5

Carbon fibres

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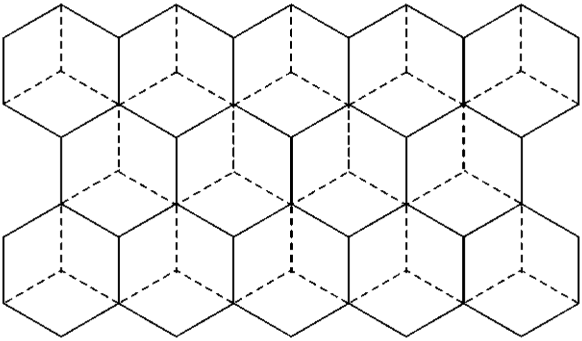
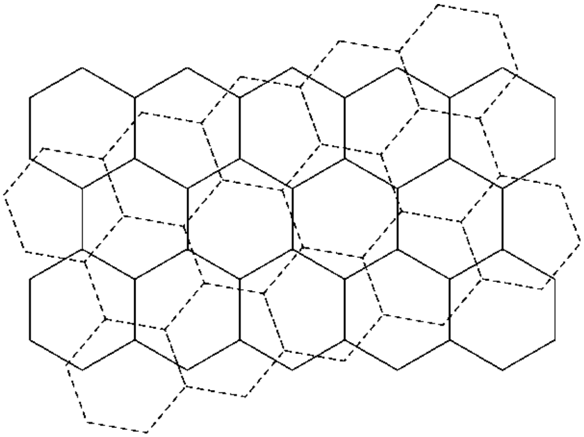
5.1 Introduction

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 Peebles[3] 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.

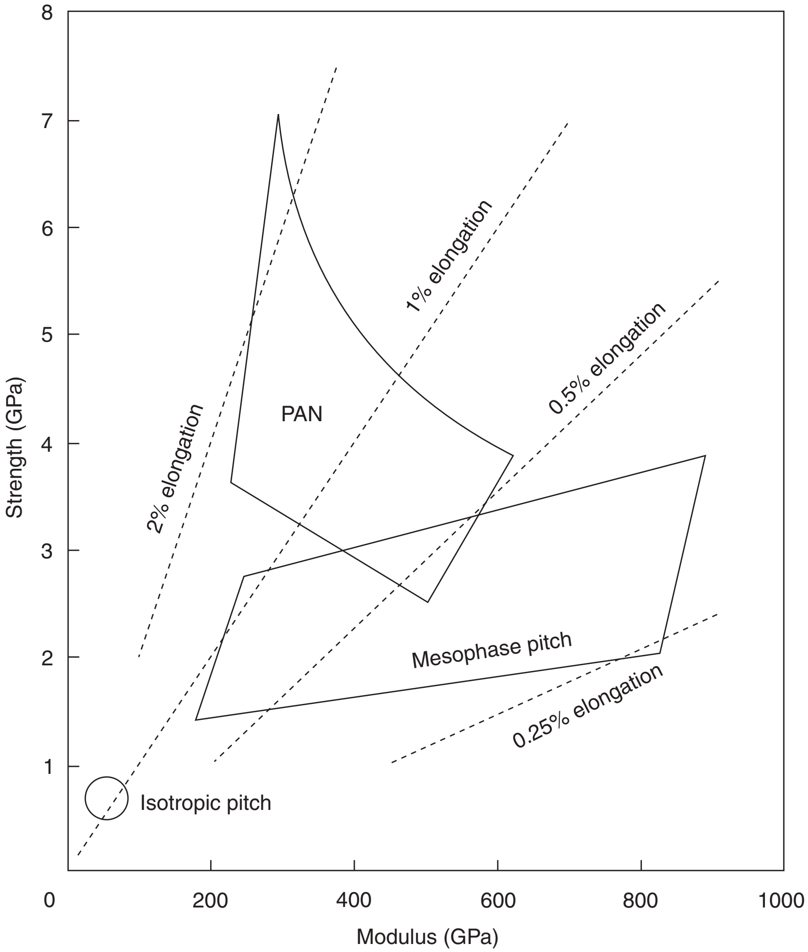
The word 'graphite' is much misused in carbon fibre literature. The word refers to a very specific structure, in which adjacent aromatic sheets overlap with one carbon atom at the centre of each hexagon, as shown in Fig. 5.1. This structure appears very rarely in carbon fibres, especially in PAN-based 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

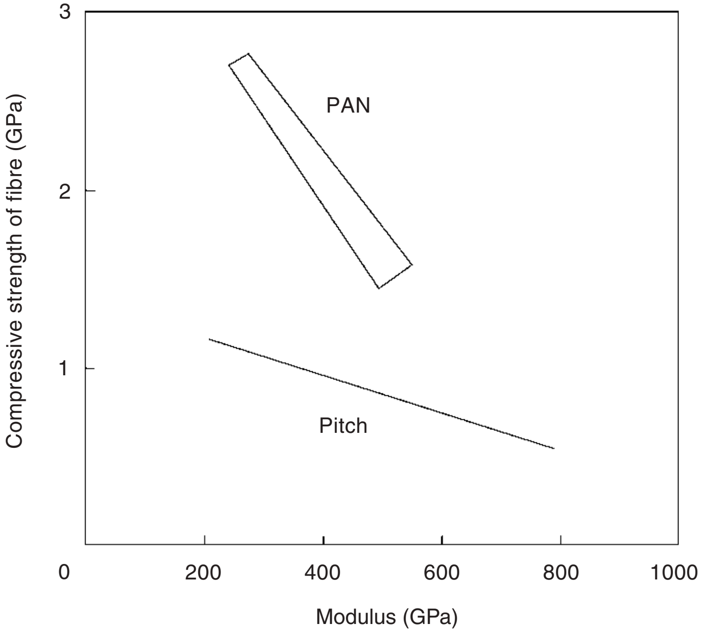
Table 5.1 Mechanical properties of selected carbon fibres

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

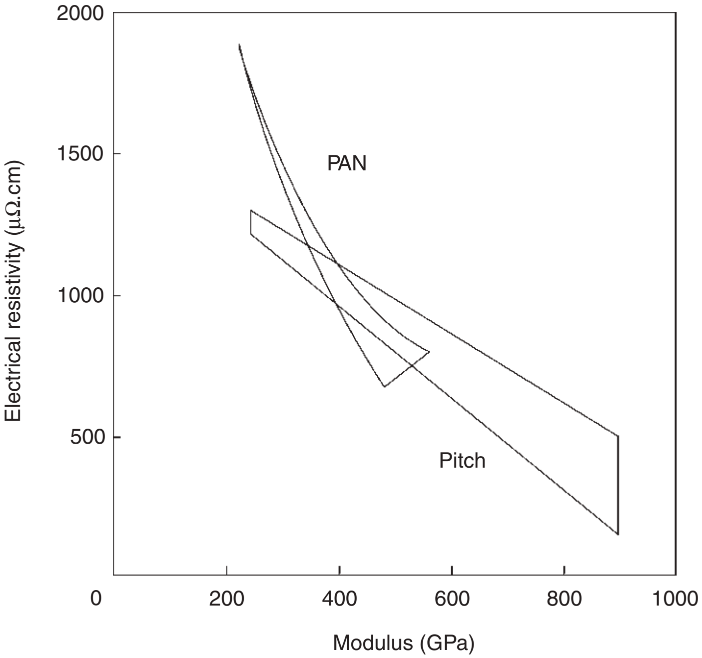


5.3 Tensile properties of carbon fibres.

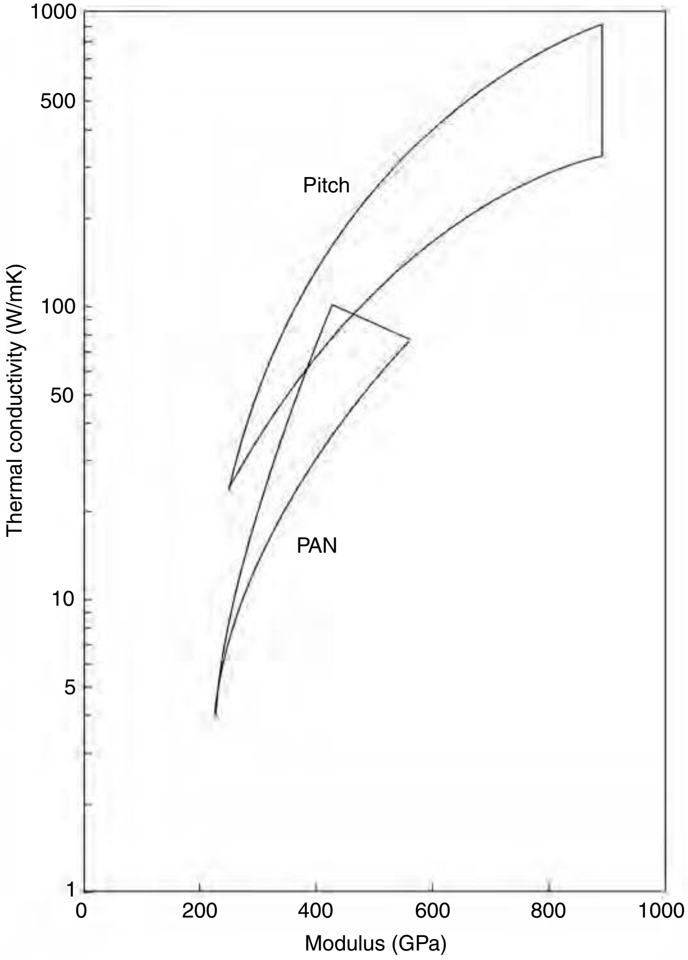
strength versus modulus. 'General purpose' fibres made from isotropic pitch have modest levels of strength and modulus. However, they are the least expensive pitch-based fibre, and are useful in enhancing modulus or conductivity in many applications. PAN-based fibres are the strongest available; however, 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.



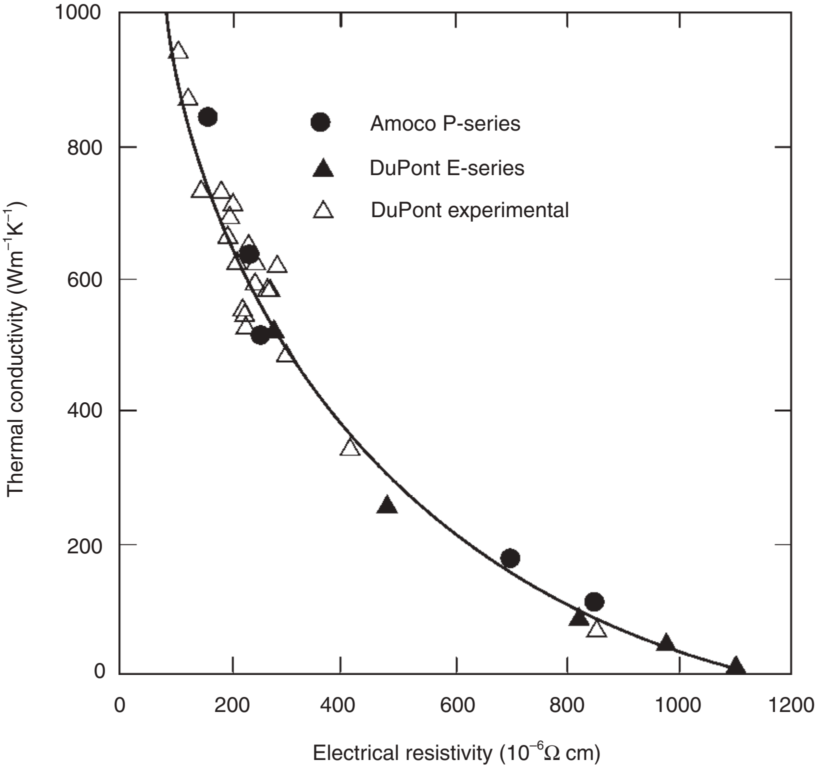
5.5 Electrical resistivity of carbon fibres.



5.6 Thermal conductivity of carbon fibres.

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

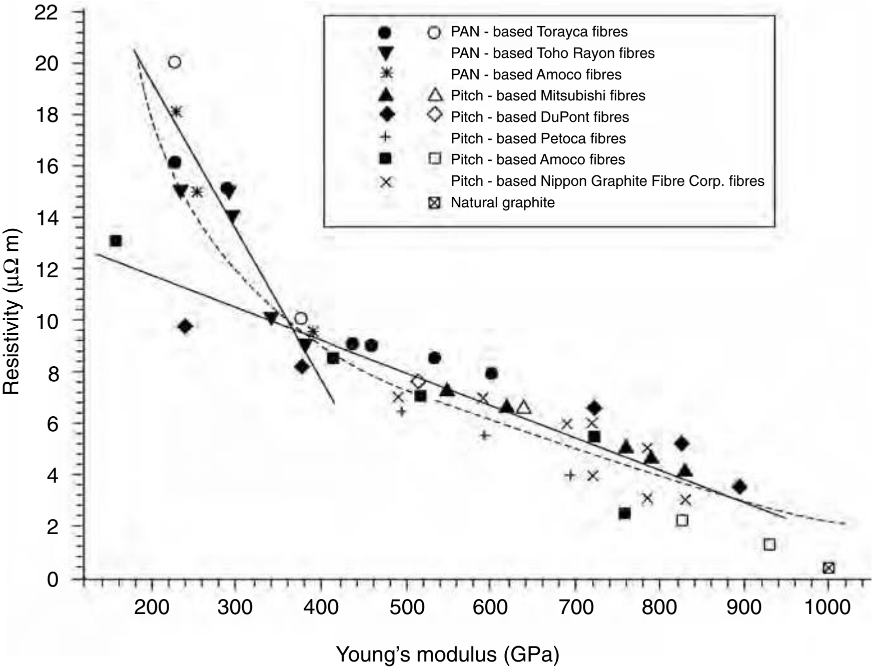
Finally, there is a property of high-performance carbon fibres, both PAN and mesophase pitch-based, which sets them apart from other materials. They are not subject to creep or fatigue failure. These are important characteristics for critical applications. In a comparison of materials for tension members 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]

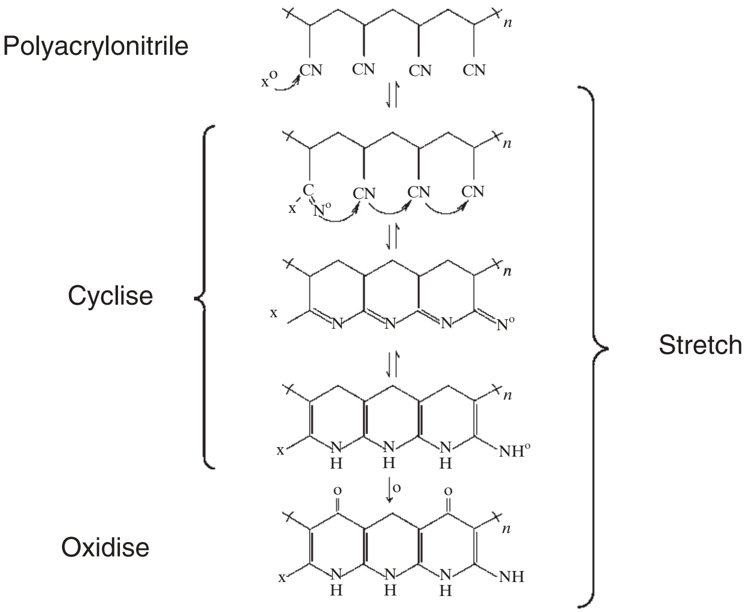


5.8 Relationship between Young's modulus and electrical resistivity in carbon fibres.[8] (Copyright 1997, reproduced with permission from Elsevier Science.)

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

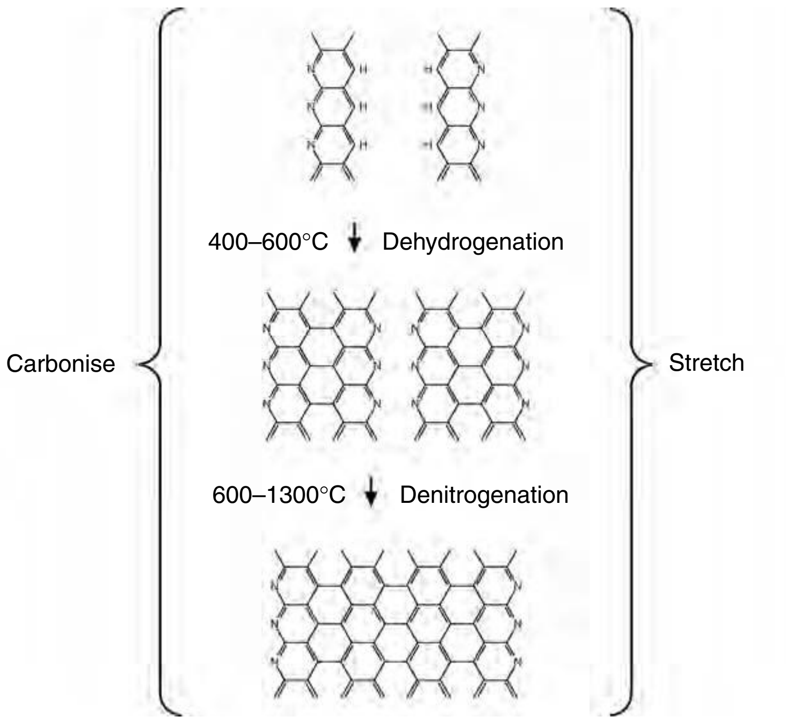


5.9 PAN-based carbon fibre chemistry: cyclization and oxidation.

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).



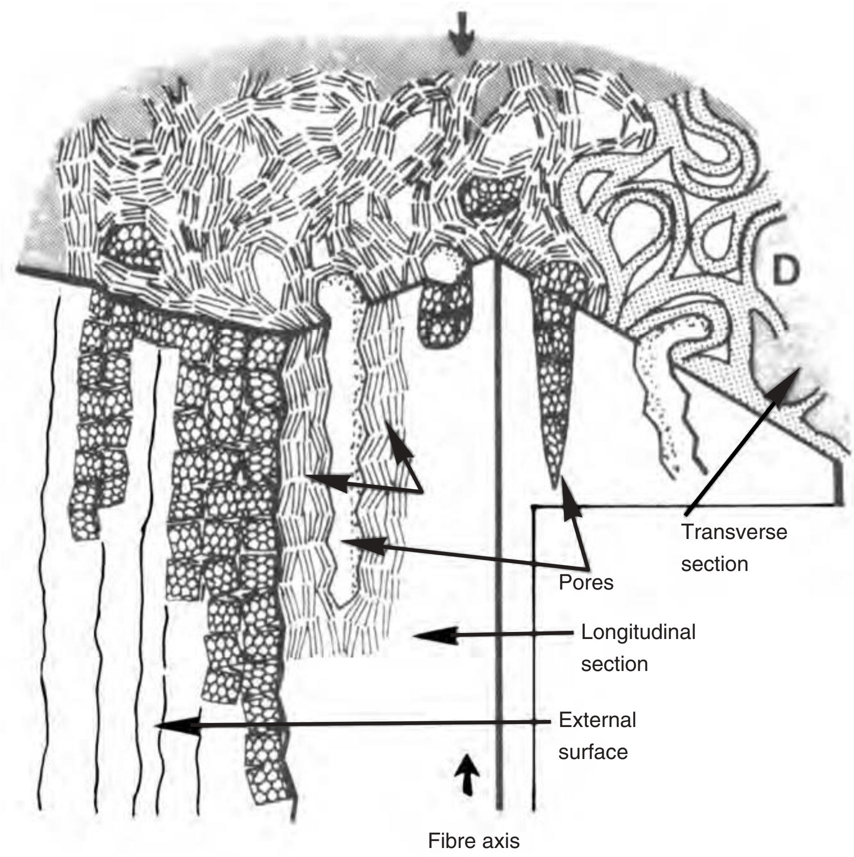
5.10 PAN-based carbon fibre chemistry: carbonisation.

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 ~1.8 g/cm^3, compared with 2.28 g/cm^3 for pure graphite, and 2.1 g/m^3 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



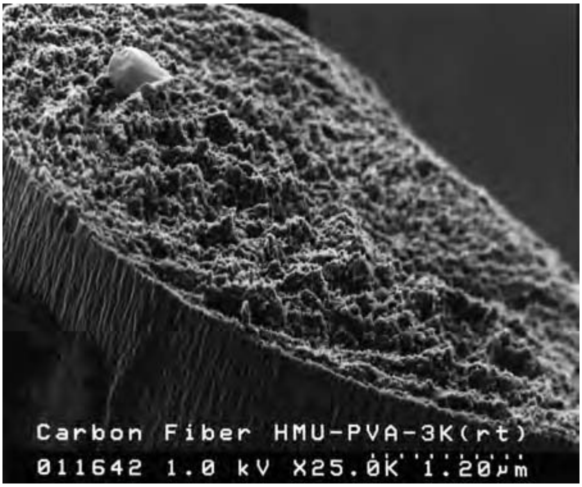
5.11 **Model of microtexture of high tensile strength PAN-based carbon fibre.[9] (Copyright 1984, reproduced with permission from Elsevier Science.)**

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.

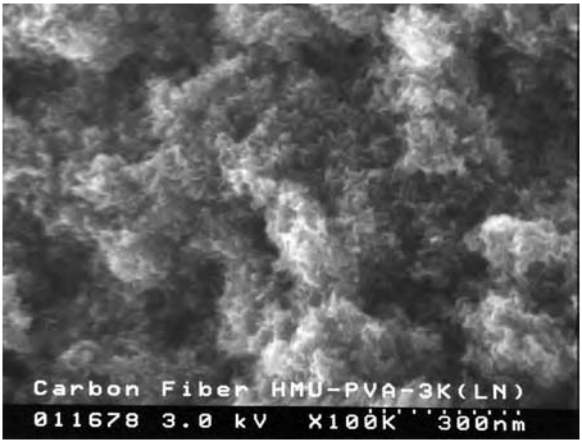
5.4 Pitch-based carbon fibres

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



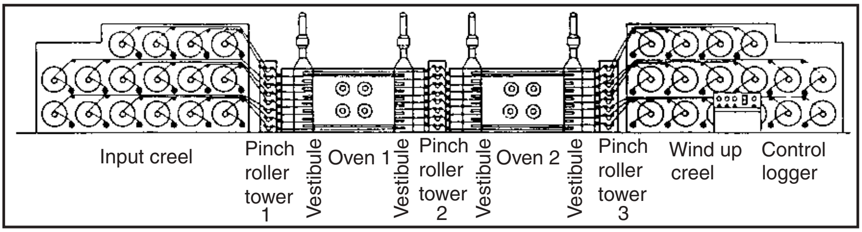
5.12 PAN-based carbon fibre fracture surface.[10]



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 Pa s 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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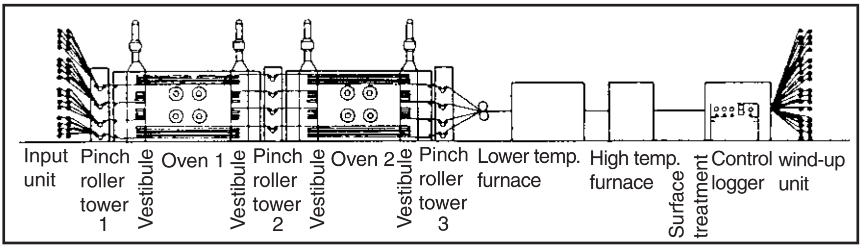


CARBONISING LINE

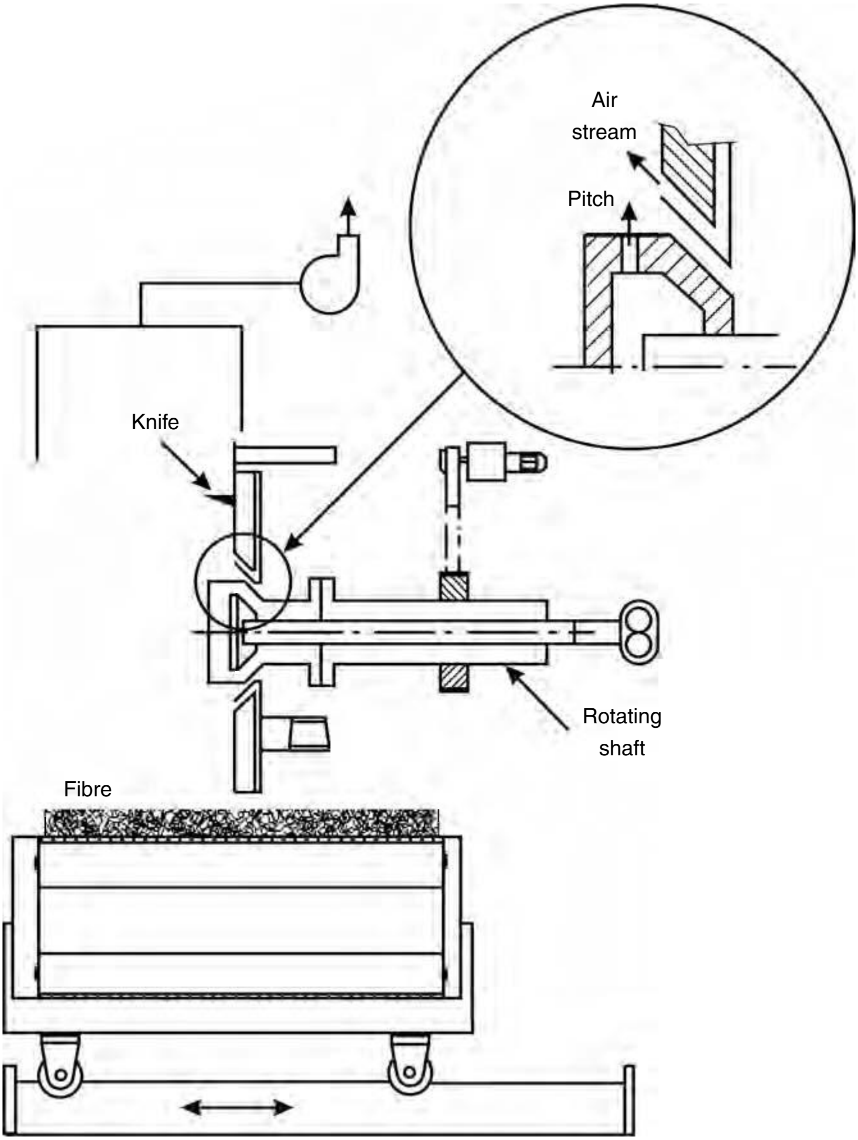
5.14 Schematic diagram of machinery for production of carbon fibres. (Reproduced from *Fiber Reinforcements for Composite Materials*, ed. A R Bunsell, Elsevier 1988, p. 103.)

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 forwarding 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]

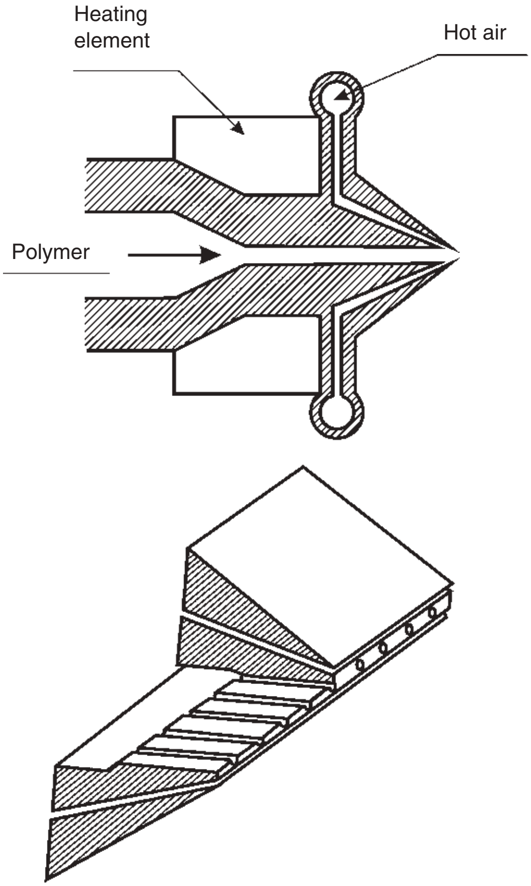
5.4.2 High-performance pitch-based carbon fibres

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.

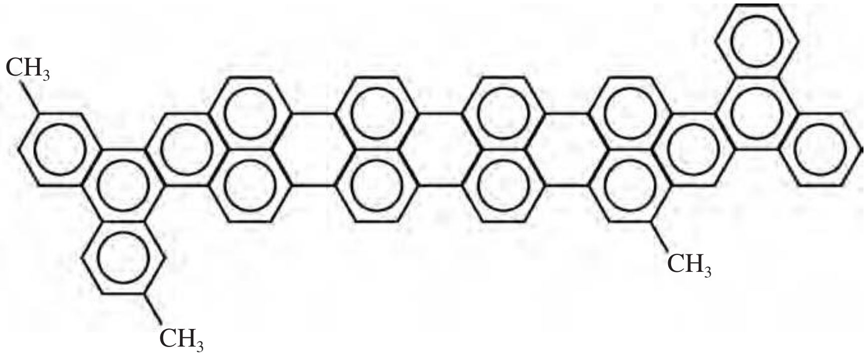


5.15 Centrifugal spinning apparatus.

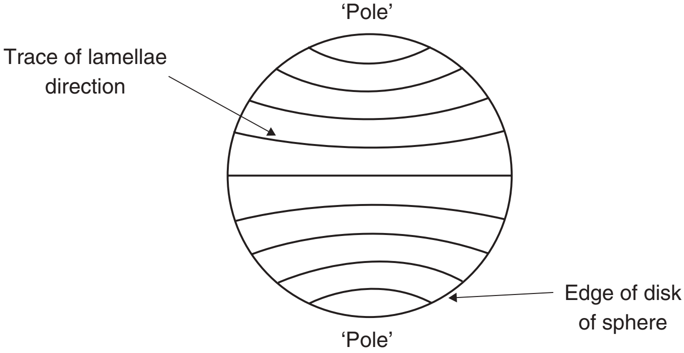
There are three common elements in pitch preparation: first, a highly aromatic feedstock; second, a process for polymerising the molecules; third, a process for separating out the unreacted feed molecules. The feedstock is typically a decant oil from cat cracker bottoms. When polymerised, the pitch molecule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

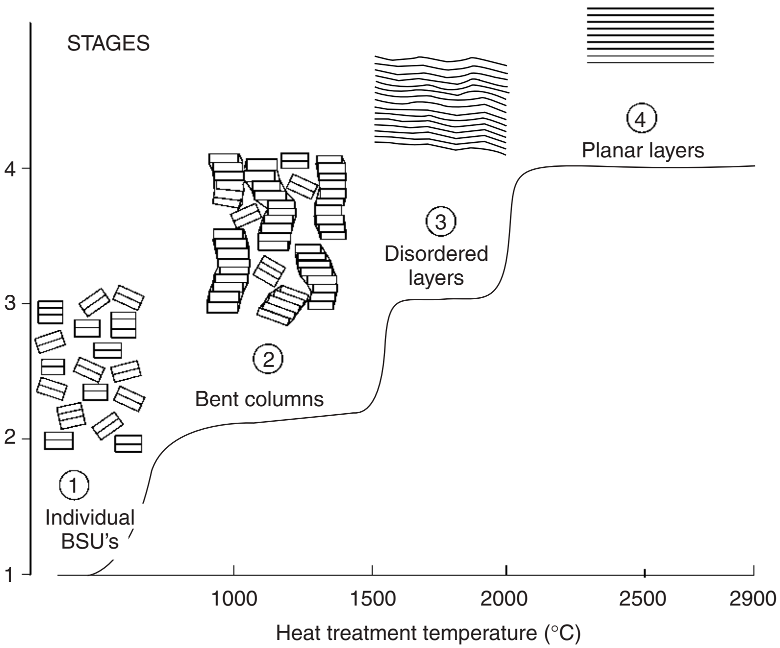


5.18 Brooks and Taylor sphere.

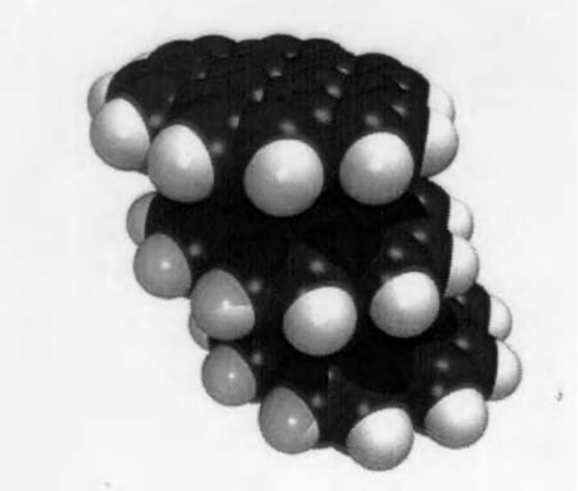
When they get sufficiently large, the pitch molecules aggregate will form 'Brooks and Taylor' spheres,[16] as shown in Fig. 5.18. These in turn coagulate to form larger spheres and then, as polymerisation continues, there is a phase inversion and a continuous nematic liquid crystalline phase, typically called mesophase (Greek for changing phase) is formed. In a classic treatise showing the various structural changes as the pitch progresses to graphite, Oberlin[17] 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.

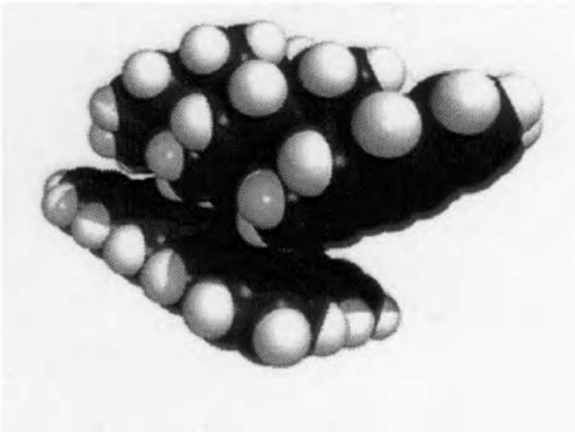
Petroleum-based pitches are typically made from the same slurry or decant oils used to make isotropic pitches. The earliest processes for making mesophase pitches used a long heat soak (typically about 30 hours at 400 °C) under an inert atmosphere, while a gas sparge was used to take away volatile compounds.[19] 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.)

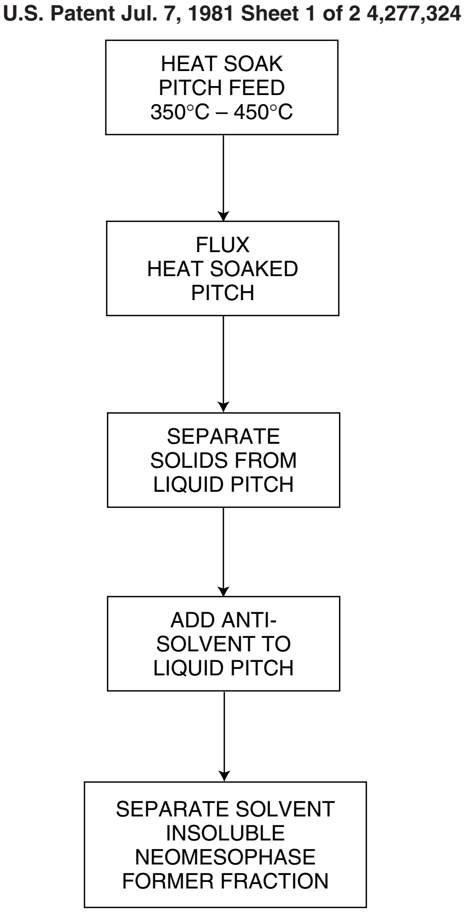
Coal-tar pitches are a by-product of coke ovens associated with steelmaking operations. They differ from petroleum pitches in their rheological properties; for a given molecular weight, the flow viscosity is much higher. Coal-tar pitches also have fewer aliphatic groups on the molecules, which gives 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 Riggs[21] 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



5.22 Process for preparation of mesophase pitch.

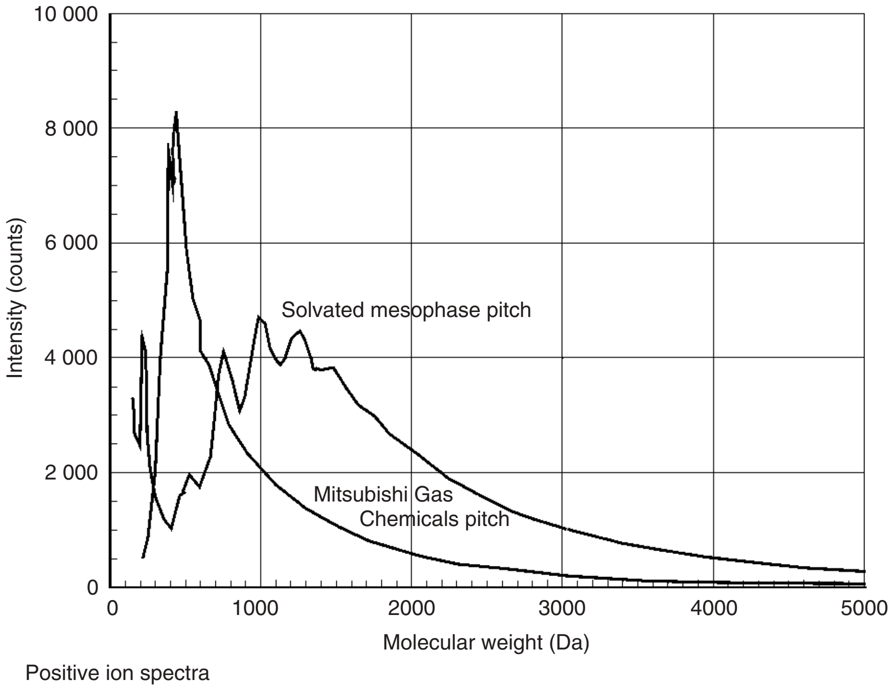
or toluene, and the insoluble fraction (high molecular weight material) rejected. Next, a poor solvent was added to the solution, causing precipitation of the higher molecular weight material remaining. The lowest molecular weight material remained in solution and was rejected. The precipitate was then 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

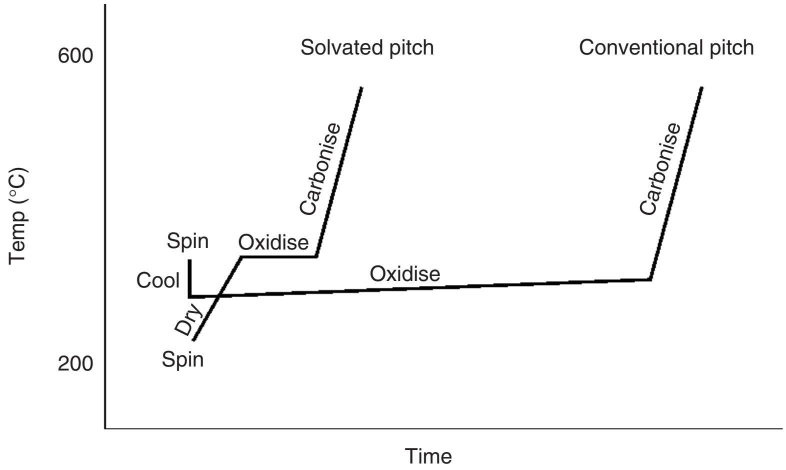
Polymerisation of aromatic molecules is known to be promoted by 'Lewis acid' catalysts such as $AlCl_3$. However, large ratios of acid to oil are needed, and it has proven difficult to remove all of the catalyst from the finished pitch. Mochida *et al.*[24] realized that a strong Lewis acid combination, 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 napthalene[24] or methylnapthalene.[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



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



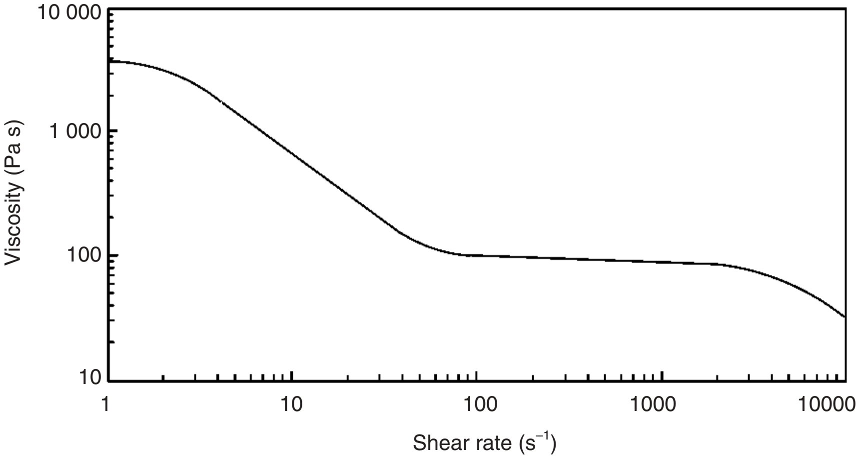
5.24 Comparative thermosetting of solvated and conventional mesophase pitch fibres.

in Section 5.4.1. Typically, melt-blown carbon fibres are curved and low in strength. However, advances in this technology[29] 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.

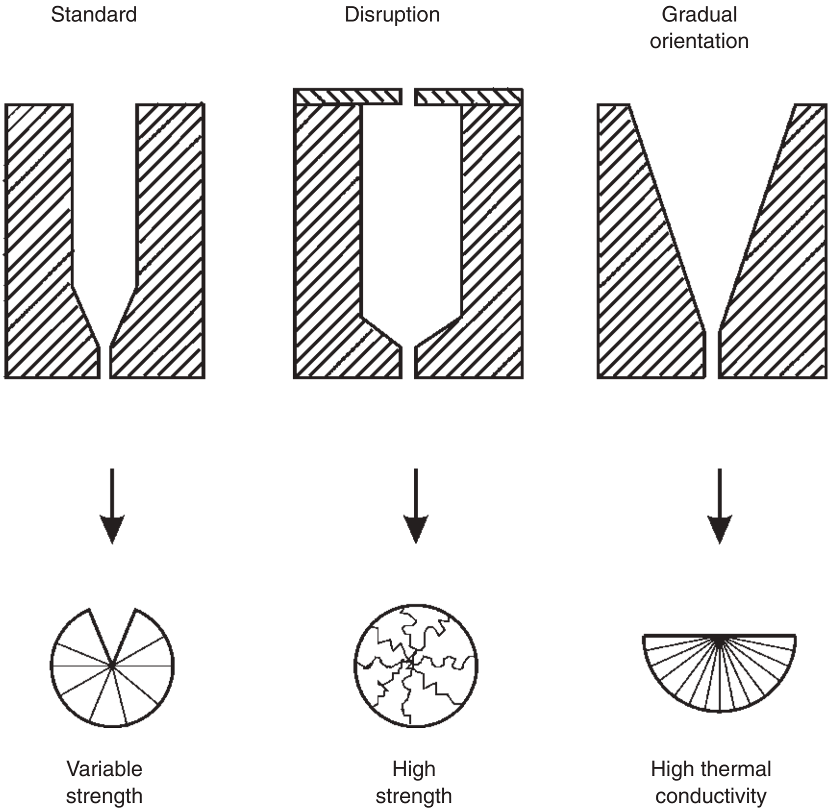
necessitates uniform treatment of bundles of fibres in downstream processing. However, processing rates are generally low and greatly depend upon the quality of the pitch feedstock. Pitch rheology and the arrangement of the discotic liquid crystal determines mesophase pitch structure[33] and resultant 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

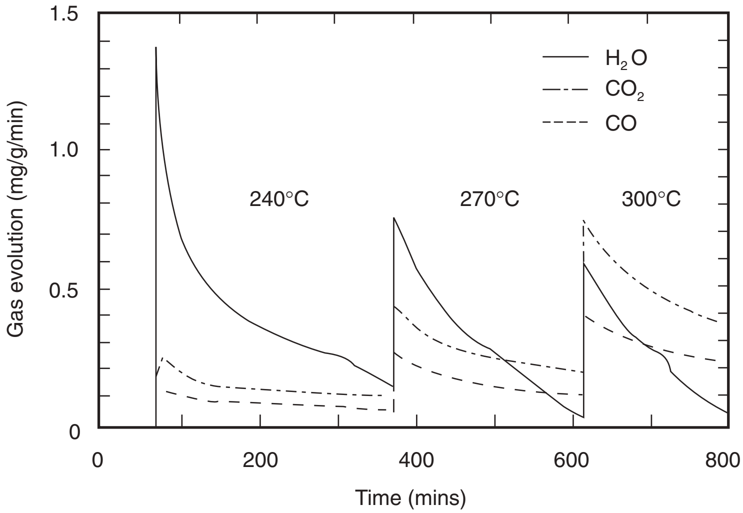


5.26 Influence of spinneret design on fibre morphology.

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.

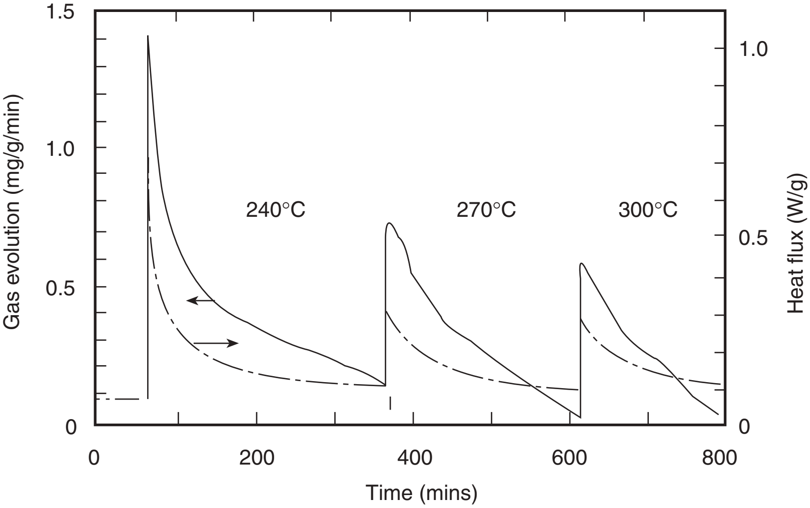
The stabilisation reaction is controlled by the diffusion of oxygen into the fibre, which is a slow process. The diffusion rate is known to increase with



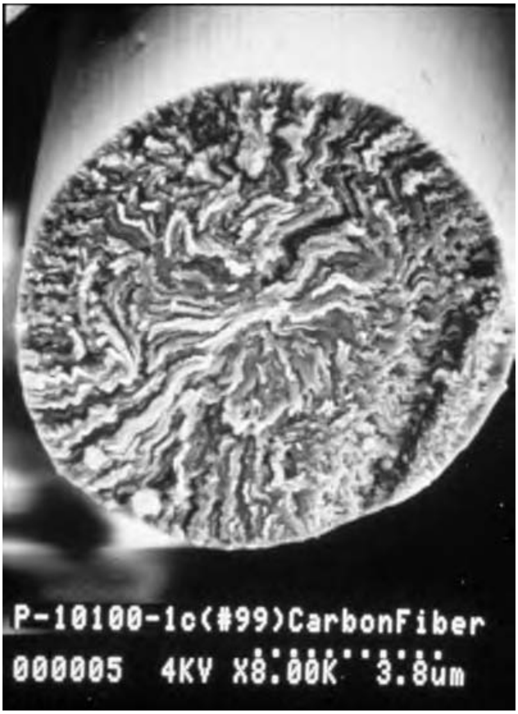
5.27 Gas evolution as a function of temperature during stabilisation.[40] (Copyright 1992, reproduced with permission from Elsevier Science.)

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 CO_2, 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.

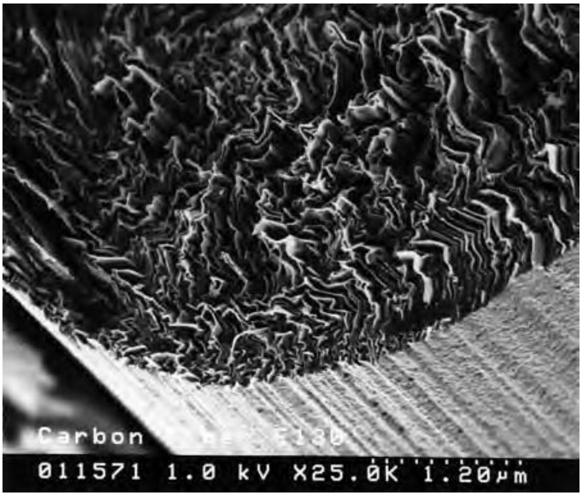
Lavin[40] shows comparative rates of evolution of water, CO and CO_2 when fibres are stabilised in air in a stepped temperature sequence. In this experiment the temperature was held at 240 °C for 6 hours, raised to 270 °C for 4 hours and then to 300 °C for 3 hours. Water evolution spiked at the beginning of each cycle, and then fell off gradually close to zero (see Fig 5.27). CO and CO_2 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



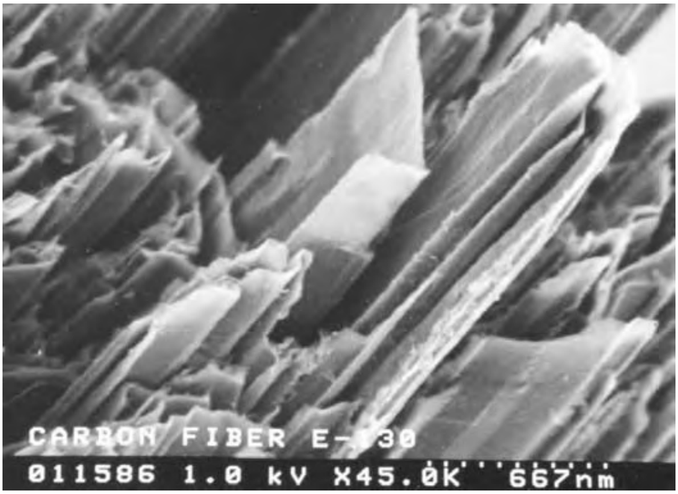
5.28 Gas evolution and heat flux as a function of temperature during stabilisation.[40] Arrows point to relevant axis. (Copyright 1992, reproduced with permission from Elsevier Science.)



5.29 Pitch-based carbon fibre fracture surface.



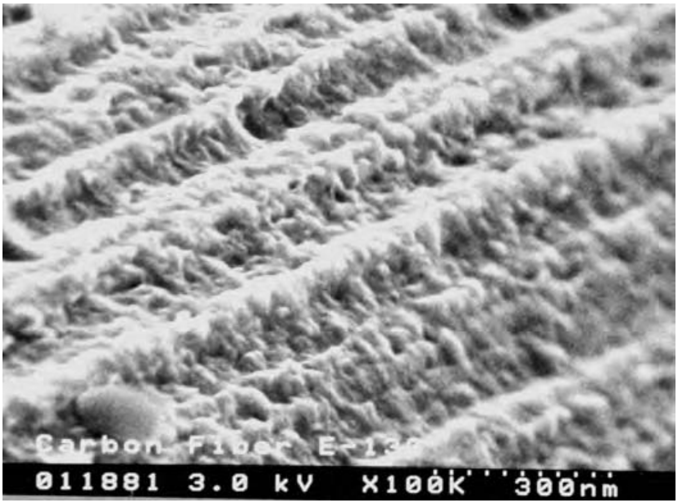
5.30 Pitch-based carbon fibre fracture surface: expanded view.



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. Lahijani[23] 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.

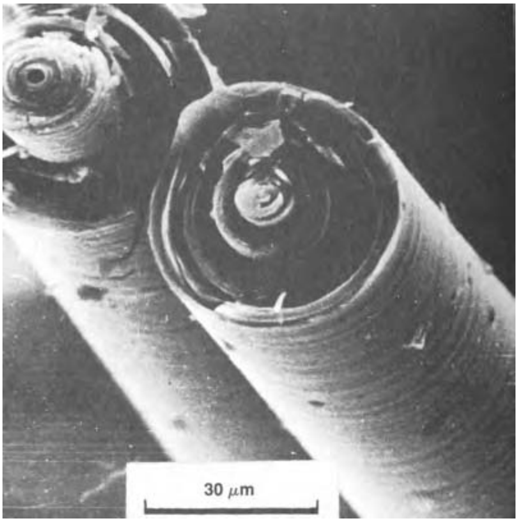
5.5 Vapour-grown carbon fibres

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.

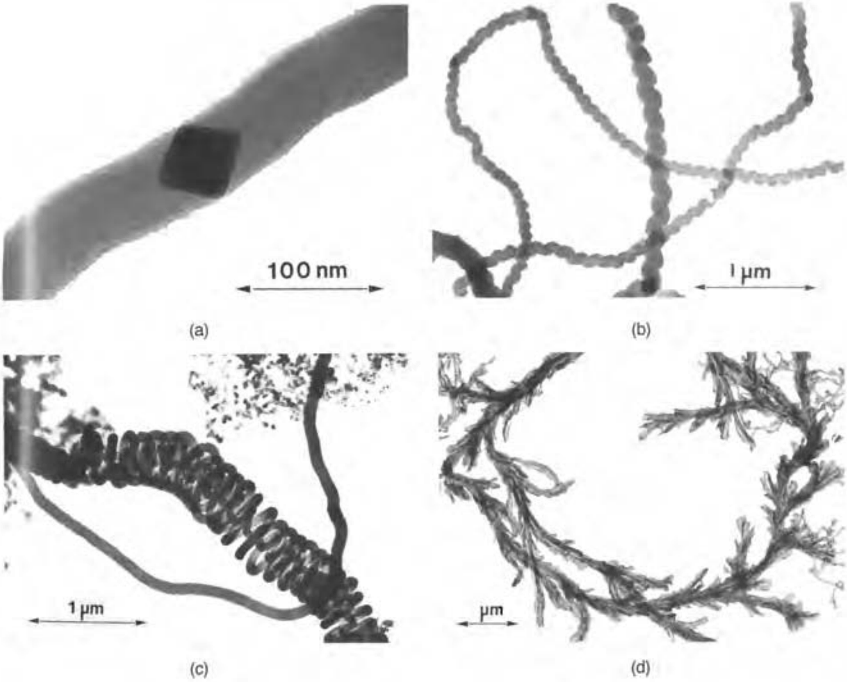
Typically, about 100 mg of powdered catalyst is placed in a ceramic boat, which is positioned in a quartz tube located in a horizontal tube furnace. The catalyst is reduced in a dilute hydrogen/helium stream at 600 °C, and quickly brought to the desired reaction temperature. Following this step, a mixture 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 formation[43] 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 hydrogen[44] is shown in Fig. 5.35.

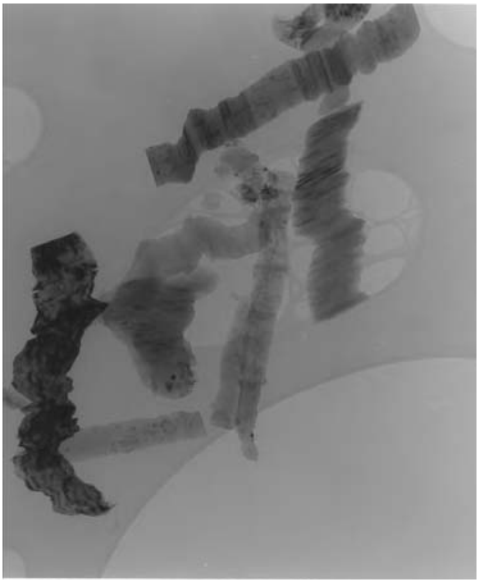
There are basically two kinds of process for producing vapour-grown fibres. The most common process is the one described above, in which the catalyst is a metal supported on a ceramic. This process produces long fibres which are tangled together in a ball that is extremely difficult to break up. A variant 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.)



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.)

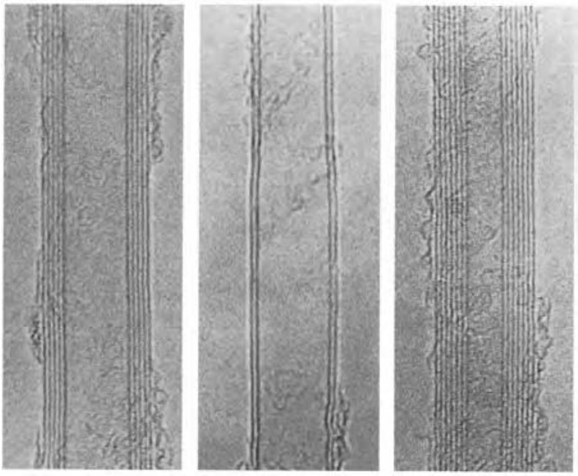


5.35 Vapour-grown carbon fibres with good hydrogen storage capability.

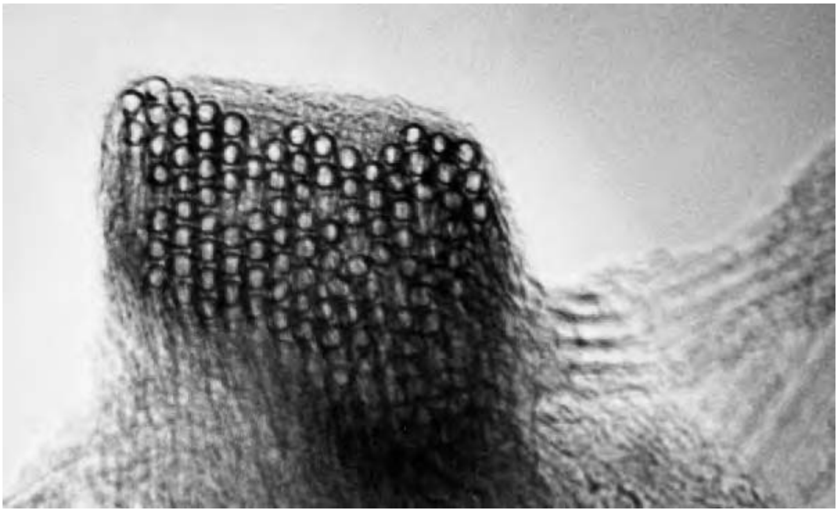
straight. However, they may be aggregated together and bound by amorphous carbon. In either case, the reinforcing capabilities of the fibre are restricted.

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 Iijima[45] 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, Iijima[47] and Bethune[48] *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 10 nm 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. Pich-based fibres have been used in Japan for large volume reinforcement of cementicious 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 m^2 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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