

Chapter 2

Fiber Reinforcement

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Composite materials mainly consist of matrixes (polymers, metals and ceramics) and reinforcements (continuous fibers, whiskers and particles) [1]. Reinforcements are the important component of composites because they contribute the main strength to the composites [2]. According to the definitions of the Air Force Materials Laboratory (AFML) and the National Aeronautics and Space Administration (NASA), high-performance fibers are fiber reinforcements with specific strengths (tensile strength/density) and specific moduli (elastic modulus/density) higher than 6.5×10^6 and 6.5×10^8 cm, respectively. Additionally, advanced composite materials are composites made from these fibers [3].

The variety of fiber reinforcements range from widely used glass fibers and plant fibers to new fibrous reinforcement varieties such as organic fibers like aramid, polyester, polybenzoxazole (PBO) and ultra-high molecular weight polyethylene (UHMWPE) fibers. Inorganic fibers like alumina, carbon, silicon carbide and specialty glass fibers are also of note [2, 3].

In the 1990s, a variety of new technologies and new equipment was developed to prepare advanced composite materials, and this promoted the development of high-performance fibers. Development is currently advancing well with regard to research, production and marketing. As a result, a new generation of high-performance fibers such as ultra-high-temperature silicon carbide fibers and carbon nanotubes are receiving much attention.

The development of high-performance fibers will accelerate the development of advanced composite materials. This chapter will briefly introduce the main types of high-performance fiber reinforcements, including their preparation, characteristics and applications. Major developments in China over the last two decades are also highlighted.

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2.1 Glass Fibers

Glass fibers are usually drawn from a molten mixture of quartz sand, limestone, dolomite and paraffin, as well as a certain fraction of soda and boric acid [4]. To facilitate the process or to achieve the desired performance, an appropriate fraction of TiO_2 , ZrO_2 or Al_2O_3 is also incorporated. The components and the drawing process greatly affect the performance of the final fibers.

Glass fibers are non-combustible and do not decompose, and they are characterized by good chemical stability, good heat resistance, high tensile strength, high electrical insulation, low tensile strain, low insulation and a low coefficient of thermal expansion. They were the first fibers to be used for the preparation of polymer matrix composites. They are commonly known to be low-cost reinforcements for fiberglass-reinforced plastics (FRP) [5]. The diameters of the glass fibers vary from 5 to 20 μm , and a finer fiber diameter generally results in better performance.

The types and specifications of commercially available glass fibers are mainly as follows:

A-glass fiber, containing high alkali metal oxides;
 C-glass fiber, resistant to chemical attack;
 D-glass fiber, with a high dielectric property;
 E-glass fiber, with high electric insulation;
 M-glass fiber, with a high Young's modulus;
 S-glass fiber, with a high tensile strength;
 AR-glass fiber, alkaline resistant and suitable for reinforcing cement matrix composites.

As reinforcements, glass fibers can be processed into yarns, cloths, belts, as well as three-dimensional fabrics, such as carpets. Table 2.1 lists the types and compositions of commercial glass fibers, and their typical properties are listed in Table 2.2. The glass fiber varieties and grades produced in China have different

Table 2.1 Types and compositions of commercial glass fibers

Type	Composition/%						
	SiO_2	Al_2O_3	B_2O_3	CaO	Na_2O	MgO	Others
A	72	0.6–1.5	–	10	14.2	2.5	0.7% SO_3
C	65	4	6	14	8	3	
D	74	0.3	22	0.5	1.0	–	0.5% LiO_2
E	52–56	12–16	5–13	16–25	0–2	0.6	0–1.5% TiO_2
E-CR	58–63	10–13	1.0–2.5	21–23	0–1.2	–	1–2.5% TiO_2 , 0–3.5% ZnO
M	53.7	–	–	12.9	–	9.0	2.0% ZrO_2 , 8% BeO_2 , 8% TiO_2 , 3% CeO_2
S	65	25	–	–	–	10	–
Z or AR	71	–	–	–	11	–	16% ZrO_2 , 2% TiO_2

Table 2.2 Properties of commercial glass fibers

Type	Diameter/ μm	Density/ (g/cm^3)	Coefficient of thermal expansion/ $(\times 10^{-6} \text{ K})$	Young's modulus/GPa	Tensile strength/GPa	Tensile strain/%	Poisson's ratio	Softening temperature/ $^{\circ}\text{C}$
E	12	2.54	5.0	72.4–76	3.6	–2.0	0.21	845
AR	12	2.68	7.5	70–80	3.6	–2.0	0.22	–
M	12	2.89	5.7	110	3.5	–	–	–
S	12	2.48	2.9–5.0	–86	4.6	–	–	968

Table 2.3 Properties of the glass fiber varieties produced in China

Property	Non-alkali	Medium alkali 5 [#]	Medium alkali 5-2 [#]	High alkali	High strength 2 [#]	High modulus M ₂	Alkali resistant R ₁₃
Tensile strength/GPa	3.12	2.68	—	—	4.10	—	—
Young's modulus/GPa	73	—	—	—	85	95	—
Density/g·cm ⁻³	2.57	2.53	2.54	2.51	2.54	2.77	2.73
Permittivity at 10 ⁶ Hz	6.6	—	—	—	—	—	—
Loss tangent angle at 10 ⁶ Hz	1.1 × 10 ⁻³	—	—	—	—	—	—
Volume resistivity/Ω·cm	1.2 × 10 ¹⁵	—	—	—	—	—	—
Surface resistivity/Ω·cm	2.2 × 10 ¹⁴	—	—	—	—	—	—

—2[#] is equivalent to No.2; 5-2[#] is equivalent to No.5-2.

Table 2.4 Properties of the high-strength glass fiber varieties produced in China

Type	Density/g·cm ⁻³	Tensile strength/GPa	Specific tensile strength/×10 ⁷ cm	Young's modulus/GPa	Specific modulus/×10 ⁸ cm
S ₁	2.55	2.8-3.10	1.10-1.20	80-83	3.14-3.25
S ₂	2.54	3.00-4.10	1.18-1.61	85-87	3.35-3.43
S ₃	2.64	3.72	1.41	89	3.38
No alkali	2.54	2.0	0.79	73	2.83

Table 2.5 Effect of heat treatment temperature on high-strength glass fibers

Type	Tensile strength/GPa					
	Room temperature	300 °C	400 °C	500 °C	600 °C	700 °C
S ₁	3.39	2.31	1.90	1.40	1.70	—
S ₂	3.40	3.35	—	2.30	2.20	1.50
S ₃	3.75	3.08	3.10	3.32	2.26	1.70

specifications, and these are listed in Table 2.3. Among these fibers, the high-strength type can be subclassified as in Table 2.4, and their tensile strength variations are listed in Table 2.5 as a function of heat treatment temperature.

2.1.1 E-Glass Fibers

E-glass fibers, also referred to as non-alkali glass fibers, were the first fiber species used for electronic insulation belts. They are a kind of Ca–Al–B–Si glass fiber with a total alkali content less than 0.8 wt%, which ensures their excellent corrosion resistance and high conductivity resistance. As a favored insulation material, they have been processed into electromagnetic wires, impregnation materials, mica products, laminated products and polymer matrix composite products. The insulation grade of these products varies from B, F and H to C, which enables their widespread use in the electric and electronic fields.

They are also the most common fiber reinforcements for polymer matrix composites. They are regarded as ideal polymer strengthening glass fibers with a high strength, high Young's modulus, low density and good water resistance. As an example, they have accounted for 90% of the glass fiber market. They can be used both structurally and functionally. For example, E-glass fiber-reinforced rubber products or filter products can be used in the cement, power, metallurgy and carbon black industries where processing temperatures reach up to 150–300 °C. However, a significant disadvantage of E-glass fibers is their limited chemical corrosion resistance to acid or alkali media, thus restricting their application in a cement matrix.

2.1.2 AR-Glass Fibers

AR-glass fibers, namely alkali-resistant glass fibers, contain about 16 wt% ZrO_2 . They are used as reinforcements for cement matrix composites with an anti-alkaline property better than that of ordinary glass fibers. Compared with unreinforced cement, AR-glass fiber-reinforced cement has a 2–3 times higher tensile strength, a 3–4 times higher bending strength and a 15–20 times higher toughness. The reinforced composite can be used for manufacturing large panels, roof slabs, corrugated tiles, balcony slabs, all kinds of pipes and permanent templates.

2.1.3 S-Glass Fibers

S-glass fibers are referred to as high-strength glass fibers with a tensile strength about 35% higher than that of E-glass fibers. Their main components are SiO_2 , Al_2O_3 and MgO . A representative S-glass fiber is “S-994” with a tensile strength of 4.3–4.9 GPa, a Young's modulus of 85 GPa, a density of 2.49 g/cm^3 and a softening point of 970 °C. Typical S-glass fibers produced in China are high-strength type I and type II with a tensile strength of 4.1 GPa and a Young's modulus of 85 GPa. Based on different purposes, the fiber diameters vary from 7 to 12 μm .

S-glass fibers can be made into a variety of twistless rovings, twist yarns, cloths and other products. If the coupling agent KH-550 is applied, they can be impregnated directly into epoxy, phenolic resins and nylon, and they act as reinforcements of polymer matrix composites that require high strength. The reinforced composites can be fabricated as weapon components such as rocket engine shells and launcher shells, plane spiral lamina and landing gear, radomes, artillery covers and fuses, deep water mine shells, bulletproof vests, and ammunition boxes. They have played an important role in improving arms performance. In civilian fields, they have been used in high-pressure containers such as air cylinders, health cylinders, lifeboats, refrigerated vessels and spiral laminas.

2.1.4 M-Glass Fibers

M-glass fibers, also referred to as high-modulus glass fibers, generally have a higher modulus than common glass fibers. Their specific modulus is much higher than that of steel because their density is about two-thirds lower. Improving the modulus of glass fibers allows their use in structural composites, which results in better performance.

For $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ glass fibers, oxides such as BeO , Y_2O_3 , ZrO_2 , TiO_2 and CeO_2 are usually incorporated to increase their Young’s modulus. However, highly toxic BeO and expensive Y_2O_3 have not been industrially used even though they are particularly effective in increasing moduli.

Chinese type “M₂” glass fibers with a Young’s modulus of about 95 GPa have been produced, and they contain CeO_2 , TiO_2 and ZrO_2 [5]. Table 2.6 shows the mechanical properties of several typical high-modulus glass fibers.

M-glass fibers have a high modulus and also a high tensile strength. Additionally, their insulation properties are good and they can be used to reinforce epoxy, phenolic resins and nylon for the production of high-performance composite materials that are widely used in the space industry as structural materials. At the same time, they have found important use in civil products such as EHV-operation

Table 2.6 Mechanical properties of several typical high-modulus glass fibers

Type	Production country	Density/g·cm ^{−3}	Young’s modulus/GPa	Specific modulus/×10 ⁷ cm	Tensile strength/GPa
M ₁	China	2.80	93–95	3.32–3.39	3.10–3.40
M ₂	China	2.77	94–95	3.39–3.43	3.20–3.81
Non-alkali	China	2.54	73	2.83	3.10
YM ₃₁ A	US	2.89	110–120	3.81–4.15	3.70
BM-1	Russia	–	93	–	3.80
BM-100	Russia	–	105	–	3.50
M-11	Russia	–	112	–	4.30
M-12	Russia	–	120	–	4.50

poles with resistance to 5,00,000 V, high jump poles and diving boards. Product forms include yarn, cloth and twistless rovings.

2.1.5 High Silica Glass Fibers

High silica glass fibers contain about 96–99 wt% SiO_2 as well as small amounts of B_2O_3 , Na_2O and Al_2O_3 . For the preparation of SiO_2 – B_2O_3 – Na_2O system glass fibers, raw materials were molten and drawn into fiber products, phase separated at 500–600 °C and then soaked in hydrochloric acid at a certain temperature. B_2O_3 and Na_2O were leached, and a porous SiO_2 skeleton was left; the skeleton was then sintered at 700–900 °C with the SiO_2 content increasing to more than 96 wt%. The high silica glass fibers have fiber diameters of 4–10 μm , a density of 2.20 g/cm^3 , a tensile strength of 1.50 GPa and a Young's modulus of 73 GPa.

The main characteristics of these products are high-temperature stability, shape stability, thermal shock resistance and chemical stability, which enable their use as a high-temperature ablation reinforcement.

For example, high silica glass fiber-reinforced phenolic resins, in various composite forms, have been used as ablation-resistant parts of missiles and rockets such as missile headgear, end skirts, shell and rocket large nozzles. High silica glass fiber carpets, fabrics and other products are superior insulation materials and can function as a thermal protection layer for missiles and rockets or as impurity filters in steel materials. In addition, because of their porous structure they can be used as catalyst supports and can be fabricated into reverse osmosis membranes for use in desalination and gas separation.

2.1.6 Specialty Glass Fibers

Characterized by high strength, superior integrated performance and low cost, glass fibers are currently the most widely used and most produced reinforcements. Special glass fibers have been developed to meet some special performance requirements:

(1) Hollow Glass Fibers

As a new type of glass fiber, hollow glass fibers have features such as lightness, high stiffness, low dielectric constants and low thermal conductivity. Their main technical indexes are hollow percentage and hollow degree. The hollow percentage refers to the ratio of the number of hollow filaments versus the total number of filaments and is expressed as a percentage; the hollow degree refers to the ratio of the inner diameter versus the outer diameter of the hollow fibers, often expressed as a K value.

Table 2.7 Properties of hollow glass fiber-reinforced epoxy phenolic laminate

Fiber type	Density/g·cm ⁻³	Thermal conductivity/ kJ·(m·h·°C) ⁻¹	Dielectric constant/ $\times 10^{10}$ Hz	Dielectric loss tan σ
Hollow fiber	1.38	2.97	2.80	0.01
Dense fiber	1.98	5.94	4.65	0.02

Hollow fibers are generally prepared from E-glass. Their tensile strength increases when the K value increases from zero to 0.8 and decreases when the K value increases more than this. For general industrially produced hollow glass fibers, $K = 0.5\text{--}0.7$.

They are characterized by low thermal conductivity and low dielectric constant, as listed in Table 2.7. Composites made from hollow glass fibers can be used in the aviation industry and in underwater facilities such as radomes, deep water containers and high pressure containers.

Additionally, hollow glass fibers with metal coatings of zinc or aluminum can be used as electronic-interference materials. Because of their excellent lightness, reliability, capacity and response time, they can float in air over long periods and proliferate over a large area while having good interference effects. These antistatic and electromagnetic shielding fields allow hollow glass fibers to be widely applied.

(2) Radiation-Resistant Insulating Fibers

These fibers are composed of SiO_2 , Al_2O_3 , CaO and MgO and characterized by a small thermal neutron capture area, high insulation resistance, excellent mechanical properties and better water resistance than E-glass fibers.

Their insulation resistance is highly stable under high doses of γ -rays or strong neutron irradiation. The fibers can thus be used at high temperatures and under strong irradiation environments. For example, they can be used as main insulation materials in high-temperature cables or radiation-resistant cables in nuclear reactors. They are also insulation materials that can be used for high-temperature wires and are important reinforcements for polymer matrix composites. They can also be applied as low dielectric loss and low-density materials for electronic components or radomes.

2.2 Carbon Fibers

Fibrous carbons include continuous carbon (graphite) fibers, carbon whiskers and the recently developed carbon nanotubes, and these are new types of nonmetallic materials [3]. Among them, carbon fibers are a kind of polycrystalline fiber with incompletely crystallized graphite arranged along the fiber axial [6].

Table 2.8 Categories and mechanical properties of carbon fibers

Property	UHM	HM	UHT	HT
Young's modulus/GPa	>400	300–400	200–350	200–250
Tensile strength/GPa	>1.70	>1.70	>2.76	2.0–2.75
Carbon content/%	99.8	99.0	96.5	94.5

All the commercial continuous carbon fibers are manufactured from carbon precursors followed by spinning into fiber form (spinning step), cross-linking using proper agents (stabilization step), and heating up to 1200–3000 °C under inert gas to remove non-carbon elements (carbonation step) [6–21].

As the most successful commercialized carbon products in the last 40 years, carbon fibers have developed into one of the most important modern industrial materials. They are mainly used as reinforcements for polymer matrixes, ceramic matrixes and carbon matrix composites. At present, most countries regard high-performance carbon fibers as important engineering materials for the twenty-first century [6, 7].

Based on their mechanical properties, carbon fibers can be classified into the following categories: high-tenacity type (HT), ultra-high-tenacity type (UHT), high-modulus type (HM) and ultra-high-modulus type (UHM). Their corresponding mechanical property ranges are listed in Table 2.8.

Based on the type of carbon precursor, carbon fibers can be classified as polyacrylonitrile (PAN)-based carbon fibers, pitch-based carbon fibers and rayon (viscose filament)-based carbon fibers, whose typical species and major mechanical properties are listed in Tables 2.9, 2.10 and 2.11.

From the above tables, the most representative manufacturer is the Toray Company, whose high-performance carbon fibers are second to none in terms of production and performance. Additionally, their fiber varieties tend to be serialized [8–12].

As functional reinforcements, in addition to high specific strength and high specific modulus [10], carbon fibers also have excellent properties like high-temperature stability, chemical corrosion resistance, heat impact resistance, electrical conductivity, thermal conductivity, anti-friction properties, anti-radiation properties, damping, shock absorption, noise reduction and weavability.

Carbon fiber-reinforced composites have been widely used in the aerospace, defense and other military fields, as well as in advanced sporting goods, medical equipment, the auto industry and in other civilian areas. Their fields of application and their characteristics are listed in Table 2.12.

There are a variety of carbon fiber precursors, but those that are industrially applied mainly include polyacrylonitrile (PAN), pitch or phenolic, and rayon. Comparative mechanical properties of different precursor-based carbon fibers are listed in Table 2.13.

Table 2.9 Manufacturers, brand names and characteristics of some typical carbon fibers

Type	Manufacturer	Brand name	Diameter/ μm	Density/ $\text{g}\cdot\text{cm}^{-3}$	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Compressive strength/GPa	Note
PAN-CF	Amoco	T-50	6.5	1.81	2.90	300	0.7	1.61–4.09	C
		T-40	5.1	1.81	5.65	290	1.8	1.88–2.7	C
		T-650/35	6.8	1.77	4.55	241	1.8	≤ 0.8	C
		T-300	7	1.76	3.45	231	1.4	2.8–2.88	C
	BASF	CelionGy-70	8.4	1.90	1.86	517	0.30	1.38–2.2	M
								1.05	C
								0.413	M
								6.2–8.3	C
	Grafil Inc.	CelionG30-500	7	1.78	3.79	234	1.62	2.76	C
		Grafil34-700	6.9	1.80	4.5	234	1.9	1.66–2.2	C
		Grafil43-750	5.0	–	5.5	305	–	0.8	M
		GrafilHM-ST	6.9	–	3.2	390	–	>2.0	C
		GrafilXA	7.0	–	3.5	230	–	1.39–2.0	C

(continued)

Table 2.9 (continued)

Type	Manufacturer	Brand name	Diameter/ μm	Density/ $\text{g}\cdot\text{cm}^{-3}$	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Compressive strength/GPa	Note
PAN-CF	Hercules	MagnamiteHMS4	7	1.80	2.34	345	0.8	1.66	C
		MagnamiteIM6	5.4	1.74	5.1	303	1.7	2.8–7.1	C
		MagnamiteIM7	5	1.80	5.3	303	1.8	6.39–8.8	C
		MagnamiteIM8	5	1.80	5.3	303	1.6	3.22	C
		MagnamiteAS1	8	1.80	3.1	228	1.3	5.9	C
		MagnamiteAS4	8	1.79	4.0	221	1.6	1.44	M
		Besfight-HTA	7	1.77	3.72	235	1.6	2.8	C
								1.9	M
	Toray	Torayca-M30	6.5	1.81	1.74	392	0.6	1.6	C
		Torayca-M40						1.2	M
		Torayca-M40J	6	1.77	4.41	377	1.2	2.33	C
	Torayca-M46							3.41	C
			6.5	1.88	2.55	451	0.6	1.4	C
								1.2	M
	Torayca-M50J		5	1.8	3.92	465	0.8	4.0	C
								1.2	M
			4.7	1.94	3.92	588	0.7	1.67	C
	Torayca-T300		7	1.75	3.53	230	1.5	2.8–3.7	C
								2.55	M
		Torayca-T300S	7	1.82	4.8	230	2.1	6.1	C
		Torayca-T800H	5	1.81	5.49	294	1.9	2.74–7.86	C
		Torayca-T1000	5	–	4.8	294	2.4	2.2	M

(continued)

Table 2.10 Other properties of typical carbon fibers

Type	Manufacturer	Brand name	Horizontal compressive strength/MPa	Horizontal fracture strain/%	Shear modulus/GPa	Damping factor	Horizontal compressive modulus/GPa
PAN-CF	Hercules Toray	Magnamite-AS4	–	–	17.0	1.10	–
		Torayca M30	–	–	1.42	–	3.2
		Torayca T40	–	–	14.0	2.00	–
					17.0	1.96	
		Torayca T40J	–	–	3.52	–	4.0
					17.5	1.98	
		Torayca T50	–	–	14.0	1.50	–
					15.0	1.36	
		Torayca T300	556	26	15.0	1.30	3.21
		Thornel P-25	600	–	–	–	–
Pitch-CF	Amoco	Thornel P-55S	300	–	6.6	0.85	–
					7.0	0.81	
		Thornel P-75S	200	–	8.0	0.85	–
					9.0	0.88	
		Thornel P-100	130	–	4.7	1.00	–
					5.0	1.04	
		FiberG-E35	80	–	8.0	0.70	–
		FiberG-E75	–	–	8.5	0.73	–
					5.7	1.00	
		FiberG-E105	–	–	6.0	1.01	–
	DuPont de Nemours				5.0	1.00	–
					5.5	1.04	
		NT-20	160	8	–	–	–
		NT-40	94.3	10	–	–	–
		NT-60	54.9	5	–	–	–
	Mitsubishi Nippon Steel						

Table 2.11 Mechanical properties of carbon yarns

Type	Production country	Density/g·cm ⁻³	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%
MT	China	1.73	2.06	188	1.0
HT-I	China	1.75	2.56	225	1.1
T300	Japan	1.76	3.34	235	1.3
Graphite	China	1.78	1.96	310	0.9
M40	Japan	1.83	2.36	387	0.6

Table 2.12 Fields of application and characteristics of carbon fiber composites

Applications	Characteristics
Aerospace, roads, transport and sporting goods	High strength, toughness and lightness
Missiles, aircraft brakes, air and spacecraft antennas	High-dimensional stability and low thermal expansion coefficient
Audio equipment, hi-fi equipment capsules and robot arms	Excellent vibration damping, strength and toughness
Covered vehicles, electrical equipment, casts and bases, brushes	Electrical conductivity
Surgery and X-ray equipment and transplantation	Biologically inert and X-ray penetrating property
Textile machinery and general engineering	Anti-fatigue, self-lubricating and high damping
Chemical industry, nuclear field, valves and sealing materials	Chemically inert and corrosion resistance
Fixed circles of large generators and radiation equipment	Electromagnetic property

Table 2.13 Mechanical properties of different precursor-based carbon fibers

Precursor	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%
PAN	3.5–8.0	230–600	0.6–2.0
Rayon	0.7–1.8	40	1.8
Homogeneous pitch	0.8–1.2	40	2.0
Mesopitch	2.0–4.0	200–850	0.3–0.7

2.2.1 Polyacrylonitrile (PAN)-Based Carbon Fibers

PAN-based carbon fibers are the main type of carbon fibers accounting for 80% of the world's total output. Seventy percentage of these fibers were produced by Japanese companies like Toray, Toho and Mitsubishi, and the rest were shared by the US companies Hexcel, BP Amoco and also China's Formosa Plastics [8, 11–13].

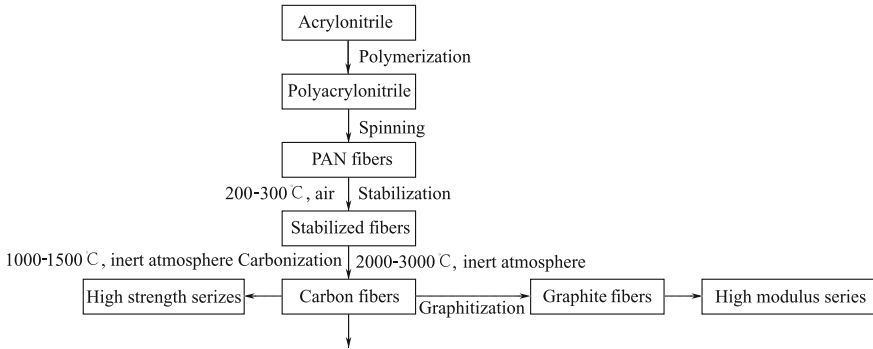


Fig. 2.1 Flowchart for PAN-based carbon fibers

PAN-based carbon fibers were invented in 1959 and were significantly improved in 1963 when the British Royal Air Research Center introduced tension into the stabilization process. They underwent rapid development in the 1990s and steady development occurred in the early twenty-first century. Currently, development is focused on high-performance PAN-based carbon fibers with higher strength, higher modulus and larger filament counts [12].

A flowchart showing PAN-based carbon fibers is shown in Fig. 2.1.

PAN-based carbon fibers are characterized by the following features: ① good weaving capability; ② low density, 1.7–2.1 g/cm³; ③ high modulus, 200–700 GPa; ④ high strength, 2–7 GPa; ⑤ fatigue resistant; ⑥ self-lubricating and wear resistant; ⑦ energy absorbing and impact resistant; ⑧ low coefficient of thermal expansion, $0\text{--}1.1 \times 10^{-6} \text{ K}^{-1}$; ⑨ good thermal conductivity without heat accumulation; ⑩ good electrical conductivity, 15–5 $\mu\Omega\cdot\text{m}$, and non-magnetic; good X-ray penetration and good biological compatibility.

Toray is the most comprehensive company in terms of PAN-based carbon fiber production, and their fiber specifications and performances are listed in Table 2.14 [8].

The performance of carbon fibers increases from T300 to T1000G and from M30S to M60 J. The company's goal is to further increase the tensile strength to 8.56 GPa. Even though their current laboratory data indicate a value of 8.05 GPa, the tensile strength can still be improved significantly because the current strength is only 4.76% that of the theoretical value. The theoretical strength of a graphite crystal is 180 GPa [13].

High-modulus carbon fibers are also referred to as graphite fibers (GrF), and they have a carbon content of 92–96%. The carbon content of ultra-high-modulus (UHM) graphite fibers is more than 99%, and the available brands and their performance are listed in Table 2.15.

Research in China on PAN-based carbon fibers started in the 1960s [12, 13]. In the mid-1970s, the tensile strength and Young's modulus reached 2.00 and 180 GPa, respectively, while in the early 1980s they reached 2.5 and 180–200 GPa, respectively, and were named HT-I. In the late 1980s, they reached 3.0–3.6 and 220

Table 2.14 Brand names and properties of Japanese company Toray’s carbon fibers

Brand name	Filament count	Tensile strength/GPa	Young’s modulus/GPa	Tensile strain/%	Size/tex	Density/(g/cm ³)
T300	1k	3.53	230	1.5	66	1.76
	3k				198	
	6k				396	
	12k				800	
T300J	3k	4.21	230	1.8	198	1.78
	6k				396	
	12k				800	
T400H	3k	4.41	250	1.8	198	1.8
	6k				396	
T600S	24k	4.12	230	1.9	1700	1.79
T700S	6k	4.9	230	2.1	400	1.8
	12k				800	
	24k				1650	
T700G	12	4.90	240	2.0	800	1.78
	24				1650	
T800H	6k	5.49	294	1.9	223	1.81
	12k				445	
T1000G	12	6.37	294	2.2	485	1.80
M35J	6k	4.70	343	1.4	225	1.75
	12k				450	
M40J	6k	4.41	377	1.2	225	1.77
	12k				445	
M46J	6k	4.21	436	1.0	223	1.84
	12k				445	
M50J	6k	4.12	475	0.8	216	1.88
M60J	3k	3.92	588	0.7	100	1.94
	6k				200	
M30S	18	5.49	294	1.9	760	1.73
M30G	18k	5.10	294	1.7	760	1.73
M40	1k	2.74	392	0.7	61	1.81
	3k				182	
	6k				364	
	12k				728	

GPa, respectively, with small quantities approaching 2.0 GPa and 280 GPa, respectively. With a graphitization temperature of 2500 °C, the Young’s modulus reached 300 GPa, but the tensile strength was only 0.8–1.2 GPa [14]. By the end of the last century, continuous fibers were produced with tensile strength higher than 2.45 GPa and a Young’s modulus higher than 392 GPa, and this is listed in Table 2.16.

Table 2.15 Brand names and properties of ultra-high-modulus (uhm) carbon fibers

Brand name	Young's modulus/GPa	Tensile strength/GPa	Tensile strain/%	Coefficient of thermal expansion/ $\times 10^{-6} \text{ K}^{-1}$	Thermal conductivity/W·(m·K) $^{-1}$	Electrical conductivity/ $\mu\Omega\cdot\text{cm}$	Density/g·cm $^{-3}$
P100S ^a	724	2.20	0.31	−1.45	520	2.5	2.15
P120S ^a	827	2.20	0.27	−1.45	640	2.2	2.18
M60J	588	3.92	0.70	−0.90	75	8.0	1.94
M70J	690	—	—	—	—	—	—
Gy-70	517	1.86	0.36	−1.10	142	6.5	1.90
Gy-80	527	1.96	0.32	—	—	6.0	1.92

^aPitch-based carbon fibers

Table 2.16 Brand names and properties of Chinese PAN-based carbon fibers

Brand name	Manufacturer	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Density/g·cm ⁻³	Diameter/ μ m	Electrical conductivity/ $\times 10^{-6} \Omega\cdot\text{cm}$
J9107	Jilin Carbon Co. Ltd.	3.49	227.6	1.63	1.68	6.3	19.6
S9206	Shanghai Carbon Co. Ltd. ^a	3.10	217.3	1.45	1.71	6.3	19.8
L8506	Lanzhou Carbon Co. Ltd. ^a	2.90	203.3	1.48	1.71	6.5	24.8

^a At a standstill

With the continuous improvement in carbon fibers as well as developments in processing and equipment, more people have come to realize that the key to high-strength carbon fibers is to control the polymer composition, to make fiber diameter finer, to produce a homogenous fiber bulk and to produce a fiber surface with few defects. With the support of national key projects, China can produce 3K or 12K T300-type carbon fibers at 100 t/a. These fibers have a tensile strength of 3.84 GPa, a Young's modulus of 235.6 GPa and a tensile strain of 1.6%.

The theoretical modulus of graphite fibers is about 1020 GPa, as listed in Table 2.15. Pitch-based carbon fibers such as P120S have reached 81.1% of the theoretical value, while PAN-based carbon fibers such as M70 J have reached 67.7%. By the end of the last century, with proper graphitization, China had produced high-modulus PAN-based carbon fibers with a tensile strength of 2.85 GPa and a Young's modulus of 382 GPa [15]. With the introduction of boron and graphitization at 2400–2900 °C, the tensile strength and the Young's modulus reached 2.53–2.89 and 400–520 GPa, respectively [16, 17].

2.2.2 Pitch-Based Carbon Fibers

As raw materials; bituminous coal, petroleum bitumen and asphalt or polyoxyethylene asphalt should be appropriately treated so that their rheological property, chemical composition and structure will meet the requirements for carbonization and graphitization.

Asphalt can be isotropic or anisotropic (such as mesopitch or LCD). Carbon fibers derived from the isotropic system generally have poor performance; for example, their tensile strength is about 950 MPa, Young's modulus is 40–45 GPa and the tensile strain is 2.0–2.2%. These fibers are referred to as common-class products and are mainly used in composites that do not require high performance. Alternatively, high-performance carbon fibers, particularly the ultra-high-modulus carbon fibers, can be manufactured from mesopitch [18–20].

Since the original carbon content of pitch is higher than that of PAN, its carbon yield is higher after carbonation. In addition to a high Young's modulus, pitch-based carbon fibers also have good thermal conductivity, electrical conductivity and a negative coefficient of thermal expansion. However, their processing properties and compressive strength are not as good as those of PAN-based carbon fibers.

High-performance pitch-based carbon fibers have unique applications in aerospace and space satellites, etc. The mechanical properties of some typical commercial pitch-based carbon fibers are listed in Table 2.17. The mechanical properties of the pitch-based carbon fibers produced by Nippon Graphite Fiber Corporation are listed in Table 2.18.

Table 2.17 Mechanical properties of some typical commercial pitch-based carbon fibers

Manufacturer	Brand name	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%
Amoco Corp.	Thornel P25	1.40	140	1.0
	Thornel P55	2.10	380	0.5
	Thornel P75	2.00	500	0.44
	Thornel P100	2.20	690	0.30
	Thornel P120	2.20	820	0.20
Osaka Gas	DannCarl F140	1.80	140	1.3
	DannCarl F60	3.00	600	0.5
Kureca	Kureca KCF100	0.90	38	2.4
	Kureca KCF200	0.85	42	2.1

The Granoc XN series are a kind of low modulus, low strength carbon fiber with a fiber diameter of about 10 μm , a Young's modulus of 55–155 GPa and a tensile strength of 1.10–2.40 GPa. However, their density is low at 1.65–2.80 g/cm^3 and their tensile strain is relatively high at 1.5–2.0%. They are mainly used for civil engineering and infrastructure in the form of sealing materials, reinforcing sheets for repairing concrete, tunnel walls and poles.

The Granoc CN series are a kind of carbon fiber mainly used for recreational sport supplies and general industrial applications. Compared with T300-type PAN-based carbon fibers, their Young's modulus is much higher and applicable to materials requiring stiffness. They can be used in electronic equipment, precision optical instruments, acoustics and audio equipment, robot arms and various rollers.

The Granoc YSH series of carbon fibers are mainly used in the manufacture of satellite antennas, satellite structure components, solar panels, joysticks, stings, missile components and rocket components.

In China, researchers mainly focus on common pitch-based carbon fibers using an isotropic pitch as the precursor as well as high-performance pitch-based carbon fibers using mesopitch as the precursor [18, 19]. The common carbon fibers have been continuously prepared with a tensile strength of 0.80–0.95 GPa, a Young's modulus of 40–45 GPa and a tensile strain of 2.0–2.5%, but these have not yet been industrialized. Because of their poor mechanical properties, they are mainly used for functional or cement matrix composites.

High-performance pitch-based carbon fibers are prepared from mesopitch by melt spinning, pre-oxidation, carbonation and graphitization [19]. Their performance depends largely on the structure and composition of the precursor. Mesopitch has been studied in-depth, and at the end of the last century, graphite fibers were produced by the modification and modulation of oil residue and coal. Spinnable pitch has a softening point of 264–278 $^{\circ}\text{C}$ and a mesopitch content above 95%. Typical mechanical properties of final continuous carbon fibers are listed in Table 2.19.

Table 2.18 Brand names and properties of carbon fibers from Nippon Graphite Fiber Corporation

Brand name	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Density/g·cm ⁻³	Diameter/ μ m	Coefficient of thermal expansion/ $\times 10^{-6}$ K ⁻¹	Thermal conductivity/W·(m·K) ⁻¹	Electrical conductivity/($\times 10^{-4}$ Ω ·cm)
XN-05	1.10	54	2.0	1.65	10	+3.4	47	28
XN-10	1.70	110	1.6	1.70	10	-0.1	-	100
XN-15	2.40	155	1.5	1.85	10	-0.8	6.3	20
CN-05	3.43	620	0.6	2.12	10	-	-	-
CN-15	3.43	780	0.5	2.17	10	-	-	-
YSH-50A10H	3.83	520	0.7	2.10	6	-1.4	140	7
YSH-50A15S	3.83	520	0.7	2.10	7	-1.4	140	7
YSH-60A	3.83	630	0.6	2.12	7	-1.4	200	6
YSH-70A	3.83	720	0.5	2.15	7	-1.5	260	5
YS-80A	3.63	785	0.5	2.15	7	-1.5	320	5
YS-90A	3.53	880	0.3	2.18	7	-1.5	500	3
YS-95A	3.53	920	0.3	2.19	7	-1.5	660	2.2

Table 2.19 Typical mechanical properties of Chinese high-modulus carbon fibers

No.	Diameter		Tensile strength		Young's modulus		Tensile strain	
	μm	C.V. %	GPa	C.V. %	GPa	C.V. %	%	C.V. %
1	13.25	12.38	2.31	20.72	525.6	17.0	0.44	18.6
2	13.68	12.33	2.18	22.70	483.2	9.95	0.46	22.5

Table 2.20 Mechanical properties of Y-shaped and circular carbon fibers

Cross section	Equivalent diameter/μm	Oxidation gas	Temperature/°C	Oxidation time/h	Tensile strength/GPa
Y-shaped	35.5	Air	300	2.0	0.882
Circular	34.9	Oxygen + air	240	10.0	0.607
Y-shaped	27.5	Air	300	0.5	0.976
Circular	29.6	Air	240	24.0	0.603

The preparation of mesopitch by the modulation of coal tar has been reported. Green filaments with a diameter of 10.3 μm and a length of 29 km were obtained after spinning, and graphite fibers with a tensile strength of 2.5 GPa and a Young's modulus of 973 GPa were obtained after pre-oxidation, carbonation and 3000 °C graphitization [18]. Additionally, Y-shaped carbon fibers have also been reported, as listed in Table 2.20 [20]. Their mechanical properties are much better than those of the circular cross-sectional fibers, but these fibers have not yet been industrialized.

2.2.3 Rayon-Based Carbon Fibers

α-Cellulose can be extracted from cellulose raw materials such as wood, cotton seed cashmere and bagasse. When they are purified with soda or carbon disulfide, dissolved in dilute NaOH, wet-spun and post-processed, viscose fibers are obtained. Carbon fibers can be obtained after oxidation in air below 300 °C and carbonization in inert atmosphere above 800 °C. If graphitized in argon above 2500 °C, their crystallinity, thermal conductivity, anti-oxidation, lubrication and heat capacity increase greatly and graphite fibers are obtained with a carbon content of more than 99% [21]. The USA and Russia are the two major producers of rayon-based carbon fibers.

Rayon-based carbon fiber products come in various forms such as short fibers, continuous fibers, yarns, fabrics, belts and clothes. They can also be divided into rayon-based carbon fibers and rayon-based graphite fibers. In addition to their high specific strength, high specific modulus, good corrosion resistance and good lubrication properties, the fibers are also characterized by low density, low thermal conductivity, high purity, high tensile strain, good flexibility, large surface area and easy activation, etc.

These fibers play an irreplaceable role in thermal insulation-resistant and ablative materials, in reinforcement materials as well as in promising biological engineering materials because of their excellent biocompatibility. Brand names and properties of rayon-based carbon fiber products are listed in Tables 2.21, 2.22 and 2.23.

Rayon-based carbon fibers are mainly used as large area ablation shielding materials for aircraft brakes, car brakes, radioisotope boxes, solid-fuel engine nozzles, reentry vehicles, rocket and missile noses or heads. They can also be used to reinforce polymer composites with applications in corrosion-resistant pumps, laminas, pipes, containers and conductive wires, heating bodies, sealing materials, catalyst supports and medical absorption materials, and colloidal materials in addition to medical bandages and anti-chemical clothes.

In China, research on rayon-based carbon fibers started in the 1980s but still lags far behind the USA and Russia. Some achievements have been made in that a production line with an annual output of 300 kg was built in 2002. In addition, there are reports on the improvement of the mechanical properties of rayon-based carbon fibers wherein SiC-coated carbon fibers were prepared after surface treatment with multi-amine fire retardant and polycarbosilane with subsequent heat treatment at 1000 °C [22]. Their tensile strength, Young's modulus, electrical resistance, diameter and density, respectively, are 1.3–2.0 GPa, 70–130 GPa, 10^{-2} – 10^{-3} Ω-cm, 4–6 μm and 1.55–1.60 g/cm³.

2.3 Ceramic Fibers

As one of the outstanding Chinese achievements, traditional ceramic material is a class of clay material that can be cast into various shapes that hardens upon high-temperature treatment. They are polycrystalline materials with a specific strength. With the scientific and technological development of ceramic manufacturing including purification and related fields, ceramics have progressed from traditional ceramics to advanced ceramics [23–27].

Advanced ceramics mainly refer to nonmetallic oxides, quasi-metal oxides, carbides, nitrides, alumina, aluminum nitride and carbon, etc. Their raw materials are generally high purity, ultra-fine synthetic inorganic compounds. Their common characteristics are high-temperature stability, oxidation resistance, erosion resistance, corrosion resistance, wear resistance, high hardness and a low creep rate as well as coupling features related to their light, electrical, magnetic, acoustic and thermal properties. They are mainly used in high-tech and military technical areas that require high-temperature stability, corrosion resistance and wear resistance, etc. Examples might be mechanical seals, ceramic bearings, ball valves, ceramic cylinders and cutting tools.

With the development of materials science and engineering, advanced ceramic materials have developed from polycrystalline bulk materials to low-dimensional materials such as fibers or whiskers. They not only retain the original characteristics

Table 2.21 Mechanical properties of Chinese rayon-based carbon fibers

Type	Diameter/ μm	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Density/ $\text{g}\cdot\text{cm}^{-3}$	Electrical conductivity/ $\times 10^{-2}\ \Omega\cdot\text{cm}$	Carbon content/%
Carbon fibers	5-7	0.40-0.60	25-35	1.5-2.0	1.4	4	91-95
Graphite fibers	5-7	0.60-0.80	60-80	1.0-1.5	1.5-1.8	4	99.6

Table 2.22 Mechanical properties of US high-performance rayon-based carbon fibers

Manufacturer	Brand name	Tensile strength/GPa	Young's modulus/GPa	Density/g·cm ⁻³
Union Carbide Corporation (UCC)	Thornel-25	1.260	175	1.40–1.45
	Thornel-40	1.750	280	1.56
	Thornel-50	1.995	350	1.60
	Thornel-100	3.500	700	1.79
HITCO Carbon Composites (HITCO)	HMG-20	1.120–2.100	154–210	1.5
	HMG-40	1.400–1.645	245–350	1.7
	HMG-50	2.100–2.205	350–427	1.8

Table 2.23 Mechanical properties of Russian rayon-based carbon fibers

Brand name	Form	Carbon content/%	Fracture load (5-cm-wide fabric strength)/GPa		Tensile strength/GPa
			Radial	Latitudinal	
YPaIT-22	Cloth or belt	≥ 99.5	1.4	0.5	1.30
YPaITp3/2-15	Fabric	≥ 95.0	1.5	–	1.00
YPaITp3/2-20	Fabric	≥ 99.5	1.5	–	1.00
YPaITM/4-22	Multilayer fabric	≥ 99.5	3.0	2.0	1.30
YPaIII0-22	One-directional belt	≥ 99.5	–	–	2.00
YPaIII0-15	One-directional belt	≥ 95.0	–	–	2.00
YPaIC	Mesh	≥ 99.5	–	–	1.80
YPaIH	Textile	≥ 99.5	–	–	1.60
YPaIIII	Sewing yarn	≥ 99.5	–	–	1.60
YPaITp3/2-152	Surface-modified fabric	≥ 96.0	1.59	–	–
YVT-2	Fabric	≥ 94.0	1.40	0.8	0.80
YTM-8	Fabric	≥ 70.0	0.60	0.2	0.60
YTIeH	Yarn	≥ 94.0	–	–	0.50

of ceramics but also have new features that greatly extend the possible applications of ceramic materials and lead to a new variety of products.

However, high-tech fields such as space, energy and chemicals demand materials with excellent mechanical properties and also require them to withstand extreme environmental conditions such as aerodynamic heating and the resultant high temperatures, high heat flux densities, high-speed particle erosion and salt spray corrosion. These materials should have excellent chemical and thermal mechanical stabilities at 1500 °C.

Much research has been devoted to the development of ceramic matrix composites and intermetallic compound matrix composites. However, because of the

inherent brittleness and poor reliability of ceramics, it is the only effective method to produce excellent ceramic matrix composites using reinforcing ceramics with high-performance fibers or whiskers. Ceramic fiber-reinforced ceramic matrix composites are currently used in the manufacture of space shuttle components, thermal protection materials, high-performance engines, high-temperature heat exchangers, and other high-temperature structure materials.

Some oxide ceramics like quartz and Al_2O_3 can be melt-spun into ceramic fibers using high purity or controlled purity and composition ceramic materials, but most ceramics cannot be directly spun into ceramic fibers because of their high melting points. The general approach is to synthesize pre-ceramic precursors, which could be either inorganic precursors or organic polymer precursors. The precursors can be easily spun into green fibers and then be transformed into ceramic fibers after firing and sintering at high temperatures.

Like organic fibers, ceramic fibers have high strength, high modulus, fine diameters and good weaving performance; however, ceramic fibers also have high-temperature stability, oxidation resistance and high hardness. Therefore, ceramic fibers are believed to be important reinforcements for advanced polymers, metals and ceramic matrix composites [23–27].

2.3.1 Alumina Fibers

The main phase of alumina fibers is $\alpha\text{-Al}_2\text{O}_3$, and small amounts of SiO_2 , B_2O_3 , Zr_2O_3 , MgO , etc. are also present. These fibers have excellent high-temperature oxidation resistance and high-temperature stability as high as 1400°C . They have been given much attention recently. As a typical example, the 3M Company in the USA produced a new Al_2O_3 fiber using iron oxide for grain refinement. The tensile strength and elasticity modulus of this fiber are as high as 3.2 and 370 GPa, respectively (Nextel610). In addition, Nextel610 has a low thermal conductivity, unique electrochemical properties and corrosion resistance properties [24].

Compared with other ceramic fibers, alumina fibers have simple processing procedures, minimal equipment requirement and no need for inert gas protection. Therefore, it is cost-effective and has great commercial value. It is an important strengthening fiber that can be widely used in the military and civilian composite materials industries. The preparation methods and compositions of alumina fibers are various, and their characteristics are different from product to product. Alumina fibers can be continuous or non-continuous and common brands, and their properties are listed in Table 2.24.

From the above table, the fiber properties are shown to differ greatly upon a variation in method and composition. Alumina fibers are mainly classified as two kinds of fibers, namely composite reinforcements or high-temperature insulation materials. Continuous fibers can be woven into sheets, braids, ropes and other special forms. They are mainly used to strengthen Al, Ti, SiC and oxide matrixes to manufacture flexible insulation composites. Because the fibers and these matrixes

Table 2.24 Properties of typical alumina fibers

Brand name	Manufacturer	Diameter/ μm	Composition/ %(wt)	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Density/ $\text{g}\cdot\text{cm}^{-3}$	Working temperature/ $^{\circ}\text{C}$
FP	Du Pont	15–20	$\alpha\text{-Al}_2\text{O}_3$ 99	1.4–2.1	350–390	0.29	3.95	1000–1100
PRO	Du Pont	15–25	$\alpha\text{-Al}_2\text{O}_3$ 80 Zr_2O_3 20	2.2–2.4	385–420	0.40	–	1400
Altel	Sumitomo	9–17	$\alpha\text{-Al}_2\text{O}_3$ 75 SiO_2 25	1.8–2.6	210–250	0.80	3.2–3.3	1250
Safil	ICI	3	$\alpha\text{-Al}_2\text{O}_3$ 95 SiO_2 5	1.03	100	0.67	2.8	1000
Nextel312	3M	11	$\alpha\text{-Al}_2\text{O}_3$ 62 SiO_2 24 B_2O_3 14	2.0 1.3–1.7	300 152	– 1.12	3.3 2.7	1000 1200–1300
ACo ₂	3M	10	$\alpha\text{-Al}_2\text{O}_3$ 70 SiO_2 29 Cr_2O_3 1	1.38	159	–	2.8	1400
Nextel440	3M	–	$\alpha\text{-Al}_2\text{O}_3$ 70 SiO_2 28 B_2O_3 2	1.72	207–240	1.72	3.1	1430
Nextel480	3M	10–12	$\alpha\text{-Al}_2\text{O}_3$ 60 SiO_2 40	1.90	220	0.86	3.05	–
Nextel550	3M	10–12	$\alpha\text{-Al}_2\text{O}_3$ 73 SiO_2 27	2.2	220	0.98	3.75	–
Nextel720	3M	10	$\alpha\text{-Al}_2\text{O}_3$ 85 SiO_2 15	2.1	260	0.81	3.4	–
Nextel610	3M	10–12	$\alpha\text{-Al}_2\text{O}_3$ 99 SiO_2 0.25	3.2	370	0.5	3.75	–

are well matched, their composites have been used in supersonic aircraft, rocket engine nozzles and gaskets. Alumina short fibers are mainly used as insulation refractory materials in metallurgical furnaces, ceramic sintering furnaces or other high-temperature furnaces.

In addition to their abilities to enhance mechanical properties and to improve the hardness and wear resistance of the matrixes, alumina fibers have low density, good insulation, low thermal capacity, are effective energy savers, and have a low coefficient of thermal expansion. Therefore, alumina fiber-reinforced aluminum matrix composites have been applied to the production of car pistons, connecting rods, brake parts, gas compressor rotating blades and helicopter transmission devices. Furthermore, the Young's modulus of alumina fibers is higher than that of glass fibers and their compressive strength is higher than that of carbon fibers. Importantly, the fibers are white and alumina fiber-reinforced polymers can thus be fabricated into colored fishing rods, golf pars, skis, tennis rackets and other items that require high intensity and high rigidity properties.

Alumina fibers are still in the laboratory stage of development in China, but aluminum silicate and aluminum borate short insulation fibers have been produced on large scale. China lags behind in high-performance continuous alumina fibers.

2.3.2 Silicon Carbide Fibers

This fiber series consists of silicon carbide (SiC) fibers, silicon nitride (Si_3N_4) fibers and new silicon-based ceramic fibers in which silicon is the main element containing small amounts of B, Ti, Zr and C [23–35].

SiC fibers are a new kind of ceramic fiber with excellent strength, modulus, high-temperature stability, oxidation resistance, corrosion resistance, antineutron radiation properties and electromagnetic transmission and absorption properties. SiC fibers are an important species that are ideal reinforcements for structural composites and have undergone rapid development for use in ceramic fibers in the 1980s.

The preparation of continuous SiC fibers is mainly carried out by chemical vapor deposition (CVD) and by the pre-ceramic polymer-derived (PPD) method. Both methods can be used to produce continuous SiC fibers [25–29]. The properties of several typical commercial and developmental SiC fibers are listed in Table 2.25, and their high-temperature resistances are listed in Table 2.26.

2.3.2.1 Chemical Vapor-Deposited (CVD) SiC Fibers

CVD was the first approach used for the production of SiC fiber core-shell composite filaments. In 1961, Gareis and coworkers applied for a patent using ultra-fine W silk as the deposition support to produce SiC (W core) fibers [28]. In 1972, US company AVCO Corporation produced large-diameter C-wire, and as a result, SiC

Table 2.25 Properties of several typical SiC fibers

Brand name	Manufacturer	Composition/ %(wt)	Density/g·cm ⁻³	Diameter/ μ m	Tensile strength/GPa	Young's modulus/GPa	Status
NL202	Nippon Carbon	Si57C31O12	2.55	14	3.0	220	C
Hi-Nicalon	Nippon Carbon	Si62C32O0.5	2.74	14	2.8	270	C
Hi-Nicalon-S	Nippon Carbon	Si68.9C30.9O0.2	3.10	12	2.6	420	C
Tyranno LoxM	Ube Industries	Si55.4C32.4 O10.2Ti2.0	2.48	11	3.3	187	C
Tyranno ZM	Ube Industries	Si55.3C33.9 O9.8Zr1.0	2.48	11	3.3	192	C
Tyranno SA	Ube Industries	Si67C31 O < 1.0Al < 2.0	3.10	10	2.8	380	C
SiBNC	Bayer	Si-B-N-C	1.8-1.9	8-14	3.0	358	C
UF SiC	3 M	SiC(98.9)O1.1	2.70	10-12	2.8	210-240	D
SCS-6	Textron	SiC(C)	3.00	140	4.0	390	C
Sylramic	Dow Corning	SiC(95) TiB ₂ (3)B ₄ C(1.3)	3.00	10	3.4	386	C
KD-I	NUDT, China	Si-C-O	2.42	12-15	2.4-3.0	150-190	D
SiC(W)	CAS, China	SiC(W)	3.4	100 \pm 3	3.7	426	D

Note C—commercialized; D—developmental

Table 2.26 High-temperature resistances of typical SiC fibers

Brand name	Composition	Highest working temperature/°C	Working temperature/°C	Application field	Price/\$·kg ⁻¹
NL202	Si–C–O	1300	1100	PMC, MMC, CMC	1295
Hi-Nicalon	Si–C	1400	1200	PMC, MMC, CMC	6900
Tyranno LoxM	Si–C–O–Ti	1400	1100	MMC	–
Sylramic	SiC, TiB ₂	1400	1200	CMC	10000
SCS-6	SiC	1400	1300	PMC, MMC	8800

Note PMC—polymer matrix composites; MMC—metal matrix composites; CMC—ceramic matrix composites

(C core) fibers were produced with better performance and lower cost. Subsequently, from 1981 to 1984, SiC (C core) fibers were successfully commercialized by AVCO. Recently, the US company Textron (formerly AVCO Corporation) was allowed to produce a series of SCS-2, SCS-6 and SCS-8 SiC (C core) fibers.

British company BP bought the original German technology for the production of SiC (W core) fibers. It produced a series of fibers referred to as SM1040, SM1140 and SM1240 with different surface coatings. These fibers were applied, respectively, to reinforce polymers, aluminum, titanium, intermetallic compounds and ceramic matrixes.

Research has been carried out in China on mercury electrode-heated CVD SiC (W core) fibers as early as 1975 [29]. The tensile strength of the fibers was 2.6 GPa, and the continuous length reached 900 m. The radio-frequency heating method was then successfully applied to produce CVD SiC (W core) fibers. Meanwhile, detailed studies on the reaction mechanism revealed characteristics such as microstructure and optimal parameters. Continuous SiC (W core) fibers with surface protection coatings were successfully manufactured with properties close to the similar US and UK products in the 1990s (see Table 2.27). The production capacity reached an annual output of 12 kg. The dispersion coefficient of the tensile strength was less than 10%, and the continuous length was longer than 1000 m.

2.3.2.2 Pre-ceramic Polymer-Derived (PPD) SiC Fibers

The precursor approach of transferring organic materials into inorganic materials by high-temperature treatment under oxygen-free atmospheres has been used since ancient times. Similar to the method to obtain carbon fibers wherein PAN or other organic fibers are carbonized in an inert atmosphere at high temperatures, this kind of precursor method has been applied to the commercial production of ceramic fibers [23].

Table 2.27 Properties of CVD SiC (W core) fibers

Location	Brand name	Diameter/ μm	Tensile strength/GPa	Young's modulus/GPa	Density/ $\text{g}\cdot\text{cm}^{-3}$	Surface coating
USA	SCS series	≈ 140	3.50	400	3.0	Si/C
UK	SM1040	100	3.50	400	3.4	N/A
UK	SM1140	107 ± 3	3.00–3.30	–	–	C
UK	SM1240	101 ± 4	3.00–3.50	–	–	C + TiB_x
CN	–	100 ± 3	3.70	>426	3.4	C

The process includes four steps: ① synthesis of pre-ceramic polymers (pre-cursors); ② melt spinning of polymers into green fibers; ③ curing of green fibers by oxidation or EB radiation, and ④ pyrolysis of the cured fibers under an inert atmosphere at high temperatures. Fine-diameter continuous SiC fibers are finally obtained from polycarbosilane precursors. Nippon Carbon Co. first realized the industrial production of a series of continuous SiC fibers under the trademark Nicalon.

Compared with CVD SiC fibers, the biggest advantage of PPD SiC fibers is their much smaller diameter, which allows easy weaving into a variety of fabrics. It can then be easily used as reinforcements in complicated composites. In addition, PPD SiC fibers are very good heat-resistant materials and can be used as insulation materials, high-temperature conveying belts, melt filters, etc. The properties of Nicalon serial fibers are listed in Table 2.28.

The successful development of SiC fibers by the PPD method resulted in a large amount of interest from material scientists. Recently, plenty of research has been carried out on Nicalon fibers and their composites resulting in an understanding of their advantages and disadvantages. This lay the foundation for further enhancements of fiber performance and a reduction in production costs. Newer silicon-based ceramic fibers have also produced such as *M*-containing SiC fibers (*M* = Ti, Zr, Al, etc.), near-stoichiometric SiC fibers, silicon nitride (Si_3N_4) and Si–B–C–N fibers [23, 25, 30–41]. China entered this field in the early 1980s, and a variety of SiC fibers have been studied including carbon-rich SiC fibers, magnetic particle-containing SiC fibers and non-circular SiC fibers.

(1) Continuous SiC fibers

In the 1970s, Professor Yajima first obtained SiC fibers from a silicon-based polymer, polycarbosilane. This is the first ceramic fiber obtained using polymer techniques. Subsequently, Nippon Carbon procured the patent and started scale-up production. A series of fibers were then commercialized and trademarked as Nicalon, as listed in Table 2.28.

Table 2.28 Properties of the Nicalon serial fibers

Property	NL-200	HVR NL-400	LVR NL-500	NL-607	Hi-Nicalon	Hi-Nicalon-S
Diameter/ μm	14/12	14	14	14	14	12
Filament count	250/500	250/500	500	500	500	500
Denier/(g/1000 m)	105/210	110/220	210	210	200	180
Tensile strength/GPa	3.00	2.80	3.00	3.00	2.80	2.60
Young's modulus/GPa	220	180	220	220	270	420
Tensile strain/%	1.4	1.6	1.4	1.4	1.0	0.6
Density/(g/cm^{-3})	2.55	2.30	2.50	2.55	2.74	3.10
Electric conductivity/ $\Omega\cdot\text{m}$	$10^3\text{--}10^4$	$10^6\text{--}10^7$	0.5–5.0	0.8	1.4	0.1
Coefficient of thermal expansion/($\times 10^{-6}/\text{K}$)	3	–	–	3.1	–	–
Specific heat/[J/($\text{kg}\cdot\text{K}$)]	1140	–	–	1140	–	–
Dielectric constant	9	6.5	20–30	12	–	–

Polycarbosilane-derived Nicalon fibers (NL-200, for example) are not pure SiC fibers as they contain oxygen (14.0 wt%) and a trace of hydrogen (0.15 wt%) in addition to silicon (55.5 wt%) and carbon (28.4 wt%). These elements are in the β -SiC (1–5 nm), SiC_xO_y and free carbon forms, respectively. In addition, the fiber surface is oxygen-rich in the form of SiO_2 .

The high-temperature mechanical properties of Nicalon fibers are limited because of the unstable SiC_xO_y phase, which will undergo decomposition upon an increase in the grain size of β -SiC at temperatures higher than 1200 °C. Therefore, Nicalon fibers are not good enough to be used as heat-resistant materials or as advanced composite reinforcements.

One effective method is to reduce oxygen incorporation using oxygen-free approaches such as electron beam curing [31, 32]. Based on this modification, oxygen-free Hi-Nicalon and Hi-Nicalon type S fibers have been produced by Nippon Carbon, and these fibers can withstand temperatures up to 1500–2000 °C.

China started to synthesize polycarbosilane from polysilane according to a modified Yajiam route at normal pressure using domestic raw materials. However, this precursor is unstable in air, and the SiC fibers obtained had low tensile strength. After several years of research, important progress was made such as the synthesis of polycarbosilane at normal pressure, multi-spinneret melt spinning, continuous curing and continuous pyrolysis. The tensile strength of the continuous fibers ranged from 2.6 to 3.0 GPa with Young's moduli of 150–190 GPa and diameters of 12–15 μm , which are close to those of the Nicalon fibers.

(2) *M*-Containing SiC Fibers (*M* = Ti, Zr, Al, B)

Another effective method to improve Nicalon fibers is the introduction of metal or other nonmetallic elements such as Ti, Zr, Al and B [32–39]. Ti-, Zr- and

Al-containing SiC fibers have been developed by Ube Industries in Japan. These SiC fibers have been commercialized and have the trade name Tyranno. Compared with the Nicalon fibers, the obvious advantages of Tyranno fibers are their higher thermal stability and good compatibility with aluminum and aluminum alloys. They are thus more suitable for reinforcing aluminum matrixes.

Ti and Zr only increase the thermal stability of SiC fibers to a limited extent, and more stable fibers are obtained upon the incorporation of Al and B. These elements act as sintering agents at higher temperatures. The Tyranno SA fibers by Ube Industries and the Sylramic fibers by Dow Corning have been produced by the sintering effect of Al and B near-stoichiometric SiC fibers, as listed in Table 2.25. They can withstand temperatures up to 2000 °C just like the Hi-Nicalon type S fibers.

China also developed Ti-containing SiC fibers and obtained continuous fibers longer than 300 m with a filament count of 400–600 [33]. The fiber diameter range is 14–16 μm, the tensile strength range is 2.20–2.80 GPa and the Young's moduli range is 160–180 GPa. The improvement in mechanical properties upon titanium introduction is due to a generation of TiC microcrystals preventing the growth of β-SiC crystals. However, more oxygen was also introduced, which has negative influence on their thermal stabilities.

China has also developed Al- and B-doped SiC fibers from polyaluminocarbosilane or a hybrid precursor of polyborazine and polycarbosilane [34, 35]. Their tensile strengths are 2.8 and 2.2 GPa, respectively, with diameters of 12 μm and 13 μm, respectively. Upon heating to 1400 °C for 1 h under argon, their retained tensile strengths are both over 95% of the original value, confirming that their thermal stabilities are better than that of the Nicalon NL201 fibers. In addition, the creep resistance of the Al-containing SiC fibers is better than that of the Nicalon fibers. Additionally, B-containing SiC fibers with improved mechanical properties can also be obtained by mixing a polycarbosilane precursor with polyborosilazane or polyborazine, or by curing polycarbosilane fibers in a B-containing atmosphere, such as BCl₃.

(3) Silicon Nitride (Si₃N₄) and Si-B-C-N Fibers

As another type of important Si-based ceramic fibers, silicon nitride (Si₃N₄) fibers also have excellent mechanical properties [25]. Furthermore, they have a low coefficient of thermal expansion, low thermal conductivity, good thermal shock resistance, good oxidation resistance and good insulation. They are mainly used in metal matrix composites (MMC), ceramic matrix composites (CMC) and heatproof composite materials.

The processing of Si₃N₄ fibers is similar to that of SiC fibers in terms of synthesis, spinning, curing and pyrolysis. Their pre-ceramic polymers are polysilazanes or polycarbosilazanes, which can be synthesized in various strategies. The composition, microstructure and properties of the Si₃N₄ fibers differ greatly depending on the polymers. There are thus two strategies for the preparation of target Si₃N₄ fibers, pure Si₃N₄ fibers and Si₃N₄-SiC fibers.

Three typical Si_3N_4 fibers are available from the Dow Corning Corporation in the USA, Toa Nenryo Kogyo K. K. (TNK) in Japan and Domaine University in France, and these represent three different preparation technologies.

In 1987, Si_3N_4 fibers were prepared by Dow Corning by the synthesis of polymers from chlorosilane and hexamethyldisilazane (HMDS), melt spinning, curing in a chlorosilane atmosphere and pyrolysis at up to 1200 °C under an inert atmosphere. The ultimate fibers are stoichiometric Si_3N_4 . Their diameter is 10–15 μm , their tensile strength is 3.1 GPa and their Young's modulus is 260 GPa.

TNK began research into Si_3N_4 fibers slightly later than Dow Corning. They synthesized a hydropolysilazane precursor via ammonolysis of dichlorosilane. The precursor only contains Si, N and H, resulting in plenty of Si–H bonds and N–H bonds and thus a very reactive material. The precursor can be cross-linked by heating giving an infusible but still soluble fiber, and therefore, it is suitable for the preparation of high-purity Si_3N_4 fibers without other elements. These Si_3N_4 fibers are good reinforcing candidates for CMCs and MMCs because of their high thermal stabilities and oxidation resistance. Their properties are listed in Table 2.29.

Domaine University used polycarbosilazane as the precursor for Si_3N_4 –SiC fibers, and this was synthesized from chlorosilanes by ammonolysis and polymerization. Because Si_3N_4 and SiC coexist in the Si–C–N–O fibers, they are expected to have new features. Their diameter, tensile strength and Young's modulus are 20 μm , 1.85 and 186 GPa, respectively. If their green fibers are cured by γ -ray irradiation, oxygen-free Si–C–N fibers can be obtained with a tensile strength and Young's modulus of 2.4 and 214 GPa, respectively. After 1600 °C treatment, their tensile strength and Young's modulus are still as high at 2.1 and 220 GPa, respectively.

Because of the limited thermal stability of Si–C–N fibers, B was introduced and an amorphous Si–B–N–C fiber, SiBN_3C , is currently being developed by Bayer HG in Germany. This fiber has high room-temperature strength and stiffness and is reported to have remarkable strength retention and creep resistance at elevated temperatures.

China has also carried out a series of similar studies and obtained Si–C–N–O fibers from chlorosilane. Low oxygen content Si_3N_4 fibers were also obtained by electron beam irradiation, but their mechanical properties need to be improved. Recently, a kind of carbon-free Si–B–N fiber has been developed in China [36].

(4) Functional SiC Fibers

Based on their high strength, high modulus, low coefficient of thermal expansion and adjustable electrical resistivity, SiC fibers are not only good reinforcements for structural composites but are also good high-temperature radar-absorbing reinforcements for functional composites.

For use as good radar absorbents, their electrical resistance should be in the range of 10^1 – 10^3 $\Omega\cdot\text{cm}$. Pure SiC is a semiconducting material with an electrical resistance lies in the range of 10^4 – 10^6 $\Omega\cdot\text{cm}$. Therefore, measures are required to adjust their electrical resistance.

Table 2.29 Typical properties of the Si₃N₄ fibers

Manufacture	Fiber	Composition/%(wt)				Density/g·cm ⁻³	Diameter/μm	Tensile strength/GPa	Young's modulus/GPa	Status
		Si	N	C	O					
TNK	Si ₃ N ₄	59.8	37.1	0.4	2.7	2.39	10	2.5	300	D
Dow Corning	HPZ	59	28	10	3	2.32	8–15	1.75–1.85	140–175	C
Dow Corning	HPZ	60	27	9	3.4	2.48	10–12	2.06	165–220	C
Rhone-Poulenc	FDBE-Ramil	56	22	15	8	2.40	15	1.80	220	C
NUDT	Si-C-N-O						15	1.5–1.8	140–165	D

Note C—commercialized; D—development

Fortunately, precursor varieties, processing parameters and ultimate microstructures (cross section of the fibers) can all be used to achieve this target, and radar-absorbing fibers with the best absorption capacities in the range of 10–12 GHz can be obtained [39–42].

For example, the electrical resistance of Nicalon fibers of low-volume-resistivity (LVR) type, NL-500, is 0.5–5.0 Ω·cm. They have good radar-absorbing properties. Another type of Nicalon fiber is the high-volume-resistivity (HVR) type such as NL-400, which has an electrical resistance of 10⁶–10⁷ Ω·cm, and can be used as an excellent radar transmission fiber. They are all reinforcements with functional properties, as listed in Table 2.28.

① Non-circular SiC fibers

A reason to change the cross section of SiC fibers from circular to non-circular can be explained using carbon fibers, which are radar reflection fibers with an electric resistance of about 10⁻² Ω·cm. They can also absorb microwaves if the shape and size of the cross section are changed.

Systematic studies were carried out on non-circular fibers by changing the shapes of the spinnerets upon melt-spinning polycarbosilanes [38]. The results showed that at the same equivalent diameters, the tensile strength of the fibers with a trilobal cross section is about 30% higher than that with a circular cross section, and the rate of tensile strength reduction upon increasing the diameter is also lower.

The electromagnetic parameters of trilobal SiC fibers measured using a rectangular waveguide approach in the X-band are listed in Table 2.30. The electromagnetic parameters of the trilobal SiC fibers are similar to those of the circular fibers (NL202) at lower pyrolysis temperatures. However, when the pyrolysis temperature was increased to 1100 °C or 1250 °C, the imaginary part of the permittivity (ϵ'') of the trilobal SiC fibers is about 30–60 times that of circular fibers. A higher ϵ'' is beneficial because it implies a better ability to transfer microwave energy to heat. The reflection curve of a composite with two-orthogonal-layered trilobal SiC fibers is shown in Fig. 2.2 [38]. The size of the composite is 80 mm × 180 mm × 4 mm.

The reflection is lower than -10 dB in the range of 11.6–18.0 GHz or lower than -15 dB in the range of 13.9–18.0 GHz. The lowest reflection of -19.8 dB is achieved at 17.2 GHz.

Table 2.30 Electromagnetic parameters of trilobal SiC fibers ($f = 10$ GHz)

Pyrolysis temperature/°C	ϵ'	ϵ''	μ'	μ''
800	3.06	0.17	1.03	0.05
900	3.47	0.11	1.04	0.01
1000	4.02	1.78	0.94	0.09
1100	4.87	8.96	1.03	0.00
1250	5.04	4.69	0.87	0.04
Comparison: NL202	3–5	0–0.15	0.98–1.03	0–0.5

Fig. 2.2 Reflection cure of a trilobal SiC fiber composite

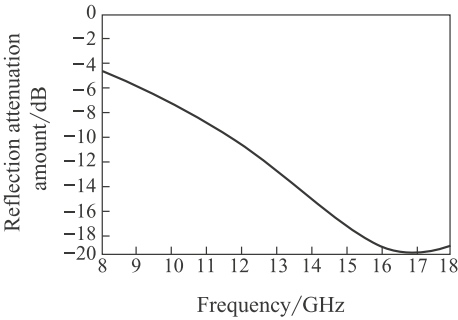
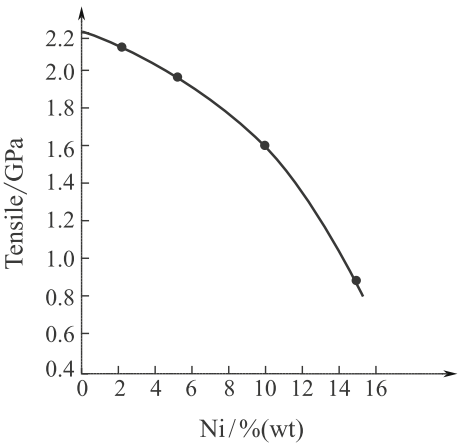


Fig. 2.3 Tensile strength of metal-containing SiC fibers as a function of Ni content



② **Metal particle-containing SiC fibers** A kind of metal particle-containing SiC fiber was produced by simply mixing metal particles with precursors followed by subsequent melt spinning, curing and pyrolysis [39–41]. Changing the metal content can change the electrical resistance and the electromagnetic parameters of the target SiC fibers. The metal particles studied were ultra-fine metal powders of Fe, Co, Ni and Ti with 30–50 nm diameters. The electrical resistance of the SiC fibers can be adjusted continuously over a wide range, as shown in Figs. 2.3 and 2.4 and Table 2.31. The electrical resistance decreases with increasing metal content, but the tensile strength decreases too.

When nano-ferrous powder was added to polycarbosilane, the electrical resistivity of the obtained SiC fibers decreased sharply. For example, 1–5%(wt) of the nano-ferrous powder effectively reduced the electrical resistance to 10^0 – $10^3 \Omega\cdot\text{cm}$. The fibers still retained a relatively high tensile strength, as listed in Table 2.31. Figure 2.5 shows the reflection curve of an epoxy matrix composite reinforced with Fe-containing SiC fibers with a thickness of 6 mm.

Fig. 2.4 Electrical resistance of metal-containing SiC fibers

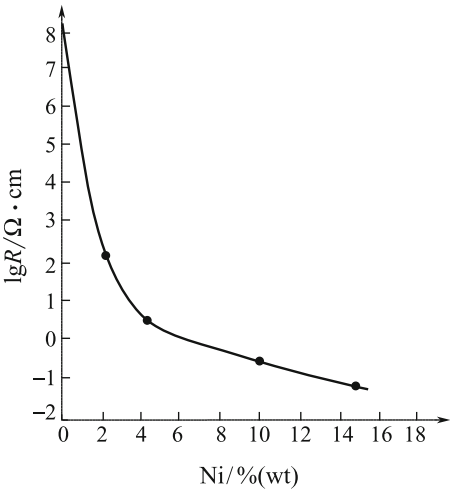
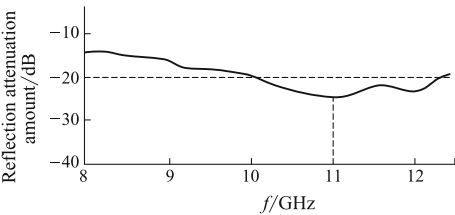


Table 2.31 Effect of addition of nano Fe, Co, Ni and Ti on the properties of SiC fibers

Amount of addition	Fe/%(wt)						Ni/%(wt)		
	0	1.0	2.0	3.0	5.0	10.0	2.0	5.0	10.0
Tensile strength/GPa	2.26	1.92	1.82	1.80	1.65	1.08	2.16	1.95	1.65
Electrical resistance/Ω·cm	7106	730	82.7	10.44	0.84	0.29	1.1		

Amount of addition	Co/%(wt)						Ti/%(wt)		
	1.0	2.0	3.0	5.0	10.0	10.0	20.0	30.0	50.0
Tensile strength/GPa	1.92	1.76	1.72	1.55	1.18	1.92	1.75	1.55	1.32
Electrical resistance/Ω·cm	5220	516.5	107.4	15.4	1.58	13500	2407	214.6	26.4

Fig. 2.5 Reflection curve of an Fe-containing SiC fiber composite



The reflections are all less than -14 dB in the range of $8\text{--}12.4$ GHz with the lowest achieved being -25.1 dB. Additionally, the reflection bandwidth at less than -20 dB is about 2.2 GHz, indicating a much improved microwave-absorbing property with the addition of magnetic ferrous powder.

Other than Fe, Ti and Zr can also be introduced to the body of SiC fibers to lower their electrical resistance while retaining their high tensile strength. Ube

Table 2.32 Properties of the Tyranno fibers

Brand name	Diameter/ μm	Tensile strength/GPa	Young's modulus/GPa	Density/ (g/cm^3)	Electrical resistance/ $\Omega\cdot\text{cm}$	Coefficient of thermal expansion/ $(\times 10^{-6}/\text{K})$
Tyranno	8–10	3.0–3.3	180–200	2.3–2.4	$10^5\text{--}10^4$	3.1
A	8–7	3.0	170	2.29	10^6	3.1
D(s)	8–10	3.3	180	2.35	10^3	3.1
E	8–10	3.3	180	2.35	10^2	3.1
F	8–10	3.3	180	2.40	10^1	3.1
G	8–10	3.3	180	2.40	10^0	3.1
LoxM	8–10	3.3	187–180	2.48	30	3.1
LoxE	8–10	3.4	206	2.55	0.8	3.1
ZE ^a	8–10	3.5	233	2.55	0.3	–

^aZr-containing SiC fibers**Table 2.33** Effect of Ti content on the properties of SiC fibers

Samples	Ti content/%(wt)	Electrical resistance/ $\Omega\cdot\text{m}$	Tensile strength/GPa
SiC	0	1.0×10^6	1.97
Si–Ti–C–O-1	1.35	1.96×10^5	1.83
Si–Ti–C–O-2	3.5	4.35×10^3	1.84
Si–Ti–C–O-3	4.0	2.98×10^3	1.79

Industries has developed and commercialized a series of Tyranno fibers for different applications, and their properties are listed in Table 2.32.

Titanium can be introduced by reacting polycarbosilane with titanium alkoxide, and the properties of the thus-obtained SiC fibers are listed in Table 2.33. It was found that the elemental composition and microstructure are closely related to the electrical resistance. With an increase in the titanium content, the resistance decreased and a relatively high strength was retained.

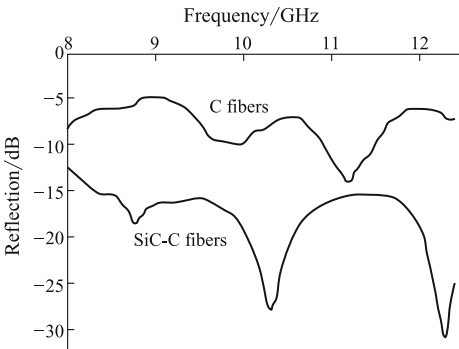
Carbon is conductive and can be introduced to the SiC fibers to change their electrical resistance. A kind of SiC–C fiber was prepared from a blended precursor consisting of polycarbosilane and pitch. Because of an easy phase detachment, the blended precursor is spun with difficulty into fine fibers. Therefore, even the electrical resistance is adjustable in the range of $10^0\text{--}10^4 \Omega\cdot\text{cm}$, and the tensile strength is relatively low at about 1.0–1.2 GPa. They cannot be used as reinforcements for structural radar-absorbing composites.

An improved method consists of the synthesis of carbon-rich polycarbosilane by the co-thermolysis of polysilane and polyvinylchloride (PVC). When PVC is pyrolyzed, plenty of double bonds are created, which can be grafted onto the main chain of Si–C bonds by a hydrosilation reaction. Therefore, carbon was dispersed into the precursor at the molecular level and the spinning property improved greatly. The properties of the SiC–C fibers are listed in Table 2.34.

Table 2.34 Properties of the SiC–C fibers

Sample	Composition/%(wt)			Tensile strength/GPa	Electrical resistance/ Ω -cm
	Si	C	O		
SiC	40	31.6	28.3	1.50	10^6
SiC–P5	46.2	40.8	12.9	1.71	35.2
SiC–P10	45.1	43.3	11.6	1.45	31.8
SiC–P30	42.9	42.1	11.8	0.87	25.8

Fig. 2.6 Reflection curve of a rayon-based SiC–C composite fiber and comparison of rayon-based carbon fibers



A substantial reduction in the electrical resistance is apparent. At a PVC content of 5 wt% the electrical resistance is low enough to meet application requirements. Additionally, the tensile strength is also slightly higher than for those without PVC addition.

A different method exists for SiC–C fiber production and comprises increasing the silicon content of the C fibers by the infiltration of carbon precursor fibers with polycarbosilane. For example, rayon filament or natural cellulose fiber was infiltrated with polycarbosilane solution, pre-oxidized and heat-treated at high temperature, and a kind of SiC–C composite fiber was obtained [22]. The carbon yield of the composite fiber was improved by up to 35–38%(wt) by the promotion of pyrolysis with flame retardants consisting of multi-amines and surfactants. Furthermore, the electrical resistance of the fibers can be adjusted by the concentration of polycarbosilane solution. The tensile strength of the fiber was as high as 1.8 GPa. Figure 2.6 shows the reflection curve of this composite fiber, indicating wideband microwave-absorbing properties.

2.3.3 Boron Nitride (BN) Fibers

As a variety of inorganic heat-resistant fiber, BN fibers are white, flexible polycrystalline fibers. According to the manufacturing method and their microstructure, they are usually divided into composite fibers and pure fibers [43, 44].

The former is prepared by CVD using borane, ammonia and boron trichloride as gas vapors, and a hot W wire as the deposition support and the core of the composite fiber. The latter usually comes from melt-spun B_2O_3 fibers after treatment with NH_3 to give unstable boron amine at low temperatures and heat resistance polycrystalline BN at 1800 °C.

BN fibers have superior thermal insulation and high-temperature stability, excellent electrical insulation and good dielectric properties; in addition, they have good resistance to radiation, infrared rays and chemical corrosion. When used as reinforcements for ceramic matrix composites, they can increase the toughness and thermal shock resistance. They have been used to fabricate microwave window components, separation rings in continuous casting technology and cell membranes in communication satellites.

For example, BN fiber-reinforced quartz has been used as a missile antenna window component and meets all the requirements of the space environment. BN fiber-reinforced Si_3N_4 can survive the erosion of carbon steel and stainless steel at 1600 °C, indicating that the composite can withstand the thermal shock generated by a tremendous temperature difference.

BN fibers can withstand long-term erosion by a 40 wt% KOH solution and as cell membranes of alkaline batteries and high-energy batteries, they are corrosion resistant, Ag_2O migration resistant and stable at high temperatures with the ability to retain the electrolyte. Therefore, BN fibers are a good cell membrane material.

Furthermore, BN fibers are ideal lubrication materials because of their good high-temperature lubrication property, which comes from their structure similarity with graphite. BN fibers can be used as protective clothing materials because they have the capacity to absorb neutrons with resistance toward ultraviolet and cosmic rays. Based on their excellent chemical stabilities, BN fibers can also be used in the form of paper and carpets as chemical filters and gas filters.

The USA was the first country to produce BN fibers. The former Soviet Union and Japan also carried out systematic studies into BN fibers. The properties of typical BN fibers are listed in Table 2.35.

In 1966, the Emery Co. in the USA was the first to produce BN fibers and they produced high-strength, high-modulus BN fibers in 1978. At the same time, various BN fiber products such as paper, felts and boards were developed. In 1976, research was carried out in China into reacting B_2O_3 with ammonia, and the relationship between microstructure and performance was systematically studied. In 1993, BN fibers with similar performance were obtained, as listed in Table 2.35.

Because of the complexity of the solid-gas reaction, the obtained BN fibers were hardly homogenous [43]. In the 1990s, research focused on the manufacture of BN fibers from polymer precursors to overcome the shortcomings of the nitridation process [44]. Currently, the tensile strength of polymer-derived BN fibers is up to 1.5 GPa.

Table 2.35 Properties of typical BN fibers

Property	USA			China short fiber
	Short fiber	Continuous fiber	High strength and high modulus	
Diameter/ μm	4–6	5.19	6	4–6
Tensile strength/MPa	350–870	302	830–1400	350–800
Young's modulus/GPa	28–84	35.7	210	18–120
Density/(g/cm^3)	1.4–1.9	1.8	1.8–1.9	1.4–1.8
Tensile strain/%	2–3	1	–	2–3

2.3.4 Boron Fibers

Boron fibers are important reinforcements for advanced composites. They are produced by CVD by depositing B on W or C fibers in the form of a continuous monofilament with an outer diameter of 100–200 μm .

The commonly used W wire has a diameter of 3.5–50 μm . At reaction temperatures of 1120–1200 $^{\circ}\text{C}$, more infiltration of B into W is found. Therefore, the composition of the core changes from W to a variety of tungsten diborides such as WB, W_2B_5 and WB_4 . As a result, only a small amount of boron is deposited into the core. However, when the temperature is increased to 1200–1300 $^{\circ}\text{C}$, the deposition rate of B increases and the target B fibers can be obtained.

During the course of deposition, the core has a pressing stress and the initial deposition layer has a drawing stress, and therefore, radial cracks form in the B fibers. To avoid the propagation of cracks and any unexpected interface reactions, a coating process is usually carried out in addition to the CVD process. Therefore, a coating of boron carbide (B_4C) is applied using a mixed gas consisting of BCl_3 , CH_4 and H_2 . The thickness of the coating is generally 3 μm . A commercialized B fiber with the trademark BoSiC is obtained when the coating is SiC.

The most promising advantages of boron fibers are their mechanical properties (tensile strength and Young's modulus are 3.5 and 400 GPa, respectively) and low density (2.5 g/cm^3). The processing maturity and reasonable price are essential reasons for their development. In addition, B fibers have good bending strength, and their corresponding compressive strength is very high at 6.9 GPa, which is twice their tensile strength. Boron fibers can survive at 500 $^{\circ}\text{C}$ in air for 1 h with no obvious change in tensile strength. However, at temperatures exceeding 500 $^{\circ}\text{C}$, their tensile strength decreases significantly.

Boron fibers are mainly used in the aviation and aerospace industries with special applications in MMC and PMC composites that have specific demands regarding weight and stiffness. Boron fiber-reinforced aluminum composites are one successful example. Boron fiber-reinforced epoxy composites have also been used to repair airplane metal bodies and to fabricate sports and entertainment items such as golf clubs and skis.

Table 2.36 Properties of typical boron fibers

Property	B						BorSiC			
	B/W			B/C			BorSiC/W		BorSiC/C	
Diameter/ μm	102	142	203	102	142	203	107	147	107	147
Density/ (g/cm^3)	2.31	2.31	2.30	2.29	2.29	2.29	2.32	2.32	2.31	2.31
Tensile strength/GPa	3.24– 3.51	3.24– 3.51	3.30– 3.50	3.10	3.10	3.17	3.24	3.24	3.17	3.17
Young's modulus/GPa	378– 400	378– 400	378– 400	345– 358	345– 358	345– 365	378– 400	378– 400	351– 365	351– 365

The USA was the earliest and most important country regarding the research and development of boron fibers. In the mid-1960s, AVCO produced W core and C core boron fibers using hydrogen and boron trichloride. The diameters of the continuous fibers were 100–200 μm . Textron Inc. then produced a high-strength, high-modulus and low-density boron fiber. In July 1985, the Japanese vacuum metallurgy company developed the world's highest tensile strength boron fiber at 5.2 GPa and established a pilot plant.

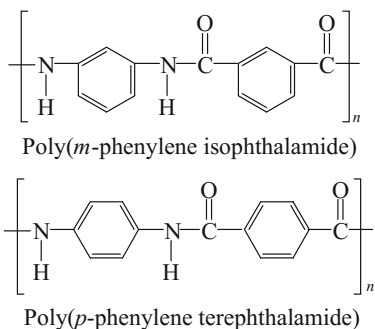
The former Soviet Union and France also carried out research and made extensive progress. China began these studies in the early 1970s, and five pilot lines have been completed. The performances of the fibers are close to those of other countries. The properties of typical boron fibers are listed in Table 2.36. Their performance is closely related to their diameters.

2.4 Aromatic Polyamide Fibers

Aromatic polyamide fibers are also referred to as aramid fibers. Aramid fibers are a class of heat-resistant and strong synthetic polymer fibers in which the fiber-forming substance is a long-chain synthetic polyamide with at least 85% amide linkages ($-\text{CO}-\text{NH}-$) attached directly to two aromatic rings. Aramids are generally prepared by the reaction between an amine group and a carboxylic acid halide group.

Polyamides in dimethyl acetamide solution can be directly spun into fibers using dry-spinning, wet-spinning or dry-wet spinning methods. After washing and drying, the fibers are heat-treated at 500–600 $^{\circ}\text{C}$ under tension to obtain the target aramid fibers [45, 56].

Aromatic polyamides were first used commercially as meta-aramid fibers in the early 1960s, and para-aramid fibers were subsequently developed in the 1960s and 1970s. Their structures are as follows:



Apart from production in the USA by DuPont, meta-aramid was also produced in the Netherlands and in Japan by Teijin under the trade name TeijinConex and in China by Yantai under the trade name New Star, and a variant of meta-aramid was produced in France by Kermel under the trade name Kermel. The most representative para-aramid fibers are *p*-phenylene terephthalamide (PPTA) fibers and their trade names are Kevlar (DuPont), Twaron (previously Akzo and currently owned by Teijin) and Technora (Teijin). After the industrialization of PPTA fibers by DuPont in the 1970s, a series of products with improved performance and higher production efficiency were made.

PPTA aramid fibers are classified as two types: one is a high-strength type with a tensile strength of up to 3.0–5.5 GPa and a Young's modulus of 60–90 GPa. This is mainly used in high-strength, middle-hardness textile materials and in flexible composite materials such as tires and industrial rubber products; the other is a high-modulus type with a Young's modulus of up to 100–170 GPa, and it is mainly used in high-strength, high-hardness textile materials and in hard composite materials [47, 48]. The world's major producers of PPTA fibers are listed in Table 2.37.

PPTA is characterized by its ultra-fine molecular structure, its high degree of orientation and the regular arrangement of long chains so that each molecule can contribute when tensile loaded. This is the reason for their excellent mechanical properties. Table 2.38 shows the main structures of the PPTA from different producers. Their statistical chain length is about 20–50 nm, bearing a large number of polar groups. The fibers have high intra-chain atomic combination energy and high inter-chain interface energy as well as many polar groups and many rigid blocks in

Table 2.37 Major producers and brand names of PPTA fibers

Manufacture	Brand name	Type
DuPont, USA	Kevlar	High strength, high modulus
Teijin, Japan	Twaron	High strength, high modulus
Institute of Synthetic fibers, Russia	Terlon	High strength, high modulus
Institute of Synthetic fibers, Russia	SVM	High modulus
Institute of Synthetic fibers, Russia	Armos	High modulus
Teijin, Japan	Technora	High strength

Table 2.38 Structural characteristics of PPTA fibers

Brand name	Molecular level	Super-molecular level	Microscopic level
Kevlar Twaron Terlon	PPTA; statistical chain length is 30–50 nm; polar group is CONH	Three-dimensional crystal structure, highly oriented, chain ratio with load is 0.5–0.7	Cross section: homogeneous, circular-shaped
SVM	Heterocyclic aromatic polyamide; statistical chain length is 20–40 nm; polar groups are CONH and –N–	One-dimensional crystal structure, highly oriented, chain ratio with load is 0.5–0.7	Cross section: homogeneous, circular-shaped
Armos	Heterocyclic aromatic polyamide copolymer; statistical chain length is 20–40 nm; Polar groups are CONH and –N–	Three-dimensional crystal structure, highly oriented, chain ratio with load is 0.5–0.7	Cross section: homogeneous, circular-shaped

Table 2.39 Representative mechanical properties of PPTA fibers

Brand name	Density/g·cm ⁻³	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Standard moisture regain/%
High-modulus type: Kevlar, Twaron, Terlon	1.44	3.0–3.5	120–170	2.5–3.0	2.0–3.0
High-strength type: Kevlar, Twaron, Terlon, Technora	1.44	3.0–3.5	60–90	3.0–4.5	3.0–3.0
High-modulus type: SVM	1.43	4.2–4.5	125–150	3.0–3.5	3.5–4.0
High-modulus type: Armos	1.43	4.5–5.5	130–160	3.5–4.0	3.0–3.5

the molecular chains. This gives the fiber a high glass transition temperature and high thermal stability. In addition, the high homogeneity of the structure and the low amount of structural defects are also one of the reasons for their good mechanical properties.

Tables 2.39 and 2.40 show the mechanical properties of world's most important PPTA fibers. Armos yarn has been regarded as one of the best types.

The first generation of Kevlar series products produced by DuPont are Kevlar RI, Kevlar29 and Kevlar49, and the second generation are Kevlar HX, which includes the high-adhesive type (Ha), high-strength type (Ht, 129), solution-colored type (Hc, 100), middle-modulus type (Hp68), high-modulus type (Hm, 149) and high-tensile-strain type (He, 119). Their typical physical properties are listed in Table 2.41.

Table 2.40 Thermal properties of PPTA fibers

Brand name	Glass transition temperature/°C	Processing extreme temperature/°C	Pyrolysis temperature/°C	Combustion temperature/°C	Spontaneous combustion temperature/°C	Limiting oxygen index (CO ± 7%)
Terlon, Kevlar, Twaron	345–360	250–270	450–550	450–500	500–600	27–30
SVM, Armos	270–280	300–330	550–600	500–600	550–650	37–43

Table 2.41 Typical physical properties Kevlar fibers

Property	Kevlar RI Kevlar29	Kevlar Ht (129)	Kevlar He (119)	Kevlar Hp (68)	Kevlar 49	Kevlar Hm (149)
Toughness/cN·Tex ⁻¹	205	235	205	205	205	170
Tensile strength/GPa	2.90	3.32	2.90	2.90	2.90	2.40
Young's modulus/GPa	60	75	45	90	120	160
Tensile strain/%	3.6	3.6	4.5	3.1	1.9	1.5
Moisture regain/%	7	7	7	4.2	3.5	1.2
Density/(g/cm ³)	1.44	1.44	1.44	1.44	1.45	1.47
Pyrolysis temperature/°C	≈500	≈500	≈500	≈500	≈500	≈500

Research into aramid fibers started in China in the early 1970s and the performance of the products are close to that of Kevlar49, with a production capacity of 200 t/a. There are two types of aramid fibers in China, Aramid I and Aramid II. Aramid II consists of four types.

Their performances are listed in Table 2.42. Although the tensile strength of Aramid II is higher than that of Aramid I, its Young's modulus is lower. Aramid I maintains its strength better at high temperatures, i.e., a better aging property, and therefore, it is a better candidate for high-temperature composites.

In addition to the p-aramid fibers, aramid copolymer fibers also exist. The introduction of a new diamine or a third monomer during the synthesis of a new aramid is an important approach to improving performance. Examples include Technora, SVM and Armos. Typical properties of Russian aramid fibers are listed in Table 2.43.

In addition to the above-mentioned continuous aramid yarns, other forms like staple fibers, short fibers, pulps, fabrics and laminates also exist. For example, KevlarT970, Twaron1070, Twaron1072, Twaron1075 and Twaron1077 are short fibers, while KevlarT979, KevlarT982, KevlarT953 and Twaron 1095 are pulps.

Aramid fibers are a kind of light, high strength, widely used high-performance organic fiber [45, 46]. They are mainly used to reinforce polymer matrix composites, rubbers, cements and metals, resulting in significant improvements in toughening aspects, and therefore, they are mainly used in the fields of space, aviation, petroleum, building materials, traffic, transportation and public security departments. They are especially used in the shells of solid rocket motors, bullet-proof vests, tires, cables and in asbestos substitutes.

Because of their superior specific strength and specific modulus compared with S-994 high-strength glass fibers, the characteristic factor, PV/W (P , blast pressure, V , vessel volume and W , vessel weight), of a Kevlar-reinforced epoxy engine shell was increased up to 30%. Kevlar-reinforced epoxy composites have also been widely used in the manufacture of advanced aircraft in the form of engine shells, central engine cowlings, wings and fuselage cowlings. In addition, aramid fibers are

Table 2.42 Typical properties of the aramid fibers produced in China

Property	Aramid I		Aramid II ^a					
	Green fiber	Heat-treated fiber	Green fiber	Heat-treated fiber	II-1	II-2	II-3	II-4
Density/g·cm ⁻³	1.42	1.46	1.44	1.45	—	—	—	—
Tensile strength/cN·dtex ⁻¹	8.8–10.1	16.0–17.7	19.5–21.2	19.5–21.2	17.7–19.4	≥ 15.9	17.7–19.4	19.4–21.1
Young's modulus/cN·dtex ⁻¹	340–400	903–1062	354–400	624–703	423	—	618–706	618–706
Tensile strain/%	5.5–6.5	1.5–2.0	3.5–5.5	2.5–3.5	3.5–3.6	≥ 6	2.5–3.5	2.5–3.5

^a Aramid II has four types: II-1, common; II-2, high tensile strain; II-3, middle-strength, high modulus; II-4, high strength, high modulus

Table 2.43 Typical properties of Russian aramid fibers

Brand name	Filament count	Young's modulus/GPa	Tensile strength/GPa	Tensile strain/%	Density/g·cm ⁻³	Mass per unit/g·km ⁻¹	Glass transition temperature/°C	Coefficient of thermal conductivity/W·(m·K) ⁻¹	Moisture regain/%
Terlon	40k	98-147	2.94-3.5	2-4	1.45	6	345-400	0.04-0.65	2.0-3.5
SVM	70k	122-132	3.72-4.12	3.5-4.5	1.42	14.3	230-250	0.045	4-7
Armos	50k	142-147	4.5-5.2	3-3.5	1.45	14.3	160-520	-	3.5-5.0

also widely used in aircraft high-pressure oil pipes. Therefore, they are very important in aviation materials.

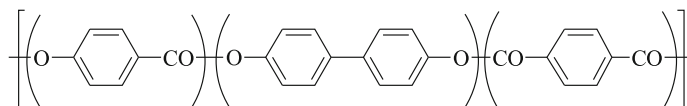
They are also applied as armored protection for warships and aircraft carriers, as well as sonar diversion covers. Aramid fibers can also be used to manufacture soft bulletproof vests, train brakes and sealing fillers.

The application of Kevlar in reinforcing cement to substitute steel bars or to reduce application of steel bars is known to be more suitable in extreme ocean conditions. When used as wall materials, their tensile strength is 5–10 times that of ordinary cement.

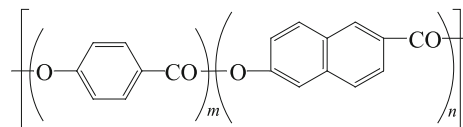
2.5 Aromatic Polyester Fibers

Aromatic polyester fibers are also referred to as polyarylate (PAR) fibers and are actually a kind of aromatic polyester copolymer fiber derived from aromatic dicarboxylic acids and diphenols. The spinnability of aromatic polyesters from one type of monomer is not good enough to obtain high-performance fibers. The copolymerizing component should be of relative low cost, low melting point and be a good spinning copolymer, which is able to maintain high strength and high modulus.

The trade names of current aromatic polyester products are Ekonol and Vectron. They were both spun from all-aromatic polyester copolymers. Ekonol fibers were commercialized jointly by the Carborundum and Sumitomo companies, and their chemical structure is as follows:



They have high strength and high modulus but also a high manufacturing cost, which restricts their further development. Vectron fibers were prepared by Kuraray exclusively in 1990, and its structure is as follows:



With the same level of strength and modulus as PPTA fibers, the most outstanding feature of aromatic polyester fibers is that their retained strength after dry-heat or wet-heat treatment is superior to that of PPTA fibers. This is because they are not hygroscopic and do not shrink after creeping or aging under dry or wet conditions. Additionally, their resistance to wear, cutting, solvents, acid and impact,

Table 2.44 Performance comparison between aromatic polyesters and PPTA monofilaments

Brand name	Density/g·cm ⁻³	Pyrolysis temperature/°C	Moisture regain/%	COI/%	Tensile strength/GPa	Tensile strain/%	Young's modulus/GPa
Vectron HT	1.41	>400	0	37	3.61	3.8	833
Vectron HM	1.42	>400	0	—	—	3.5	—
PPTA common	1.44	>400	4.9	42	3.72	3.6	788
PPTA HM	1.45	>400	44.3	39	3.20	3.0	1228
Ekonol	1.40	—	—	—	3.83	2.6	968

Table 2.45 Performance comparison between Vectron and PPTA yarns

Brand name	Denier/ (dtex/filament count)	Tensile strength/GPa	Tensile strain/%	Young's modulus/GPa	Sintering strength/N·dtex ⁻¹
Vectron HT	1667/300	3.23	3.8	746	6.0
Vectron HM	1667/300	2.90	3.5	1043	—
PPTA Common	1667/300	2.67	3.9	709	6.2
PPTA HM	1578/1000	2.69	2.7	1121	5.7

Table 2.46 Types and applications of Vectron fibers

Type	Code	Structure	Application
Filament Yarn HT	T-101	8333/1667/1111/556/278-28 (dtex)	General industrial supplies
Filament Yarn HM	T-117	1667(dtex)	Ropes, cords, tension components
Filament Yarn HM	T-150	1667/556/278-28(dtex)	Harnesses, fishing lines, sutures
Filament Yarn NT	T-155	1111(dtex)	Tension components
Original spun yarn	AP	10/20(S)	Protective clothing, gloves, aprons
Core-sheath yarn	CY	3.7/7.4(S)	Fishing lines
Short fiber	CF	1/3/6(mm)	Advanced composite materials
Puple	HP	1-3(mm)	Asbestos substitutes
Puple	NP	1-3(mm)	Synthetic paper, speaker cones
Fabric	—	—	Advanced composite materials, general industrial supplies
Laminate	—	UD fabric	Advanced composite materials

as well as vibration absorption, is also better than that of PPTA fibers. Their spontaneous combustion stability, non-melting ability upon combustion and weather resistance are similar to those of PPTA fibers. Performance comparisons of aromatic polyester and PPTA fibers, in monofilaments and yarns, are listed in Tables 2.44 and 2.45, respectively.

Aromatic polyester fibers hardly absorb water and have good dimensional stability, but their interface bonding and fatigue resistance are relatively poor when used to reinforce rubbers and polymers. Aromatic polyester fibers are used in speaker cones, tennis rackets, table tennis bats, safety helmets and pipes, as these items take advantage of their high modulus, high shock absorbance and vibration attenuation properties.

Table 2.46 shows the types and applications of Vectron fibers. To date, no related fiber development has taken place in China. These fibers should be developed further because they are high-performance reinforcements for composite materials, and generally their performance is better than that of PPTA fibers. More importantly, their cost is also lower.

2.6 Heterocyclic Polymer Fibers

Although aramid fibers have been used as aerospace structural materials, bullet-proof materials, automotive structural materials, tire cords, etc., they have a clear weakness in that they possess poor environmental stability, which limits their application. This comes from the amide bonds in the main chain of the molecule, which tends toward oxidation and hydrolysis.

Modern theory and practice show that, surprisingly, rod-like heterocyclic polymer fibers spun from a liquid crystal phase solution have superior mechanical properties compared with aromatic polyamide fibers, and also have much improved thermal stability, which is close to the theoretical limit of organic polymer crystals [48, 49].

As representatives of the heterocyclic polymer fiber family, poly(*p*-phenylene benzobisoxazole) (PBO), poly(*p*-phenylene benzobisthiazole) (PBT) and poly(*p*-phenylene benzimidazole) (PBI) are considered to be a new generation of polymer fiber, which have high strength, high modulus and high-temperature stability. Their main chains contain rigid-rod-like units of benzene and heterocyclic structures like oxazole, thiazole and imidazole [49]. A new PBO-like heterocyclic polymer fiber, polypyridobisimidazole (PIPD or M5), is believed to have more promising applications than general PBO fibers. These fiber products will be fully commercialized in the twenty-first century, and more applications will be targeted. Table 2.47 shows some typical characteristics of heterocyclic polymer fibers.

2.6.1 Polybenzoxazole (PBO) Fibers

PBO is poly(*p*-phenylene-2,6-benzobisoxazole), and its *cis* and *trans* structures are shown below:

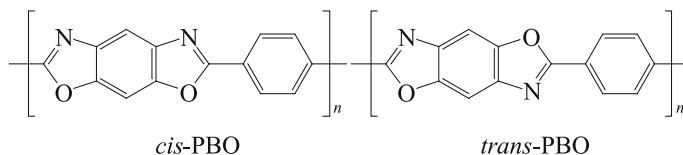


Table 2.47 Typical characteristics of heterocyclic polymer fibers

Type	Molecular cross-sectional area/($\times 10^{-2}$ nm ²)	Theoretical Young's modulus/GPa	Measured Young's modulus/GPa
<i>cis</i> -PBO	19.17	730	350
<i>trans</i> -PBO	19.21	707	–
<i>cis</i> -PBT	20.68	580	–
<i>trans</i> -PBT	20.60	605	300
<i>cis</i> -PBI	20.89	630	–
<i>trans</i> -PBI	20.90	640	–
PPTA	20.20	182	125
UHMPE	18.20	362	160

There is a high degree of orientation of molecular chains because they are spun in the liquid crystal state, which gives them a high tensile strength of 4.8–6.2 GPa and a high Young's modulus of 280–380 GPa. Their moisture uptake is less than 1%, and their decomposition temperature is as high as 670 °C. They do not melt. In addition, they are abrasion resistant and have a low creep rate.

The fibers are very thin and feel good and can be prepared in various forms such as yarns, worsted yarns, cloths, fabrics, chopped fibers and pulps. Similar to other rigid polymers, the fibers are also processed from anisotropic solutions. The solvent is polyphosphoric acid. Because of their much higher rigidity than aramids as well as the lack of amide bonds, their thermal properties and mechanical properties are much improved. However, because of expensive ingredients and the highly aggressive solvent combined with extremely high solution viscosities of 30 dl/g, they cost much more than aramid fibers. Typical properties of PBO fibers compared with other fibers are listed in Table 2.48.

The series of PBO fibers include the PBO-AS fibers by Dow Chemical Company, Zylon and the PBO-HM fibers by Toyobo, and others by DuPont. Their most striking characteristics are their high strength and high modulus, which is nearly two times that of PPTA fibers. Their LOI is also much higher.

The applications of PBO fibers are mainly in the following areas [50]:

- ① High-strength ropes, as well as high-performance canvases;
- ② High-strength composite materials. PBO fibers are a new generation of high-performance fibers because they meet the requirements of light weight, high strength, high modulus and high humidity resistance. They are prospective materials for use in pressure vessel structural materials and advanced sports goods;
- ③ Bulletproof anti-shock materials. PBO fiber composites have excellent performance in terms of impact resistance, as shown in Figs. 2.7 and 2.8. Therefore, they have been used in impact energy absorption devices such as aircraft fuselages, bulletproof vests and helmets;

Table 2.48 Property comparison between PBO fibers and other fibers

Property	PBO	PBO-AS	PBO-HM	M5	PBT	PBI	Kevlar49	Kevlar129
Density/(g/cm ³)	1.57	1.54	1.56	1.70	1.57	1.40	1.47	1.45
Young's modulus/GPa	406	180	280	330	373	5–6	143	99
Tensile strength/GPa	3.4	5.8	5.8	–	3.5	0.40	2.3	2.4
Tensile strain/%	–	3.5	2.5	1.2	1.3	30	1.5	3.3
LOI	–	68	68	75	–	41	26	26
Decomposition temperature/°C	650	650	650	–	600	550	555	555
Highest usage temperature/°C	350	350	350	–	350	–	250	250

Fig. 2.7 Mechanical properties of PBO/epoxy composites

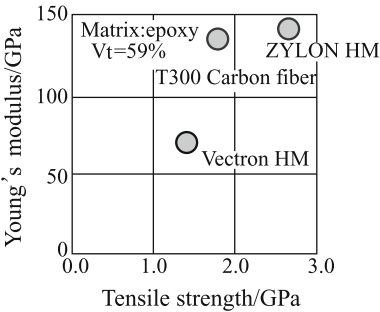
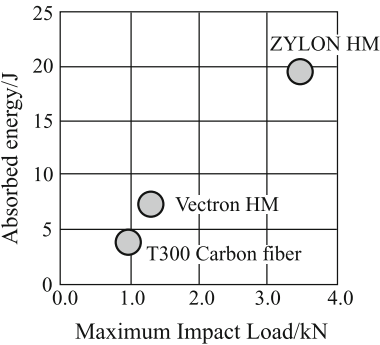
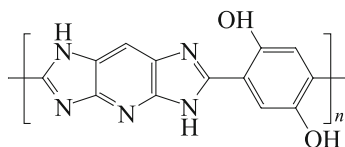


Fig. 2.8 Impact property of PBO/epoxy composites



- ④ Other special protective materials. Because of their superior heat resistance, flame-retardant properties, cut resistance, wear resistance, etc., they can be used to create light, soft products such as optical cable protection materials, safety gloves, thermal blankets, special conveyors, fireproof clothes and footwear.

PBO fibers have excellent performance, but they also have some shortcomings such as poor compressive performance, which is mainly caused by the tangling of the microfiber structures under compressive stress. This leads to fibrillation. Improvements are focused on eliminating the severe temperature changes in the preparation process and to use different monomers for copolymerization. The most successfully strategy so far is to create polymers that are rigid-rod-like as in PBO, but with strong intermolecular hydrogen bonds. This has been done for the recently developed PIPD or M5 fibers with a structure as follows:



Polypyridobisimidazole(PIPD)

PIPD is a polypyridobisimidazole made from 2,3,5,6-tetraamino pyridine and 2,6-dihydroxy-terephthalic acid. It was developed by Akzo-Nobel upon correcting the above-mentioned problem by maintaining the rigid-rod structure while adding extra hydrogen bonding sites. The restructuring of Akzo-Nobel led to this project being abandoned, and Magellan Systems International was formed to commercialize this product using A-N equipment. Composites made from this fiber show much improved impact resistance, damage tolerance and wear resistance.

Another reason for the poor performance of PBO fibers is that the bonding performance between PBO fibers, and polymer matrixes are generally lower than that of aramid, which limits their application in high-performance composite materials.

Therefore, surface treatment is usually applied to improve the interface bonding strength, mainly including plasma treatment, the formation of microfibers on surfaces, chemical grafting and blending. One method reported in China is to modify the surface structures by applying both reactive monomers and high-energy radiation technologies. It is a promising surface modification method because it can deal with large-scale fibers resulting in good improvements.

Modified PBO fibers still have high rigidity and high strength, excellent resistance to oxidation, ultraviolet and moisture. They are particularly suitable for high-performance composite materials such as the insulation components of rockets and engines. They can also be used to reinforce cement. Because of their low creep rate and good abrasion resistance, they can be used to reinforce rubbers and heat-resistant equipment. Composite materials reinforced by modified PBO fibers are especially suitable for aircraft, transport machinery, electrical machinery, etc.

In short, modified PBO fibers are superior to polyester, nylon and high-strength polyolefin fibers in terms of heat resistance and mechanical properties. They are a new type of advanced synthetic fiber. It is thought that PBO fibers have started a revolution in new organic fibers. An increasing number of researchers in China are involved in the development of PBO fibers, but no pilot production has been

Table 2.49 Property comparison between Zylon fabrics and aramid fabrics

Name	Type	Yarn count, Warp/s	Yarn count, Weft/s	Yarn count, Warp/cm	Yarn count, Weft/cm	Thickness/mm	Density/(g/m ²)
Zylon	Plain weave	20	20	33.9	19.7	0.35	170.1
Meta-aramid	Plain weave	20	20	34.3	19.3	0.39	171.4
Para-aramid	Plain weave	20	20	34.3	20.1	0.40	176.7

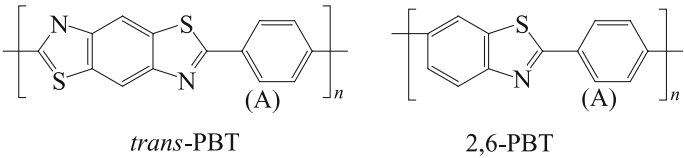
Table 2.50 Mechanical properties of Zylon fabrics and aramid fabrics

Name	Tear strength/kN		Tensile strength/(N/cm ³)		Tensile strain/%		Rupture strength/MPa	Abrasion resistance/cycles
	Warp	Weft	Warp	Weft	Warp	Weft		
Zylon	≥ 125.4	≥ 125.4	2.283	1.497	17.0	6.6	≥ 4.1	441
Meta-aramid	83.3	83.3	1.412	0.998	17.7	5.3	2.4	236
Para-aramid	68.6	39.2	0.807	0.481	46	29.8	2.1	193

reported to date. A property comparison between Zylon fabrics and aramid fabrics is listed in Tables 2.49 and 2.50.

2.6.2 Polybenzothiazoles (PBT) Fibers

Polybenzothiazole (PBT) is a high-temperature, high-modulus heterocyclic polymer whose main chain contains benzothiazole repeat units. It is obtained by reacting mixed toluides, sulfur and 4-aminophthalimide. PBT has two types of structures: *trans*-PBT and 2,6-PBT, as shown below:



For these structures, “A” stands for aromatic or aliphatic hydrocarbons. In the former case, PBT is not soluble in common organic solvents but only soluble in polyphosphate acid, mesylate acid, chlorosulfonic acid and concentrated sulfuric acid; in the latter case, PBT can be soluble in *m*-cresol and methanoic acid. PBT is a

Table 2.51 Typical properties of PBT fibers compared with other fibers

Type	Young's modulus/GPa	Tensile strength/GPa	Tensile strain/%	Density/(g/cm ³)
PET	5–12	1	10–16	1.38
Nylon	5	1	18	1.14
Glass	55	3.5	4	2.55
Steel	180–200	2–3	2–3	7.9
Kevlar29	60	3.7	3–4	1.44
Kevlar49	120	4.1	2.5	1.44
PBT	250	2.4	1.5	1.50

kind of incombustible lyotropic liquid crystal polymer with a density of 1.42–1.60 g/cm³.

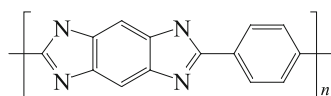
Air Force Wright Aeronautical Laboratories, referred as AFWAL, carried out an industrialization assessment of PBT fibers. The synthesis process starts from *p*-phenylenediamine (PPD), and an intermediate product of 2,5-diamino-1,4-benzenedithiol salt (DABDT) is obtained after four steps. DABDT needs to be refined by recrystallization and then polycondensation with terephthalic acid (TA) in a solution of polyphosphate acid. After PBT synthesis, its fiber can also be obtained after dry–wet spinning and heat treatment. Typical properties of PBT fibers are listed in Table 2.51.

In addition to the necessary heterocyclic aromatic chemical structures, another reason for the high performance of PBT fibers is their degree of orientation along the axial direction of molecular chains. This orientation is the result of spinning in the lyotropic liquid crystal state, which enables the obtained fiber structure to be close to the ideal structure of the fibers.

PBT fibers are a new type of high-performance composite reinforcement and can be used to substitute asbestos and cables. Their fabrics can be used to prepare bulletproof suits, space rocket engines, solar arrays, pressure valves and space frame structures. They are, therefore, prospective aerospace materials. However, their complicated synthesis procedure and the high cost of the solvent limit their development and application, especially in China.

2.6.3 Polybenzimidazole (PBI) Fibers

Polybenzimidazole fibers are stable at high temperature and comprise a variety of flame-retardant synthetic fibers. They are known as PBI with the trade name Togyon. Their main chain contains heterocyclic units, as shown below:



The polymer is usually synthesized by solid-phase polymerization in vacuum or by a two-step polycondensation method. The PBI fibers are gold in color. Two types of these fibers are available, yarns and staple fibers, and their deniers are 11–200 tex and 0.12–0.44 tex, tensile strength is 300–500 and 250–400 MPa, tensile strain is 15–20% and 20–30%, respectively. Additionally, their Young's modulus, density, boiling water shrinkage, LOI and moisture uptake are, respectively, 18 GPa, 1.43 g/cm³, 46.2 and 13–14%. These fibers are neither combustible nor melt in a flame, and they do not give off-gases even at 560 °C. They have good chemical resistance and a good fire-retardant property. They remain soft and retain their insulation property even after carbonation.

They are mainly used as suits or uniforms for fire services, steel-making, welding, aerospace and military applications as well as protective gloves, aprons, flame-retardant decorations, high-temperature tracks, fire-retardant composite reinforcements, high-performance threads, asbestos substitutes and deceleration cables.

In addition, these fibers have been used as moon-landing suits and expansion structures for spacecraft reentry into earth. As hollow forms, these fibers are pressure resistant, semi-permeable and heat resistant and can thus be used as a reverse osmosis desalination film for boiling water.

2.7 Ultra-High Molecular Weight Polyethylene (UHMWPE) Fibers

Ultra-high molecular weight polyethylene (UHMWPE) fibers are gel-spun from UHMWPE and have a molecular weight of more than 10⁶ D, and this is followed by a stretching technique [51]. Gel spinning includes both melt spinning and dry spinning, which forces the entangled molecules of the gel polymers to fully unwrap and thus affords fibers with high strength and high modulus.

UHMWPE fibers have been developed since the 1980s and were commercialized quickly because of the low cost of the raw materials as well as their prospective application in the development of high-strength, high-modulus light composites. Their strength and modulus are around 4 and 120 GPa, respectively. However, their density is less than 1.0 g/cm³.

Table 2.52 shows trade names and production companies of commercial UHMWPE fibers, and their properties are compared in Table 2.53.

The densities of the commercialized UHMWPE fibers are all less than 0.97 g/cm³, which is two-thirds those of aramid fibers and half that of high-modulus carbon fibers, as shown in these tables. Their densities are the lowest among all the developed high-performance fibers. For example, the specific tensile strength of Spectra1000 is higher than that of all other high-performance fibers as it is nearly 135% that of Kevlar fibers and 150% that of carbon fibers; in addition, their specific Young's modulus is 2.5 times that of Kevlar fibers.

Table 2.52 Manufacturers and trade names of commercial UHMWPE fibers

Manufacturer	Brand name	Type/ (dtex/f)	Tensile strength/ (cN/dtex)	Young's modulus/ (cN/dtex)	Tensile strain/%
Togobo	DyneemaSK60	36–154	26.5	882.3–1650	3.0–6.0
DSM	DyneemaSK76	1760	37.0	1200.0	3.8
Allied	Spectra900	1333/98	26.5	1235.2	–
	Spectra1000	722/120	30.9	1764.6	–
Mitoui	Tekmilon I	111/200	29.1	997.0	3.0
	Tekmilon II	555/60	25.0	897.3	–

Table 2.53 Properties of UHMWPE fibers compared with other selected fibers

Property	Spectra900	Spectra1000	Kevlar LM	Kevlar HM	HS carbon fiber	HM carbon fiber	S-glass fiber
Diameter/ μm	38	27	12	12	7	7	7
Density/(g/cm^3)	0.97	0.97	1.44	1.44	1.81	1.81	2.50
Tensile strength/GPa	2.50	3.0	2.8	2.8	3.0–4.5	2.4	4.6
Young's modulus/GPa	117	172	62	124	228	379	90
Tensile strain/%	3.5	2.7	3.6	2.8	1.2	0.8	5.4
Specific tensile strength/ ($\times 10^8$ cm)	2.67	3.09	1.94	1.94	1.76	1.32	1.84
Specific Young's modulus/ ($\times 10^8$ cm)	120.6	117.8	43.05	36.11	125.9	209.3	36.0

UHMWPE fibers were invented by DSM, patented in 1979 and were piloted in 1990. The fibers have the trade name Dyneema. Subsequently, Mitsui Oil Company built its own pilot line of 300 t/a in 1999 and started to produce Tekmilon fibers. The Allied company bought the patent from DSM and built an improved pilot line producing Spectra900 and Spectra1000 fibers. DSM also undertook a joint enterprise with Toyobo and produced DyneemaSK-60 fibers. China also built a production line in 2000 and produced high-modulus fibers with the trade name Qianglun. Additionally, a new pilot line of 100 t/a was also built to produce high-strength fibers with a tensile strength of 36.83 cN/dtex, a Young's modulus of 1309.6 cN/dtex and a tensile strain of 3.7%.

UHMWPE fibers have excellent mechanical properties and dielectric properties, as listed in Table 2.54. Their dielectric constant and dielectric loss are very low, and therefore, the electromagnetic wave transmission of their composites of close to 100% is higher than that of glass fiber composites. They are the best reinforcement

Table 2.54 Dielectric properties of high-performance fibers

Type	Dielectric constant (ϵ)	Dielectric loss tangent/ $\times 10^{-4}$
UHMWPE	2.3	4
Kevlar	2.8	–
E-glass	6.0	60
PA66	3.0	23
PET	3.0	90

Table 2.55 Impact properties of selected composites

Property	Spectra900	E-glass	Kevlar	Graphite
Total absorption energy/J	45.2584	46.7758	21.8287	21.6981
Specific absorption energy/J	16.4	8.9	6.3	5.4

candidates for the preparation of radar radomes and for fiber optic cable cores. Among all the high-performance fibers, UHMWPE has the highest impact strength, as listed in Table 2.55.

The specific absorption energy of the UHMWPE fiber composite is twice that of the E-glass fiber composite and three times those of Kevlar and carbon fiber composites [45–47, 51]. Therefore, they are important fibers for bulletproof vests, cut-resistant clothing, police shields and bulletproof helmets, bulletproof vehicles, tanks and other armors.

Other advantages are their good solvent resistance and lower price, which gives them great potential for development. For example, Spectra fibers had an original price of 49–61 \$/kg and this will be further lowered as a result of their recent major breakthrough in gel spinning, which enabled a thousand times increase in productivity. The potential application fields of UHMWPE fibers are listed in Table 2.56.

The interface bonding performance of UHMWPE fibers and fabrics in polymer matrixes can be improved by surface treatment. The biggest advantages of UHMWPE fiber composites are their significantly lower weight and their significantly higher impact strength. Therefore, they can be used to manufacture many excellent protection products such as protective shields, bulletproof vests, protective helmets, aircraft structural components and tank anti-debris linings. Table 2.57 illustrates the comparative impact strengths of UHMWPE fiber and Kevlar fiber-reinforced composites.

Additionally, because they are chemically inert, they can be used in medical equipment such as sutures and artificial muscles. Other than the above-mentioned attractive features, UHMWPE fibers also have shortcomings such as their poor thermal stability, high creep rate and bad interface bonding property.

The melting point of polyethylene fibers is around 134 °C, and a higher melting point of 144–154 °C can be observed in highly oriented UHMWPE fibers. Because of these low melting points, their strength and modulus vary according to changes in temperature. At temperatures lower than 100 °C, their strength is higher than that

Table 2.56 Potential applications of UHMWPE fibers

Application fields	Fabrics	Knitwear	Non-woven fabrics	Ropes	Composites
Protective supplies		Protective gloves, cut-resistant clothing			Motor covers
Maritime supplies	Sails			Departure ropes, mooring cables, trawls	Hulls
Transportation	Tapes, balloons			Lift cable, cables	Lightweight armor, ships
Bulletproof products	Shelter, protection products		Bulletproof, anti-riot vests		Helmets, board materials, armor
Sports goods	Sails	Fencing clothes, skating clothes		Speedboat ropes, fishing lines	Skiing board, hockey sticks, fishing rod

Table 2.57 Comparative impact strength of UHMWPE fiber and Kevlar fiber-reinforced composites

Type	Number of layers	Impact rate/ (m/s)	Maximum load/N	Absorbed energy/J
UHMWPE	1	4.2	3500	1040
Spectera900	3	4.3	4370	540
Kevlar	1	4.3	830	40
	3	4.5	1650	120

of the aramid fibers; however, at temperatures higher than 100 °C it is lower than that of the aramid fiber. Resistance to a constant tensile load also drops rapidly at temperatures close to 100 °C. Therefore, UHMWPE fibers are not suitable for extended tensile load at 90–100 °C. Studies have shown that their thermal stability and creep resistance can be improved by physical or chemical cross-linking such as high radiation modification.

Additionally, even though shrinkage between UHMWPE fibers and the epoxy resin composite matches well, the interface property of the composite is worse than that of aramid fibers. Surface modifications are necessary to improve this performance. Methods include washing, drying, chemical erosion treatment, flame treatment and low-temperature plasma processing. Improved UHMWPE fibers can undoubtedly be used in a wide variety of applications. They are very promising new generation of high-performance fibers, particularly because they are cost-effective.

2.8 Characterization Methods for Long Fibers

Because fiber characterization methods are very specific, it is necessary to discuss these in a separate section. As reinforcements of composite materials, mechanical properties such as tensile strength, the Young's modulus and tensile strain are of interest; additionally, for specific composite performance their density, coefficient of thermal expansion, thermal conductivity, resistivity, etc. are of concern. This section briefly introduces the main characterization methods for long-fiber reinforcements such as monofilaments and yarns. Short fibers such as whiskers are not considered because of different testing approaches.

2.8.1 Mechanical Characterization Methods

2.8.1.1 Monofilaments

The mechanical property of monofilaments is generally measured by placing a monofilament of specific length in a paper frame followed by tensioning until fracture under a specific tensile strain rate using a constant pulling machine. Tensile strength and Young's modulus can be calculated from the recorded fracture load and the tensile strain curve. Adhesions or coatings on the surface of the fibers, if any, are removed by washing with suitable solvents, and the fibers are dried before measurement.

Specifically, fibers 4–5 cm long are cut randomly from fiber yarns, and monofilament samples are separated undamaged and then stuck onto the center line of the paper frame, as shown in Fig. 2.9. The space and thickness of the paper frame are 25 ± 0.5 mm and 0.07–0.3 mm, respectively. The outer side width and length should be in accordance with the clip size of the testing machine. According to the standard, the laboratory temperature and the relative humidity should be 23 ± 5 °C and 50–70%, respectively. The paper frame is then fixed using a clip and cut using a small pair of scissors. The monofilament is subjected to tensile pulling at a constant speed of 5 mm/min, and the extension curve is recorded until fracturing occurs.

Fig. 2.9 Illustration of a paper frame with a monofilament (A sticking position, B fixed position)

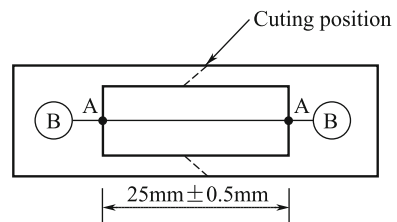
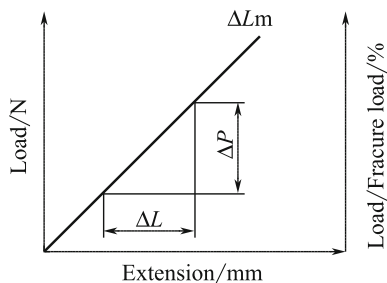


Fig. 2.10 Load–extension curve from a monofilament tensile test



A typical tensile load–extension curve for a monofilament is shown in Fig. 2.10. For a confidence level of 90% and a precision of 4%, no less than 25 samples should be collected.

The cross-sectional area of a monofilament is measured in accordance with Chinese standard GB/T3364, using a transmission microscope or a projector to investigate the diameters of fibers scattered on a slide. If the number of monofilaments is known for a given yarn, the cross-sectional area can also be obtained according to Appendix C, GB/T3362, in which the monofilament cross-sectional area is derived from the yarn cross-sectional area. The tensile strength of a monofilament can be calculated as follows:

$$\sigma = \frac{P}{A} \quad (2.1)$$

Here, σ is the tensile strength in MPa; P is the fracture load in N; A is the monofilament average cross-sectional area in mm^2 .

When the apparent Young's modulus is required, the middle part of the load–extension curve, which is 20–90% of the fracture load, is selected and tangled, as shown in Fig. 2.10. Then, ΔP and ΔL can be calculated, and Young's modulus is obtained using Eq. (2.2).

$$E_a = \frac{\Delta P}{A} \times \frac{L}{\Delta L} \quad (2.2)$$

Here, E_a is the apparent Young's modulus in MPa; ΔP is the intercept of the load increment in N; L is the length of the sample in mm; ΔL is net extension corresponding to the load increment ΔP in mm.

The tensile strain, ε , is related to the fiber length and the maximum extension (ΔL_m in Fig. 2.10), namely:

$$\varepsilon = \frac{\Delta L_m}{L} \times 100 \quad (2.3)$$

According to standard GB8170, the arithmetic mean value of the results should be reported to three significant digits, the standard deviation and the coefficient of variation to two digits.

2.8.1.2 Yarns

The tensile strength, Young's modulus and tensile strain of reinforcements can also be obtained through yarn tensile measurements. The samples are prepared with epoxy resin-impregnated yarns, as shown in Fig. 2.11. Both ends are stuck onto 0.2- to 0.4-mm-thick paper frames and fixed using any room-temperature curing adhesive.

The samples should be smooth, straight, uniform and without defects. The amount of epoxy resin should be in a control of 35–50%. If an inertia-free tensile machine is used the relative error should be less than $\pm 1\%$; if an automatic load record machine is used, the error in paper recording rate should be no more than $\pm 1\%$. Standard environmental conditions for the measurement are as follows: temperature of $(23 \pm 2)^\circ\text{C}$ and an air relative humidity of $50 \pm 5\%$. Ten samples are included in each test, and if a fracture occurs at the fixed position, the sample result is invalid. The tensile strength can be calculated as follows:

$$\sigma_t = \frac{P}{A} \quad (2.4)$$

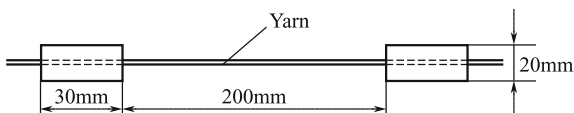
where σ_t is the tensile strength in MPa; P is the load in N; A is the yarn cross-sectional area in mm^2 (or m^2). A is obtained from the yarn axial density divided by the yarn volume density.

The apparent Young's modulus can be obtained as follows:

$$E_a = \frac{\Delta P}{A} \times \frac{L}{\Delta i} \quad (2.5)$$

where E_a is the apparent Young's modulus in MPa (or GPa); ΔP is the intercept of the selected load from the load–extension curve in N; L is the length of the specimens in mm; Δi is the incremental extension within the gauge corresponding to ΔP in mm.

Fig. 2.11 Illustration of a yarn sample



The tensile strain is calculated by Eq. (2.6):

$$\varepsilon = \frac{\Delta L}{L} \times 100 \quad (2.6)$$

where ε is the tensile strain %, and ΔL is the apparent tensile extension in mm.

2.8.2 Physical Characterization Methods

2.8.2.1 Density

The linear density of yarns can be measured with a balance of 0.1 mg accuracy. The samples should be three 1-m-long yarns, accurate to ± 0.5 mm. As for volumetric density, the floating method or the density gradient method can be used.

(1) Floating Method

Surface adhesives are removed with appropriate solvents, and the samples are dried for measurement. A mixed solution is prepared using a high-density solvent, e.g., dibromoethane, and a low-density solvent, e.g., *n*-heptane. The density should be close to the assumed density of the samples. The solution is put into a plugged graduated cylinder. Fiber samples are cut 0.5–1.0 mm long and put into the above-mentioned cylinder and stirred using a glass rod until fully dispersed in the solution. The cylinder is then put into a water bath at $(25 \pm 1)^\circ\text{C}$.

If the fibers float upward (or sinking downward) in the mixture, more *n*-heptane (or dibromoethane) is required to decrease (or increase) the density of the mixture until the fibers are evenly distributed. After 4 h in the water bath, the solution density will be regarded to be the same as the fiber density if they are still dispersed uniformly.

A densitometer is then used to measure the solution density. This will be the fiber density value.

(2) Density Gradient Method

A density gradient tube is prepared using a high-density solvent and a low-density solvent. Both the solvents can be pure solvents or mixture solvents. Their volumes are calculated as follows:

$$d \cdot V = A \cdot a + B(V - a) \quad (2.7)$$

where d is density of the mixture in g/cm^3 ; V is the volume of the mixture in cm^3 ; A is the density of the heavy solvent in g/cm^3 ; B is the density of the light solvent in g/cm^3 ; a is the volume of the heavy solvent in cm^3 ; $(V - a)$ is the volume of the light solvent in cm^3 .

Different mixtures with different densities are checked with a densitometer of 0.001 g accuracy, and densities are adjusted by the addition of a heavy solvent or a light solvent until they reach the required accurate density.

From the lower-density to the higher-density solvents, the mixtures are transferred to a scaled gradient tube through a funnel and a long capillary of 0.8–1.0 mm in diameter. After the last mixture, i.e., the heaviest mixture is added, the capillary is removed from the gradient tube. The gradient tube is covered with a lid and placed in the water bath at $(25 \pm 0.5) ^\circ\text{C}$ and held still for 24 h.

The density gradient tube is checked as follows: four to five small balls with standard densities are put into the tube in turn, from higher to lower densities. After 4 h, the relative heights of the balls are measured using an altimeter, and then, a curve of height versus density can be obtained based on the known densities of the small balls. The linear part of the curve should be no less than 5 cm, and the density difference between each 1-cm height graduation should be lower than 0.002 g/cm^3 .

The tube is then ready for sample preparation and measurement. The fibers are organized into small-fiber yarns and then bent into four circular rings of about 0.5 cm in diameter. No broken fibers are permitted to guarantee the smoothness of the rings. The rings are then immersed in an appropriate solvent such as acetone for 4 h to become unglued. The rings are then dried for 2 h at $60 ^\circ\text{C}$ and cooled to room temperature in a dryer. The dried fibers are submerged in a solution with a density similar to the fiber and placed into the centrifuge tube and degassed for 15 min at 2000 r/min. The degassed samples are then ready for the test. They are quickly placed in the gradient tube and left for 4 h. The height of the fiber samples, as well as the heights of the standard balls, is obtained using an altimeter.

The fiber density can be obtained using the interpolation method as follows:

$$d_x = \frac{x - b}{a - b}(d_a - d_b) + d_b \quad (2.8)$$

Here, d_x is the fiber sample density in g/cm^3 ; x is the height of the fiber sample in mm; a is the height of the heavy ball in mm; b is the height of the light ball in mm; d_a is the density of the heavy ball in g/cm^3 ; d_b is the density of the light ball in g/cm^3 .

2.8.2.2 Electrical Resistivity

Electrical resistance can be determined using a resistance instrument, which requires that the fibers be pressed into a measurement box. Resistance is an intrinsic property of a conductor. According to the resistance law, the resistance of a conductor, R , is proportional to its length, L , and inversely proportional to the cross-sectional area, S , as shown below:

$$R = \rho_v \frac{L}{S} \quad (2.9)$$

Here, ρ_v is the resistivity, also known as the volume resistivity, and its unit is $\Omega \cdot \text{cm}$.

$$\rho_v = R \frac{S}{L} \quad (2.10)$$

Because air is present in the fibers in the measurement box, the real area of the plate is not S , but SF , where F is the filling factor and can be calculated as below:

$$F = \frac{v_f}{V_r} = \frac{\frac{m}{d}}{SL} = \frac{m}{SLd} \quad (2.11)$$

Here, v_f is the real volume of the fiber; V_r is the volume of the measurement box; m is the mass of the fiber sample; d is the density of the fiber sample.

The volume resistivity is calculated as follows:

$$\rho_v = R \frac{SF}{L} = R \frac{m}{L^2 d} \quad (2.12)$$

The volume resistivity is the resistance when the current transfers through a material with a volume of 1 cm^3 , while the mass resistivity, ρ_m , is the resistance when the length of a material is 1 cm and the mass of the material is 1 g . The relationship between volume resistivity and mass resistivity is shown below:

$$\rho_m = d \rho_v \quad (2.13)$$

The unit of mass resistivity is $\Omega \cdot \text{g/cm}^2$, and its value is calculated as follows:

$$\rho_m = R \frac{m}{L^2} \quad (2.14)$$

The electrical resistivity of the fibers can also be obtained directly by measuring the resistance of the monofilament that is fixed on the paper frame and is calculated according to Eq. 2.10.

2.8.2.3 Coefficients of Thermal Conductivity and Thermal Expansion

Heat conduction is based on the thermal property of the materials coefficient of thermal conductivity. Heat conduction along an infinite flat material with a thickness of x can be described using the Fourier equation as shown below in a one-dimensional manner:

$$Q = -\lambda \cdot \Delta T / \Delta x \quad (2.15)$$

Q represents the unit area heat flow caused by the temperature gradient ΔT over the thickness Δx . Two factors are related to the coefficient of thermal conductivity, λ . Under stable temperature gradient and material geometry conditions, λ expresses the amount of heat required to maintain the temperature gradient.

Many methods and instruments exist to measure the coefficient of thermal conductivity. The Fourier equation is used to describe steady-state conditions, and instruments using this equation are only suitable for testing low thermal conductivity at middle-range temperatures. Equipment that use dynamic (transient) methods such as the hotline or laser light scattering method can be used to measure high thermal conductivity at high temperatures.

A fiber's coefficient of thermal expansion is of great significance in the selection of fibers for matching with ceramic matrixes. For example, reinforcements should have at least the same high-temperature performance as the matrix, and the fiber coefficient of thermal expansion should be slightly higher than that of the matrix. Some thermal expansion testing instruments such as the DIL 402C produced by NETZSCH (temperature range -180 to 2000 °C) can provide a special monofilament support, which is convenient when determining the fiber's coefficient of thermal expansion.

2.9 Whiskers

Whiskers are single-crystal short fibers grown under controlled conditions. They are usually defect-free with diameters ranging from $0.1 \mu\text{m}$ to several microns, and their lengths range from dozens to thousands of microns [52].

Each whisker has a characteristic shape and structure relevant to its intrinsic material property. Good whiskers have perfect crystal structures, highly ordered atomic structures, and contain the least internal defects, e.g., dislocations and impurities. Therefore, they are high-purity short fibers with strengths close to the atomic bonding strength. They are regarded as a pillar reinforcement family for advanced composite materials.

Whisker-reinforced composites have enhanced microstructures, leading to excellent resistance to sliding and wearing. Some whiskers also have special physical properties such as electrical insulation or a negative coefficient of thermal conductivity. Whisker-reinforced high-performance composites have become an important integration composite in structural and functional materials [53].

Recent applications of whisker-reinforced composites have spread greatly, which in turn has promoted research and development into a variety of whiskers, particularly in the manufacturing of cost-effective whiskers.

More than 100 species of various whiskers have been developed to date, and these include organic whiskers, metal whiskers and ceramic whiskers. These are the

Table 2.58 Physical properties of general whiskers

Whisker	Melting point/ $^{\circ}\text{C}$	Density/ (g/cm^3)	Tensile strength/GPa	Young's modulus/GPa
BeO	2570	2.85	13	350
B_4C	2450	2.52	14	490
α -SiC	2316	3.15	–	480
β -SiC	1600	3.19	3–14	400–700
Si_3N_4	1690 (sublimation)	3.18	13.7	380
C(graphite)	3650	1.66	19.6	710
TiN	–	5.20	7	200–300
AlN	2199	3.30	6.9	340
MgO	2799	3.60	–	340
$\text{K}_2\text{O}[\text{TiO}_2]_n$	760–1370	3.29	5.7–7.0	280
Cr	1890	7.20	9	240
Cu	1080	8.91	3	120
Fe	1540	7.83	13	200
Ni	1450	8.97	4	210
$9\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$	1420–1480	2.93	7.8	392
ZnO	1720 (sublimation)	5.78	>10	354
Polyoxymethylene	184	1.42	–	>100

three major categories, among which ceramic whiskers are superior to the other two in terms of strength, modulus, heat resistance and wear resistance. Therefore, ceramic whiskers have more industrial use and have become the focus of research and development. The physical properties of general whiskers are listed in Table 2.58.

2.9.1 Ceramic Whiskers

As a kind of special fibrous single-crystal material, the growth mechanisms of whiskers are also unique as they are completely different to the formation of continuous fibers. The vapor–solid (VS) mechanism and the vapor–liquid–solid (VLS) mechanism are the two most common types. However, whisker growth mechanisms and their preparation methods are closely linked. For example, in the VS mechanism, in addition to the chemical reaction conditions and the choice of raw materials, oversaturation in the vapor reactant also plays an important role. The growth mechanisms of selected whiskers and their preparation methods are listed in Table 2.59.

In the VLS mechanism, catalysts are necessary for the fast growth of whiskers. A good catalyst should be able to form a low-melting eutectic liquid, which can

Table 2.59 Growth mechanisms of selected whiskers and their preparation methods

VS mechanism		VLS mechanism		
Whisker	Preparation method	Whisker	Preparation method	Catalyst
Al ₂ O ₃	AlF ₃ hydrolysis	Si ₃ N ₄	CVD	Fe
β-SiC	Carbon thermal reduction	β-Si ₃ N ₄	CVD	Cr
Mullite	Vapor	α-Al ₂ O ₃	CVD	Mo, Fe
Mullite	Sol–gel	β-Sialon	Carbon thermal reduction	Fe

significantly reduce the growth energy. This is why the VLS growth rate is faster than the VS growth rate, because no catalyst takes part in the VS mechanism. By properly controlling the droplet location, type and chemical composition of the low eutectic liquid, a variety of whiskers with different shapes, types and properties can be obtained. Therefore, the VLS growth mechanism is currently the most important and mostly used approach to a number of commercialized whiskers. Typical ceramic whiskers and their performance are listed in Table 2.60.

In addition to basic whisker properties such as high tensile strength, high Young’s modulus and high heat resistance, the typical ceramic whiskers listed in Table 2.60 also have unique characteristics such as high hardness (SiC) or a low coefficient of thermal expansion (Si₃N₄) [53]. It is very important to select appropriate whiskers to meet the specific requirements of different composites.

2.9.1.1 SiC Whiskers

There are two kinds of crystal isomers in SiC whiskers, hexagonal α-SiC and cubic β-SiC [54]. Compared with α-SiC whiskers, β-SiC whiskers maintain whisker length better because of the lower likelihood of fracture upon loading; therefore, they are preferred in most industrial fields. In addition to their high strength, high modulus, high hardness and good chemical stability, SiC whiskers also have good wear resistance, corrosion resistance and high-temperature anti-oxidation properties. For these reasons, they are known as “king of the whiskers.”

SiC whiskers are at the practical application stage, and many satisfactory results have been obtained. For example, SiC whiskers can greatly improve the Young’s modulus and wear resistance in aluminum matrixes. Additionally, it improves their low-temperature and high-temperature strength and their fatigue strength. These composites are now widely used in the automotive, aerospace and military industries as structural parts and wear-resistant parts such as engine pistons, connecting rods, bearings, bulletproof plates and shielding materials.

Research into SiC whiskers started in the 1960s, and in the 1980s SiC whiskers were extensively applied as polymer, metal and ceramic matrix reinforcements. Many production reports have been published, and most come from the USA and Japan. In addition to their successful application as cutting tools (SiCw/Al₂O₃), piston engines (SiCw/Al), aircraft landing gear parts and sporting equipment such as golf clubs (SiCw/polymer), SiC whisker composites have begun to be used as

Table 2.60 Some typical ceramic whiskers and their performance

Whisker	Density/ (g/cm ³)	Diameter/ μ m	Length/ μ m	Tensile strength/GPa	Young's modulus/GPa	Mo's hardness	Coefficient of thermal expansion/ (10 ⁻⁶ /K)	Melting point/ $^{\circ}$ C	Thermal stability/ $^{\circ}$ C
SiC	3.18	0.05–7	5–200	21	490	9	4.0	2690	1600
K ₆ Ti ₁₃ O ₆	3.30	0.1–1.5	10–100	7	280	4	6.8	1370	1200
Al ₁₈ B ₄ O ₃₃	2.93	0.5–1	10–20	8	400	7	4.2	1950	1200
ZnO	5.78	5	2–300	10	350	4	4.0	1720	–
Si ₃ N ₄	3.20	0.1–0.6	5–200	1.4	350	–	3.0	1900	1700
MgO	3.60	3.0–10	200–300	1–8	–	–	13.5	2850	2800

Table 2.61 Manufacturers and brand names of SiC whiskers in the USA and Japan

Manufacturer	Brand name
Advanced Composite Materials Co. (ACMC)	AC ₁ , AC ₂
American Mterix Co.	AM ₁ , AM ₂ , AM ₃ , AM ₄ , AM ₅ , AM ₆ , AM ₇ , AM ₈
Advanced Ceramic Technologies	AI ₁
Alcan Co.	CN ₁
Huber Co.	Hu ₁ , Hu ₂ , Hu ₃
Clermont Co.	KE ₁
Kobe Steel Co.	KS ₁ , KS ₂ , KS ₃ , KS ₄
Tateho Chemical Industries Co.	TA ₁ , TA ₂ , TA ₃
Tokai Carbon Co.	TK ₁ , TK ₂ , TK ₃ , TK ₄ C, TK ₅ , TK ₆ , TK ₇
Los-Alamos Co.	ARCo

Table 2.62 Typical properties of SiC whiskers

Property	ARCo	Tateho	ToKai	BP, China
Tensile strength/GPa	8.4	–	3–14	4–13
Young's modulus/GPa	580	–	400–700	–
Diameter/ μm	0.6	0.05–0.20	0.2–1.0	0.1–1.0
Length/ μm	10–80	10–40	30–200	10–200
Crystal type	α	$\alpha + \beta$	β	β

filter materials in the chemical industry recently. However, since they are carcinogenic, it is necessary to take protective measures during production and application.

Research into these materials started in China in the early 1970s, and a number of SiC whisker products have been produced. The carbon thermal reduction method has also been used to prepare SiC whiskers, and a pilot plant was commissioned and delivered a product quality close to that of other countries. In addition, using carbon black and rice husk as a carbon source for the growth of SiC whiskers has also been reported.

Manufacturers, brand names and typical properties of SiC whiskers in the USA, Japan and China are listed in Tables 2.61 and 2.62. Morphological characteristics of typical SiC whiskers are listed in Table 2.63. All the products have similar mechanical properties but with some obvious differences in morphology.

2.9.1.2 Si₃N₄ Whiskers

Morphologies of Si₃N₄ whiskers vary according to preparation methods. In general, there are three types of preparation methods:

Table 2.63 Morphology characteristics of typical SiC whiskers

Characteristic	US AM ₁	USAC ₁	China BP	Japan TK ₁	Japan TA ₁
Extremely straight crystal/%	97	99	97	54.5	98
Straight crystal/%	3	1	3	35.5	2
Bent crystal/%	–	–	–	8.5	–
Extremely bent crystal/%	–	–	–	1.5	–
Extremely smooth whisker/%	10.5	89.5	16.5	47.5	5.0
Smooth whisker/%	20.5	5.0	19.5	6.5	45.0
Coarse whisker/%	48.5	5.0	54.5	44.5	19.0
Extremely coarse whisker/%	20.5	0.5	9.5	1.5	31.0
Particle content/%	4	1.0	4.0	1.0	4.0

- ① In the vapor-phase method, a mixed gas of SiCl₄, H₂ and N₂ is used, and Si₃N₄ whiskers are grown on an Fe-coated graphite base heated to 1250 °C. These whiskers are amorphous with regular spiral bodies and spherical ends and are thus the smallest coil springs;
- ② In the liquid-phase method, silicon is heated to 1550–1600 °C to a liquid state and reacts with the nitrogen atmosphere to give Si₃N₄ whiskers;
- ③ In the solid-phase method, a mixture of solid SiO₂ and C is heated in nitrogen or a mixture of solid SiO₂ and Si is heated in a N₂ and H₂ atmosphere affording the target Si₃N₄ whiskers.

Another method exists for the preparation of defect-free Si₃N₄ whiskers; that is, Si₃N₄ and high-pressure NH₃ are mixed at room temperature and then heated to remove the ammonium nitrogen, and this is further heated gradually to decompose the amide affording Si₃N₄ ultra-fine powders with high activity and high purity. If they are further heated to 1400–1450 °C, straight and smooth Si₃N₄ whiskers are obtained. Their oxygen content is less than 1%, and their aspect ratio depends on the heating temperature. For example, at a heating temperature of 1400 °C, the diameter and length are 0.02–0.08 and 50–100 μm, respectively, whereas at 1450 °C these parameters are 0.1–0.3 and 10–30 μm, respectively. In addition, their typical tensile strength, Young's modulus and coefficient of thermal expansion are 13.8, 390 GPa, and $2.75 \times 10^{-6} \text{ K}^{-1}$, respectively.

Si₃N₄ whiskers can be used to reinforce aluminum matrix composites and also to reinforce a large number of various ceramics such as glass, aluminum, silicon nitride and silicon carbide. These ceramic matrix composites have good high-temperature performance and excellent toughness; for example, Si₃N₄ whisker-reinforced SiC ceramic has a maximum working temperature up to 1400 °C. In addition, the toughness of 20%(wt) Si₃N₄ whisker-reinforced Al₂O₃ is 1.5 times that of its matrix.

2.9.1.3 Potassium Titanate Whiskers

Even though their tensile strength and Young's modulus are relatively low, potassium titanate whiskers are a kind of low-cost material with good integrated performance. Their aluminum composites are easily cut-processed, which is attractive. They are mainly used in the manufacture of polymer matrix composites because they improve the friction and insulation properties of the polymers.

Potassium titanate whisker reinforcement composites meet the requirements of automobile, chemical and military applications such as high strength, low attrition rate, good high-temperature and low-temperature stability, and good resistance to strong acids and strong bases.

Additionally, potassium titanate whiskers have high infrared reflectivity and very low thermal conductivity and are thus widely used in the automobile, electrical, electronic and instrumentation industries as corrosion resistance paints, lubricants, insulation materials and anti-corrosion materials.

As a kind of general reinforcement, there is a demand for a further reduction in the production cost. According to expert analysis, only when the price reaches 11,100 US dollars/ton, large-scale use will be possible in the automobile industry. A conductive potassium titanate whisker recently produced in Japan can apparently be used in the manufacture of static electricity prevention or electromagnetic shielding electronic components.

Since potassium titanate whiskers have been adopted as reinforcements in resins such as POM, PBT, Nylon 66, Nylon 6, specialty Nylon, PPS, ABS, PVC and PP, there are many applications for these plastic composites: ① reinforced POM as watch gears, camera gears, micromotor gears and tape recorders; ② reinforced PBT as telegraph key switches, posts, motor parts, relays, cams and plugs; ③ reinforced Nylon 66 as bearings, cams, gears, winding pipes, wheels and bearing retainers; ④ reinforced Nylon 6 as bearings, gears, industrial posts, automatic closing door devices, winding pipes and buttons; ⑤ reinforced specialty Nylon as sliding parts, silence gears, thin-walled parts, and sporting goods; ⑥ reinforced PPS as copier parts, sliding parts and auto parts; ⑦ reinforced ABS as copier parts, electroplating products, watches and clock parts and sporting goods; ⑧ reinforced PVC as pearls, decorative bands and coating pipes; ⑨ reinforced PP, as audio components, vacuum-forming parts and auto parts.

The general formula of potassium titanate whiskers is $K_2O(TiO_2)_n$ in which $n = 1, 2, 4, 6$ and 8 . Best stability is usually obtained when $n = 6$. Typical characteristics of one type of stable potassium titanate whiskers are listed in Table 2.64.

The biggest drawback of these whiskers is that they readily react with metal melts at the interface, and furthermore, these whiskers are not stable at higher temperatures because of decomposition. Further in-depth studies are needed to extend their application in reinforcing metals.

Table 2.64 Typical characteristics of potassium titanate and aluminum borate whiskers

Property	$K_2O \cdot 6TiO_2$	$9Al_2O_3 \cdot 2B_2O_3$
Appearance	White, needle-like	White, needle-like
Density/(g/cm ³)	3.3–3.4	2.93
Melting point/°C	1370	1440
Young's modulus/GPa	280	400
Tensile strength/GPa	7	8
Mo's hardness	4	7
Linear expansion coefficient/($\times 10^{-6}/K$)	–	4.2
Axial direction	–	2.6
Cross-sectional direction	–	5–6
Coefficient of thermal conductivity/[W/(cm/K)]	–	0.04–0.05
Thermal diffusion coefficient/(cm ² /s)	–	0.01
Dielectric constant	3.5–3.7	5.6

2.9.1.4 Aluminum Borate Whiskers

Aluminum borate whiskers have two kinds of structures, namely $9Al_2O_3 \cdot 2B_2O_3$ and $2Al_2O_3 \cdot B_2O_3$. They are new emerging high-tech whiskers with high performance and low price. For example, their production cost is only 1/10th to 1/30th that of SiC whiskers.

Aluminum borate whiskers are widely used as new inorganic fillers in light-metal alloys, functional plastic composites, ceramic fibers and coatings. Because of resource conditions in China, the state attaches great importance to the further research and development of these whiskers.

Typical physical properties of $9Al_2O_3 \cdot 2B_2O_3$ whiskers are listed in Table 2.64. These whiskers have good tensile strength, Young's modulus, heat resistance, chemical resistance, neutron absorption and electrical insulation properties. They are not only used for insulation and heat-resistant materials but also used as reinforcements in thermoplastic resin, thermosetting resins, cements, ceramics and metals.

After treatment with coupling agents such as silane, aluminum borate whiskers can significantly improve the mechanical properties of a variety of engineering plastics such as Nylon 6 and polycarbonate. Aluminum borate whiskers improve the tensile strength, wear resistance and heat resistance and also result in isotropic products with smooth surfaces. Satisfactory results have also been obtained in a number of small precise parts with complicated shapes such as the components of clocks, watches and cameras.

Aluminum borate whiskers can be used as reinforcements in metals and alloys, especially aluminum alloys, which have good abrasion resistance and a low thermal expansion rate. These have found application in cycling operation components in vehicles and compressors.

Aluminum borate whisker-reinforced aluminum composites have competitive strength, modulus and thermal expansion properties compared with SiC and Si₃N₄ whisker-reinforced aluminum and even have better wear resistance. For example, whisker-reinforced aluminum composites can be used to manufacture automobile engine pistons that substantially increase engine power, save fuel and reduce noise and exhaust emissions.

These high-performance, low-cost whiskers are important composite reinforcements, especially in the automotive industry [53]. However, measures must be taken to control the interface between the whiskers and alloys. They also can be used in ceramic matrix composites as they improve their mechanical properties and high-temperature stabilities. In addition, they are also applied to flame-retardant or fire-resistant coatings, electronic materials and electromagnetic shielding materials.

2.9.1.5 ZnO Whiskers

As a kind of *n*-type semiconductor, ZnO whiskers are mainly divided into two categories, mono-needle-like and multi-needle-like. Mono-needle-like ZnO whiskers have similar properties and applications to those of SiC whiskers or potassium titanate whiskers. Tetra-needle-like ZnO whiskers, which are typical multi-needle-like ZnO whiskers, have more interesting properties and applications [55].

They have a central body and four protruding needle-like crystals with a general length of 3–300 μm, a root diameter of 0.1–14 μm and an angle between protruding crystals of about 109°. Their crystal structure is a hexagonal Wurtzite structure, and the protruding needles grow along the *c* axis of hexagonal crystal. Their typical physical properties are listed in Table 2.65. Their average volume resistance is 10⁴–10⁸ Ω·cm indicating a semiconductive property.

ZnO whiskers have many functional properties such as electrical conductivity, thermal conductivity, piezoelectric activity, pressure sensitivity, microwave absorption, sound absorption, vibration attenuation and anti-bacterial and catalytic properties. They are widely used as reinforcements in metals, ceramics and polymers, with the ability to improve their tensile strength, bending strength, shear

Table 2.65 Typical physical properties of tetra-needle-like ZnO whiskers

Property	Value
Formula	ZnO
Shape	Tetra-needle-like
Intrinsic density/(g/cm ³)	5.78
Apparent density/(g/cm ³)	0.05–0.50
Boiling point/°C	1720
Length of protruding needle/μm	3–300
Root diameter of protruding needle/μm	0.1–14
Volume resistance/Ω·cm	7.14
Coefficient of thermal expansion/ (×10 ⁻⁶ /K)	4.0

strength, abrasion resistance and high-temperature chemical stability, as well as many other functional properties [56].

For example, because of their conductive and piezoelectric properties, ZnO whiskers are widely used as conductive fillers, conductive layers, anti-electrostatic materials, radio wave-absorbing materials and piezoelectric materials [56]. Also, because of their good isotropic structures and isotropic physical properties, tetra-needle-like ZnO whisker-reinforced composites have good isotropic mechanical properties, electrical properties and optical properties, which are unmatched by other whiskers, particularly in the field of functional materials. Furthermore, the whiskers are also widely used as noise shielding, sound absorption and damping materials in the automotive, construction, industrial equipment, office equipment and household appliance fields.

In addition, ZnO whiskers are also sensitive to combustible gases, especially when doped with Li^+ , which can significantly increase their sensitivity. The apparent density of ZnO whiskers is very low, and they are thus attractive fillers for insulation materials as well as unique vibration attenuation fillers in music instruments.

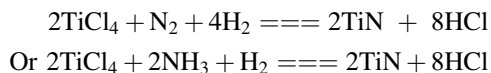
ZnO whisker research began in the mid-1980s, and Matsushita Electric Industrial is one of the most successful companies in the preparation of ZnO whiskers, devices and their applications.

Research started in China in the early 1990s, and the tetra-needle-like ZnO whiskers obtained have an average protruding needle length of 51 μm , a root diameter of 15 μm , a specific heat of 5.52 J/g·K, heat resistance of 1720 $^{\circ}\text{C}$, an apparent density of 0.01–0.50 g/cm³, electrical resistivity below 50 $\Omega\cdot\text{cm}$, bending strength of 12 GPa and a Young's modulus of 350 GPa.

2.9.1.6 TiN Whiskers

TiN whiskers are cubic crystals, and their density is 5.21 g/cm³ at 25 $^{\circ}\text{C}$, their specific conductivity is 8.7 $\mu\Omega^{-1}\cdot\text{m}^{-1}$ at 20 $^{\circ}\text{C}$, their microhardness is 2000–2400 kg/mm², and they have melting points up to 2950 $^{\circ}\text{C}$. They have low-temperature superconductivity and excellent thermal conductivity, and their linear expansion coefficient is as high as $9.4 \times 10^{-6}/\text{K}$.

TiN whiskers are prepared by chemical vapor deposition (CVD) at 1000–1450 $^{\circ}\text{C}$ using a mixed vapor system of $\text{TiCl}_4\text{--H}_2\text{--N}_2$ or $\text{TiCl}_4\text{--H}_2\text{--NH}_3$ [57] as follows:



The TiN whiskers thus prepared are cubic crystals with high purity and good chemical stability. The macroscopic shape of the whiskers is four-prism or eight-prism. In the 1980s, much research was carried out in the USA, Japan, Poland, the former Soviet Union and China. The TiN whiskers produced in China

have a tensile strength distribution of 1.5–10 GPa and a Young's modulus distribution of 30–200 GPa. Their Young's modulus is a magnitude of order higher than that of the bulk crystal and is 10 GPa.

TiN whiskers have good compatibility with alumina, boron nitride, tungsten carbide and stainless steel, as well as a number of metal alloys. In particular, they are ideal reinforcements in zirconia ceramic matrix composites because their coefficients of thermal expansion are very close; for example, the coefficient of thermal expansion of zirconia is $9.5 \times 10^{-6}/\text{K}$. The whiskers can greatly improve the high-temperature toughness of zirconia.

In addition, TiN whiskers have high hardness and good abrasion resistance and can thus be used to improve the hardness of super-tough ceramics. For example, TiN whisker-reinforced WC cutting tools have a higher bending strength of 750–1050 MPa compared with 650 MPa without reinforcement and also show a reduced wearing rate of the cutting edge.

2.9.2 Carbon Whiskers

Carbon (graphite) whiskers are prepared from low boiling point hydrocarbon compounds, which act as carbon resources. Oxygen or an inert gas is used as the carrier gas, and transition metals such as Fe, Co or Ni are used as the catalyst in the form of ultra-fine powder. The whiskers are grown at 500–1100 °C in the form of monocrystals [58, 59].

Carbon nanotubes are seamless hollow tubes formed by rolling graphite sheets. They are classified as single-walled nanotubes or multi-walled nanotubes. They are a new kind of carbon material with chirality. They can be considered to be special hollow carbon whiskers because of their diameter, length, as well as their single-crystal form.

2.9.2.1 Carbon (Graphite) Whiskers

Carbon (graphite) whiskers are also referred to as carbon (graphite) nanofibers because their diameters are about 50–200 nm, and they have a relatively longer length than general whiskers [58]. For example, their length varies from 50 μm to several millimeters.

The growth of carbon whiskers from hydrocarbon gases was observed more than 100 years ago, and in the mid-1950s they began to receive much more attention. Over the last two decades, a considerable amount of research has been carried out mainly in Japan, the USA and France.

The vapor growth of carbon whiskers has been mostly studied in Japan and the USA. Currently, the production and sales of carbon (graphite) whiskers are dominated mainly by Showa Denko, Hyperion Catalysis International and Applied Sciences Inc. No extensive research has been carried out or reported in China.

Because vapor growth carbon whiskers are obtained at high temperature from hydrocarbon compounds, their structures are denser than general carbon fibers. They have a much smaller surface and less internal defects as well.

Additionally, carbon whiskers have a high aspect ratio and a large surface area and are easily graphitized. This makes them superior to other carbon fibers in mechanical properties, electrical conductivity, thermal conductivity and chemical and thermal stabilities. Table 2.66 lists some typical characteristics of carbon whiskers (preheat treatment) and graphite whiskers (post-heat treatment).

Additionally, carbon (graphite) whiskers are excellent heat insulation materials, brake sealing abrasion materials, corrosion-resistant chemical filtration materials and electromagnetic shielding materials [58]. Carbon (graphite) whiskers are mainly used as additives to increase conductivity, as reinforcements to improve mechanical properties and additives to control the coefficient of thermal expansion. Their specific applications are listed in Table 2.67.

Carbon (graphite) whiskers are thus a new kind of sub-micron additive material. In the current market, they are mainly used as electromagnetic shielding materials for automotive fuel tanks, semiconductor and electronic products. There is also a large market in lithium batteries, large-capacity capacitors and fuel cells. They are not generally used as reinforcements in structural components yet but are used as additives to improve mechanical properties, electrical and thermal conductivities, interlaminar shear strength (ILSS) and the coefficient of thermal expansion. Over the next 10 years with large-scale production and lower prices, carbon (graphite) whiskers are expected to become major reinforcements of composite structures.

2.9.2.2 Carbon Nanotubes

It was generally believed that there are three kinds of carbon allotropes existed, namely diamond, graphite and amorphous carbon. Kroto, a professor in Britain, and Curl and Smalley, two professors in the USA, discovered C_{60} in 1985 [60] and received the Nobel Prize for Chemistry in 1996. Professor Iijima from Japan discovered carbon nanotubes (CNTs) in 1991 using a high-resolution transmission electron microscope [59]. These two new allotropes were thus included in the carbon family as fullerenes and carbon nanotubes. Recently, a two-dimensional graphene was also added [61].

Since the discovery of CNTs, widespread interest has been expressed because of their excellent performance and their potential applications, which then makes them a very hot topic around the world. In the USA, large investments have resulted and much research has been carried out in fields from medical to electronics and composite materials. The response has been similar in Japan and China, with a focus on electronics.

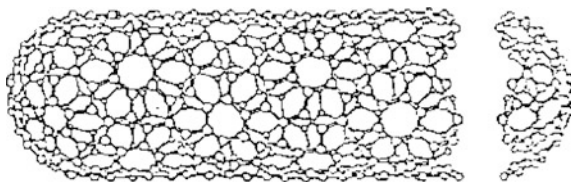
Significant progress has been made in preparation methods and in the study of CNT characteristics. Mass production has begun, and studies continue into the application of CNTs.

Table 2.66 Typical characteristics of carbon whiskers and graphite whiskers

State	Tensile strength/GPa	Young's modulus/GPa	Tensile strain/%	Density/(g/cm ³)	Electrical resistivity/ $\mu\Omega\cdot\text{cm}$	Thermal conductivity/W/(m·K)
Carbon whiskers	2.7	400	1.5	1.8	1000	20
Graphite whiskers	7.0	600	0.5	2.1	55	1950

Table 2.67 Specific applications of carbon (graphite) whiskers

Role	Area	Specific applications
To increase electrical conductivity	Static electricity dissipation	Oil pipelines, automotive systems, electronic assembly, weapons and electrostatic control of satellites
	Electrostatic painting	Aircraft, vehicle body components, vessels and other vehicles
	Anti-EMI	High-speed computers, communication systems, aerospace control systems and electronic systems
	Anti-lightning	Aircraft, ground structures, ships, radomes and weapon warehouses
	Soft contact	Scanning electron microscopes and fuel cells
To improve mechanical properties	Synthetic rubber	Tires, vessels, ship structures and sporting goods
	Thermoplastic components	Aircraft, vehicles, satellites, ships and sporting goods
	Thermosetting components	Aircraft, vehicles, satellites, ships and sporting goods
	Carbon/epoxy components	Aircraft bodies, automobiles, aerospace components and sporting goods
To control the coefficient of thermal expansion	Optical	Injection molding low-cost optical components and laser components
	Frames	Frames of aircraft, vehicles, satellites and ships
	Electrical	Electronic equipment, instrument panels, computers and controlling equipment

Fig. 3.21 Synthesis of PT resins

Carbon nanotubes are seamless nanotubes spirally coiled from single- or multilayered graphite sheets at a certain angle along the central axis [62, 63]. As shown in Fig. 2.12, each layer of the nanotube is a cylinder surface composed of many hexagonal planes, which are formed from carbon atoms by SP^2 hybrid bonding. The border length of the planular hexagonal cell is 0.246 nm, and the shortened C–C bond is 0.142 nm, which is close to the atomic stacking distance of 0.139 nm. Both ends of the cylinder are closed with pentagon or heptagon atomic cycles. During graphite sheet rolling, suspended bonds on the border combine randomly, which leads to randomness in the tube axis. As a result, the carbon atoms are arranged spirally in the hexagonal lattice in the general structure of carbon nanotubes, and there is thus a certain degree of spirality in the CNTs.

Based on the number of layers, CNTs can be divided into two categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). MWCNTs are composed of a number of coaxial cylindrical structures with inter-layer stacking like ABAB, and its layer distance of 0.34 nm approximates that of graphite.

Studies on the electrical properties of SWCNTs have shown that their performance is strongly dependent on their geometric structure, that is, their diameter or chirality (i.e., m , n). When the difference between m and n is an exact integer dividable by 3, the SWCNTs act as metals or semimetals. For example, (n, n) “chair” structural SWCNTs are metallic. In other cases, SWCNTs are semiconductors and the band gap is proportional to the inverse of the diameter. Among all CNTs, about one-third are metallic and two-thirds are nonmetallic.

For practical applications, their preparation should meet the following requirements: continuous mass production, low cost and environmental friendliness. Additionally, the products obtained should be of high purity and have uniform structures with good control. Currently, three main methods are used: arc discharging, catalytic pyrolysis and laser evaporation.

The arc discharging system mainly consists of a power supply, a graphite electrode, a vacuum system and a cooling system. Catalysts are usually introduced to the cathode to increase production efficiency, and sometimes laser evaporation is also applied. For arc discharging, the temperature inside the reaction vessel can be as high as 2700–3700 °C, and the CNTs generated have a high degree of graphitization close to the expected theoretical state. However, the CNTs prepared this way have uncertain growth directions as well as a high impurity content, and they are easily sintered. Research shows that discharge stability is the key to high yields and high-quality CNTs. The adoption of a uniformly rotating progressing anode or cathode can improve the discharge conditions, which promotes the mass production of CNTs.

Catalytic pyrolysis is a widely applied method for the preparation of CNTs. The necessary equipment and processes are relatively simple, while the key is the preparation and dispersion of the catalysts, which are mainly transition metal catalysts. It is suitable for the large-scale preparation of CNTs with the advantage of a high content of CNTs in the final products. However, many defects exist in these CNTs.

Current research into catalytic pyrolysis is mainly focused on two areas: the large-scale preparation of disordered, randomly directed CNTs and the preparation of discretely distributed, order directed arrays of CNTs. The former process gives SWCNTs or MWCNTs in large quantities at 530–1130 °C when using Fe, Co, Ni or their alloys as catalysts and using clay, silica, diatomite, alumina or magnesium oxide as carriers as well as acetylene, propylene or methane as carbon sources, and hydrogen, nitrogen, helium, argon or ammonia as dilution gases. Free carbon ions form nanotubes under the effect of catalysts.

Research into arrays of CNTs is also currently a hot topic, and the important step is the preparation and dispersion of catalyst nanoparticles. Currently, catalysts and catalyst supports with a high density of active sites, a high surface area and a high

pore volume are mainly used. For example, Pan successfully prepared a very long array of CNTs of more than 2 mm using catalyst nanoparticle-incorporated porous silica gel, which was prepared by the hydrolysis of a TEOS solution mixed with a transition metal salt [64]. There is no doubt that this is an important step toward the application of CNTs.

Laser evaporation is an effective method for the preparation of SWCNTs, and a high-energy CO₂ laser or a Nd/YAG laser is used to evaporate the carbon target that has been mixed with Fe, Co, Ni or their alloys resulting in SWCNTs and their bundles. The diameter of the SWCNTs can be controlled by laser pulses. However, the shortcomings of laser evaporation (ablation) are the low content of SWCNTs in the products as well as excessive tangling of the SWCNTs. Solar energy has also been reportedly used for preparation of SWCNTs.

Since the emergence of CNTs much interest has been shown in their special morphologies and structures. The nature of the various forms has been of interest to ultimately realize their applications. Based on theoretical calculations and experimental studies, CNTs have been found to have important physical properties and attractive applications in the following areas:

(1) Electrical Properties and Their Applications

The electrical properties of CNTs are very strange. Their axial resistance is very small, and they can be transformed into superconductors at low temperatures and can thus be observed as one-dimensional quantum wires. In 1992, researchers discovered semiconducting or conducting properties that vary according to the different rolling structures. Deforer and coworkers have successfully prepared horizontal carbon nanotube transistors that work at room temperature. The volume of the carbon nanotube transistor is only one-tenth that of the semiconductor transistor. This is bound to lead to a new computer revolution if computer chips are replaced with carbon-based molecular electronic devices. CNTs can also be used as nanowires, as coherent electronic sources in electron microscopy, as efficient electronic sources in field emission and as super-capacitors.

(2) Mechanical Properties and Their Applications

Experimental and theoretical calculations show that carbon nanotubes have high strength and great toughness. The Young's modulus of SWCNTs is estimated to be as high as 5 TPa, and the experimentally measured average Young's modulus and bending strength of MWCNTs are 1.8 TPa and 14.2 GPa, respectively. Although their density is only one-seventh that of steel, their tensile strength is 100 times that of steel.

As one-dimensional materials and compared with carbon fibers, CNTs have less defects, higher purity, higher strength and a higher modulus. Their aspect ratio is as high as 100–1000. They have self-resilience after bending, and scientists use them as CNT tips in scanning tunneling microscopes as well as in nanometer balances that can weigh a single virus of 2×10^{-16} g in weight, making use of the excellent rigidity and flexibility of CNTs.

Because of their excellent mechanical properties, CNT-reinforced composites are expected to have excellent strength, flexibility, anti-fatigue and isotropic properties. For example, carbon fiber sports equipment can easily fracture under low amounts of stress with a tensile strain of only 1%. For MWCNTs, the tensile strain before fracture can be as high as 15%.

(3) Siphon Phenomenon and Its Applications

CNTs with open ends possess a siphon phenomenon, which can be used as a particle absorbent. If highly active particles are adsorbed, CNTs become molecular-scale catalysts, which are in high demand and are widely applied in the oil industry.

CNTs also have excellent hydrogen storage properties, and a hydrogen storage capacity up to 4.2%(wt) was reported based on a large amount of SWCNTs with a diameter of 1.85 nm. These could release 80% of the absorbed hydrogen at ambient pressure [65].

(4) Other Properties and Their Application

CNTs are resistant to acid and alkali, with good high-temperature stabilities. In addition, they can be modified to become soluble, and so can be used in the preparation of composite materials, chemical sensors and artificial muscles. If added to light-emitting polymers, they can improve light-emitting performance.

CNTs are also a good thermal conductive material. However, heat does not transfer from one tube to another even when a bundle of nanotubes are bound together, which means that CNTs can only transfer heat in one dimension.

CNTs can also be used in stealth materials and batteries. For example, helical CNTs absorb light with a higher absorbing capacity than general materials. Therefore, they can be used in stealth weapons. CNTs with a layered structure can also be used as cathodes in lithium batteries.

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