

Introduction to Carbon Fibers

Carbon fibers refer to fibers which are at least 92 wt.% carbon in composition [1]. They can be short or continuous; their structure can be crystalline, amorphous, or partly crystalline. The crystalline form has the crystal structure of graphite (Figure 1.1), which consists of sp^2 hybridized carbon atoms arranged two-dimensionally in a honeycomb structure in the x - y plane. Carbon atoms within a layer are bonded by (1) covalent bonds provided by the overlap of the sp^2 hybridized orbitals, and (2) metallic bonding provided by the delocalization of the p_z orbitals, i.e., the π electrons. This delocalization makes graphite a good electrical conductor and a good thermal conductor in the x - y plane. The bonding between the layers is van der Waals bonding, so the carbon layers can easily slide with respect to one another; graphite is an electrical insulator and a thermal insulator perpendicular to the layers. Due to the difference between the in-plane and out-of-plane bonding, graphite has a high modulus of elasticity parallel to the plane and a low modulus perpendicular to the plane. Thus, graphite is highly anisotropic.

The high modulus of a carbon fiber stems from the fact that the carbon layers, though not necessarily flat, tend to be parallel to the fiber axis. This crystallographic preferred orientation is known as a fiber texture. As a result, a carbon fiber has a higher modulus parallel to the fiber axis than perpendicular to the fiber axis. Similarly, the electrical and thermal conductivities are higher along the fiber axis, and the coefficient of thermal expansion is lower along the fiber axis.

The greater the degree of alignment of the carbon layers parallel to the fiber axis, i.e., the stronger the fiber texture, the greater the c -axis crystallite size (L_c), the density, the carbon content, and the fiber's tensile modulus, electrical conductivity, and thermal conductivity parallel to the fiber axis; the smaller the fiber's coefficient of thermal expansion and internal shear strength.

The carbon layers in graphite are stacked in an AB sequence, such that half of the carbon atoms have atoms directly above and below them in adjacent layers (Figure 1.1). Note that this AB sequence differs from that in a hexagonal close packed (HCP) crystal structure. In a carbon fiber, there can be

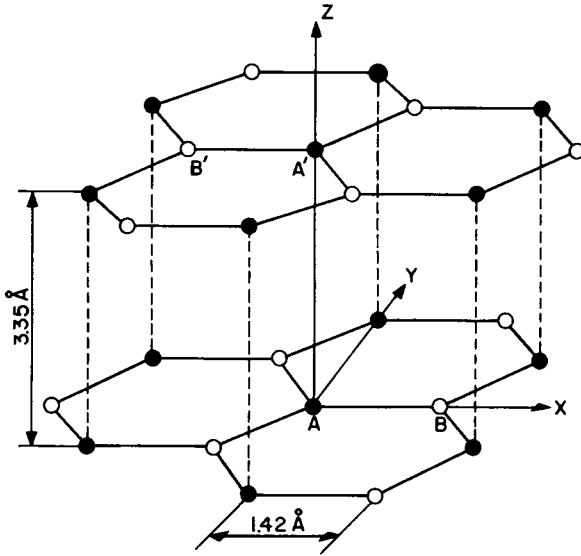


Figure 1.1 The crystal structure of graphite.

graphite regions of size L_c perpendicular to the layers and size L_a parallel to the layers. There can also be crystalline regions in which the carbon layers, though well developed and parallel to one another, are not stacked in any particular sequence; the carbon in these regions is said to be turbostratic carbon. Yet another type of carbon that can exist in carbon fibers is amorphous carbon, in which the carbon layers, though well developed, are not even parallel to one another.

The proportion of graphite in a carbon fiber can range from 0 to 100%. When the proportion is high, the fiber is said to be graphitic, and it is called a graphite fiber. However, a graphite fiber is polycrystalline, whereas a graphite whisker is a single crystal with the carbon layer rolled up like a scroll. Because of their single crystal nature, graphite whiskers are virtually flaw-free and have exceptionally high strength. However, the production yield of graphite whiskers is too low for them to be commercially significant. This book only deals with fibers—not whiskers.

Table 1.1 [2] compares the mechanical properties, melting temperature, and density of carbon fibers with other types of fibers. There are numerous grades of carbon fibers; Table 1.1 only shows the two high-performance grades, which are labeled “high strength” and “high modulus.” Among the fibers (not counting the whiskers), high-strength carbon fibers exhibit the highest strength while high modulus carbon fibers exhibit the highest modulus of elasticity. Moreover, the density of carbon fibers is quite low, making the specific modulus (modulus/density ratio) of high-modulus carbon fibers exceptionally high. The polymer fibers, such as polyethylene and Kevlar fibers, have

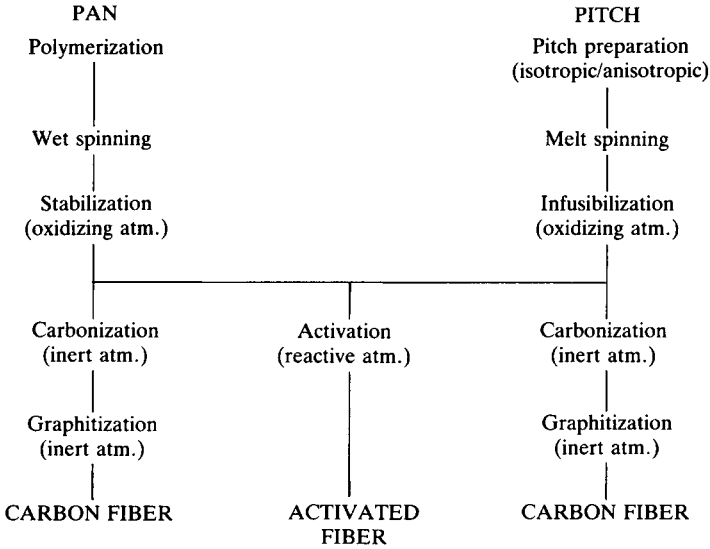
Table 1.1 Properties of various fibers and whiskers.

<i>Material</i>	<i>Density^a</i> (g/cm ³)	<i>Tensile strength^a</i> (GPa)	<i>Modulus of elasticity^a</i> (GPa)	<i>Ductility</i> (%)	<i>Melting temp.^a</i> (°C)	<i>Specific modulus^a</i> (10 ⁶ m)	<i>Specific strength^a</i> (10 ⁴ m)
E-glass	2.55	3.4	72.4	4.7	<1 725	2.90	14
S-glass	2.50	4.5	86.9	5.2	<1 725	3.56	18
SiO ₂	2.19	5.9	72.4	8.1	1 728	3.38	27.4
Al ₂ O ₃	3.95	2.1	380	0.55	2 015	9.86	5.3
ZrO ₂	4.84	2.1	340	0.62	2 677	7.26	4.3
Carbon	1.50	5.7	280	2.0	3 700	18.8	19
(high-strength)							
Carbon	1.50	1.9	530	0.36	3 700	36.3	13
(high-modulus)							
BN	1.90	1.4	90	1.6	2 730	4.78	7.4
Boron	2.36	3.4	380	0.89	2 030	16.4	12
B ₄ C	2.36	2.3	480	0.48	2 450	20.9	9.9
SiC	4.09	2.1	480	0.44	2 700	12.0	5.1
TiB ₂	4.48	0.10	510	0.02	2 980	11.6	0.3
Be	1.83	1.28	300	0.4	1 277	19.7	7.1
W	19.4	4.0	410	0.98	3 410	2.2	2
Polyethylene	0.97	2.59	120	2.2	147	12.4	27.4
Kevlar	1.44	4.5	120	3.8	500	8.81	25.7
Al ₂ O ₃ whiskers	3.96	21	430	4.9	1 982	11.0	53.3
BeO whiskers	2.85	13	340	3.8	2 550	12.3	47.0
B ₄ C whiskers	2.52	14	480	2.9	2 450	19.5	56.1
SiC whiskers	3.18	21	480	4.4	2 700	15.4	66.5
Si ₃ N ₄ whiskers	3.18	14	380	3.7	—	12.1	44.5
Graphite	1.66	21	703	3.0	3 700	43	128
whiskers							
Cr whiskers	7.2	8.90	240	3.7	1 890	3.40	12

^aFrom Ref. 2.

densities even lower than carbon fibers, but their melting temperatures are low. The ceramic fibers, such as glass, SiO₂, Al₂O₃ and SiC fibers, have densities higher than carbon fibers; most of them (except glass fibers) suffer from high prices or are not readily available in a continuous fiber form. The tensile stress-strain curves of the fibers are straight lines all the way to fracture, so the strength divided by the modulus gives the ductility (strain at break) of each fiber, as shown in Table 1.1. The main drawback of the mechanical properties of carbon fibers is in the low ductility, which is lower than those of glass, SiO₂, and Kevlar fibers. The ductility of high-modulus carbon fibers is even lower than that of high-strength carbon fibers.

Carbon fibers that are commercially available are divided into three categories, namely general-purpose (GP), high-performance (HP), and acti-



Scheme 1.1 The processes for making carbon fibers from PAN and pitch precursors.

vated carbon fibers (ACF). The general-purpose type is characterized by an amorphous and isotropic structure, low tensile strength, low tensile modulus, and low cost. The high-performance type is characterized by relatively high strength and modulus. Among the high-performance carbon fibers, a higher modulus is associated with a higher proportion of graphite and more anisotropy. Activated carbon fibers are characterized by the presence of a large number of open micropores, which act as adsorption sites. The adsorption capacity of activated carbon fibers is comparable to that of activated carbons, but the fiber shape of activated carbon fibers allows the adsorbate to get to the adsorption site faster, thus accelerating the adsorption and desorption processes [3]. The amount adsorbed increases with the severity of activation. Severe activation may be achieved by treating commercial ACF with sulfuric acid followed by heating at up to 500°C [4].

Commercial carbon fibers are fabricated by using pitch or polyacrylonitrile (PAN) as the precursor. The processes for both precursors are shown in Scheme 1.1 [5].

Precursor fibers are fabricated by conventional spinning techniques, such as wet spinning for PAN and melt spinning for pitch. They must be converted to a form which is flameproof and stable at the high temperatures ($> 700^{\circ}\text{C}$) involved in carbonization. Therefore, before carbonization (pyrolysis), they are stabilized for the case of the PAN precursor, or infusibilized for the case of the pitch precursor. Both stabilization and infusibilization are carried out in an oxidizing atmosphere. After that, general-purpose and high-performance fibers are obtained by carbonization in an inert atmosphere, followed by graphitization at $> 2500^{\circ}\text{C}$ in an inert atmosphere if a high modulus is desired, whereas

activated carbon fibers are obtained by activating in a reactive atmosphere, such as steam at elevated temperatures. To enhance the preferred orientation in the high-performance carbon fibers, graphitization can be performed while the fibers are under tension. The higher the graphitization temperature, the greater the preferred orientation.

For the case of pitch as the precursor, isotropic pitch gives an isotropic carbon fiber, which belongs to the category of general-purpose carbon fibers, whereas anisotropic pitch (such as mesophase pitch) gives high-performance carbon fibers which have the carbon layers preferentially parallel to the fiber axis.

Table 1.2 shows the tensile properties of various carbon fibers on the market. Among the high-performance (HP) carbon fibers, those based on pitch can attain a higher modulus than those based on PAN, because pitch is more graphitizable than PAN. In particular, the HP fiber designated E-130 by du Pont exhibits a modulus of 894 GPa, which is over 80% of the theoretical value of a graphite single crystal (1 000 GPa). A higher modulus is associated with a lower elongation at break, as shown by comparing the group of Amoco HP fibers in the order P-25, P-75S, and P-120S, and the group of du Pont HP fibers in the order E-35, E-75, and E-130. The du Pont HP fibers exhibit higher tensile strengths and greater elongations than the Amoco HP fibers of similar moduli. Among the high-performance (HP) fibers, those based on PAN can attain a higher tensile strength and greater elongation than those based on pitch, because (1) shear is easier between the carbon layers in a graphitized fiber, (2) pitch is more graphitizable than PAN, and (3) the oriented graphitic structure causes the fibers to be more sensitive to surface defects and structural flaws. In particular, the HP PAN-based fiber designated T-1000 by Toray exhibits a tensile strength of 7 060 MPa and an elongation of 2.4%. The general-purpose (GP) fibers tend to be low in strength and modulus, but high in elongation at break.

Table 1.2 also shows the diameters of various commercial carbon fibers. Among the HP fibers, those based on PAN have smaller diameters than those based on pitch.

Pitch-based carbon fibers (GP and HP) represent only about 10% of the total carbon fibers produced worldwide around 1990 [6], but this percentage is increasing due to the lower cost and higher carbon content of pitch compared to PAN. The costs of precursors and carbon fibers are shown in Table 1.3. Mesophase pitch-based carbon fibers are currently the most expensive, due to the processing cost. Isotropic pitch-based carbon fibers are the least expensive. PAN-based carbon fibers are intermediate in cost.

Figure 1.2 [7] shows the prices and tensile strengths of carbon fibers, aramid fibers, and glass fibers. Although carbon fibers are mostly more expensive than aramid fibers or glass fibers, they mostly provide higher tensile strengths. Among the different grades of carbon fibers, the prices differ greatly. In general, the greater the tensile strength, the higher the price.

The price of carbon fibers has been decreasing, while the consumption

8 CARBON FIBER COMPOSITES

Table 1.2 Tensile properties and diameters of commercial carbon fibers.

Type	Fiber designation	Tensile strength (MPa)	Tensile modulus of elasticity (GPa)	Elongation at break (%)	Diameter (μm)	Manufacturer
GP	T-101S	720	32	2.2	14.5	Kureha Chem.
	T-201S	690	30	2.1	14.5	Kureha Chem.
	S-210	784	39	2.0	13	Donac
	P-400	690	48	1.4	10	Ashland Petroleum
	GF-20	980	98	1.0	7–11	Nippon Carbon
HP (PAN)	T-300	3 530	230	1.5	7.0	Toray
	T-400H	4 410	250	1.8	7.0	Toray
	T-800H	5 590	294	1.9	5.2	Toray
	T-1000	7 060	294	2.4	5.3	Toray
	MR 50	5 490	294	1.9	5	Mitsubishi Rayon
	MRE 50	5 490	323	1.7	6	Mitsubishi Rayon
	HMS-40	3 430	392	0.87	6.2	Toho Rayon
	HMS-40X	4 700	392	1.20	4.7	Toho Rayon
	HMS-60X	3 820	588	0.65	4.0	Toho Rayon
	AS-1	3 105	228	1.32	8	Hercules
	AS-2	2 760	228	1.2	8	Hercules
	AS-4	3 795	235	1.53	8	Hercules
	AS-6	4 140	242	1.65	5	Hercules
	IM-6	4 382	276	1.50	5	Hercules
	HMS4	2 484	338	0.7	8	Hercules
HMU	2 760	380	0.70	8	Hercules	
HP (pitch)	P-25	1 400	160	0.9	11	Amoco
	P-75S	2 100	520	0.4	10	Amoco
	P-120S	2 200	827	0.27	10	Amoco
	E-35	2 800	241	1.03	9.6	du Pont
	E-75	3 100	516	0.56	9.4	du Pont
	E-130	3 900	894	0.55	9.2	du Pont
	F-140	1 800	140	1.3	10	Donac
	F-600	3 000	600	0.52	9	Donac
ACF	FX-100	—	500 ^a	18 ^b	15	Toho Rayon
	FX-600	—	1 500 ^a	50 ^b	7	Toho Rayon
	A-10	245	1 000 ^a	20 ^c	14	Donac
	A-20	98	2 000 ^a	45 ^c	11	Donac

^aSpecific surface area (m^2/g).

^bAdsorption amount of benzene (%).

^cAdsorption amount of acetone (%).

Table 1.3 Cost of PAN-based, mesophase pitch-based, and isotropic pitch-based carbon fibers. From Ref. 6.

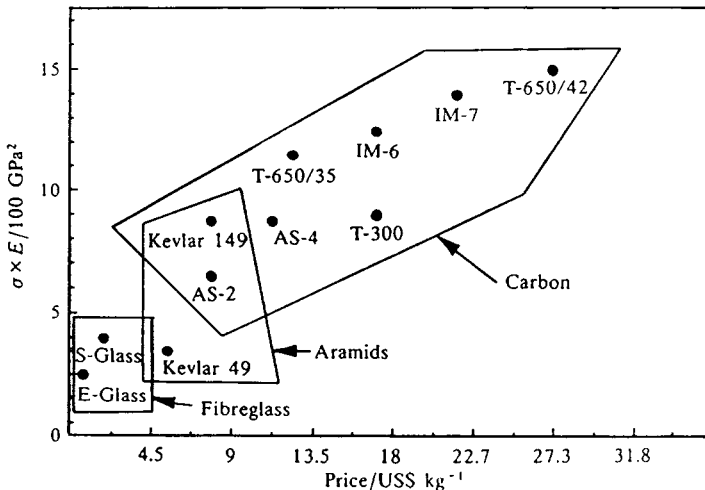
	Cost of precursor (\$/kg)	Cost of carbon fibers (\$/kg)
PAN-based	0.40	60
Mesophase pitch-based	0.25	90
Isotropic pitch-based	0.25	22

has been increasing, as shown in Figure 1.3 [7]. The decreasing price is broadening the applications of carbon fibers from military to civil applications, from aerospace to automobile applications, and from biomedical devices to concrete structures.

Under rapid development are short carbon fibers grown from the vapor of low-molecular-weight hydrocarbon compounds, such as acetylene. This process involves catalytic growth using solid catalyst particles (e.g., Fe) to form carbon filaments, which can be as small as $0.1 \mu\text{m}$ in diameter. Subsequent chemical vapor deposition from the carbonaceous gas in the same chamber causes the filaments to grow in diameter, thus resulting in vapor grown carbon fibers (VGCF) or gas-phase grown carbon fibers.

Carbon fibers can alternatively be classified on the basis of their tensile strength and modulus. The nomenclature given below was formulated by IUPAC.

- UHM (ultra high modulus) type: carbon fibers with modulus greater than 500 GPa

**Figure 1.2** The product of tensile strength (σ) and tensile modulus (E) versus price for various commercial carbon fibers. From Ref. 7. (By permission of Pion, London.)

10 CARBON FIBER COMPOSITES

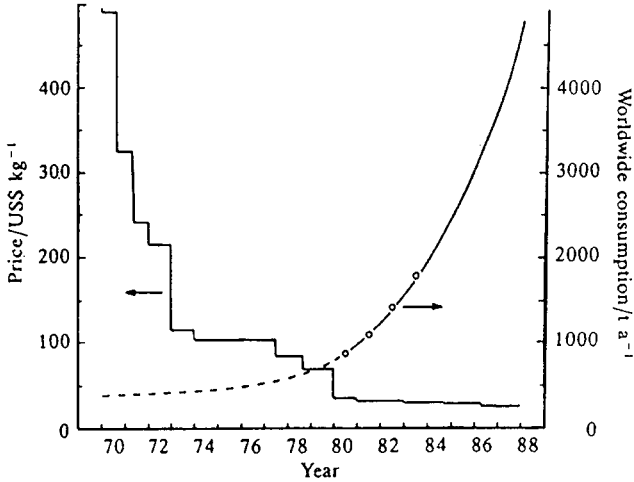


Figure 1.3 Changes in carbon fiber price and consumption over the last 20 years. From Ref. 7. (By permission of Pion, London.)

- HM (high modulus) type: carbon fibers with modulus greater than 300 GPa and strength-to-modulus ratio less than 1%
- IM (intermediate modulus) type: carbon fibers with modulus up to 300 GPa and strength-to-modulus ratio above 1×10^{-2}
- Low-modulus type: carbon fibers with modulus as low as 100 GPa and low strength. They have an isotropic structure
- HT (high strength) type: carbon fibers with strength greater than 3 GPa and strength-to-modulus ratio between 1.5 and 2×10^{-2}

There is overlap between the IM and HT categories, as shown by the above definitions.

Commercial continuous carbon fibers are in the form of tows (untwisted bundles) containing typically 1 000–12 000 fibers (filaments) per tow, or yarns (twisted bundles). They may be sized or unsized. The sizing improves the handleability and may enhance the bonding between the fibers and certain matrices when the fibers are used in composites.

High-performance carbon fibers are widely used in polymer-matrix composites for aircraft which are lightweight for the purpose of saving fuel. The aircraft Voyager has 90% of its structure made of such composites and achieved a nonstop, unfueled, round-the-world flight in 1986. The use of such composites in passenger aircraft is rapidly increasing. High-performance carbon fibers are also used in carbon-matrix composites for high-temperature aerospace applications, such as in the Space Shuttle, as the carbon matrix is more temperature resistant than a polymer matrix. These fibers have started to be used in metal matrices, such as aluminum, for aerospace applications, as aluminum is more temperature resistant than polymers.

Short general-purpose pitch-based carbon fibers are used for the reinforcement of concrete, because low cost is crucial for the concrete industry. Because this is a large-volume application of carbon fibers, the tonnage of carbon fibers used is expected to increase markedly as this application becomes more widely accepted. General-purpose carbon fibers are also used for thermal insulation, sealing materials, electrically conducting materials, antistatic materials, heating elements, electrodes, filters, friction materials, sorbents, and catalysts [8].

References

1. E. Fitzer, in *Carbon Fibers Filaments and Composites*, edited by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, and K.J. Huttinger, Kluwer Academic, Dordrecht, 1990, pp. 3–41.
2. D.R. Askeland, *The Science and Engineering of Materials*, 2d ed. PWS-Kent, 1989, p. 591.
3. L.I. Fridman and S.F. Grebennikov, *Khimicheskie Volokna* **6**, 10–13 (1990).
4. Isao Mochida and Shizuo Kawano, *Ind. Eng. Chem. Res.* **30**(10), 2322–2327 (1991).
5. K. Okuda, *Trans. Mater. Res. Soc. Jpn.* **1**, 119–139 (1990).
6. D.D. Edie, in *Carbon Fibers Filaments and Composites*, edited by J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, and K.J. Huttinger, Kluwer Academic, Dordrecht, 1990, pp. 43–72.
7. E. Fitzer and F. Kunkeler, *High Temp.–High Pressures* **22**(3), 239–266 (1990).
8. R.M. Levit, *Khimicheskie Volokna* **6**, 16–18 (1990).