

Fibers for Polymer-Matrix Composites

3.1 Overview

As a result of their strong directional interatomic bonds, elements of low atomic number, including C, B, Al, and Si, can be formed into stiff, low-density materials. These materials may be made entirely from the elements themselves (e.g., C or B), or from their compounds (e.g., SiC), or with oxygen or nitrogen, (e.g., Al_2O_3 , SiO_2 or Si_3N_4).

The strong bonding¹ also inhibits plastic flow, at least at temperatures below around half the melting temperature. Because these materials are unable to relieve stress concentrations by plastic flow, they are markedly weakened by sub-microscopic flaws, particularly those open to the surface. Thus, it is generally only when made in the form of fibers that the inherent very high strength of these materials can be realized.^{2,3} There are several reasons for this, including the following:

- The probability of a flaw being present (per unit length) in a sample is an inverse function of volume of the material, as described by Weibull statistics.⁴ Hence a fiber having a very low volume (per unit length) is much stronger on average than the bulk material. However, the bulk material, having a much higher content of weakening flaws, exhibits a much lower variability in strength, as shown in Figure 3.1. It follows similarly that the smaller the fiber diameter and the shorter the length, the higher the average and maximum strength, but the greater the variability.
- Flaws can be minimized by appropriate fiber manufacturing and coating procedures to minimize surface damage. Also, the precursor materials used in fiber making must be of a high purity, including freedom from inclusions. The effect of flaws on strength can be estimated from thermodynamic (energy balance) and elasticity considerations.
- Fiber manufacturing processes that involve drawing or spinning can impose very high strains in the direction of the fiber axis, thus producing a more favorable orientation of the crystal or atomic structure.
- Some fiber manufacturing processes involve a very high cooling rate or rapid molecular deposition to produce metastable, often ultra-fine grained structures, having properties not achievable in the bulk material.

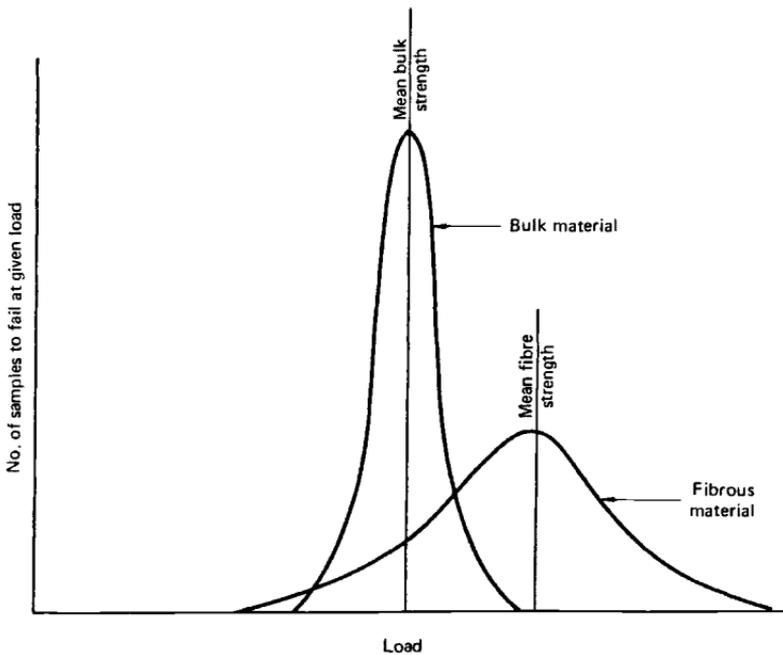


Fig. 3.1 Effect of sample cross-section on distribution of strength.⁴

Polymeric materials, based on a suitable carbon backbone structure, can also form strong, stiff fibers. Some of these materials rely on a very high drawing ratio to orientate the polymer chains, as well as high purity to develop their stiffness and strength.

Finally, some polymeric fiber materials can be used as precursors for producing inorganic fibers, through a process of controlled pyrolysis.

Thus, commercially available continuous fibers used in structural polymer-matrix composites (PMCs) for aerospace applications can be loosely classed as ceramic or as polymeric. Ceramic fibers, for the purposes of this discussion, include silica, carbon, and boron, although strictly these last two are not classed as ceramics. True ceramic fibers include silicon carbide and alumina, whereas polymeric fibers include aramid and high-density polyethylene.

Ceramic fibers, including glass, are typically flaw-sensitive and fail in an elastic brittle fashion from surface or internal flaws and inclusions.

Polymer fibers exhibit a complex fibrous type of fracture, as they essentially are made of a bundle of relatively weakly bonded sub-filaments or fibrils. As a result these fibers, compared with the ceramic fibers, are relatively insensitive to flaws. However, under compression loading they can defibrillate, resulting in poor compression properties.

Figure 3.2 summarizes the specific properties of several fiber types and includes, for comparison, structural metals. As a result of fiber volume fraction

and other limitations, maximum properties for a PMC with unidirectional fibers are around 60% of the values shown. It is apparent from this plot that significant improvements in specific stiffness compared with the metals are achieved only by using some of the more advanced fibers, including carbon and boron. More details on fiber properties are provided in Table 3.1.

3.2. Glass Fibers

3.2.1 Manufacture

Glass fibers,⁵ based on silica (SiO_2) melted with oxides, are the mainstay of PMCs because of their high strength and low cost. High-strength glass fibers have been used in demanding structural applications such as pressure vessels and rocket casings since the early 1960s. Structural applications in airframes are limited because glass fibers have a relatively low specific stiffness, as shown in Table 3.1 Nevertheless, they are widely exploited for airframes of gliders and other aircraft, where their low specific stiffness is not a design limitation, and in secondary structures such as fairings, with which relatively low cost (compared with the high-performance fibers) is attractive. Because of the suitability of their

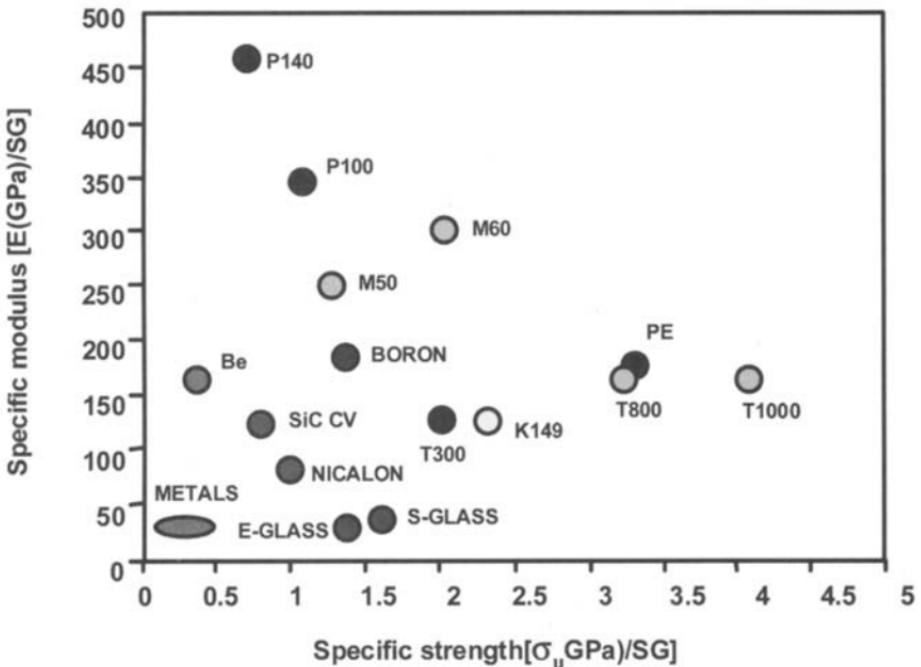


Fig. 3.2 Plot of specific fibers versus specific strength; the zone in which structural metals fall is shown for comparison. SG, specific gravity.

Table 3.1 Details of the Mechanical Properties of Various Fiber Types (the Temperature Column is the Nominal Maximum Operating Temperature in an Inert Environment)

Fiber	Fiber diameter (μm)	Specific gravity	Stiffness (GPa)	Specific stiffness	Ultimate strain (%)	Strength (GPa)	Specific strength	Coefficient of thermal expansion ($\times 10^{-6}$ m/m/ $^{\circ}\text{C}$)	Maximum use temperature ($^{\circ}\text{C}$)	Commercial name
Glass										
E-Electrical	5–20	2.6	73	1.1	3.5	3.5	11.2	5.0	350	
S-High strength	8–14	2.5	87	1.3	4.5	4.6	15.3	5.6		
Carbon PAN based										<i>Toray</i>
High strength*	8	1.76	230	4.9	1.5	3.5	16.6	-0.4		T300
Intermediate modulus	5	1.80	294	6.1	2.4	5.9	32.9	-1.0	>2000	T800
High modulus	8	1.90	490	9.7	0.5	2.5	11.0	-1.0		M-50
High modulus	6	1.94	588	14.3	0.7	3.9	16.8	-1.2		M-60
Carbon pitch based										<i>Amoco</i>
High modulus	10	2.03	520	9.6	0.4	2.1	8.6	-1.4		P-75
High modulus	10	2.15	725	12.7	0.3	2.2	8.5	-1.4	>2000	P-100
High modulus	10	2.18	830	14.3	0.3	2.2	8.4	-1.4		P-120
Boron CVD	140	2.50	400		0.7	2.8	9.3	4.9	1500	<i>Textron</i>
Silicon carbide										<i>Textron</i>
Monofilament	140	2.50	430	6.5	0.8	3.4	11.3	—	1400	SCS8
										Nippon Carbon
Multifilament	15	2.60	200	2.9	1.5	2.8	9.0	3.1	1200	Nicalon

Alumina											<i>Du Pont</i>
Monofilament	20	3.90	380	3.7	0.5	1.8	3.8	5.7	1000		FP
											<i>Sumitomo</i>
Multifilament	17	3.30	210	2.4	0.7	2.1	5.3	4.0	1100		Alumina
Aramid											<i>Du Pont</i>
Ballistic	12	1.43	80	2.1	3.6	2.9	9.7	16.9	250		Kevlar 29
Structural	12	1.45	120	3.1	2.8	2.9	9.7	17.1			Kevlar 49
High modulus	12	1.47	185	4.7	1.5	2.3	7.7	17.3			Kevlar 149
Polyethylene											<i>DSC</i>
	10–12	0.97	87	3.4	3.5	2.7	9.0	23.2	120		Dyneema
											<i>Allied Signal</i>
	38	0.97	117	4.5	3.5	2.6	8.7	22.3	100		Spectra 900
	28	0.97	172	6.7	2.7	3.0	10.0	25.8			Spectra 1000

N.B. The specific stiffness and strength is normalized to aluminum alloy 2024 T3; strength is based on stress at nominal yield.

dielectric properties, glass-fiber PMCs are also widely used in applications in which transparency to electromagnetic radiation is required, including radomes and aerial covers.

Glass is an amorphous solid produced by cooling a viscous liquid at a sufficiently high rate to prevent the formation of ordered or crystalline regions. Compounds that make up the glass in glass fibers can include (in addition to silica) oxides of aluminum, boron, calcium, magnesium, sodium, and potassium. Additives are used to lower the melting point of silica so that the required viscosity is obtained at a lower temperature. In addition, they facilitate the removal of gas bubbles and have a significant effect on the mechanical and chemical properties of the final product.

Glass fibers are manufactured by a viscous drawing process depicted in Figure 3.3 in which glass, melted in a furnace at temperatures of about 1400 °C, flows into an electrically heated platinum-rhodium alloy bushing or spinneret, containing a large number (400–8000) of holes in its base. The emerging glass drops are drawn into fibers by pulling at speeds of up to 50 m s⁻¹. They are then cooled by a fine water spray and coated with a size by contact with a rotating applicator. Finally, the fibers are combined into a strand as they are wound onto a take-up spool.

The fiber diameter, typically around 5–20 μm, is a function of the size of the holes in the bushing, the viscosity of the melt (which is dependent on the composition of the glass and the temperature), the head of glass in the furnace, and the rate of winding. Depending on the number of holes in the bushing, the strand typically consists of 52, 102, or 204 fibers.

The cooling rate experienced by the fibers is very high, >10,000 °C s⁻¹. A parameter⁵ called the *fictive temperature* is the apparent temperature at which

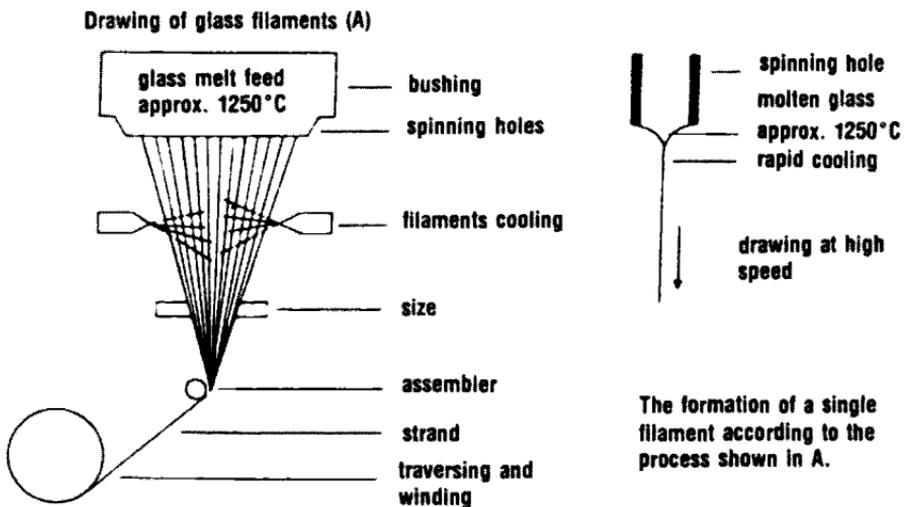


Fig. 3.3 Schematic illustration of the process used to manufacture glass fibers.

the glass is frozen, generally found to be 200–300 °C above the liquidus. As a result, the fiber structure is somewhat different from that of bulk glass, resulting in a higher tensile strength but lower elastic modulus and chemical resistance.

3.2.2 Effect of Flaws

Glass fibers, being essentially monolithic, linearly elastic brittle materials, depend for their high strength on the absence of flaws and defects. These take the form of sub-microscopic inclusions and cracks. The inclusions can often be seen with a scanning electron microscope, but “cracks” sufficient to reduce strength significantly can be very difficult to find because they are of nanometre dimensions. The origin of flaws is, however, generally obvious when examining the fracture surface because growth starts from the region of the flaw as a flat (mirror) surface and transforms to hackles radiating from this region as growth accelerates.

Commercial glass fibers are particularly prone to the formation of flaws by abrasion against other fibers, resulting in a reduction in strength of the order of 20% compared with pristine fibers made under laboratory conditions.

The tensile strength is probably significantly dependent on the composition, structure, and internal stresses in the surface layer, all of which differ significantly from those in the internal structure due in part to the high cooling rate. Although this layer is only of the order of a nanometer thick, it is of the order of the size of the flaws that control the strength of high strength fibers > 2 GPa. Generally, surface flaws have a similar strength-reducing effect compared with internal flaws of twice the length.

Humid environments reduce the strength of glass fibers under sustained loading, as the moisture adsorbed onto the surface of the flaw reduces the surface energy, thus facilitating slow growth to critical size. This phenomenon in glass is called *static fatigue*.

The strength of the glass fibers is reduced by about a further 50% when they are formed into a polymer-matrix composite. However, because of the bundle effect described in Chapter 2, this reduction is not noticeable. Essentially, the gauge length for a bundle of fibers is the length of the bundle, whereas, due to load transfer from the matrix, for a composite it is only of the order of 1 mm, depending on fiber diameter and fiber/matrix bond strength. Further reductions in strength can occur if the composite is exposed to wet conditions because components leached out of the polymer can cause acidic or basic conditions to develop at the fiber surface.

3.2.3 Types of Glass Fiber

The compositions of glass made into fibers for PMCs are listed in Table 3.2. There are two types of glass fiber used for structural applications: “E,” a calcium

alumino-borosilicate glass, and "S," a magnesium alumino-silicate glass. *E* stands for electrical grade, because compared with other standard forms of glass, its electrical resistivity is high and its dielectric constant low. These are by far the most widely exploited in structural applications, particularly in the non-aerospace area, because of their relatively low cost and high strength. A modified (low boron and fluorine) version of E glass fiber, ECR (E glass chemically resistant), is used where improved chemical properties are required. *S* stands for high-strength grade, although stiffness is also somewhat increased. These fibers can also withstand significantly higher temperatures than E glass fibers. Thus S glass fibers are used in more demanding structural applications. However, this marginal increase in stiffness is obtained at a relatively high cost. Where high specific strength and stiffness are required (with good dielectric properties) aramid fibers, described later, may be more attractive. More recently, a boron-free E glass has been developed that has markedly improved resistance to corrosive environments, but with no loss in mechanical properties.

3.2.4 Glass Fiber Coatings

As mentioned earlier, glass fibers are highly sensitive to surface damage. Because the coefficient of friction between glass fibers is around unity, mechanical damage sufficient to cause a significant loss in strength can result from fiber-to-fiber abrasion during the forming process. To prevent contact damage, within milliseconds of solidifying, the fibers are coated with a protective size that also serves to minimize losses in strength due to atmospheric moisture absorption. For example, the tensile strength of as-drawn fibers can be reduced by over 20% after contact with air during drawing under normal ambient conditions. It seems likely that the atmospheric moisture is absorbed into microscopic flaws, reducing fracture energy because time would be too limited for chemical attack. In any case, the tensile strength of the glass fibers drops significantly during the manufacturing process, from as high as 5 GPa immediately after drawing to typically around 2–3 GPa postproduction.

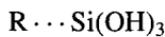
The size consists of several components. The simplest is a lubricant, such as a light mineral oil for protection and to aid further processing such as weaving, filament winding, and pultrusion. Binders such as starch and polyvinyl alcohol

Table 3.2 Chemical Composition of the Two Main Glass Fiber Types

Glass type	Si	Al ₂ O ₃	CaO	B ₂ O ₃	MgO	Na ₂ O K ₂ O
E-Electrical	53	14	18	10	5	<1
S-High strength	65	25	—	—	10	—

(PVA) are included in the size to bond or hold the filaments together into strands and tows. Finishes, also called primers, are used in the size to improve the adhesive bonding between the fiber and the polymer matrix. Primers may be added to the size or applied later after removal of the size components by heat treatment.

The finish is often based on a coupling agent that for most polymer-matrix resins is an organo-silane compound. Organo-silanes effectively have dual functionality, with their organo portion interacting with the organic resins or adhesives and the silane portion interacting with the inorganic fibers. Thus, these compounds are used to improve the interfacial (resin/fiber) properties of PMCs. Briefly, the silane molecule on hydration in water can be represented by the following simplified formula:



The $\text{Si}(\text{OH})_3$ bonds with the oxide film at the surface of the inorganic fiber-glass in this case, while the organic functional group R is incorporated into the organic matrix during its cure. R must therefore be a group that is chemically compatible with the matrix resin. For example, for an epoxy resin, an epoxy silane may be used. The following lists some of the coupling agents used as finishes for various resins:

- Vinyl silane (methacrylate silane), suitable for polyester resins
- Volan (methacrylate chromic chloride), suitable for polyester and epoxy resins
- Amino silane, suitable for epoxy, phenolic, or melamine resins
- Epoxy silane, suitable for epoxy and phenolic resins

3.3 Carbon Fibers

3.3.1 *Manufacture*

Carbon fibers are widely used for airframes and engines and other aerospace applications. High modulus (HM, Type I), high strength (HS, Type II) and intermediate modulus (IM, Type III) form the three broad categories of carbon fibers available commercially, shown in Table 3.3

The name *graphite* for these fibers is sometimes used interchangeably with carbon, but this is actually incorrect. Graphite is a form of carbon in which strong covalently bonded hexagonal basal planes are aligned in a three-dimensional lattice. The weak dispersive atomic Van der Waals' bonding allows easy slip between the basal planes, the basis for the lubricating properties of graphite. As discussed later, the atomic structure of carbon fibers differs in that the basal planes have only a two-dimensional order, which inhibits slip.

Table 3.3 Typical Properties for the Major Types of Commercial Carbon Fibers

Property	HM Type I	HS Type II	IM Type III
Specific gravity	1.9	1.8	1.8
Tensile modulus (GPa)	276–380	228–241	296
Tensile strength (MPa)	2415–2555	3105–4555	4800
Ultimate strain (%)	0.6–0.7	1.3–1.8	2.0
Coefficient of thermal expansion ($\times 10^{-6} \text{ mm}^{-1} \text{ K}^{-1}$)	-0.7	-0.5	N/A
Thermal conductivity ($\text{Wm}^{-1} \text{ K}^{-1}$)	64–70	8.1–9.3	N/A
Electrical resistivity ($\mu\Omega \text{ m}$)	9–10	15–18	N/A

Carbon fibers are made from organic precursor materials by a process of carbonization. The bulk of carbon fibers used in aerospace and other structural applications, are made from polyacrylonitrile (PAN) fibers.⁶ Carbon fibers are also made from various forms of pitch.⁷ Early carbon fibers were manufactured from rayon, however, these fibers have been gradually phased out due to their low carbon yield (20–25%) and their generally poorer mechanical properties compared to PAN and pitch-based carbon fibers.

3.3.2 PAN-Based fibers

PAN is an acrylic textile fiber produced by wet or dry spinning of the basic polymer or copolymer. Dry spinning produces round smooth fibers whereas wet spinning (extrusion into a coagulating bath) produces a variety of cross-sections, including dog-bone, elliptical, and kidney-shaped. There are some advantages in the non-circular cross-sections; for example, the larger relative surface area improves effective bonding. The fibers are stretched during the spinning process. The greater the stretch, the smaller the fiber diameter and the higher the preferred orientation of the molecular chain along the fiber axis, resulting in a stiffer carbon fiber when processed. PAN fiber tows typically contain around 10^4 fibers, although much larger or smaller tows are also produced. The finished carbon fibers are between 5–10 μm in diameter.

Figure 3.4 schematically illustrates the process of conversion of the PAN fibers into carbon fibers. The PAN is first stabilized in air at around 250 °C by oxidation to form a thermally stable ladder polymer, having a high glass transition temperature (T_g), which is resistant to melting at the higher temperatures. The cyclic groups in the ladder polymer are rather similar in molecular structure to the carbon basal plane, except that they also contain nitrogen and hydrogen atoms. The fibers are maintained under tension to prevent them from contracting during oxidation and, through the resulting deformation, to align further the ladder structure with the fiber axis.

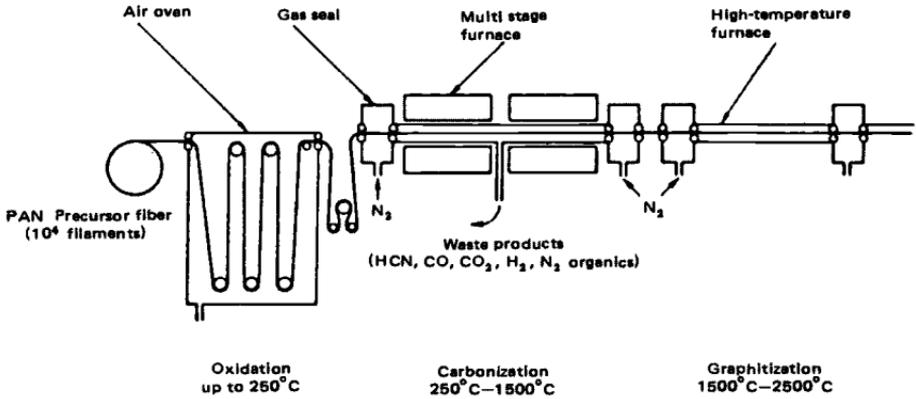


Fig. 3.4 Schematic illustration of the process used to make carbon fibers from PAN.

The next step in the process is carbonization in the temperature range of 1200–1600 °C in an inert nitrogen atmosphere. This removes the nitrogen, oxygen, and hydrogen from the ladder.

As the heat treatment proceeds, benzene aromatic rings link to form polynuclear aromatic fragments, with the basal planes aligned along the fiber axis. Gradually the aromatic network transforms to mainly carbon atoms and becomes denser through cross-linking with the evolution of N₂ through open pores in the fiber. At 120 °C the transformation to carbon is almost complete and closed pores remain in the fiber. Finally, at around 1500–1600 °C the strength of the fiber reaches its peak.

Although the basal planes in carbon fibers are aligned (with varying degrees of perfection) parallel to the axis of the fibers, ordering of the planes is largely two-dimensional, having extended two-dimensional ribbons of basal carbon. Crystalline order in the third dimension, Figure 2.5, is very limited, as the alignment of one ribbon with another is generally very low. This structure is referred to in the literature as turbostratic carbon.

The strength and stiffness of carbon fibers are a function of the degree of perfection of the structure and the alignment of the ribbons of basal planes with the fiber axis. These depend on several processing factors, including the heat treatment temperature as well the nature and content of weakening voids and flaws—determined to a large degree by the purity and freedom from inclusions in the PAN precursor. Of course there is a high cost penalty if ultra-high-purity PAN is required, which sets a high baseline cost for high-performance carbon fibers.

After heat treatment at 1500–1600 °C the strain capability of the fibers is then over 1.5% with an intermediate value of the Young's modulus of around 240 GPa, Table 2.3.

If higher modulus is required, which will be at the expense of strength and strain capability, the fibers undergo a final graphitisation stage of heat treatment

up to 2500 °C. This treatment is generally carried out in a clean and more inert atmosphere, such as argon, to prevent the formation of flaws through chemical reactions and/or local graphitisation. During this process, the aromatic carbon basal layer planes grow, by further coalescence of adjacent layers, resulting in an increase in preferred orientation along the fiber axis and thus in elastic modulus. As indicated in Table 2.1, strain capacity is then reduced to around 0.7% and the Young's modulus up to 380 GPa.

3.3.3 Pitch-Based Fibers

Pitch is a relatively cheap precursor material for the manufacture of carbon fibers.⁷ However, although low cost fibers can be produced from isotropic pitch, they have rather poor mechanical properties. Pitch can also be used as a precursor for ultra high-stiffness fibers, however these involve much more elaborate processing, so are very expensive.

Commercial pitch, made of mixtures of organic compounds, is subjected to prolonged heating to form a liquid crystal phase known as mesophase (MP) prior to spinning into precursor fibers. Heat is applied at approximately 400–450 °C in an inert atmosphere for an extended period in order to transform isotropic pitch to mesophase pitch. This is then melt-spun into filamentary form. The draw ratio employed during spinning determines the degree as well as uniformity of molecular orientation of the fiber. To reduce relaxation of the orientated structure, the pitch fibers are cross-linked by heat-treating at 300 °C for a short period in an atmosphere containing oxygen. Pre-carbonisation at 1000 °C to reduce the rate of gas evolution (and hence the creation of surface flaws), precedes carbonisation and graphitisation at temperatures ranging between 1200–3000 °C.

The main advantage of this process over the PAN processing route, is that no tension is required to develop or maintain the molecular orientation required to achieve high modulus and strength. Owing to the anisotropic liquid crystal nature of the pitch, molecular orientation is achieved in the spinning process and is enhanced, or at least preserved, throughout processing without the need to use tension.

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MP-based fibers in general exhibit higher tensile modulus than their PAN-based counterparts. This is due to the more highly graphitizable character of the former precursor. However, this results in relatively lower compression and shear properties. The structure of MP-based fibers is also more porous, leading to lower

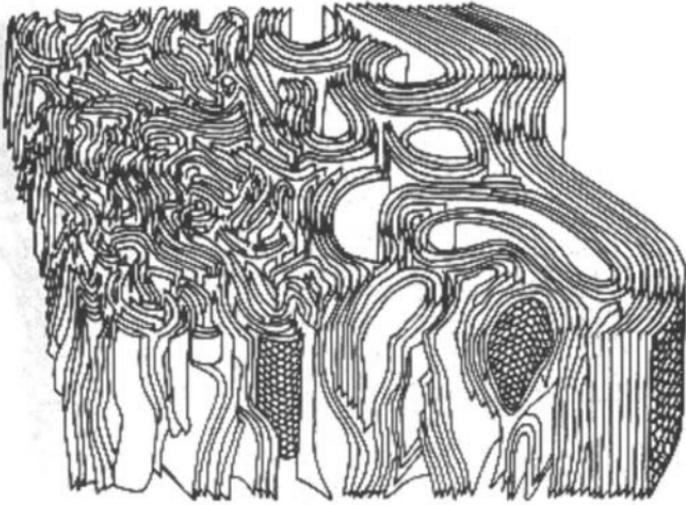


Fig. 3.5 Schematic illustration of the structure of carbon fiber.⁴

achievable strengths. Their carbon content is much higher, however, being around 80% compared with 50% for PAN precursors.

Very high values of Young's modulus and thermal and electrical conductivities can be obtained from pitch fibers as shown in Table 3.1. Therefore, they are widely used in space-based applications where ultra-high stiffness and conductivity are highly advantageous.

The other main continuous inorganic fibers⁸ in production are boron and various types of silicon carbide. Continuous alumina fibers are also manufactured, but are not discussed here, although some properties are included in Table 3.1 for completeness. These fibers are of interest for the development of metal-matrix and ceramic-matrix composites, as discussed in Chapter 1. For these applications, retention of high static and creep strength and resistance to attack by the matrix material are important requirements. Ideally, they should also match the matrix in thermal expansion properties to minimize residual stresses—this is only feasible with ceramic-matrices.

Their low electrical and thermal conductivity make them preferred options to carbon fibers for some applications.

3.4 Boron Fibers

Boron fibers⁹ are large monofilaments around 125–140 μm in diameter, compared with around 10 μm for carbon. Because boron is almost as hard as diamond, PMCs based on this fiber are difficult to drill and machine. Therefore, carbon fibers which are much cheaper as well as being more machinable and formable, have largely replaced boron fibers for aerospace PMC applications.

However, several recent U.S. aircraft such as the F-14, F-15, and B-1 contain a number of important boron/epoxy components. Boron is also used to reinforce aluminium metal-matrix composites (Chapter 1).

Boron fibers are made by chemical vapor deposition (CVD) of boron onto a fine incandescent tungsten or a pitch-based carbon fiber, around $10\ \mu\text{m}$ in diameter. The carbon fiber is coated with a thin layer of pyrolytic graphite to alleviate internal stresses by promoting relative movement.

Deposition is usually achieved through hydrogen reduction of a boron trichloride gas at a temperature of above $1000\ ^\circ\text{C}$ at atmospheric pressure in a glass reactor; alternatively, boron bromide, iodide, or fluoride can be used. The process, illustrated in Figure 3.6, involves gradual growth of the boron deposit, which is quite slow, around $3\text{--}4\ \mu\text{m}\ \text{min}^{-1}$, and therefore very expensive.

Because tungsten has a high density and is also expensive, the boron monofilament must have a large diameter to minimize fiber density and cost. Even if a carbon fiber substrate is used, the economics dictate the formation of large-diameter fibers. For some reason, the use of carbon precursor fibers is not common, although carbon is used for the core in the CVD of silicon carbide fiber, described next.

The traverse speeds for producing the fibers are critical. At relatively low temperatures, around $1200\ ^\circ\text{C}$, the desired near-amorphous form of boron is deposited. Above this temperature, at slow traverse speeds, some crystalline boron is formed, which has an adverse effect on mechanical properties. The final fiber has a distinctive corncob appearance, typical of solids made by CVD, resulting from multiple nucleation of boron and growth from the substrate. The properties of boron fibers are listed in Table 3.1.

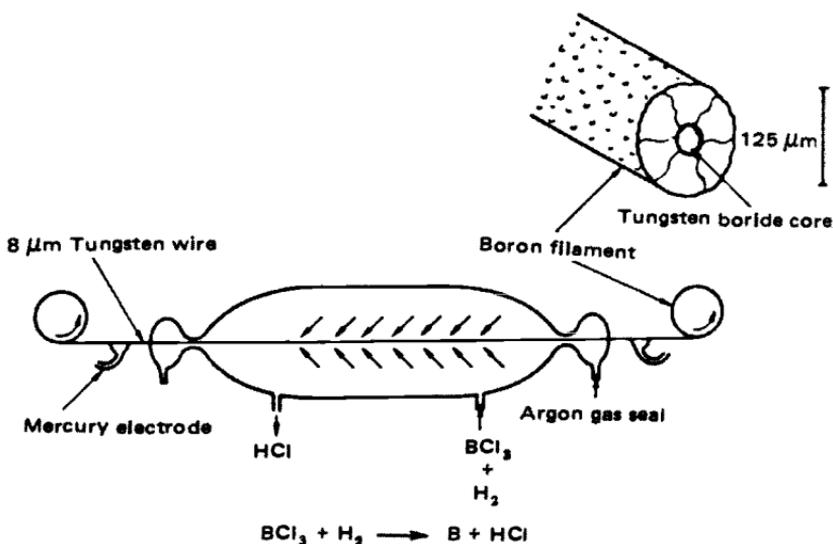


Fig. 3.6 Schematic illustration of the process used to make boron fibers.

Detailed X-ray studies show that the preferred form of the boron is actually not amorphous but a microcrystalline b-rhombohedral, with a crystal size of around 2 nm. In the reaction process with tungsten wires, the boron diffuses into and reacts with the tungsten core to produce various tungsten boride compounds, including WB_4 and W_2B_5 . These have a greater volume than the tungsten fiber and so produce quite severe internal tensile stresses that can lead to internal cracking. However, the CVD process apparently leaves compressive stresses on the fiber surface that should reduce sensitivity to surface flaws.

Strength is reduced by the presence of flaws such as microscopic dust particles enveloped during fiber manufacture, or localized growth of coarse crystals caused by undesirable temperature fluctuations during manufacture. Strength can be enhanced by smoothing the surface, using chemical etching, or dissolving the fiber core. However, these processes are not used industrially because of the cost. Boron fibers made by deposition onto a carbon fiber substrate are much smoother, which may be a result of the smoothness of the carbon fiber or an increase in the number of nucleation sites.

Boron fibers undergo significant anelastic deformation (apparent creep) under prolonged loading at elevated temperature that is recovered upon unloading.

Because boron was the first fiber capable of reinforcing metals, considerable effort was made to use this fibers in this application. To improve chemical compatibility with aluminum and titanium matrices, the use of a nitride or silicon carbide coating was developed. The silicon carbide coated fiber was called "Borsic" and offered some improvement over the uncoated fibers. However, the inherent temperature limitations of the core boron fiber resulted in the focus for development of metal-matrix composites moving to silicon carbide fibers.

3.5 Silicon Carbide

Silicon carbide fibers are produced by a CVD process similar to boron or by a polymeric precursor route. The highest strength and chemical stable fibers are produced by CVD, which produces fibers suitable for reinforcing aluminum and titanium alloys. CVD silicon carbide fibers are also highly suited for reinforcing ceramics, as mentioned in Chapter 1, notably silicon carbide, silicon nitride, or glass.

3.5.1 CVD-Based Silicon Carbide Fibers

CVD fibers are produced by the reaction of hydrogen with a mixture of chlorinated alkyl silanes (such as methyltrichlorosilane) at the surface of a resistivity-heated substrate fiber. In this case, the substrate fiber is a spun carbon monofilament, around 30 μm in diameter, coated with a thin layer of pyrolytic graphite. The resulting fiber is polycrystalline β -SiC, having a fairly coarse grain

compared with the microcrystalline boron. Internal stresses in CVD silicon carbide fibers are fairly low, in contrast to the high stresses found in boron fibers.

Since the cost of carbon core is much lower than tungsten and the deposition rate is significantly greater, the potential cost of the silicon carbide fibers is about one third that of boron. Properties of CVD SiC fibers are listed in Table 1

The fibers retain most of their room temperature strength up to about 900 °C then maintain a strength of around 1 GPa up to 1300 °C. Also ambient temperature strength is recovered on cooling after exposure at temperatures up to 1400 °C. Above this temperature, coarsening of the SiC crystal structure occurs, resulting in permanent weakening. The fibers undergo creep deformation at temperatures below 1400 °C, this is attributed to grain boundary sliding due to the presence of free silicon between the grains. Heat treatment above 1400 °C improves creep resistance at the cost of reduced strength by coarsening of the β -SiC grains and possibly by disrupting the weak layers between the grains.

The key issue in the use of fibers to reinforce metals in MMCs, is chemical compatibility and the need to form a strong stable surface bond (See Chapter 1). To achieve this, three types of CVD fibers are produced, each having a carbon-rich zone of several microns close to the surface. For example, SCS-6 is designed for reinforcing aluminium alloys, while SCS-8 is designed for reinforcing titanium. The carbon-rich layer at the grain boundaries in these versions of the SiC CVD fiber, improves creep-resistance by reducing grain-boundary-sliding and also inhibiting grain growth.

3.5.2 Silicon Carbide Fibers Based On A Polymeric Precursor

The polymer-precursor textile route to the manufacture of silicon carbide fibers¹⁰ is based on a high molecular weight polymer (made by polymerisation of dichlorodimethylsilane) containing silicon and carbon. A similar polymer precursor/textile route can be used to make a range of multi-filament ceramic fibers, including alumina and silicon nitride.

The polycarbonylsilane polymer is melt spun to form a multi-filament tow and then pyrolysed in two temperature stages; 550 °C to stabilise the precursor to be infusible and 850 °C to form an impure form of silicon carbide, containing a non-stoichiometric form of SiC, SiO₂ and free carbon.

Table 1 lists typical properties for Nicalon (trade name, see Table 1), which is the most well-known and used version of these fibers. As a result of the low fiber diameter and tow size, the fiber can be produced in a wide variety of textile forms and allows similar flexibility in manufacture to PAN-based carbon fibers.

Due to the impurities and the crystalline form of SiC produced, the elastic modulus of the fiber is lower than monolithic SiC; 220 GPa compared with 450 GPa. It also tends to decompose at temperatures above 1200 °C and has low retained strength above 1400 °C. The fibers are also prone to oxidise at temperatures above around 1000 °C to form surface SiO₂. As may be expected, the presence of SiO₂ at the grain boundaries has a negative impact on creep

properties. Creep resistance is also a function SiC grain size, and improves as the grain size increases.

Some of the disadvantages of Nicalon have been overcome in a version called Hi-Nicalon, which is produced from the same precursor material, but cured by electron-beam radiation. The improvement results from the lower oxygen content leading to a reduced level of SiO₂, but the non-stoichiometric form of SiC and excess carbon, remain. Further improvements were made by heat-treating the fiber at a high temperature to produce a near-stoichiometric form of SiC with coarser grains, without significant loss of strength. Hi-Nicalon retains a high level of strength even after exposure at 1600 °C and has significantly improved creep properties. Presumably, this version of the fiber would also have improved compatibility with aluminum and/or titanium, so, is more suited to formation of metal-matrix composites.

Silicon carbide is a semiconductor; in the case of the fibers resistivity depends on impurity content and crystal structure. The resistivity of Nicalon fibers can be controlled in the range 10–10⁶ Ω mm⁻¹ according to the heat treatment.

Finally, although Nicalon fibers exhibit significant creep at elevated temperatures and do not have the required high chemical compatibility with metals of CVD SiC, they are substantially cheaper than the CVD fiber and are suitable for some modest temperature applications in metals and ceramics.

3.6 Aramid Fibers

Aramid fibers,¹¹ trade name Kevlar (Du Pont), were the first organic fibers with sufficient stiffness and strength for use in PMCs suitable for airframe applications. Table 3.1 lists the important physical and mechanical properties of three types of Kevlar. This shows that Kevlar aramid fibers significantly exceed the specific strength and stiffness of glass fibers. PMCs based on aramid fibers have attractive tensile properties for temperatures of over 400 °C; however, they have poor compression strength. This is a major limitation for applications subject to significant compression loading, including those requiring high bearing strength.

A major advantage of aramid fibers is their ability to absorb large amounts of energy during fracture, which results from their high strain-to-failure, their ability to undergo plastic deformation in compression, and their ability to defibrillate during tensile fracture. The fibers exhibit plastic behavior at around 0.3% compression strain, and deformation is linear up to failure at strains greater than 2% in tension. Hence aramid PMCs are used for ballistic protection and also for engine containment rings. The most common use of aramid PMCs in aerospace has been in fairings, but it is also used as the skins or face sheets for honeycomb panels. Aramid PMCs are also used in radomes and other applications requiring structural efficiency and suitable dielectric properties.

Kevlar fibers are based on an aromatic polyamide (poly para-phenylene terphalamide; PPD-T) polymer chain. Nylon is a generic name for textile fibers based on a linear form of polyamide. In PPD-T, the aromatic rings contribute high thermal stability and result in a crystalline rigid, rodlike polymer. The strong covalent bonds in the polymer chain and the weak hydrogen bonding between these chains result in highly anisotropic properties; the polymer structure is depicted in Figure 3.7. The polymer rods, as in mesophase pitch, aggregate in solution to form liquid crystals.

When PPD-T, as a 20% solution in concentrated sulphuric acid, is extruded through a spinneret at around 100°C the liquid crystal zones or domains align in the direction of the flow. The fiber precipitates in a short air gap after emerging from the spinneret and then coagulates by passing through a cold water bath that removes the acid. Some rotation of domains occurs during the spinning process. The fiber structure thus consists of highly crystalline, aligned polymer chains separated, on a larger scale, into distinct zones or fibrils. The fiber structure is essentially made up of a bundle of these fibrils that are relatively weakly bonded together.

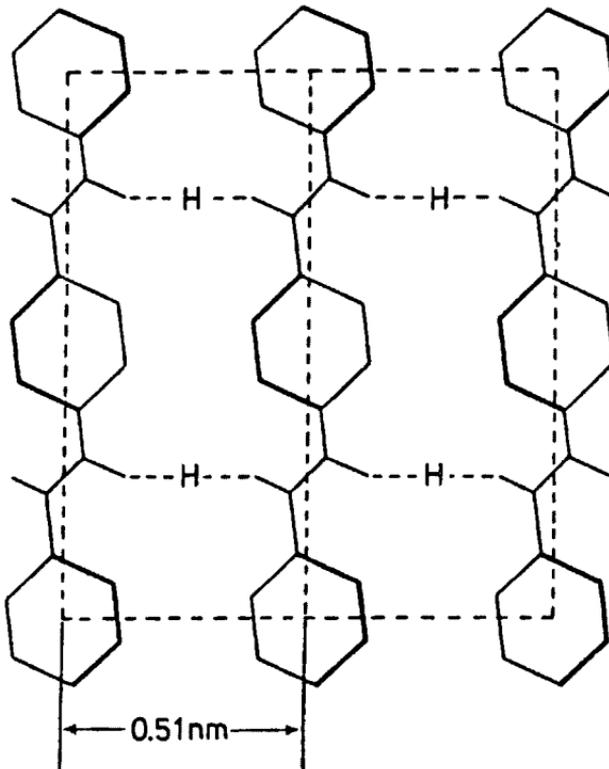


Fig. 3.7 The polymeric structure of aramid fibers. Note the hydrogen bonding between the polymer chains. Taken from Ref. 3.

Under tensile loading, failure occurs by a defibrillation process (due to the presence of weak interfaces) that reduces flaw sensitivity in individual fibrils and is therefore highly effective for energy absorption. The strength of aramid fiber falls to around 80% of room temperature strength at 180 °C, followed by a more rapid decline above this temperature. However, as mentioned earlier, under compression loading, aramid fibers exhibit pronounced non-linear behavior. This is caused by the formation of kink bands resulting from in-phase compressive buckling of the fibrils. As a result, compression strain-to-failure is only about 25% of the tensile value.

Aramid fibers have a high tendency to absorb moisture. For Kevlar 49, moisture absorption is around 4% at 60% relative humidity, while for Kevlar 149, it is around 1.5%, but the effect on tensile strength at ambient temperatures does not appear to be significant.

Aramid fibers are prone to significant short-term creep even at modest temperatures, however, long-term creep is negligible. The fibers are also prone to stress rupture under prolonged loading but are much less sensitive to this mode of failure than are glass fibers.

Finally, aramid fibers are degraded in strength by prolonged exposure to ultraviolet radiation but, although this can be a serious concern with cables having exposed fibers, it is not a significant problem for aramid PMCs because the fibers are protected by the resin matrix.

3.7 Orientated Polyethylene Fibers

High modulus polyethylene fibers¹² can be produced with a specific gravity below that of water (Table 3.1). Two types of fiber are currently commercially available—Spectra by Allied Signal and Dyneema by DSM. Polyethylene fibers are produced by the drawing of melt-crystallized polyethylene to very high draw ratios. Other routes to manufacturing these fibers include solution and gel spinning of very high molecular weight polyethylenes.

In common with aramid fibers, polyethylene fibers exhibit low compression strength and fail under compression by a process involving the formation of kink bands. On a specific basis, polyethylene fibers have tensile properties that exceed those of most other fibers including aramid (Table 3.1). However, the fibers are prone to creep deformation and creep rupture under long-term loading, particularly at modest temperature, which limits their use in applications involving high, prolonged static loading. Creep occurs in part because the fibers cannot be drawn to their full extent in commercial production; however, sliding of the polymer chains encouraged by the weak inter-chain bonding also makes a significant contribution.

Polyethylene fibers are limited to temperature applications under 100 °C; Spectra, for example, melts at 150 °C. Nevertheless, they have exceptional chemical resistance and low moisture absorption characteristics. It is difficult for

the resin matrix to form strong adhesive bonds to the fibers as a result of their non-polar nature; however, bonding can be improved by various pre-bonding etching techniques, including corona discharge.

As with PMCs based on aramid fibers, high toughness is a very attractive feature of PMCs based on polyethylene fibers. Thus, the fibers are being developed for use in PMCs with applications requiring ballistic protection or very high impact resistance.

3.8 Dry Fiber Forms

Continuous carbon, glass, aramid, and other multi-filament fibers are produced in various dry forms¹³ (no matrix precursor added) for subsequent processing into high-performance PMCs using pre-impregnation (pre-preg), resin film, or liquid resin injection techniques. The forms include continuous rovings, woven rovings, yarns, and woven cloth (see Fig 3.8). The various types of resin pre-impregnated fiber forms are mentioned briefly here, and a more detailed discussion of the subject is given in Chapter 5. The monofilament CVD fibers are available in the dry form either as a single-fiber spool or as a tape or cloth, which is held in place by polymeric fibers and sometimes attached by a light resin coating to a very fine glass fiber cloth.

3.8.1 Rovings and Tows

Rovings, a term generally used in association with glass fibers, consist of an untwisted bundle of strands that in turn consist of a collection of more than one continuous glass filament. Rovings are made by collating ends from several primary strand creels and then, using a precision winder, winding them onto a cylindrical package.

In the case of carbon, the bundle of fibers is called a *tow* and results directly from processing the PAN precursor. Typically, a carbon fiber tow contains between 1000 and 48,000 individual filaments.

It is very important that the strands in the roving or tow are maintained under even tension because uneven tension markedly affects later processing. Uneven tension in processes such as filament winding and pultrusion can result in strands sagging and becoming entangled. Importantly, fiber tension in the finished component will vary significantly, reducing the reinforcing efficiency.

3.8.2 Yarns

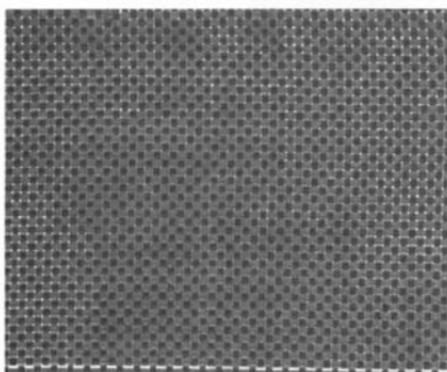
Yarns are made by twisting a collection of strands (usually smaller than rovings) or filaments as they are pulled off the creel under tension. The twist, approximately one turn per centimeter, holds the fibers in place and maintains even tension during subsequent processes such as weaving and filament winding.



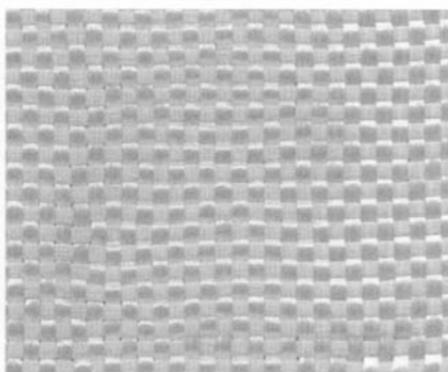
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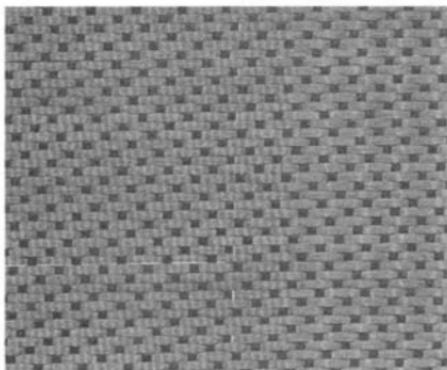
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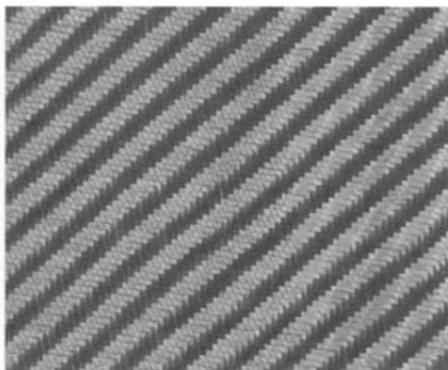
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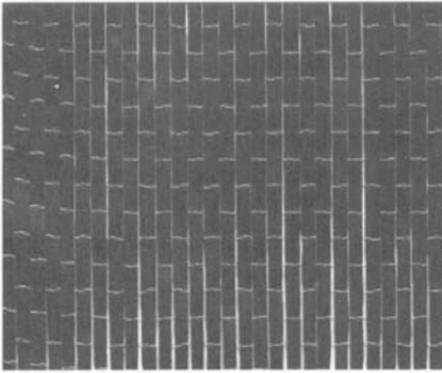


e)

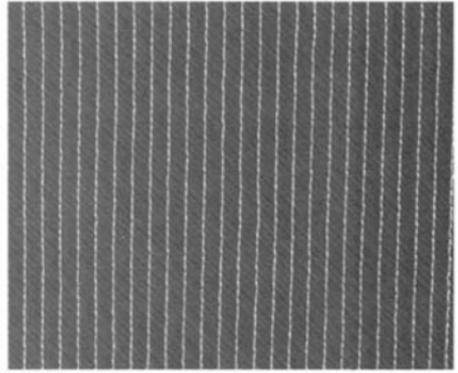


f)

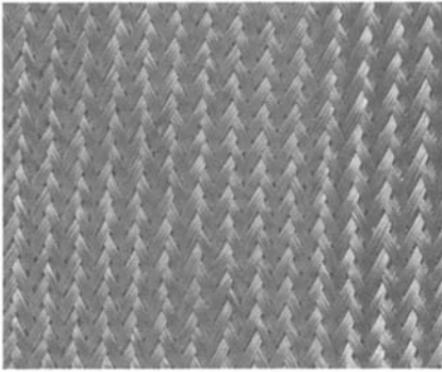
Fig. 3.8 Fiber forms: *a*) Carbon tows of various weights (Torayca brochure); *b*) non-wovens (CSM); *c*) plain woven; *d*) 4×4 basket woven; *e*) five-harness satin woven; *f*) 4×4 twill woven.



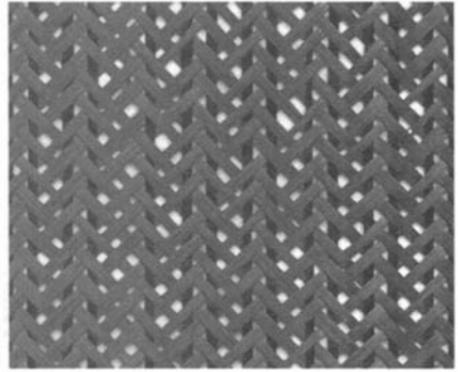
g)



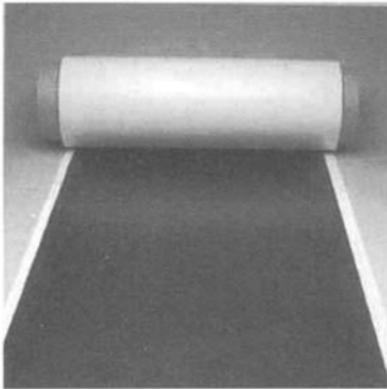
h)



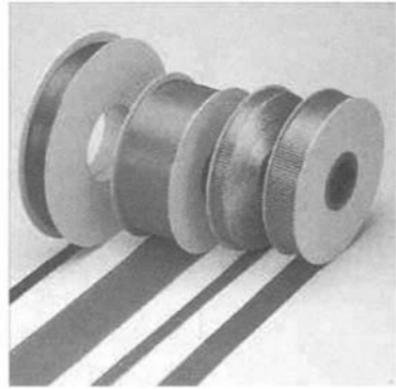
i)



j)



k)



l)

Fig. 3.8 (continued) Fiber forms: g) uniweave; h) non-crimp; i) biaxial braided; j) triaxial braided; k) pre-pregs (Torayca brochure); l) narrow fabrics/tapes (Torayca brochure).

Where heavier yarns are required, two or more stands may be twisted together and then plied by re-twisting several twisted yarns together in the opposite direction of the strand twist. The directions of the twist are denoted by S- or Z-type twist. Hence two or more strands with an S-twist are plied with a Z-twist to maintain balance.

3.8.3 Non-woven Fabrics

Mats are non-woven fabrics that provide near isotropic properties and come in either chopped or continuous strand form. The former consists of fibers cut to lengths typically up to 50 mm and randomly deposited onto a moving belt. Continuous strand mats, on the other hand, are manufactured by swirling continuous strands of fibers onto a moving belt. The reinforcements, usually glass, in both forms of mat are held together with a polymeric binder. Stitch-bonded and needle felt fabrics are two other kinds of non-wovens.

3.8.4 Woven Fabrics

A wide variety of textile cloths are made using conventional textile weaving looms. The type of weave influences the formability/drapability and reinforcing efficiency of the fibers. The weave is made up of warp fibers that run in the direction of the loom and the weft (or fill) fibers that are normal to the direction of the warp.

The main styles of woven fabric reinforcement are plain, twill, satin, and basket weaves (Fig. 3.9). In the plain weave, each warp yarn alternately crosses over and under each weft yarn (i.e., 1×1). This is by far the most common structure used and affords relatively good fabric stability. Twill (e.g., 2×2 and 4×4) and satin (e.g., 5-harness and 8-harness) weaves are woven such that yarns go over and under multiple warp yarns. Twill weaves involve warp and weft interlacing in a programmed sequence so that a pattern of diagonal lines is obtained on the fabric. Satin weaves, on the other hand, offer a reduced amount of

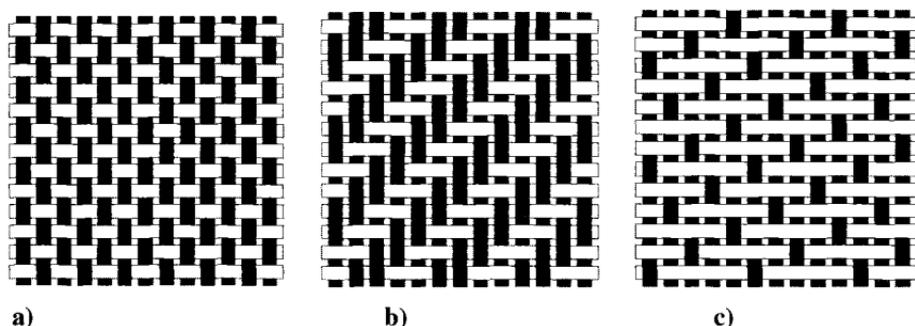


Fig. 3.9 Various commonly used weave architectures: a) plain; b) twill; c) satin.

interlacing, whereby the weft yarns pass over several (4 in the case of 5-harness satin and 7 in the case of 8-harness satin) warp yarns. Twill and satin weaves have lower degrees of fiber crimp than plain weave and hence are heavier fabrics due to better packing density. They also have better drapability, formability, and in-plane properties. As a result of the lower degree of interlacing, these fabrics are also less stable and can create some difficulty during handling. Basket weaves have two or more warp yarns interlacing with two or more weft yarns. In some cases, the woven fabric has a highly biased fiber content in the warp direction, whereby the warp yarns are held by sparingly introduced weft yarns that are also normally much thinner than the warp yarns. These are referred to as *uni-weaves*.

Woven fabrics are also available in a number of hybrid (mixed-fiber) forms. For example, a cloth could be made in any of the forms previously discussed, having carbon fibers in the warp direction and glass or aramid in the weft direction. Alternatively, carbon and one or more of the other fiber types may alternate in the warp or weft direction. Hybridization may be desirable for either property or cost reasons.

Woven fabrics can be produced from rovings (and hence they are called *woven rovings*), or from finer yarns. Woven fabrics come in either wide or narrow forms; the latter is convenient for localized, selective reinforcement.

Woven fabrics may also be produced in a form in which the main fibers are mixed (comingled) with thermoplastic polymer fibers. During consolidation of the fabric, the thermoplastic fiber melts and flows to form a thermoplastic matrix.

Weaving causes a periodic out-of-plane undulation of the fibers, resulting in a significant loss of reinforcing efficiency because the optimum reinforcing efficiency is obtained only when the fibers are absolutely straight and in plane. Compression strength is particularly compromised with undulating fibers. However, as may be expected, through-thickness strength including delamination resistance is improved.

3.8.5 Braided Fabrics

Braids are generally more expensive than woven fabrics due to the more complex manufacturing process. However, they also usually offer greater strength per fabric weight. Produced in either the flat or tubular forms, braided fabrics can have at least one axial yarn that is not crimped, thereby allowing $[0, \pm \theta]$ orientations to be achieved. Due to limitations imposed by the size of braiding machines, the widths of these fabrics are normally much narrower than those of woven fabrics and are only suitable for selective reinforcement and production of components with small cross-sections, such as poles and tubes. Chapter 14 provides information on braided composites.

3.8.6 Non-crimp Fabrics

Also known as multiaxial, multilayer warp-knit fabrics, non-crimp fabrics consist of fibers that are held straight and in plane by a stitched or knitted

thermoplastic polymer (typically nylon or polyester) fiber or a flexible high-performance fiber such as glass or aramid. The material is not crimped as in the case of woven material, and as such, the fibers are arranged in a more optimal fashion. These important fabrics are further discussed in Chapter 14.

3.8.7 Tapes

Tapes are essentially narrow dry fiber fabrics having widths of less than 100 mm. The tape may be a woven cloth or it may contain mainly warp, unidirectional fibers with a light cross weave or knit of polymer fibers to hold the tows in place. Another alternative is to bond the fibers onto thin supporting fiber mat or cloth, using a low-volume fraction of a thermoplastic polymer or uncured thermoset that is later absorbed into the matrix. Monofilament tapes are often made this way. If the tape is held together by woven or knitted fibers, it usually has a stitched or reinforced edge to keep it from falling apart. This is generally trimmed off after the composite has been cured.

3.8.8 Three-dimensional Textiles Preforms

Three-dimensional textiles preforms are dry fiber forms in which the complete reinforcement is manufactured as a single product. The finished component then requires only the addition of resin and curing. Three-dimensional preforms can be woven, braided, or knitted. All these textile techniques are capable, within limits, of producing fully-fashioned or net-shaped preforms with improved formability/drapability and can potentially reduce production times, particularly for complex-shaped components. These processes are also discussed in Chapter 14.

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