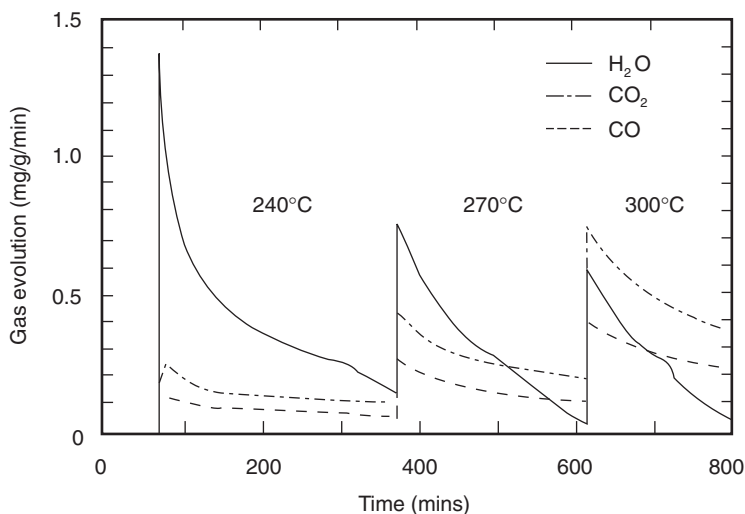


5.26 Influence of spinneret design on fibre morphology.

and the fibre becomes infusible. This occurs at 450 to 600°C. However, if the fibre were simply heated, it would melt. In commercial processing this is avoided by a 'stabilising' or 'infusiblising' step in the process.

There are a number of alternative process routes to accomplish stabilisation,³⁹ but the most common process is air oxidation. The fibre is heated in the presence of oxygen (typically a mixture of air and nitrogen) which diffuses into the core and reacts with the pitch molecules, preferentially at aliphatic or alicyclic sites. There are two chemical mechanisms involved. The first mechanism is that whenever oxygen is added to an aromatic molecule, its melting or boiling point is raised (e.g. benzene boils at 80°C, but phenol boils at 182°C). In the second mechanism, the oxygen molecule bridges two pitch molecules; this replaces two small molecules with one large one twice the size, which is a very powerful method of raising the melting point.

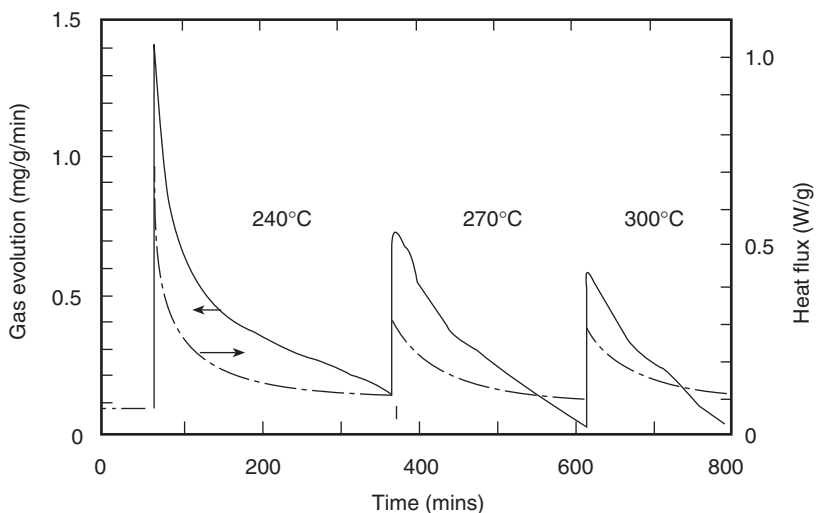
The stabilisation reaction is controlled by the diffusion of oxygen into the fibre, which is a slow process. The diffusion rate is known to increase with



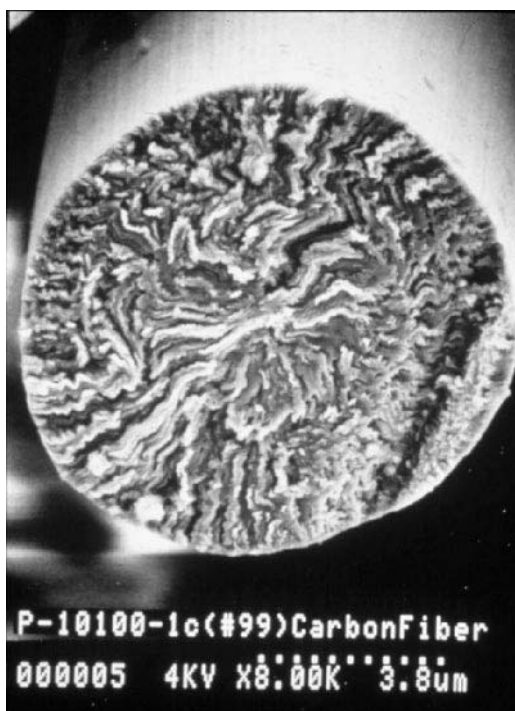
5.27 Gas evolution as a function of temperature during stabilisation.⁴⁰
(Copyright 1992, reproduced with permission from Elsevier Science.)

temperature, so there is a temptation to raise the temperature and drive the reaction. However, there are several problems associated with doing this. The first is that the heat released in the stabilising process is large – of the order of 500 calories/g of fibre – and the reaction can become autocatalytic, creating the equivalent of a charcoal fire and destroying the fibre. Also, at about 270 °C, the Boudouard reaction becomes important. In this reaction, oxygen is chemisorbed onto the surface of the fibre and reacts with the carbon. It is then removed as CO and CO₂, removing carbon from the surface of the fibre. In extreme cases, pitting of the fibre may be seen and the fibre fails to achieve maximum strength. Oxygen uptake reactions are believed to take place at aliphatic side chains to produce a variety of compounds by oxygen insertion and dehydrogenation.²⁵ Since coal-tar pitches are relatively deficient in aliphatic and alicyclic groups, longer cycle times are required.

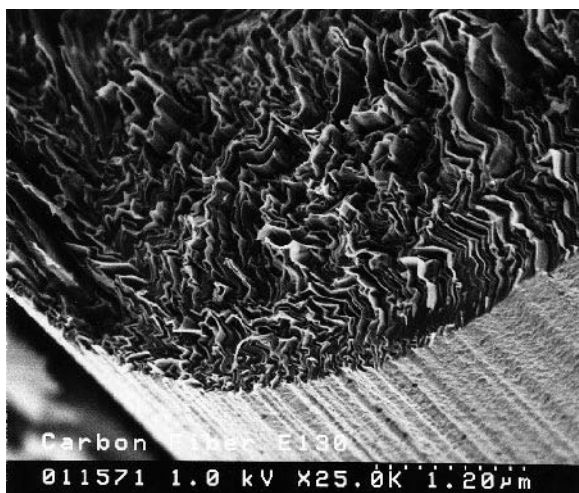
Lavin⁴⁰ shows comparative rates of evolution of water, CO and CO₂ when fibres are stabilised in air in a stepped temperature sequence. In this experiment the temperature was held at 240 °C for 6 hours, raised to 270 °C for 4 hours and then to 300 °C for 3 hours. Water evolution spiked at the beginning of each cycle, and then fell off gradually close to zero (see Fig 5.27). CO and CO₂ evolution spiked at the beginning of each cycle, and then fell to an asymptotic value about half of the initial spike. Water evolution accounted for most of the heat generation (see Fig. 5.28). These data suggest that only a certain number of reaction sites are available for beneficial



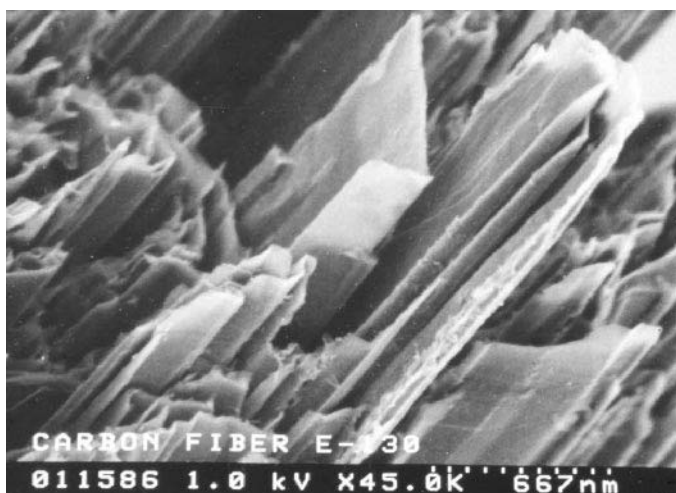
5.28 Gas evolution and heat flux as a function of temperature during stabilisation.⁴⁰ Arrows point to relevant axis. (Copyright 1992, reproduced with permission from Elsevier Science.)



5.29 Pitch-based carbon fibre fracture surface.



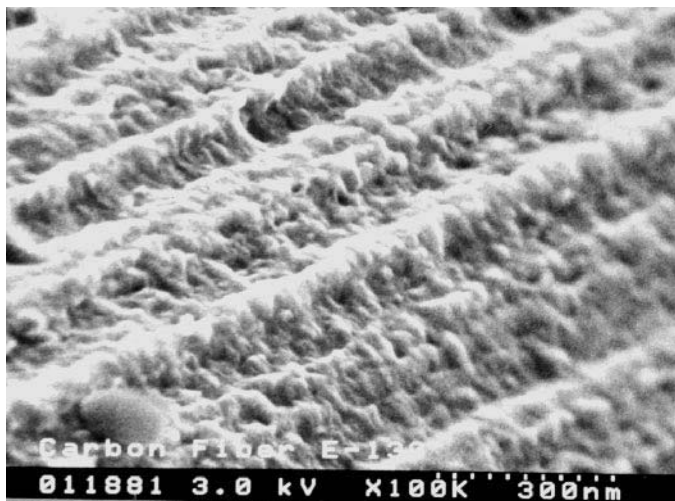
5.30 Pitch-based carbon fibre fracture surface: expanded view.



5.31 Pitch-based carbon fibre fracture surface: view of large crystallites.

reactions between pitch molecules and oxygen at any given temperature. Such reactions are characterised by evolution of water. When water is no longer being evolved, the only reactions taking place are the harmful Boudouard reactions. This suggests a method of monitoring the stabilisation process for effectiveness.

The great advantage of pitch-based carbon fibre over PAN based fibre is



5.32 High-resolution scanning electron micrograph of pitch-based carbon fibre surface.

that carbonisation and graphitisation can be accomplished with the fibre in the relaxed state. Following stabilisation, the fibre is first heated above the coking temperature (450 to 600 °C) in an inert atmosphere to remove some hydrogen and light oils. It is then heated above 1000 °C to remove the remaining hydrogen, oxygen, sulphur and nitrogen, and to form the structures which give the desired balance of breaking strength and modulus. General purpose fibres are heat treated to about 1000 °C.

Commercially useful fibres are made from mesophase pitch at heat treatment temperatures of 1600 °C and above. As heat treatment temperatures are increased, the modulus of mesophase pitch fibres increases and modulus values close to the theoretical modulus of graphite (1 TPa) are possible. The term ‘graphitisation’ is frequently applied to heat treatment above 2500 °C. However, this does not mean that the structure is converted to graphite. Most carbon fibres, even those with a modulus above 700 GPa, are made mostly of turbostratic carbon with small graphitic domains. The inert gases used in carbonising furnaces are nitrogen and argon. Nitrogen is preferred because of cost. However, above about 2000 °C, significant quantities of cyanogens are produced by the reaction of nitrogen with the graphite of the furnace, so argon, which is completely inert, is used instead. Lahijani²³ shows how a two-stage carbonisation can be used to make a mesophase pitch fibre with very high modulus and strength. In the first stage the fibre is heat treated to 2400 °C, and in the second, to 2600 °C or greater, depending on the desired final modulus.

A SEM image of the fracture surface of a pitch-based carbon fibre is shown in Fig. 5.29.¹⁰ It will be noted that there are many zig-zag features, which allow the fibre to sustain a 40% reduction in surface area during heat treatment without introducing damaging hoop stresses. The large, flat crystals that make up the fibre are evident in Figures 5.30 and 5.31, and the nature of the surface is shown in Fig. 5.32.

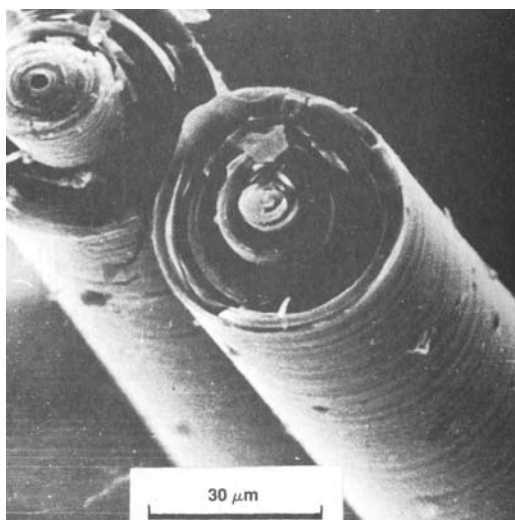
5.5 Vapour-grown carbon fibres

Pure carbon fibres may be grown by a catalytic process from carbon-containing gases. The catalysts are typically transition or noble metals, and the gases are CO or virtually any hydrocarbon. The fibres were first identified in 1890,⁴¹ and they were the subject of study within the oil industry more recently, with the objective of preventing their growth in petrochemical processes. The fibres may take a variety of forms, depending upon the catalyst system and the constituents of the feed gas. The interested reader is referred to an excellent review article by Rodriguez,⁴² which includes a description of a generic process for catalytic formation of carbon fibres.

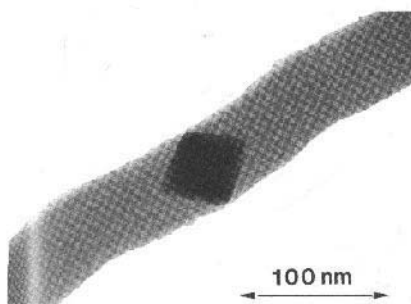
Typically, about 100mg of powdered catalyst is placed in a ceramic boat, which is positioned in a quartz tube located in a horizontal tube furnace. The catalyst is reduced in a dilute hydrogen/helium stream at 600°C, and quickly brought to the desired reaction temperature. Following this step, a mixture of hydrocarbon, hydrogen and inert gas is introduced into the system, and the reaction is allowed to proceed for about 2 hours. This approach will produce about 20 g of carbon fibres from the more active catalyst systems. In this process, the fibre diameter is typically related to the catalyst particle size. The process proposed for fibre formation⁴³ involves adsorption and decomposition of a hydrocarbon on a metal surface to produce carbon species which dissolve in the metal, diffuse through the bulk, and ultimately precipitate at the rear of the particle to produce the fibre. This process is described as tip growth. There is an analogous process in which the catalyst particle remains attached to the support.

Vapour-grown fibres typically have a hollow centre and multiple walls, which are arranged like tree rings, as shown in Fig. 5.33. However, they may be grown in many other shapes, as shown in Fig. 5.34. A shape particularly useful for storage of hydrogen⁴⁴ is shown in Fig. 5.35.

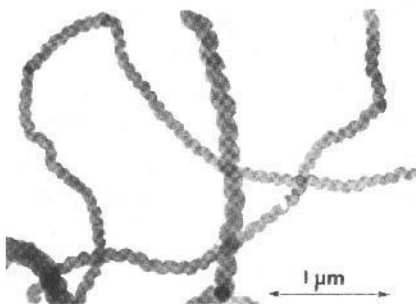
There are basically two kinds of process for producing vapour-grown fibres. The most common process is the one described above, in which the catalyst is a metal supported on a ceramic. This process produces long fibres which are tangled together in a ball that is extremely difficult to break up. A variant of this process is one in which the catalyst is an organometallic, injected into a chamber containing the gas mixture. These fibres tend to be short and



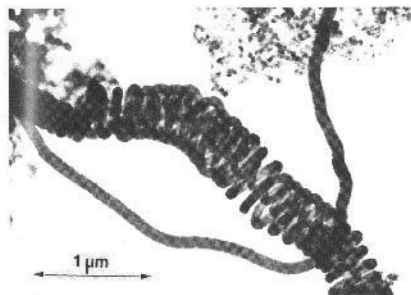
5.33 Vapour-grown carbon fibre fracture surface. (Reprinted with permission from Endo M, 'Grow carbon fibres in the vapour phase', *Chemtech* Vol. 18(9), 568–576. Copyright 1988, American Chemical Society.)



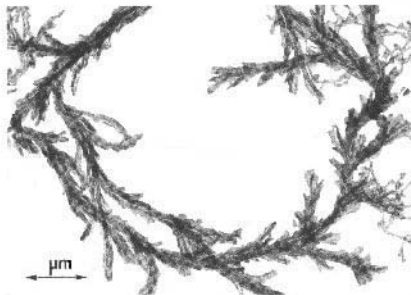
(a)



(b)

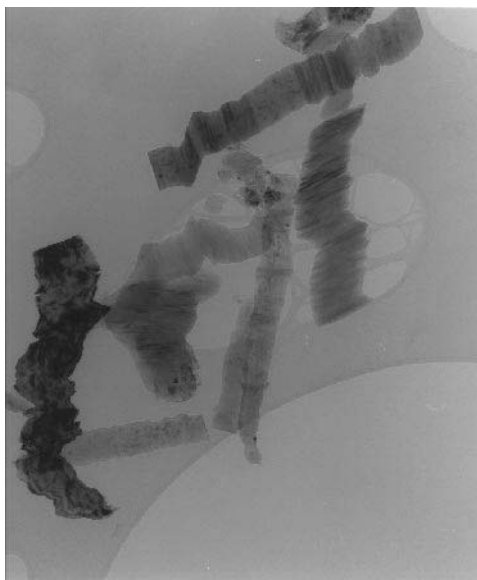


(c)



(d)

5.34 Transmission electron micrographs of different types of carbon nanofibres: (a) bidirectional; (b) twisted; (c) helical; and (d) branched. (Reprinted from Ref. 42 by permission of the author. Images (a) and (b) originally appeared in the *Journal of Catalysis*. Permission to reproduce them was also granted by Harcourt, Brace & Co.)

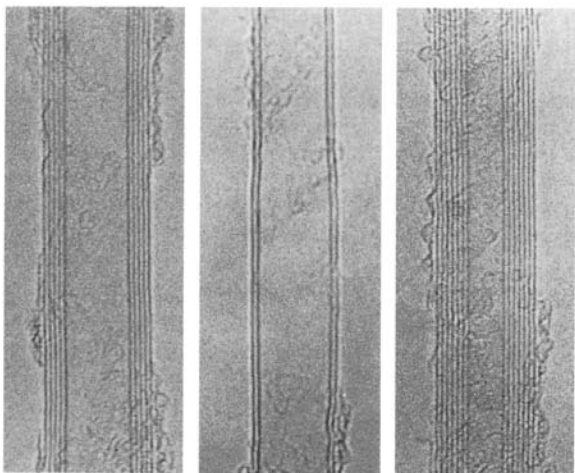


5.35 Vapour-grown carbon fibres with good hydrogen storage capability.

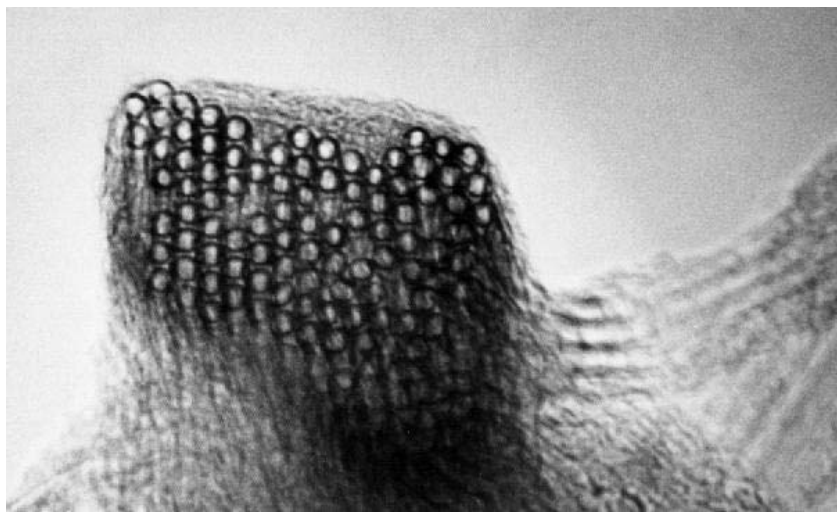
straight. However, they may be aggregated together and bound by amorphous carbon. In either case, the reinforcing capabilities of the fibre are restricted.

5.6 Carbon nanotubes

The last decade has seen the genesis of extremely small fibres of pure carbon which, based on their physical properties, might truly be called superfibres. The first important discovery was made in 1991, when Iijima⁴⁵ analysed the cathode deposit from a carbon-arc process used to make C_{60} , and found carbon fibres with diameters in the range of 4 to 50 nanometers (nm), and lengths of several micrometers (μm). The fibres had well defined, multiple walls, as shown in Fig. 5.36. Multi-wall carbon nanotubes (MWCNT) as they were called, were quickly found to be extremely stiff and strong. They were also electrically conductive and because of these characteristics found application as electron emitters in field emission devices.⁴⁶ In 1993, Iijima⁴⁷ and Bethune⁴⁸ *et al.* simultaneously discovered that when transition metal catalysts were introduced to the carbon arc, single wall carbon nanotubes (SWCNT) were made, which were of almost infinite length. The individual SWCNT had diameters in the range of 1.5 nm. Later, Guo *et al.*⁴⁹ made similar products in a laser ablation process. These fibres were aggregated into ropes (see Fig. 5.37) which typically included about 100



5.36 Multi-wall carbon nanotubes.⁴⁵ (Copyright 1991, reproduced with permission from *Nature*.)



5.37 Ropes of single-wall carbon nanotubes.⁵⁰ (Reprinted with permission. Copyright 1996, the American Association for the Advancement of Science.)

individual SWCNT, and measure about 10nm across.⁵⁰ The SWCNT have subsequently been found to have a Young's modulus of 1.2 TPa, which makes them the stiffest material known to man. The interested reader is referred to a comprehensive review of carbon nanotubes by Harris.⁵¹

The arc and laser ablation processes are not scaleable to industrial production levels and consequently attention is being given to chemical vapour deposition manufacturing processes for the same product. Of particular note is a process based on disproportionation of CO under high pressure,⁵² which produces pure single-wall carbon nanotubes of a quality similar to the laser ablation process. Also noteworthy is a process based upon production of nanometer-scale catalyst particles via an aerogel route.⁵³ These particles are then used to make single wall carbon nanotubes by the process described in Section 5.5.

While the term 'nanotube' was originally applied to products from carbon arc and laser ablation processes, it is now being used also for vapour-grown fibres of 100 nm or less. In general, vapour-grown fibres made at high temperatures (say 1000 °C) are relatively defect-free and resemble carbon arc and laser ablation nanotubes. Vapour-grown fibres made at say 600 °C and below are highly defected and inferior in physical properties to the true nanotubes.

5.7 Applications

As shown in Fig. 5.3, there is a wide range of choice of carbon fibres, which are suited to different applications. The properties of some commercially available carbon fibres are given in Table 5.1.

Development of PAN-based carbon fibres was driven during the 1980s by use in composites for military aircraft. Since carbon fibre composites allowed for reduction in weight, and improvement in range, payload and performance, their value-in-use was very high. Adoption in commercial aircraft followed quickly. Because they made new levels of performance possible, carbon fibres also found their way into sporting goods, medical devices, industrial applications and infrastructure. PAN-based carbon fibre was classified into two groups: aerospace grade, with tight specifications for critical applications, and commercial grade, made in very large tow sizes (46K filaments). With the end of the cold war, military requirements diminished. However, there was still demand for carbon fibre for commercial aircraft and sporting applications expanded rapidly. Carbon fibre found its way into tennis racquets, golf club shafts, fishing rods, skis and many similar applications, to the extent that virtually all major producers authorised capacity increases. Next, the Asian crisis of 1998 struck, slowing demand in all markets at the time new capacity came on line. In the year 2000, PAN fibre capacity is estimated at 45 000 metric tons, while shipments are less than 25 000 metric tons. Prices of aerospace grade fibre fell from over \$60/kg in 1992 to \$17/kg in 2000, while commercial grade fell to \$14/kg. One large producer has set a goal of \$11/kg in 2000–2001.

Pitch-based carbon fibre capacity is difficult to estimate, but is probably

less than 2500 metric tons. Pitch-based fibres have been used in Japan for large volume reinforcement of cementitious matrices. During the Japanese construction boom of the 1980s the industry had sufficient value for lighter-weight and more durable, premium, exterior, building panels. More than 400 000 m² of carbon-reinforced cement curtain walls have been deployed over the last 10 years. Benefits included greater resistance to corrosion, spalling, and freeze-thaw cycling. These curtain walls were deployed in dozens of high-rise buildings.⁵⁴ A large potential market for pitch-based carbon fibres appears to be petroleum production in deep water. Current materials technology, centred mainly around steel, appears to be limiting deepwater production to water depths of about 1800 m. The two major technologies being pursued to develop and produce deepwater reserves are tension leg platforms (TLPs) and floating production submersible (FPS) systems. The use of carbon fibre composites in TLP and FPS technologies, in components such as tendons, production risers and drilling risers, has led to significant improvements in weight, cost, durability and environmental reliability. Significantly, a single TLP needs 14 000 tonnes of high-strength carbon fibre composite, requiring a significant increase in installed capacity in the industry.

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6.1 Introduction

6.1.1 Historical perspective

The drawing of glass into fine filaments is an ancient technology, older than the technology of glass blowing. Winding coarse glass fibres onto a clay mandrel was used as an early manufacturing route for a vessel. With the advent of glass blowing, similar fibre technologies were used to decorate goblets.

In the 1700s, Réaumur recognised that glass could be finely spun into fibre that was sufficiently pliable to be woven into textiles. Napoleon's funeral coffin was decorated with glass fibre textiles. By the 1800s, luxury brocades were manufactured by co-weaving glass with silk, and at the Columbia Exhibition of 1893, Edward Libbey of Toledo exhibited dresses, ties and lamp-shades woven from glass fibre.

The scientific basis for the development of the modern reinforcing glass fibre stems from the work of Griffiths,¹ who used fibre formation to validate his theories on the strength of solids.

Glass fibres are used in a number of applications which can be divided into four basic categories: (a) insulations, (b) filtration media, (c) reinforcements, and (d) optical fibres.

6.1.2 Fibreglass for insulation and filtration

For insulation, the thermal conductivity or sound transmission ability of a fibrous 'wool' is of the most importance. Clearly, the thermal performance will be directly related to the low thermal conductivity of the glass itself but also to the density of the material. In other words, the entrapped air provides the insulating properties but the fibres provide the supporting structure. The efficiency of air entrapment is determined by the fibre diameter and its configuration, which is a function of the fibre spinning technique.

Table 6.1 Typical compositions (in weight %) for glass fibres used for thermal and acoustic insulation¹

	Typical mineral or slag wool	Typical fibre glass insulation	Typical high- temperature grade
SiO ₂	50	63	50
Al ₂ O ₃	10	} 6	} 40
Fe ₂ O ₃	1		
CaO	25	7	6
MgO	14	3	4
Na ₂ O	—	14	—
K ₂ O	—	1	—
B ₂ O ₃	—	6	—
F ₂	—	0.7	—

For filtration, the surface area of the fibres and the size of the spaces between them are the important factors. A number of spinning techniques have been developed, to produce fibres with a range of diameters from 0.05–25 μm . The finest diameter fibres provide the most insulation and filtration effectiveness² as a result of the pore size of the mat.

Fibre spinning for insulation and filtration materials can be achieved by flame attenuation, developed by Owens-Corning Fiberglass in the late 1940s, and the improved Toration process. Steam fiberisation was the basis of the mineral wool process which operated in the 1930s in Toledo, Ohio. This was adapted for glass, in the steam-blown process, which uses high-pressure steam jets below a tank of molten glass to attenuate the glass drops falling from the bushing into fibres. Subsequent techniques involve the free fall of a glass melt onto a fiberising roller (spinning process), air jet (rotary process), or spinning drum (Schuller). In all of these, the fibres are bound into a 'wool' or mat with a phenolic resin binder. The glass source can be a cupola or tank of glass melt above a bushing (in later techniques) or precast marbles, which are melted directly above the bushing. These historical developments are discussed in detail by Mohr and Rowe.²

The formulations for the glasses are shown in Table 6.1.

6.1.3 Reinforcing fibres

For reinforcements, it was recognised by Griffiths¹ that the strength of any material was determined by the presence of flaws of critical dimension. Glass was an obvious material for demonstrating that increasing the surface to volume ratio would lead to increased strength, by reducing the number of flaws of critical dimension. Thus, high strength materials will be filamentary of fine diameter.³

Furthermore, within a bundle of fibres, the individual filaments will have differing strengths, giving rise to progressive failure that can be harnessed in the formation of a composite material. The Young's modulus of inorganic glass is about 20 times that of the polymer resin that holds the fibres together as a composite (originally referred to simply as 'fibreglass' or glass fibre-reinforced plastic). The development of so-called advanced composites occurred with the discovery of high-strength and high-modulus carbon fibres in 1965.⁴ However, reinforced materials had been known since biblical times. The best way of comparing the performance of differing fibres (and of their composites) is through their specific stiffness and strength E_f/ρ and σ_{fu}/ρ , where E_f is the Young's modulus of the fibre, σ_{fu} the strength of the fibre and ρ the density. As shown in Table 6.2, the specific strength of glass fibres is significantly higher than that of conventional bulk materials. However, even after dilution with a resin to give composites of fibre volume fraction 35–60% there is still an advantage in specific strength and specific stiffness for structural applications, especially where low weight, high strength and high stiffness are critical design parameters.⁵ Another advantage is their corrosion resistance.⁶ This chapter will describe their fabrication, properties, applications and performance.

6.1.4 Optical fibres^{7,8}

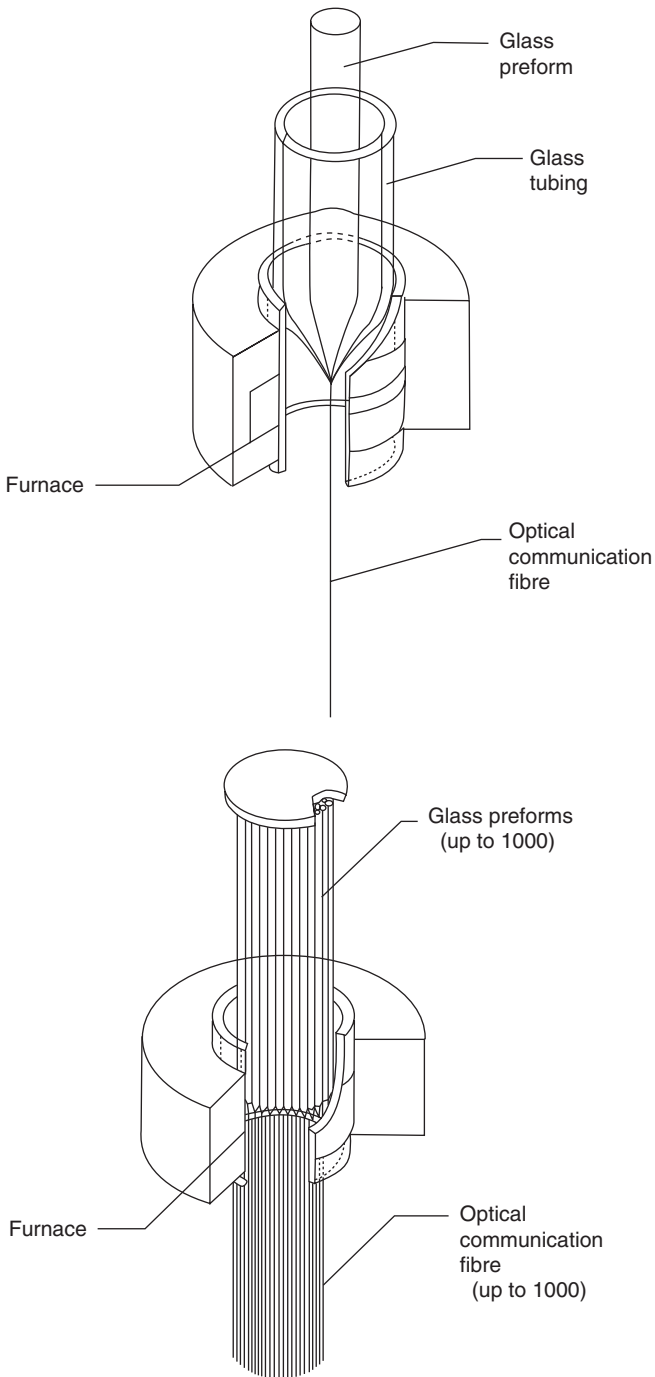
Optical fibres can be made from polymeric (e.g. polymethyl methacrylate) and inorganic glasses. The latter have initiated a revolution in information technology, because they are an effective means of transmitting digitalised data as an electromagnetic wave. Clad optical fibres allow transmission over many kilometres without the need for signal boosting. The high frequency of optical signals allows a bandwidth of 10^5 MHz, permitting significantly higher data capacity than conventional copper cables, while appropriate fibre design allows signal dispersion to be minimised.

Most commercial optical fibres consist of a silica glass core-clad structure, made as a bulk preform and drawn down into an optical fibre of diameter $125\mu\text{m}$, as shown in Fig. 6.1. Ge, P and B are introduced as dopants to give the required refractive index profile, *viz* a core of approximately $8\mu\text{m}$ diameter with a refractive index enhancement of 0.001 to give a monomode fibre. The efficiency of light transmission depends on the wavelength of light employed. Pure fused silica has low loss windows at 1.3 and $1.5\mu\text{m}$ with transmissions down to 0.2dB km^{-1} and possible transmission distances of hundreds of kilometres. In the near-UV, this increases to $>10\text{dB km}^{-1}$. Chemical vapour deposition (CVD) techniques allow the manufacture of preforms with the required refractive index profile and purity levels of better than 0.1 ppb for critical absorbing transition metal impurities. Wide

Table 6.2 Specific properties of glass and other fibres in comparison to other materials

		E (GPa)	σ_u (GPa)	ρ (g/cm ³)	E/ρ (Mm)	σ_{fu}/ρ (km)	ϵ_u (%)	$d_f/(\mu\text{m})$
E-glass fibre		72	1.5–3.0	2.55	2.8–4.8	58–117	1.8–3.2	10–20
S-glass fibre		87	3.5	2.5	3.5	140	4.0	12
S2-glass fibre		86	4.0	2.49	3.5	161	5.4	10
Carbon fibre		220–350	2.3–3.7	1.8–2.0	12–18	130–190	0.7–1.7	7
High-performance polymer fibres:	Aramid	60–180	2.65–3.45	1.44–1.47	4.0–12.2	180–235	4–1.9	12
	PBT	250	2.4	1.5	17.0	160	1.0	20
	PE	60–120	1–3	1.0	6–12	100–300	—	—
Steel		210	0.34–2.1	7.8	2.7	4.3–27	—	—
Aluminium		70	0.14–0.62	2.7	2.6	5–22	—	—
Bulk glass		60	0.05–0.07	2.6	2.3	1.9–2.7	0.08–0.12	—
Resins (epoxy)		2–3.5	0.05–0.09	1.2	0.16–0.29	4–7.5	1.5–6	—
High-density polyethylene (PE)		1.3	0.027	0.96	0.135	2.8	—	—

E = Young's modulus, σ_u = tensile strength, ρ = density, E/ρ = specific modulus, σ_u/ρ = specific strength, ϵ_u = failure strain, d_f = fibre diameter.



6.1 Schematic of single and multimode optical fibre forming (after Mohr and Rowe²).

core, multimode optical fibres have been developed where fibres of high numerical aperture are needed, such as for image transmission in medicine. The latter fibres are unsuitable for telecommunications because of the signal dispersion that arises from the many possible light paths.

Recent advances have concentrated on rare earth doping to produce fibre lasers for optical amplification, fibres with Bragg reflection gratings built into their core for signal multiplexing, and both fluoride and chalcogenide glasses that have extended infrared transmission and enhanced amplification characteristics.

6.2 Glass for fibres

6.2.1 Formulations

These inorganic glasses are all based on silica, because it is an excellent glass former. Polymerisation means that $(\text{SiO}_{4/2})_n$ three-dimensional networks form which do not have a sharp melting point and which start to soften at 1200°C but are not fluid enough for spinning as fibres until they reach 2000°C . When silica crystallises, it forms networks made up of cyclic groups such as $(\text{Si}_6\text{O}_{18})^{12-}$ containing 6 SiO_4 tetrahedra, sharing corners, and as embodied in crystalline forms of SiO_2 such as tridymite and cristobalite. Smaller rings occur in various silicate minerals and probably contribute to the disorder present in vitreous silica. Further additives are introduced to reduce the melting temperatures needed for these glasses. Al_2O_3 and B_2O_3 are present in significant concentrations and act as network formers, i.e. are built into the silica network as tetrahedra, as found, for example, in the mineral albite, $\text{NaAlSi}_3\text{O}_8$. These oxides are oxygen deficient compared with silica. Consequently, there will be some oxygen ions in the network with unsatisfied charges. Neutrality can be achieved by incorporating so-called network modifiers such as CaO , BaO , Na_2O or K_2O . Such modifier ions are located near the unsatisfied oxygen ions in the interstices in the network. At higher concentrations they can also start to break up the network, forming non-bridging oxygens. Such alkali boroaluminosilicate glasses can form stable glasses that can be spun at temperatures between 1300 and 1600°C and have high chemical durability.

Intermediate oxides such as MgO and TiO_2 can be found in both locations described above, i.e. as network formers or modifiers. This is a brief description of glass chemistry and the reader is referred to a fundamental text.⁹

Na^+ and K^+ are relatively mobile and therefore will contribute to the electrical conductivity of the glass. Only at high temperatures is the bulk conductivity significant, but surface conductivity can occur at ambient conditions. The volume resistivity of A-glass, which is an alkali glass, is $10^{10}\ \Omega\text{m}$. E-glass was developed principally for its good electrical properties

Table 6.3 Typical fibre-forming E-glass compositions¹⁰

Constituent	Weight %
SiO ₂	52–56
Al ₂ O ₃	12–16
B ₂ O ₃	5–10
TiO ₂	0–1.5
MgO	0–5
CaO	16–25
Na ₂ O + K ₂ O	0–2
Fe ₂ O ₃	0–0.8
F ₂	0–1

($10^{15} \Omega\text{m}$) but it has become the universal glass for fibre reinforcement as a consequence of its excellent chemical durability.

More than 99% of continuous glass fibres are spun from an E-glass formulation. A typical range of formulations is given in Table 6.3. A-glass is an economically attractive alternative because it utilises plate glass scrap, made in a remelt process rather than the direct melt process, but the fibres only have half the strength of E-glass. However, E-glass is not resistant to acid or alkalis, and a chemically-resistant C-glass is available for use in applications where acidic environments are met. C-glass is also used as an alternative to E-glass in the reinforcement of bitumen for roofing mat. In practice, E-glass dominates because of the scale of manufacture.¹⁰

The range of compositions of other specialist glasses is given in Table 6.4. For high-strength composites, S-glass (Owens-Corning Fiberglass) and R-glass (Vetrotex), which have similar compositions, are used. However, the high cost of manufacture means that they are only used where this can be justified, e.g. in aerospace, military components and specialist sports equipment.

*Cemfil*¹¹ and *AR*¹² glass are alkali resistant and were developed for the reinforcement of cement and related products. *Cemfil* was originally developed from the glass composition identified by Majumdar¹¹ and commercialised by Pilkington Fibreglass. This has now been transferred to Vetrotex who have also utilised the acid-resistance of the *AR* glass formulation to spin a universal chemically-resistant fibre glass called *Chem Glass*, principally to compete with the chemically resistant E-glass (*ECR*) developed by Owens-Corning. *ECR* glass was a result of the continued developments in formulations for E-glass fibre given in Table 6.5. Commercialisation was prompted by the observation of environmental-stress corrosion cracking of GRP (glass fibre-reinforced plastic) in late 1970s, when demanding corrosion-resistant applications (such as chemical plant and sewer pipes) were being explored.

Table 6.4 Compositions (in weight %) of typical glasses for fibres, with some properties (after Loewenstein¹⁰ and Jones⁵)

Constituent or property	E	ECR	C	A	S	R	Cemfil ¹¹	AR ¹²	AR
SiO ₂	55.2	58.4	65	71.8	65.0	60	71	60.7	61
Al ₂ O ₃	14.8	11.0	4	1.0	25.0	25	1	—	0.5
B ₂ O ₃	7.3	0.09	5	—	—	—	—	—	—
ZrO ₂	—	—	—	—	—	—	16	21.5	13.0
MgO	3.3	2.2	3	3.8	10.0	6	—	—	0.05
CaO	18.7	22.0	14	8.8	—	9	—	—	5.0
ZnO	—	3.0	—	—	—	—	—	—	—
TiO ₂	—	2.1	—	—	—	—	—	—	5.5
Na ₂ O	0.3	—	8.5	13.6	—	—	11	14.5	—
K ₂ O	0.2	0.9	—	0.6	—	—	—	2.0	14.0
Li ₂ O	—	—	—	—	—	—	—	1.3	—
Fe ₂ O ₃	0.3	0.26	0.3	0.5	tr	—	tr	tr	—
F ₂	0.3	—	—	—	—	—	—	—	—
Liquidus temp. ^a (°C)	1140	—	—	1010	—	—	1201	1172	—
Fiberising temp. ^b (°C)	1200	—	—	1280	4.7	4.5	1470	1290	—
Single fibre tensile strength at 25°C, (GPa)	3.7	3.4	3.4	3.1	—	—	2.9	—	2.5
Single fibre tensile modulus (GPa)	76.0	73.0	—	72.0	86.0	85.0	—	—	80
Density, (g/cm ³)	2.53	2.6	2.49	2.46	2.48	2.55	—	2.74	2.74
Refractive index <i>n</i> _D	1.550	—	—	1.541	1.523	—	—	—	1.561
Coefficient of linear thermal expansion (10 K)	5.0	—	7.1	9	2.85	4.10	—	—	—
Volume resistivity (Ω cm)	10 ¹⁵	—	—	10 ¹⁰	10 ¹⁶	—	—	—	—
Dielectric constant at 25°C and 10 ¹⁰ Hz	6.11	—	—	—	—	6.2 ^c	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.

^bIndicates temperature at which the viscosity of the glass is 10³ P.

^cMeasured at 10⁶ Hz.

Table 6.5 E-glass compositions 1940–1990 (weight %) (after Loewenstein¹⁰)

	Original E glass ¹⁶	'Improved' E glass ¹⁷	621 glass ¹⁸	MgO-free glass	816 glass ²⁰	F-free glass ²¹	B&F-free glass ²²	Low n_D glass ²³
SiO ₂	60	54.0	54.0	54.3	58.0	55.3	59	55.8
Al ₂ O ₃	9	14.0	14.0	15.1	11.0	13.9	12.1	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	—
CaO	27	17.5	22.0	22.1	22.5	21.4	22.6	21.0
ZnO	—	—	—	—	2.6	—	—	—
Na ₂ O/K ₂ O	—	1.0	1.0	0.4	1.0	0.4	0.9	1.4
Fe ₂ O ₃	—	trace	trace	0.2	0.1	0.2	0.2	n.d.
F ₂	—	0.5	0.5	0.6	0.01	—	—	0.5

Table 6.6 Compositions (in weight %) for dielectric glass (D-glass) (after Loewenstein¹⁰)

Constituent/properties	Japan ¹³	USA	Europe (Vetrotex)
SiO ₂	45–65	75.5	72–75
Al ₂ O ₃	9–20	0.5	—
B ₂ O ₃	13–30	20.0	20–23
CaO	—	0.5	—
MgO	—	0.5	—
CaO + MgO + ZnO	4–10	—	—
Li ₂ O + Na ₂ O + K ₂ O	0–5	3.0	1 (max)
Other	—	—	4 (max)
Dielectric constant at 10 ¹⁰ Hz	4.3–4.9	3.8	3.85
Loss tangent at 10 ¹⁰ Hz (10 ⁻³)	—	—	0.5

To meet the requirements of fast-response electronic circuit boards, D-glass with lower dielectric constant than E-glass has been introduced over the last decade. Typical compositions are given in Table 6.6. A further discussion of other aspects is given in Section 6.8.2.

6.2.2 E-glass

E-glass is basically a calcium aluminoborosilicate glass containing less than 1% alkali calculated as Na₂O. Actual content varies, as do the presence of trace elements, with the choice of minerals, which will mainly be locally sourced. Most contain a small quantity of fluoride to assist dissolution of raw materials and to lower the liquidus temperature (the liquidus temperature is the highest temperature at which a glass would develop crystals if held there for a long time). Crystal formation is disastrous for glass fibre manufacture because submicroscopic particles will behave like strength-reducing flaws and cause problems in fibre spinning. Fluoride-free E-glass has been developed by optimising the MgO content at 1.8%, when the liquidus temperature is at a minimum of 1083 °C and the fibre-forming temperature is lower than for traditional E-glass (1212 °C). Fe₂O₃ is an adventitious component that increases the rate of heat loss through infrared radiation when the molten glass leaves the bushing and can assist fibre forming. However, Fe in the glass may be involved in acidic degradation reactions.^{14,15}

Fluoride is one of the components in the glass composition that presents a pollution hazard since it volatilises as fluorosilicic acid, hydrofluoric acid and fluoroborates.

As shown in Table 6.5, the composition has moved in the direction of boron- and fluoride-free. The ‘original’ composition represents the early attempt to find an alkali-free formulation.¹⁶ The ‘improved’ composition

has a lower liquidus temperature¹⁷ as discussed above. '621' glass¹⁸ has MgO eliminated through replacement by CaO. Of importance was its ability to accommodate ZrO₂ from refractory dissolution without devitrification.¹⁹ Developments in refractory technology have led to significant improvements in corrosion resistance, so that higher temperatures can be used in the process with the reduction or elimination of B₂O₃ from the compositions – '816' glass.²⁰ Fluoride-free composition is a Japanese glass²¹ whereas the boron and fluoride free (B&F free) composition is American.²² However, according to Loewenstein¹⁰ the extent of use of these boron-free glasses in the USA is uncertain since most manufacturers have used pollution control rather than composition refinement to meet legislative requirements.

A special glass of low refractive index designed for translucent sheeting²³ falls just outside the E-glass definition.

6.3 Fibre manufacture

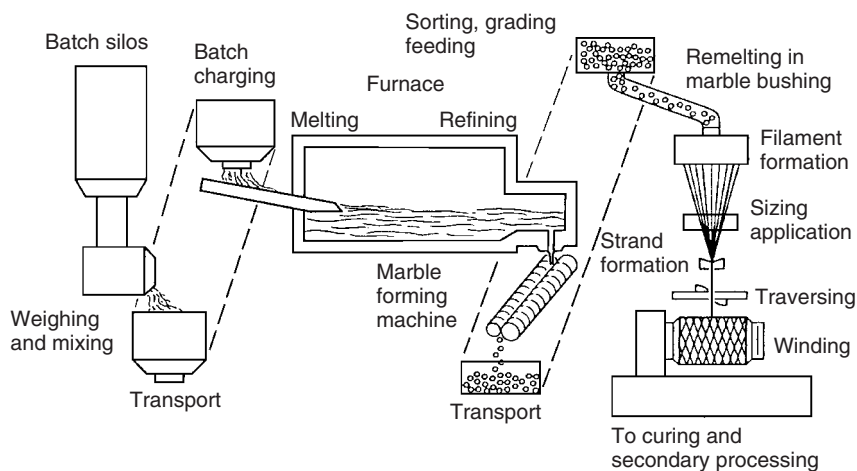
The fibre manufacturing process has effectively two variants. One involves the preparation of marbles, which are remelted in the fiberisation stage. The other uses the direct melting route, in which a furnace is continuously charged with raw materials which are melted and refined as that glass reaches the forehearth above a set of platinum–rhodium bushings from which the fibres are drawn. The two processes are described in Figures 6.2 and 6.3.² Glass fibres are produced by rapid attenuation of the molten glass exuding through nozzles under gravity. The glass melt has to have a narrow range of viscosity between 600 and 1000 P. The rate of fibre production at the nozzle is a function of the rate of flow of glass, not the rate of attenuation, which only determines final diameter of the fibre.

The flow of molten glass through a nozzle can be described by the Poiseuille's equation:

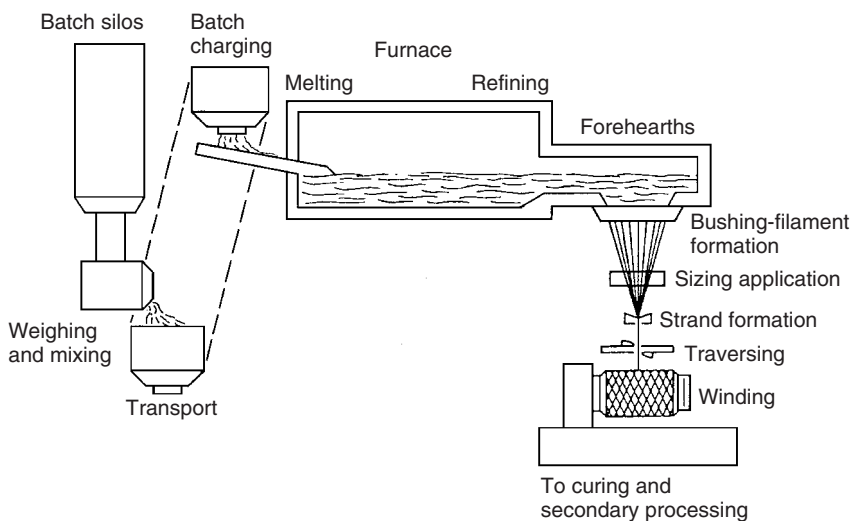
$$F \propto \frac{r^4 h}{l \eta}$$

where F is the rate of flow, r is the radius of the nozzle at its narrowest cylindrical section, l is the length of the cylindrical section, h is the height of the glass above the nozzle and η is the viscosity of the glass. Modified equations for nozzles of different geometry are given by Loewenstein.¹⁰ As the melt cools, it increases in viscosity, which varies along the nozzle making exact predictions of the flow rate difficult. Iterative procedures can be used to determine the dimensions of a nozzle of a selected design. Direct melt spinning is more predictable because of the complexities introduced by remelting preformed marbles.

The bushing is made from typically 87 Pt/13 Rh to 90 Pt/10 Rh alloys. The rhodium additions increase the hardness and stiffness of the alloy, which significantly enhances the lifetime of the bushing by reducing creep



6.2 Schematic of marble melt process for continuous filament (after Mohr and Rowe²).



6.3 Schematic of direct melt process for production of continuous filaments (after Mohr and Rowe²).

at the high temperatures employed. An additional benefit is the increased contact angle with the molten E-glass.

With a soft alloy, the size of bushing and hence of the number of holes is limited. Thus, the standard bushing is used to produce 200–204 fibres. However, as the number of fibres is increased, the stiffness of the bushing

Table 6.7 Typical commercial fibre strands (after Loewenstein¹⁰)

USA ^a	Strand designation		Number of filaments per strand	Average filament diameter (µm)
		Metric ^b		
D	1800	EC5 2.75	50	5.33
D	900	EC5 5.5	100	5.33
D	450	EC5 11	200	5.33
D-E	150	EC6 33	400	6.35
E	300	EC6 16.5	200	6.35
E	450	EC7 11	100	7.32
E	225	EC7 22	200	7.32
G	150	EC9 33	200	9.14
G	130	EC9 38	200	9.65
G	75	EC9 66	400	9.14
H	110	EC11 45	200	10.67
H	55	EC11 90	400	10.67
J	90	EC12 55	200	11.75
J	45	EC12 110	400	11.75
J	23	EC12 220	80	11.75
K	31	EC14 160	400	14.19
K	16	EC14 320	800	14.19
K	10	EC14 480	1200	14.19
K	8	EC14 640	1600	14.19
M	6	EC16 800	1600	15.86
M	5	EC16 1000	2000	15.86
N	4	EC17 1200	2000	17.38
N	2	EC17 2400	4000	17.38
T	2	EC24 2200	2000	23.52
T	1	EC24 4400	4000	23.52

^aFilament designation and count.^bE = E glass, C = continuous, then nominal filament diameter and tex.

needs to be increased. This is being achieved by using composite alloys containing dispersed zirconia, yttria, or thoria.^{24,25} 4000 filaments can now be spun at one bushing and 6000 filaments are planned.¹⁰

The collected bundle of fibres is known in the industry as roving, which is commonly produced by assembling multiples of 200 filaments into the required size of roving as a separate operation. However, with the development 2–4000 nozzle bushings, direct rovings can be formed into a final package immediately.

A typical haul-off rate of 2500m/min is employed to attenuate the fibre to the required diameter. The fibres are immediately cooled by sprayed water at the bushing, coated with a size, assembled into a 'strand' and wound onto a culet to produce a cake, as shown in Fig. 6.3.

In the metric system, rovings are defined by the fibre diameter and the

number of filaments per strand, which defines the total linear density (tex) of the roving. Tex is the number of grams per kilometre ($1 \text{ tex} = \text{g}/1000 \text{ m}$) and is preferred to the older textile unit of denier ($\text{g}/9000 \text{ m}$). In the American system, a standard alphabetic letter followed by the 'count', which is the number of hundred yards per pound, is used.

$$\text{Count} = 4961/\text{tex}$$

Thus, in the metric system EC14 160 refers to E-glass continuous roving with fibres of nominal diameter $14 \mu\text{m}$ of tex 160. The American designation is K 31. It contains 400 filaments per strand. A list of typical roving definitions is given in Table 6.7.

The fibre diameter, d_f (in μm) can be computed from roving tex according to the equation:

$$d_f = 15.8 \left(\frac{T}{0.4961N} \right)^2$$

where $T = \text{tex}$ and N is the number of filaments per strand.

The term tow is used to define the smallest unitary element of the strand and represents the number of filaments drawn from a single bushing, which was commonly equal to 200 or 204. The number of fibres in a strand is made up from multiples of the bushing number. However, rovings (other than direct rovings) are reassembled from a number of strand-cakes in a separate operation. A typical roving could have a tex of 2300 and consist of 30 strands.

6.4 Fibre finish

6.4.1 Sizes and finishes

Immediately after cooling with water the fibres are coated with an aqueous size (usually an emulsion) in contact with a rubber roller. Typical designs for sizing applicators are given in the literature.¹⁰ The size (or finish) is crucial to the handleability of the fibres and their compatibility with the matrix. The size is chosen to suit the application or further processing. For example, for chopped fibres (see Section 6.6), strand integrity may be a particular requirement. As a result, the number of formulations is extensive. An additional binder would be used to hold chopped or continuous fibres in a mat (see Section 6.6). The 'finish' therefore may consist of:

- (i) an adhesion promoter or coupling agent,
- (ii) a protective polymeric size or film former,
- (iii) lubricant(s),
- (iv) surfactant(s),
- (v) antistatic agent(s), and
- (vi) an optional polymeric binder (emulsion or powder) used for fibre mats.

The solids content of the emulsion employed for sizing will be of the order 10% of which 0.3–0.6% will be the coupling agent. The film former is a polymer that may contain a plasticiser (a high-boiling compound such as dibutyl phthalate). The lubricant, surfactant and antistat are usually present in the emulsion at 0–0.3%, 0–0.5% and 0–0.3% respectively. There is some confusion over the use of the term ‘size’. It is often used to refer to the film former including all of the additives (including coupling agent) in an aqueous base. Others use the term to refer to the solids deposited on to the fibres at the bushing, whilst it can also mean the compounded film former without coupling agent. The term ‘finish’ universally refers to the deposited solids including any optional binder, used for mats.

6.4.2 Film former

Items (ii)–(vi) in the list in Section 6.4.1 impart good handleability and controlled wet-out kinetics with matrix resins in composites and are therefore chosen for compatibility with the fabrication process. For specialist applications such as environmental resistance, the chemical nature of the film former in the size and the binder are crucial and are selected accordingly. Good economical design can be achieved by combining fibres with differing finishes in different laminae. Typical film formers and binding resins are given in Table 6.8.

The film former is chosen for one or more of the following criteria:

- compatibility with coupling agents and other components
- stability of the emulsion during application
- handling characteristics after drying
- unwind potential for repackaging
- wet-out rate in the resin matrix
- dry and wet properties of the composites.

These emulsions clearly contain emulsifying agents (surfactants) that contribute to the complexity of the deposit on the fibre. A typical surfactant is polyoxyethylene monophenyl ether. Commercial emulsions of film formers are not always used. Often in specialist applications, the manufacturer will prepare their own emulsion.

6.4.3 Lubricants and antistatic agents

Typical lubricants are based on fatty acid amides, which, in the presence of the acetic acid used to adjust the pH of the sizing emulsion to approximately 4, will be protonated. Cationic quaternary ammonium sites are positively charged and will have an affinity to the negatively charged glass surface. Polyalkylene glycols are also used and often a complex blend is required to give the correct requirements.

Table 6.8 Typical sizing resins and binders for glass fibres (after Jones⁵)

Glass type	Polymeric size	Polymeric binder	Application
E	PVAc	—	General purpose roving
E	PVAc	PVAc emulsion	General purpose CSM
E	Polyester	—	Environmentally resistant GRP
ECR	Polyester	—	Environmentally resistant GRP
E,ECR,S,R	Epoxy	—	High-performance composites
E	Epoxy/ polyester copolymer	—	High-performance composites with wide range of compatibility
E,ECR	Polyester	Various powder	CSM, environmental resistant GRP CSM processing with controlled wet-out, CRM
E	Polyurethane	—	Roving for thermoplastics – short fibre moulding compounds (e.g. nylon)
C		Polyacrylate Polystyrene	Reinforcing veils for gel coats, chemically resistant barrier layers

PVAc = polyvinyl acetate, CSM = chopped strand mat, CRM = continuous random mat.

Since glass is a non-conductor, static electricity can build-up during the use of the rovings at the high speeds used in the manufacturing process. Antistatic agents such as alkyl trimethyl ammonium chloride (*Arquad S50*) and quaternary ammonium methyl sulphate (*Neoxil AO 5620*) are used to impart surface conductivity.

6.4.4 Sizings for yarns and fabrics

A yarn is an assembled roving in which a twist has been imparted onto the strands. These are used for weaving or knitting. In most applications, such as braiding for wire insulation, a starch size including a vegetable oil and surfactants is used. For composites the woven fabric would be desized and resized before use. Similarly for rubber reinforcement in tyres, heavy cord is manufactured and desized prior to being given an appropriate finish.

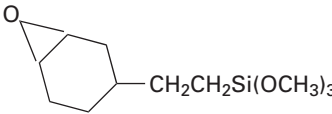
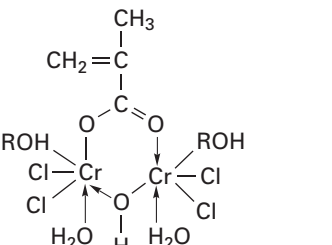
6.4.5 Silane and other coupling agents

Adhesion promoters are added to the sizing emulsion to provide the glass with compatibility and potential coupling of the glass surface to the matrix resin. The role is the following:

- (i) Displace adsorbed water on the glass surface.
- (ii) Create a hydrophobic surface of the correct thermodynamic characteristics for complete wetting by the matrix resin.
- (iii) Develop strong interfacial bonds between the fibre and resin. These may involve covalent bonding or, in the case of thermoplastics, long compatible molecular chains that are completely solubilised into the polymer, in analogy to graft and block copolymers employed in polymer blends.

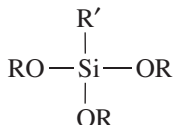
Typical adhesion promoters or coupling agents are given in Table 6.9. The chrome complex was one of the original ones. It is still used in some applications, for example it improves the abrasion and flexure resistance of

Table 6.9 Typical coupling agents for glass fibre-resin adhesion (after Jones⁵)

Vinyl	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$
Epoxy	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$
Methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$
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	$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2)\text{Si}(\text{OCH}_3)_3\text{HCl}$
Cationic methacrylate	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{Cl}^- \\ \qquad \qquad + \\ \text{CH}_2=\text{C}-\text{COOCH}_2\text{CH}_2-\text{N}(\text{Me}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$
Cycloaliphatic epoxide	
Titanate	$[\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}]_3\text{TiOCH}(\text{CH}_3)_2$
Chrome complex	

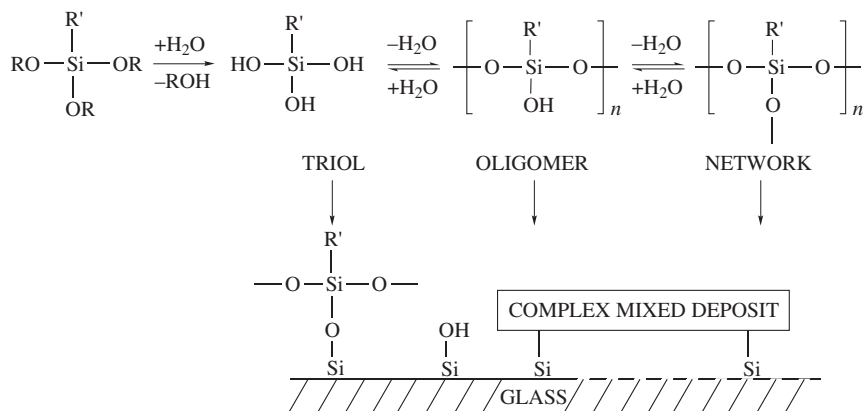
'starch' sized fibres used in yarns and fabrics,²⁸ but it has been largely replaced now by the alternative silanes.^{26,27}

The silanes given in Table 6.9 all have the following structure:



Where R' is a polymer-compatible or -reactable organic group. R is either ethyl or methyl.

In aqueous solution and usually in the presence of acetic acid which is used to adjust the pH (of the sizing emulsion) to approximately 4, the alkoxy (RO) groups are hydrolysed and can polymerise to give linear and branched poly (hydroxy siloxane).



This equilibrium polymerisation is strongly dependent on the nature of R' so that the concentration at which only the silane triol exists in aqueous solution (in the absence of the film former) varies. For example with γ -aminopropyltriethoxysilane (γ -APS), the triol will only exist at concentrations below 0.15%.²⁹ For most sizings, the concentration is closer to 0.5% so that it is expected that the hydrolysed 'silane' will be a mixture of monomeric triol and oligomers of differing degrees of polycondensation. The further away from the floor concentration, the more polymeric is the hydrolysed silane. The extent of this varies from silane to silane.

Examination of Table 6.10 shows that the glass fibre surface is silica-rich and that aluminium tends also to be enriched.^{5,30} The calcium on the other hand is depleted relative to the bulk. Since the glass is made in the presence of water, the silicon at the surface will have hydroxyl groups attached. Therefore, the hydrolysed silane will be in competition for condensation with silanols on the glass surface or through self-condensation.

Table 6.10 Typical bulk (ICP) and surface (XPS) percentage elemental composition for heat-cleaned polished E-glass plate* and as-received non-treated, water-sized fibres† (after Jones⁵)

Element	Uncoated plate		Uncoated fibre	
	Bulk	Surface	Bulk	Surface
Si	22.3	25.1	22.8	22.4
Al	7.4	8.4	7.0	8.5
Ca	16.4	9.6	17.6	8.6
O	49.6	56.9	50.4	60.5
Mg	0.4	—	0.5	—
B	2.1	—	1.4	—
Fe	0.6	—	0.3	—

— Below the detectable limit of X-ray photoelectron spectroscopy (XPS).

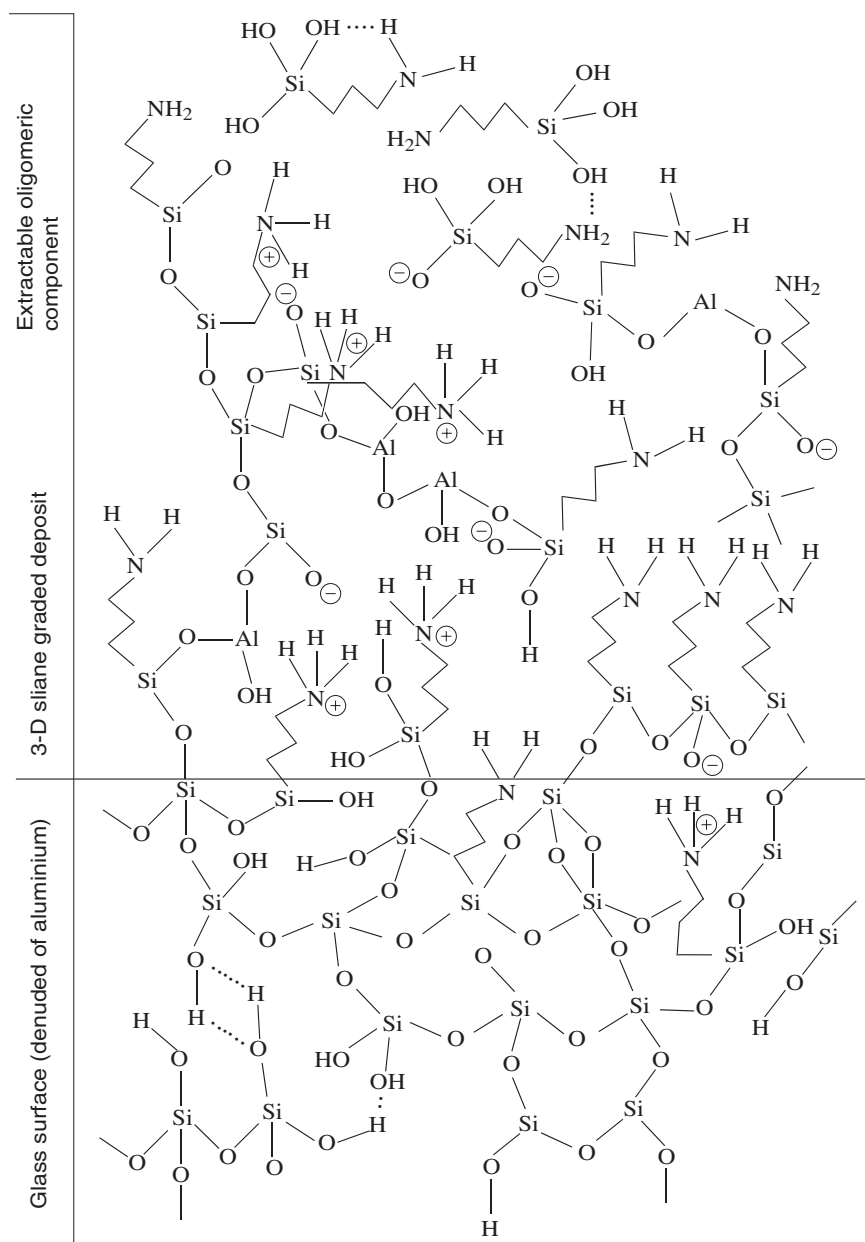
* Cast from E-glass marbles.

† Commercial fibres treated only with water during manufacture.

ICP = Inductively coupled plasma technique.

The important factor, therefore, is to differentiate between the potential for polycondensation or adsorption of the 'silane' at the surface. For strongly active surfaces, such as silicate minerals, the triol will tend to be adsorbed. For example, with γ -APS, additional internal hydrogen bonding stabilises the adsorbate, forming a monolayer. However, with glass surfaces, multilayers are deposited. Typically, more than 100 molecular layers might be deposited, of which 90% would readily be extracted in water at 50°C. Approximately three to six molecular layers remain after more rigorous hydrolytic extraction at 80–100°C. This leaves a deposit that is highly hydrolytically-resistant.^{29–38} These components or layers have been referred to respectively as: (i) the physisorbed layers, (ii) the loosely chemisorbed layer, (iii) the strongly chemisorbed layer. Wang and Jones^{30,33,34} confirmed the presence of differing components using changes in the mass of the secondary ions sputtered from the silanised surfaces in the time-of-flight surface ionisation mass spectroscopy (ToF SIMS) spectra. In this way they demonstrated that the deposit was a graded network of higher density at the fibre surface. They also found that the concentration of aluminium was enhanced at the fibre surface which lead them through thermodynamic argument to suggest that the strongly chemisorbed material was a copolymer with aluminium hydroxide extracted from the fibre surface.³⁴

The graded network model had further confirmation in the observation that phenolic resins of higher molecular weight penetrated less efficiently into the hydrolysed γ -APS deposit.³⁵ They also demonstrated that the amino group was ionised to an extent of 40%. This lead to a modification of the

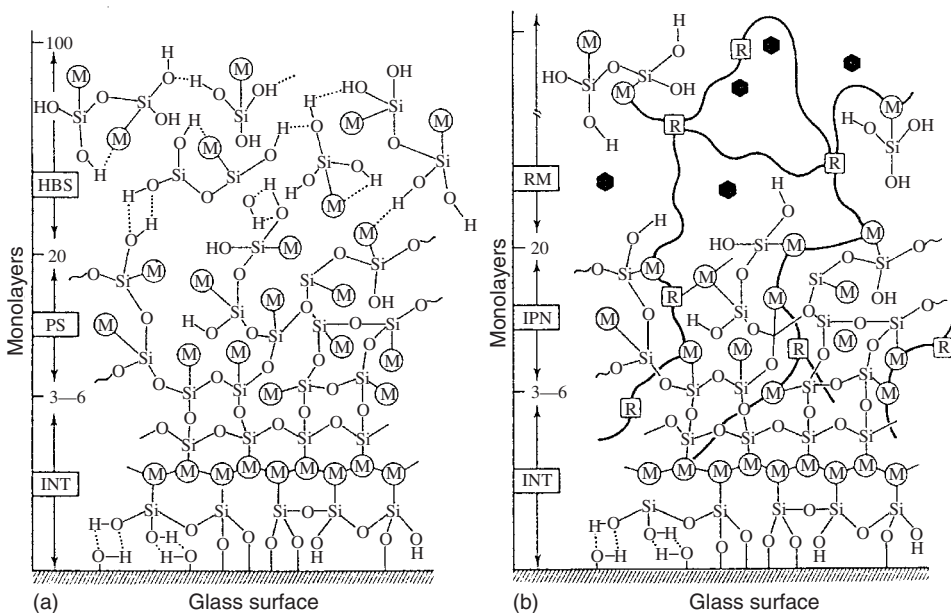


6.4 Schematic of the structure of hydrolysed γ -APS on E-glass, showing the presence of the denuded glass surface and quaternary ammonium ions.³⁵ (Reproduced with permission of VSP International Science Publishers.)

structure of hydrolysed γ -APS previously reported.³⁵ The latest schematic diagram, given in Fig. 6.4, also proposes that the silane can penetrate the denuded glass surface to provide a rather diffuse 'interphase' region.

The above model has been derived from studies on γ -APS because the nitrogen atom enables a detailed surface analysis with XPS and to some extent SIMS.

Other common silanes such as γ -methacryloxypropyl trimethoxysilane (γ -MPS) and vinyltrimethoxysilane have received less attention, but Fourier transform infrared (FTIR) studies have proved valuable. These two silanes behave differently from each other on hydrolysis. γ -MPS behaves very similarly to γ -APS with a deposit consisting of about 200 molecular layers that can be readily desorbed at 80°C to leave a deposit of about 7–20 molecular layers thick, which is hydrolytically stable. Ishida and Koenig³⁶ also observed that polymerisation through the methacrylate group may have occurred at the glass fibre interface. In the ToF SIMS Analysis of commercially silanised fibres (without film former),³⁹ evidence for this mechanism was also observed.



6.5 Schematic of γ -methacryloxypropyl triethoxysilane deposit on (a) glass fibre surface showing presence of oligomeric hydrogen bonded silane (HBS) and graded polysiloxane 3D deposit (PS), (b) after impregnation with resin (R) and dissolution of sizing (black hexagons). IPN is the semi-interpenetrating network between resin and silane; RM is the copolymer of silane oligomer and resin.

Jones⁴⁰ interpreted this data in the form of a schematic diagram of the deposit (Fig. 6.5a) and its interaction with resins as shown in Fig. 6.5b.⁵ Recent work³⁵ suggests that the interface between the glass and silane is more diffuse, as shown in Fig. 6.4.

Vinyltrimethoxysilane (VTS) on the other hand behaves completely differently. Ishida and Koenig³⁷ showed that the deposit was much more hydrolytically resistant. Thus, it is concluded that the hydrolysed VTS deposit was one of a crosslinked network with only limited oligomers present.

6.4.6 Structure of the interphase

The previous section discusses the structure of the hydrolysed silane on the glass surface in the absence of the film former. The presence of the film former will influence the nature of the deposit. Thomason^{41,42} has studied these aspects using extraction procedures, thermal analysis and surface analysis techniques. It is generally accepted that the silane is partitioned at the glass surface leaving the film former to diffuse to differing degrees into the matrix during fabrication of the composite.⁴³ Add to this that there will be an oligomeric component to the silane that will also be mobile, and it is clear that a complex interphase will form at the interface between fibre and matrix. Fig. 6.5(b) gives a schematic of how the interphase might be configured. Briefly, on embedding in a liquid resin, the soluble components of the sizing on the fibre will diffuse into the resin to a varying degree, depending on the thermodynamic compatibility of the 'blend' and the rate of diffusion which will also be a function of molecular weight of each component. Since the silane oligomers are likely to be mobile, the chemisorbed 'silane' will, in effect, be rather like a molecular sponge with molecular pores that can accept the resin molecules. Therefore, the best representation of this structure is one of a bonded semi-interpenetrating network.

6.4.7 Mechanisms of adhesion

Several theories of adhesion were identified by Erickson and Plueddemann,⁴⁴ viz:

- (i) chemical bonding
- (ii) deformable layer hypothesis
- (iii) surface wettability hypothesis
- (iv) restrained layer hypothesis
- (v) reversible hydrolytic bonding mechanism.

Chemical bonding (i) invokes the simplistic formation of chemical coupling between the components. This would produce a distinct interface, which from the forgoing is difficult to justify. The deformable layer theory (ii)

recognises the presence of an interphase where stress relaxation can occur and is probably one of the most important contributing factors. The restrained layer hypothesis (iv) is effectively equivalent except that the interphase exhibits a higher modulus than the matrix, through a higher degree of crosslinking. Surface wetting (iii) alone is unsatisfactory, but in order to achieve a strong interface this aspect must be satisfied. The reversible hydrolytic bonding theory (v) was favoured by E P Plueddemann^{26,44} to explain the reduction in wet strength and its recovery on drying, by reformation of hydrolysed siloxane bonds. With recent knowledge, it is clear that it is not necessary to invoke chemical bond hydrolysis to explain the reversibility of transverse strength because we now know that the stress transfer between fibre and resin is strongly influenced by the presence of a thin interphase.^{45,46} With differential plasticisation of the interphase and matrix, the effect of water can be explained.

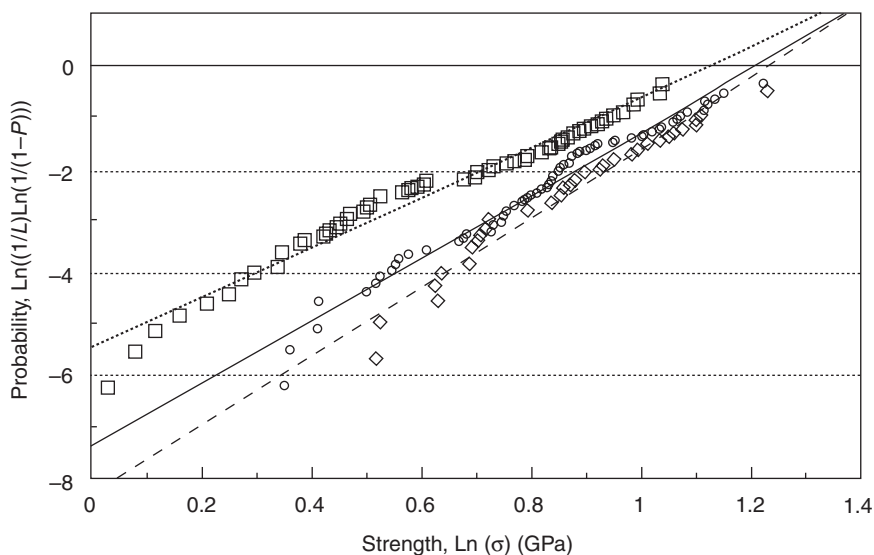
6.4.8 Characterisation of the interface/interphase

The assessment of interfacial response is an essential aspect of sizing development. Most commercial work generally involves simple composites such as impregnated bundles. Optimisation therefore involves relevant tests such as tensile or interlaminar strength. For short-fibre reinforced materials, other specific tests such impact strength may be utilised. Attempts have been made to assess performance using single filament tests such as pull-out, microdebond, push-in and fragmentation. The test methods have been reviewed recently.⁴⁷ Problems arise from the complexity of interfacial response under shear, which was also reviewed.⁴⁸ Certainly for sized glass fibres, debonding is not always observed so that yield of an interphasal region limits the stress transfer at the interface. As a consequence, without full knowledge of the interphase properties it is often difficult to interpret single filament test data. It is, however, clear that careful study illustrates that 'sizing' formulations influence composite micromechanics.⁴⁵

6.5 Glass fibre properties

6.5.1 Strength and stiffness

The mechanical properties of glass fibres are shown in Table 6.2. The modulus is very much dominated by the chemical forces operating within the amorphous inorganic glass and has a value of around 70–80 GPa. Higher modulus can be achieved only with crystallisation into a glass-ceramic or ceramic. The strength of any solid is dominated by the presence of flaws that grow under stress. At a critical size given by the Griffith equation,^{1,3} rapid fracture occurs. The population of flaws and their size therefore deter-



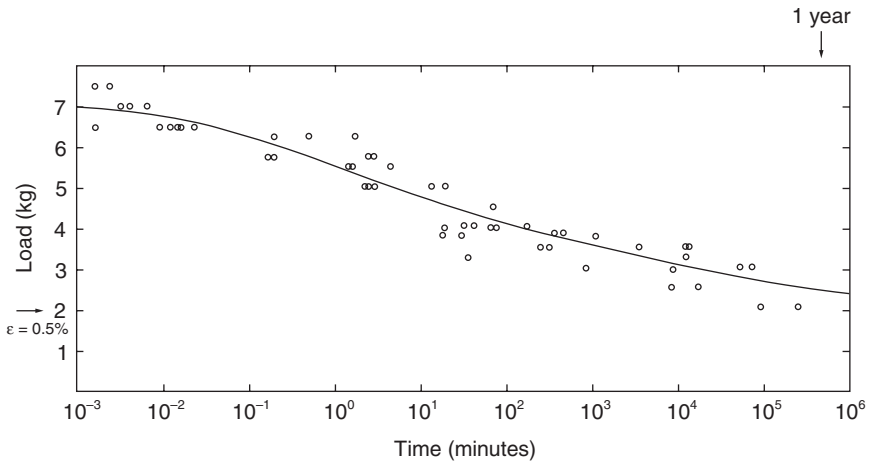
6.6 Weibull plots for three laboratory coated E-glass fibres showing differing protective abilities. \square = Pure γ -APS (Sigma Chemicals); \circ = commercial γ -APS (A1100); \diamond = polydimethyl siloxane. The values of the Weibull parameter m and the characteristic strength σ_0 are, respectively 4.88, 3.1 GPa; 6.1, 2.4 GPa; 6.7, 3.4 GPa. L = gauge length of fibres tested (= 6.35 mm); P = probability of failure.

mines the failure of the material, so a fine filament, which will have a lower density of critical flaws, will be stronger than the bulk solid. Furthermore, the strength of a fibre will therefore be gauge dependent and a bundle of fibres will fail progressively because each individual filament will have a different strength.

As a rule of thumb, the theoretical strength will be approximately $E/10$. For glass this will be about 7 GPa, but the practical strength would be significantly less at about 0.07 GPa. Filaments provide a method of realising a significant fraction of the ideal strength. A typical E-glass fibre can have a strength of 3 GPa. However, the introduction of surface flaws during manufacture and storage can reduce the fibre strength significantly. Hence, the 'finish' is applied to the fibres at the bushing immediately after spinning to provide maximum protection.

As-drawn glass fibres have been shown to exhibit three populations of flaws both by Bartenev⁴⁹ and Metcalfe and Schmitz.⁵⁰ In a statistical analysis, the latter authors concluded that the population of fibres with:

- (i) average strength of 3 GPa could be attributed to severe surface flaws of 20 mm spacing;
- (ii) average strength of 3–5 GPa could be attributed to mild surface flaws



6.7 Static fatigue of E-glass strands in distilled water (after Aveston *et al.*⁵²). Reproduced with permission.

of 0.1 mm spacing associated with a tempered layer 10 nm thick which is fractured to expose an inner core whose strength is determinant;

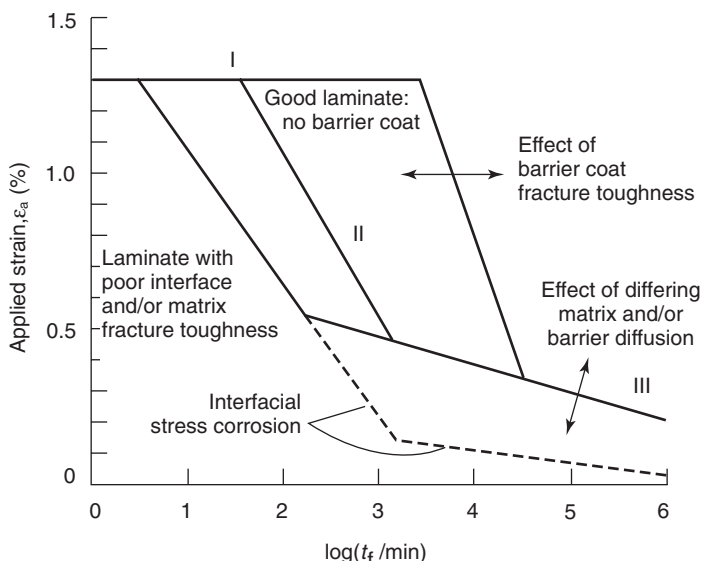
- (iii) average strength of 5 GPa could be attributed to internal defects of 10^{-4} mm spacing, characteristic of defect-free filaments with an uninterrupted surface layer.

Bartenev, however, attributed (ii) to internal defects. Despite this, the presence of a tempered surface is generally accepted.

The Griffith flaws have been associated with the structure of the glass network.⁵¹ In the analysis of commercial fibres it is generally assumed that one population exists and a single parameter Weibull distribution is used. Figure 6.6 gives a typical set of strength data for a glass fibre with a Weibull analysis. From the Weibull parameter, m , and the characteristic strength, σ_0 , it is possible to predict the strength of fibres of differing length. This approach is commonly employed in the analysis of fragmentation test data for adhesion assessment.⁴⁸ It can also be shown by these studies that the 'finish' on glass fibres is an effective protective coating for strength retention (Fig. 6.6).

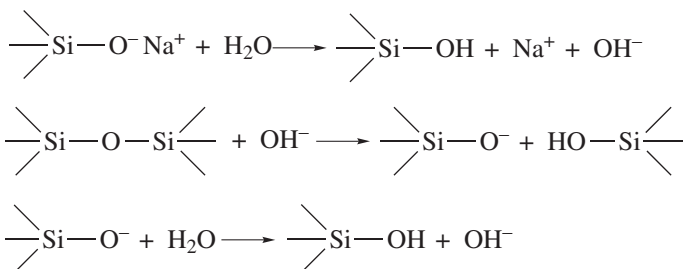
6.5.2 Static fatigue

Glass fibres are subject to static fatigue, which is the time-dependent fracture of a material under a constant load, as opposed to a conventional fatigue test where a cyclic load is employed. This phenomenon is illustrated in Fig. 6.7⁵² where the failure times of fibre bundles under stress in distilled



6.8 Schematic failure map for a unidirectional E-glass fibre composite under acidic environmental stress corrosion conditions, illustrating the three stages of failure I, II, and III and the influence of composite variables.

water are given. The same trend is found for immersion in air. Generally, it is considered that there is no time-dependence of strength in a vacuum,⁴⁹ so that the reduction in strength is a stress corrosion mechanism in the presence of water and not creep rupture as in polymer fibres. The reactions are:



Thus the Na^+ acts as a catalyst for the degradation of the silica network which is propagated by the OH^- ion.

The stress versus time curve has the general form shown in Fig. 6.7 (this is illustrated in Fig. 6.8 for a 0° composite in an acidic environment where these effects are amplified) in which three stages are seen:⁵³

- I *Stress dominated region* at high stresses, where crack propagation is more rapid than the corrosion at the crack or flaw tip. Here the

rate of diffusion of Na^+ to the surface is considered to be rate determining.

- II *Stress corrosion cracking* region, where the rate of corrosion is similar to the rate of crack propagation. Here the crack remains sharp and propagates into a weakened glass.
- III *Stress-assisted corrosion* region, where the effect of stress on the failure time is much less significant because the rate of hydrolysis of the silica network is higher than the rate of crack growth: the chemistry at the crack tip causes a rounding of the crack tip and a reduction in potential to propagate according to the well-known equation

$$\alpha_{\max} = 2\sigma_a(x/\rho)^{1/2}$$

where σ_{\max} stress at the crack tip, σ_a = applied stress, x and ρ are the flaw depth and radius, respectively.

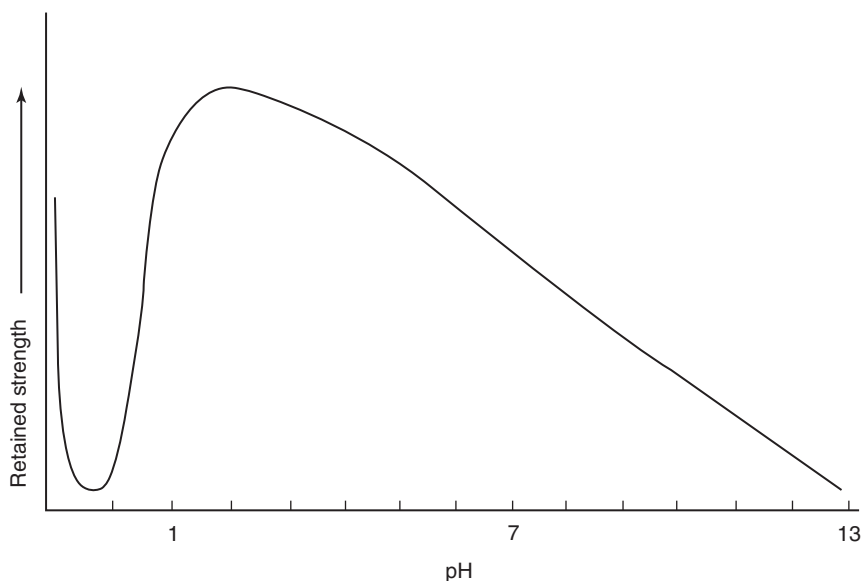
The static fatigue of the glass fibres is clearly determinant of the minimum life of a structural composite under load. Thus, the rate of moisture diffusion, even from humid air, can determine the protective effectiveness of a well-bonded matrix. This can also explain the need for a good interfacial bond, otherwise rapid ingress from an environment could reduce the durability to the minimum for a composite under load in service.

Typically a bundle of E-glass fibres can have a lifetime of 10^7 mins (19 years) at a typical strain of 0.5%, providing the minimum for a composite (see Fig. 6.7).

6.5.3 Environmental stress corrosion cracking (ESCC)

As shown in the previous section, E-glass fibres have a reduced lifetime under load and this is more severe in an acidic environment. This is generally referred to as environmental stress corrosion cracking or ESCC. Here, a synergism between stress and chemistry occurs as described in the previous section under II. At low loads and in alkaline environments, chemical corrosion dominates but is stress assisted. Figure 6.8 illustrates this effect, where the left-hand line approximates to the fibres. Corrosion of the glass is clearly pH dependent, with the network modifiers becoming involved. It is well established that leaching of Ca^{2+} , Al^{3+} , Fe^{3+} , Na^+ , K^+ and other residuals leaves a weakened sheaf. It is now possible to explain ESCC in an analogous mechanism to that given previously for static fatigue.

Leaching also leads to spiral cracking of unstressed fibres after storage in aqueous acid for a short period. It is not clear whether the crack forms prior to optical or SEM examination or after removal from the environment. The latter is favoured and the spiral or multiple cracks form when the hydrated sheaf dries out. However, not all of the fibres in a bundle suffer from this phenomenon. This would appear to confirm that the leaching of the network modifiers is also stress dependent and that variable residual



6.9 Illustration of the retained strength of unloaded E-glass in environments of differing acidity and alkalinity (after Cockram⁵⁵). Reproduced with permission of The Society of Glass Technology.

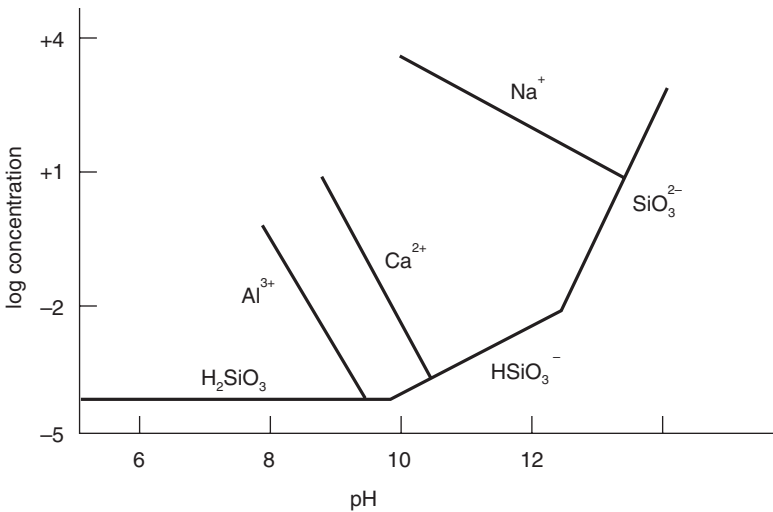
stresses are built into the fibres as a result of the water-cooling regimes employed in manufacture. This is further complicated by the complexation of leachable ions such as Fe(III) in the aqueous solution, which promotes the process. This may be the mechanism by which ultraviolet illumination can accelerate ESCC of E-glass filaments.^{15,54}

6.5.3.1 Corrosion of E-glass fibres

As shown in Fig. 6.9, the retained strength of the filaments is strongly dependent on the pH of the environment.⁵⁵ Of note is the lowest durability at a pH of 0.2. This can be explained by the thermodynamics of the glass/aqueous solutions interaction. Fig. 6.10 shows how the solubility of different glass modifiers varies with pH. For example, $\text{Ca}(\text{OH})_2$ can be precipitated above a pH of 10,⁵⁶ thereby explaining the dominance of ESCC in acids and corrosion in alkalis. The rate of corrosion in the latter is so high that zirconia glasses are preferred.

6.5.3.2 ESCC of E-glass fibres

Most studies have been conducted in acidic environments, when rapid failure occurs. But studies on composites confirm that the effect of pH on



6.10 Thermodynamic calculations of the aqueous solubility of differing glass components at differing pH (after Fox⁵⁶).

ESCC of E-glass fibres shows a similar trend to Fig. 6.9. For example, corrosion appears to dominate at high pH whereas at low pH, ESCC dominates. However, *AR* glass and *ECR* glass fibres show improved resistance to stress corrosion cracking in aqueous acidic environments. This phenomenon can be applied to the design of glass fibre composites with resistance to ESCC (see Section 6.8.3).

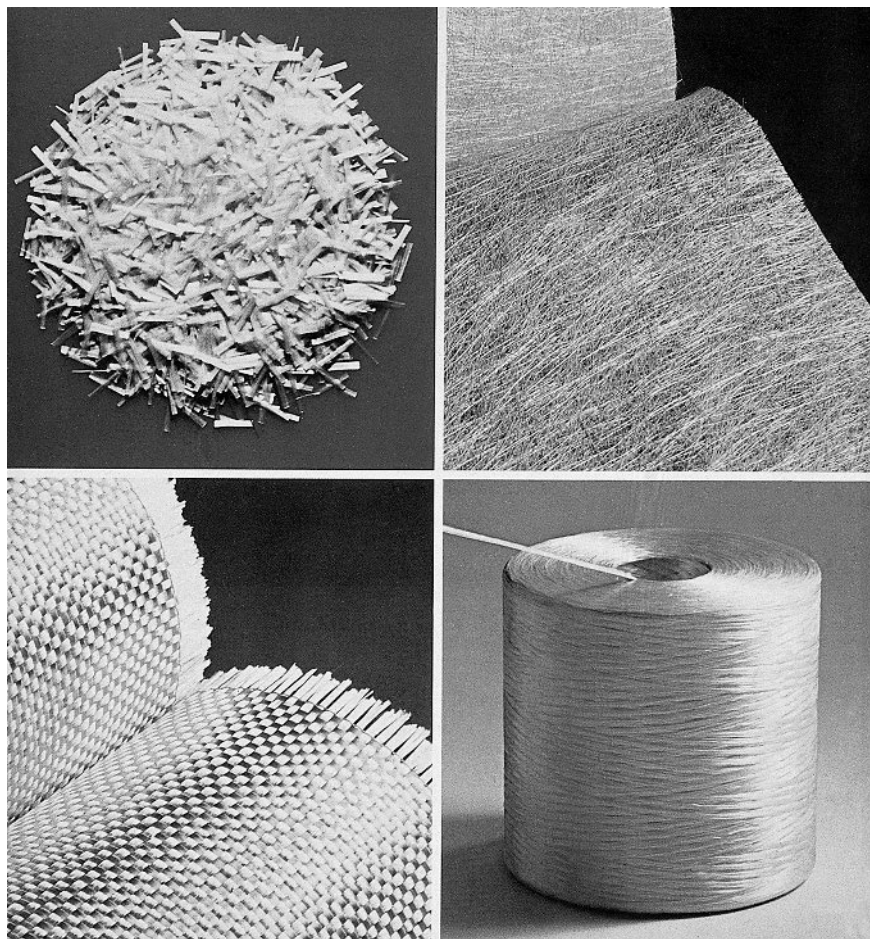
6.6 Fibre assemblies

6.6.1 A variety of types

As shown in Fig. 6.11(a) and (b), the form of fibres used for composite manufacture is quite varied. As discussed in Section 6.4, the strands can be compiled at the bushing to make direct rovings that, when unreeled do not have a twist and are ideal for advanced composites made from prepreg, or by filament winding and pultrusion. Alternatively, the fibres are collected on a culet, where they are dried and sent for further packaging.

6.6.2 Mats

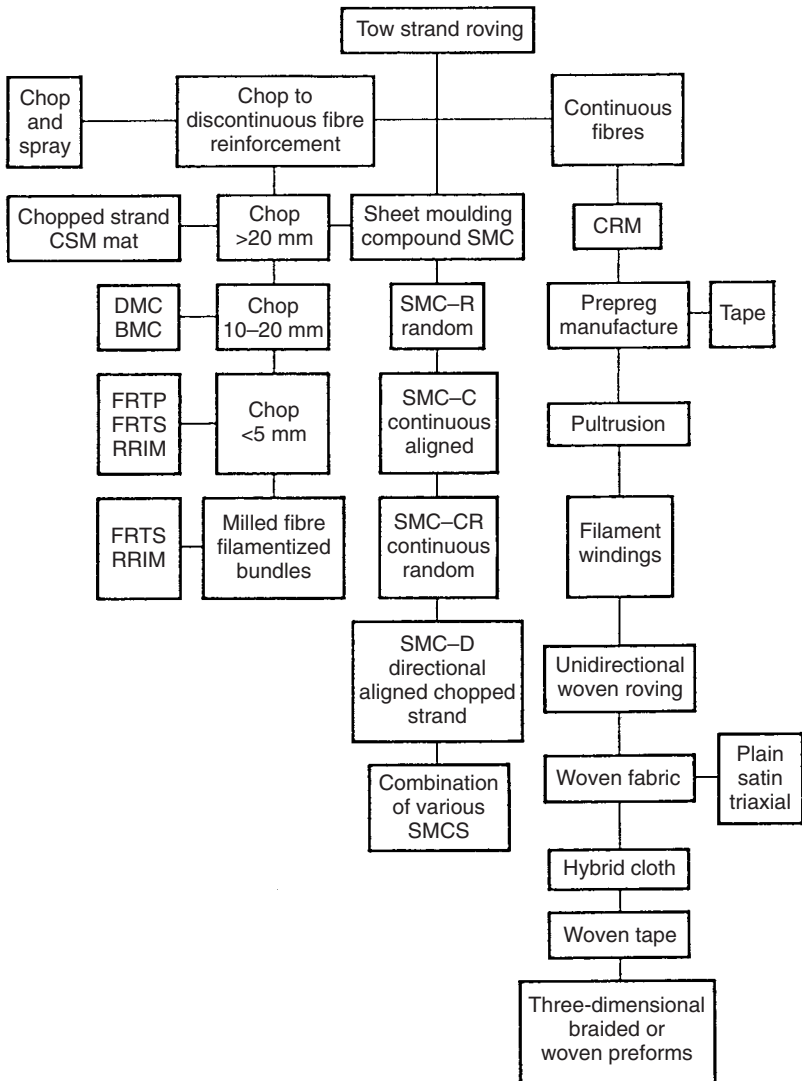
Chopped strand mat (CSM) is a non-woven fabric that is formed by chopping the rovings into strands of 20–50 mm in length, compacting them in a random orientation on a foraminous moving belt and binding them



6.11 (a) Photograph of differing forms of glass fibres as reinforcements.

together with either an aqueous polymer emulsion or a fused powder binder. These mats are used in hand lay-up or related fabrication techniques.

Continuous random mat (CRM) is analogous to chopped strand mat but *unchopped* strands are assembled into an interlocked spiral and bound together with a powder binder or needled to provide a proportion of through-thickness fibres that mechanically bond the assembly. The benefit of the former is in its drape onto a mould surface combined with good surface finish. The needled CRM is used for thermoplastic sheet product where mechanical stability during melt impregnation is crucial.



Types and forms of glass fibre products. R = random; D = directional; C = continuous; CR = continuous random, CRM = continuous (filament) random mat, CSM = chopped strand mat, DMC = dough moulding compound, BMC = bulk moulding compound, SMC = sheet moulding compound, FRTTP = fibre reinforced thermoplastics, FRTS = fibre reinforced thermosets, RRIM = reinforced resin injection moulding (after Jones⁵).

6.11 (b) Schematic of fibre forms and composite fabrication routes.

Fine continuous random mats are used as surfacing *tissue* for resin-rich liners or gel-coats. *Overlay mat* is a heavier grade where more robust handling is encountered, as in press moulding.

Roofing mat or *tissue* is a CSM with binders specific to bitumen or similar matrices used in building products, or for a reinforcement of PVC flooring.

Needled mat consists of chopped fibres as strands, bonded to a glass fabric by needling.

6.6.3 Continuous roving

A typical roving is an assembly of parallel strands (typically 30 at a tex of 2300) for unwinding during fabrication to give a non-twist product. Often these are unwound from the inside of the package and care is needed to ensure that the numbers of twists in the final composite is low. They can be subsequently processed into unidirectional reinforced composites through filament winding or pultrusion (see Section 6.7), woven into various fabrics (see Fig. 6.12), or chopped into short lengths for spraying directly into a mould with the resin or deposition with the resin into a secondary moulding product such as dough or bulk moulding compound (DMC or BMC) or sheet moulding compound (SMC).

Direct rovings are assembled at the bushing. These are generally used for advanced composites where the memory of the tows is a distinct disadvantage and where twists need to be absent.

6.6.4 Woven rovings

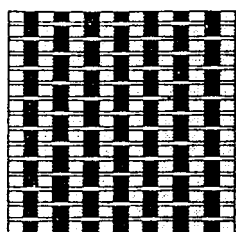
Rovings can be woven in a variety of fabrics of differing configurations as shown in Fig. 6.12. For example, satin weaves are chosen where drape onto a mould surface without distortion of the fibre orientation is required and therefore are often used in advanced composites in the form of a prepreg. The weave pattern can be chosen to ensure appropriate fibre orientation in the moulding. The properties of a fibre composite are dominated by the alignment of the fibres to the principal stress axes.

6.6.5 Combination mats

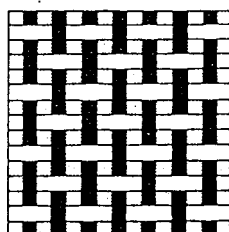
These combine CSM and woven rovings, or needled mat and woven rovings to provide specialist products for specific applications.

6.6.6 Yarns

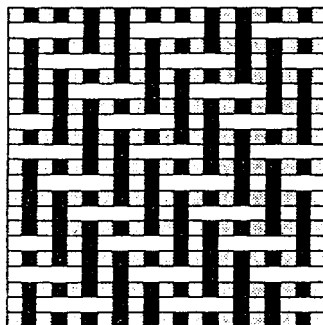
Glass fibre yarns are analogous to other textile fibres in which a twist is incorporated into the rovings and doubled for weaving of glass fabrics.



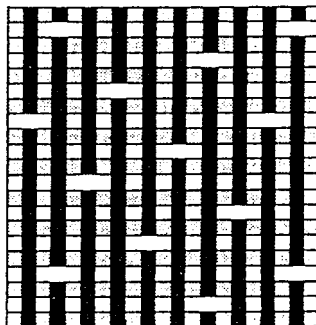
Unidirectional



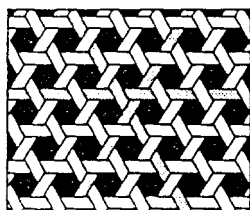
Plain



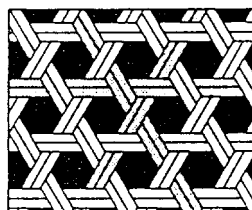
Twill 2.2



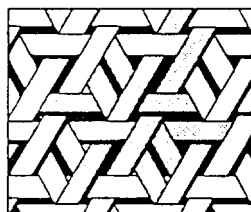
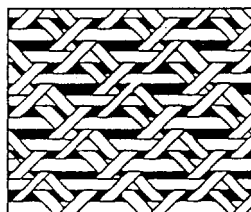
Satin 8



Basic (triaxial) weave



Basic basket weave

Bi-plain weave
(filling 60° to warp)Bi-plain weave
(filling 45° to warp)

6.12 Schematic of glass fibre fabric weaves (after Jones⁵).

Typical examples are heavy cords for reinforcing elastomers, electrical insulation laminates for electrical circuit boards, and fireproof curtains.

6.6.7 Chopped strands

These are fibres which have been chopped to lengths of 1.5 to 50 mm, depending on the application. These are combined with thermoplastic or thermosetting resins for moulding compounds. Chopped strands are either soft- or hard-sized, depending on the moulding application. Optimum impact strength is often achieved by energy absorption from bundle disintegration so that the glass finish is designed to keep the chopped bundles intact. Alternatively, for most applications (such as thermoplastic injection moulding granules) soft sizings are used which diffuse efficiently giving finely dispersed filaments.

6.6.8 Milled fibres

These are made by milling chopped strands to filamentise the bundle and provide a reinforcement without maintenance of bundle integrity, to give good dispersion. Fibre length is also degraded during milling but fortunately, with complete dispersion, the reinforcing efficiency can be maintained because it is the length-to-diameter ratio of the reinforcing element which is critical. These fibres are often used in reinforced reaction injection moulding (RRIM), where the fibres are dispersed in one of the reacting components (the polyol in a polyurethane) for mixing with the other component at a rapid mixing head. They are also used in short-fibre reinforced phenolic and related fibre-reinforced thermoset mouldings (FRTS).

6.6.9 Knitted reinforcements

Knitted fabrics are now being used for composite fabrication, especially by resin infusion on transfer. These present an opportunity for manufacture of 3D structural preforms. Knitted structures based on fibrous glass yarn are fast becoming a technological solution to the fabrication of one-piece complex shapes such as a T-joints and flanges. The interlooped nature of the reinforcement leads to relatively poor reinforcement efficiency so that attempts to include planar elements are being researched.

6.7 Composites

6.7.1 Fabrication

The fabrication of composite materials, of which glass fibre reinforced plastics form a major part, is the main application of E-glass and other fibres.

Glass fibres are used to reinforce rubber for conveyor belts and some tyres. AR glass fibres are used for the reinforcement of cementitious products such as spun pipe. This is essentially analogous to the centrifugal casting process used in the plastics industry. Sprayed chopped strands are also used in other reinforced concrete processes for more complex shapes such as ovoid sewers. Bundle integrity appears to be an important aspect and sizes are chosen accordingly.

The range of fabrication routes to glass fibre reinforced plastics is extensive. Those described here illustrate the basic principles, but for detailed discussions of each technique the reader is referred to other texts.^{5,57}

The fabrication routes can be discussed in terms of primary or direct routes, where the artefact is fabricated from its component fibres and resins, and secondary or indirect routes, where the fibres are preimpregnated to form a moulding material prior to the moulding stage.

6.7.2 Direct or primary impregnation methods

6.7.2.1 *Hand lay-up*

This is the 'original' manufacturing route to so-called 'fibreglass', where E-glass fibres in the form of CSM (woven rovings and combination mats can improve the product stiffness) are placed into a mould that had been pre-coated with a layer of gelled resin or gel-coat. Depending on the requirements, the gel-coat is generally an unfilled resin with relevant properties, but it may be reinforced with a fine glass veil or scrim. Glass fibre mat is then placed upon it and impregnated with catalysed liquid resin, using a paint brush, and consolidated with a roller. The resin 'cold' cures in a specified time. The resins employed are generally from the family of styrenated unsaturated polyester resins which are cured with a peroxide catalyst (e.g. methylethylketone peroxide) and redox accelerator, such as cobalt octoate. Other resins are used for special purposes or to improve consolidation. Variations, which improve consolidation, combine hand-lay with application of pressure to the impregnated glass through a plastic film, using a positive gas pressure or evacuation through the tooling. Hand-lay moulding is rather labour intensive but provides an economic flexible manufacturing route for large mouldings from low cost tooling.

6.7.2.2 *Spray-up*

This process is a semi-automated version of the hand-lay process, where the rovings are chopped and sprayed directly into the mould with the liquid resin. However, consolidation routes are generally the same as in hand-lay.

6.7.2.3 *Centrifugal casting*

In this related technique to spray-up, the chopped fibres and resin are introduced into a rotatable cylindrical moulding to manufacture a pipe. The fibre volume fraction can be adjusted by varying the speed at which the mould is rotated. Alternate layers of sand reinforcement can be readily included for rigidity. Furthermore, the matrix resin properties can be graded to provide high fracture toughness at the surface in contact with the environment.

6.7.2.4 *Pultrusion*

This technique is used to fabricate continuous lengths of product at constant cross-section. These are usually linear but a degree of curvature can be introduced by placing the impregnated fibres onto a large diameter wheel prior to completion of the cure. Clearly, arcs of a circle can be cut from the product. In this simple process the fibrous reinforcement is impregnated with thermosetting resin (unsaturated polyester and related resins, epoxy or phenolic resins) and pulled through a heated die that shapes the section and initiates the curing chemistry. The major difficulty is in controlling the curing kinetics of the resin to ensure that the shape introduced at the die is stabilised after full resin impregnation. The partially cured resin needs to have good mechanical properties and release from the tooling to provide a good finish to the product. Normally, unidirectionally reinforced pultrudates of high stiffness and flexural strength, which rely on aligned fibre properties, are manufactured. However, for improved transverse properties, a CRM can be incorporated as a surface layer. The proportion of unidirectional rovings will determine the balance of properties. Typical applications are tension members such as supports for optical fibre cables.

6.7.2.5 *Filament winding*

There are two variants: wet and dry filament winding. In the former, the fibres are impregnated by pulling them through a resin bath, similar to pultrusion, onto a rotating mandrel. The tension on the fibres determines the consolidation and fibre volume fraction. Generally, a winding angle of 53° is used, with several passes to manufacture an angle plied material and optimise the properties of the pipe. Hoop winding can also be used, providing a principally circumferentially reinforced pipe. In practice, the angle will be approximately 8° . These are often referred to as flexible pipes. However, to achieve axial stiffness and strength, unidirectional woven rovings can be applied to provide fibres in the axial direction. In applications such as sewer pipes, fillers can be added to provide stiffness at eco-

conomic cost. Chemical plant and other containers are often manufactured from filament wound pipes onto which hand-layed bases and tops (dished-ends) are adhered, using overwind technology.

Dry filament winding is commonly employed to provide fibre orientation at various angles on complex-shaped mandrels. (For enclosed artefacts such as a sphere, the mandrel would be a foamed polymer which can be left *in situ* after manufacture.) Because of the practical difficulties of wet winding, these are dry wound into a preform and impregnated with resin in a separate procedure, such as resin transfer moulding. Planetary whirling arm, or tumble winders, are often used in combination with a robot to secure the fibres to a mandrel of complex curvature with adhesive, in the manufacture of complex-shaped preforms, with controlled reinforcement angle.

6.7.2.6 Resin transfer moulding (RTM)

Resin infusion or impregnation of a preform of fibres is usually carried out in a process called RTM (the term resin injection is reserved for the related RIM process (see Section 6.7.2.7)). In the RTM process, the preform is placed into a mould which is closed, and the catalysed liquid resin is pumped into it. The resin usually cold-cures so that the artefact can be demoulded. In a variation, the infusion is done under vacuum assist. This technique is referred to as vacuum assisted resin injection (VARI) or vacuum assisted resin transfer moulding (VARTM). The SCRIMP process employs a stitched preform with angle ply configuration. The clamping pressures in the mould are low because of the low viscosity of the resins used in the process and, as a consequence, the tooling requirements are relatively low in cost, providing economic manufacture of large structural components such as car bodies of low volume production cars (e.g. the *Lotus Elan*). Reactive processing (fast curing monomers replacing the resin) can be used to increase the rate of production and this is referred to as structural reaction injection moulding (SRIM).

6.7.2.7 Reinforced reaction injection moulding (RRIM)

RRIM refers to the technique of reactive processing where monomer(s) are polymerised immediately after injection into the mould cavity. Reaction injection moulding (RIM) was developed from the rapid polymerisation of ϵ -caprolactam into nylon 6. However, a range of polyurethane materials which are formed by rapid reaction of a polyol with di-isocyanate at a fast mixing head are the most common matrices employed. Demoulding can be achieved in less than 20s. In RRIM, short fibres (often milled glass fibres) are included in the polyol monomer stream (rather than in the isocyanate because of its sensitivity to residual water on the glass surface). A common

application has been for the manufacture of large, medium-volume production body components for automobiles, with high impact performance. In structural reaction injection moulding, SRIM, a fibre preform is placed in the mould cavity prior to injection of rapidly mixed reactants. Fast curing epoxy resins have also been used in the manufacture of structural composites by these methods.

6.7.3 Indirect impregnation

These manufacturing processes employ resin or polymer preimpregnated glass fibres or compounded moulding material.

6.7.3.1 *Prepreg*

Prepreg (or preimpregnated fibres) is commonly used in the aerospace industry where high-performance or advanced composites are employed. The advantage of this approach is the ease with which laminates of differing configurations can be manufactured, by stacking plies of unidirectional prepreg at appropriate angles for consolidation.

Prepreg is manufactured by either hot-melt or solution impregnation. In both, a liquid film of the resin including latent hardeners is cast onto a roller and brought into contact with the fibres, in the form of unidirectional or woven rovings, at the nip of additional rollers. Recently hot-melt impregnation has tended to replace the use of solvents, which have to be removed carefully, otherwise voidage can be created in the cured laminate. However, since the resins are designed to be heat cured, they have to be carefully formulated for hot-melt casting otherwise partial cure of the resin can lead to a variable viscosity and problems during consolidation of the laminae.

Epoxyes, bismaleimides, cyanate ester and related resins can be impregnated in this way to provide a feedstock for the lamination industry. Thermoplastics can also be used as matrices for prepreg but these are mostly manufactured by a hot-melt pultrusion technique. Thermoplastic prepregs employing glass fibres are mostly based on polypropylene.

6.7.3.2 *Sheet moulding compound (SMC)*

The unsaturated polyesters and related resins are unsuitable for prepregging because of their low viscosity and cure mechanisms which involve a reactive solvent. As a result, for equivalent preimpregnated fibres, thickening agents and particulate fillers are employed. Thus chopped random, continuous random, discontinuous and continuous aligned fibres are impregnated with a filled resin between release films. Magnesium oxide is incorporated into the resin, which chain extends the unsaturated polyester

through ionomer bond formation with the end-groups to increase the viscosity of the resin during maturing, to give a practical preimpregnated sheet material for hot-press moulding. Typical recipes are given elsewhere.⁵ The fibres are mostly arranged in plane. Hard-sized (resin insoluble) strands are used so that bundle integrity is maintained in the final moulding.

6.7.3.3 *Dough or bulk moulding compounds (DMC, BMC)*

These are formulated similarly to SMC except they do not contain the thickening agent, have a higher proportion of mineral fillers (such as chalk) and are prepared into a dough which can be compression or injection moulded.⁵ The fibre length is shorter than for SMC and is typically about 6mm in length, compared to 25–50mm in SMC. Again, hard sizing is employed. Both terms DMC and BMC are employed for the same material but BMC tends to infer longer glass fibres.

6.7.3.4 *Long glass fibre thermoplastic sheet (RTS)*

These are the analogous thermoplastic sheets for thermal processing (hot stamping) or compression moulding. The preimpregnation process can be through lamination of extruded polymer films and random continuous fibre mat, but an alternative process involves the *in situ* consolidation of the glass rovings and particulate thermoplastic powder into an impregnated mat. These are referred to as glass mat reinforced thermoplastic sheet (GMT). Structural thermoplastic composites (STC) are random short-fibre sheets that have been manufactured by the wet slurry process, which was developed from traditional paper making technology and uses an aqueous dispersion of polymer particles and chopped fibres.⁵

6.7.3.5 *Moulding granules*

These are generally made by compounding chopped fibres into either short-fibre thermoplastics (SFRTTP) or short-fibre thermosets (SFRTS) to produce granules for moulding by compression, injection or extrusion processing. The fibres can be incorporated in a number of mixing techniques, passed through an extruder and chopped into granules. The extrusion process introduces some alignment into the fibre orientation but the fibre length is generally extremely low (e.g. ~0.2mm). Long-fibre thermoplastic moulding granules (fibre length typically ~10mm) are made by pultrusion impregnation followed by chopping, to give an aligned discontinuous fibre granule. This is generally referred to as the Verton process. With this, after injection moulding, the artefact contains fibres with higher average fibre length, and consequently improved strength.

6.7.4 Consolidation or moulding techniques

6.7.4.1 *Vacuum bag moulding*

This composite fabrication employs prepreg to manufacture advanced structural components. Prepreg is stored between release film in a freezer (to maintain the life of the latent hardened resin) and has to be brought to room temperature before unwrapping, to avoid excess moisture absorption. After stacking on the tooling at an appropriate angular configuration, the prepreg is covered in a porous release layer, resin absorber, breather cloth (to equalise the pressure) and a membrane which forms the vacuum-bag when vacuum is applied through a valve. On application of the vacuum, the bag conforms to the tooling and places the prepreg stack under 1 atm pressure, where consolidation and curing can take place in an oven.

6.7.4.2 *Autoclave moulding*

This is the standard fabrication route for advanced composites and involves the procedures of Section 6.7.4.1 except that the ‘bagged-up’ component is placed in the pressure chamber where it can be connected to the vacuum. In this way vacuum pressure and gas pressures of >1 MPa can be applied at appropriate times during the heating schedule in order to optimise the consolidation process and minimise void formation, while maintaining precise fibre angles in the structural composite. The tooling used is often manufactured from composite materials, in order to match the thermal expansion/contraction of the tooling to the component. The prepreps used for tooling may be cured at low temperatures followed by free-standing post-curing after manufacture to appropriate temperatures to ensure their thermal stability during component manufacture.

6.7.4.3 *Compression moulding*

This is a standard moulding technique where a weighed charge is placed into a heated, matched die mould and subjected to mechanically applied pressure. The artefact can be removed after a defined curing schedule (fusion and cooling in the case of a thermoplastic).

6.7.4.4 *Injection moulding*

In this standard plastics process the granules are plasticised in a screw and barrel and then metered into a closed mould. For thermoplastics, homogenisation in the barrel is followed by cooling in the mould. For thermosets, such as DMC or short fibre-reinforced phenolics (SFRTS), the resins have

to cure within the heated tooling after injection. The barrel temperatures are chosen to provide plasticisation and controlled advancement of cure but are not sufficient to gel the resin; they are lower than that of the mould.

6.7.4.5 Extrusion

This is the classic process whereby the homogenised or plasticised melt is forced through a die continuously to give a product of constant cross-section. This technique is used mainly for thermoplastics materials.

6.7.4.6 Fibre management by shear controlled orientation

It is important to control fibre orientation in any moulding process. This can be achieved by careful mould design to provide appropriate flow paths. Allan and Bevis^{5,58} have, however, developed a live feed technology that applies shear forces onto the melt within the mould. In this way, short fibres can be orientated within the artefact to optimise the strength of the component. The same technology has also been applied to extruded pipes, where the fibres can be organised to give high axial or high circumferential stiffness.

6.7.5 Mechanical property of glass fibre composites

6.7.5.1 Continuous fibre reinforcements

The stiffness of a composite artefact can be predicted using the theories presented elsewhere.^{3,5,59-61} For fibres aligned unidirectionally, the modulus in the fibre, 0° or longitudinal direction (E_l) is given to within <1% by the law of mixtures:

$$E_l = E_f V_f + E_m V_m \quad [6.1]$$

where E is the modulus, V is volume fraction, and the subscripts m and f refer to matrix and fibres, respectively.

At 90° to the fibres, the predictions of E_t from equivalent laws of mixtures are poor because the matrix properties dominate. The Halpin-Tsai equation includes corrections for non-uniform fibre distribution (ξ):

$$E_t = E_m (1 + \xi_\eta V_f) (1 - \eta V_f) \quad [6.2]$$

where $\eta = (E_f/E_m - 1)/(E_f/E_m + \xi)$

At angles (θ) other than 0° and 90°, E_θ varies non-linearly and has a rapid fall-off with rotation away from 0°.

The strength of a fibre-reinforced composite is also highly anisotropic

with fibres dominating in the 0° direction but the resin or matrix at most other angles. At 90° , the resin or interface is determinant and the strength is often 50% of the resin alone. As a result, it is necessary to arrange the fibres at angles to each other, either in laminates, with woven rovings or random mat in order to meet the complex stresses encountered.

A consequence of these lay-ups is that the failure of a fibre-reinforced plastic or composite involves in order, multiple transverse (or matrix) cracking, interlaminar or intralaminar shear failure (delamination) and multiple fragmentation of the fibres, before final fracture. In this way, large energies can be absorbed in fracture, which provides the explanation for the toughness of a composite made from these brittle components.

6.7.5.2 Short fibre reinforcement

With GRP, short fibres are often employed in industrial applications for economic and design reasons. The mechanics differ from those of long fibres because the fibre length reinforcing efficiency is reduced. This is because the build up of stress from the end of the fibre occurs over a transfer length (l_t). As the fibres become shorter, the average stress carried by the fibre is reduced because the transfer length at each end becomes more and more dominant.

The simple constant shear model of Kelly and Tyson,³ can be used to define the critical length (l_c) of a fibre for it to be loaded to fracture.

To be 95% efficient, the actual length has to be $>10 l_c$. In short-fibre reinforced plastics a distribution of fibre lengths exists within the moulded artefact. Sub-critical fibres will not break and tend to pull out on fracture of the composite, whereas the super-critical ones will break and become progressively sub-critical. As a result, the stress-strain curves will invariably be non-linear.

The law of mixtures, Equation [6.1], can be modified to account for the reduced reinforcing efficiency of the fibres with length (η_l) and orientation (η_θ)

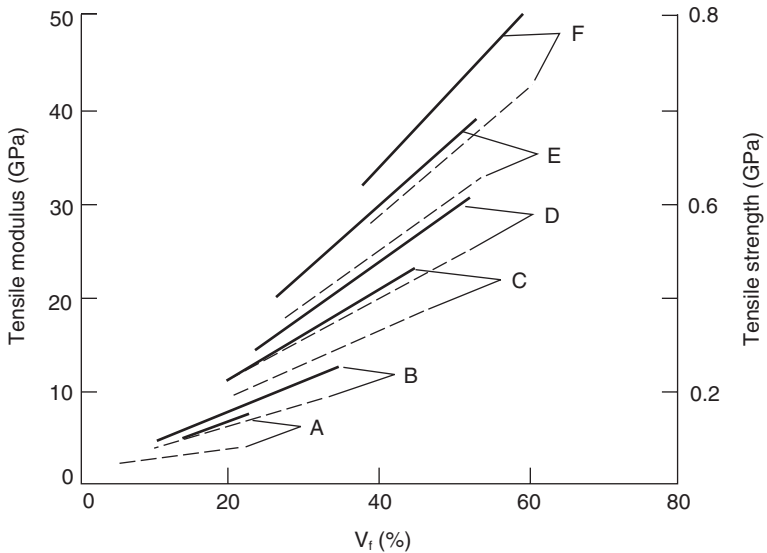
$$E_c = \eta_\theta \eta_l E_f V_f + E_m V_m \quad [6.3]$$

However, this requires knowledge of the fibre length and angle distributions, making predictions of strength and modulus difficult.

For the materials referred to as GRP or 'fibreglass', $l \gg l_c$ as in chopped strand mat and similar reinforced composites, a simple estimate can be obtained from

$$E_c = \frac{3}{8} E_l + \frac{5}{8} E_t \quad [6.4]$$

Typical properties of GRP with differing fibre reinforcements are presented in Fig. 6.13.



6.13 Stiffness (—) and tensile strength (----) of polyester-glass laminates, showing effect of different forms of reinforcement over practical ranges of glass content. A, random short fibre plastic; B, chopped strand mat; C, balanced woven roving; D, crossplied laminate or woven rovings; E, unidirectional woven roving; F, continuous aligned roving (after Jones⁵).

6.8 Design of fibre glass composites

The selection of glass fibres for a particular application depends on the economics and the application process. Two examples will be considered that illustrate some of the aspects.

6.8.1 General aspects

Fig. 6.13 illustrates the fundamental issues because short fibre mouldings (A) clearly have the poorest mechanical performance but can be rapidly moulded into a complex-shaped artefact by injection moulding. An example is a glass fibre-reinforced phenolic water pump housing for an automobile, or a glass reinforced polyamide (nylon) used for inlet manifolds. The best performance is achieved with unidirectional reinforcement (F) but only simple shapes can be manufactured in slow, labour-intensive processes, such as using an autoclave. Pultruded materials need to be cut and assembled into useful components. Thus, the basic competition between performance, processing and economics determines the choice of reinforcement and manufacturing route. The beauty of composite usage is that a variety of low cost/low volume routes (e.g. hand-lay) exist along side high-performance and high-volume solutions. From a direct comparison of material's cost, the

composite solution does not appear to be economic. However, comparison of the overall costs of manufacture shows that significant gains can be made through waste saving, assemblage costs where complex shapes can often be manufactured in one stage, in maintenance costs (helicopter rotor blades), or where improved design and performance not achievable in metals is possible (aerodynamically shaped helicopter rotor blades). Fuel savings through lightweight structures (aircraft or motor vehicles) or corrosion-resistance (yachts, ships, containers and pipes) are other important design requirements.

6.8.2 Electrical circuit boards

Here, shape is not really an issue, but for insulating performance, crucial thermal and mechanical stability is. The choice of matrix resin determines thermal stability and the use of balanced woven rovings will provide the latter. The one issue which is important is the maintenance of insulation. Specialist D-glass formulations are available (Table 6.6). Interfacial stability is required to prevent moisture-induced conduction paths. Thus, the industry utilises starch-sized woven rovings as the reinforcement. These are heat-cleaned prior to deposition of an appropriate coupling agent in the absence of a film former, to provide optimum adhesion without the variability that could be introduced with as-sized fibres.

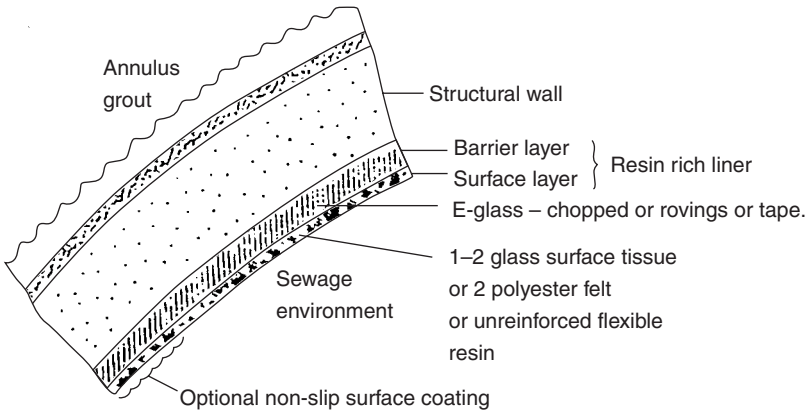
6.8.3 Chemical plant and related products

Environmental stress corrosion of GRP is of major concern. Fig. 6.8 demonstrates how differing composite parameters can be optimised for durability in acidic conditions at differing loading regimes.

For environmental durability, the more durable ECR glass can be used but at a cost penalty over standard E-glass. However, the composite can be designed to utilise the structural properties of E-glass with protection from a more chemically resistant C-glass reinforced gel-coat or barrier layer. The typical structure of a pipe for effluent is shown in Fig. 6.14. Here the important aspect is to prevent stress-corrosion initiated fibre breaks from propagating through the structure. Thus, C-glass veils coupled with chopped fibre-reinforced surface layers can inhibit a brittle crack from forming and protect the structural E-glass of the composite. In combination with higher fracture toughness resins, a durable structure can be manufactured.

6.9 Conclusions

Fibres from a number of glass formulations are available. E-glass fibres can be converted into a number of forms for reinforcement of resins, rubbers



6.14 Typical construction of a durable GRP pipe in corrosive environments.⁶² (Reproduced with permission of Mechanical Engineering Publications, now known as Professional Engineering Publishing Ltd.)

or polymers to give durable structural composites, with a wide range of application. They can also be used to reinforce cementitious products, but for durable structures alkali-resistant zirconia glass should be used. However, there is a growing application of GRP rebars for concrete using pultruded E-glass rod, where there is resin protection.

A-glass fibres are used as insulants in thermal or acoustic applications. E-glass fibres are also used in fire resistant textiles, which can be coloured using dyeable sizing.

The other major and growing application is SiO_2 -based glass for optical fibre communications.

In conclusion, fibres from glass represent a major technical resource.

6.10 Acknowledgements

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ANTHONY R BUNSELL AND
MARIE-HÉLÈNE BERGER

7.1 Introduction

The need for reinforcements for structural ceramic matrix composites (CMC) to be used in air at temperatures above 1000°C, as well as for the reinforcement for metals (MMCs), has encouraged great changes in small-diameter ceramic fibres since their initial development as refractory insulation. There now exists a range of oxide and non-oxide fibres with diameters in the range of 10 to 20µm which are candidates as reinforcements.¹ There are also large-diameter ceramic fibres with diameters over 100µm made by chemical vapour deposition (CVD) and by epitaxial growth from the melt which are also potential reinforcements. Applications envisaged are in gas turbines, both aeronautical and ground-based, heat exchangers, first containment walls for fusion reactors, as well as uses for which no matrix is necessary such as candle filters for high temperature gas filtration.

For all of these applications the structures have to withstand very high temperatures, so excluding the use of organic or glass fibres. The oxidising and corrosive environments in which such structures must operate also prohibit the use of carbon fibres, which would be degraded above 300°C. Ceramic fibres can withstand such demanding conditions but also are often required to resist static or dynamic mechanical loading at high temperature, which can only be achieved by a close control of their microstructures.

Ideally, ceramic fibres should show sufficient flexibility so that preforms can be made by weaving and subsequently infiltrated by the matrix material. This can be achieved with ceramics, which have high Young's moduli, if the fibres have sufficiently small diameters, because flexibility is related to the reciprocal of the fourth power of the diameter. A diameter of the order of 10µm is therefore usually required for ceramic reinforcements, together with a strain to failure of around 1%. As the choice of a ceramic material imposes a Young's modulus of 200 GPa or more, this implies a room temperature strength of more than 2 GPa. The fibres are destined to be used at

high temperature in air so that long-term chemical, microstructural and mechanical stability and creep resistance above 1200°C are often required.

Alumina and silicon carbide bulk ceramics are widely used for their high stiffness and good high temperature mechanical properties in air; however, they are generally weak due to the presence of critically sized defects. The low strength of these materials is significantly increased when the ceramics are in the form of fine filaments because the microstructures of the fibres are much finer, being composed of sub-micron grains. This precludes the existence of large defects. The requirements for high-performance reinforcements would therefore be fulfilled if such bulk ceramics were transformed into fibres. However, small diameters required for the fibres impose production processes which result in specific microstructures and properties which are not necessarily those of the bulk ceramics.

Conventional processes for the fabrication of bulk ceramics, which include powder compaction and sintering, cannot be extended to fine fibres. Thermoplastic polymer fibres and glass fibres are obtained by the spinning and drawing from a melt of the desired final composition, a process which is precluded for refractory materials as their melting points can exceed 2000°C . The production of fine ceramic fibres requires the spinning of an organic or mineral precursor fibre, which is then heat treated and pyrolysed for a very short time. The first ceramic fibres for very high temperature structural applications were commercialised at the beginning of the 1980s and, since then, the fibres have undergone great changes and shown improved properties. This chapter will describe the evolution of both oxide and non-oxide ceramic fibres and show how the small variations in the fabrication processes which have been introduced have induced major modifications in the microstructure and mechanical behaviour of these fibres.

7.2 Silicon carbide-based fibres

7.2.1 Fabrication of silicon carbide-based fibres

7.2.1.1 General

Fine-diameter SiC fibres are made from precursor fibres that are spun from the melt of an organosilicon polymer, such as a polycarbosilane (PCS) or one of its derivatives. This family of polymers is principally formed of rings of six atoms of Si and C, prefiguring the architecture of the blende structure of SiC. Methyl groups and hydrogen atoms are grafted onto these rings and, in part, remain in the fibres after their conversion to ceramic fibres by pyrolysis above 1200°C . However, before this process can take place, crosslinking of the precursor fibre is necessary to avoid the softening or melting of the fibre during pyrolysis. The choices of the precursor polymers

and of the crosslinking processes have a great influence on the final composition and microstructure of the ceramic fibres.

7.2.1.2 *Fibres cured by oxidation*

The elaboration of the first fine SiC-based fibres was reported by Yajima and his colleagues in Japan in the mid-1970s² and commercialised under the name of *Nicalon* fibres by Nippon Carbon at the beginning of the 1980s. They were produced from a PCS fibre for which crosslinking was achieved by a heat treatment in air at around 200°C. Lateral Si-H and C-H bonds were oxidised and new Si-O-Si or Si-O-C bonds were created linking pairs of polymer chains. This curing process introduced oxygen into the structure of the precursor fibre which already had hydrogen and methyl side groups in addition to the Si-C of the main chain. This deviation from stoichiometry was reduced during the heat treatment owing to the outgassing of hydrogen, carbon oxides and alkyls between 300 and 900°C. However, after the pyrolysis at around 1200°C, significant amounts of oxygen (12% wt) and excess carbon ($C_{at}/Si_{at} = 1.3$) still remained in the ceramic. The fibres that were obtained were described as SiC-based fibres, although their appearance and mechanical properties were not those which could be expected from SiC. The *NL-200 Nicalon* fibres, which are the most representative of this class of ceramic fibres, have a diameter of 14 µm, a glassy appearance, as shown in Fig. 7.1, a Young's modulus of 200 GPa, as shown in Table 7.1, that is half that of bulk SiC, and they show much inferior creep properties as creep is observed from 900°C. This is explained by the microstructure of the fibre. Only 55% of the fibre is composed of β-SiC, which is in the form of grains of about 2 nm. Oxygen, introduced during curing, forms with carbon and silicon, a metastable Si-C-O phase representing 35 to 40% of the fibre by weight, the rest of the fibre consisting of free carbon particles.³ The Si-C-O phase impedes grain growth and permits creep. This phase begins to decompose from 1200°C. Excess carbon and oxygen are lost in the form of oxides of carbon but no densification of the remaining growing SiC grains is possible so that the fibre loses all strength. This degradation of the fibre is more rapid in an inert atmosphere than in air as the outer silica layer that is formed by oxidation slows down the outgassing of the decomposition. However, bubbles of CO which build up at the SiC/SiO₂ interface reduce the fibre strength.

Ube Industries produced a series of fibres from a polytitanocarobosilane (PTC) precursor which was obtained by the grafting of titanium alkoxide between the PCS chains.⁴ PTC was reported to be more easily spinnable. *Tyranno LOX-M* fibres, with diameters down to 8.5 µm and containing 13% oxygen by weight, were produced after oxidation, curing and pyrolysis at around 1300°C. Moreover, it was expected that the germination and growth



7.1 Fracture morphology of a *Nicalon NL-200* oxygen-cured SiC-based fibre. The fibre has a diameter of $14\mu\text{m}$ and shows a glassy appearance when observed in SEM (scanning electron microscopy).

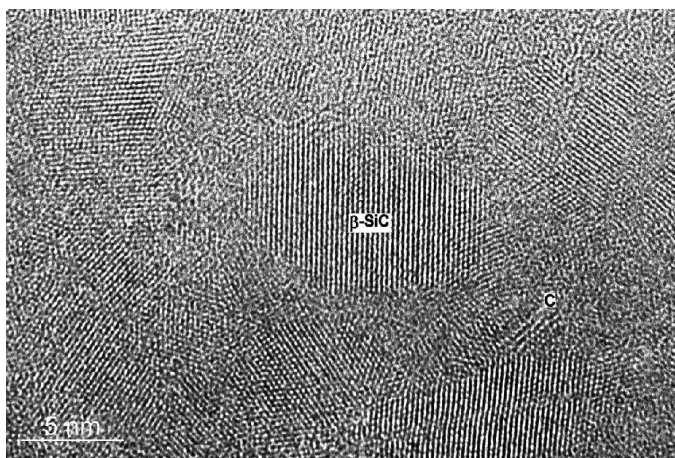
of evenly distributed small grains of TiC could trap excess carbon and inhibit the SiC grain growth responsible for strength loss. Growth of large TiC particles was observed from 1200°C but no remarkable improvements in the microstructural stability and mechanical properties were noticed and higher oxidation rates were reported.

7.2.1.3 *Fibres cured by irradiation*

The further improvement of SiC-based fibres required the elimination of oxygen from the structure. This was achieved by Nippon Carbon by irradiating precursor PCS fibres with a 2 MeV electron beam. Si and C atom sited radicals were formed and radical–radical recombination reactions allowed the chains to be crosslinked without introduction of oxygen. These *Hi-Nicalon*⁵ fibres were pyrolysed up to about 1400°C . The oxygen content was decreased to 0.5% wt but the fibre contained more free carbon ($C_{\text{at}}/Si_{\text{at}} = 1.39$) as less oxides of carbon could leave the fibre during heat treatment. The fibre encloses ovoid β -SiC grains of 5 to 20 nm, surrounded by poorly organised Si–C and turbostratic free carbon, as seen in Fig. 7.2. The lower oxygen content induced a better chemical stability at high temperature compared to oxygen-cured fibres. The threshold temperature for creep was pushed to 1100°C and lower creep rates were measured. Creep resistance could further be enhanced by a post heat-treatment for 5 hours in argon

Table 7.1 Properties and compositions of silicon-based fibres. Compositions and densities are those given by the manufacturers

Fibre type	Manufacturer	Trademark	Composition (wt %)	Diameter (μm)	Density (g/cm ³)	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
Si-C based	Nippon Carbide	Nicalon NLM 202	56.6% Si 31.7% C 11.7% O	14	2.55	2.0	1.05	190
	Nippon Carbide	Hi-Nicalon	62.4% Si 37.1% C 0.5% O	14	2.74	2.6	1.0	263
	Ube Industries	Tyranno Lox-M	54.0% Si 31.6% C 12.4% O 2.0% Ti	8.5	2.37	2.5	1.4	180
	Ube Industries	Tyranno Lox-E	54.8% Si 37.5% C 5.8% O 1.9% Ti	11	2.39	2.9	1.45	199
Near stoichiometric SiC	Nippon Carbon	Hi-Nicalon Type-S	68.9% Si 30.9% C 0.2% O	13	3.0	2.5	0.65	375
	Ube Industries	Tyranno SA1	SiC Al < 1%	10	3.0	2.6	0.75	330
		SA3	+small amounts of C + O	7.5	3.1	2.9	0.8	340
	Dow Corning	Sylramic	SiC ~ 96% TiB ₂ ~ 3.0% C ~ 1.0% O ~ 0.3%	10	3.1	3.0	0.75	390



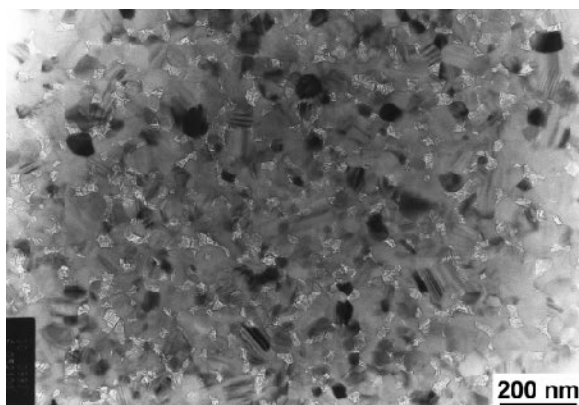
7.2 High-resolution transmission electron microscopy (TEM) image of a *Hi-Nicalon* fibre, showing β -SiC grains of about 10 nm, surrounded by a poorly organised Si-C phase, and turbostratic carbon.

at 1450°C, a temperature just above the pyrolysis temperature, so as to increase the crystallinity. Turbostratic carbon has been seen to grow preferentially parallel to some of the SiC grain facets and could in some cases form cages around them, so limiting their growth.

The radiation curing process was also used by Ube Industries to crosslink PTC fibres. After a pyrolysis at around 1300°C, the *LOX-E* fibre that was obtained contained 5% wt of oxygen. This higher value of oxygen in the *LOX-E* fibre compared to that of the *Hi-Nicalon* was due to the introduction of titanium alkoxides for the fabrication of the PTC. As a result, this fibre possessed a microstructure and high-temperature behaviour that were comparable to those of the previous oxygen-rich fibres.⁶ A subsequent series of *Tyranno* fibres was obtained from a PCS polymer onto which zirconium acetylacetonate was grafted.⁷ The use of these compounds introduced less oxygen and allowed the oxygen content to be decreased to 2% wt. The microstructure and creep behaviour of the *Tyranno ZE* fibres obtained by radiation curing were close to those of the *Hi-Nicalon*.

7.2.1.4 Sintered fibres

Three new sintered fibres, referred to by their manufacturers as being stoichiometric, have been developed by Ube Industries, Dow Corning and Nippon Carbon and called respectively, *Tyranno SA*,⁸ *Sylramic*⁹ and *Hi-Nicalon Type-S*.¹⁰ Ube Industries and Dow Corning start with precursor fibres cured by oxidation, as for the first generation of fibres, but introduce



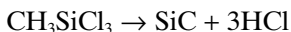
7.3 Microstructure of a *Hi-Nicalon Type-S* fibre revealed by TEM. The fibre is composed of SiC grains of 50 to 100 nm and pockets of free carbon.

sintering aids in the precursor, by reaction of aluminium acetylacetonate with PCS for Ube Industries or by doping the PTC with boron for Dow Corning. By these processes, ceramic fibres containing an oxygen-rich intergranular phase, similar to the first generation of fibres, are produced. These fibres are then pyrolysed up to 1600 °C for the *Sylramic* and 1800 °C for the *Tyranno SA*, so that the excess carbon and oxygen can be lost as volatile species. Unlike in the previous generations of fibres, densification of the fibres can take place because of the sintering aids. Grain sizes are of 200 nm, with TiB₂ particles in the *Sylramic* fibres whereas no crystallised aluminium compounds are formed in the *Tyranno SA* fibres. The process adopted by Nippon Carbon is reported as being a ‘modified *Hi-Nicalon* process’. The PCS precursor fibres are cured by irradiation and pyrolysed in a hydrogen-rich atmosphere up to 1500 °C to reduce the free carbon content. The grain sizes are 50 to 100 nm, as seen in Fig. 7.3. Sintering aids cannot be detected in these fibres. The three types of fibres contain a significant amount of free carbon, located at pockets between clusters of SiC grains, which explains why their Young’s moduli are still lower than that of bulk sintered SiC. The three fibres show much improved creep properties, with creep rates of the order of 10⁻⁸ s⁻¹ at 1400 °C when compared to the earlier generations of fibres which have rates of 10⁻⁷ s⁻¹ at the same temperature. The *Nicalon Type S* fibre shows lower creep rates than the other two fibres and this fibre is also seen to maintain its room temperature strength up to 1400 °C. The use of the electron-curing process for the PCS precursor is clearly of benefit, although it imposes a cost penalty. The sintering aids used in the other two fibres are seen to increase creep rates by increasing diffusion rates.

As the composition of the fibres approaches stoichiometry, lower creep and oxidation rates are obtained. Nevertheless, this family of fibres are likely to be limited by oxidation to a maximum temperature of 1400°C.

7.2.1.5 *SiC fibres made by chemical vapour deposition*

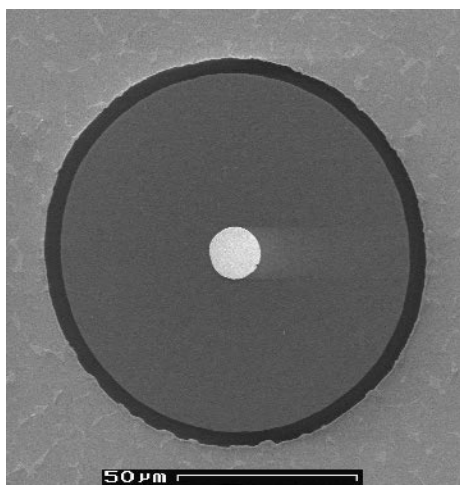
Silicon carbide fibres made by CVD are produced on both tungsten and carbon cores.¹¹ In commercial production, the gas mixture is introduced at multiple injection points of the vertical reactor, which is about two metres in length. The temperature along the reactor passes through a maximum between 1400 and 1500°C at an early stage of deposition. Passage through the reactor is of the order of one or two minutes and results in a fibre with a diameter greater than 100µm. Various carbon-containing silanes have been used as reactants. In a typical process, with CH₃SiCl₃ as the reactant, SiC is deposited on the core as follows:



SiC fibres produced on a tungsten core of 12µm diameter show a thin reactive layer between the SiC and tungsten which forms reaction products of α-W₂C and W₅Si₃. Heating above 900°C leads to growth of this reactive layer and degradation of the properties of the fibre.

The carbon fibre cores of 33µm diameter, which are used for the CVD production of SiC fibres, are themselves coated with a 1–2µm thick layer of pyrolytic carbon which covers surface defects on the core and produces a more uniform diameter. The fibres on a carbon core show a gradation of composition, which is richer in carbon near the interface and becomes stoichiometric SiC towards the fibre surface. The fibres on a tungsten core have a mantle of stoichiometric SiC. The specific gravity of a 100µm diameter SiC-W fibre is 3.35 whilst that of a 140µm diameter SiC-C fibre is around 3.2.

Early SiC fibres were found to have a wide scatter in tensile strengths and this was alleviated by coating them with a thin layer of carbon. This had the disadvantage, however, of reducing interfacial bonding, particularly with light alloys. To overcome this, the SiC fibres made on a carbon core and destined to reinforce light alloys, are produced with a surface coating, the composition of which is made to vary from being carbon rich to silicon carbide at the outer surface. The fibres which are to be used to reinforce titanium have a protective layer which varies from being rich in carbon to being rich in silicon to a composition which is again rich in carbon at the surface. The outer sacrificial layer protects the fibre during contact with the molten and highly reactive titanium during composite manufacture. This type of fibre is produced by Textron under the designation SCS-6, as the



7.4 Cross-section of a SiC fibre made by CVD onto a tungsten core.

coating increases the fibre diameter by $6\mu\text{m}$. The fibre shows no degradation after 5 hours at 900°C when embedded in Ti (6Al4V) matrix. A cross-section of a typical $100\mu\text{m}$ diameter SiC fibre on a tungsten core, made by DERA, is shown in Fig. 7.4. This fibre has surface coating that is $3\text{--}4\mu\text{m}$ thick and that varies from being carbon rich to becoming a thin layer of less than $1\mu\text{m}$ of TiB_2 at the surface.

The room-temperature strengths of the fibres are around 4GPa . Low failure stresses are due to surface flaws whereas higher strengths are controlled by defects at the core mantle interface. Strength decreases in air when the fibres are heated to above 800°C for long periods most probably due to oxidation of the carbon-rich outer layers. At temperatures above 900°C , interfacial reactions between tungsten cores and mantles cause degradation of properties. At higher temperatures still, grain growth in the SiC mantle may be the cause of further falls in strength.

7.3 Other non-oxide fibres

Various non-oxide fibres have been developed at a laboratory or pilot scale from other silicon containing precursors such as polysilazane. The fibres obtained have amorphous structures based on Si–C–N–O, Si–N or Si–B–N–C, but recrystallise from 1200°C or show poor oxidation resistance. Boron nitride fibres with oriented turbostratic structures are also being developed for specific applications, but they are intrinsically not adapted to resist oxidation.

7.4 Alumina-based fibres

If high-performance fibres are to be exposed to oxidising atmospheres and temperatures above 1400°C, they will have to be made from oxides with high melting points. α -alumina is widely used for its refractory properties. Its complex structure provides large Burgers vectors so that high stresses are necessary to generate plasticity in monocrystals. Monocrystalline α -alumina fibres showing no creep up to 1600°C can be obtained if the fibre axis strictly corresponds to the [0001] axis. However no viable processes exist at present to produce fine and flexible continuous monocrystalline fibres. Therefore, only polycrystalline fibres can be considered for the reinforcement of ceramics. Various processing routes exist for making such fibres and these lead to a large range of microstructures and behaviours at high temperature. The properties of such fibres are shown in Table 7.2.

7.4.1 Fabrication of alumina fibres

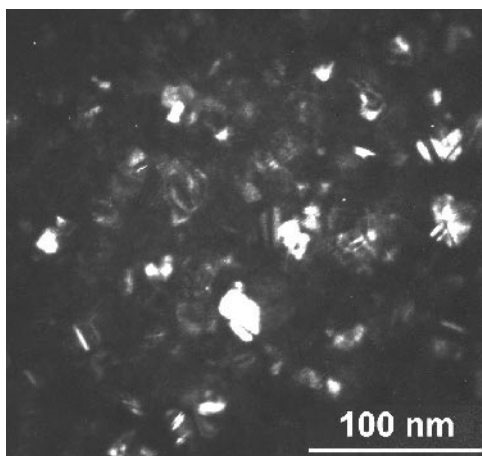
Precursors of alumina are viscous aqueous solutions of basic aluminium salts, $\text{Al}X_n(\text{OH})_{3-n}$, where X can be an inorganic ligand (Cl^- , NO_3^- . . .) or an organic ligand (HCOOH^- . . .).¹² Spinning of the precursor produces a gel fibre which is then dried and heat treated. Decomposition of the precursor induces the precipitation of aluminium hydroxides, such as boehmite $\text{AlO}(\text{OH})$, and the outgassing of a large volume of residual compounds. The associated volume change and porosity at this step has to be carefully controlled. It is also possible to spin aqueous sols based on aluminium hydroxides directly. Above 400°C and up to around 1000°C the fibre is composed of grains, in the range of 10 to 100 nm, of transitional forms of alumina associated with finely divided porosity. Above 1100°C, stable α -alumina nucleates and a rapid growth of micron-sized grains occurs together with the coalescence of pores. The fibres become extremely brittle owing to large grain boundaries emerging at the fibres' surfaces and cannot be used in this form. The use of alumina fibres above 1100°C therefore requires the control of the nucleation and growth of α -alumina and porosity. This has been achieved by adding either silica precursors or seeds for α -alumina formation to the fibre precursors and has led to two classes of alumina-based fibres, one consisting primarily of α -alumina grains and the other of transitional alumina phases together with another phase.

7.4.2 Alumina-silica fibres

Alumina-silica fibres were the first ceramic fibres produced in the early 1970s, for thermal insulation applications. A small amount of silica ($\approx 3\%$ wt in the *Saffil* short fibres from ICI) allows the sintering of the transitional

Table 7.2 Properties and compositions of alumina-based fibres. Compositions and densities are those given by the manufacturers

Fibre type	Manufacturer	Trade mark	Composition (wt %)	Diameter (μm)	Density (g/cm^3)	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
α - Al_2O_3 fibres	Du Pont Mitsui Mining	<i>FP</i>	99.9% Al_2O_3	20	3.92	1.2	0.29	414
		<i>Almax</i>	99.9% Al_2O_3	10	3.6	1.02	0.3	344
	3M	<i>Nextel 610</i>	99% Al_2O_3 0.2%–0.3 SiO_2 0.4–0.7 Fe_2O_3	10–12	3.75	1.9	0.5	370
Alumina-silica fibres	ICI	<i>Saffil</i>	95% Al_2O_3 5% SiO_2	1–5	3.2	2	0.67	300
	Sumitomo	<i>Altex</i>	85% Al_2O_3 15% SiO_2	15	3.2	1.8	0.8	210
	3M	<i>Nextel 312</i>	62% Al_2O_3 24% SiO_2 14% B_2O_3	10–12 or 8–9	2.7	1.7	1.12	152
	3M	<i>Nextel 440</i>	70% Al_2O_3 28% SiO_2 2% B_2O_3	10–12	3.05	2.1	1.11	190
	3M	<i>Nextel 720</i>	85% Al_2O_3 15% SiO_2	12	3.4	2.1	0.81	260
Alumina-zirconia fibres	3M	<i>Nextel 650</i>	89% Al_2O_3 10% ZrO_2 1% Y_2O_3	11	4.1	2.5	0.7	360



7.5 Dark field image of an *Altex* fibre revealing γ -alumina grains that are embedded in amorphous silica.

forms of alumina and delays the nucleation and growth of α -alumina to 1300°C .¹³ Larger amounts (15% wt in the *Altex* fibre from Sumitomo) produce γ -alumina grains of around 25 nm in amorphous silica,¹⁴ as shown in Fig. 7.5. Mullite, with a composition between $2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, crystallises above 1100°C , before the formation α -alumina, the growth of which is then restricted. The α -alumina formation can be totally suppressed if enough silica is added to consume the metastable alumina by mullite formation. 3M began to produce the *Nextel* series of fibres having the composition of mullite. Boria additions lowered the temperature of mullite formation, helped sintering and increased the fibre strength. Various degrees of crystallinity can be obtained according to the amount of boria and the pyrolysis temperature. *Nextel 312*, with 14% B_2O_3 , is a quasi-amorphous fibre,¹⁵ the high temperature properties of which are limited by the volatilisation of boron compounds from 1100°C . *Nextel 440* contains 2% B_2O_3 and is composed of γ -alumina in amorphous silica. The same fibre composition, heated above the mullitisation temperature, yields fully dense crystallised mullite with 50 to 100 nm grain sizes.¹⁶ However, the good high-temperature creep resistance which could be expected from the complex mullite structure is not obtained owing to the presence of an amorphous borosilicate intergranular phase.

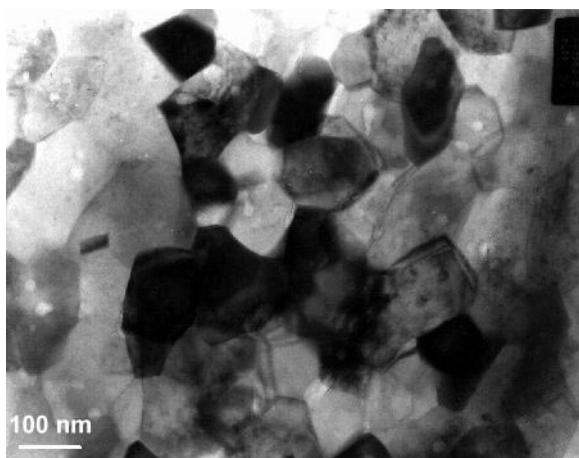
The effect of silica on the room-temperature properties of alumina fibres is to reduce their overall stiffness ($E(\text{SiO}_2) \approx 70 \text{ GPa}$, $E(\text{Al}_2\text{O}_3) \approx 400 \text{ GPa}$) and to increase their room temperature strength by avoiding the formation of large grains.¹ This results in flexible fibres that can be used in the form of bricks or woven cloths for thermal insulation. Strength loss at high tem-

perature occurs from 1000°C. The main drawback of silica is that it facilitates creep, which begins from 900°C so that these fibres cannot be used for structural applications above this temperature.

7.4.3 Single phase α -alumina fibres

To obtain creep-resistant alumina fibres, they have to be deprived of intergranular silicate phases. This imposes processes other than the addition of silica to control α -alumina growth. A pure α -alumina fibre was first produced by Du Pont in 1979.¹⁷ *Fiber FP* was obtained by the addition, to an alumina precursor, of more than 40% wt of α -alumina powder having a grain size of less than 0.5 μm . The use of a lower fraction of precursor reduces the porosity owing to its decomposition and to the dehydration of hydrous aluminas. α -alumina particles act as seeds for the growth of α -alumina and so remove the problems associated with the delay of nucleation and rapid grain growth. In the case of *Fiber FP*, the grain size of the powder included in the precursor precluded the spinning of fine filaments. The *Fiber FP* had a diameter of 20 μm , and this, added to the intrinsic high stiffness of α -alumina ($E_{\text{FP}} = 410 \text{ GPa}$) and low strength (1.5 GPa at 25 mm) owing to its large grain size (0.5 μm), made the fibre unsuitable for weaving. Flexible α -alumina fibres require diameters of around 10 μm . This was first achieved by Mitsui Mining by reducing the size of the α -alumina powder.¹⁸ However, this affected the control of porosity and the resulting *Almax* fibre encloses a significant amount of pores inside alumina grains, which are of 0.5 μm in size.¹ Later, 3M produced the *Nextel 610* fibre,¹⁹ which is a fully dense α -alumina fibre of 10 μm in diameter, as seen in Fig. 7.6, with a grain size of 0.1 μm and possesses the highest strength of the three α -alumina fibres described, as shown in Table 7.2.

The high-temperature behaviours of these three fibres are controlled by their microstructures, which are made of fine isotropic grains.²⁰ Plasticity occurs from 1000°C and superplastic behaviour can be obtained at 1300°C with the *FP* fibre. No intragranular plasticity can develop in these fibres as the small distances between two grain boundaries, perpendicular to the load axis, prevent the formation of dislocation sources and pin dislocation movement. However, the large number of boundary surfaces allows the relaxation of the imposed stress by grain boundary sliding. This mechanism involves movement of intergranular dislocations and is accommodated by interfacial controlled diffusion mechanisms. Amongst the three fibres, the lowest deformation rates are obtained with the *FP* fibre ($\sim 10^{-3} \text{ s}^{-1}$ at 1300°C). Diffusion and deformation are facilitated by porosity in the *Almax* and by grain size in the *Nextel 610*, which is five times smaller than in the other two fibres. Damage occurs by the growth of cavities at triple points and the coalescence of intergranular microcracks induces failure. The times



7.6 Microstructure of a *Nextel 610* fibre composed of α -alumina grains of around 100 nm.

to failure in creep are considerably reduced in the *Almax* fibre by the build-up of large intergranular pores.

These three fibres are stiff and chemically stable. They can therefore be used to reinforce matrices, such as light alloys, working in intermediate temperature ranges, or for applications at higher temperatures for which no load bearing capacity is required, as in thermal insulation. They were not developed to work in the conditions for which their poor creep behaviours have been demonstrated. However, the creep mechanisms that have been revealed have allowed the microstructure that would improve the high temperature behaviour of α -alumina based fibres to be better defined. These fibres must have fine grains, as large grains are detrimental to the fibre strength, but grain sliding has to be inhibited. Inclusions of second phases and fine but elongated oriented grains have been considered as possible solutions to achieve these goals.

7.4.4 α -alumina/zirconia fibres

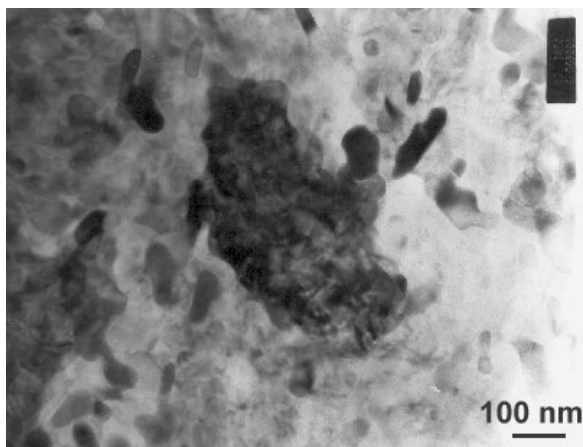
The dispersion of small particles of tetragonal zirconia between α -alumina grains was first employed by Du Pont, with the aim of producing a modified *FP* fibre with improved flexibility. This fibre, called *PRD-166*,²¹ was obtained by the addition of zirconium acetate and yttrium chloride to the blend of the alumina precursor and α -alumina powder. The fibre had a diameter of 20 μm and contained 20% wt of tetragonal zirconia in the form of grains of 0.1 μm , which restricted the growth of α -alumina grains to 0.3 μm , on average.²⁰ The Young's modulus was lowered to 370 GPa because

of the lower stiffness of zirconia ($E(\text{ZrO}_2) \sim 200 \text{ GPa}$). Tetragonal to monoclinic transformation of zirconia around the crack tip at room temperature toughened the fibre and a higher strength was obtained. However, this was not sufficient to ensure flexibility and production did not progress beyond the pilot stage. A flexible α -alumina-zirconia fibre, *Nextel 650* has been announced by 3M, with the aim of increasing the creep resistance with respect to that of the α -alumina *Nextel 610* fibre.

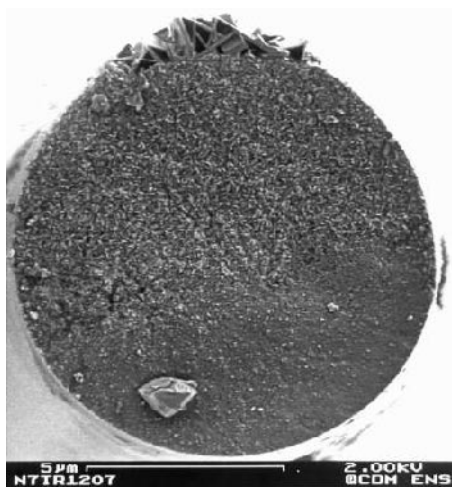
The effect of the addition of zirconia on the high-temperature mechanical behaviour is to delay the onset of plasticity to 1100°C and to decrease the strain rates in creep. The mechanisms proposed have been the pinning of the grain boundaries by the intergranular zirconia particles and the modification of the Al^{3+} diffusion rates at the alumina/alumina grain boundaries by the presence of Zr^{4+} ions. However, these mechanisms are less efficient as the temperature exceeds 1100°C and at 1300°C the creep rates of *FP* and *PRD 166* fibres are similar.²⁰

7.4.5 α -alumina/mullite fibres

The complex crystalline structure of mullite provides creep resistance materials if a sintered microstructure can be obtained without the help of an excess of silica. 3M produced a dense mullite/ α -alumina fibre, called *Nextel 720*,²² by using an aqueous sol composed of intimately mixed silica and alumina precursors, with iron compounds used as the seeds for α -alumina. The fibre is composed of a continuum of mullite mosaic grains of about $0.5 \mu\text{m}$ with wavy contours, with no silicate intergranular phase. Each mosaic grain consists of several mullite grains that are slightly mutually mis-oriented, and encloses spherical and elongated particles of α -alumina of respectively 50 nm in diameter and 100 nm in length, as can be seen in Fig. 7.7. The elongated particles show some preferential alignment with respect to the fibre axis and their long facets correspond to the basal plane of α -alumina. After heat treatment, from 1300°C , the microstructure evolves towards faceted mullite ($3\text{Al}_2\text{O}_3:2\text{SiO}_2$) grains deprived of intragranular alumina particles, together with larger α -alumina particles which become intergranular. Some of the elongated α -alumina grains show exaggerated growth. This evolution of the microstructure is accelerated by the combination of temperature and load. When tested in creep, these fibres show much reduced creep rates as compared to pure α -alumina fibres and creep rates of the order of 10^{-6} s^{-1} have been measured at 1400°C .²³ This remarkable behaviour is attributed to the high creep resistance of mullite and to the presence of the elongated and oriented α -alumina grains. The fibres are, however, very sensitive to alkaline-containing environments. Mullite decomposes in the presence of a low concentration of alkalines to form aluminosilicate phases of melting points lower than 1200°C . The fast growth



7.7 Microstructure of a *Nextel* 720 fibre revealing diffracting mullite aggregates and α -alumina grains that are enclosed in other non-diffracting mullite grains. Some of these alumina grains are elongated and oriented preferentially parallel to the fibre axis.



7.8 Fracture morphology of a *Nextel* 720 fibre at 1200°C in the presence of alkaline contaminants.

of large alumina grains, under load, occurs by liquid transportation leading to large platelets as can be seen in Fig. 7.8 and which are detrimental to fibre strength. This observation could seriously limit the use, in real environments at high temperature, of fibres based on the Al_2O_3 - SiO_2 system.

7.5 Other polycrystalline oxide fibres

Attempts to produce creep-resistant oxide reinforcements have led to the experimental development of polycrystalline fibres from complex crystallographical systems such as mullite, chrysoberyl or garnet-like structures. Among them, yttrium aluminium garnet (YAG) ($\text{Y}_3\text{Al}_5\text{O}_{12}$) fibres seem the most promising.

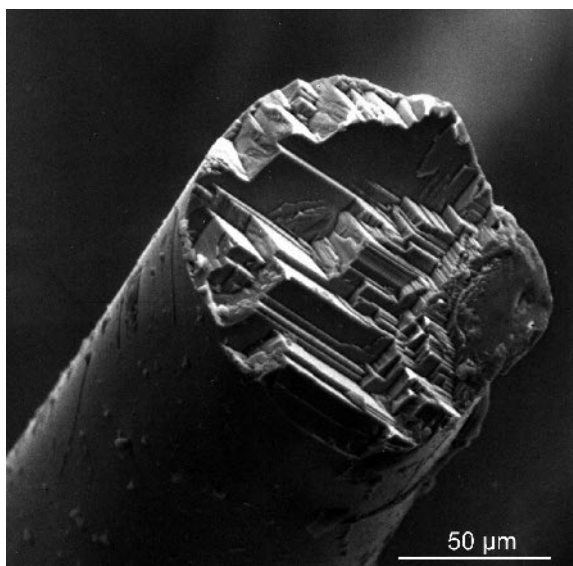
7.6 Single-crystal oxide fibres

Continuous monocrystalline filaments have been developed by the Saphikon company in the USA.²⁴ These filaments are grown from molten alumina, either heated in a crucible or from the end of an alumina rod heated by a laser, and, as a consequence, are produced at a slow rate and high cost and with large diameters usually in excess of $100\text{ }\mu\text{m}$. The stoichiometric composition of these fibres with the absence of grain boundaries means that they should be able to better withstand high temperatures above 1600°C . Careful orientation of the seed crystal enables the crystalline orientation to be controlled so that creep resistance can be optimised. Published data on the strength of *Saphikon* fibres as a function of temperature reveal that strength variation is not a simple function of temperature. The observed fall in strength around 300°C , which is then followed by an increase in strength around 500°C , could be due to stress corrosion followed by crack blunting.²⁴ These fibres are not without defects and characteristic bubbles can be seen in the fibres, most probably due to convection during fibre growth at the meniscus point between the solid and the melt. The crystalline fracture morphology of these fibres is shown in Fig. 7.9.

The same manufacturing processes have been employed to produce an eutectic fibre consisting of interpenetrating phases of α -alumina and YAG. The structure is lamellar and oriented parallel to the fibre axis. This fibre does not show the same fall in strength seen with the single-phase alumina fibre. However, such fibres are seen to relax from 1100°C but do not have as strong a dependence on temperature as the polycrystalline oxide fibres.²⁵

7.7 Conclusions

The requirement to have reinforcing fibres capable of operating at very high temperatures and under corrosive environments has been addressed by the development of two families of small-diameter reinforcements and large-diameter fibres made by CVD or grown from the melt. The former SiC- and alumina-based fibres have been improved by a greater knowledge and control of the relationships between process and microstructure that governs the ultimate mechanical properties. The reduction of amorphous



7.9 Room-temperature fracture morphology of a monocrystalline α - Al_2O_3 fibre produced by *Saphikon*.

phases, in both classes of fibres, has largely overcome the poor creep behaviour and structural instability at high temperatures of earlier generations of these fibres. The latest SiC fibres have sintered microstructures showing excellent creep resistance and strength retention up to 1400°C . These fibres are, however, limited by oxidation. The large diameter SiC fibres made by CVD are of primary interest for reinforcing titanium. Polycrystalline alumina fibres do not suffer from this limitation but can exhibit superplastic behaviour at 1300°C . The addition of second phases, such as zirconia or mullite, can inhibit grain boundary sliding.

The large diameter oxide fibres resist much better the effects of very high temperatures but their high costs and the inability to weave such fibres means that they have attracted little industrial interest. The development of polycrystalline oxide fibres for very high temperatures is still in its infancy and considerable advances may be expected from the production of fibres based on oxides with complex crystallographic structures.

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A RICHARD HORROCKS (8.1–8.3, 8.5–8.7)
BRUCE McINTOSH (8.4)

8.1 Introduction (ARH)

Chemically resistant organic polymeric fibres include those which are designed to resist chemical attack for acceptable periods during their service lives at both ambient and elevated temperatures. As a consequence of their generally inert structures they may also be flame resistant and so address markets where that property is also desirable.

Obviously, some members of this group will overlap with other fibres more often considered to be high-temperature resistant fibres, such as the aramids, arimids and others dealt with elsewhere in this text. Although primarily chosen for their strength and stiffness, many of the fibres described in Chapters 2 to 7 have good chemical resistance, albeit somewhat selectively. In this chapter, reference will be made only to applications and characteristics of these fibres which enable them to be used in environments where chemical resistance is the major priority.

Because chemical reactions have rates that increase with temperature, the main application areas will be those where the combined effects of heat and reactive chemical agencies operate, such as in wet and dry filtration. However, longer term durability to less corrosive environments is demanded in the geotextile and geomembrane sectors, where ambient conditions prevail. Protective clothing applications requiring specific chemical resistance will also seek to exploit members of this fibre group.

The essential chemical structural features of the members of this group will be general inertness as a consequence of the presence of strong chemical bonding systems within the polymeric backbone and/or the presence of no or unreactive side groups. In addition, because the presence of aliphatic chain hydrogen atoms increases the tendency of the polymer towards oxidation, their presence should be minimal. Consequently, fibres produced from poly(ethylene) and poly(propylene), while having acceptable resistance to many chemicals at ambient temperatures, are limited in resistance to temperatures much in excess of 50°C, especially if oxidising agents are

present. Fibres based on these polymers are excluded from this chapter. Furthermore, the polymer backbone should be free of hydrolysable functional groups such as ester and amide, and so fibres based on aliphatic polyamide and polyester structures lack sufficient chemical durability to be included. Aromatic analogues, however, show greater resistance and so the polyaramids, for example, may be considered to belong to this group as well as to the high-temperature resistant group.

Thus, the fibres discussed within this chapter do not belong to a single fibre genus and do not have a simple commonality of polymer backbone structure or a common set of chemical properties. However, they do present a most interesting and almost disparate group, linked together by the general property of chemical inertness extending over a range of temperatures. They tend also to see service in applications that are of a very similar character, differentiated only by the severity of thermal and chemical inertness demanded. For instance, hot gas and liquid filtration fabrics, braiding materials in chemical plant, gaskets, protective textiles, conveyer beltings and high performance sewing threads are typical end-uses.

8.2 Chlorinated fibres: PVDC (ARH)

The major fibres of importance here are those based on poly(vinylidene chloride) or PVDC. The chemical structure of the polymeric repeat unit $-\text{CCl}_2\text{.CCl}_2-$ creates a polymer with a high degree of chemical resistance and a high degree of order. This latter makes the polymer difficult to process and so in commercially useful forms, copolymers with other vinyl and acrylic comonomers, such as vinyl chloride, acrylonitrile and methyl acrylate (usually present at <15% w/w), are utilised. Dow Chemical Company developed the *Saran* fibre based on this polymer in the 1940s and the name *Saran* is a registered trademark with respect to the polymer which is used in coatings, films, monofilaments and other extrusions. Currently, the resin *Saran 510* is that recommended for monofil applications and it is, in fact, a copolymer of vinylidene chloride and vinyl chloride. Fibres have been marketed under the names *Permalon* and *Velon*. Similar fibres, such as *Fugafil* produced in Germany by Saran GmbH, are also available.

The polymer melts over the range 160–170°C and is melt spun at about 180°C by conventional melt-spinning methods to yield both multi- and monofilaments. It softens over the range 115–160°C, depending upon its copolymeric character and this limits its service temperature limit. The inherently golden-yellow coloured fibres have acceptably high tenacities, up to 0.25 N/tex, with breaking strains of 15–30%. The moderately low modulus (0.9N/tex) ensures that even the coarsest filaments have a high level of flexibility. With a moisture regain of less than 1%, tensile properties are main-

Table 8.1 Typical properties of PVDC fibres¹

Property	Value
<i>Thermal:</i>	
Melting point, °C	171
Softening temperature, °C	115–160
Sticking temperature, °C	99–104
<i>Tensile:</i>	
Tenacity, N/tex	0.20
Tenacity (100 °C), N/tex	0.13
Tenacity (loop), N/tex	0.06–0.10
Tenacity (knot), N/tex	0.09–0.15
Breaking strain, %	15–30
Elastic recovery at 3% strain, %	98.5
Elastic recovery at 10% strain, %	95
Modulus, N/tex	0.44–0.88
<i>General:</i>	
Specific gravity	1.6
Moisture regain, %	<1
Colour	Golden-yellow
Cross-section	Round
Limiting oxygen index, %	60

tained under wet conditions and permeation by chemicals is low. Table 8.1 summarises the main properties of these fibres.

Resistance to chemicals such as salts, acids, most alkalis, aliphatic hydrocarbons and alcohols is excellent at temperatures up to 100 °C. However, resistance to aromatic and halogenated hydrocarbons, ketones, ethers and esters is less, with temperature playing an important part.

Coupled with its chemical resistance is an inherently low flammability and a limiting oxygen index value of 60%. When in a fire, however, it gives off hydrogen chloride, which is both toxic and corrosive.

Apart from some discoloration, PVDC fibres have excellent sunlight and weatherability resistance.

Main end-uses are those which demand a high level of chemical, and sometimes soil resistance and so car-seat covers, outside furniture, public vehicle upholstery and wet filtration are typical.

8.3 Fluorinated fibres: PTFE, PVF, PVDF and FEP (ARH)

While fluoropolymeric fibres tend to be very expensive, their extreme chemical inertness has ensured that a number of variants find use within filtration applications, where extreme chemical, and in some cases thermal

resistance are required. The most notable generic example is poly(tetrafluoroethylene) or PTFE, although other examples exist such as poly(vinyl fluoride), PVF, poly(vinylidene fluoride), PVDF and various fluorinated ethylene polymers or FEP types. Table 8.2 summarises the properties of a selection of these fibres which are often available as both continuous filament and staple forms.

While each fibre type in Table 8.2 is marketed essentially for a defined level of chemical resistance, the effect of temperature on chemical reactivity is also important and is quite different for each, although generally, these fibres are renowned for their excellent resistance to a variety of chemical environments at temperatures well in excess of 100 °C. Resistance to the combined effects of temperature and chemical action is a combination of the inherent stability and unreactivity of the polymer chain structure, coupled with the efficiency of intermolecular forces and chain order. These latter determine the magnitude of softening (T_s) and melting (T_m) temperatures, which determine the ease of accessibility to chemical agencies as well as the upper limits of the ability of respective fibres to remain as coherent, load-bearing structures. Not surprisingly, therefore, there is often a link between inherent unreactivity by virtue of a high degree of fluorine presence and hence polar C–F bond density in a polymer, the degree of chain order and the ability to withstand the combined agencies of temperature and chemical attack.

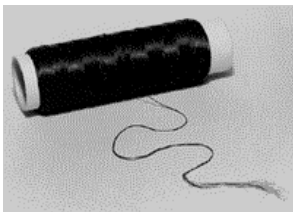


It is evident from Table 8.2 that PTFE fibres have the highest melting points. This, coupled with their insolubility, requires that conversion to fibres is via non-standard methods. The original DuPont *Teflon* filaments were, and still are, produced by the extrusion of fibrillar polymeric suspensions in a viscose (cellulose) dope followed by high temperature sintering to generate a coherent fibre structure.⁴ This gives brown fibres because of the charred cellulose remnants present, so may be followed by a bleaching process if desired. This process, developed in the 1950s, generates fibres that are available in staple, continuous filament and flocked fibre forms, as Fig. 8.1 shows.

A recent review by Schick⁵ contrasts this process with the so-called paste extrusion technology, used by companies such as W L Gore, and the split-peel process of Lenzing. In the paste-extrusion process, PTFE powder is mixed with a lubricant and preformed into a cylinder, which, after placing in an extruder, may be transformed into film or rod forms. The calendered film is slit, sintered and stretched to give high-tenacity fibres. This technology enables additives to be incorporated, such as graphite to improve internal lubrication properties in applications such as packings. The low density and open structure are ideal for medical applications including dental floss, as well as yielding lower thermal expansion coefficients ideal for high-temperature gland packings. The third method, split peel formation,

Table 8.2 Selected fluorine-containing, chemically resistant polymers^{2,3}

Genus	Example	Manufacturer	Tenacity, N/tex	Breaking strain, %	T_m , °C	T_s , °C	Max. temp. usage, °C	LOI, % O ₂
PTFE	<i>Teflon</i>	Du Pont	0.14	20	347	177	290	98
	PTFE	Lenzing	0.08–0.13	25	327	200	280	98
	PTFE	Albany	0.13	50	375	93	260	98
PVF			0.19–0.39	15–30	170	100	150	—
PVDF	<i>Kynar</i>	Albany	0.43	25	156	100	149	44
	<i>Solef</i>	Solvay	—	40	178	150	160	—
	<i>Trofil</i>	Dynamit	—	10–50	165	—	120	—
FEP	<i>Halar-ECTFE</i>	Albany	0.3	25	241	149	180	48
	<i>Teflon-FEP</i>	Du Pont	0.05	50–60	290	—	—	—
	<i>Tefzel-ETFE</i>	Albany	0.3	25	271	177	195	—

Notes: T_m is the melting temperature and T_s is the shrinkage temperature; LOI is the limiting oxygen index.

Form	Image	Characteristics and uses
Continuous filament yarn		<ul style="list-style-type: none"> • Low coefficient of friction • High thermal and chemical resistance • Woven fabrics / tubes • Knitted fabrics / tubes • Combination with other yarns
Staple		<ul style="list-style-type: none"> • High thermal and chemical resistance • Low coefficient of friction • Used for needle-felting • Hot gas filtration • Low friction / high temperature resistant parts in office equipment • Performance enhancement in blends with other fibres
Floc		<ul style="list-style-type: none"> • Low coefficient of friction • Blends / compounds with other polymers for moulding • High chemical resistance for chlor-alkali electrolysis

8.1 Continuous filament, staple and floc forms of *Teflon*® PTFE. (*Teflon*® is a registered DuPont trademark; figure reproduced with permission of DuPont.)

involves the precision turning of a continuous outer film layer from a cylindrical PTFE billet, followed by slitting and sometimes coating with PTFE and/or graphite dispersions. This yields extremely regular filaments with good pressure and temperature resistance, although with poorer ability to withhold surface-dispersed additives.

All PTFE fibres and yarns show excellent thermal properties in terms of shrinkage, and maximum service exposure temperatures result from their wholly fluorinated ($-\text{CF}_2\text{CF}_2-$) and extremely ordered polymer chains, which ensure maximum efficiency of the polar intermolecular chain forces of attraction present. This, coupled with the chemical inertness of the C—F chemical bond, enables these fibres to have some of the highest chemical resistances of all fibres, especially at high temperatures. They consequently find use in filtration, braiding, gaskets, packing and similar end-uses that demand this combination of resistances for long periods. They find particular use in chemical engineering applications where direct contact with and

resistance to corrosive chemicals at high temperatures are essential. For instance, braiding packings for pump shafts exposed to fuming (103%) nitric acid will last up to seven months and when used in pumps handling >50% caustic soda at 165°C, will last several days.⁴ Essentially, PTFE fabrics and yarns are attacked to any extent at ambient and moderate temperatures only by other fluorine-containing species, such as the element itself and chlorine trifluoride. Their high LOI value (Table 8.2) of 98% again demonstrates the almost complete flame resistance, and hence resistance to oxidation, of PTFE fibres and fabrics. One major drawback with all PTFE fibres is their high creep at elevated temperatures and, to overcome this, they may be combined with low creep fibres such as para-aramids and arimids, although these may reduce acid and/or alkali resistance. In addition, in composite yarn formation with a range of other fibres, where the PTFE provides the chemical resistance, a harder core enables varying yarn densities and hardnesses to be generated thereby modifying compressibility in packing applications.⁵

PVDF, PVF and FEP fibres have lower melting points and so lend themselves to melt extrusion with all the advantages of being able to produce monofilaments in addition to the more conventional continuous filament and staple forms. They also have lower LOI values and hence increased flammability, which reflects their reduced resistance to oxidation compared with PTFE. Unfortunately, very little is published about these fibres outside of the technical data sheets provided by manufacturers. However, PVF and PVDF in particular, because of their excellent tensile properties, are used where a combination of good tensile properties and chemical resistance is required. Both find particular use as monofilaments in filter media that combine these characteristics with excellent abrasion and fatigue resistances.⁶

FEP fibres have structures and properties which may vary from type to type because they include copolymers of tetrafluoroethylene ($-\text{CF}_2\text{CF}_2-$) and hexafluoropropylene ($-\text{CF}(\text{CF}_3)\text{CF}_2-$) [PTFE-FEP]; ethylene and chlorotrifluoroethylene ($-\text{CFClCF}_2-$) [ECTFE];⁷ and ethylene and trifluoroethylene ($-\text{CHF}\text{CF}_2-$) [ETFE]. These copolymers have reduced crystallinity and hence easier processibility compared to their respective homopolymers, while retaining the chemical inertness of the fluorinated groups present. This is especially the case for *Teflon-FEP* in Table 8.2, where its melting point of 290°C is less than that of homopolymeric PTFE or *Teflon*.

ECTFE and ETFE fibres (also sold in engineering polymer resin forms) have superior mechanical properties, similar to those of other synthetic fibres such as the polyamides. Because of their greater thermoplasticity than PTFE, however, they are unable to retain significant tensile strength much above 180°C, which is similar to these same conventional synthetic fibres.

Table 8.3 Resistance of *Tefzel* ETFE fibres to selected chemicals after 7 days' exposure⁸

Chemical	Boiling pt., °C	Test temp., °C	Retained properties, %		
			Strength	Elongation	Mass gain
<i>Acids:</i>					
Acetic acid	118	118	82	80	3.4
Trichloroacetic acid	196	100	90	70	0
Hydrochloric acid (conc)	106	23	100	90	0
Hydrofluoric acid (conc)	—	23	97	95	0.1
Sulphuric acid (conc)	—	100	100	100	—
Nitric acid (70% conc)	120	120	0	0	—
Chromic acid	125	125	66	25	—
<i>Bases:</i>					
Aniline	185	180	95	90	—
<i>N</i> -butylamine	78	78	71	73	4.4
Pyridine	116	116	100	100	1.5
Ammonium hydroxide	—	66	97	97	0
Sodium hydroxide (50%)	—	120	94	80	0.2
<i>Halogens:</i>					
Bromine	59	23	90	90	1.2
Chlorine	—	120	85	84	7
<i>Solvents:</i>					
Carbon tetrachloride	78	78	90	80	4.5
Chloroform	62	61	85	100	4.0
Dichloromethane	40	40	85	85	0
Dimethylformamide	154	90	100	100	1.5
Dimethyl sulphoxide	189	90	95	95	1.5
Mineral oil	—	180	90	60	—
Benzene	80	80	100	100	0

Their chemical resistance is similar to that of *Teflon-FEP* and superior to PVDC, PVF and PVDF. These latter will degrade in 98% sulphuric acid, 70% nitric acid and 50% caustic soda solutions at elevated temperature, whereas ECTFE is resistant. The resistance of *Tefzel* ETFE to a number of organic and inorganic chemicals at temperatures upto 180°C in some cases has been well documented.⁸ The selected examples of chemical resistance listed in Table 8.3 show behaviour considerably inferior to that expected of PTFE fibres but still superior to other chemically resistant fibres, including others within the fluorinated group.

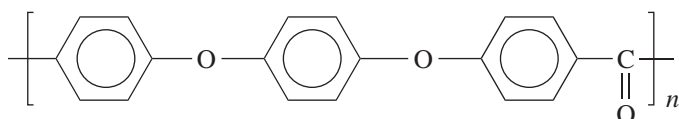
Thus, both ETFE and ECTFE fibre types are ideal for use in filter screens and cloths, column packings, braided sleeveings, gaskets and conveyor belt-ings, for example, where extreme chemical resistance at temperatures as high as 150°C is required.

8.4 Poly(etheretherketones): PEEK (BM)

8.4.1 Polyetherketones

PEEK (polyetheretherketone) is the foremost member of a family of semi-crystalline aromatic thermoplastic polymers, the polyetherketones (PEKs). It is capable of being formed into an extensive range of monofilaments and fibres using high-temperature melt-spinning techniques. The glass-rubber transition temperature (T_g) and the melting point (T_m) are given for the principal members of the series in Table 8.4.

Chemically, PEEK has a polymer repeat unit of one ketone and two ether groups. This provides a linear, fully aromatic, highly stable structure containing only carbon, hydrogen and oxygen atoms:



Although some experimental work was carried out in the 1960s, PEEK polymer was first manufactured⁹ and commercialised¹⁰ by ICI Advanced Materials in the late 1970s and early 1980s under the brand name *Victrex PEEK*. The first emphasis was on injection moulding application, but work by ICI¹¹ and Leeds University¹² showed the polymer's potential for producing high-specification fibres.

Although other manufacturers introduced pilot plant developments of competitive polyetherketones through the 1980s, notably BASF with PEKEKK,¹³ DuPont with PEKK¹⁴ and Hoechst with PEEKK,¹⁵ PEEK proved to be the only polymer to survive and prosper in an expanding range of applications through the 1990s. The technical difficulty of polymerising and the high cost of purifying polyetherketones to a quality suitable for processing into finer components has limited competition. PEEK is now

Table 8.4 Thermal transitions of the various PEK polymers, where E signifies an ether and K a ketone segment

Polymer	T_g , °C	T_m , °C
PEEK	143	334
PEEKK	150	365
PEK	152	365
PEKEKK	170	381
PEKK	165	391

well established with a long development lead-time advantage over other polyetherketones. It is principally produced by Victrex Ltd – an independent company formed from the break-up of ICI Advanced Materials in 1993.

8.4.2 PEEK fibre-performance factors

As an introduction to the general bulk properties of PEEK as a thermoplastic material, Table 8.5 will be a useful reference.

The general factors which characterised the acceptance and underpinned the successful growth of PEEK as a new thermoplastic material can be set out briefly as:

- *Temperature performance*: a continuous operating temperature for many applications of up to 260°C, with short excursions to 300°C being possible, and a non-brittle low temperature performance down to –60°C.
- *Chemical inertness*: it is unaffected by high-temperature steam and most fluids and chemical reagents. However, it is dissolved by concentrated sulphuric acid (>50%) and degraded by strong oxidising agents such as nitric acid.
- *Abrasion resistance*: it has a tough, low friction, low wear, cut-resistant surface and is particularly good at resisting abrasion at elevated temperatures and relatively high surface speeds.
- *Dimensional stability*: it exhibits low creep and low shrinkage, especially below its T_g (143°C). It has excellent dynamic recovery and flex fatigue performance.
- *Polymer purity*: fibres are exceptionally pure, without the need for stabilising additives, and they have EEC and FDA approval for medical

Table 8.5 Properties of PEEK

Property	Value/parameter
Colour	Beige (thick section) Golden (thin section)
Specific gravity	1.30
Melting point, T_m , °C	334
Glass transition, T_g , °C	143
Crystallinity, %	30–35
Moisture regain, 65% rh 20°C, %	0.1
Dielectric strength, kV/cm	190
Resistivity, ohm-cm	5×10^{16}
Heat capacity, kJ/kg/°C	1.34
Thermal conductivity, W/m/°C	0.25

and food-contact use.^{16,17} A good low surface energy self-cleaning characteristic minimises contamination in use.

- *Flammability*: fibres are self-extinguishing with an LOI of 35% while emitting one of the lowest levels of smoke and toxic gases.
- *Processability*: the room temperature physical properties of PEEK fibres are similar to those of both polyester and nylon, so textile processes such as weaving and braiding can be conveniently performed.
- *Sustainability*: recovery and recycling of PEEK as a material can be carried out under certain conditions with little loss of key physical properties.¹⁸

8.4.3 Fibre products

Starting in the early 1980s, a number of companies set out to produce PEEK fibres of various different types for commercial sale. Initially, circular cross-section monofilaments in the diameter range 0.4 to 1.0mm were extruded at high temperature, cooled, drawn and relaxed to give low-shrinkage products with physical properties in the range 0.3 to 0.4N/tex tenacity and 30 to 40% extension-to-break, with hot-air shrinkages below 2% at 180°C.

By the mid-1980s the polymer quality had improved sufficiently to allow multifilament products in the range 5 to 15 dtex per filament to be viably produced. These, depending on the process employed, could be spun with tenacities up to 0.65N/tex at extensions below 25% and shrinkages below 1% at 180°C. Modulus values at about 4 to 5N/tex are typically intermediate between similar polyester and polyamide products.

Finer and heavier monofilaments were also developed, with some specialist products in the 0.2 to 0.3mm range having tenacities up to 0.60 N/tex at extensions below 20%, and some of the larger diameter products being made with higher shrinkages at about 10% so that they could be conveniently heat-set into spiral structures in subsequent processing.

The first crimped filament staple products with a fineness range from 3 to 25dtex and staple lengths of 40 to 80mm were also developed at this time. Finer individual monofilaments and progressively finer multifilament yarns down to 100 dtex and filament finenesses of 3dtex (20µm) have been refined through the 1990s, yielding further improvements in tenacity. Additionally, a wider range of cross-sectional types, including rectangular and hollow filaments and an increasing range of colour pigmented monofilaments, have become available for the main monofil diameters (0.20 to 1.50mm).

The manufacturer with the most comprehensive range of PEEK fibre products through this period has been ZYEX Limited.¹⁹ Other producers, such as Teijin, Kosa, Shakespeare, Luxilon and Albany International, have

at different times been active in different segments of the PEEK fibre business but none other than ZYEX has yet attempted to cover more than a small part of the potential product range.

8.4.4 Fibre properties

The value of PEEK fibre products does not normally lie in their measured starting properties or with their short-term performance. As has been indicated, PEEK monofil, yarns and fibres are in fact similar to polyester or nylon products in these respects. It is rather PEEK's ability to retain useful properties at an extreme condition or throughout an extended working life that differentiates it from mainstream industrial fibres.

The thermal, chemical and abrasive endurance of PEEK sets it apart from comparable industrial fibres, as is indicated in the following tables. This is especially true in real industrial processing situations where a combination of these factors, rather than just one, may be causing standard materials to fail prematurely.

Table 8.6 shows the resistance to hot air exposure over a 28-day period, and Table 8.7 the ability of PEEK fibres to withstand steam for 7 days. Clearly, PEEK can perform well at temperatures up to 300°C in both dry air and steam, thus indicating its oxidation and hydrolysis resistance.

Table 8.6 PEEK and other fibres exposed to elevated temperatures for 28 days in air

Fibre Temperature	% Strength retained			
	150 °C	200 °C	250 °C	300 °C
PEEK	100	100	95	90
m-aramid	100	95	75	0
PPS	100	90	0	melted
PET	90	30	0	melted

Table 8.7 PEEK and other fibres exposed for 7 days in pressurised steam

Fibre Temperature	% Strength retained				
	100 °C	150 °C	200 °C	250 °C	300 °C
PEEK	100	100	100	95	80
PPS	100	100	90	0	disintegrated
m-aramid	100	90	0	0	0
PET	90	0	0	0	disintegrated

Table 8.8 Cycles to failure for PEEK and other fibres as threads – thread on thread abrasion at 120 °C loaded at 0.05 cN/tex

Fibre	Cycles to failure
PEEK	900
PA	600
PET	500
m-aramid	250
PPS	50

Its resistance to abrasion is also superior to many competing fibres, as Table 8.8 shows.

Table 8.9 ranks the chemical resistance of PEEK fibres at three different temperatures. Generally, the most common or the most potentially vulnerable situations have been covered. It is probable that a ‘no attack’ category is very likely for other chemical situations, but, if in doubt, the latest technical data should be consulted.²⁰

8.4.5 Fibre applications

Applications relate to industrial and technical end-uses where a combination of good physical properties and inertness to the environment are essential features:

- *Process conveyor belts:* The mainstream application for PEEK fibres is in industrial conveyor belts that carry product through aggressive processing stages effectively on a continuous basis, in particular, in the manufacture of paper or nonwoven fabric products where pressing, bonding or drying stages can involve temperatures up to 300 °C at line speeds up to 300 m/min. In some situations, significant flex and surface abrasion is also experienced by the conveyor belt as it passes around pulleys and drive rolls, or through nip restrictions. Here again, PEEK belts may well deliver cost-effective increases in life expectancy or process flexibility when compared with other high-tech fibre or steel belts.

Initially, PEEK was used in the most vulnerable part of such conveyor belts – at the joint or on the edges. Joints are often made using PEEK monofil, heat-set as interlocking spirals and joined by a larger diameter straightened PEEK ‘pintle pin’ monofil. Subsequently, PEEK has been used more as a substantial part of the belt, up to 100% of the construction, products normally being woven from monofil although some multifil yarns or needled staple felts are also used, especially in narrow

Table 8.9 The chemical resistance of PEEK fibres at various temperatures

Chemical	23 °C	100 °C	200 °C
Acetic acid, 10%	A	A	
Carbonic acid	A	A	
Citric acid	A	A	
Formic acid	B	B	
Hydrochloric acid, 10%	A	A	
Nitric acid	A	A	
Nitric acid, 30%	B		
Phosphoric acid, 50%	A	A	A
Sulphuric acid, <40%	B	B	B
Ethanol	A	A	A
Ethylene glycol	A	A	B
Ethylene glycol, 50%	A	A	A
Acetone	A	A	
Formaldehyde	A	A	
Methylethyl ketone (MEK)	A	B	C
Ammonia, aqueous	A	A	A
Sodium hydroxide, 50%	A	A	A
Aluminium chloride	A	A	
Carbon monoxide (gas)	A	A	A
Ferric chloride	B	B	
Hydrogen sulphide (gas)	A	A	A
Iodine	B		
Ozone	A	B	
Phosphorous pentoxide	A	A	
Potassium bromide	A	A	
Sulphur dioxide	A	A	A
Carbon tetrachloride	A	A	
Chloroform	A	A	
Trichlorethylene	A	A	
Aromatic solvents	A	A	
Benzene	A	A	
Brake fluid (mineral)	A	A	A
Dowtherm ht			B
Methane (gas)	A	A	A
Motor oil	A	A	A
Naphthalene	A	A	
Oils (petroleum)	A	A	
Dimethyl formamide	A	B	
Pyridine	A	A	
Dimethylsulphoxide (DMSO)	B	B	
Diphenylsulphone (DPS)	B	C	C

Note: A = no attack, B = slight attack, C = severe attack. Where no concentration is given for the chemical it may be assumed that 100% or a saturated solution was used.

woven tape belts. Complete belts of interlocking coils are also increasingly being specified where maximising open area is important. Other industries where PEEK conveyor belts are used include textile printing and heat setting, food drying and filtering and laundry ironing.

- *Press filters*: Fine woven screens of PEEK are used in frame filters, or slow-moving press filter applications for the production of board products or the dewatering of chemical powders. Dimensional stability and the ability to survive many more pressure cycles than equivalent metal screens are important here.
- *Protective braids*: PEEK braids, made mainly from coloured/pigmented monofilaments are increasingly important in aerospace, automotive and industrial applications. In particular, the additional chafe resistance and temperature stability delivered are ideal for electrical wiring looms associated with engine components in aircraft and motor vehicles. In addition, in any enclosed situations where toxic fumes from burning wiring could pose a threat to life, PEEK as a cable covering is ideal.

Industrial applications include the wiring for robotics in nuclear installations where high levels of gamma radiation would degrade conventional plastics, and hydraulic-pressure hosing reinforcement, where the monofilament diameters used are heavier.

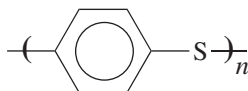
- *Reinforced rubber gaskets*: A multifilament PEEK scrim fabric is used to reinforce synthetic rubber gaskets and bellows. The fibre's unique combination of good flex fatigue performance and resistance to the chemical breakdown products of the rubber at high temperature greatly extends component lifetime in specialised applications.
- *Industrial bristles*: Brush bristles used for hot-cleaning extruders and injection moulds are sometimes preferred as PEEK monofilaments, rather than soft metal wires.
- *Protective clothing*: Multifilament PEEK sewing threads have found niche markets in industrial protective clothing, associated with their chemical inertness. Also, hook and loop fasteners utilising both monofilament and multifilament PEEK products are used in quick-release garments in high-temperature environments.
- *Sports strings*: The possibility of manufacturing fibres that exhibit deformation and rapid recovery from high stress rates has given rise to PEEK's use in up-market tennis, squash and racquet ball strings.²¹
- *Music strings*: The unique tonal quality and tension-holding that can be achieved from specified PEEK products have given rise to their adoption for guitar, violin and other stringed instruments.²²
- *Thermoplastic composites*: PEEK fibres can also be used as a source of the matrix in composites. Intimately mixed with carbon fibres, PEEK fibres provide an ideal feedstock for the production of advanced thermoplastic composites. In the pressurised high-temperature moulding

stage, PEEK remelts and flows to encase and protect the carbon fibres, becoming the matrix phase of the composite. In addition to aerospace components, medical tools and bone replacements are being made to take advantage of PEEK's excellent biocompatibility and *in vitro* performance.

8.5 Poly(phenylene sulphide), PPS (ARH)

The presence of aromatic groups within the polymeric chains bonded together by relatively inert groups is not only a feature of PEEK, discussed above, but also of poly(phenylene oxide), PPO. PPO and its derivatives are mainly used as engineering plastics although some academic interest has been shown in wet-spun filaments.²³ Because of lack of commercial interest to date, they are not considered to be within the scope of this chapter. The related polymer, poly(phenylene sulphide), PPS, is more important as a fibre.

Developed in 1973, the first commercial fibres from PPS appeared in the early 1980s with the introduction of *Ryton* by Phillips Fibers Corp.,²⁴ and subsequently by other companies such as Bayer,²⁵ Teijin,²⁶ Toyobo as *Procon*, Toray as *Torcon*^{27,28} and Celanese as *Fortron*.²⁹ Scruggs and Reed³⁰ reviewed this then new fibre in 1985 and described its chemistry of polymerisation, conversion into fibres, and their characteristic structure and properties. Its chemical structure is:



which, because of its aromatic backbone will anticipate challenges during the polymerisation and processing stages. Phillips Fibers pioneered the means of producing polymer with molecular weight high enough to enable fibres having tenacities as high as 0.35 N/tex to be melt spun above its melting transition of 278°C. During drawing, the fibre melting temperature shifts to 285°C, reflecting the effects of increasing orientation and crystallisation accompanying the process. This melting point, which is similar to those of the more conventional synthetic fibres, precludes the fibre from use in very high temperature-resistant applications. Its second order transition of about 93°C also places a higher limit on useful service temperatures of this order when used under stressed conditions. Table 8.10 summarises the main physical properties of PPS fibres.

It is evident that PPS fibres have an acceptable balance of properties for many end-uses in terms of tensile properties under dry and wet conditions. The applications at high temperatures depend on the levels of applied stress during service; obviously for high stress end-uses, the second order

Table 8.10 Physical properties of PPS fibres^{28,30}

Property	Staple	Monofilament
Tenacity, N/Tex	0.27–0.47	0.27–0.37
Tenacity retention, %:		
at 100 °C	70	
at 150 °C	58	
at 200 °C	52	
Tenacity (knot), N/tex		0.18–0.23
Breaking strain, %	25–35	12–16
Initial modulus, N/tex	2.7–3.7	4.1–5.0
Elastic recovery, %:		
at 2% strain,	100	
at 5% strain	96	
at 10% strain	86	
Boiling water shrinkage, %	0–5	
Moisture regain, %	0.6	
Specific gravity	1.37	1.37
Melting point, °C	285	285
Colour	Golden	Golden
Limiting oxygen index, %	34–35	
Autoignition temperature, °C	590	
Maximum service temperatures, °C	93 (high stress) 182–190 (low stress) 232 (surges)	93 (high stress) 182–190 (low stress)

transition temperature will define the upper useful limit, whereas in lower stressed applications, such as gas filtration bags, long-term exposures above 180 °C are possible. Exposure to sudden elevated temperature changes shows that these fibres can withstand up to 230 °C for very short periods. Experimental exposures to hot air show that PPS fibres retain 60% of their original strength after 1000 hours, at 260 °C and 90%, 70% and 60% retention after 2000, 5000 and 8000 hours, respectively at 204 °C.

The relatively high LOI of 34–35% (although LOI values as high as 39–41% have been claimed³¹) indicates an acceptable level of inherent flame resistance. However, the general ease of oxidation of the sulphur atom present in the polymer chain is indicated by this value being less than observed for PPO fibres (LOI = 68%) and the susceptibility of PPS fibres to oxidising agents.

During light exposure it is discoloured but compares favourably with poly (meta-aramid) fibres in terms of retention of tensile properties; in general, however, light resistance may be said to be poor.³¹

Table 8.11 Chemical and solvent resistance of PPS fibres³⁰

Chemical	Temp., °C	Strength retained after one week's exposure, %
<i>Acids:</i>		
48% Sulphuric acid	93	100
10% Hydrochloric acid	93	100
conc. Hydrochloric acid	60	100
conc. Phosphoric acid	93	95
Acetic acid	93	100
Formic acid	93	100
<i>Alkalis:</i>		
10% Sodium hydroxide	93	100
30% Sodium hydroxide	93	100
<i>Oxidising agents:</i>		
10% Nitric acid	93	75
conc. Nitric acid	93	0
50% Chromic acid	93	0–10
5% Sodium hypochlorite	93	20
conc. Sulphuric acid	93	10
Bromine	93	0
<i>Organic solvents:</i>		
Acetone	B.Pt	100
Carbon tetrachloride	B.Pt	100
Chloroform	B.Pt	100
Ethylene dichloride	B.Pt	100
Perchloroethylene	B.Pt	100
Toluene	93	75–90
Xylene	B.Pt	100

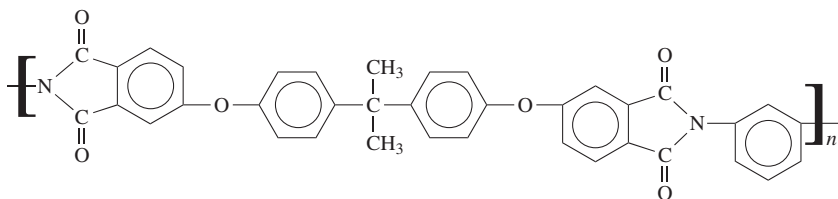
The excellent chemical resistance of these fibres is demonstrated in Table 8.11. Resistance to non-oxidising acids is excellent, as is that to hot alkalis, thereby showing that in spite of PPS being a condensed polymer, it has considerable resistance to hydrolysis. However, exposure to oxidising agents shows that its durability is reduced as a consequence of the vulnerability of the sulphur chain group. Organic solvent resistance is variable, although still high. When compared with conventional fibres such as polyester, acrylic and polypropylene, its resistance to both hot acid (50% sulphuric acid) and alkali is demonstrated even after only short exposures of 24 hours or so. After exposure periods of several days or so, its superiority to the aromatic heat-resistant fibres polyaramid and even poly(benzimidazole) becomes apparent.³⁰

Applications for poly(phenylene sulphide) fibres lie primarily in the wet and dry filtration areas, where they have proved to be exceptionally durable

for coal-fired boiler gas filtration at temperatures in the region of 150–200°C, in the presence of ash and acidic, high-sulphur flue gases. During pulsed jet cleaning, needle-punched fabrics prove to be more efficient in not only their filtering capacity but also their resistance to wear during cleaning. In some cases, lifetimes of up to 3 years have been reported for bags under these conditions,³² where they have proved to be superior to homopolymeric acrylic fibre-containing filter bags. Other uses include felts used in the drying operation of paper production, as well as for battery separators and filter cloths (as felts or woven constructions) for filtering hot, corrosive chemicals such as organic chemicals, acids and bases. Sewing threads for use in these products are also valid applications.

8.6 Poly(ether imide), PEI^{33,34} (ARH)

Like PEEK, poly(ether imide) is really an engineering plastic which has found application as fibres in some applications where chemical and temperature resistance are required. Although its temperature resistance is slightly inferior to that of PEEK, PEI is a cheaper material. Currently, both Teijin and Acordis (formerly Akzo) have reported commercial fibres based on PEI. The chemical structures of both commercial forms are believed to be similar and as outlined below:^{33,34}



With its less than ideally regular polymer chain structure, PEI is essentially an amorphous polymer which may be melt-spun to yield fibres having only moderate tenacities (0.25 N/Tex) and breaking elongations of about 40%. Fibres can resist temperatures up to 190°C for long periods and also possess high LOI value of 45%, which is higher than the values for PEEK and PPS. A comparison of the properties of PPS, PEEK and PEI is presented in Table 8.12.

As for all these fibres, mono- and multifilament forms are preferred for PEI, although staple forms (e.g. 6 mm, 2.8 dtex; 60 mm, 8.3 tex) are available. Their high LOI value again represents a stability at high temperatures and resistance to oxidation and so they are used in hot gas filtration applications, especially where aggressive chemical environments are present. However, chemical resistance is specific rather than general and so fibres should be tested before use.

Table 8.12 Comparison of properties of PEI with PPS and PEEK fibres^{33,34}

Fibre	T_m , °C	T_{max} , °C	LOI, %	Tensile strength, N/tex
PEI	215–225 (= T_g)	170–190	44–45	0.19–27
PPS	285	190	34	0.45
PEEK	334	260–300	35	0.60–0.65

Note: T_{max} = maximum continuous-service life temperature.

Table 8.13 Chemical resistance of PEI fibres³⁴

Chemical	Concentration	Strength retention after 1500 h at 20 °C, %
HCl	10%	101
HNO ₃	10%	99
H ₂ SO ₄	10%	95
HF	10%	106
CH ₃ COOH	10%	104
NaCl	Saturated	101
Mineral oil		104
Borax	pH 9	110
(NH ₄) ₃ PO ₄	pH 10	104
NH ₃	pH 11	96
Ca(OH) ₂	pH 12.5	107
NaOH	pH 13.5	84

Table 8.13 lists some chemical resistance data for these fibres, from which it is seen that these fibres have very good resistance to dilute acids and alkalis although resistance to concentrated acids is poor. Resistance to organic species is variable and may be poor for aromatic solvents and vapours.

8.7 Others (ARH)

Other fibres in this group include the polyaramids (both meta- [e.g. *Nomex*, DuPont] and para-derivatives [*Kevlar*, DuPont; *Twaron*, Acordis]), polyarimid [*P84*, Inspec Fibers], poly(aramid-imide) [*Kermel*, Rhodia], poly(benzimidazole) [*PBI*, Celanese] and the oxidised acrylics [*Panox*, RK Textiles/SGL UK]. Most of these are primarily marketed and used as high-temperature fibres and will be discussed in detail in the next chapter. However, primarily because of their oxidation resistance, they find application in

high-temperature gas filtration applications. Their resistance to chemicals such as acids and bases is often poor, however, because the majority are condensed polymers and so are susceptible to hydrolysis.

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A RICHARD HORROCKS (9.1, 9.3, 9.6, 9.7),
HANS EICHHORN (9.2),
HASSO SCHWAENKE (9.2),
NEIL SAVILLE (9.4), AND
CHARLES THOMAS (9.5)

9.1 Introduction (ARH)

Thermally resistant organic polymeric fibres include those that resist thermal degradation and some degree of chemical attack, notably oxidation, for acceptable periods during their service lives. As a consequence of their generally inert structures, like the chemically resistant fibres in the previous chapter, they may also be flame resistant and so address markets where that property is also desirable. Their thermal resistance derives from their possessing aromatic and/or ladder-like chain structures that offer a combination of both physical and chemical resistance and the former is quantified in terms of high second order temperatures, preferably above 200°C or so, and very high (>350°C) or absence of melting transitions.

Obviously, this group overlaps with the HM-HT polymer fibres described in Chapters 2 to 4, in which strength and stiffness are primary properties. In this chapter, reference will be made only to applications and characteristics of these fibres that enable them to be used in environments where thermal resistance is of prime importance. Some aspects of the metaaramids, which are not HM-HT fibres, are included in Chapter 2. The only HM-HT fibres that do not have good thermal resistance are the polyethylene fibres described in Chapter 3 and Section 4.5. The inorganic fibres covered in Chapters 5 to 7 also have, in varying degrees, high thermal resistance. The fibres described in this chapter are those in which high strength is not a primary requirement, and includes some where lower stiffness is needed to give good textile properties in clothing and upholstery.

Fibres in this group tend, however, to see service in applications which are often differentiated only by the severity of thermal environments and their respective resistance to it and the degree of protection and/durability demanded by the end-user. For instance, and again like the chemically resistant fibres discussed previously in Chapter 8, hot gas and liquid filtration fabrics, braiding materials, gaskets, protective textiles, conveyer beltings and

high-performance sewing threads are typical end-uses. The major difference here is that temperature upper limits extend often to service temperatures well above 400 °C, and higher if shorter times of heat exposure are evident. Protective clothing, for example, may be required to give protection to flame temperatures (>1000 °C) for a few minutes while hot-gas filtration fabrics may require continual service exposure temperatures of 120–150 °C or so and be expected to sustain these for days, weeks and even months.

9.2 Thermosets (HE and HS)

The thermoset polymeric fibres are sensitive to heat in that they continue to polymerise and even crosslink when heated. However, depending upon their respective reactivities and opportunities for crosslinking via reactive side groups, this may give rise to rapidly crosslinking polymers like the melamine–formaldehydes or relatively unreactive polymers like heat-cured novolac phenol–formaldehydes. Both these polymers, although not fibre-forming in the manner that linear polymers tend to be, can give rise to fibres that have acceptable textile properties, each of which reacts to heat in different ways. Both types on heating will continue to crosslink and eventually char, hence giving rise to high levels of fire resistance. Under controlled heating, novolac-derived fibres, or novoloids, can give rise to carbon fibres in their own right.

9.2.1 Melamine–formaldehyde fibres: *Basofil* (BASF) (HE)

Condensation products made from melamine are used in a wide range of applications in the textile, paper, leather and adhesive industries. *Basofil*®, a synthetic melamine fibre produced by BASF is the result of a condensation reaction between melamine, a melamine derivative and formaldehyde, which form a three-dimensional network typical of thermosetting resins. From its chemical structure, the fibre has inherited the characteristic properties of melamine/formaldehyde condensation resins such as high temperature and flame resistance, low flammability and chemical resistance. *Basofil* is the only commercial member of this recently generated class of melamine fibres.

Originally developed at BASF's central research laboratories in Ludwigshafen/Germany, the fibre is now produced in a 1500-tonnes capacity plant at Enka, North Carolina, USA.

9.2.1.1 Chemistry of condensation reaction

In general, one mole of melamine reacts with six moles of formaldehyde at pH 8.0–9.5 at elevated temperatures under general acid–base catalysis to

form methylol compounds. In a slightly exothermic reaction, the reaction mixture turns into a clear solution whose viscosity strongly increases with temperature and reaction time. The initially formed methylol compounds then react with each other by oligocondensation and elimination of water and formaldehyde to form methylene ethers and methylene bridges. The ratio of methylene to dimethylene bridges is pH and temperature dependent.¹ During further processing, the reaction has to be interrupted at a certain viscosity when a curing step follows by pH reduction at elevated temperatures.

9.2.1.2 *Resins and fibre manufacturing*

Melamine–formaldehyde condensation resins can be extruded to filaments at high viscosity;² the high viscosity stabilises filament formation and also stabilises the fragile primary fibre. Depending on external conditions, melamine–formaldehyde resins can be spun into fibres within a viscosity range of 300 to 3000 P.³

For textile applications, the resulting fibre would, however, be far too brittle. To increase the elongation to a level required for processing the fibre in usual textile machinery, specially modified melamine derivatives have to be added. These derivatives are substituted melamines which act as an internal plasticiser by reducing the degree of crosslinking and hence improving mechanical properties such as elongation-at-break and tensile strength.⁴

The manufacturing process can be divided into two sections, the condensation section and the subsequent spinning as outlined above to produce the finished fibre.

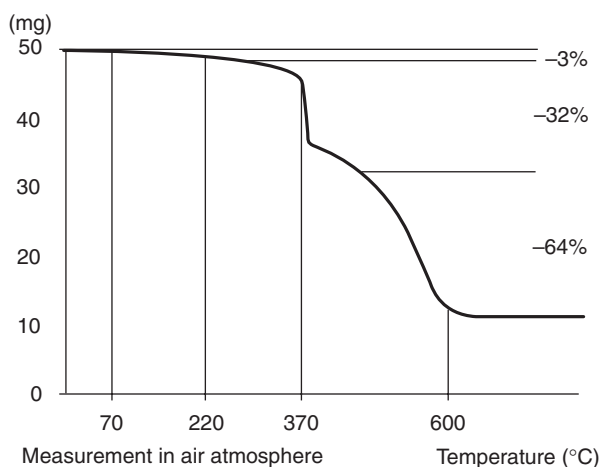
9.2.1.3 *Properties of fibres*

The property profile and the characteristics of *Basofil*[®] fibre are essentially related to its chemical building blocks and to its manufacturing process. The important physical properties are shown in Table 9.1. The most important properties of the *Basofil*[®] fibre are its high limiting oxygen index, LOI, low thermal conductivity and excellent heat dimensional stability. Thermogravimetric analysis (TGA) of *Basofil*[®] (see Fig. 9.1) shows that at 250 °C the residual mass of the fibre is reduced by only 3%. Under exposure to flames, the fibre does not melt and also does not produce burning drips.

In common with melamine condensation resins, the fibre shows good hydrolysis stability. Comparative tests on woven fabrics according to DIN 53857 after storage under a standard atmosphere and after immersion in water for 12 hours show no change in tensile elongation and only a minimal reduction in tensile strength. The chemical resistance of a woven *Basofil*[®] fabric to various solvents, acids and bases in terms of tensile strength loss

Table 9.1 Physical properties of *Basofil*® fibres

Strength, cN/dtex	2–4
Modulus, nominal, N/tex	6
Elongation-at-break, %	15–20
Density, g/cm ³	1.4
Moisture regain, 23 °C & 65% RH, %	5
Limiting oxygen index, LOI, %	32
Hot air shrinkage, 1 hr @ 200 °C, %	<1
Continuous use temperature, °C	190



9.1 Thermogravimetric analysis of *Basofil*®.

after exposing to the test medium for 28 days at room temperature is shown in Table 9.2. The results indicate that, although the fibre is only moderately resistant to acids, it displays an excellent chemical resistance, especially with regard to organic and aromatic solvents and to bases.

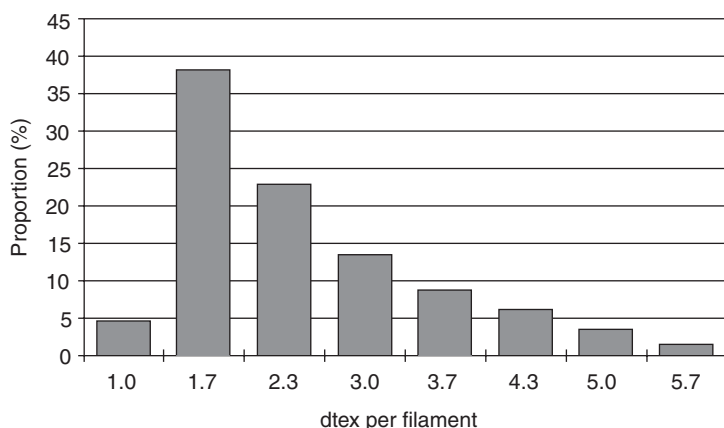
Within its recommended temperature use, the tensile strength of the fibre is hardly affected by exposing it to higher temperatures. Also, measurements of the tensile strength of *Basofil*® samples exposed to elevated temperatures indicate only minimal changes in tensile properties.

Because its manufacturing process is by spinning the condensation resin through a rotating disk, the fibre is produced as a staple fibre with some variation in staple length and also in diameter. Typical fibre diameter distribution and staple length distribution are shown in Figs. 9.2 and 9.3.

As shown in a scanning electron micrograph (SEM) (see Fig. 9.4), the cross-section of the fibre is variable, and to some extent elliptical, with a smooth fibre surface.

Table 9.2 Chemical resistance of *Basofil*® fibres after 28 days exposure at room temperature

Chemical	Strength loss (%)
Acetone	0
Butyl acetate	0
Gasoline	0
Methanol	0
Demineralized water	0
Sodium chloride solution, 5%	7
Sodium hydroxide solution, 20%	0
Hydrochloric acid, 20%	48
Sulphuric acid, 20%	48

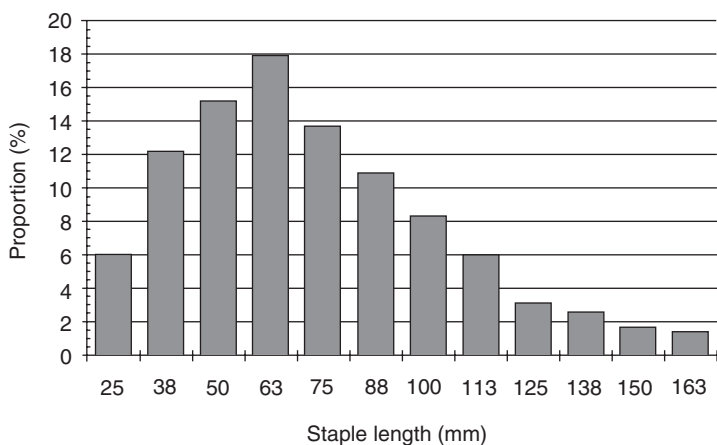


9.2 Diameter distribution of *Basofil*® fibres.

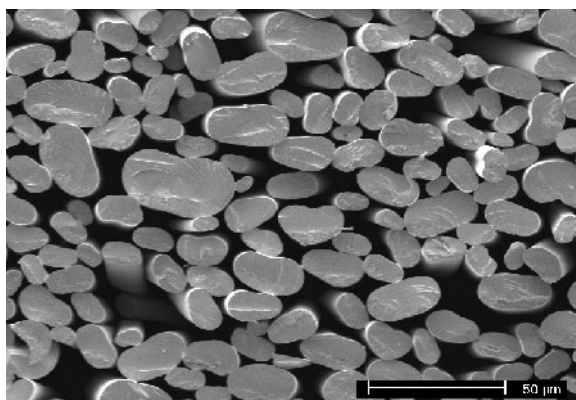
For fibres used in heat and flame protective applications, for instance in aircraft fire blocking, smoke toxicity in the event of a fire is an important characteristic. Analysis of smoke and gas samples taken according to ASTM E662-79/BSS 7239 after four minutes flaming of a *Basofil*® fabric are shown in Table 9.3. Results show the *Basofil*® fabric to be well under FAA requirements. The specific density of the smoke, according to the same test, is 25 (DS) after 4 minutes flaming. A DS value of less than 200 is required to pass FAA standard.

9.2.1.4 Processing

In common with other staple fibres, *Basofil*® can be processed into nonwovens and woven textiles. It can also be blended with other technical



9.3 Staple length distribution of *Basofil*® fibres.



9.4 Cross-sections of *Basofil*® fibres.

and natural fibres, depending on end-use applications. The property profile of the *Basofil*® fibre clearly indicates that the fibre can be used on its own wherever strength does not have to be the dominant characteristic. The breaking strength is equal to the level of natural fibres such as cotton. Likewise, *Basofil*® can be spun into yarns, woven into fabrics or processed into felts by common fibre and textile processing technology. If there are special requirements towards the tenacity of the yarn, fabric or nonwoven to be produced from *Basofil*, blending with other technical fibres is recommended. Other characteristics of the fibre, such as staple length distribution and diameter distribution are governed by the fibre production process and have therefore to be taken into account.

Table 9.3 Smoke toxicity of *Basofil*[®] fibres (ASTM E662-79/BSS 7239)

Toxic gas (4 min flaming)	Basofil fabric (ppm)	Boeing limit (ppm)	Airbus limit (ppm)
CO	100	3500	3500
NO _x	12.5	100	100
HCN	62.5	150	150
HCl	0	500	150
HF	0	150	100
SO ₂	0	100	100
Formaldehyde	0.35	—	—

In general, no processing problems should be encountered on producing needled felt and fleeces from *Basofil*[®]. It can also be spun in yarns, in particular in yarn counts up to Nm 60 (>17tex), using state-of-the-art high-speed carding equipment. If yarns with counts less than Nm 10 (>100tex) are to be produced, it is recommended that *Basofil* be blended with a higher tenacity fibre.

One important additional question relating to the end-use of *Basofil* concerns the dyeability of the fibre and its final products. *Basofil*[®] fibres can be dyed with best results only with selected small-molecular disperse dyes in a high-temperature process comparable to HT dyeing with disperse dyes on polyester.⁵ Colour yields range from 60–80%, depending on the species and the amount of dye used. Lightfastness following xenon arc irradiation (DIN 54002) show ratings in the range of 4–6.

9.2.1.5 End-uses

Typical end-use applications of *Basofil*[®] can be found in all areas where heat and flame resistance properties and chemical resistance are required. Some examples include:

- high-temperature filtration
- fire blocking and heat insulating felts
- heat and flame protective apparel.

In high-temperature filtration applications, *Basofil* is used in a nonwoven felt based on an intimate blend of approximately 50% *Basofil*[®] with meta-aramid fibres. As seen in variable environmental simulation analysis (VESA) and also in baghouse applications, filter media from *Basofil* enhances filtration performance by simultaneously lowering particulate

emission levels and reducing pressure drop compared to standard meta-aramid filtration media.⁶

Also in blends with other technical fibres, *Basofil*[®] enhances the fire blocking and heat insulating performance of needled felts and hydroentangled fleeces used for protective clothing and as fire blockers in transportation and furniture applications.⁷

In protective clothing, such as industrial workwear for the chemical, utility and automotive industries, and in fire fighting apparel, *Basofil*[®] is used in blends with meta- and para-aramids, FR (flame retardant) viscose or with cotton. The good heat insulation properties and low thermal conductivity of *Basofil*[®] allows construction of thinner fabrics with equal protection and good wear comfort due to the fibre's low stiffness and high moisture regain.

9.2.2 Novoloid fibres: *Kynol*[®] (HS)

9.2.2.1 Properties

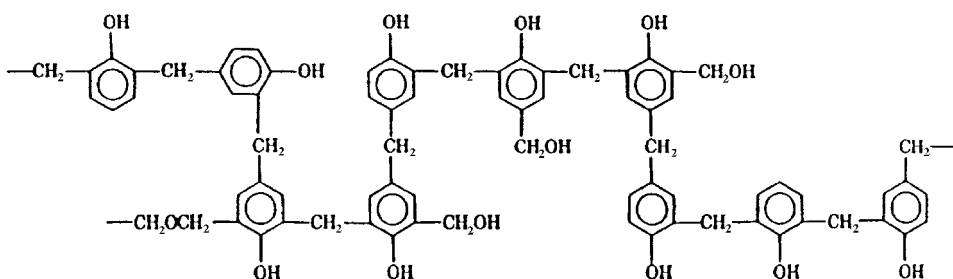
Kynol novoloid fibres are amorphous, crosslinked, phenol-aldehyde (novolac) fibres made by the Kynol Corporation of Japan. Chemically, the fibres contain approximately 76% carbon, 18% oxygen and 6% hydrogen (see Fig. 9.5). They embody many of the characteristics of the well-known phenolic resins, such as:

- excellent thermal/electrical insulation, because of low conductivity;
- retention of properties at low (even cryogenic) temperatures;
- outstanding resistance to acids, alkalis, solvents, fuels, steam;
- low specific gravity (1.27);
- high compatibility with resins, elastomers, adhesives; and
- being an excellent precursor for carbon and activated carbon fibres and textile materials;

and in the presence of heat or flame:

- high resistance: non-melting at any temperature;
- minimal smoke generation, little or no shrinkage;
- retention of textile integrity and no embrittlement or breakage; and
- practically no toxic off-gassing (no HCN, halogens, etc.).

Kynol fibres are generally elliptical in cross-section and are light gold in colour. The fibres feel soft and are available with or without crimp, in different lengths. They are highly flame resistant but are not high-temperature fibres in the usual sense of the term. For example, a 300 g/m² fabric withstands 2500 °C for 12 s or more without breaking, but the practical temperature limits for long-term application are 150 °C in air and 250 °C in the absence of oxygen. This is because the fibre is reactive above 150 °C and, in the absence of oxygen, crosslinks and slowly carbonises.



9.5 Polymer structure of *Kynol* novoloid fibre.

Table 9.4 Typical properties of *Kynol* fibres

Colour	gold
Standard diameter, μm	15, 18 (2 and 3 denier)
Standard fibre lengths, mm	standard 51 or 70
Specific gravity	1.27
Tensile strength, cN/tex	12–16
Elongation, %	30–50
Modulus, cN/tex	260–350
Loop strength, cN/tex	19–27
Knot strength, cN/tex	10–13
Elastic recovery, %	92–96
Moisture regain at 20°C, 65% rh %	6
Limiting oxygen index, LOI %	30–34

The typical properties of *Kynol* fibres are listed in Table 9.4.

The chemical structure of these fibres includes only carbon, oxygen and hydrogen and so when *Kynol* products are exposed to flame, the products of combustion are principally water vapour, carbon dioxide and carbon char. There is no emission of HCN, HCl, bromine- and phosphorus-containing compounds and other toxic products of combustion typical of many other inherently flame-resistant and FR-treated organic fibres. Moreover, since the fibre chars without melting and produces few volatiles, smoke emission is also minimal and is less than that of virtually any other organic fibre.

These characteristics have led not only to their use as asbestos-replacement fibres and in safety-related textiles, but also to a number of other end-uses which will be explained briefly.

9.2.2.2 Applications

The applications of *Kynol* fibres and derived textile materials can be roughly divided in two groups: safety materials and industrial uses. In many

industrial applications, safety is also a primary reason for the use of *Kynol* products. A more detailed breakdown may be given as follows:

- *Flame resistant safety products and smoke barriers:* Protective garments incorporating *Kynol* woven and nonwoven linings and waddings are used in a wide variety of flame, heat- and chemical-resistant fields where safety is required. Welders, racing drivers and fire fighters use not only regular *Kynol* garments, hoods and gloves, but also aluminised *Kynol* clothing. These are often more comfortable to wear than other aluminised materials and provide excellent heat insulation as well.

Kynol materials have also replaced asbestos in protective curtains for flame, radiant heat and metal splash hazards, as well as in flame-resistant ventilation ducts, and insulation of roofs and walls.

An important application of *Kynol* felts and fabrics are flame and smoke barriers and insulation in aeroplanes. The materials have been approved by leading aircraft producers such as Airbus Industries and Boeing. This is because of their low specific gravity and hence felt area densities, virtually no emission of toxic gases in flame (no HCN, etc.), extremely low smoke generation and high flame resistance.

In addition to aircraft, such insulations and barriers are used in other transport, e.g. cars, trains, ships, ferries and submarines. In public facilities such as theatres, cinemas, hotels, discotheques, airports and hospitals, they are also of use as fire blockers, seat linings, smoke barriers, curtains, escape hoods, bed covers, emergency bags and aprons.

- *Applications requiring heat insulation and resistance to extremely low temperatures:* Certainly there are many other areas in which the combination of flame protection and thermal insulation is required by modern life and industry. *Kynol* materials are excellent thermal insulators thanks to their low thermal conductivity and retention of their textile properties at extremely low temperatures, even after immersion in liquid nitrogen. These factors have led to the use of *Kynol* felts in flexible insulation for liquid natural gas piping, as well as in military sleeping bags – two examples in which protection against both flame and cold extremes are required.
- *Industrial sealings and packings:* Asbestos-free sheet gaskets, both calender- and beater-processed, were among the first products to be produced with milled or short-cut *Kynol* fibres, in order to increase not only compressive strength and recovery but even more importantly, steam, heat and chemical resistance.

Their outstanding resistance against acids, alkalis, solvents, fuels, steam and even hydrofluoric acid has led also to their highly successful use in braided packings of extremely high durability. For gaskets and packings, and certainly also for brake-bands and fabric-based seals, it is

of great importance that fibre-to-matrix wetting and adhesion of *Kynol* fibres are excellent. In fact, an actual chemical crosslinking reaction occurs between the fibre and matrix resins and elastomers, in which the methylol groups formed during curing of the fibre play a key role, and this leads to improved characteristics in the final product.

- *Composites, including friction materials:* The crosslinking property mentioned above underlies the usefulness of *Kynol* fibres in composites. Frequently unexpected synergistic improvements in properties may be displayed in such composites; for example, *Kynol* fabrics coated with chlorinated polyethylene (CPE) or other elastomers and friction materials and similar moulded products with phenolic (resole) resin binders.

Again, the low specific gravity of *Kynol* fibres often leads to a reduction in weight of such composites, while properties such as heat, steam and chemical resistance, impermeability, compressive strength, shock resistance, dimensional stability and hardness are improved. Similarly, lightweight friction materials have given rise to high-performance disc pads, clutch facings and textile-based industrial friction materials with reduced weight, more stable coefficients of friction, greatly reduced wear to mating surfaces and better noise absorption.

The properties of many other materials based on thermoplastic and thermosetting resins can be improved by adding *Kynol* fibres in the same way.

- *Cables:* *Kynol* fibres are used in flame resistant and smoke-free filler yarns, wrapping tapes and coatings for communication and power cables where maximum circuit integrity must be maintained for safety reasons. They are found in highway and railway tunnels, underground concourses and subways, high-rise buildings and in industrial complexes. Because of good resistance to radioactive emissions, these fibres are extremely useful for cabling in nuclear power stations.
- *Carbon fibre products:* Since *Kynol* fibres are non-melting and have an inherently high carbon content of about 76 wt%, they are excellent precursors for carbon fibres and other carbon textile products. Carbonisation is a simple, one-step process, which is routinely performed on completed textile structures such as woven fabrics and needled felts. Yields are on the order of 55 to 60 wt%, with carbon contents up to 99.8%.

The resulting carbon fibres are amorphous in structure and have a low modulus. They are soft, pliable, produce little dust or fly on processing, have good electrical conductivity and possess even higher resistance to heat and chemicals than the precursor fibre.

Kynol-based carbon products perform even better than their *Kynol* precursors in a number of the applications mentioned previously, such as heat- and chemical-resistant braided packings. *Kynol* carbon fabrics are employed in significant quantity in composites for rocket motor exit

nozzles. Other applications include brushes and similar products for static elimination in copying machines.

- *Activated carbon fibre products:* Again due to the high carbon content, *Kynol* fibres and products are used as a precursor for activated carbon materials. *Kynol* fibres and textiles are transformed into activated carbon by a one-step process and the effective surface area can approach $3000 \text{ m}^2/\text{g}$.

The following important technical advantages can be obtained in comparison with granular activated carbon and other fibres:

- highly efficient and cost-effective removal of very small amounts of impurities from large amounts of air or liquids;
- high fibre surface-to-volume ratio and direct connection of micropores to the fibre surface significantly shorten diffusion distance and increase speed of adsorption and desorption;
- pore dimensions and surface characteristics can be tailored to the application;
- depending on the target material, excellent rates of removal may be obtained even at ppb concentration levels;
- fibres can be locked into textile structures, preventing 'channelling' and minimising loss and contamination due to interparticle abrasion;
- textile structures are often convenient for filter design and assembly, and compared to textiles impregnated with powdered carbon there is less shedding of particulates and no pore blockage by binders;
- shed particles tend to be fibre fragments with a minimum of $10 \mu\text{m}$ dimensions, easily trapped in particulate filter media;
- the strength of all activated *Kynol* products is superior to similar viscose products, especially when wet.

Such technical considerations make activated carbon fibres highly useful in specialised filtration applications, such as air filtration, solvent recovery, radioactive iodine filtration, ozone elimination, medical and military (nuclear, biological and chemical [NBC] agent) applications, industrial safety and water treatment.

Kynol activated carbon products perform extremely well in electrical and electronic applications. Taking one example, the capacitance of a simple two-layer capacitor is linearly related to the surface area of its two electrodes. This means that even very small quantities of such fabrics achieve outstanding results in capacitors.

9.3 Aromatic polyamides and polyarimids (ARH)

Of all the inherently heat- and flame-resistant fibres developed since 1960, this group is perhaps the most well known and exploited. In the main, they

are typified by having aromatic repeat units bonded together by amide—CONH—groups, the polyaramids, generally, shortened to ‘aramids’, imide—CON<groups, the polyarimids or arimids, or both in alternating manner, the poly(aramid-arimid)s. Their resistances to heat are dependent, therefore, on the weakest or most reactive bond present. In the polyaramids this is the single C—N bond in the amide group, whereas in polyarimids, this same C—N bond is strengthened by the presence of increased conjugation. Thus, polyaramids have inferior heat resistances to polyaramid analogues as will be shown below. All members of this group are typified by having thermal resistances in excess of 300°C for short-term exposures and high levels of inherent flame resistance.

9.3.1 Aramid fibres

Perhaps the most well known of the thermally resistant fibres are the aromatic polyamides or aramids which originated with the commercial development of DuPont’s *Nomex* fibre in the early 1960s. While Chapter 2 reviews the aramid group of fibres in detail, it is useful to summarise some of their types and characteristics here in order to give an overall coherence to this chapter. In addition, their thermal and flame-resistant properties are often considered as benchmarks against which all other fibres in this group are measured.

For the purpose of this summary, a number of reviews describe the development of this group up to the mid-1970s,⁸ more recently⁹ and those produced in the former USSR.¹⁰

Commercially available fibres based on poly(*m*-phenylene isophthalamide), in addition to the well-established *Nomex*, are *Conex* (Teijin), *Apyeil* (Unitika) and *Fenilon* (former USSR) and variations having modified tensile properties (e.g. *Inconex*, Teijin) and antistatic properties (*Apyeil-α*, Unitika). Most versions of these fibres have had improved dyeing properties, introduced during the last 10 years or so to enable them to compete effectively with flame-retardant versions of conventional fibres (e.g. flame-retardant cotton, viscose and wool), which are available in full colour ranges. However, their thermal resistances are very similar and defined by the physical and chemical features of the all-*meta* aromatic polymer chains. Their rigid structures and efficient intermolecular forces ensure that the fibres have minimal thermoplastic characteristics, with second order transition temperatures (T_g) of about 275°C and an ill-defined melting point accompanied by thermal degradation starting at 375°C. Together, these enable the fibres to be used in textiles where shrinkage should be minimal at temperatures of continuous use of 150–200°C and to shorter exposures as high as 300°C. Thus they are ideal for use in hot gas filtration and protective clothing applications respectively, although their resistance to acidic and basic environments is limited by the hydrolytic sensitivity of the amide links present in the polymer

chains; however, continuous exposures up to 150°C and higher are still possible.⁹ Other important uses include their incorporation as very short fibres or flocs in papers and similar materials, from which a variety of heat and flame-resistant gaskets, tapes, honeycomb structures, insulation materials and similar products can be fabricated. Such has been the impact of the meta-aramids in certain industries such as aerospace, for example, that without the lightweight honeycomb board and composite structures available comprising them, modern aircraft development toward higher capacity and greater fuel efficiency could not have taken place.

Most commercial meta-aramid examples, typified by *Nomex* for example, are available in floc, short staple and continuous filament forms as well as a range of finesses and even cross-sections. *Nomex* Type 450, for example, has served the filtration industry for over 30 years, is available in 1.7 and 2.2 decitex and has a bean-shaped cross-section. However, as the desire for improved filtration has increased, so the tendency to reduce fibre fineness has given rise to fibres such as *Nomex Delta FF* and *Delta Micro*, with fineness values respectively of 1.1 and 0.78 decitex. While specific surface areas and hence filtration efficiencies of fabrics incorporating these fibres have increased, their fundamental thermal resistances have remained the same as all the other members of the *Nomex* family. It is merely the changes in physical dimensions that have enabled improvements in product performance and new applications for this fibre genus to be generated.

When heated above 400°C or so, thermal decomposition proceeds via the formation of a tough, carbonaceous char that still provides a coherent heat-protective layer to underlying surfaces, thereby maintaining its protective character. This char formation ensures that all meta-aramid fibres have low flammabilities with limiting oxygen index values in the range 28–31%.⁹ They, therefore, compete effectively with many other non-thermoplastic flame-retardant fibres such as flame-retarded cotton and wool, which have similar LOI values, although they are inferior to the highly crosslinked (e.g. *Kynol*) and ladder (e.g. semi-carbon and PBI) aromatic fibres.

This combination of excellent thermal and flame resistance ensures that meta-aramids are used in both flexible (e.g. protective clothing) and inflexible (e.g. honeycomb-structured composites for the aircraft industry) protective materials which demand, in addition, little or no thermoplasticity and good tensile and other mechanical properties. However, in order to improve thermal properties further, blending with small amounts of para-aramid fibres (e.g. *Nomex III*) enables the thermal protective behaviour to increase, primarily through increasing the char tensile strength. Notwithstanding these advantageous features, all aramid fibres are expensive and, within the area of fire resistance, attempts to blend meta-aramids with lower cost flame-retardant fibres such as flame-retardant viscose, have given rise to protective fabrics such as *Karvin* (30% *Nomex*, 5% *Kevlar* para-aramid

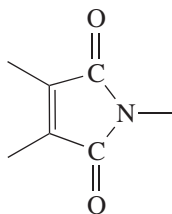
and 65% *Viscose FR* (Lenzing)) and similar blends (e.g. *Viscose FR/Twaron* (Acordis) para-aramid). These have similar flame retardancy to their respective parent single-aramid components, but their char structures are weaker and so do not offer sustained fire protection at high heat fluxes and temperatures as the 100% meta-aramid fabrics do.

The para-aramids, typified by *Kevlar* (DuPont) and *Twaron* (Acordis) and their modifications (see Chapter 2) which are based on poly(*p*-phenylene terephthalamide), while having enhanced tensile strengths and moduli as a consequence of the extreme symmetry of their polymer chains and hence order or crystallinity, also have enhanced thermal performance. The increased structural chain rigidity and order raises the second order transition temperature to about 340 °C and melting point to about 560 °C, before decomposing above 590 °C. Furthermore, higher continuous working temperatures of 180 °C and above are possible with resistance to short term exposures to temperatures as high as 450 °C being achievable. However, thermal degradation to carbonaceous char is similar to that occurring in the meta-aramids and so the LOI values are similar at 30–31%. However, as indicated above, the improved tensile properties coupled with this char-forming ability yield fabrics that can resist higher temperatures than the meta-aramid analogues to yield charred structures of superior tensile strength. Again, the higher cost, poorer textile processing properties and higher modulus of para-aramid fibres ensure that their use in applications such as protective textiles and filtration fabrics is limited to 100% contents only when performance demands are exceptional. As mentioned above, however, additions of small amounts of para-aramid to meta-aramid and indeed non-aramid fibres, can significantly add a combination of enhanced tensile and heat and flame resistance.

9.3.2 Arimid fibres

Arimid fibres were researched during the 1960–70 period as alternatives to the contemporaneous aramid fibre developments discussed above and in Chapter 2 of this book. Attempts to produce high-temperature resistant arimid fibres at this time focused on the aerospace industries and these have been reviewed up to 1976 by Hughes *et al.*⁸ Not surprisingly, both the USA and former USSR research efforts produced similar products, under names such as *PRD-14* (Du Pont, similar to their *Kapton H* aromatic polyimide film) and *Arimid T*, respectively. These latter have been more fully reviewed by Duobinis.¹⁰

As stated previously, arimid fibres derive their extremely high heat resistance from the presence of the imide nitrogen, >N–, which not only lacks the active hydrogen present in the polyamide functional group, but also introduces the possibility of rigid and stable heterocyclic rings in the polymer chain, of the type:



Synthesis of these groups typically involves the condensation reaction of an aromatic tetracarboxylic dianhydride and an aromatic diamine, and Du Pont's original *PRD-14* fibre was considered to be based on pyromellitic anhydride and a diamine similar to *p*-phenylene diamine, 4,4'-diaminodiphenyl, 4,4'-diaminodiphenylether, substituted derivatives, or a mixture thereof. More recently, diisocyanates have been found to be more acceptable in place of the diamines. Thus, the number of single bonds per unit length of polymer chain is reduced compared to the aramids and this gives rise to high chain rigidity and hence high second order transition temperatures and greater resistance to pyrolytically induced chain scission reactions. Arimid polymers rarely start to break down below 500°C under nitrogen and 450°C in air, and this latter characteristic is complemented by a high degree of flame resistance.

Although Table 9.5 lists a selection of polyimide fibres reported to date, the major development has been by Lenzing of Austria, which introduced the polyarimid fibre *P84* during the mid-1980 period.¹¹ The development of arimids, and of this fibre in particular, has been reviewed.^{12,13} *P84* fibres are now produced by Inspec Fibres (USA).

All polyimide polymers and fibres tend to be very intractable and so are often produced as reaction intermediate fibres, which although unstable, are soluble in appropriate solvents such as dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Once extruded, the filaments are trans-

Table 9.5 Selected examples of polyarimid fibres⁹⁻¹³

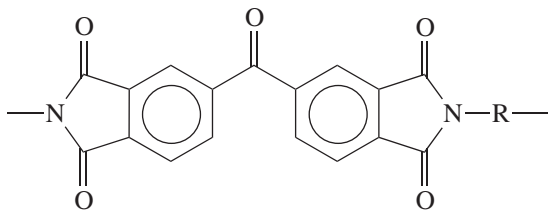
Fibre	Origin	Tenacity, N/tex
<i>PRD-14</i>	Du Pont, USA	>0.26
Polypyromellitimide (high strength)	Du Pont, USA	1.13–1.30
<i>Arimid T</i>	Russia	>0.35
<i>Arimid T-TK 160</i>	Russia	>0.50
<i>P84</i>	Lenzing, Austria (now Inspec Fibres, USA)	0.35–0.38

formed to fully reacted and imidised polymer chains by use of high temperatures (up to 300 °C) or chemically.¹² The properties of the resulting polymers are dependent upon the exact structure of the tetracarboxylic acid dianhydride and the diamine. For instance, physical properties such as tensile strength and modulus, and thermal stability, increase with the increasing simplicity and symmetry of the former, and for polyimides containing pyromellitic dianhydride (PMDA), 3,4,3',4'-biphenyl tetracarboxylic acid dianhydride (BPDA) and benzophenone tetracarboxylic acid dianhydride (BTDA), the order of improving tensile behaviour and thermal stability generally is:



which also reflects their order of increasing insolubility. Therefore, poly(pyromellitimide) filaments, initially produced as *PRD-14* by Du Pont, have also been produced as high strength and modulus forms.

Because of their high insolubility and hence need for a two-stage production method outlined above, successful commercialisation followed the development of the use of copolymeric polyimides which enabled directly soluble polymers and hence more easily and economically processible ones to be produced. *P84* is the major outcome of this development and is produced from benzophenone tetracarboxylic acid dianhydride and a mixture of aromatic tolylene and diphenylmethane diisocyanates. The *P84* polymer has the following structure representative of poly (4,4'-diphenylmethane-*co*-tolylene benzophenonetetracarboxylic imide):



where R = $\text{C}_6\text{H}_4.\text{CH}_2$ or $\text{C}_6\text{H}_4.\text{CH}_2.\text{C}_6\text{H}_4$

The fibre is produced by dry-spinning to yield typically gold-coloured fibres with lobed, irregular cross-sections. After drying and hot drawing, the fibres achieve moderate tenacities (see Tables 9.5 and 9.6). These fibres, as staple, continuous filament and with or without crimp, are produced solely for their thermal performance and their complete properties are presented in Table 9.6.

Their profiled cross-section and high specific surface area make *P84* fibres ideal candidates for hot gas filtration and thermal insulation. In addition, the TGA-derived onset of degradation in air at about 450 °C, coupled with an LOI value superior to those of the polyaramids (see Table 9.14,

Table 9.6 Properties of commercial polyimide and poly(amide-imide) fibres^{8,11-15}

Property, unit	<i>P84</i> polyimide	<i>Kermel</i> poly(amide-imide)
<i>Tensile</i>		
Tenacity, N/tex	0.35–38	0.245–0.588
Breaking strain, %	33–38	8–20
Initial modulus, N/tex	3–4	4.9–9.4
<i>General</i>		
Boiling water shrinkage, %	<5	<0.5%
Thermal shrinkage, %	At 250 °C for 30 min, <1	At 200 °C <0.5%
Specific gravity	1.41	1.34
Moisture regain, 20 °C, 65% rh, %	3	3–5
Colour	Gold/yellow	Pale yellow
Second order temp., T_g , °C	315	<315
Maximum continuous temp., °C	160	150–180
Decomposition temp., °C	450	380
Limiting oxygen index, %	36–38	32

later) make *P84* fibres excellent candidates for high temperature end-uses in oxidative environments.

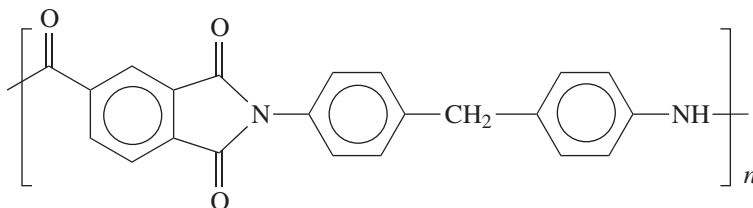
While the arimid fibres are not designed to be chemically resistant in the sense that the majority of fibres in Chapter 8 are, they do exhibit acceptable levels, even in the presence of strong acids and bases where hydrolysis of the imide linkages will be catalysed. Generally, the performance of *P84* is superior to that of the polyaramid fibres. For instance, immersion in the oxidising acids, sulphuric and nitric acids at 10–20% concentrations, can yield between 85–95% strength retentions after room temperature exposures of up to 100 hours. At elevated temperatures, retentions drop to, e.g. 75% after 20% sulphuric acid exposure at 50 °C. Resistance to hydrochloric acid is similar to that in these former acids at low concentrations and temperatures but is not so good at higher concentrations; only 45–55% retention is observed after 100 hours exposure to a 37% solution at room temperature.¹² On the other hand, resistance to dilute (5%) alkali at room temperature, even after 1000 hours exposure, is acceptable, with 85–95% strength retention. As might be expected of an all-aromatic structured polymer, solvents such as alcohols, ketones, chlorinated hydrocarbons and benzene have little, if any, adverse effect. However, aprotic solvents like DMF, DMSO, dimethylacetamide and *N*-methyl-pyrrolidone will swell and dissolve *P84* fibres.

The main arimid fibre applications exploit the high temperature and flame-resistant properties and are summarised as follows:

- *Protective clothing:* Outerwear, underwear and gloves may be made from 100% *P84* or blended with lower cost fibres such as flame retardant viscose (e.g. a 50/50 *P84/Viscose FR* (Lenzing) blend is used for knitted underwear with high moisture absorbency) or with high tenacity polyaramids to increase wear and tensile characteristics. Spun-dyeing of *P84* fibres enables their natural colour to be replaced by those demanded by customers who may, for instance, require more appropriate bright safety colours. The protective character of these arimid-containing fabrics is not only their tendency not to decompose at high temperatures but also to provide high levels of thermal insulation which may be improved by increasing fibre crimp levels.
- *Braided packings:* *P84* fibres are ideal candidates for high-temperature seals and packings, which may be impregnated with lubricants and PTFE dispersions when requiring higher levels of chemical resistance.
- *High temperature filtration:* Hot gas filter bags may be used up to 260°C for prolonged periods; experience has shown that continuous use for periods of years is possible at temperatures as high as 160°C with peaks up to 180°C being permissible.
- *Aircraft and other transport interiors:* Three-dimensional components with structural rigidity may be fabricated from nonwoven fabrics following heating above the second order transition temperature (Table 9.6), which causes fibre contraction and consolidation of the structure with some fibre-to-fibre adhesion occurring. These low density, rigid and fire-resistant structures can replace conventional materials where low weight is at a premium, such as in aircraft and high-speed trains.

9.3.3 Poly(aramide-imide) fibres

If the tetracarboxylic acid dianhydride component in a polyimide is replaced by a tri- or even dicarboxylic acid, then reaction with a diisocyanate produces a poly(amide-imide), the prime example of which is the *Kermel* fibre, which has been produced by Rhone-Poulenc of France since 1971.⁸ *Kermel* is now produced by Rhodia Performance Fibres. The chemical structure of *Kermel* is reported to be:⁸



and the diamino component is based on the diphenyl methane moiety. This chain segment is not very symmetrical and so the ability to crystallise is not high and hence the specific gravity is on the low side (see Table 9.6). However, this low order enables the polymer to be wet or dry spun from aprotic solvents such as dimethylacetamide, DMA. Furthermore, by incorporating isophthalate links in the chain, base dye affinity can be created.⁹ In 1993, a so-called third-generation *Kermel* was announced, which claimed to have superior colouration properties.¹⁵

Properties are included in Table 9.6 and it is seen that a range of tensile properties are possible that are similar to those of conventional polyamides and the poly(meta-aramids) (see Chapter 2). Like the poly(meta-aramids), however, *Kermel* has poor UV stability, and so must be protected from intense radiation sources. Its lower second order and decomposition temperatures reflect the lower chain rigidity and the weaker polyamide bond structure; again, these properties are similar to those of the poly(meta-aramids). Its behaviour to chemical exposure is similar to that of the poly(meta-aramids), with good resistance to strong acids when cold, poor resistance when hot, but very good organic solvent resistance except for aprotic species as seen for *P84* previously.¹⁴

Flammability, measured as limiting oxygen index, (LOI = 32%) is lower than seen for the arimid fibres but comparable to the aramids (see Table 9.14, later, and Chapter 2). Like these same fibres, it competes for the same end-uses, although it has found a special market in protective clothing⁹ where it is used as 100% *Kermel* or as blends with other fibres including FR viscose. The presence of the latter adds to the comfort and so is recommended for underwear like the similar *P84*/FR viscose blends outlined previously. Blends with wool have been shown to be ideal for uniforms, jerseys and pullovers. The years between 1971 and the present time have seen significant improvements in fibre quality and tensile properties, and these have been complemented by developments in colouration. As with the meta-aramids, this is usually carried out by spin or solution dope dyeing to yield bright, fast colours. A higher performance version, *Kermel Tech*, has been developed, with improved thermal resistance and designed for use in hot gas filtration where useful lifetimes of up to 20000 hours at 180°C are achievable.¹⁵ Production of composite yarns with high modulus aromatic fibres such as the poly(para-aramids) (*Kermel HTA*) enables the strength and abrasion resistance of fabrics to be increased.

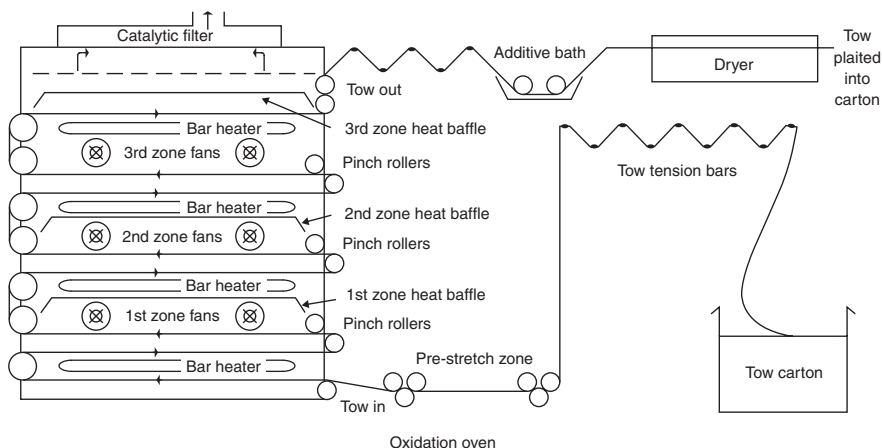
As an end-point to this group, while *Kermel* has been the only commercial example of a poly(aramide-imide) fibre to date, there is some interest being shown in the medical sector in hollow fibre membranes for blood purification.¹⁶ Commercial exploitation, however, has yet to follow.

9.4 Semi-carbon fibres: oxidised acrylics (NS)

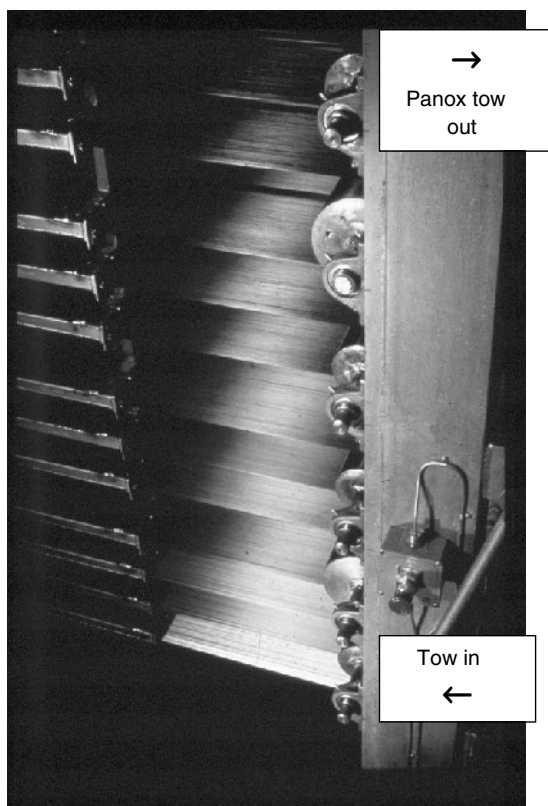
9.4.1 Development and manufacture

During the 1960–70 period, a number of carbonised or semi-carbon fibres were developed for high-temperature and flame-resistant end-uses. While these included carbonised viscose,¹⁷ only those based on semi-carbonised or oxidised acrylics have survived and continue to be developed today. The oxidised acrylics represent a group of ladder polymer fibres that are produced following controlled high-temperature oxidation of acrylic fibres during the first stages of carbon fibre production (see Chapter 5 for full details). First reported about 1970 as ‘*Black Orlon*’,¹⁸ they became of commercial interest as potential high temperature-resistant fibres during the early 1980s. During this time a number of commercial versions were announced including *Celiox* (Celanese), *Grafil O* (Courtaulds), *Pyron* (Stackpole), *Sigrafil O* (Sigri Elektrographit, now SGL) and *Panox* (SGL UK Ltd., formerly R K Textiles). Other examples were produced, including one from Toho Rayon in Japan. There are presently large production plants for oxidised acrylics in North America, UK, France, Germany, Hungary, Israel, Korea, Taiwan and Japan. Oxidised polyacrylonitrile (PAN) yarns are in regular production in the USA, UK, France, Germany and Japan in 100% form and in blends with aramids and/or glass. More sophisticated blends can be obtained and a list of producers and products is available.¹⁹

All are produced by similar means to yield black fibres that, while retaining some of the fibre physical properties of their acrylic fibre precursors, have very high thermal resistances and inherent flame resistance because of their partially carbonised structures. For example, *Panox* fibre is manu-



9.6 Schematic diagram of acrylic tow oxidation.

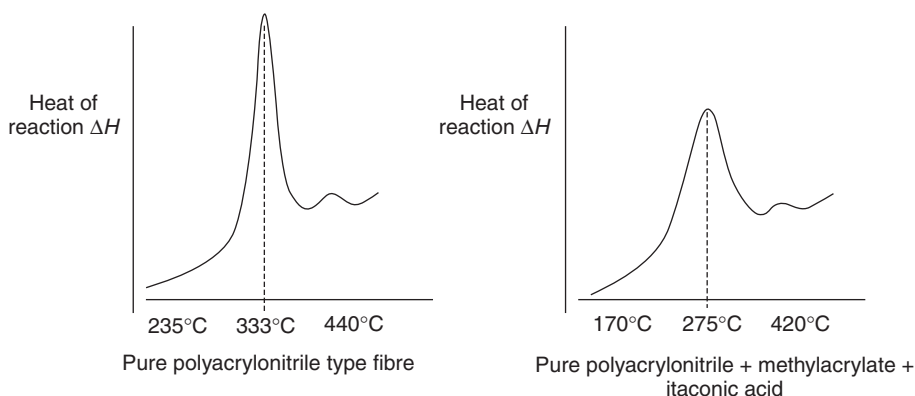


9.7 Acrylic tow passing through an air oven at 200 °C.

factured by the controlled oxidation of a *Courtelle* (Acordis) acrylic precursor textile fibre made specifically for the carbon fibre industry. The preferred acrylic precursor is a copolymer of the major monomer acrylonitrile, $\text{CH}_2=\text{CHCN}$ and methyl acrylate, $\text{CH}_2=\text{CHCOOCH}_3$ and the co-monomer originally introduced to promote base dye affinity, itaconic acid, $\text{CH}_2=\text{C}(\text{COOH})(\text{CH}_2\text{COOH})$. Conversion to oxidised fibres occurs in continuous form during slow passage through an oven at about 210–220 °C. Figures 9.6 and 9.7 show schematically and visually the passage of acrylic tows through an oven and, in the latter, the gradual change from a white acrylic to the black, fully oxidised acrylic fibres is clearly seen.

9.4.2 Theory of oxidation of polyacrylonitrile

The oxidation of PAN was first really studied by Hantz²⁰ in 1950, and since that time its role in the production of carbon fibres has been reviewed by

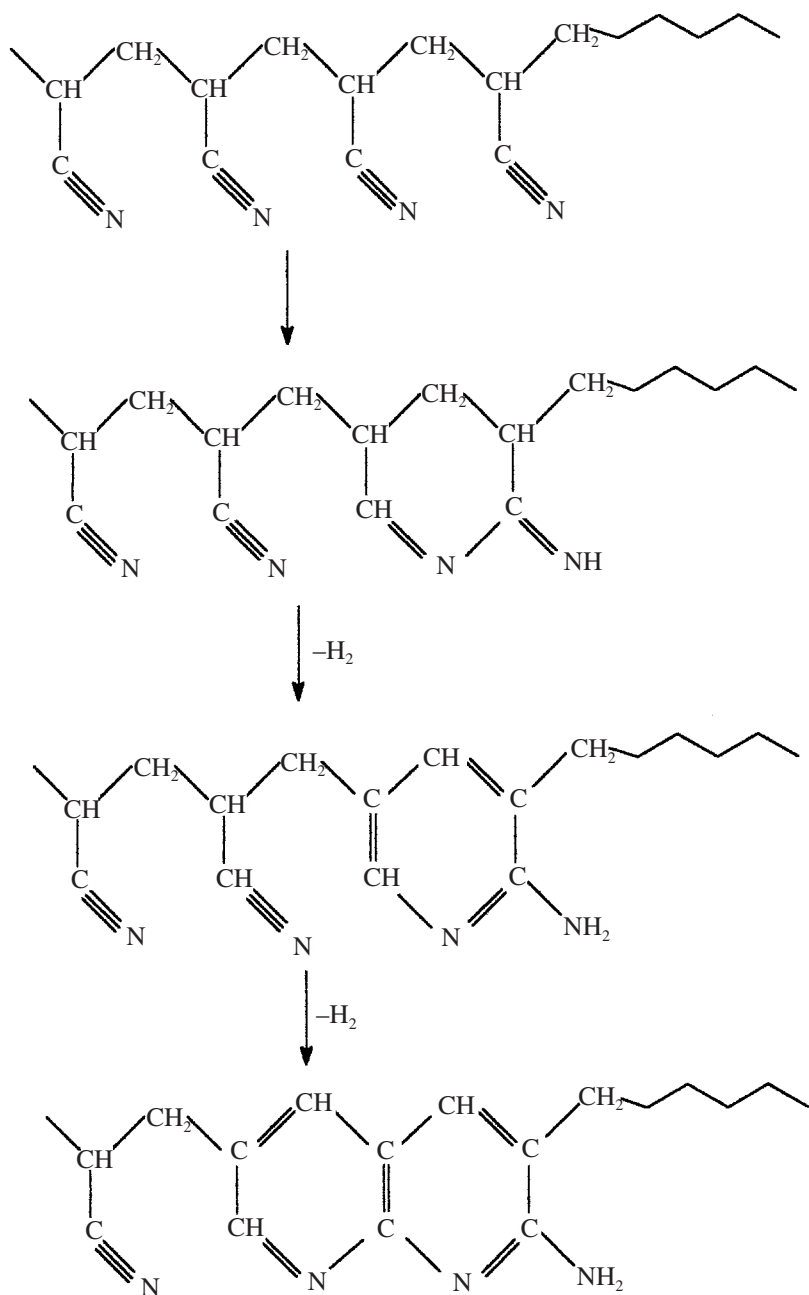


9.8 Typical differential scanning calorimeter curves (heating rate 20°C/min).²³

a number of authors.^{21,22} Morgan²³ has described how pure PAN, when heated in air, has a sharp exothermic reaction, that is, a change in enthalpy by releasing heat from the tow's mass. This can be seen in Fig. 9.8, which shows how the temperature of the tow mass reacts to heat when examined in a differential scanning calorimeter. This clearly shows how the presence of itaconic acid comonomer helps to give a less pronounced exotherm peak, and at a lower temperature. This co-monomer also assists in promoting cyclisation of the pendant nitrile groups. If the acrylic fibre is heated in air too rapidly, a destructive exotherm occurs and there is a thermal run-away of the reaction inside the oven. Hence, the oxidation process must be very carefully controlled by a very sophisticated thermal control, or flash-over will occur in the oven, causing fire at worst or incorrect density of the threaded tow if mere overheating occurs.

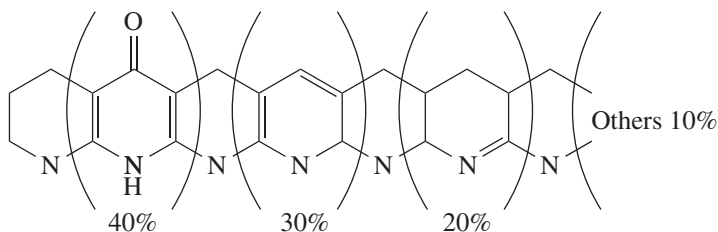
Ammonia, water, carbon dioxide, carbon monoxide and hydrogen cyanide are evolved in the oxidation process and about 2.5 molecules of oxygen enter the fibre for every molecule of hydrogen cyanide evolved. Since the acrylonitrile repeat unit has a completely saturated hydrocarbon chain, the addition of oxygen will involve the elimination of hydrogen and nitrile groups. The hydrogen cyanide that is evolved can account for one half of an oxygen molecule of the 2.5 molecules entering the polymer, leaving four hydrogen atoms to be eliminated, possibly as water. The hydrogen loss, however, is greater than that due to removal by oxygen, and some crosslinking or hydrocarbon chain unsaturation must also occur. While the original mechanism of Hantz²⁰ shown in Fig. 9.9 is still considered to be correct, others have been published.^{21,22}

After the oxidation process there is still about one third of the original hydrogen content remaining in the fibre product, which also retains half



9.9 The structure of polyacrylonitrile chain segments cyclising and transforming into a ladder-like, oxidised chain.²⁰⁻²²

of its exothermicity. Carbon dioxide is both evolved and consumed and ammonia is known to inhibit the oxidation reaction. While there appears to be no generally accepted formula for oxidised fibre it is thought to be of the general form:^{21,22}



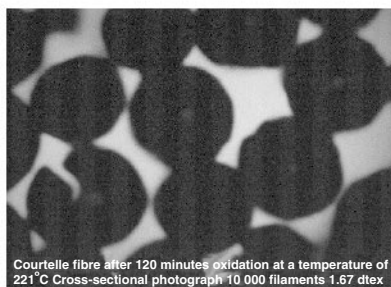
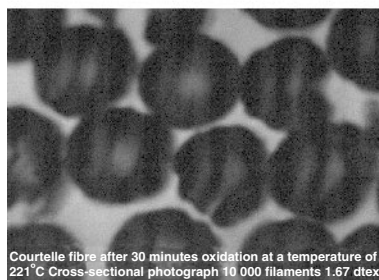
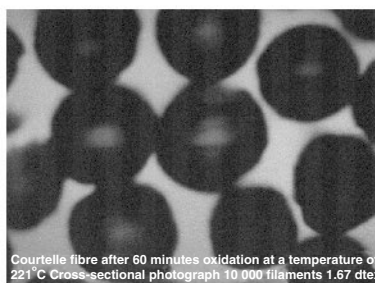
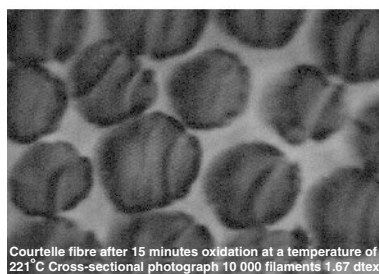
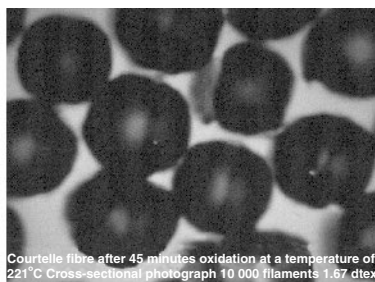
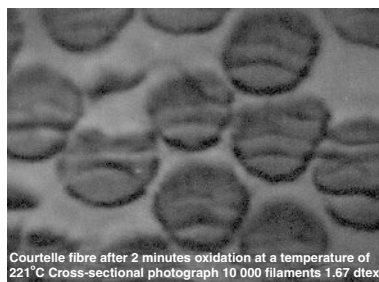
The cyclisation and oxidation processes are not considered to be separate reactions, but rather as progressing in parallel. In the oxidised form, hexagonal rings are believed to occur in groups of 7 to 10, which is probably due to co-monomer groups within the basic acrylic fibre structure interfering with the cyclisation along the chains. Subsequent carbonisation reactions involve the linking together of parallel chains of hexagonal groups, displacing oxygen and nitrogen atoms. The mechanism is best explained by reference to the photographs in Fig. 9.10 of the cross-sections of the polymer at different stages of oxidation.

The oxidation thus appears to occur in three stages:

- (i) Oxygen rapidly diffuses into the outer zone of the fibre with resultant oxidation of the polymer.
- (ii) A relatively slow cyclisation of the outer zone of the pre-oxidised polymer occurs without any observed progression of the zone boundary.
- (iii) The final reaction occurs with the zone boundary moving towards the centre of the filament following a diffusion-controlled reaction obeying a 'square root of time' relationship. At the same time the outer zone darkens further to become black.

9.4.3 The oxidation process

The oxidation of the special *Courtelle* fibre is performed in an electrically heated oven shown previously in Figures 9.6 and 9.7. Figure 9.6 shows the passage of the tow through the oven. The tow is taken from the box and threaded over various tension bars to open it out to its full width (approximately 30 cm); the tow is then stretched by 8–10% prior to entering the oven. This will give an optimum extension of 11–13% in the oxidised tow. The tow then enters the oven at the bottom level and is fed backwards and forwards up through the oven, passing through three separate heater zones, set at gradually increasing air temperatures between 185°C and 220°C.



9.10 Cross-sectional micrographs of *Courtele* fibres exposed to (a) 2 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 120 min oxidation at a temperature of 221°C, 10 000 filaments, 1.67 dtex.

The tow is driven through the oven and tensioned by 'pinch' rollers; these are rollers that can be moved horizontally to increase or decrease tension on the tow. It emerges from the oven at the top and is then passed through a bath to apply additives, dried and plaited back into a tow carton. A catalytic filter at the top of the oven removes the burnt tar and gases. The heating zones are heated by electric bar heaters. Fans and baffles keep the zones at uniform temperatures. All controls for the production process are incorporated in a data logger system that continuously monitors temperature distribution and tow speed.

Table 9.7 General properties of oxidised acrylic fibres

Property	Value
<i>Tensile:</i>	
Tenacity, GPa	0.2–0.3
Breaking strain, %	15–21
Modulus, GPa	7–11
<i>General:</i>	
Moisture regain, %	10
Specific gravity	1.35–1.40
Limiting oxygen index, %	55

9.4.4 Properties

After carbonisation, a major indicator of the overall fibre properties and suitability for end-use is the density. This is in spite of other physical and morphological characteristics being influenced by the degree of carbonisation achieved and shrinkage accommodated during the oxidation process.²⁴ The higher the density, the greater is the degree of carbonisation and the higher is the limiting oxygen index. Ideally, fibres having a LOI of 55% are considered to be acceptable. Table 9.7 shows the general properties of oxidised acrylic fibres, which may vary, of course, between manufacturers and types. Apart from continuous filament tows having individual fibre finenesses in the range 1.7 to 5 dtex, staple fibres are the more usual form with average lengths typically in the range 60 to 90 mm. Fibre flocs with lengths of 4 mm and below are also available.

As Table 9.7 shows, oxidised acrylic fibres have acceptable tensile properties for textile processing, a surprisingly high moisture regain and hence comfort factor of resulting fabrics, and a very high level of inherent flame resistance. Hence, they are used where a combination of acceptable physical properties and extreme heat and flame resistance are essential characteristics.

9.4.5 Applications

The fibres converted into fabrics satisfy the following end-uses: high temperature packings, anti-riot suits, tank suits, FR underwear, fire blockers for aircraft seats, heat-resistant felts (insulation), hoods and gloves, fire entry/fire proximity suits when aluminised, flexible hot air ducting, protection against phosphorus and sodium splash, welding blankets, components on aircraft side-walls and decorative double cloths for aircraft and ships.

The oxidised fibres/fabrics can be further carbonised by heat treatment and are then used as a valuable component in carbon-carbon composites that are essential components of aircraft brakes. They also find use as interface components for clutches and transmissions, reinforcement for plastics and composites, rocket motors, filters and electrical heating elements.

Oxidised PAN fibre-containing fabrics can be successfully printed and coated. They can also be flocked with fire-resistant coloured fibre for decorative FR end-uses. For molten sodium and phosphorus resistance, the fabric requires multiple fire-resistant coatings. Similar materials can be used for resistance against napalm. Special polymers can be impregnated to give strength and flexibility to the fabric after it has been burnt.

No one fibre has all the necessary properties for every fire-resistant application and, in the case of oxidised acrylic fibres, the best treatment is to blend them with other fibres to enhance colour and abrasion resistance, handling and wear characteristics.

Panox fibre is oxidatively degraded after prolonged periods at 210°C and it is vulnerable to flexing, crushing and abrasion in 100% form for yarns finer than 90tex. However, for non-apparel end-uses it may be spun to give yarns of about 38tex and can be woven commercially. The fibre can be spun on a wide range of machinery but essential modifications have to be made to prevent fibre breakage and crushing.

9.4.6 Economic considerations

When comparing oxidised acrylics with competitive fibres such as PBI (Section 9.5), while their LOI values and carbon contents are very similar, the cost per kilo of the former is less than a tenth of the cost of PBI. *Panox* is also half to a quarter of the cost of a range of aramid fibres and double the cost of the modacrylics. One aspect of the true cost of a fibre is to consider the cost-advantages of using it during the product lifetime. Since a significant market for these fibres is their use in aircraft seat barrier fabrics, the weight and fuel savings may be calculated. Table 9.8 presents details for British Airways aircraft for 1986 which shows the weight and associated costs of seat fire-blocking fabrics in a range of commercial aircraft.

These figures show that in 1986 it cost around £45.00 per kilo of fabric per year in aircraft fuel charges. In terms of oxidised acrylic lightweight fire blockers for the seats, the cost of the fuel to fly the material over a four year period ($= 4 \times £808870$) is twice as much as the fabric price (£1.53m). It is clear, therefore, that high carbon content fibres allow fire-blocking fabrics to be made at lower weights per square metre than fibres having lower carbon contents, which means they are more economic as well as more protective.

Table 9.8 Operational costs of fire-blocking fabrics fitted to passenger seats in selected British Airways aircraft in 1986 (reproduced with kind permission of British Airways)

Aircraft(A/C) type	No. of seats	No. of A/C	Fabric mass per A/C, kg	Cost of fabric mass: £/kg/yr	Cost per A/C £	Cost per fleet £
<i>Selected aircraft:</i>						
B737	114Y	35	68	26	1768	61880
B737 (Airtours)	130Y	8	78	26	2028	16224
B757	189Y	15	113	17	1921	28815
B757	195Y	9	117	17	1983	17847
B747	18F/90SC/262Y	28	267	57	15219	426132
B747 (Combi)	22F/92SC/220Y	2	250	57	14250	28500
Concorde	100F	7	100	65	6500	45500
Others	—	50	—	—	—	173972
Total aircraft		154	—	~45 (ave)	—	808870

Notes: F = first; SC = super club, Y = club and economy class seats.

Weight increase for fire blocking fabrics:

First Class seat: 1.1 kg per seat place

Super Club seat: 1.0 kg per seat place

Economy and Club seat: 0.6 kg per seat place

Concorde seat: 1.0 kg per seat place

9.4.7 Heat-treated oxidised acrylics

The Dow Chemical Company have shown that further heat treatment of oxidised acrylic fibres in an inert atmosphere promotes a further improvement in heat and flame resistance. One product, produced under licence from this technology, is *Curlon* (Orcon Corporation) whose properties have been reviewed recently.²⁵ The fibres have a crimp, hence the name, are circular and are available in diameters of 8 and 11 μm . While the tensile strength (0.5 GPa) and extensibility (4.5%) are closer to those values more typical of carbon fibres, and the specific gravity of 1.54 reflects this as well, the Limiting Oxygen Index has increased to 56%. Because of its increased degree of carbonisation, toxic gas emissions, particularly those of HCN, when heated to temperatures up to 1000 °C, are claimed to be less than for normal oxidised acrylics. The higher density improves the acoustic insulating qualities and so this fibre is finding application in thermal-acoustic, fire-blocking, nonwoven fabrics in aircraft and marine environments.

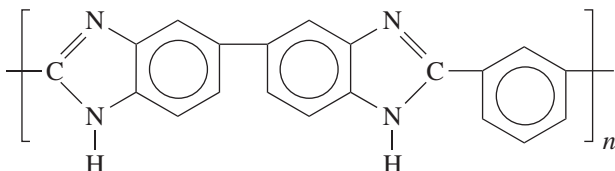
An even more recent version of this fibre is *Quiesse* (Quiescent Technologies, UK) which appears to have similar characteristics to *Curlon*.

9.5 Polybenzimidazole, PBI (CT)

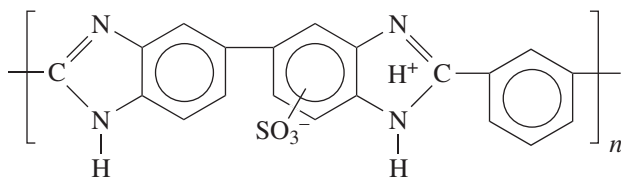
9.5.1 Development and structure

PBI fibre manufactured by Celanese Americas, USA, is a high-performance fibre recognized for its exceptional thermal stability and chemical resistance. These two qualities, along with its excellent textile processing characteristics, have secured *PBI* fibre a unique position in the high-performance fibre markets. Since around 1990, *PBI* fibre has found acceptance and is known as the premium product for many performance-based applications. These include fire protective fabrics for personnel, friction products, and fire-blocking substrates for aircraft. While *PBI* fibre is relatively new to the civilian market place, the story of *PBI* goes back to the early 1960s.^{26,27} It was then that the US Air Force Materials Laboratory (AFML) contracted with the former Celanese Corporation to develop the polymerization and spinning processes for a high-temperature resistant fibre. Later, after the 1967 fire in the Apollo spacecraft, AFML and NASA examined *PBI* fibre as a non-flammable material for flight suits that would afford maximum protection to astronauts or pilots in oxygen-rich environments. After years of pilot scale manufacturing and use in highly specialized military and aerospace applications, Celanese, in 1983, built a full-scale manufacturing plant for the production of *PBI* polymer and fibre. It was then that Celanese began developing civilian markets for the various *PBI* products.

Polybenzimidazoles are a class of polymers that exhibit high thermal and chemical stability. The polybenzimidazole or PBI referred to in this report is poly (2,2'-(*m*-phenylene)-5,5'-dibenzimidazole) and it is the only commercially available polybenzimidazole. This particular PBI was commercialized because of its combination of excellent thermal stability and processability. PBI gains much of its thermal stability from the fact that it is a wholly aromatic, ladder-like polybenzimidazole structure.



Most PBI fibre sold today is treated with sulphuric acid to increase the flame stability of the fibre. Sulphonated PBI shrinks less than 10% when exposed to direct flame.

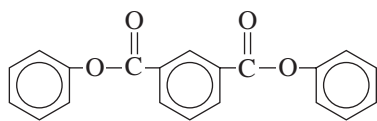


Even greater flame stability can be achieved by substituting the sulphuric acid treatment with a phosphoric acid treatment. Phosphonated PBI is available but it is only used in super critical applications.

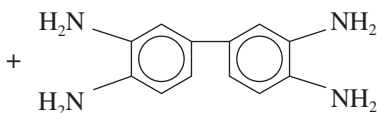
9.5.2 Synthesis and fibre manufacture

PBI polymer is synthesized from tetra-aminobiphenyl (TAB) and diphenylisophthalate (DPIP) (see Fig. 9.11) in a two-stage reaction process.^{23,28} In the first stage, equimolar amounts of the monomers are heated and melted in an inert atmosphere. As the monomers react and begin to build the PBI prepolymer, the by-products water and phenol evolve, causing the prepolymer to foam. After heating at 260 to 275 °C for 1–2 hours, the foam is allowed to cool and is then crushed into a fine powder. In the second stage, this PBI prepolymer is heated for an additional 2–3 hours at 375–400 °C to complete the polymerization process and provide the desired molecular weight for further processing. The resulting PBI polymer is in the form of a fine gold/brown powder.

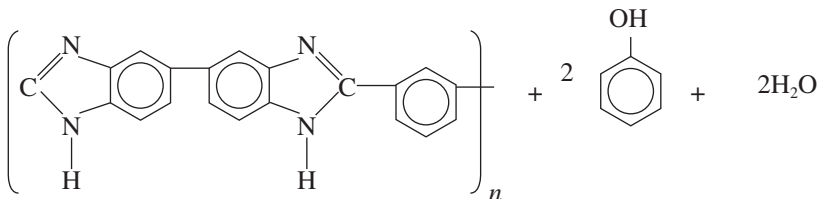
Solutions of PBI dope are made by dissolving PBI polymer powder and lithium chloride under pressure and temperature in dimethylacetamide, DMAC, in an inert atmosphere. A typical dope solution contains 25% solid



Diphenylisophthalate
M.W. = 318.31
M.Pt. = 136–137 °C



Tetra-aminobiphenyl
M.W. = 214.5
M.Pt. = 175–178 °C



Poly[2,2'-(*m*-phenylene)-5,5'-dibenzimidazole]
M.W. = (308.03)_n
M.Pt. = Chars
Intrinsic viscosity = 0.7 +

Phenol

9.11 PBI polymerisation.

PBI polymer by weight and has a viscosity of about 1500P at room temperature. The lithium chloride is added to stabilize the solution, increasing the shelf life from days to several months. Before further processing, the PBI dope is filtered to remove particulates that could interfere with downstream processing.

Fibre forming involves the dry extrusion of the polymer solution through a fine-holed spinneret into a heated inert atmosphere. As the dope solution exits the spinneret, the DMAC evaporates and the solution begins to form into a semi-solid fibre. The resulting bundle of fibres (or 'ends') is drawn through a heated chamber to complete the fibre formation and remove most of the DMAC. The DMAC vapour is recovered through a vapour-recovery system. As individual fibre ends exit the heated chamber, they are combined with other ends to form a sub-tow. The sub-tows are laid and stored in a creel to await further processing.

After the required number of sub-tow creels are produced, they are brought together to form a heavy denier tow band for final processing. This final processing, known as tow finishing, consists of five major continuous steps:

- (i) **Washing:** The tow band is run through a heated water bath to remove residual DMAC and lithium chloride left in the fibre from spinning.

- (ii) *Drawing*: After washing, the tow band is drawn and heated to orient the PBI fibre and produce a final fibre denier value of 1.5.
- (iii) *Sulphonating*: The PBI tow band is submerged in a weak solution of sulphuric acid and subsequently heated at high temperature in an inert atmosphere to bond the sulphur chemically to the PBI molecule. Sulphonation reduces fibre flame shrinkage to less than 10%.
- (iv) *Crimping, finishing, and cutting*: Depending on the customer requirements, the PBI has finish added, is crimped and is cut to various staple lengths, or is collected uncrimped and without finish for short-cut applications.
- (v) *Packaging*: The finished product is packaged for delivery to the customer.

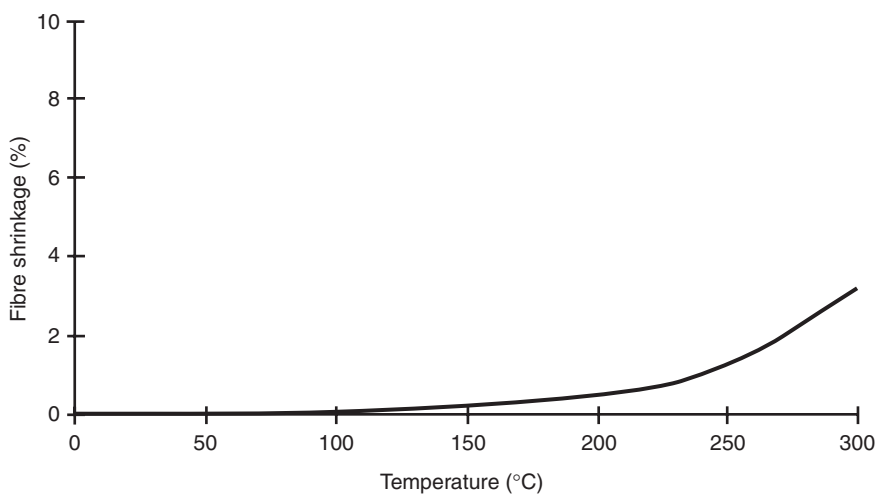
9.5.3 Fibre properties and applications

The full properties and fibre characteristics are fully described elsewhere but may be addressed with respect to the context of this particular discussion below.^{27–30}

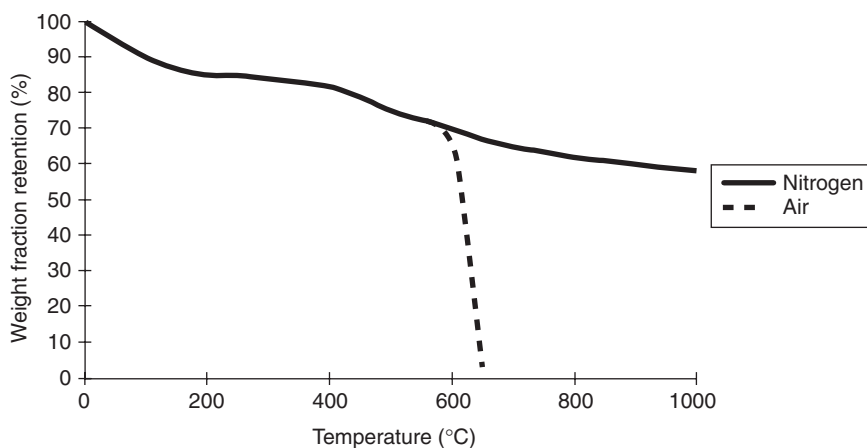
- *Flame and thermal stability*: PBI fibre will not undergo sustained burning in air, as demonstrated in the limited oxygen index test. The lowest concentration of oxygen that will sustain burning is 41%. Another standard test used to evaluate fire or flame resistance is the vertical flammability test (FSTM 191–5903). In this test, a fabric sample is exposed to a high flame temperature for a set time. Flammability performance is determined by measuring the after-flame time on the fabric and the length of fabric destroyed by the flame (char length). Fabric produced from PBI fibre exhibits no after-flame and minimal char length (10mm or 0.4 inches), further confirming PBI's exceptional flame resistance.

PBI fibre maintains its physical and mechanical integrity during and after exposure to a wide range of severe temperatures, and thermal stability has been examined in numerous high-temperature exposure tests. In these tests, where fibres are exposed to a range of temperatures for a predetermined duration followed by physical characterisation such as strength, mass and length retentions, PBI shows exceptional high-temperature stability. Figures 9.12 and 9.13 and Table 9.9 summarize some of these results. The thermogravimetric (TGA) analysis of PBI shown in Fig. 9.13 indicates that PBI retains integrity up to 450°C (840°F) in air and over 1000°C (1830°F) in nitrogen.

- *Heat release and smoke and gas generation*: Heat release is a measure of how much energy a material adds to pyrolysis and the burning reaction. In applications where a material is used to protect people and/or



9.12 Thermal linear shrinkage of PBI fibre after 24-hours exposure.

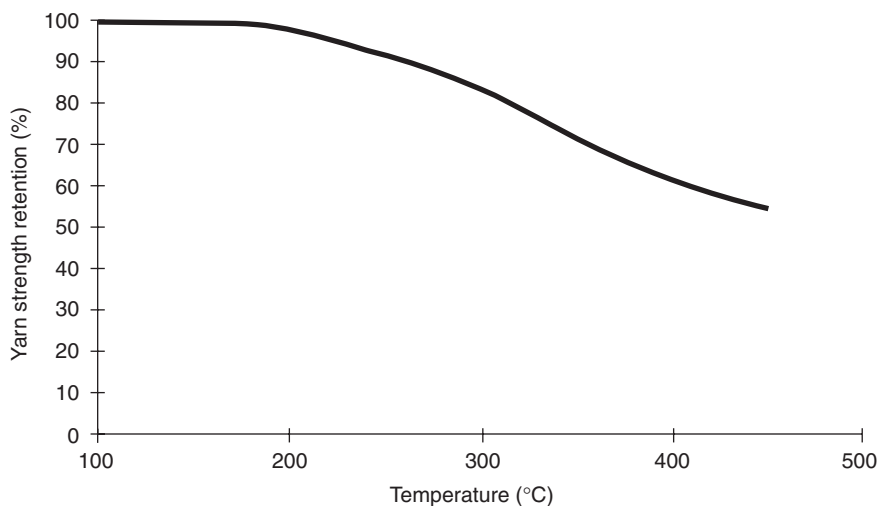


9.13 Thermogravimetric analysis of PBI fibre in air and nitrogen.

property from flame, it is important that the protecting material does not add to the danger by increasing the amount of available fuel. PBI fibre has negligible heat release as measured by the US Federal Aviation Administration (FAA) version of the Ohio State University heat release apparatus specified in FAA specification JAR 25.853 Part IV Appendix F(1). The two-minute average heat release is less than 10 kW/m^2 compared to the FAA's required maximum value of 65 kW/m^2 .^{31,32}

Table 9.9 Thermal stability of PBI fibre

Temperature, °F/°C	Useful life
1100/600	3–5 seconds
840/450	5 minutes
750/400	1 hour
625/330	24 hours



9.14 Acid vapour resistance of PBI fibre after exposure to sulphuric acid vapour, 75% (w/v) concentration.

Furthermore, because PBI fibre does not burn in air, it releases little or no smoke and off-gases up to its decomposition temperature. The specific optical smoke density (ES or D_s) of PBI is 2 compared to values of 3 to 8 for other common high-temperature fibres.³³

- *Chemical resistance:* PBI fibre has excellent chemical resistance to a whole host of inorganic acids and bases, and organic chemicals. Chemical resistance is demonstrated by exposing PBI fibre to specific compounds and then measuring the strength retention of the fibre after the exposure. Results in Fig. 9.14 and Tables 9.10 and 9.11 show this resistance to some of the more common chemicals.
- *Physical properties:* PBI fibre has a large number of desirable physical properties that, along with the aforementioned thermal and chemical properties, make it the fibre of choice in many critical performance-based applications (see Table 9.12). In particular, its combination of high

Table 9.10 Tensile strength after immersion in inorganic acids and bases

Compound	Concentration, %	Temperature, °C/°F	Time, hr	Tensile strength retained, %
Sulphuric acid	50	30/85	144	90
Sulphuric acid	50	70/160	24	90
Hydrochloric acid	35	30/85	144	95
Hydrochloric acid	10	70/160	24	90
Nitric acid	70	30/85	144	100
Nitric acid	10	70/160	48	90
Sodium hydroxide	10	30/85	144	95
Sodium hydroxide	10	93/200	2	65
Potassium hydroxide	10	25/77	24	88

Table 9.11 Tensile strength after immersion in organic chemicals

Compound	Strength retention, %
Acetic acid	100
Methanol	100
Perchlorethylene	100
Dimethylacetamide	100
Dimethylformamide	100
Dimethylsulphoxide	100
Kerosene	100
Acetone	100
Gasoline	100

* All exposures at 30°C (85°F) for 168 hours.

moisture regain, low modulus, and good tensile strength makes it an excellent candidate for textile applications.

- *Textile properties:* PBI fibre has excellent textile properties and processes easily on conventional textile equipment. The properties of PBI fibre lend themselves to other fibres, making it an excellent candidate for blending. Products made from PBI and PBI blends are known for their superior flame resistance and soft hand and cotton-like feel. In many cases, PBI fibre will improve the processability of its partner fibre.

Table 9.13 lists the PBI fibre products that are available, along with the major applications and end-use. PBI fibre is available in a short-cut form for applications that require uncrimped, cut fibre. Short-cut PBI can be dis-

Table 9.12 Typical physical properties of PBI fibre

Property	English	Metric
Denier per filament (dpf)	1.5 denier	1.7 dtex
Tenacity	2.7 g/d	2.4 dN/tex
Breaking elongation	28.5%	28.5%
Initial modulus	32.0 g/d	28.0 g/d
Crimp (for crimped staple)	28.0%	28.0%
Finish	0.25%	0.25%
Specific gravity	1.43	1.43
Moisture regain, 20 °C, 65% rh	15.0%	15.0%
Boiling water shrinkage	<1.0%	<1.0%
Hot air shrinkage, 205 °C	<1.0%	<1.0%
Specific heat	0.3 BTU/lb °F	1.0 K/kg °C
Limited oxygen index (LOI)	>41.0%	>41.0%
Surface area resistivity, 21 °C, 65% rh		1×10^{10} ohms/cm
Colour	Gold	Gold
Standard cut lengths for crimped staple	1 $\frac{1}{2}$, 2, 3 and 4 inch	38, 50, 76 and 102 mm
Thermal conductivity	0.022 BTU/hr.ft. °F	0.038 W/m °C

Table 9.13 PBI fibre available products

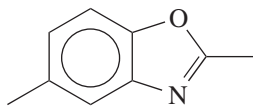
Product description	Availability	Applications	End-uses
Crimped cut staple	1.5, 2.0, 3.0 and 4.0 inch (38, 51, 76 and 102 mm)	1. Textile yarns and fabrics 2. Nonwovens	1. Fire-fighting turnout gear 2. Industrial flash-fire protective clothing 3. Aircraft fire blocking 4. Heat resistant thread
Short cut staple (uncrimped and unfinished)	0.125, 0.25 and 0.5 inch (3, 6 and 12.5 mm)	1. Compounds 2. Nonwovens	1. Friction products 2. High-temperature paper products 3. Nonwoven insulative products
Phosphonated fibre	Same as above	Where increased thermal stability is required	Aerospace applications

persed and compounded with other materials, and is used in nonwoven insulative media, friction product formulations, and high-temperature paper products. A small percentage addition of PBI short-cut fibre can substantially improve the thermal performance of many products. PBI short-cut is available in $\frac{1}{8}$ (3 mm), $\frac{1}{4}$ (6 mm) and $\frac{1}{2}$ (12.5 mm) inch lengths.

PBI is also available in the raw polymer form and solution dope. For more information on the PBI products available, see the PBI website.³⁴

9.6 Polybenzoxazoles, PBO (ARH)

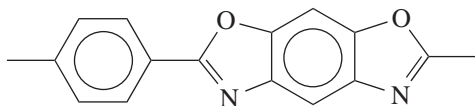
In the quest for improved polymer thermal and physical properties, introduction of the rigid benzoxazole segment:



within polymer chain backbones has been shown to improve significantly these characteristics, although problems of conversion to fibres have arisen, as they have for all linear aromatic-chain polymers.⁸ Chapter 4 discusses this generic group of fibre-forming polymers in detail and so here they will be considered from the thermal property viewpoint only.

As early as 1973, Judge and Montgomery³⁵ had demonstrated that fibres derived from complex polybenzoxazole polymers synthesised earlier by Lindsey *et al.*, showed superior thermal degradative behaviour compared to the meta-aramid *Nomex*, with negligible mass loss occurring until above 500 °C when heated in a TGA instrument. Furthermore, these fibres showed good resistance when heated at temperatures up to 250 °C in terms of tenacity retention. This extreme temperature resistance has been referred to more recently where stabilities in air up to 650 °C and well above 700 °C in inert atmospheres have been reported.³⁶

At the present time, there is one commercial example of a PBO fibre, poly(*p*-phenylene benzobisoxazole) or *Zylon*®, manufactured by Toyobo. It is evident from simple examination that the rigid and linearly symmetrical repeating aromatic structure



will have very high thermal stability and, because of the absence of aliphatic CH groups, excellent inherent flame resistance. The properties of this fibre discussed in Chapter 4 and published elsewhere^{35–38} show that fibres do indeed exhibit the very high onset of thermal decomposition temperature

of 650°C and a LOI value of 68. While there are at least two variants of fibre, *Zylon-AS* and *Zylon-HM*, of which the latter has the higher modulus, they both have these same thermal and burning parameter values. These properties demonstrate that PBO fibre is the most thermally stable and flame resistant of all organic polymer fibres commercially available at the present time, as summarised in Table 9.14. This thermal stability is shown also by their greater strength retention when heated to temperatures above 200°C, compared to the meta- and para-aramids.³⁸ Thus, when heated to 300, 400 and 500°C, *Zylon-HM* retains about 65%, 50% and just below 40% respectively, of its normal ambient tenacity. In addition, when heated at temperatures as high as 400°C for periods as long as 3 hours, the fibres lose only about 5% of their mass. Clearly, these properties, coupled with a very good resistance to hydrocarbon (e.g. gasoline), polar (e.g. dimethylformamide, methyl ethyl ketone) and hydrogen-bonding (e.g. methanol) solvents makes the fibre ideal for end-uses such as hot gas filtration.

The fibre is available in staple, filament and chopped forms and finds applications in the area of thermal and fire resistance products where a combination of these properties with high tenacity and modulus are required. Principal examples are heat-protective clothing including gloves, hot gas filtration media, high temperature conveyor beltings and reinforcements, and aircraft fragment/heat barriers.

9.7 Final comments (ARH)

This chapter has demonstrated that a significant number of fibres exist that have high levels of heat resistance and, usually, accompanying high levels of flame or fire resistance. Furthermore, as Table 9.14 shows, the range and level of fibre performances are considerable. Usually, however, the selection of a particular fibre for a specified use is governed by a balance of the overall properties, ease of processibility and, of course, cost. In the case where very high levels of thermal resistance, fire resistance, or both, are essential, then these respective fibre properties will be major selection criteria.

It should be mentioned at this point that, while the design and selection of flame and fire resistance of textiles comprising these fibres is made on data such as that presented in Table 9.14, there is now an increasing tendency to measure heat-release rates determined by calorimetric techniques. This has been driven by the recognition that fire spread is determined by the heat release of ignited component materials, and the definition of minimal heat-release values using standard calorimetric methods^{31,32} has been enshrined in civil aviation authority regulations since the late 1980s.⁴⁰ The latter define values measured using the Ohio State University (OSU) calorimeter whereas the more recently developed cone calorimeter finds

Table 9.14 Summary of thermal and flammability parameters³⁹

Fibre genus	Second order temperature, °C	Melting temperature, °C	Onset of decomposition, °C	Maximum, continuous use temperature, °C	LOI, %
Melamine–formaldehyde	NA	NA	370	190	32
Novoloid	NA	NA	>150	150/air; 250/inert	30–34
<i>m</i> -Aramid	275	375–430 (decomp)	425	150–200	28–31
<i>p</i> -Aramid	340	560 (decomp)	>590	180–300	29–31
Arimid (P84)	315	—	450	260	36–38
Aramid-arimid	<315	—	380	NA	32
Semicarbon	NA	NA	NA	~200/air	55
PBI	>400	NA	450/air; 1000/inert	~300 (est)	>41
PBO	—	—	650; >700/inert	200–250 (est)	68

Notes: NA = not applicable; (decomp) = with decomposition; (est) = value estimated from data in cited references.

Table 9.15 Peak heat release (PHR) values for selected heat-resistant fibres and polymers⁴¹⁻⁴⁵

Fibre/blend	PHR, kW m ⁻² (OSU; 35 kW m ⁻² incident flux)	PHR, kW m ⁻² (cone calorimeter, 50 kW m ⁻² incident flux)
Wool	—	286
63% oxidised acrylic/17% aramid/ 20% pvc	34	—
80% oxidised acrylic/ 20% aramid	38	—
33% modacrylic/ 35% FR viscose/ 32% aramid	47	—
Mixed m- and p- aramid	—	53
Oxidised acrylic	—	77
PBO (film)	47	—
PBO (carbon fibre (40%)/PBO(60%)) composite	—	50

greater acceptability in the wider fire science community.³¹ Unfortunately, there is not very much published data regarding heat-release rates either as peak values (PHR) or average values available for the fibres discussed in this chapter. Such PHR values that are available are listed in Table 9.15 for incident heat flux values of 35 kW/m²,^{32,45} or 50 kW/m².⁴¹⁻⁴⁵ A value for wool is included merely to provide a reference PHR value more representative of a moderately flammable fibre.⁴⁴ The values for PBO are for film and composite variants. In order to pass civil aviation authority requirements, peak heat-release rates of samples subjected to 35 kW/m² incident heat flux must emit 65 kW/m² or less^{32,40} and fabrics having the lowest values are those that comprise fibres having the highest degradation temperatures and LOI values (see Table 9.14).

An observation that is perhaps worthy of note is the very large number of speciality fibres reported in the literature and often patented since the 1960 period, of which only the fibres described in this chapter have survived as commercial examples. Furthermore, not until very recently has the general commercial availability of these fibres increased, as reductions in costs coupled with increasing performance demands have enabled them to displace the more conventional fibres. For example, before the 1960s, in high temperature uses such as hot gas filtration, because synthetic fibres were thermoplastic with only moderate to good thermal degradation resistance, their use was and still is limited to constant exposure temperatures of less

than 120°C or so. One exception, however, is the homopolymeric polyacrylic group by *Dralon T* from Bayer. This fibre type competed with the meta-aramids during the 1970–1990 period and could be used at constant temperatures as high as 150°C in hot air atmospheres. This fibre genus seems not to be available today and, as shown in Table 9.13, the fibres discussed therein are clearly superior in terms of both temperature and fire resistance.

Another acrylic-related fibre which has recently ceased to be a commercial entity⁴⁶ is the polyacrylate *Inidex* (Acordis),⁴⁷ which is a zinc ion crosslinked acrylic polymer-based fibre often referred to generically as a polyacrylate. This non-thermoplastic, naturally pinkish-coloured fibre, unfortunately, while having a minimum LOI value of 31% with values as high as 41–45% being reported,⁴⁷ was relatively weak (0.12–0.15 N/tex) and so lent itself only to nonwoven fabric production methods. It has seen application in barrier products such as fire blankets, protective clothing and heat shields. However, a recent French development by Tecfibres SA is an improved polyacrylate, *Tecstar FR*, which is claimed to be available in a range of colours and have excellent processibility.⁴⁶

Evidently, the improvements in thermal performance have been significant during the last 20 years and these have not only enabled longevity of many textile and related products to be increased but also higher limits of performance to be achieved. It will be interesting to see whether further improvements in performance will be forthcoming during the next 20 years and whether the performance limits expected of fibre-forming organic polymeric structures have already been reached in structures such as the semi-carbon oxidised acrylic, PBI and PBO fibres.

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Appendix

Quantities and units

The quantities and units used to describe properties of high-performance fibres have a diversity based on technical, historical and cultural factors. No attempt has been made in editing this book to enforce uniformity. Authors have used the terminology with which they are most comfortable, and this has an educational value for readers. This Appendix describes the factors involved and provides guidance for interconversion.

The size of fibres can be expressed either spatially or gravimetrically. Dimensions are normally expressed as diameters in μm , though sub-multiples of inches are found in older literature. Fibre densities are normally expressed in g/cm^3 , though strict SI uses kg/m^3 , which gives numbers 1000 times larger. For yarns, account must be taken of the space between fibres, defined by the packing factor, so that linear dimensions are not used as a specification, though they are needed in calculations of fabric geometry.

For both fibres and yarns, the linear density, namely, the mass per unit length, is the best way of characterising the size. Historically, there are many units: both direct 'weight per unit length' units and indirect counts, which derive from the number of hanks of a given length making a certain weight. In the glass fibre industry, there is use of yardage, namely yards per pound. Strand count is defined as yardage/100. The manufactured textile fibre industry adopted the silk unit of *denier*, but later a rational metric unit, *tex*, which is accepted by SI, was introduced and is now the preferred form. Because of the similarity in magnitude to denier, the sub-unit *decitex* (*dtex*) is widely used. These units are:

$\text{tex} = \text{gram per kilometre (g/km)}$

$\text{decitex} = 0.1 \text{ gram per kilometre}$

$\text{denier} = \text{gram per 9000 metres} \quad 1 \text{ denier} = 0.11 \text{ tex} = 1.1 \text{ dtex}$

$\text{strand count} = 100 \text{ yards per pound} = 4960/\text{tex}$

The diversity becomes enormous when covering stress and related strength and stiffness values.

Table A1 Unit conversions

Specific stress	Stress: density in g/cm ³ times
1 – N/tex, kJ/g, GPa/g cm ⁻³ , (km/s) ² – 10 cN/dtex, 10.2 gf/dtex, 11.3 gf/den – 102 gf/tex, kmf, kgf mm ⁻² /g cm ⁻³ 239 cal/g, 430 Btu/lb	1 – GPa, J/mm ³ – – 102 kg/mm ² 145 ksi
10 ³ – mN/tex, J/g, MPa/g cm ⁻³ – – 145 000 psi/g cm ⁻³	10 ³ – MPa, N/mm ² – 10 ⁴ bar, 9869 atm – 145 000 psi (psi = lbf/in ²)
*10 ⁶ – N/kg m ⁻¹ , J/kg, Pa/kg m ⁻³ – 3.94 × 10 ⁶ inchf, psi/(lb/cu in) –	10 ⁶ – – 7.5 × 10 ⁶ mm Hg –
10 ⁹ – – 10 ¹⁰ dyn/g cm ⁻¹ , erg/g	*10 ⁹ – Pa, N/m ² , J/m ³ , kg m ⁻¹ s ⁻¹ – 10 ¹⁰ dyn/cm ²

Notes: * strict SI units.

Other multiples are also used.

Gravitational units, written above as gf etc, are also found in forms such as: g, e.g. d/den, gm, or g-wt; lb or lb-wt; km, km-wt or Rkm.

First, either volume or mass measures may be used. In physics and engineering, stress is defined as force/area. Because of the uncertainty in the area of cross-section of yarns and fabrics and, even for solid fibres, the fact that linear density is easier to measure than area, the use of specific stress, namely force/(linear density) is preferred. Unless drastic changes occur, the linear density at zero stress is invariant, whereas packing factors can vary. It is also easy to compare the conversion of properties from molecules to fibres to yarns to fabrics: at all levels the mass is known.

Second, gravitational force units, often abbreviating g-wt or gf to g or gm, may be used instead of the physically correct inertial units. Third, quantities that are dimensionally identical can be defined and used in different ways. Fourth, there is a choice of unit systems: CGS or SI metric units or the old Imperial units, which are still widely used in USA. It is not uncommon to find mixtures, such as psi/(g/cm³).

The preferred unit for specific stress, specific modulus and tenacity is N/tex. Expressed in other ways, this equals stress/density in GPa/(g/cm³) and energy per unit mass in kJ/g. The modulus in N/tex equals the wave velocity in (km/s)². Strength can also be expressed in terms of break length, namely the length of material that will break under its own weight. Kilometre-force is most used, but brochures of one fibre manufacturer give strength in inches. Finally, for the first 50 years of manufactured fibres, the common unit was g/den. Because of the similarity in size, the use of cN/dtex, equal to 1.13 g/den, is common.

Table A1 gives the conversion factors between the above units and many others, which may be found in the literature or used in particular contexts.

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