3
Superfibers

3.1 Description of superfibers

Superfiber has been produced by intensive research and development to achieve the ultimate strength of fibrous materials, and is mainly applied for industrial uses in the non-clothing field.

It is defined as fiber possessing a tenacity of over 20 g/d (2.2 GPa) and a modulus of over 500 g/d (55 GPa). (d denotes denier and denier corresponds to the weight in g of a fiber of 9000 m in length.) The mechanical performance of the second generation superfibers will soon be increased to a tenacity of more than 40 g/d and a modulus over 1,000 g/d. Zylon® (PBO fiber commercially available from Toyobo) is classified as a second generation superfiber. Presently available superfibers are summarized in Table 3.1.

Gel spinning and liquid crystalline spinning, developed for polyethylene and Kevlar, respectively, are two important technologies for producing superfibers. Kevlar molecules are rigid and rod-like because of hexagonal benzene rings connected by amino linkage, whereas polyethylene chains are flexible and bend almost freely.

In Japan, all superfibers are commercially produced by gel spinning and liquid crystalline spinning, and are used in various industrial fields, including the railway, civil engineering, automobile, sports goods, office automation, machinery/machine parts, and the space/aeronautical industries.

3.1.1 Conventional fibers and superfibers

The maximum theoretical mechanical strength of fibrous materials (the tenacity and modulus) can be estimated from the chemical structure of the parent polymer molecules assembling in an ideal extended form. However, the mechanical strength of conventional fibers is much less than the theoretically expected value as shown in Table 3.2. For example, the ideal polyester fiber should have a tenacity and a modulus 232 g/d, and 1023 g/d, respectively, whereas a conventional polyester filament has a tenacity 9.0 g/d and a modulus

Table 3.1 Presently available superfibers

Type	Polymer	Trade name	Manufacturer	Strength (g/d)	Modulus (g/d)	Melting point/ decomposition temperature (°C)
Rigid polymer	*para*-type aramid[*1]	Kevlar	Du Pont	22–27	430–1110	560
		Twaron	Teijin Twaron	22	850	↑
		Trevar	Hoechst (USA)	23	657	
		Technora	Teijin	28	560	500
	Polyallylate	Vectran	Kuraray	20–25	680–840	330
	Heterocycle containing polymer	Zylon (PBO)	Toyobo	42	2000	650
Bending polymer	Polyethylene	Dyneema	Toyobo DSM			
		Spectra	Honeywell (USA)	30–45	900–2000	145–155
PAN-based CF	Carbon fiber	Torayca	Toray			
		Besfight	Toho Tenax	20–45	1400–3500	
		Pyrofil	Mitsubishi Rayon			
Pitch-based CF	Carbon fiber[*2]	Granoc	NGF (Japan)	13–19	700–4500	
		Dialead	Mitsubishi Chemical			

Note: *1 *meta*–type (heat resistant) and *2 isotropic pitch (conventional use) are not included in superfiber

Table 3.2 Mechanical strength and modulus of fibers

	Theoretical value (g/d)		Products on market (g/d)		High strength product (g/d)	
Fiber	Tenacity	Modulus	Tenacity	Modulus	Tenacity	Modulus
Polyethylene	372	2775	9	100	71	2400
Nylon	316	1406	9	50	17	50
Polyester	232	1023	9	160	10	203
Polyacrylo-nitrile	196	833	5	85	25	
Polyvinyl alcohol	236	2251	9	250	19	546
Cellulose	133	1010	5	160		
Kevlar	235	1500	23	1000		

Source: Kunigi, Ota, Yabuki, *High-strength high tenacity fibers,* p58, Kyoritsu Shuppan, Tokya (1988).

160 g/d, respectively. Other conventional fibers such as polyethylene, nylon, polyvinyl alcohol and polypropylene are in the same position with respect to the gap between the theoretical and practical mechanical strength.

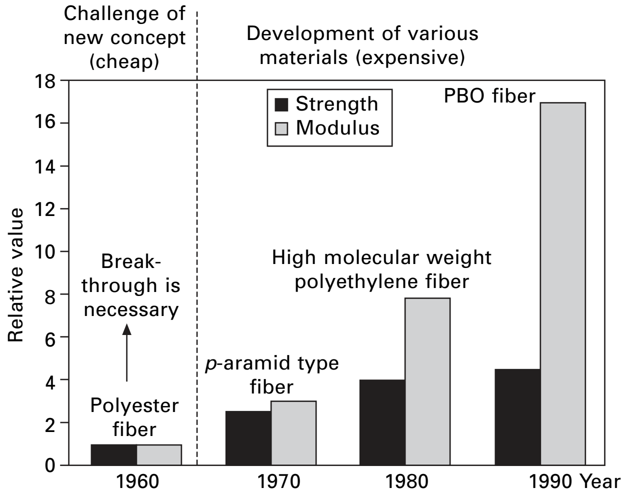
3.1.2 Ultimate strength of conventional synthetic fiber

High performance fiber

Active investigation is being carried out to develop fibers possessing the tenacity of about half that of the superfiber from polyacetal, polyvinyl alcohol, polyacrylonitrile, polyethylene terephthalate and nylon. Superfiber was developed by a new spinning technology such as liquid crystalline spinning (Kevlar®) or gel spinning (Dyneema®). Inspired by these new methods, a similar attempt has been made to improve the mechanical properties of conventional fibers to their ultimate limits for the past ten years but with minimum success. Conventional fibers for industrial use have a tenacity of about 10 g/d and a further improvement in the mechanical properties has not been successful, despite the large expense on this project. The tenacity and modulus of fiber improvement is shown in Fig. 3.1, where the polyester filament for tire cord is taken as a reference and set to 1.

Extensive applications of high performance fiber

If the mechanical performance of the conventional fibers such as polyester and nylon can be improved by a factor of three, conventional fibers can be applied not only for clothing but also for industrial uses. At present only 4.1% and 15.6% of the theoretical strength and modulus, respectively, are



3.1 Improvement of tenacity and modulus of fibers.

realized in conventional polyester fiber. Here we should understand the correlation between mechanical characteristics and high-order fiber structure.

As high-tenacity polyethylene fiber, the *shish-kebab* structure may be a key for nylon or polyester. If the *shish-kebab* structure is well controlled during spinning, the tenacity will increase considerably. The flexibility and/or large surface area of fiber are suitable for membrane and filter materials.

3.2 Development of superfiber in Europe, the United States and Japan

There are three main directions in the development of superfibers. In Europe, the development of superfiber started from the purely academic research on the *shish-kebab* type crystals of high molecular weight polyethylene as emerged from dilute solution. The results led Professor Pennings (Groningen University, The Netherlands) and his co-workers to develop the gel spinning of flexible polymer of high molecular weight that forms a gel-like solution.

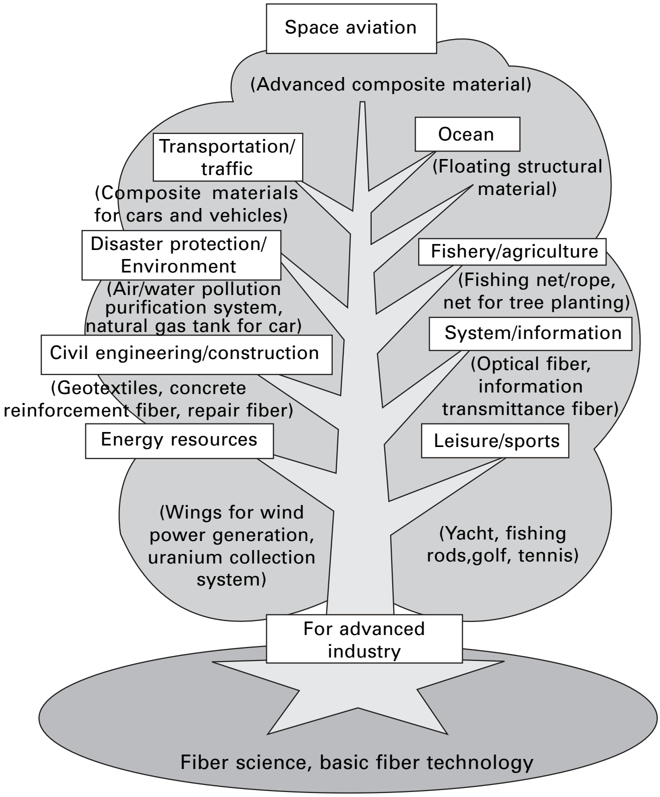
The development of heat-resistant polymer has been one of the main research targets in the United States since the 1950s because of the Cold War. In the process of developing heat-resistant polymer, polyaramid fiber and PBO fiber emerged. Carbon fiber was developed initially from rayon as a starting material in the 1950s in the United States, while PAN-based carbon fiber was developed in the early 1960s in Japan by Dr A. Shindo (former Government Industrial Research Institute, Osaka, now changed to National Institute of Advanced Industrial Science and Technology (AIST)). Pitch-based carbon fiber was also developed in Japan by Emeritus Professor S. Otani (Gunma University). Global production volumes of carbon fibers combining PAN-based and pitch-based are estimated at around 17,000 tons/year, of which around 50% is produced in Japan. Both PAN-based and pitch-based carbon fibers have expanded in their industrial applications. An example of carbon fiber composites usage is in the weight-saving of trucks where carbon fiber composite plays a part in achieving weight reduction of the floor and wing-roof (Figure 3.2). Among these composites, consumption of PAN-based carbon fibers is remarkable in their use in civil engineering and construction and pitch-based carbon fibers are used for the anode of secondary cell of lithium batteries. Those carbon fibers exceed the performance of rayon-based carbon fibers, and account for most of market. Carbon fiber, aramid fiber and polyethylene fiber constitute three main currents in the development of superfiber, developed respectively in Japan from 1959 to 1960, in the United States in 1964 and in Europe from 1966 to 1969.

3.2 A truck using carbon fiber composites (Toray)

The first satellite (Sputnik 1) was launched from the USSR in October 1957. The post-Sputnik space development in the United States promoted joint research among government institutes, universities, and industries. There were many important innovations in the field of fiber and textiles. An early result was polyaramid fiber produced by liquid crystalline spinning, developed by Dr Kuolek of Du Pont. Later came PBO fiber, first developed in the United States and now produced commercially in Japan. In these 30 years, vast quantities of heat-resistant polymers were synthesized, and the main concern has been how to achieve the theoretically expected values of the tenacity and modulus of polymer molecules when polymer is made into fiber.

3.3 Superfiber as a reinforcing material

The application of superfiber for advanced materials is summarized in Fig. 3.3. Superfiber is applied more for industrial use than for clothing. Thus we



3.3 Application of superfibers for advanced materials.

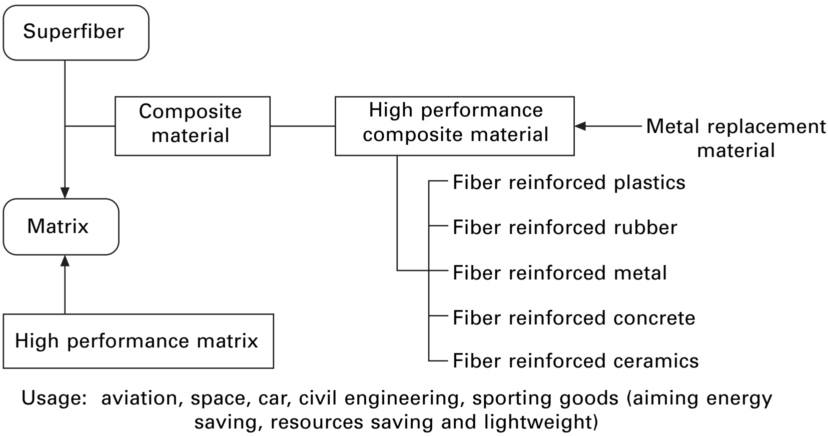
do not perceive superfibers directly, since they are used mostly in composite materials to reinforce, for example, rubber, resin, and concrete. Superfiber is incorporated in those materials in various shapes and forms to improve their mechanical performance. Figure 3.4 shows the high performance composite materials as metal replacements. Superfiber is used in the form of short staple, cord, meshed fabric or 3D woven fabric for reinforcement. The global need for synthetic fiber in the non-clothing field is expected to expand as shown in Figs 3.5 and 3.6. Table 3.3 summarizes the expected application areas of superfiber.

3.3.1 Application for transportation (bicycle and car)

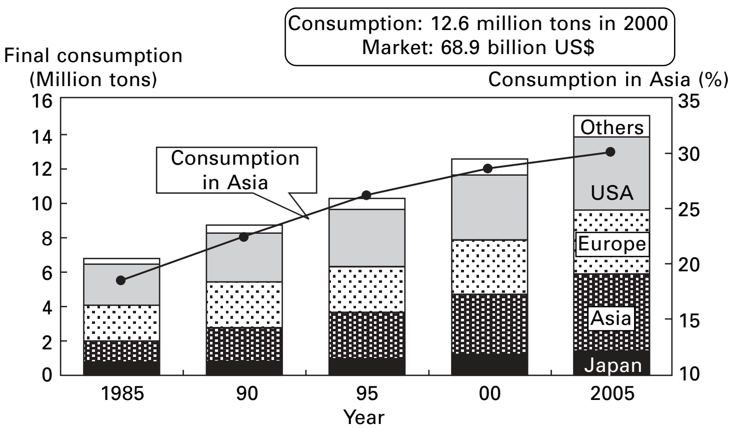
Superfiber-reinforced rubber is used as the spring belt to replace the bicycle chain, and for the tire of mountain bikes. Some lightweight racing bicycles have composite frames.

In order to improve the petrol consumption efficiency, cars have become lighter and lighter, as superfiber-reinforced rubber is used for tires, belts, and structure. Steel cord was common for tires, but as highway networks extended, and faster driving conditions prevailed, heat friction led to many of the steel wire-lined tires bursting. Thus the reinforcing materials for tires are now composed mostly of nylon and polyester fiber.

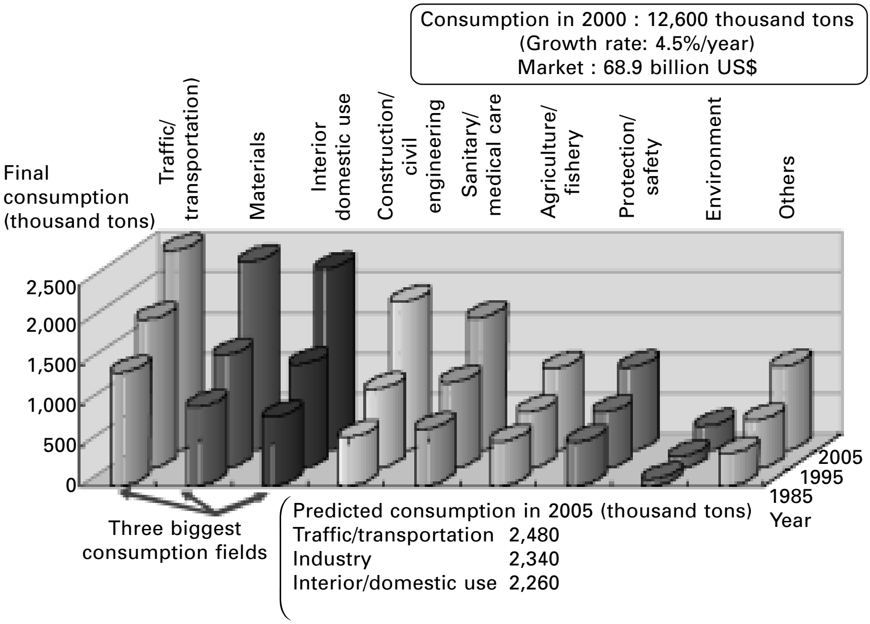
Tires are good examples of mass-produced continuous fiber composites. They are made of a rubber polymer matrix, reinforced by continuous fiber, which could be nylon cord, polyester cord, or superfiber. This composite is called RMC (rubber matrix composite). The tire is made up of sections: tread, carcass, belt, and bead. Figure 3.7 shows the position of fiber, materials in the carcass section. Continuous fiber, such as aramid fiber, is used for the structural material of the carcass, which is the basic foundation of the tire, and is made of the laminated aligned cord fabrics, whereas cross-ply tires use cross-laminated fabrics and the radial tires radial-laminated fabrics. As



3.4 High performance composite materials as metal replacements.



3.5 Global consumption trend of fiber in non-clothing field (Toray).



3.6 Consumption trend of non-clothing fiber in different application fields (Toray).

Table 3.3 Expected application areas of superfiber

Field	Application
Aviation/space industry	Composite materials for aviation and space development
Transportation	Advanced composite material reinforced materials (cars, trains, ships)
Civil engineering/construction	Geotextiles, fiber for concrete reinforcement
Ocean development	Floating structure, artificial tideland, artificial ocean farm
Medical field	Artificial organs, fiber for health, bioreactor
Sports/leisure	Various goods
System/information	Electronics–related field, optical fiber
General industrial material	High performance fiber, high functionality fiber

the radial tire becomes more popular, more aramid-type superfiber is introduced into the carcass. Nylon cord is mostly used for the cross-ply tire, is suitable for driving on a bad road at a low speed. The radial tire ensures a stable revolution and high-speed driving, but requires more suppression of friction and reduction of rolling resistance. Aramid fiber is also employed for the belt of the continuous velocity transformer (CVT) and has also replaced asbestos as the friction material for the brakes.

3.7 Position of fiber materials in the carcass section.

3.3.2 Applications in sports goods

Carbon fiber is applied to the frame of a tennis racket and the shaft of a golf club. The hybrid of aramid and carbon fiber was used initially in order to complement the respective weak points of aramid (compression resistance) and carbon (impact resistance) fiber. Those fibers are compounded with epoxy resin matrix for practical use. The ski stock and ski board are also made of superfiber. The soles of ice skates also contain carbon fiber.

3.3.3 Aerospace technology

Lightness is a key factor in this field. Composite materials with glass or carbon fiber are commonly employed. Advanced composite materials (ACM) are becoming more and more important, where aramid or carbon fiber is applied. For example, the Boeing 777 is built with 13.5 tons of carbon fiber composites in order to reduce its weight. The composite materials and applications in the field of aerospace technology are listed in Table 3.4.

3.3.4 Civil engineering

The Kansai-Awaji Earthquake in January 1995 stimulated concerns about the safety of domestic infrastructure. Thus composite sheet composed of

Table 3.4 The composite materials and applications in the field of aerospace technology

Term	Materials	Applications
Short to middle	Lightweight structure materials for ACM Seat molding compounds Heat-resistant flame proof fiber	Aviation/space devices Cars, aircraft Interior material in aircraft, uniform
Middle to long	Lightweight structure materials for ACM (SST for next generation) Oxygen enrichment membrane/fiber Membrane material for airship	Space base camp, Large aircraft engine by one molding Sky-net plan

aramid or carbon fiber has been used to reinforce the concrete columns of a bridge girder because it is easy and lighter to handle.

Geotextiles are the textile products used for civil engineering. The practical application of geotextiles was advanced in Europe and the United States, but the introduction of superfiber to geotextiles was made in Japan. Aramid fiber reinforced composite is also applied in ground fill. A reinforcing iron rod is gradually replaced with aramid or carbon fiber reinforced composite material, which is free from rust. Staple-fiber reinforced concrete (FRC) is also now becoming popular.

3.3.5 Need for standard specifications

Composite materials reinforced by superfiber have expanded steadily into the fields of aerospace engineering, ocean engineering, civil engineering, transportation engineering, sports/leisure engineering and medical engineering. The development of fiber/textile for industrial use takes at least five to six years, since no technical data is available for new materials. The required specifications for fiber/textile for industrial use are listed in Table 3.5. When the specifications and regulations are well established, the production of fiber/textile for industrial use can be expected to expand enormously. However, each engineering field has its own regulations, and no standard specification has been established. Here the basic technical data should be gathered from the various industries and standardized in order to spread the application in various industrial fields. Close cooperation is required among government institutions, civil engineering industries and chemical fiber industries.

It must be recognized that superfiber is a new material in the industrial field in comparison with concrete or metal. Table 3.6 shows the potential superfiber applications in the field of civil engineering.

Table 3.5 Required specifications of fiber/textile for industrial use

Required specifications	Original fiber Strength	 Modulus	 Toughness	Heat shrinkage High	 Low	Adhesion	Heat resistance	Processing durability	Flame resistance	Anti-weatherability
Tire cord	◎	○			○	◎	○	◎		
V-belt	○	◎			◎	○		◎		
Conveyor belt	◎	○			○	◎		○		
Ropes/net	◎		○							○
Heavy cloth	◎				○					
Bags/wrapping			○							
Sewing	○								○	
Base for artificial leather								○		
Electric material	○				○		◎			
Filtration			○				○		◎	
Safe belt	◎		○							◎
Felt								○		
Non-woven fabrics								○		
Hose	◎	○			○	◎		○		
Thread for *tatami*	◎				○		○			
Carpet										
Curtains										
Sheet for car									○	
Required specification	10	4	4		7	4	4	7	3	2

◎ Very important specification.
○ Important specification.

Table 3.6 Potential superfiber applications in the field of civil engineering

Term	Material	Application
Short to middle	Cement reinforcement fiber	Construction/civil engineering
	Asbestos replacement material	Heat retention, heat insulation packings
	Optical spectrum conversion material	Agriculture, fishery
Middle to long	High strength, low density, heat resistance (>500°C), durability, anti-weatherability	Anti-weatherability covering material Filter (heat resistant, chemical resistant) Flame proofing, heat proofing cloth (clothes, sheet) Radioactive rays protection Electronic base material, robot

3.4 Frontiers of superfiber applications

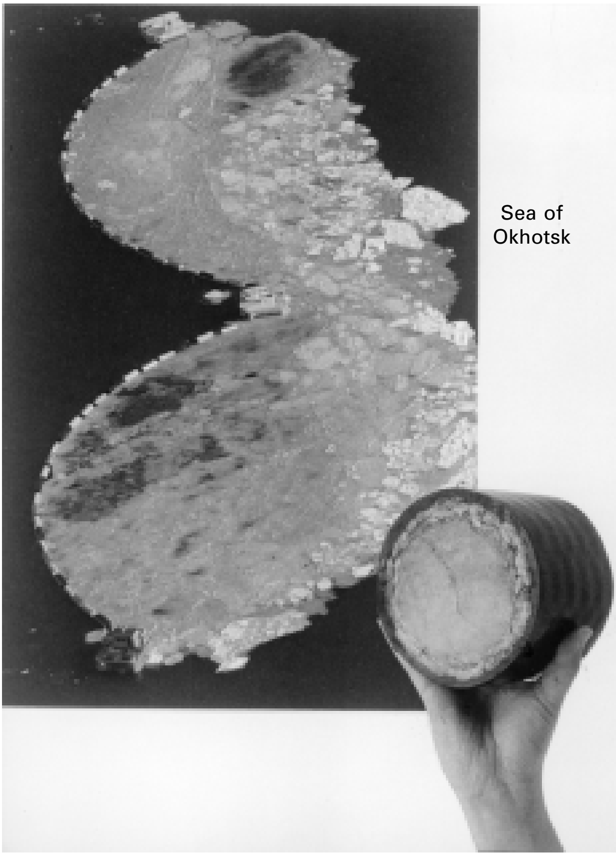
The information/communication industries and biotechnology could be leading industries in the first half of the twenty-first century. Superfiber will be a leading technology in the fiber/textile field and the following examples demonstrate the frontiers of superfiber applications in these areas.

3.4.1 Kevlar, liquid crystal spun para-aramid fiber

Ultra-thick Kevlar wire to fence the ocean culture farm from floating ice

About 60 000 tons of scallops are produced every year and earn a total of about US$ 10 million in Lake Saroma in Hokkaido. Since Lake Saroma is directly linked to the Sea of Okhotsk, floating ice will surge into the lake in late January, and may damage the farm. In fact about US$ 22.2 million was lost by the damage caused by the floating ice surge in 1974. Global warming continues, and in recent years floating ice has often surged into the lake, even in late March.

Hokkaido Development Bureau investigated how to cope with floating ice surges, and adapted the ice boom proposed by Professor H. Saeki's group (Hokkaido University). The ice boom is a floating wire fence. A single boom is 100 m long, and consists of a main wire with 28 floats (1.2 m in diameter and 3 m in length) and 4 m wire net underneath the water. Since a large quantity of floating ice will surge into the lake, the steel wire should be thick enough to cope with an ice surge, and become too heavy for the floats of practical size to sustain. Since Kevlar is about five times lighter than steel in terms of the same tensile strength, a Kevlar ice boom can be made lighter and become practical. Kevlar has another advantage, since it does not rust in seawater. The main wire, produced by a rope manufacturer in Gamagori (Aichi Prefecture), is made of ultra-thick Kevlar fiber, 13 mm in diameter, which can stand a load of 500 tons. The bird's-eye view of this ice boom



3.8 Bird's-eye view of ice boom set in Lake Saroma to protect from floating ice, and the cross-section of Kevlar wire (Du-Pont Toray).

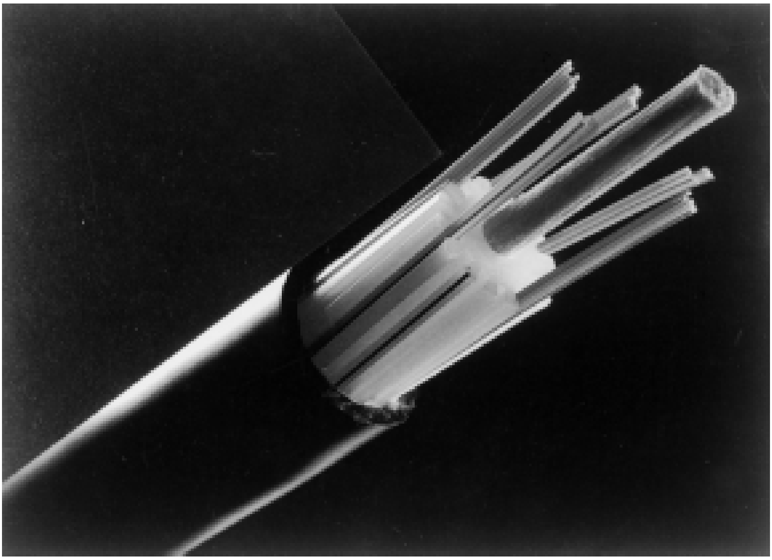
looks like an oil fence (see Fig. 3.8). The cross-section of Kevlar wire is also shown in Fig. 3.8.

Kevlar tension member for optical fiber

The twenty-first century is the era of high-speed information, so that optical fiber is indispensable. The information transmission capacity of optical fiber is about 1000 times that of conventional metal cable. Two types of optical fiber are available. One is the inorganic type of quartz fiber, and the other is made of organic polymethyl methacrylate (PMMA). The quartz optical fiber is suitable for long distance transmission, and its network extends from Hokkaido to Kyushu as well as from Japan to the United States. Superfiber supports this optical fiber network. Optical fiber is extremely thin and thus is weak against tension. When optical fiber is stretched, the optical transmission characteristics can be damaged. The high Young's modulus of Kevlar can be utilized to support such optical fibers. The optical fiber cable is composed of Kevlar fiber axis as a tension member and optical fibers arranged spirally around Kevlar as shown in Fig. 3.9.

3.4.2 Technora®, wet-spun para-aramid fiber

Teijin developed wet-spun Technora in 1973, and has produced almost 1600 tons per year in its Matsuyama Plant since 1987. Technora is synthesized by copolymerization of the same components as Kevlar (terephthalic acid chloride and *para*-phenylene diamine) and the third component diamine containing an ether linkage. Technora is wet-spun and drawn. The ether linkage in its molecular structure makes Technora more flexible than liquid-crystalline-spun Kevlar. Since Technora has improved characteristics with regard to solubility and drawability, the filament surface is smooth and no fibrillation takes place. Technora is used for ropes and nets for fisheries and civil engineering, and for protective clothing, including bullet-proof jackets, knife-proof clothes and gloves, where not only high-density woven fabric but also sheet-like structure is used. Technora is also used as FRP tension materials to reinforce rod-concrete construction against a big earthquake.



3.9 Kevlar fiber as a tension member for optical fibers (Du Pont-Toray).

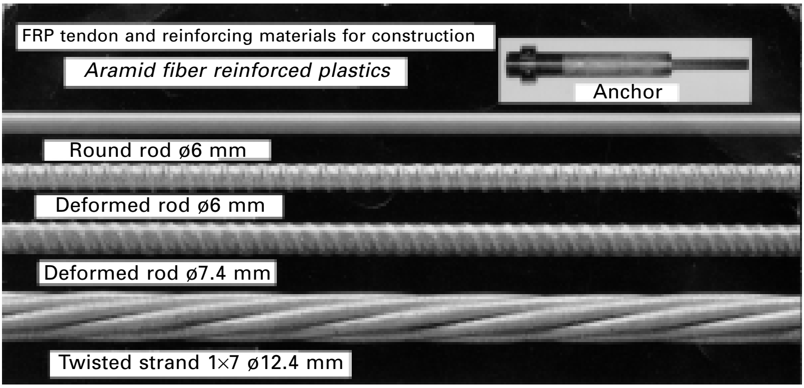
The application to printed circuit boards deserves a special mention. Conventionally, glass/epoxy resin is used for printed circuit boards for electronic equipment. Recently the light and easy-processed circuit boards from *para*-aramid paper have been developed and are replacing the conventional glass/epoxy resin boards.

We should also mention examples of high-durable aramid FRP rod applications. Aramid FRP is a composite of polyvinyl ester resin matrix reinforced by Technora-fiber. Aramid FRP rod has a rugged surface with wound aramid fiber, or by twisting in order to achieve a good adhesion to concrete. Aramid FRP rod possesses almost equal or even higher tensile strength than PC steel. Its modulus is about a quarter that of steel and has no yielding point. Its weight is about a sixth that of steel. Aramid FPR rod exhibits no deterioration in water, seawater, or alkaline solution, so no anti-rust processing is required. Figure 3.10 shows the aramid FRP rod anchor to protect the river bank in the Kyushu district, where 5160 m of aramid FRP rod of 7.4 mm in diameter was used. Figure 3.11 shows the application examples of aramid FRP.

3.4.3 Thermotropic liquid crystalline spun Vectran® fiber

Kuraray produce the polyarylate superfiber Vectran. Polyarylate contains aromatic aryl groups. By controlling the molecular structure, polyarylate melts at a certain temperature and forms thermotropic liquid crystals. Vectran is melt-spun from such polyarylate.

One of the most novel applications of Vectran was as an airbag for the Mars Pathfinder. NASA (National Aeronautics and Space Administration) announced a large space science project (the Origin Plan) in 1996. This project aims to explore the origins of space, and planned to launch a series of space probes. Mars Pathfinder was launched from the Kennedy Space



3.10 Aramid FRP rod (Teijin).

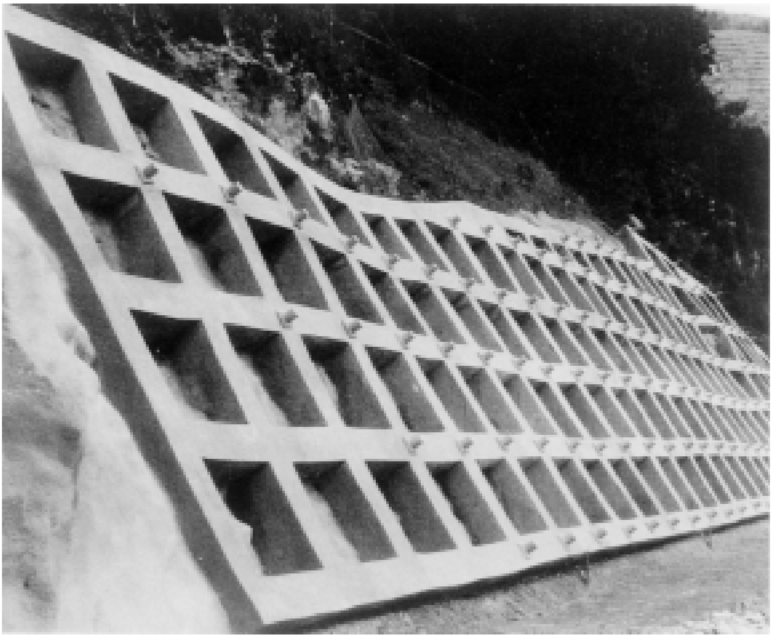


Figure 3.11 Application examples of aramid FRP (Teijin).

Center in Florida on 4 December 1996 in order to arrive on Mars on Independence Day (4 July 1997). The most difficult part of this project was how to soft-land on Mars. The staff at JPL (Jet Propulsion Laboratory, NASA) was asked to develop a less expensive soft-landing device quickly. They innovated and produced a new soft-landing device utilizing an airbag, which costs US$ 600 million, compared with US$ 1000 million for the conventional soft-landing device. This airbag is made of four-layered woven fabrics of Vectran fiber laminated inside with silicon polymer. Various designs were tested at NASA's Lewis Research Center, including the shape of the airbag, the fabric materials and the seam. The red surface of Mars is covered with rocks of various sizes and shapes. Thus the surface of the airbag is loosely seamed in order to adjust its position according to the external load and to absorb the impact shock. Vectran fiber of 200 d was woven into five-layer high-density fabrics laminated with silicon polymer with warp directions shifted 45° with respect to each layer. The outer two to three layers are designed to yield at certain impact strength and to absorb the impact energy. The fifth layer (innermost layer) is made completely airtight and possesses high strength. Figure 3.12 shows the space probe Mars Pathfinder covered with the Vectran airbag.

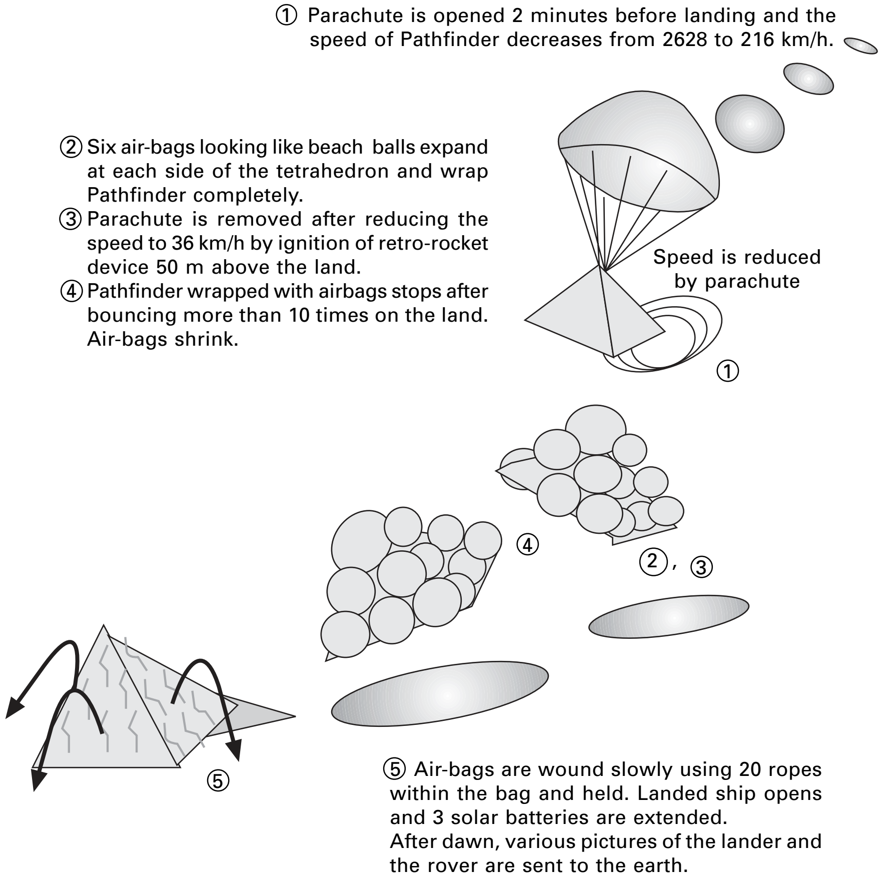
When the Mars Pathfinder (its front is protected with heat-resistant shield) is separated from the spaceship, it descends into the Martian atmosphere.

3.12 Space probe Mars Pathfinder covered with Vectran airbag (NASA).

Several minutes before soft-landing, the heat-resistant shield is cut off and Mars Pathfinder descends by parachute. At 300 m above the surface (8 s before landing), four airbag sets (each composed of six beach-ball-like bags) inflate within 0.5 s at each side of tetrahedral Mars Pathfinder. A retro-rocket device is ignited immediately and the speed of descent is reduced. Mars Pathfinder falls on to the Martian surface, bounces up and down several times and then stops. The Vectran rope then folds the airbags to the space probe surface. The outline of this landing is shown in Figure 3.13. This Mars Pathfinder system is made up of the tetrahedral landing device (the lander) and the rover. Total weight, including airbags, must be less than 360 kg, because of the limit of load to the airbags. The landing craft opens to expose its interior when landed, and the rover is sent to explore the surface (see Fig. 3.14 showing Mars surface probing car 'Rover').

3.4.4 Zylon®

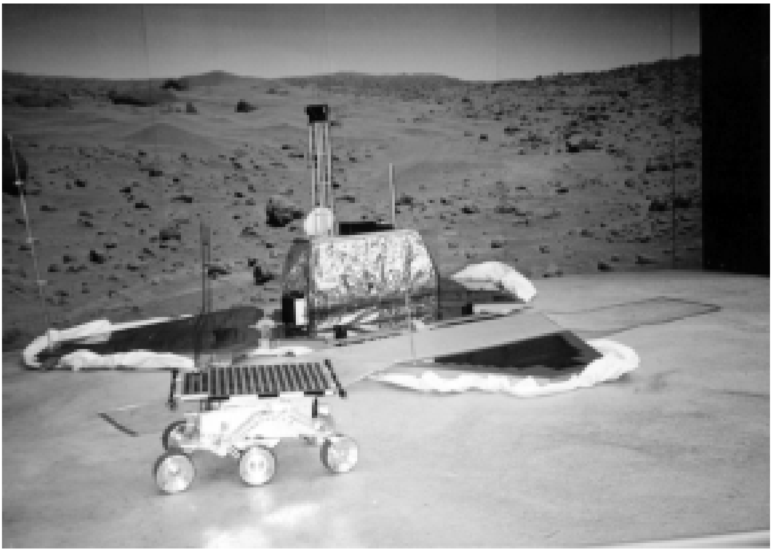
Zylon is a commercial name for PBO (poly-*p*-phenylene benz-*bis*-oxazole) fiber. Toyobo started Zylon production at its Tsuruga Plant in October 1998. The production started with 200 tons/year at the beginning and increased to 360 tons/year by 2002. The fiber is gold-colored and its appearance is similar to Kevlar. The characteristics of Zylon are an extremely high tensile strength, an extremely high modulus, high heat resistance, and a high flame resistance. The material is a rigid molecule, and its processing is difficult.



3.13 Outline of Mars Pathfinder landing (Yomiuri Shinbun, 5/7/1997).

PBO fiber from Toyobo

PBO fiber had a long history before its commercialization. When *p*-aramid fiber (Kevlar) appeared in the 1970s, the researchers at Air Force Materials Research Institute (USA) started a new challenge to synthesize polymers having higher modulus and better heat-resistance than Kevlar. They published the basic results in 1979, and PBO was one of the heterocyclic polymers developed in this project. Dr Wolf patented PBO at Stanford Research Institute. Dow Chemical bought the rights of this patent and attempted to make fibers from PBO for seven years without success. Consequently, Dow Chemical was looking for a partner to develop PBO fiber. During this period, however, Dow Chemical found a new method to improve the monomer (*p*-phenylene diamine) yield and a more efficient polymerization to form PBO.



3.14 Mars surface probing car 'Rover' (Taken at Tokyo Big Site exhibition hall).

Toyobo were interested in PBO, and proposed a joint venture with Dow Chemical to develop PBO fiber. At that time, the tenacity of PBO fiber was similar to that of Kevlar but its modulus was higher. Toyobo was confident that PBO fiber could be made stronger because of its higher modulus. Later Dow Chemical withdrew from the development of PBO fiber because of a change in the company's business strategy. Figure 3.15 shows a yacht's sail made using Zylon®.

Tenacity of PBO fiber

The tenacity of PBO fiber was initially 20 to 22 g/d. The tenacity was improved to over 40 g/d during the period of the joint development, and now commercial Zylon has an average tenacity of 45 g/d, twice as strong as Kevlar.

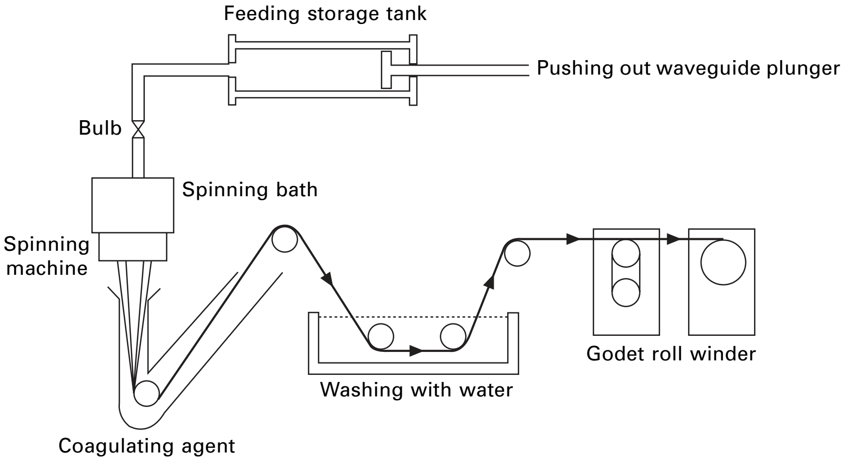
Kevlar activated further research into high-tenacity polycondensates including nylon and polyester. Conventional polyester fiber for industrial use has a tenacity of 6.5 to 10.0 g/d. The tenacity is still lower at 4.5 to 6.5 g/d for synthetic fiber use for clothing. However, the tenacity of polyester is calculated from the fully extended ideal structure as 230 g/d. Many research projects have been initiated to develop superfiber from such conventional polymers.

3.15 Race yacht sail made by Zylon® (Toyobo).

Unique spinning of Zylon

How is PBO fiber spun? PBO is a heterocyclic polymer, classified as poly benzazole, polymerized from diamino and terephthal acid in polyphosphoric acid. Zylon melt is dry-wet spun into fiber. The PBO spinning is shown schematically in Figure 3.16, as presented by Ledbetter. At the initial stage of the project at the Air Force Materials Research Center, the researchers examined theoretically how to design rigid and heat-resistant polymer molecules prior to the actual experiments. However, major innovations are often done by serendipity, and we will notice that the PBO case is rare.

NASA planned ULDB (Ultra Long Duration Balloon), a program to float a pumpkin-shaped balloon (see Fig. 3.17) at an altitude of 33.5 km for up to 100 days and obtain scientific data by atmospheric observation. The balloon is composed of a layered polyester and polyethylene film about the thickness



3.16 Outline of PBO spinning (H. D. Ledbetter *et al.*, MRS **134**, 253 (1989).

3.17 Pumpkin-shaped balloon for atmospheric observation (NASA).

of ordinary plastic food wrap (62 g/m^2). Two rings on the top of the balloon are pulled by Zylon pulling members to reduce the required strength of the membrane at planning.

Another application example of Zylon is a bullet-proof vest as shown in Fig. 3.18.

3.18 Bullet-proof vest made of Zylon (Toyobo).

Tension member for optical fiber

As mentioned previously, two types of optical fibers are available commercially. In either type, plastic or quartz, the optical fiber is extremely thin, and breaks easily by bending or stretching. In practical use optical fibers are protected with a tension member. The tension member is conventionally made of steel wire, but steel is not ideal since it picks up noise from thunder and cars. Non-conductive superfiber is an ideal material for acting as the tension member.

An optical cable for long distance communication is made of a few hundreds to a few thousands of optical fibers bundled around a rod and covered with the protective material. Another advantage of using superfiber for this purpose is its weight. Since PBO fiber has twice the tenacity and modulus of other superfibers, the tension member can be made thinner and lighter. For example, a conventional optical cable of 80 mm diameter will be reduced to 50 mm by using PBO fiber.

Balloon for Venus probe

JPL (Jet Propulsion Laboratory, NASA) is planning to send a planetary probe to Venus in about 2006. Venus is covered with a sulfuric acid cloud, and the distance between the cloud and the surface of Venus is about 48 km. The temperature of Venus's surface is 460°C, but the temperature is as low as –10°C in the sulfuric acid cloud. The atmosphere is mainly composed of carbon dioxide, containing a small amount of sulfurous acid gas. In order to transmit information gathered on the surface of Venus back to Earth, the balloon probe needs to rise above the cloud. The balloon should go up and down several times from the surface of Venus above the sulfuric acid cloud. This up-and-down movement will be controlled by inflating or deflating the balloon. PBO fabric or PBO film, for this reason, is the only candidate for the flexible heat-resistant membrane for the balloon probe.

The balloon probe will be launched with a satellite and be parachuted down to the surface of Venus through the sulfuric acid cloud. Since PBO is weak against acid, PBO fiber will be coated with gold. Thus Zylon could help in the achievement of a considerable scientific goal.

3.4.5 Gel spinning of flexible polymer

Dyneema® stands for a strong fiber

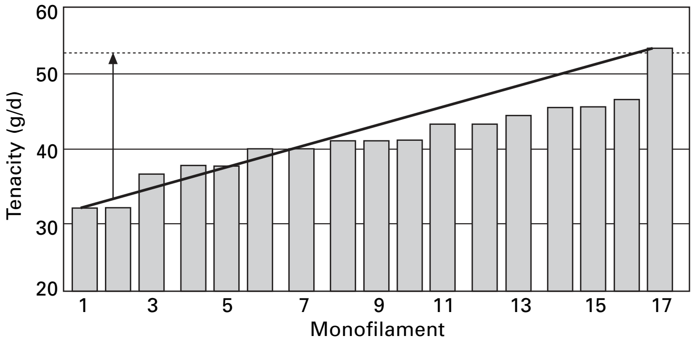
Three major fiber industries in the world are producing high tenacity polyethylene fiber. DSM (Holland) and Toyobo (Japan) jointly developed and produce Dyneema®. Allied Signal Inc. produces Spectra®.

Dyneema® is a composite Latin word made up from 'dyne' (power) and 'neema' (fiber). Dyneema thus means 'a strong fiber'. Professor Pennings, Dr P. Smith (formerly-Professor of California Institute of Technology) and Professor Lemstra (Eindhoven Technical University) collaborated to develop gel spinning of high molecular weight polyethylene. Commercial high tenacity polyethylene fiber is based on this basic process developed by these three scientists in 1979.

Dyneema SK60 has a tenacity of 30 to 35 g/d. In 1999 Toyobo first put Dyneema SK71 on the market, having a tenacity of over 40 g/d. The basic concept of gel spinning is to reduce crystalline defects. Chain ends, entanglements and the folded chains in the amorphous region are counted as defects. The tenacity of each filament fluctuates considerably, so that the filaments should be produced without tenacity fluctuation. The tenacity fluctuation of high tenacity polyethylene fiber is shown in Fig. 3.19.

Characteristics of Dyneema

The density of Dyneema is less than one, and it floats on water. Commercially available Dyneema (Dyneema SK71) is made of flexible polyethylene, and its elongation at break is around 4%. High tenacity polyethylene fiber has a good balance of tenacity and elongation, so that it is easy for later processing including fabrication and knitting. Its impact strength is excellent, and is used for protecting and reinforcing materials. Polyethylene is chemically



3.19 Tenacity fluctuation of high tenacity polyethylene fiber.

stable and has a good chemical resistance in a wide range of pH except for some organic solvents. No degradation will take place in water, so that it is suitable for use in humid places exposed to the sun. The molecular weight of high tenacity polyethylene is over 1 000 000, and its shape stability is good. However, the melting point is low (150°C) and it creeps at higher temperature.

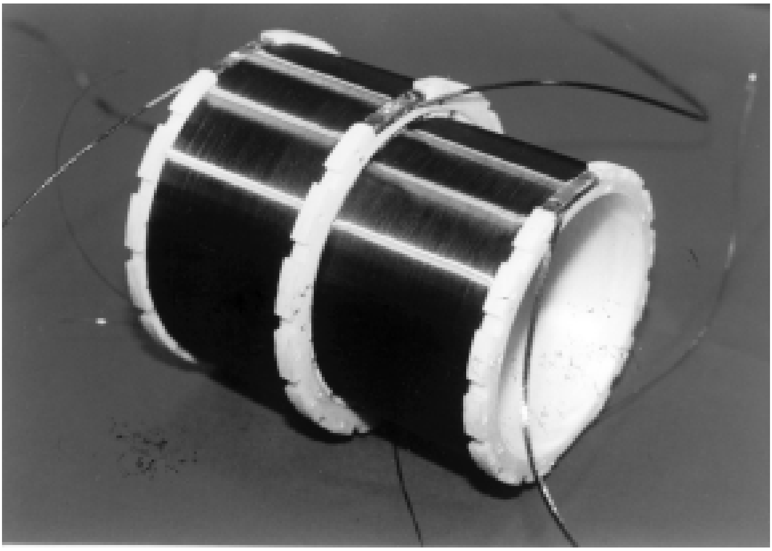
These characteristics should be taken into account in any application. Since high tenacity polyethylene is light and strong, it is mostly used for ropes. Anchoring rope and tag rope for ships made of high tenacity polyethylene is light and not water-absorbent. A fishing line is a high value-added application of high tenacity polyethylene fiber. Since Dyneema has a high sonic modulus, a bite can be detected quickly, resulting in advantageous fishing conditions.

Application to superconductive materials

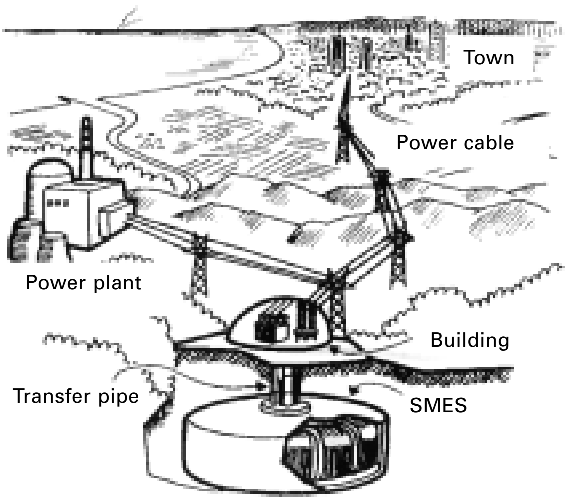
Dyneema is highly crystalline and highly oriented. Thus its filament shrinks with lowering temperature. That is, its line thermal expansion coefficient is negative. By integrating with other resins of normal thermal expansion behavior, a composite can be made, which deforms in any direction as the temperature changes. A bobbin for a superconductive coil can be made from high tenacity polyethylene fiber and epoxy resin composite (see Fig. 3.20). The bobbin will expand a little in a radial direction at liquid helium temperature, so that superconductive coil will not become loose even when the superconductive coil stretches by Lorenz forces at liquid helium temperature. A superconductive energy storage system for electric power peak saving is shown schematically in Fig. 3.21.

3.4.6 Prospects for superfiber

Superfiber applications are capable of serving a great need within our society. Energy and resource conservation will require lighter materials of higher

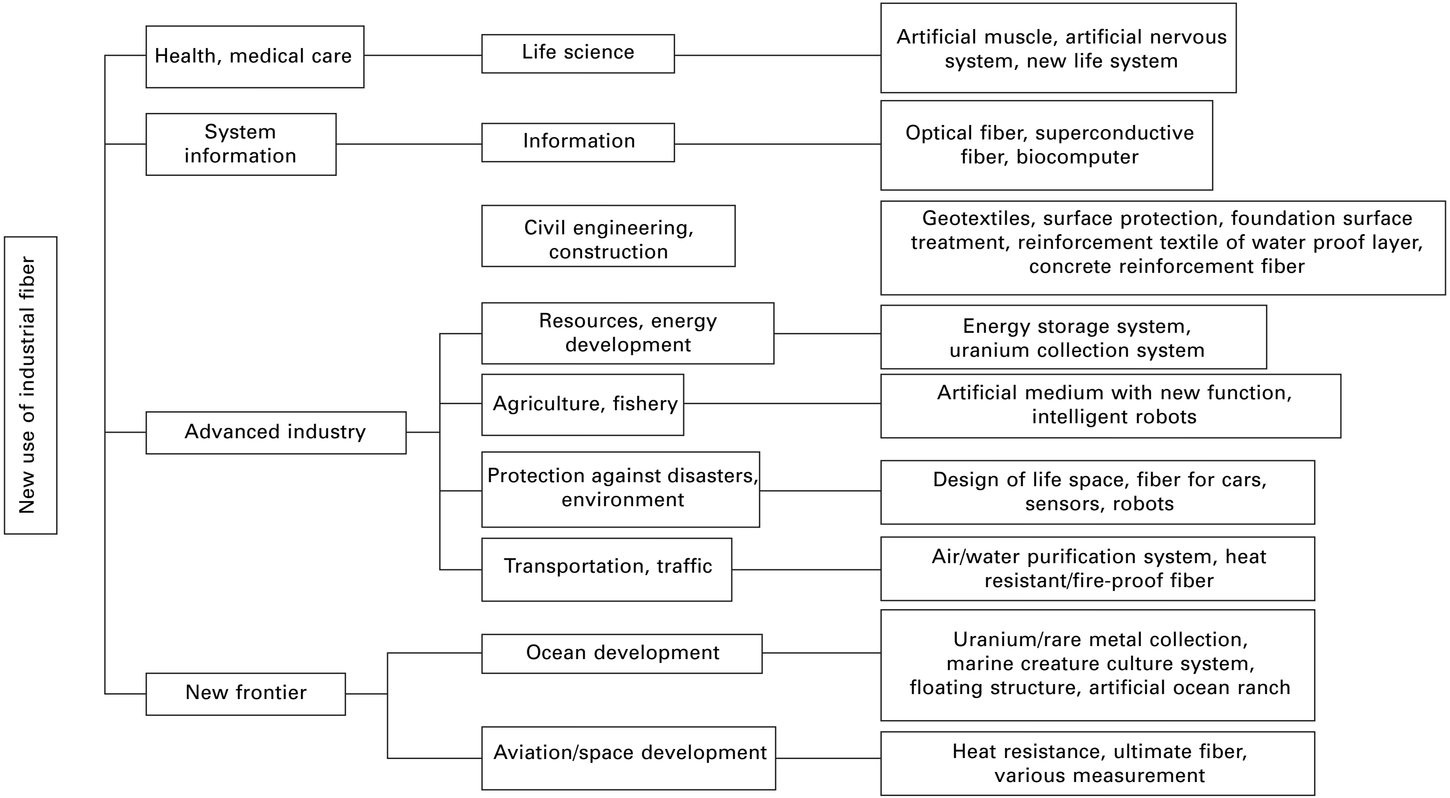


3.20 A bobbin for a superconductive coil made from high tenacity polyethylene fiber and epoxy resin composite (Toyobo and Kyushu University).



3.21 Superconductive energy storage system for electric power peak saving (Toyobo).

performance. The prospect of such superfiber needs in non-clothing fields is summarized in Fig. 3.22.



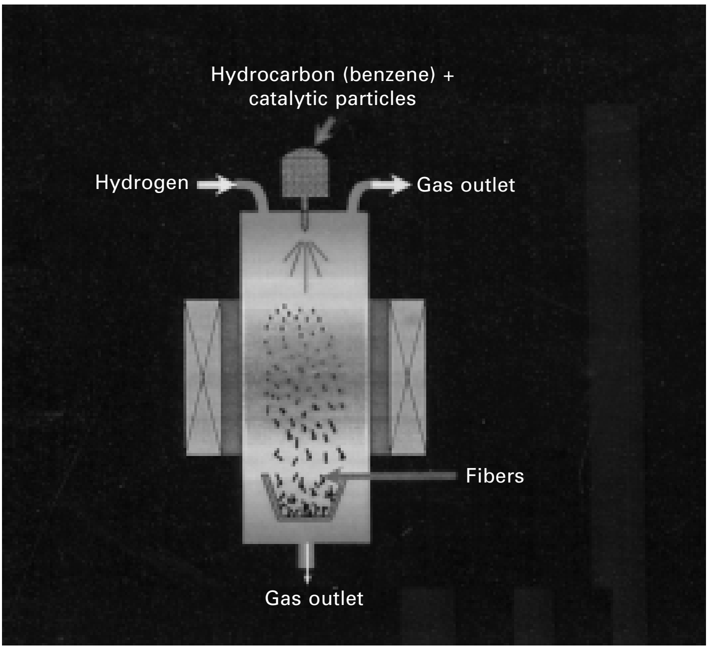
3.22 The prospect of superfiber needs in non-clothing fields.

3.5 Nanofiber (carbon nanotube)

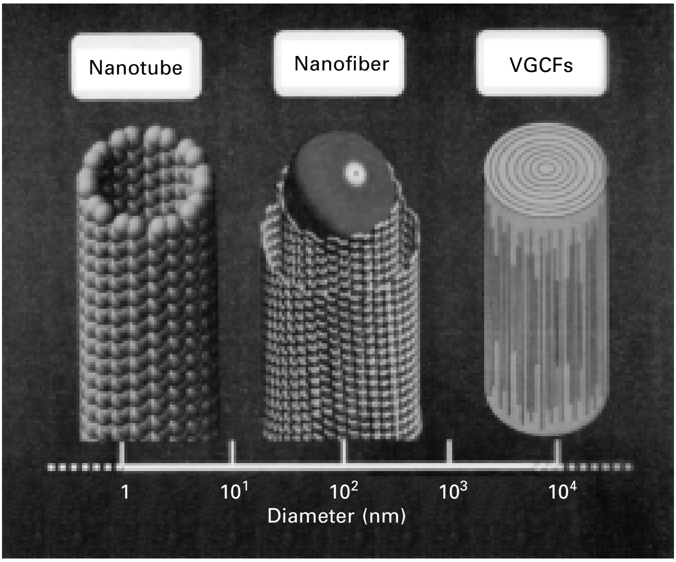
While nanofiber refers to DNA (deoxyribonucleic acid) in the field of biology, it stands for a carbon nanotube (CNT) in the field of fibers. CNT consists of carbon atoms connected in a cylindrical manner with a diameter of several nm to several tens nm and a length of several μm. Aspect ratio (ratio of length to diameter) is in the range of 1000 to 10 000, and the strength of the nanotube is expected to be 40 times of that of carbon fiber, judging from the crystal structure. It belongs to a new group of molecular fibers. CNT is classified into two types according to the thickness of the wall of the tube: single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). The former attracts attention from the academic point of view.

The method of synthesis of CNT includes arc discharge, laser ablation method and chemical vapor deposition methods. Professor M. Endo (Shinshu University) first discovered the carbon nanofiber. The fiber formation system using the floating catalyst method is shown in Figure 3.23. Dr S. Iijima (NEC) discovered the carbon nanotube and he showed transmittance electron micrographs of MWCNT and SWCNT in 1991 and 1993, respectively. A schematic model of the carbon nanotube is shown in Fig. 3.24.

SWCNT consists of a cylindrical graphite sheet with a diameter of 0.6–1.8 nm and a length of several μm. MWCNT is composed of several concentric



3.23 Fiber formation system using floating catalyst method (Professor M. Endo, Shinshu University).



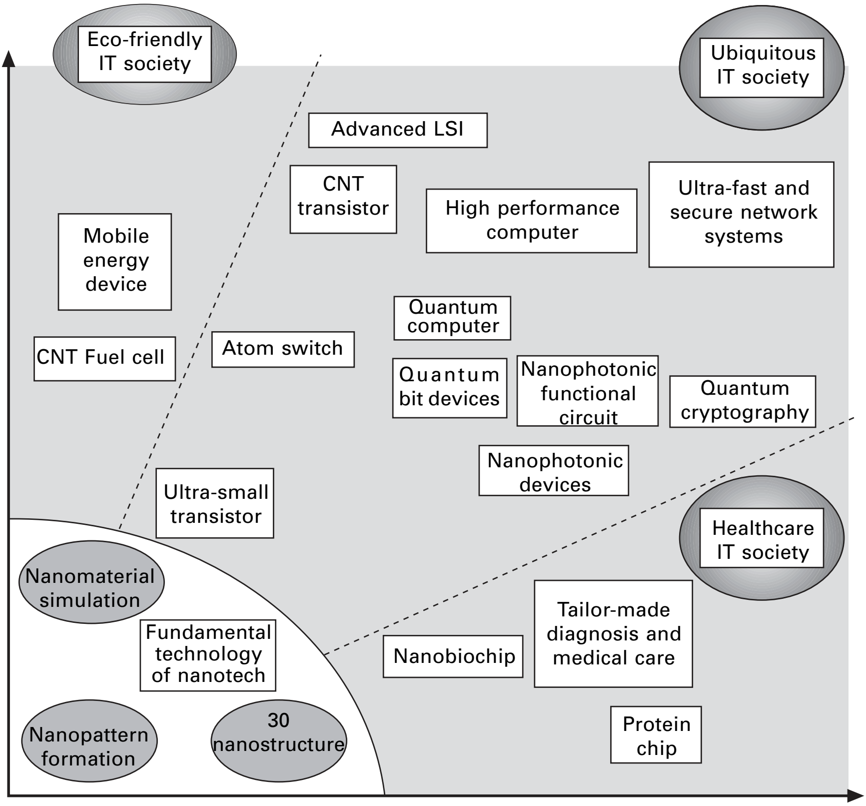
3.24 Schematic model of the carbon nanotube (Professor M. Endo, Shinshu University).

cylinders with diameters of 5–30 nm. CNT did not attract attention at first, but has attracted considerable attention subsequently, particularly when the electric conductivity of CNT was measured successfully. As a material, it has very fine structure, high tenacity strength and modulus, and specific properties in heat resistance, electric conduction and heat conduction. As a result, it is expected to be a material to drive science and technology in the twenty-first century. It is already used as the cathode plate of lithium ion batteries, hydrogen-occlusion material, electro-conductive filler in resin and paint, field emission display material (FED), in atomic force microscopes (AFM) and nano-tweezers.

Carbon fiber with carbon nanotube as a core and optional diameters in the range of several tens to several hundreds nanometers is now almost ready for manufacture. Nano composite fiber, composed of nylon and CNT as the carbon fiber, is used for the smallest gear of the second hand in a watch. Future possibilities look almost endless. The technology fields shown in Fig. 3.25 will be opened by nanotechnology.

3.6 High polyketone fiber

Asahi Kasei got off to a bad start in the high strength fiber field. But now it regards polyketone fiber as a high strength fiber such as aramid fiber and has a project to develop it with the support of NEDO. The polyketone fiber could be a masterpiece of new millennium fiber.



3.25 Technology fields that will be opened by nanotechnology (NEC).

High costs have held back multipurpose development of aramid type materials. The high price is due to the special raw materials used and the special and complex equipment and methods necessary. Asahi Kasei, however, has now developed low price high strength fiber of polyketone fiber with strength and durability as good as aramide fiber. According to the company announcement and patents, this fiber has a molecular structure which includes carbon monoxide and is also composed of ethylene. Thus it contains only carbon, oxygen and hydrogen, so it has a low manufacturing cost compared to other high strength fiber containing other atoms such as nitrogen. Figure 3.26 shows reactions of the polyketone polymer. The low price raw materials and the simple structure of this polymer have reduced the price by 40%.

$$CO + CH_2{=}CH_2 \longrightarrow -\!\!\left(CH_2CH_2\overset{\overset{\large O}{\|}}{C}\right)_{\!n}\!-$$

3.26 Reaction of polyketone polymer.

So far there has been only one polyketone polymer produced, but it is difficult to spin to form fiber. Only Asahi Kasei has developed a low cost inorganic solvent, used in the spinning process and have successfully fabricated polyketone fiber. Table 3.7 shows comparison of performance between polyketone fiber and other fibers.

Polyketone is excellent in strength and has a high affinity for rubber within raw fibers. This feature has opened up a demand for reinforced fibers in composite materials which include plastics and concrete, and especially with rubber, in tire cords. For the tire cord, steel and nylon and polyesters are usually used.

The price of polyaramide fiber is ten times that of polyester fiber. It has a market share of less than 1%. Asahi Kasei can now move into a new market for low cost new fiber to reinforce materials for optical fibers or materials for tire cord.

The demand for *para*-type aramide fiber is about 36 000 tons a year for industrial applications throughout the world. 10 000 tons of aramide is used as reinforcing material for optical fiber. In 2005, global demand will increase to 50 000 tons a year, with 20 000 tons being used as a reinforcing material for optical fiber.

Teijin aramide fiber, which ranks second in global market share, will increase its turnover to 35 000 000 000 yen a year as a reinforcing material for optical fiber and construction materials. Asahi Kasei makes use of its strong affinity to rubber for tapping demands for tire cord and for reinforced material for optical fiber as the largest market in high strength fibers. Asahi Kasei had not previously produced a high strength fiber, but hereafter rallied with the development of the polyketone fiber.

Toyobo developed a high strength and high heat proof fiber (Zylon) in 1998 and now manufactures 200 tons a year for firemen's uniforms and bullet-proof vests.

Table 3.7 Comparison of performance between polyketone fiber and other fibers*

	Polyketone fiber	Ester	Rayon	Aramid
Tenacity (g/d)	20	3	6	23
Stretch (%)	5	13	11	4
Elasticity (g/d)	400	120	130	490
Heat contraction at 150°C (%)	0.5	3.9	1.7	0.5
Density	1.5	1.4	1.5	1.4

*Nikkei Industry Newspaper on 25 July 2002.

3.7 Bibliography

3.1 Description of superfibers

Hongu T. and Phillips G.O., *New Fibers*, 2nd edn, p. 6, Woodhead Publishing, Cambridge, 1997.

Kunugi T., Ohta T. and Yabuki K., *Ko-Kyoudo Ko-Dannseiritsu Sen'i (High-Strength High-Tenacity Fibers)*, p. 58, Kyoritsu Shuppan, Tokyo, 1988.

3.3 Superfiber as a reinforcing material

Carbon Fiber – aerospace (CFRP)

Brewer D., *Advanced Composites*, p. 58 (Jan./Feb., 1987).

Boeing, *7J7 Program Review*, Oct. 1987.

Hardness J.T., *14th National SAMPE Tech. Conf., 26* (1962); *Performance Materials*, 1987-10-19, p. 3

Williams J.G., O' Brine T.K. and Chapman III A.J., *NASA CP2321*, p. 51 (1984).

Masters J.E., Courtier J.L. and Evans R.E., *31st Int. SAMPE Symp.*, p. 844 (1986).

Smith B.D., *Aerospace Composites Materials*, 61 p. 20, Shephard Press, 1992.

Aircraft Engineering and Aerospace Technolology, p. 29, MCB University Press Ltd, 1989.

Stover D., *Advanced Composites Sept./Oct.*, p. 30 (1991).

Mendon H., *13th SAMPE Europe Int. Symp.*, p. 13 (1992).

Carbon fiber – vessel (CFRP)

Momoshita S., *Proc. of ICCM IV*, p. 1710 (1982).

Carbon fiber – technical textile (vehicles)

Siejak V., *Conference of 'Bag & Belt 2000', 6th Int. Symp. on Automotive Occupant Restraint Systems*, Cologne, Germany, March 2000, p. 287.

Kitamura M. and Siejak V., *Conference of 'Bag & Belt 2000', 6th Int. Symp. on Automotive Occupant Restraint Systems*, Cologne, Germany, March 2000.

Tanaka K. and Isoda H., *Function and Materials* (Japanese edn), Feb. 1997, p. 31.

Oka T. and Ohta Y., *The 53th Annual Symp. of Tex. Mach. Soc. Jpn.*, Osaka, June 2000, p. 80.

Geosynthetics

Koener R.M., *Designing with Geosynthetics*, 3rd edn, Prentice-Hall, 1994.

Ochiai H., *et al., Proc. of Int. Symp. on Earth Reinforcement (IS Kyushu 96)*, Vol. 2, 1997.

Giround J.P., *Proc of the 5th Int. Conf. on Geotextiles, Geomembranes and Related Products, Special Lecture & Keynote Lectures*, p. 3, 1998.

Knipschild F.W., *Proc. of Int. Conf. on Geomembrance*, **2**, 739 (1984).

Imaizumi S., Yokoyama Y., Takahashi S. and Tsuboi M., *Proc. of the 12th Southeast Asian Geotechnical Conference*, **1**, 57 (1996).

Imaizumi S., Futami T. and Nomoto T., *Proc. of the 12th Southeast Asian Geotechnical Conference*, **1**, 325 (1998).
Koerner R.M., *Designing with Geosynthetics*, 4th edn, Prentice-Hall Inc., 1998.
Janson L.E., *et al., ASCE Int. Conf. on Underground Plastic Pipe*, 1981.
Kimura K., *Engineering Materials,* **48** (10), 49 (2000).

3.4 Frontiers of superfiber application

para-oriented aramid fibers – Kevlar

Cooper J.L. and Sakai H., *Sen'i Gakkaishi*, **43** (4), 125 (1987).
Kwolek S.L., *Liquid Crystalline Polyamides*, 179th Am. Chem. Soc. Natl. Meet, Houston (1980).
Du Pont, Japanese Patent (Examined) 1980-14170, 1975-8474.
Tanner D., *Proc. of the Int. Sym. on Fiber Sci. and Tech.*, Hakone, 1985.
Dobb M.G., *et al., Polymer*, **22** (7), 960 (1981).
Koralek A.S., *et al., 19th Annual OTC*, Houston, 1987.
Ghosh T.K. and Barker R.L., *J. Ind Fabrics,* **4**, 20 (1986).
Hoiness D.E. and Frances A., *32nd Int. SAMPE Sym. & Ex.*, 1987.

para-oriented aramid fibers – applications of aramid fibers to digital communication device and cable

Sakamoto K., *et al.*, *The Evolution on Continuing Development of ALIVH High-Density Printed Wiring Board*, IPC Printed Circuits EXPO Program Committee, April 2000.
Kato S., *Sen-i Gakkaishi*, **43** (4), 130 (1987).

para-oriented aramid fibers – Technora

Teijin, Japanese Patent (Examined) 1977–39719.
Hiratsuka S., *TEIJIN TECHNOLOGY REPORT*, 1985.
Murayama S., *et al., Sen'i Gakka-shi*, **13** (1), 58 (1998).
Noma T., *Sen'i Gakkaishi*, **56** (8), 245 (2000).
Fujita K., *NIKKEI ELECTRONICS*, **1** (13), 15 (1997).

para-oriented aramid fibers – Towaron

Picken S.J., *Macromolecules*, **22**(4), 1766 (1989).
Picken S.J., Aerts J., Visser R. and Northolt M.G., *Macromolecules,* **23** 3849 (1990).
US Patent 3,767,756 (1973), US Patent 3,869,429 (1975).
Yang H.H., *Aromatic High-Strength Fibers*, John Wiley & Sons, 1989.
Aramid Profile: U.S., R.M. Kossoff & Assoc., Inc.

Polyarylate fiber (Vectron)

Ueda K., *Sen'i–Gakkaishi*, **40**, 135 (1987).
Nakagawa J., *Proc. of Int. Conf. on Advanced Fiber Materials*, p. 31, 1999 Ueda, Japan.

Nakajima T., *Advanced Fiber Spinning Technology*, pp. 161–171, Woodhead Publishing Ltd., Cambridge, 1994.
Nobile M.R., Amendola E., Nicolais L., Acierno D. and Carfagna C., *Polym. Eng. Sci.*, **29**, 244 (1989).
Blizard K.J. and Baird D.G., *Polym. Eng. Sci*, **27**, 653 (1987).
Mithal A.K., Tayebi A. and Lin C.H., *Polym. Eng. Sci*, **31**, 1533 (1991).
Kiss C.G., *Polym. Eng. Sci*, **27**, 410 (1987).
Crevecoeur G. and Groeninkx G., *Polym. Eng. Sci*, **30**, 532 (1990).
Dornheim M.A., *Aviation Week & Space Technology*, 14 July 1997.

PBO Fiber (Zylon)

Yabuki K., *Proc. of Int. Conf. on Advanced Fiber Materials*, p. 27, 1999 Ueda, Japan.
Kato K., *Kobunshi*, **48**, 20 (1999).
SRI, US Patent 4, 225, 700; 4, 533, 692; 4, 533, 693.
Teramoto Y. and Yabuki K., *Kogaku-Sochi*, **8**, 83 (1997).
Radler M.J., *et al., Polym. Mater, Sci. Eng.*, **71**, 328 (1994).
Wierschke S.G., *Mater. Res. Soc. Symp*, **134**, 313 (1989).
Wierschke S.G., *et al., Polymer*, **33**, 3357 (1992).
Kuroki T., *et al., J. Appl. Polym. Sci.*, **65**, 1031 (1997).
Fujishiro H., *et al., Jpn. J. Appl. Phys.*, **36**, 5633 (1997).
Kitagawa T., *et al., J. Polym Sci. Polym. Phys.*, **36**, 39 (1998).
Yabuki K., *Sen'i Gakkaishi*, **54**, 16 (1998).

Polyethylene

Pennings A.J., *et al., Colloid Polym. Sci.*, **253**, 452 (1975).
Lemmstra J., *et al.*, in *Developments in Oriented Polymers: 2*, I.M. Ward (ed.), p. 39, New York, 1987.
DSM, Japanese Patent (Examined) 1985-47922, 1989-8372, 1989-4887 etc.
Ohta Y., *Sen'i Gakkaishi*, **54** (1), 8 (1998).
Ohta Y., *Series of Basic Lectures on Fiber & Textile*, p. 66, The Society of Fiber Science and Technology, Japan, 2001.
Ikaga T. and Ohkoshi Y., *et al., Sen'i Gakkaishi*, ***58,*** 16 (2002).
Yamazaki Y., *Proc. of the 6th Spring Seminar* p. B1, The Textile Machinery Society of Japan, 2000.

3.5 Nanofiber (carbon nanotube)

Dresselhaus M.S., Dresselhaus G., Sugihara K., Spainm I.L. and Goldberg, H.A. *Graphite Fibers and Filaments*, Spring-Verlag, Berlin, Heidelberg (1988).
Oberlin M., Endo *et al., J. Cryst. Growth*, **32**, 335 (1976).
Endo M., *Chem. Tech.*, p. 568, ACS, 1988.
Speck J.S., Endo M. and Dresselhaus M.S., *J. Crystal Grouwth*, **94**, 834 (1989).
Endo M., *et al., Sen'i Gakkaishi*, **51**, 412 (1998).
Ohya A., *Engineering Materials*, **50** (4), 98 (2000).
Dresselhaus M.S., Dresselhaus G. and Eklund P.C., *Science of Fullerenes and Carbon Nanotubes*, p. 764, Academic Press, 1995.

Endo M., in *CHEMTECH*, pp. 568–576, ACS, 1988.
Iijima S., *Nature*, **354**, 56
Endo M., *Proceedings of 1st Int. Congress on Nanofiber Sci., Tech.*, ‘Aim for the practical Application’ p. 2 On Fiber Sci. Tech. Japan, June 28, 2004.

3.6 High polyketone fiber

Nikkei Industry Newspaper, 24 July 2001.
Morita T. and Kato J., JPNPAT 2001-115007.
Taniguchi R. and Kato J., JPNPAT 2001-295134 and other 10 materials.