1

Introduction

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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-

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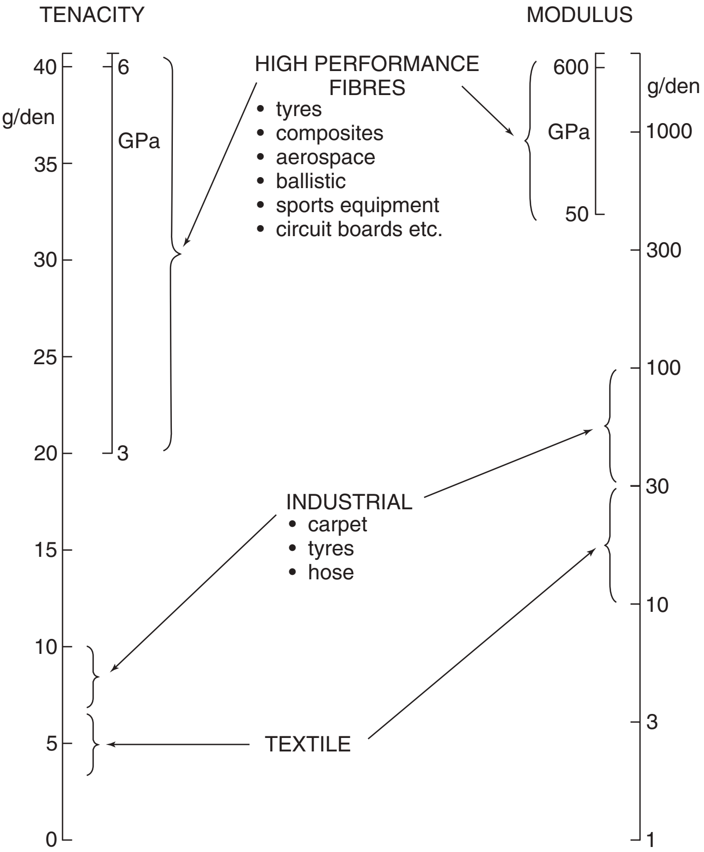
* See Appendix for a note on units.



1.1 The step change in strength and stiffness from first generation to second generation manufactured fibres. (After Mukhopadhyay[1])

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

12 N/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 2 N/tex and moduli up to 80 N/tex. Other polymer fibres have now reached tenacities over 3.5 N/tex and moduli over 150 N/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 (3 N/tex) and moduli over 800 GPa (400 N/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 (1.6 N/tex) and moduli 90 GPa (35 N/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 (100 N/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, Staudinger[5] 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 kg/mm^2 were calculated in the direction of primary bonds, but only 45 kg/mm^2 (~0.5 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 40*x*. 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.

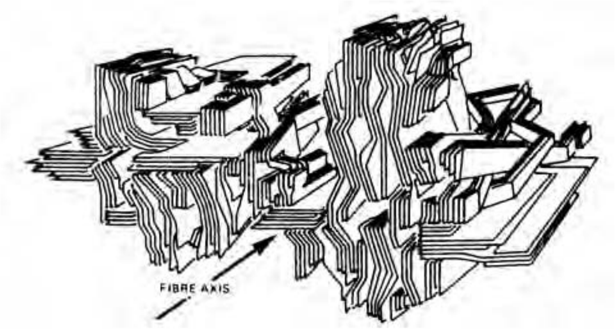
Both routes to HM-HT fibres have drawbacks. Except for the copolyesters, the rigid rod polymers are difficult to process, because they decompose chemically before they melt and require strong acid solvents. The HMPE fibres have a low melting-point, which limits their utility. Unfortunately, no way has 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.

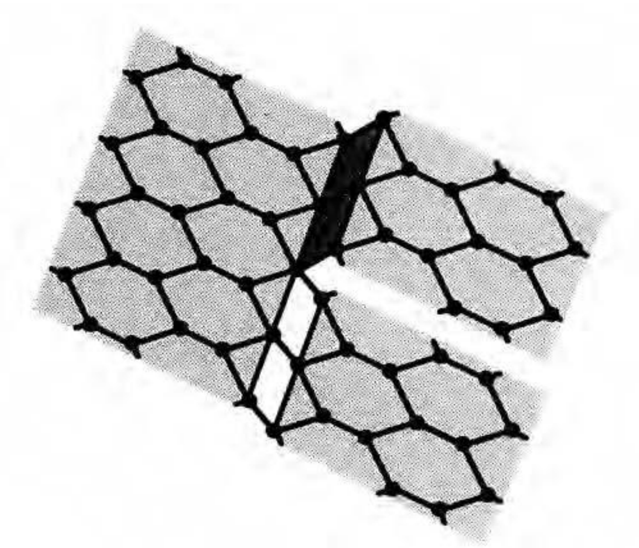
1.2.3 Graphitic sheets

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])

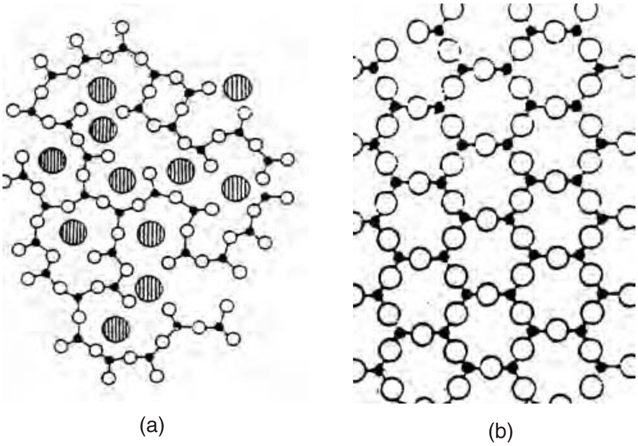


1.4 Possible interconnection between graphite planes. (Hearle[10])

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.

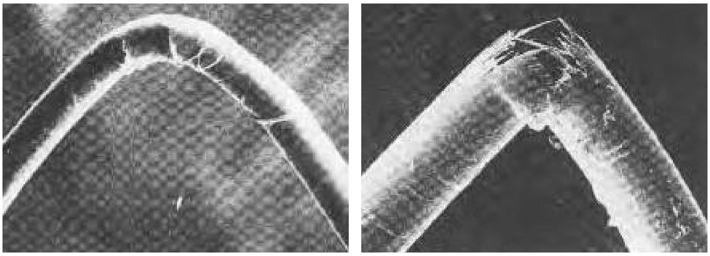
Carbon fibres tend to be closer to the 3D model, though their compressive properties are weaker than their tensile properties.

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 Skelton[12] 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 bending[12]

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
Kevlar 49	3.0	100
X-500	2.6	4.3
Steel, annealed	11.2	100
Boron, 92 μm	0.7	0.9
Polyester	7.0	100


(a) (b)

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.

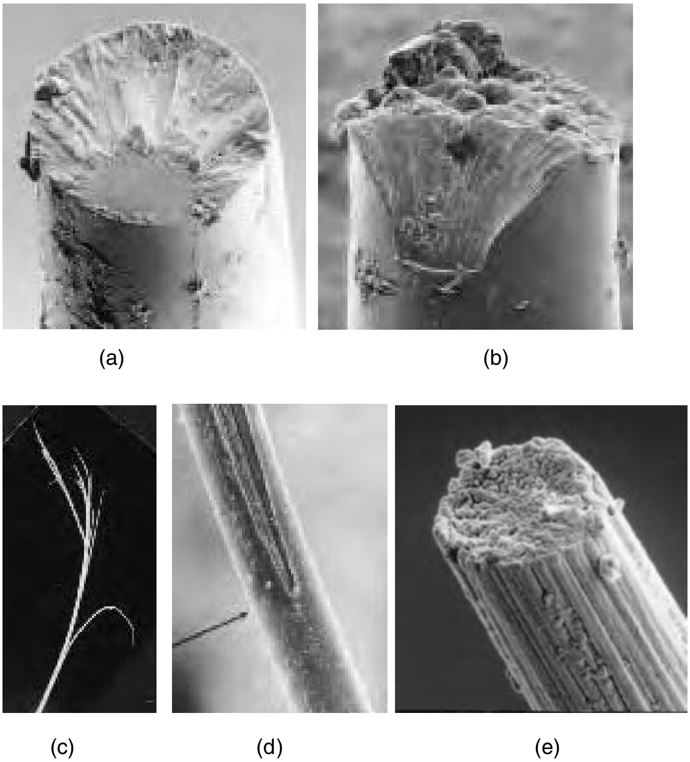
fatigue failures. In tension–tension cycling of ropes, it is possible for a component to go into compression, due to uneven loading or rope twisting, which causes the fibres as a whole to buckle into sharp kinks – and in turn to kink bands at the molecular level inside the fibres. For this reason, it is recommended[13] 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


(a) (b)

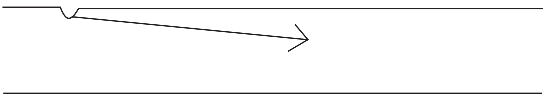
(c) (d) (e)

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.

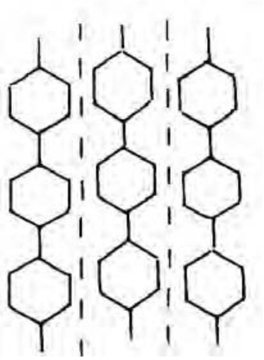
mirror region until multiple new crack initiation forms the final hackled region. This contrasts with ductile crack propagation in common melt-spun fibres, such as nylon and polyester, where a slow ductile crack propagation causes a V-notch to open up, with extensive plastic yielding on the other side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

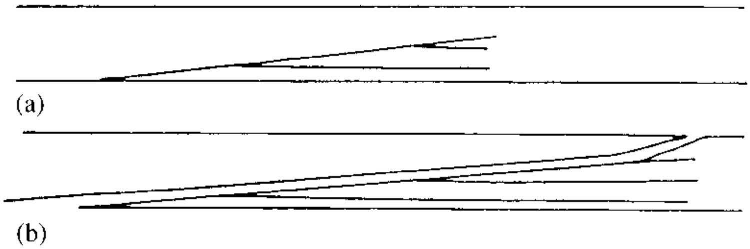
Yang,[15] in his classic text on *Kevlar*, refers to three basic forms of fracture: 'type (a), pointed break: type (b) fibrillated break: type (c) kink band break'. Type (a) corresponds to the single split and type (b) to the multiple split, which may be opposite sides of the same break. The kink-band 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. Yang[15] 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 compresion 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 5000 m/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 patent[18] refers to speeds of less than 50 m/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 patent[18] 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
Polyester	3
High-modulus polymer fibres	
para-aramid	25
meta-aramid	20
HMPE	25
Vectran	47
Zylon (PBO)	130
Tensylon (SSPE)	22–70
Carbon	
PAN based	14–17
pitch based – general purpose	15
– highest modulus	2 200
oxidised acrylic	10
Glass	3
E-glass	15
S-2 glass	
Ceramics	
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	1 070
Thermally and chemically resistant fibres	
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 100 kg of weight saved in an aircraft reduces fuel costs by $20 000 per year and increases the range by 100 km.[19] Or will routes be found to lower-cost production that compete with fibres for the large-volume market for technical 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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