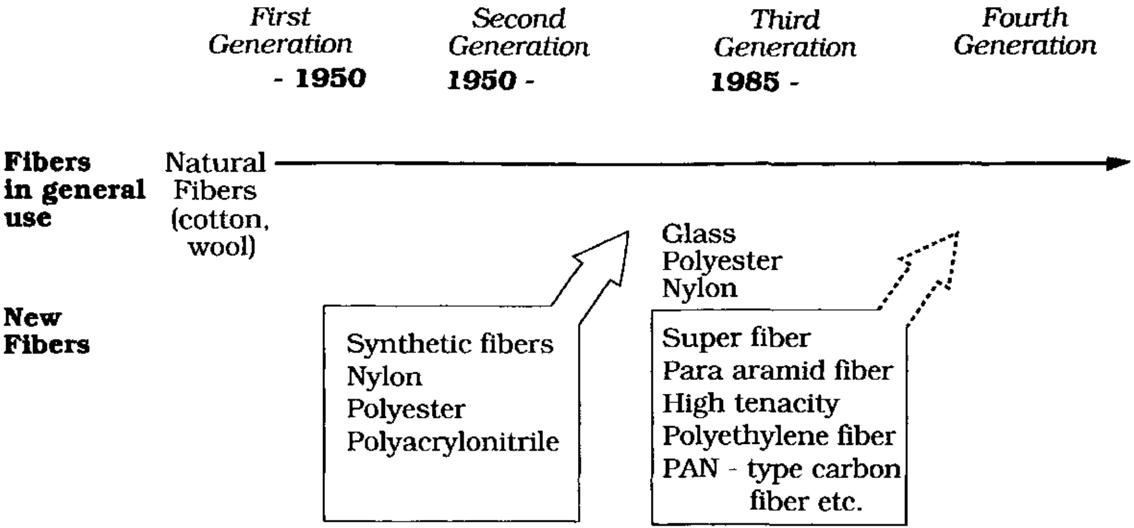
1 Birth of the new fibers

1.1 Background

Two types of fibers are currently available to human society: natural fibers, which have existed for 4,000 years or more, and synthetic fibers, which first appeared about 100 years ago, when Count Chardonnet invented artificial silk, an achievement that had been only a human dream previously. Dr Carothers of the Du Pont Company first produced nylon in 1935, which was claimed to be "finer than spider's thread, stronger than steel and more elegant than silk". Today, synthetic fibers are not a mere alternative to natural fibers, but are new materials of high functionality and high performance which play a key role in the field of high technology. Now these new materials can be designed and produced according to the nature of their utilisation.

Macroscopically, the era of natural fibers, which existed up to the 1950s, can be identified as the first generation; the synthetic fibers such as nylon, polyester, polyacrylonitrile, etc. that appeared during the 1950s were the second generation (see Fig. 1.1). These were the chemist's copy of natural fibers, in order to replace them, and to some extent they succeeded in this purpose. However, the fiber materials of high performance in use today provide the potential for developing a new technology. These fiber materials can be classified as third generation. Fibers of high modulus and high strength can now be further produced from synthetic polymers of light weight, and are widely employed in space technology, as, for example, high-tenacity fibers of polyethylene, polyaramid and polyarylate. Although carbon fiber is in nature inorganic, it is conventionally classified as a synthetic fiber, since it is mainly produced from polyacrylonitrile (PAN).

Thus synthetic fibers of the third generation are not simply alternatives to natural fibers, as the synthetic fibers of the second generation were. The need for ultra-light fibers of high strength is increasing as high technology responds to changes in the social environment, for example, by the demands of energy



1.1 Fiber development in each generation.

conservation. Such fibers are also needed in various sports, leisure, transportation, and ocean/air/space developments, leading out from Earth to space. In future decades, metals are expected to be replaced by newly developed synthetic fibers of the third generation, which can be superior to metals with respect to strength and modulus. These fibers are already being employed as strengthening materials in composites in main wings and/or other body parts of aircraft and space shuttles.

1.2 Transition to new fibers

Various fibers of different performances and/or functions have been developed continuously. Although those fibers are referred to today as super-fibers, the name "super-fiber" was coined only during the 1980s, as illustrated in Fig. 1.2. Fibers before 1980 were either identified as general-purpose fibers or designated as speciality fibers. Carbon and aramid fibers were classified, for example, as speciality fibers.

High-value-added products of polyester fiber were first developed in Japan in the 1980s. Mono-filament of conventional polyester filament is 2–3 denier. Here 1 denier is defined as the weight of a filament of 9,000 metres in length, and was used to designate the coarseness of filament of raw silk or nylon. The coarseness of natural fibers such as cotton, ramie, silk and wool is expressed in terms of count, which is determined from the length of a 1 kg fiber. For example, one count is equivalent to a 1 km fiber of 1 kg weight. Cotton fiber of 240 counts is as fine as silk. Most men's shirts are made from blended fabrics of cotton and polyester, containing 35% cotton and 65% polyester,

until 1980 Speciality fiber

↓

1980 - 84 High-performance/high-functional fiber

↓

Since 1984 High-technology fiber

↓

Since 1985 Super fiber at present :
tenacity > 20g/D (or 2.5 GPa)
modulus > 50g/D (or 55 GPa)

1.2 History of super-fibers.

although the fabrics of various blend ratios are commercially available according to the use and performance required. Polyester fiber, 1.5 denier, is normally used for blended fabrics, but additionally today, 0.5 denier fiber and 1.0 denier filament are available owing to further technical developments. Fibers of smaller denier or larger counts are technically more difficult to produce. Polyester filament became finer, reducing from 2–3 denier to the 1 denier produced now. Polyester fiber staple of blended fabrics for men's shirts or women's blouses came down from 1.5 to 0.5 denier. It is not always appreciated that it is technically difficult to spin fine polyester filament or staple. In fact, the spinning technique for forming synthetic fibers becomes more critical with shrinking denier, since the process requires three established technologies to spin homogeneously synthetic fibers as fine as human hair.

The three technologies that must be combined are:

1 Fine spinning.
2 Fine processing.
3 A highly reliable production technology to combine the above two technologies without producing any defect.

Engineers established these technologies as a result of consistent and intensive efforts over a considerable period. New products only come into existence when produced, sold and successfully evaluated by market forces. Synthetic fiber companies have accepted the challenge to spin finer and finer fibers. As the result of competition, many new products were put on the market, such as silk-like, bulky or good-to-touch textiles of nylon or polyester. These products are referred to as high-value-added or speciality products. Although the speciality fibers were deemed to be 0.5 denier, to distinguish them from conventional fibers of over 1.5 denier, consumers became confused and treated both high-performance fibers and high-value-added fibers of fine denier as speciality fibers.

Thus there was a move during 1980–84 to define the terms specifically in order to distinguish high-value-added fibers from high-performance/high-function fibers, specifying, on the one hand, polyester fibers of fine denier, and on the other, high-performance fibers such as carbon fibers and aramid fibers. High-performance/high-function fibers were later (in 1984) redeemed as high-tech fibers, as "high technology" became a term in common use. High-tech fibers now include new functional fibers such as biodegradable fibers, chemical absorbance fibers, fibers from biomaterials and activated carbon fibers, which are not of high modulus and high strength, but have other new performance advantages.

Therefore, high-tech fibers can now be redefined as fibers produced by high-technology, which are superior to those produced by conventional fiber technology, arising from the application of the newer developments in fiber science and technology. A survey on "high-tech fibers" and a book "high-technology fibers" appeared in the USA in the spring of 1985 (see Further reading at the end of the book). Since then, the term "high-tech fibers" has been generally accepted in Japan. This survey defines high-tech fibers as the fibers used in, and produced with, high technology. In this context, a super-fiber that is outstanding in certain physical properties such as high strength and/or high modulus can be defined as a high-tech fiber. Fibers with specialist chemical functions are not regarded as super-fibers. For example, high-performance fibers with biodegradable or chemical absorbance function are classified as "high-tech fibers" and not as "super-fibers".

This book reviews all new fibers, which include "super-fibers" and "high-tech fibers", classified according to the definitions given here, and additionally the new cellulose technology developed to process cellulose into speciality polymers. These moves have resulted as a direct consequence of cellulose being re-evaluated world-wide as a renewable resource following the oil crisis.

2 The super-fiber with new performance

2.1 Two streams of super-fiber

The Society of Fiber Science and Technology, Japan, organised ISF'85 (International Symposium of Fiber Science and Technology) at Hakone, Japan, in 1985 to celebrate its 40th anniversary. The main interest of the distinguished international gathering centred on the super-fibers, which were being developed competitively by many research institutes throughout the world. It is commonly thought that super-fibers emerged rather suddenly. Their development, however, was the result of merging fundamental scientific and technical knowledge which seemed at the time not related to fiber science. This was necessary to overcome a series of technical barriers. The history of science and technology teaches us that a new technology is frequently developed by a group of people obsessively concentrating on a particular problem. In this respect, a director of research and development needs to be an organiser, in addition to being a manager. Often, the future of an industrial development in high technology depends on a technical "conductor" who plans and leads the new technical development.

There are several influences in the development of super-fibers, among which two groups deserve special mention. One is the research group of the Du Pont Company in the USA, which developed the *para*-aramid fiber named "Kevlar". This material is seven times stronger than steel and, when it appeared, was the most sensational fiber since nylon. The second is the research group at DSM in The Netherlands, which developed polyethylene fiber of even higher tenacity than Kevlar. Du Pont started its research and development on heat-resistant polymers in the 1960s, in response to space development needs. A new process of liquid crystalline spinning was developed to spin Kevlar from rigid polymer by Kwolek's group in Du Pont. Gel-spinning was developed in the late 1970s by the DSM group headed by Smith (now at University of California, Santa Barbara, USA) and Lemstra (later Professor at Eindhoven Technical University) to spin extremely high molecular weight polyethylene. The molecular weight of polyethylene is of the order of 10^4 when used for plastic containers or bags. It is of the order of 10^6 for super-fibers, which are spun from gel-like solutions of high molecular weight polyethylene. Gel spinning was known in 1969, but its industrial application came in 1978 when DSM introduced polyethylene fiber of high strength. Later Allied Chemical Corp. in the USA developed polyethylene of high strength by another gel-spinning process. During ISF'85 at Hakone, scientists from DSM and Allied Chemical Corp. intensively discussed the mechanism of gel-spinning, and demonstrated the urgent need for a super-fiber of high strength and light weight.

Chemists have learnt a great deal from silkworms, and emulated them in spinning synthetic polymers. However, they have not yet been able to develop ambient temperature spinning, which would be more advantageous from an energy conservation viewpoint. For example, a silkworm swings its head in the shape of a figure 8 and spins silk fiber at room temperature. Although natural fibers such as silk, cotton and wool have been extensively investigated scientifically, the mechanism of their formation is not yet fully understood. However, the gap between the natural and the synthetic is now being continually reduced.

2.2 The quest for a strong fiber

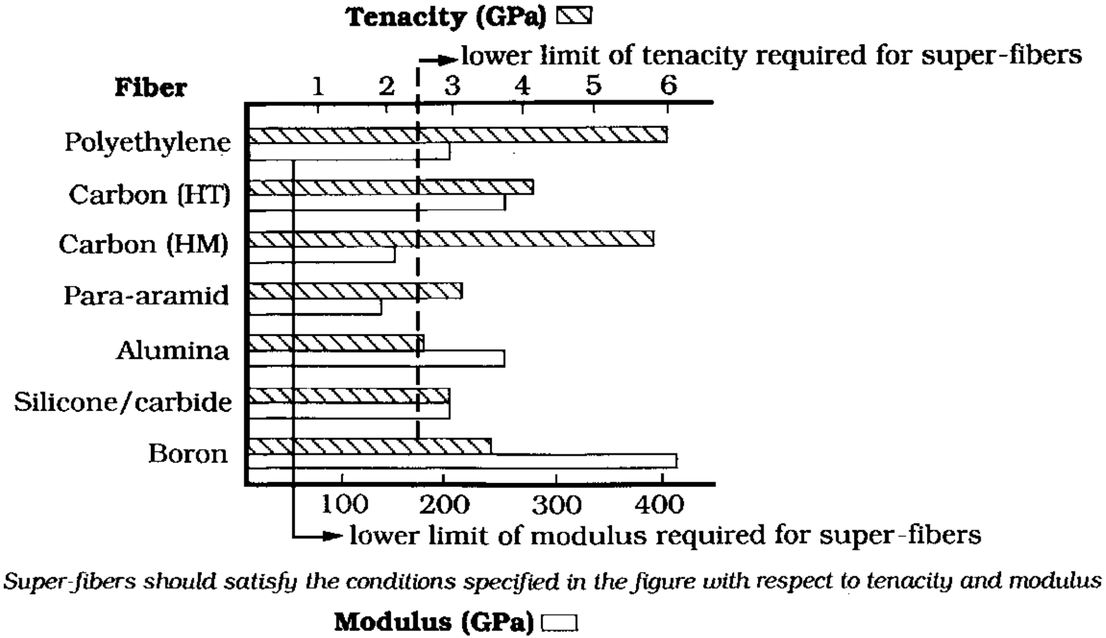
Various functions are required from fibers. Each industry is developing its own fibers for specific functions. Increased high strength is always a goal of fiber scientists, who continually seek something stronger. A fiber should be strong not only with respect to its tensile strength, but also in its resistance against deformation (high modulus) and wear resistance. The development of higher-performance fiber for composite reinforcement is also urgently needed in space and ocean technologies. These are areas where there is intense competition between the European countries, the USA and Japan. Fiber strength can be defined either in terms of tensile strength, which controls mono-filament characteristics, or tear strength, which significantly influences film characteristics. However, it is deformation resistance, i.e. having a high Young's modulus, that is the most necessary property for composite enforcement. For example, a space shuttle can be rolling violently because of atmospheric pressures when plunging into the atmosphere, so it must be resistant to deformation. Young's modulus is defined as the ratio of the unit cross-sectional applied force (stress) to the strain in the force direction. It is, therefore, a measure of deformability, with larger values indicative of lower deformability.

High-technology composite materials are expected to serve as fundamental materials for supporting the technologies required for the 21st century, as demanded by the automobile/aircraft industries, and space technology. These will allow a significant extension to the range of human activity. As a by-product, the high-performance materials developed for aerospace technology have also opened up improvements in the fiber materials used in the leisure field, such as golf, tennis, skiing and sailing, particularly in Japan. Not only are these materials light and strong but they also provide the specialist performances needed by the particular application and/or environmental conditions encountered, as in space or on the ocean. Here the mechanical properties can be tailor-made by producing a composite, and as a result new advanced composite materials (ACMs) are being developed by many industries in Europe and USA. For example, carbon fiber possesses good tensile strength, but lacks impact strength, whereas high-tenacity aramid fiber is weak against compression. Thus the mechanical weaknesses of carbon fiber (low impact strength) and aramid fiber (poor compression resistance) can be compensated for by making a composite of both fibers in an epoxy resin matrix. This type of composite material is widely employed as an ACM of light weight for energy conservation in space and ocean developments. Composite materials are superior in physical properties and performance when compared with single materials, and are used in tonne quantities in aircraft. Composite materials could well account for about 60% of the primary and secondary structural materials used in aircraft, etc. in the 21st century.

These reinforcing fibers are assessed in terms of their modulus and tenacity. Super-fibers must have a modulus greater than 55 GPa and a tenacity of 2.5 GPa (see Fig. 2.1). GPa is an international unit of modulus or tenacity; 1 GPa corresponds to the strength equivalent to approximately 100 kg per 1 mm^2. Super-fibers such as high-tenacity polyethylene fiber, para-aramid fiber and PAN-based carbon fiber satisfy this condition which is required of a reinforcing ACM fiber. The tenacity of the super-fiber Kevlar is 25 g/denier, which is seven times stronger than that of steel of the same weight (3.5 g/denier). Kevlar even possesses a higher tenacity per cross-section than steel.

2.3 From "shish kebab" to "gel-spinning"

Shish kebab is a typical Turkish–Armenian grill dish of marinated lamb on skewers, where "shish" and "kebab" denote the skewer and meat, respectively. In 1966, Pennings (subsequently Professor at Groningen State University, The Netherlands), then at the DSM Company, observed a shish kebab-shaped crystal while stirring dilute solutions (of a few per cent) of high molecular



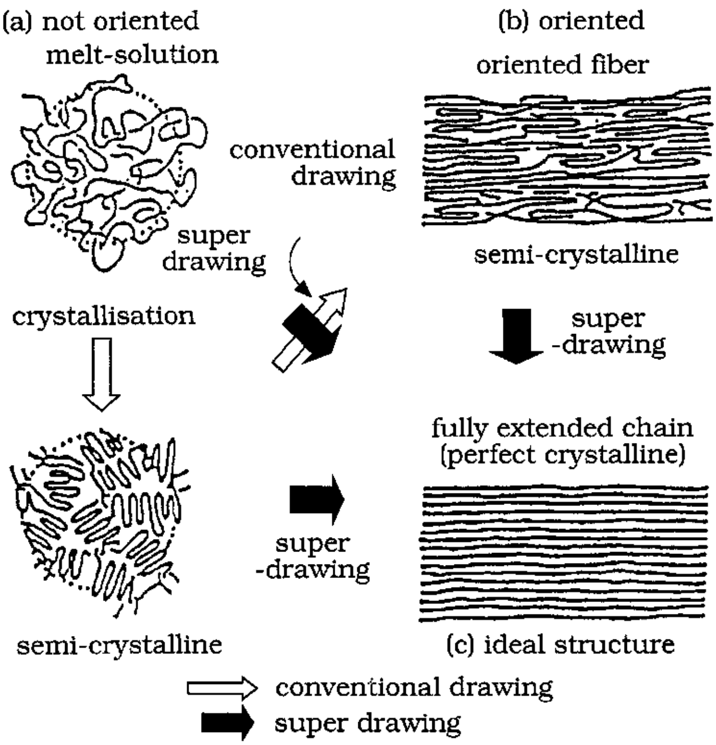
2.1 Physical properties of super-fibers.

weight polyethylene. He considered how he might make a high-tenacity fiber from this shish-part, and over many years worked energetically to separate the shish-part from the kebab-part, eventually succeeding.

Propane, used as a domestic fuel, is a gas with a low molecular weight of 44. This hydrocarbon compound becomes liquid and eventually solid like a wax candle when polymerised to increasing molecular weight. When its molecular weight becomes of the order of 10^4, the olefin compound, or plastic, is called polyethylene, which is rather hard and widely used for polybags and polyethylene bottles. There are now two types of polyethylene available for domestic use; one is the soft, branched, low-density polyethylene and the other is the hard, linear, high-density polyethylene. High-density polyethylene is produced using a polymerising catalyst at low pressure, and is used, for example, in making beer caskets. Super high molecular weight polyethylene can be classified as high-density polyethylene having a molecular weight of the order of 10^6. Its physical properties are very different from the ordinary 10^4 molecular weight product. Its chain length is almost a hundred times greater and its molecular weight two orders of magnitude greater. Polyethylene chains in this super-class product are coiled as in woollen yarn with greater entanglement. It becomes less fluid with increasing molecular weight, and it was first thought that this super high molecular weight polyethylene could not be spinned. However, in 1976, Pennings succeeded in continuously removing the shish-part, and Smith and Lemstra of DSM developed a practical method of gel-spinning by applying Pennings' technique. The method involves both spinning and drawing, in which a dilute solution (a few per cent) of polyethylene of high molecular weight is extruded into water to form a gel-like soft fiber, which is then heated and drawn out about 30 times in length. Ordinary polyethylene of molecular weight *ca.* 10^4 is drawn only up to 10 times in length and its Young's modulus is 1 or 2 GPa at most. However, the gel-like fiber of high molecular weight polyethylene drawn over 30 times can yield a Young's modulus of 90 GPa. This revolutionary method of "gel-spinning" attracted much attention from all over the world as a method for producing super-fibers.

Gel-spinning requires two steps. First, a dilute solution of polyethylene is prepared to reduce entanglement, and, secondly, a gel is formed from the solution to produce order in structure so that it does not entangle. The role of solvent is thus most important in gel-spinning. Drs Smith and Lemstra succeeded by using xylene or decalin as the solvent for this process.

Polyethylene is made up of regular crystalline regions and irregular amorphous regions when prepared by weak drawing, as shown in Fig. 2.2(a). When highly drawn upon heating, the crystalline region becomes oriented in



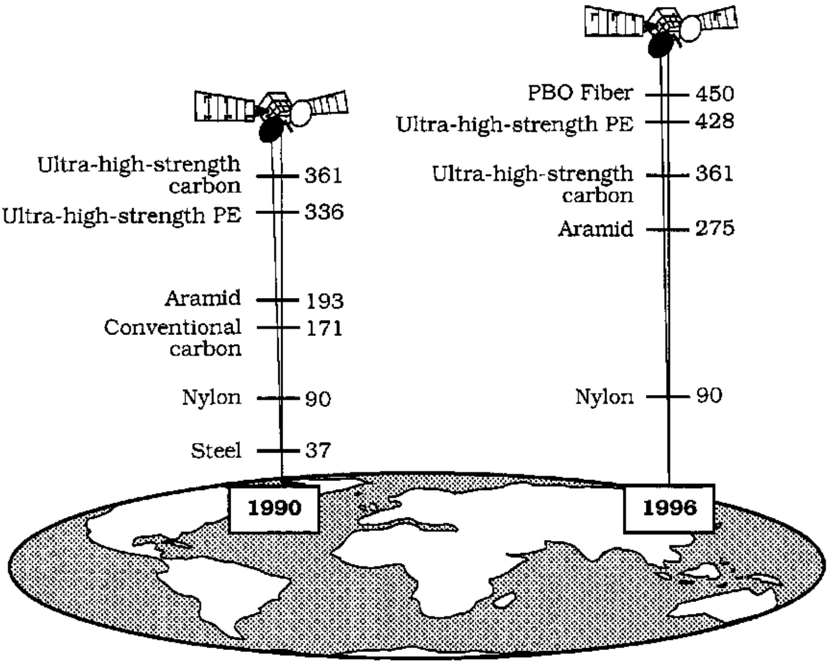
2.2 High-order structure of polyethylene.

one direction only (Fig. 2.2b). Further drawing increases the tenacity by approaching an ideal structure of extended chains, as shown in Fig. 2.2(c). Highly oriented polyethylene produced in this way can be used for packing tape, for example. An upper limit of the value of the modulus or tenacity of polyethylene can be calculated on the basis of an ideal chain structure of polyethylene molecules. Only 5% or 10% of this limit is reached in terms of the modulus or tenacity for ordinary polyethylene. Gel-spinning thus provided the first method capable of preparing polyethylene fiber with a tenacity and modulus that approached the theoretical maximum values. Although polyethylene molecules are flexible, they tend to crystallise when aligned in a parallel orientation. Once crystallised, the strong intermolecular interactions maintain the alignment of the polyethylene molecules. The problem, therefore, is how to align polyethylene chains in parallel alignment to make super-fiber of high modulus and high tenacity from conventional polyethylene.

This objective was achieved using the method of gel-spinning first patented world-wide by DSM. Although Toyobo Inc. (Japan) and Allied Chemical Corp. (USA) were pursuing their own research projects on gel-spinning simultaneously, they judged it impossible to escape from the basic patent applied for by DSM. They were forced, therefore, to enter into a technical association with DSM. Toyobo Inc. linked with DSM in March 1984, and set up a joint venture company Dyneema in The Netherlands in May 1986. In October of the same year, Toyobo Inc. completed a pilot plant at its Research Centre in Ohtsu, Shiga Prefecture, Japan, and started pilot-production of polyethylene super-fiber, eventually expanding the plant to commercial scale to produce 300 tonnes annually. DSM in The Netherlands increased production of polyethylene super-fibers to 1,000 tonnes per year in 1996 by constructing a new plant.

Allied Inc. (USA) was also investigating the production of polyethylene of high modulus and high tenacity independently. However, for the same reason, it was also forced to seek a licence for gel-spinning using the DSM process in 1984. Dr Prevorsek of Allied Inc. changed the solvent to paraffin oil, and developed high-tenacity polyethylene fiber Spectra 900 and later a higher performance fiber Spectra 1000. This material is used for a wide variety of industrial products such as helmets, suitcases and rope. Gel-spun Dyneema SK60 is a high-modulus and high-tenacity fiber of light weight, which is far superior in its impact strength to conventional fibers and exhibits the highest anti-fatigue breaking among the high-tenacity fibers. High-tenacity polyethylene is chemically stable and needs no special coating, but its melting point, varying from 145 to 155 °C, depends on the stressing conditions. It is also mechanically stable for a short period even at a temperature close to the melting point, and is used on its own as a fiber or as a composite material to reinforce other polymers. Considering its characteristics of light weight, high tenacity, anti-wearing, high ultraviolet light stability and electrical insulation, the ropes and cables made from high-tenacity polyethylene are expected to be used widely in future in the field of ocean industries and sports.

Dyneema SK71 is ten times stronger than steel in terms of the free breaking length, which is 428 km (see Fig. 2.3). Since the density of polyethylene is less than unity, its free breaking length is infinite in water. Fabrics made from this material possess high impact strength, high weather resistance and good hydrophobic properties, and as a result the material is widely employed for making bullet-proof clothing, protective wear, filters, sailing cloth and parachutes and for building materials. This high-tenacity polyethylene is also used as reinforcing material in composites for loudspeaker cones, archery bows and helmets, in order to exploit its high sonic propagation characteristics, vibration damping and high impact strength.



2.3 Free breaking length in air (km) of various fibers.

Mitsui Petrochemical Co. has developed a super high-tenacity polyethylene fiber Tekmilon, in collaboration with the Japan Research Institute for Polymers and Textiles, and has a pilot plant producing 5 tonnes per month in its Iwakuni plant. This polyethylene is used for the preparation of tennis racket gut, skis, playing clubs, bowstrings, FRP (fiber-reinforced plastics), etc.

Stimulated by the success of gel-spinning high molecular weight polyethylene, researchers in various countries have attempted the gel-spinning of other polymers, but without positive results. Allied Chemical Co., for example, developed gel-spun polyvinylalcohol (PVA) but not with the same success as polyethylene. Today Mitsui Chemical Co. of Japan, Hoechst of Germany and Hercules of the USA are commercially producing polyethylene of super high molecular weight, whose production amounts to 12,000–13,000 tonnes annually throughout the world. Nisseki Chemical Co. has developed a new method of mass production for high molecular weight polyethylene by combining its original know-how in polymerisation and catalysis techniques. The method, however, has not entered into full production since it does not proceed efficiently owing to the high viscosity of the polymer melt. The processing technology is still under development. Several other methods are being investigated currently to process high molecular weight polyethylene into fiber. Since the density of polyethylene (0.95) is considerably lower than that of Kevlar (1.45), high molecular weight polyethylene is more suitable for ACMs. The materials used in aerospace technology must be light as well as having high heat-resistance. Consequently, polyethylene cannot be used for this purpose.

2.4 The aramid fiber race in Europe, the USA and Japan

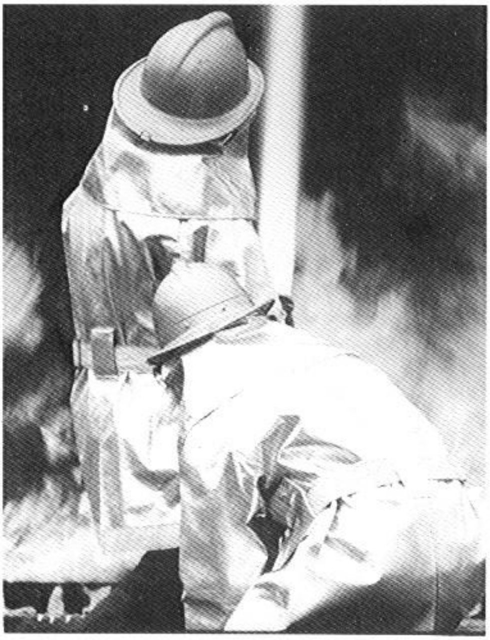
Commercial aramid fiber today now available is represented by Kevlar of Du Pont (USA) and Twaron of Akzo (The Netherlands). Approximately 2000 tonnes of Kevlar were imported and sold annually in Japan by Toray until domestic production of Kevlar started in 1988. Twaron is imported to Japan through the Japan Aramid Co., which is a joint corporation of Sumitomo Chemical Co. and Enka (a subsidiary of Akzo). Although a patent dispute between Du Pont and Akzo lasted for 11 years, it was eventually resolved. In Japan, Teijin Ltd. developed its own aramid fiber Technora, and started its commercial production in September 1987 at the Matsuyama plant, constructed in 1986.

2.4.1 Birth of liquid crystal-spun "Kevlar"

Space development projects started in the 1960s led to extensive joint research among industries, universities and governmental institutes in the USA to develop new materials. Among them, research and development leading to heat-resistant polymers by Du Pont was the most successful. For example, the heat-resistant polyimide resin Capton opened up a new field of application such as the construction of desk calculators, cameras and watches, in forms that are smaller, lighter, thinner and shorter. This is possible because the electric circuits can be printed on flexible polyamide film. Aromatic polyamide resins which have been developed by Du Pont include the zigzag-linked *meta*-type, called Nomex and the linear *para*-type named Kevlar.

The commercial production of Nomex was started in 1965, and this fiber is used for fire-fighting apparel, to allow fire resistance against flame, smoke and high radiation heat (see Fig. 2.4). This polyamide fiber is also used for protective garments worn at smelting furnaces or in oil refineries. The heat-resistant polymer has a molecular structure that is thermally stable, and stands up to long-term use at temperatures over 300 °C.

Developments always appear easier in hindsight. Nevertheless, their origination calls for enormous effort: it requires inspiration or a leap of the



2.4 Firefighter uniform of *meta*-type aramid fiber (Du Pont, Japan).

imagination to break through at a certain stage of development. Du Pont of USA developed in 1964 the *para*-type aramid fiber hailed as "...a new fiber of dreams stronger than steel..." which was then acclaimed as the most sensational fiber since nylon. The original development of this fiber originated with Dr Stefany Kwolek. Many researchers abandoned the task of dissolving the aramid resin in organic solvents, which were suggested by its molecular structure. Kwolek found, by accident, that a suitable solvent was one containing salt (sulphuric acid was eventually used in commercial production). She reported this finding to her supervisor, who did not believe her at first. When extruded from this dilute solution through a nozzle, there formed the epoch-making aramid fiber, which could hardly be cut by scissors. The term "epoch-making" is justified since this aramid fiber requires no drawing process, whereas conventional synthetic fibers such as nylon, polyester and acrylonitrile fibers must first undergo a drawing process after spinning through a nozzle. This drawing process is generally important in the synthetic fiber industry to furnish fiber in its finished form. Not only is the superficial shape controlled in this way, but the fundamental structure of the fiber will also be changed by drawing. During the drawing process, the molecular chains in polymer crystals will be aligned in the direction of drawing, and the Young's modulus and the tenacity of the fibers will increase.

Conventional synthetic fibers cannot attain sufficient strength without drawing, and would not find practical use. However, when aramid is spun from this concentrated sulphuric acid solution, the fiber shows high tenacity/high Young's modulus without the need for drawing and additionally exhibits high heat resistance.

Kevlar is spun from sulphuric acid solution where extremely rigid Kevlar molecules form a lyotropic mesophase. When the liquid crystals are extruded through a nozzle, Kevlar chains orient in the direction of the fiber axis and form fiber in the coagulating bath. Drawing is, therefore, not required to increase the tenacity by chain orientation in the direction of the fiber axis. This form of spinning is referred to as "liquid crystal spinning". The American Chemical Society Prize for Creative Invention in 1980 was awarded to Stefany Kwolek for her invention of this new process. Kevlar produced by this new technology of "liquid crystal spinning" provided an entirely new super-fiber which exhibits extremely high tenacity/high modulus as well as high heat-resistance. The impact of Kevlar proved so dramatic that researchers throughout the world rushed to synthesise rigid polymers and their subsequent liquid crystal spinning. Du Pont alone invested US$300 million over 10 years to get the aramid fiber Kevlar on to the market. The term "aramid" was adopted for the allaromatic polyamides first by the US Trade Committee in 1974, and subsequently approved by the ISO (International Organization for Standardization) to distinguish the group from the aliphatic polyamides (nylon 6). Although the commercial success of aramid fiber cannot be attributed to one particular person, Jeorge Lanzel, Managing Director responsible for the textile/fiber R&D of Du Pont, must surely take the main credit for this success. One might comment that Du Pont was well equipped with talent, funds and facilities, but these assets are only part of the story. What is important is a readiness to cultivate the small seed of an idea into a large tree that bears fruit. In this respect, the role of a technical coordinator, such as the head of the R&D section, is vital to stimulate and control talented researchers without suppressing their interest. No success can be expected in industry without the harmony of stimulation and control. R&D in Japan is often said to be no more than yielding a small-scale technical improvement. The Japanese are essentially a conservative farming race and a group consensus weighs more in their decision making than individual opinion. Once a potentially creative young Japanese of strong individuality enters the well-organised industrial society, he or she soon becomes accustomed to the environment and aims towards being a manager rather than using his or her creative talent. This might well be a consequence of the uniform education system in Japan, whereas in Europe and the USA individual creativity seems to be given greater scope in the educational system. The Europeans are a hunting race, and prefer to be different from others, with respect to originality. Since industrial internationalisation is inevitable, creative talent should be valued more in Japanese industries.

Du Pont produces Kevlar at its plant on the outskirts of Richmond in Virginia, and production capacity was increased to 21,000 tonnes/year in 1996. It also started Kevlar production at a plant in Maydown, Northern Ireland, in 1988. Production in 1996 was 5,000 tonnes per year. Toray–Du Pont, a joint company of Toray and Du Pont, has been importing Kevlar to Japan since January 1985, and it is sold through Toray Co. A newly joint company of Toray–Du Pont Kevlar was established in February 1989. A building was completed in 1991 in Tokai, Aichi Prefecture, Japan, to house a new production facility for Kevlar (2,500 tonnes/year). There are plans now to extend the application of Kevlar to produce rope for special uses, cables for optical fiber, safety helmets for sports and motorbikes and other wear-resistant materials. Approximately half of the Kevlar produced in Japan is used for cords of radial tyres for passenger cars, and the rest for industrial and sports/leisure materials such as protective working clothes and gloves, and tennis, golf and sailing equipment. Kevlar's major use throughout the world in 1984 was for composite materials in aerospace technology (51%) and tyres (21%). Since the consumption of ACMs has increased 30% annually over the past 10 years, Du Pont is actively expanding its capacity for Kevlar production. Du Pont also expects the ACM markets for aerospace technology, car industries, general industrial parts, construction materials, ceramics and electronics to increase dramatically. While *para*-type aramid fiber is mostly applied to heavy industrial uses, its physical properties are attractive for the clothing industry also. It is used for special clothing such as bullet-proof jackets, safety jackets and protective gloves. Aramid fiber is five times stronger in terms of the tensile strength and one-fifth lighter in terms of the density than steel, and exhibits high wear-resistance. Goldwin, a sportswear maker, uses aramid fiber to make trousers for mountaineering and anoraks of blended fabrics with wool or cotton. Kevlar–wool blended fabrics with 10 wt.% Kevlar are used for autumn/winter trousers, and Kevlar–cotton blended fabrics with 40 wt.% Kevlar (Kevlar filling yarns and cotton warp ends) for spring/summer trousers and anoraks. Kevlar is being expanded now into the aerospace, car, and optical communication industries, and for producing safety/protective clothing, wear-resistant materials, and ocean technology, construction materials, etc to exploit its special physical characteristics. After the big Kobe earthquake of 1995, concrete structures such as highways, railroads, subways and buildings needed to be quickly reinforced. Aramid fiber was one of the materials used because of its high tenacity and modulus, ease of working and its non-conductivity. Kevlar sheets were applied to reinforce highway columns, chimneys, lighthouses, etc. It will shortly also be applied to railway columns.

2.4.2 A new product: "Kevlar 149"

Du Pont has succeeded in developing a new *para*-type aramid fiber, Kevlar 149. Original Kevlar material is polymerised from *para*-phenylenediamine and terephthalic acid chloride using a catalyst. Wet/dry spinning from sulphuric acid solution yields highly oriented Kevlar 29 without drawing. Kevlar 149 is produced by heat processing of Kevlar 29. Kevlar 149 exhibits approximately 40% greater tensile modulus and 50% less moisture absorption than other high-modulus aramid fibers. It is thus able to replace steelwire cords in the rope/cable industry because of its high tensile strength and good creep characteristics. Kevlar 149 is a new generation that exhibits special characteristics as an advanced composite material with carbon fiber in applications that require high modulus and light weight.

2.4.3 Twaron

Akzo Co. of The Netherlands started research on the *para*-type aramid fiber in 1969, and as a result developed Twaron. Enka Co., a subsidiary of Akzo, built a pilot plant in 1976 to promote production and applications of Twaron. A Twaron plant with a production capacity of 5,000 tonnes/year (expandable to 10,000 tonnes/year) was completed in Emen, The Netherlands, at the end of 1985, and commercial production was started a year later. This production process for Twaron is similar to that of Du Pont, but Enka uses a less expensive solvent. The physical properties and special characteristics of Twaron are also similar to those of Kevlar, apart from one: it can yield an activated aramid which is preprocessed to increase the adhesion towards rubber. Akzo has developed strongly in Japan; the Japan Aramid Co. is a joint company formed by Enka and Sumitomo Chem. Co., which has imported and sold Twaron since January 1987.

2.4.4 Technora

The co-polymer type *para*-aramid fiber Technora was developed by Teijin Ltd in 1974. The production plant in Matsuyama with a capacity of 700 tonnes per year was completed in September 1994. Production capacity will be increased to 1,500 tonnes per year by 2,000 (see Fig. 2.5).

Aromatic polyamides (aramid fibers) are prepared basically from

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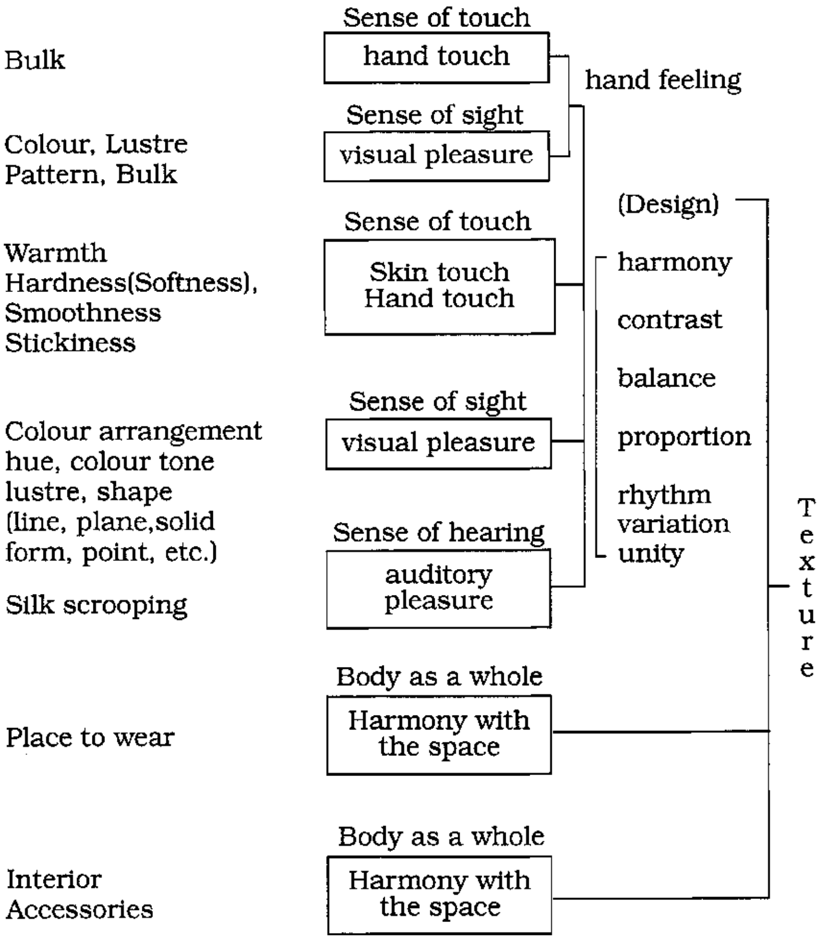
3 High-touch fibers

Among speciality fibers, the "high-touch fiber" is defined as a fiber that especially appeals to human sensitivity, such as the senses of touch, sight and hearing. The touch of a fiber is determined by its mechanical strength, bulk, warmth, softness, smoothness and/or stickiness of the material. Visually, the colour arrangement, hue, colour tone, lustre, shape, pattern and bulk are important factors. Silk-scrooping is pleasant to the ear. The finesse or texture of the whole determines the quality of the clothes.

Figure 3.1 shows the relation between the cloth-texture and the five human senses. In the first illustration, the material is improved to give a good hand-touch feeling and texture. The example includes hygroscopic polyester and nylon yielding the cool impression given by cotton, acrylic textiles, and polyester fibers, and having a better quality than silk. The second example adds the visual characteristics in order to give an unexpected impression. The third example shows the fibers with new functions such as the ceramic-blended fibers with high heat-insulating characteristics to counter the deep penetrating effect of far infra-red radiation. Better conducting fibers are used for dust-proof clothes in the electronic industry where high precision is required. The fourth example is clothes for fun, represented by scented textiles and optical and polarising fabrics that change colour according to temperature or the visual angle, so polarising light. The following sections will illustrate representative examples of these high-touch fibers.

3.1 A silk-like fiber that surpasses natural silk

Silk is distinguished by its characteristic lustre, vivid colouring, puffiness, draping and silk-scrooping. A silk-like fiber is defined as a chemical fiber that generally possesses at least some of these silk characteristics, or that which specifically provides characteristics of silk as a whole.



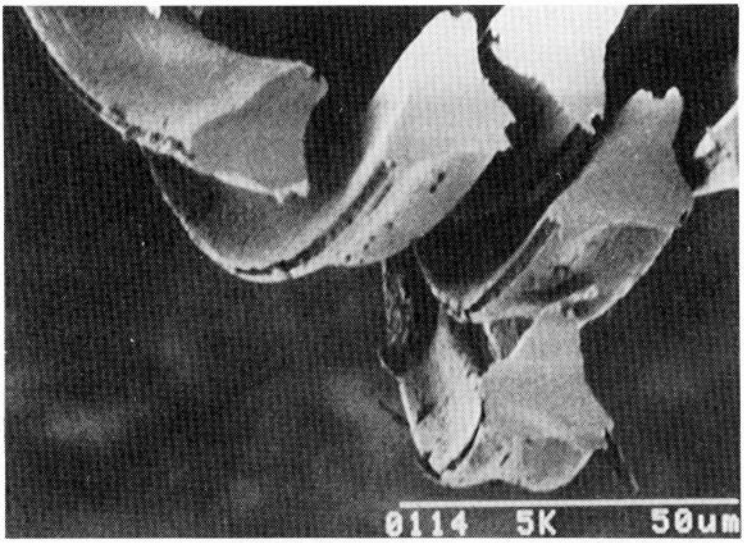
3.1 Cloth texture and the five senses.

The production of artificial silk has long been attempted. The first artificial silk chemical fiber started its production in 1891, following Count Chardonnet's invention of a silk-like fiber (rayon) derived from nitrocellulose. In 1938, Carothers of Du Pont developed the polyamide fiber "nylon" from an investigation designed to synthesise the amide-link present in silk. Nylon was an epoch-making fiber with silk-like characteristics, and even now is widely used as one of three big synthetic fibers, which include polyester and acrylic fibers. These two inventions, although on a different time-scale, were motivated by an affection for silk, and produced completely new types of fiber.

The commercial production of synthetic fibers in Japan started in 1951 with vinylon, followed by nylon in 1952, acrylic fibers in 1957 and polyesters in

Table 3.1. Development of silky polyesters: history and technology

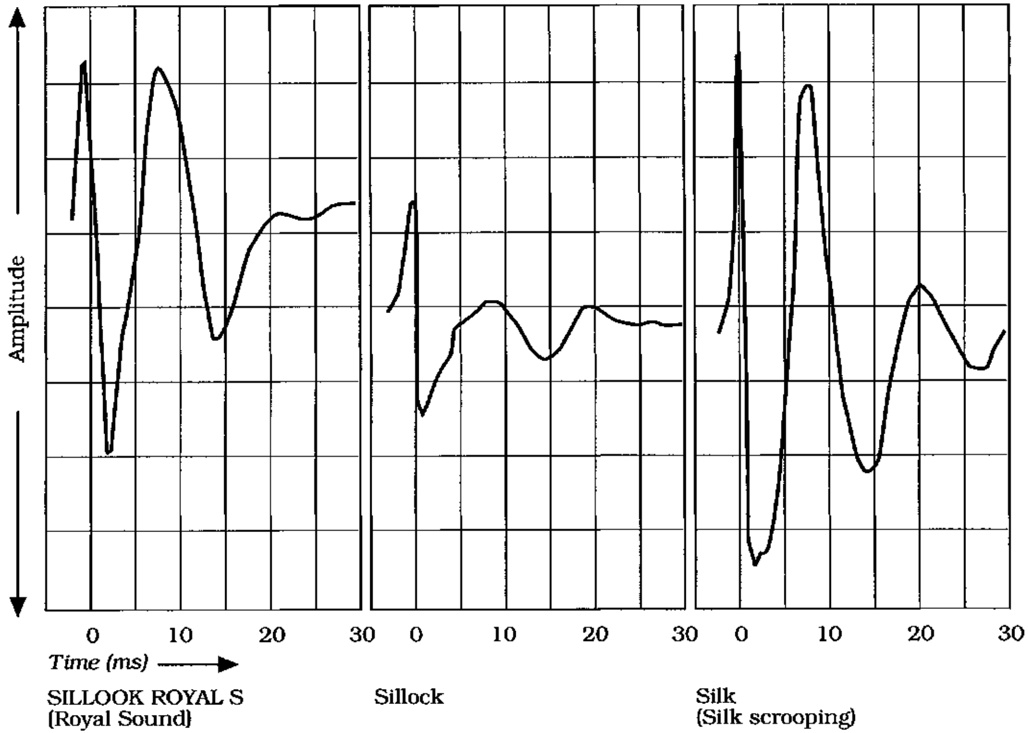
Year	Technology developed	Aim	Effect
1960	Triangular cross-section	Silk-like cross-section	Silk-lustre, silk-crispness
1970	Alkali treatment	Sericin-removal imitation	Drape
1971	Multiple fibers	Silk fineness (1 denier)	Fineness, elegance
1975	Blended fibers of different shrinkage	Silk puffiness	Silk softness, puffiness
1976	Change of surface structure	Imitation of wild silk surface	Silk-scrooping
1985	Unevenness	Silk unevenness	Natural silk-like



3.2 Sillook Royal S (Toray Industry Co.).

1958. These synthetic fibers have a round cross-section, and give a flat and paper-like touch. Since natural silk has a triangular cross-section, each company competed to produce fibers with a triangular or non-circular cross-section. Indeed, most of the textile technologies available today were established in the course of developing silk-like materials.

The history of silk-like material development can be divided into four or five generations, as analysed in Table 3.1 in terms of the development concept and the technical characteristics. The production of cleaner polymer and triangular cross-sectional fibers enabled an increase in transparency, lustre and crispness in the first generation to approach natural silk. Silk-like puffiness was achieved by varying the mono-filament length in the second

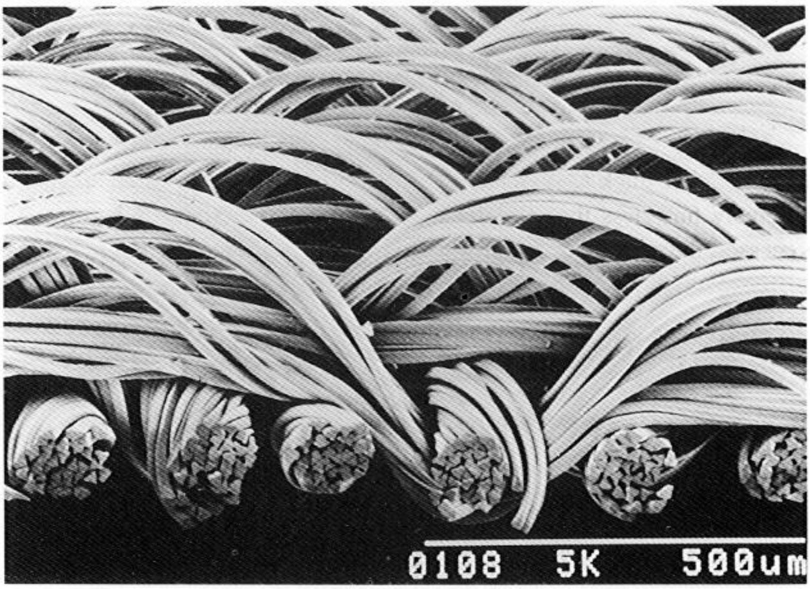


3.3 Sound wave of Royal sound (Toray Industries Co.) (comparison with silk scrooping).

generation. Combined temporary twisting and irregular drawing techniques were adopted in the third generation to gain the unevenness of natural silk and produce spun silk. Microscopic technology was applied in the wave of high technology to develop the three-petal cross-section (see Fig. 3.2) or irregular cross-section technology to produce ultra-fine fibers and imitate the silk-scrooping sound.

Toray developed the silky polyester fiber Sillook Royal S, which has a three-petal shaped cross-section with micro-slits of the order of 0.1 mm at each petal top. These micro-slits absorb the reflected light, and provide the vivid deep colour and elegant anisotropic lustre simultaneously. The micro-slits effectively prevent the worn-out shaping of the cloth, and introduce the elegant silk-scrooping and the pleasant cloth-rustling sound when two edges of a micro-slit are touched and rubbed. Sillook Royal is silk-like, not only from its hand touch, but also from a visual and auditory standpoint.

Cloth rustling and silk scrooping are generated by rubbing clothes or fibers against each other. Here the rubbing operation gives the rustling sound (high-frequency sound) by high-speed rubbing and scrooping (low-frequency sound) by low-speed rubbing (graphically shown in Fig. 3.3). The silk-like materials generated over these years were developed, not only to imitate natural silk, but also to create a new hand touch and elegance that only synthetic fibers can provide. For example, new technology was developed to

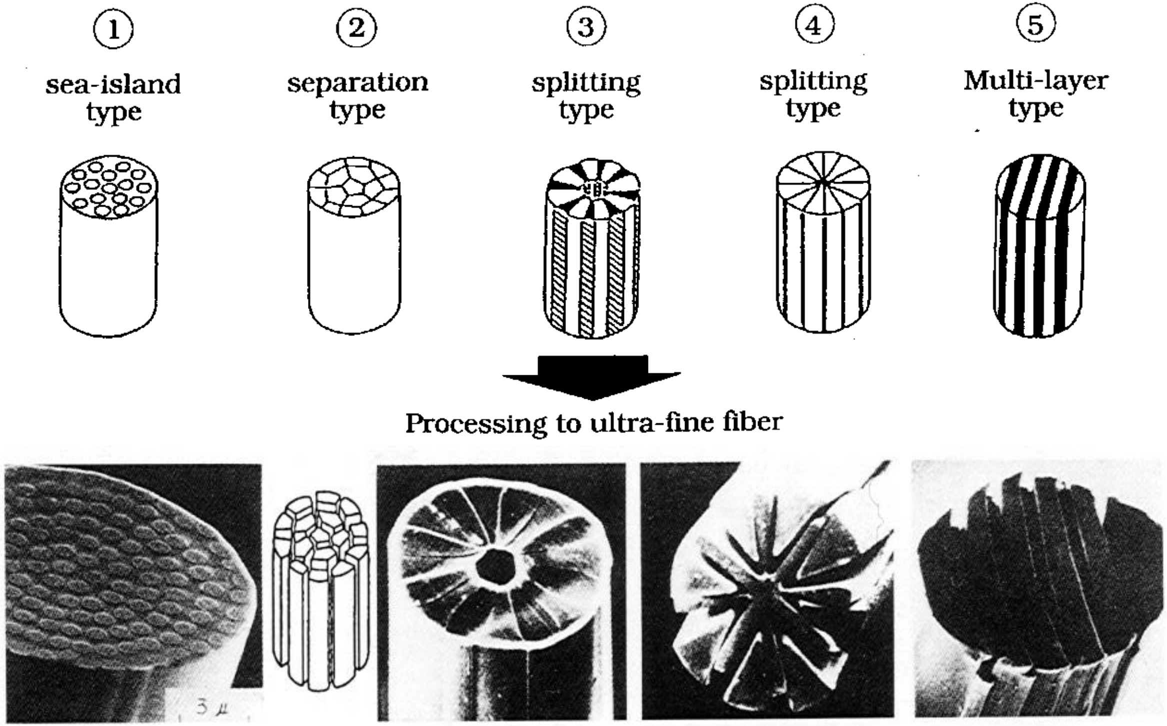


3.4 Sillook-Sildew (Toray Industry Co.).

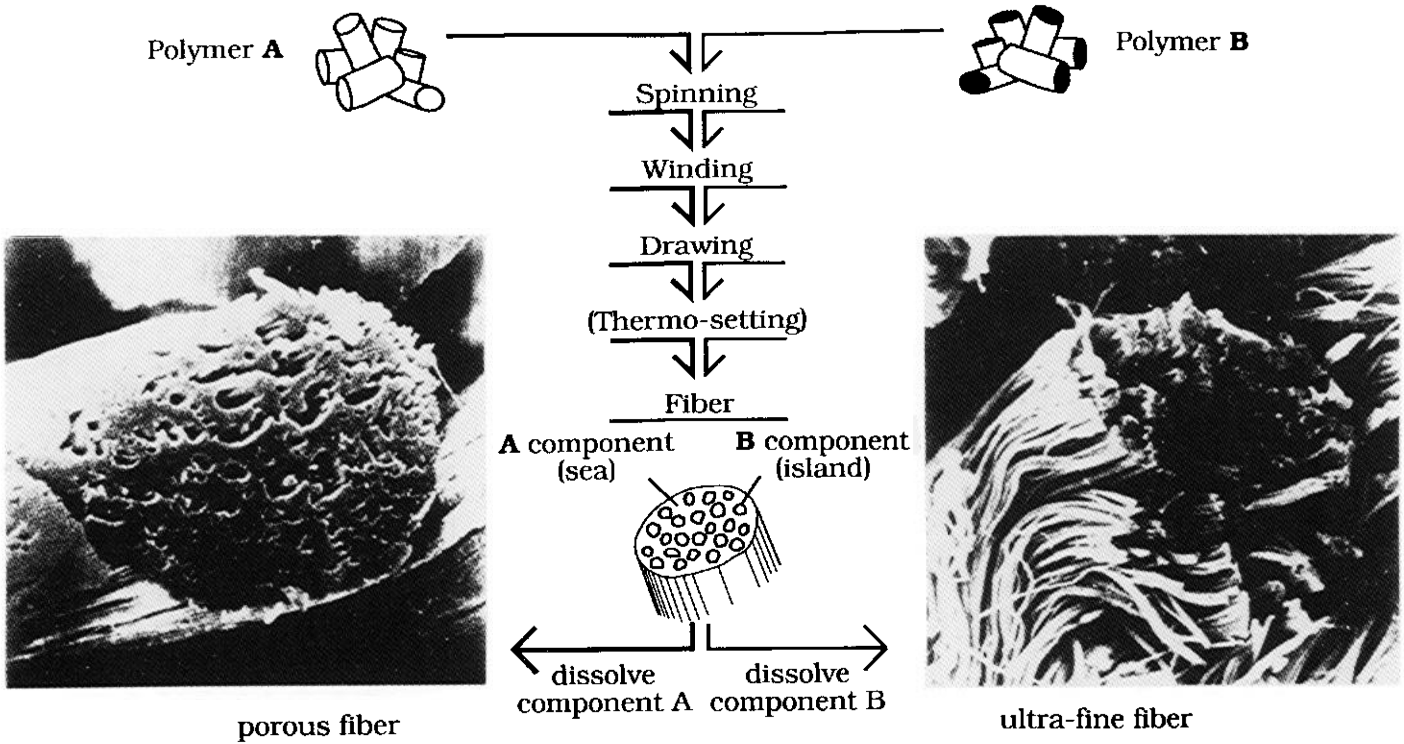
spin ultra-fine fibers, to form slits on the fiber surface, to spin the fibers with uneven cross-section (thick and thin in parts), etc. and in an unexpected way created a new type of elegance quite different from natural fibers. Toray developed the conjugate yarn with different shrinking characteristics (Sillook-Sildew) which consists of high- and low-shrinking fibers. When the fabric or knit product of this yarn is heated after the dyeing process, the high-shrinking fibers shrink and relax the low-shrinking fibers. As a result, the fabric becomes puffy and yields a new hand touch different from natural silk (see Fig. 3.4). Although the molecular design of polymers and fibers will be re-evaluated from a stand-point different from that mentioned above, the fabrication of silk-like materials is an evergreen subject for textile engineers.

3.2 The challenge of ultra-fine fibers

Several new microfibric technologies have been developed in Japan, represented by the "sea–island (islands-in-the-sea)" type (Type 1), the "separation" type (Type 2), the "fiber-splitting" type (Types 3 and 4) and the "multi-layer" type (Type 5) as schematically shown in Fig. 3.5. Type 1 shown here is somewhat different from the "sea–island types" currently employed by Toray and Kuraray, and even for these two companies production techniques are different. In this first classification the fiber is composed of two component polymers A (sea) and B (cores or islands). Toray arranges them in parallel, with polymers A and B in the conjugate spinning nozzle prior to spinning-out, but Kuraray blends them randomly in the extruder. When spun and fabricated, the A component (polystyrene) is removed by dissolving in a solvent to produce ultra-fine fibers of the B component (polyester or polyamide by Toray and nylon by Kuraray). Although the initial mono-filament (AB composite fiber) is rather thick (3–5 denier), the mono-filament of the B component is extremely fine (less than 0.1 denier). Owing to the difference between the processes, the microfiber of Toray is continuous and homogeneous in terms of its thickness (0.1 denier), whereas Kuraray's varies from 0.01 to 0.1 denier discontinuously but can be processed in the reversed "sea–island" to produce the lotus-root-shaped (porous) fiber (see Fig. 3.6). These different "sea–island" type fibers are commercialised for artificial leather such as Ecsaine (Toray, known as Alcantara in Europe and Ultrasuede in the USA) and Kurarino (Kuraray). Type 2 (the "separation type") can be considered as a variation of the "sea–island" type or the "fiber-splitting" type. The recent developments in this area are described in Chapter 7. Types 3 and 4 in Fig. 3.5 are termed the fiber-splitting" type, whereas polyester and nylon are composite-spun and then split into their respective components. Type 3 is a



3.5 Ultra-fine fiber technology by composite spinning.



3.6 Fiber formation and shape (Kuraray Co.).

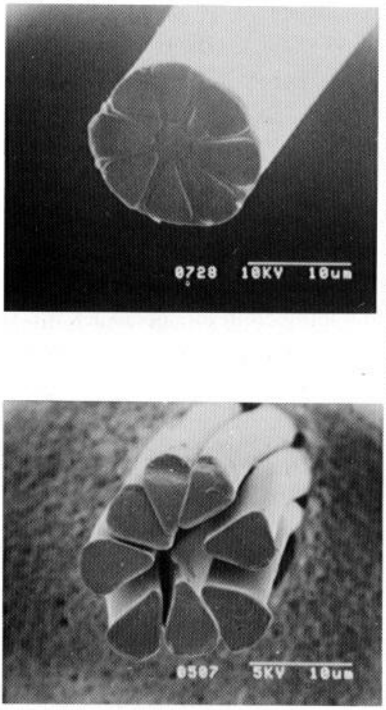
hollow composite fiber of polyester and nylon developed by Teijin (commercially available as Highlake and Elec). The composite fiber is split mechanically into 16 sections, and its mono-filament after splitting has a homogeneous cross-section of 0.23 denier. Kanebo developed Type 4 microfiber with nylon in the core and polyester (commercially available as Belleseime and Savina), and its mono-filament after splitting is on average 0.15 denier thick.

Melt-blow spinning, tuck spinning, super-drawing, etc. are also employed to produce microfibers. These microfibers are mostly applied to the hair fabrics such as non-woven (artificial leather) or knit fabrics and high-density fabrics for special functions such as water repellency. Based on the high technology of microfibers, each company in its own way is looking for a market for new types of high-touch fibers with specific characteristics. Microfibers have opened up a new field of applications and expanded the expression potential of fibric materials.

Although ultra-fine fiber technology was developed first to produce artificial leather, its know-how was further developed to produce even finer fibers, which found an unexpected application as a wiping cloth for spectacles. The cloth can also be applied to clean car mirrors, remove oily dirt from windows, clean computers and electro-optics devices, polish and clean jewels and noble metals, polish crystals, clean showcases and frames, clean panels of audio/visual devices and optical discs, remove fingerprints on photos and films, and clean plastic products, etc. Here high-density fabric is variously processed into puffs, gloves, quilts and even into tapes, according to the handling convenience needed. For example, high-density fabric tape is used as a built-in type cleaner for machines. High-density fabric is thus a new frontier fabric, which may find even wider applications.

3.2.1 High-touch material Zepyr 200

Kanebo developed the conjugate yarns Belima and Belima X and an artificial leather/suede Belleseime by imitating the bicomponent structure of silk or wool. Belima and Belima X are produced from the radial conjugate fibers of multi-layer bicomponent filament by splitting into ultra-fine fibers of 0.1–0.5 denier. The radial conjugate fibers were further developed to a highly soft-touch nylon fabric Zepyr 200. The conjugate fiber for Zepyr 200 is composed of 75% nylon (0.67 denier) in eight triangular segments and 25% polyester (0.17 denier) in a radial segment. When the woven or knitted fabrics of the radial conjugate fiber are alkali-treated, the polyester portion is removed and the fiber is split (Fig. 3.7). Then the fabrics become 100% nylon, and they can



3.7 Electron microscopic view of Zepyr 200 cross-section: top, before splitting; bottom, after splitting (Kanebo Ltd).

be finished by the conventional nylon processing to Zepyr 200, which has an extremely soft touch and an elegant appearance. For example, when the original yarn of 50 filaments, 100 denier in total, is alkali-treated, the resulted yarn is then composed of 400 filaments, 75 denier in total, i.e. each filament is extremely fine nylon of 0.18 denier. The cross-section of the fiber shows fine flower petals of several micrometres as displayed in Fig. 3.7. Because of its characteristic cross-section shape, Zepyr 200 is highly bulky, extremely soft and brilliantly coloured. Since nylon is lower in Young's modulus and density than polyester, nylon is much softer and lighter than polyester of the same fineness. Thus Zepyr 200 is a real new fabric which offers the following:

1 A silk-like soft touch and rich drapability without the rustling noise of polyester fabrics.
2 A mild and decent colour of brilliance without a see-through effect (owing to the characteristics of an assembly of eight petal-like cross-sections).

The extremely fine denier technology accumulated in developing artificial leather has thus been applied to general fabrics for clothing in the development of Zepyr 200, which pioneered a new era of nylon which expanded its application to the field of ultra-fine fiber fabrics for high-quality garments and sportswear.

3.2.2 Perfect cleaning with ultra-fine fibers

Dirt or smudges on spectacles are always a nuisance to those who wear them. Such dirt can spread over the entire glass surface when wiped with a handkerchief, or the glass may be scratched when wiped with a tissue paper. As mentioned previously, a special wiping cloth for spectacles was developed by utilising high-density fabrics of ultra-fine fibers, which now sells by the million.

Kanebo launched the first spectacles-wiping cloth made of ultra-fine fiber fabric (Belleseime) in 1978. Kanebo developed its first ultra-fine fiber Belinu in 1974, and then Belima X in 1975. These fibers are composed of polyester radially divided into eight sections by polyamide (Fig. 3.5, Type 4), and split in 8–13 mono-filaments by a technology that involves temporary twisting or swelling. The basic ultra-fine fiber cloth is knit, with each mono-filament after splitting 0.1–0.2 denier thick.

Teijin developed the hollow splitting-type composite fiber utilised for spectacles-wiping cloth in 1982. This ultra-fine fiber Highlake is also made of polyester and polyamide, radially sectioned and arranged around a hollow fiber (Fig. 3.5 Type 3). The original fiber is split into 16 mono-filaments, with each component mechanically woven into cloth. Each mono-filament is 0.23 denier thick.

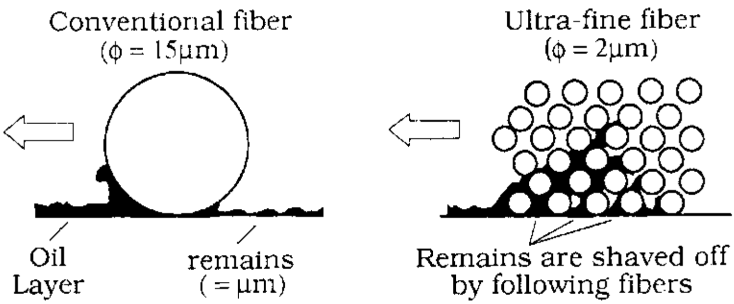
Kuraray adopted a multi-layer type (Fig. 3.5, Type 5), where nylon and polyester form 11 layers alternatively. The composite fiber is longitudinally split into 11 flat ultra-fine mono-filaments (0.2–0.3 denier each) in the dyeing process, after being woven into cloth. Although the ultra-fine effect is less apparent in comparison with other types, the composite fiber of Type 5 can be split easily, and the cloth of this composite fiber is soft because of the extremely flat shape of filaments (1–2 μm thick and 10-15 μm wide). Nylon shrinks during the splitting process to add extra soft handling to the cloth.

Toray started research and development in 1976 into the ultra-fine fiber cloth UT-C and the wiping cloth Toraysee, applying the technology developed for the "sea–island" type composite fiber. As described, these have numerous cores and were developed for the non-woven artificial leather Ecsaine in 1970.

Each company developed its own composite-spinning know-how for producing ultra-fine fibers and as a result the respective products have their own characteristics. Here, the cleaning mechanism of the ultra-fine fiber wiping cloth will be demonstrated by using as an example the Toraysee series developed by Toray. Most of the sticky dirt is caused by dust accumulating on thin layers of fat, which merely spreads and is barely touched by conventional wiping cloths, such as the chamois leather (natural leather) or waste cloth. This is because the fiber of these wiping cloths is normally 10 mm thick and is unable to capture the 1 μm thick oil layers. Toray offers many types of Ecsaine (Alcantara, Ultrasuede); a standard type is made from a composite fiber with 16 core components and a soft-thin type made from composite fiber with 36 core components. They developed the composite fiber with 70 core components for the Toraysee and UT-C series. Since 10 sea–island type composite filaments are twisted into a fiber and woven, a single fiber of the fabric consists of 700 micromono-filaments after the seam components have been removed by dissolving in a solvent. The filament density of the resulting fabric is, therefore, approximately 220,000 filaments per inch. A mono-filament of this fabric is only 0.05 denier or 2.0 μm thick, and is claimed to be the finest continuous filament commercially available in the world. These ultra-fine filaments can penetrate into the thin fatty layer of dirt and trap it within the micro-pockets among the filaments. Another reason for the excellent wiping effect is because of the good compatibility of the Toraysee series (made of polyester) with skin fat (fatty acid ester). The dirt trapped in the micro-pockets can be removed and the wiping characteristics can be regenerated by washing.

The wiping mechanism of the Toraysee series can be attributed to the following effects according to Dr Okamoto, Toray Industry Inc.:

1 *Sharp-shaving effect*. The fatty layer of dirt attached to the spectacle surface is about 1 μm thick. When wiped with a conventional cloth with thick filaments, the fatty dirt is caught and stays on the surface of the filaments. Thus, the cleaning effect deteriorates considerably when the whole surface

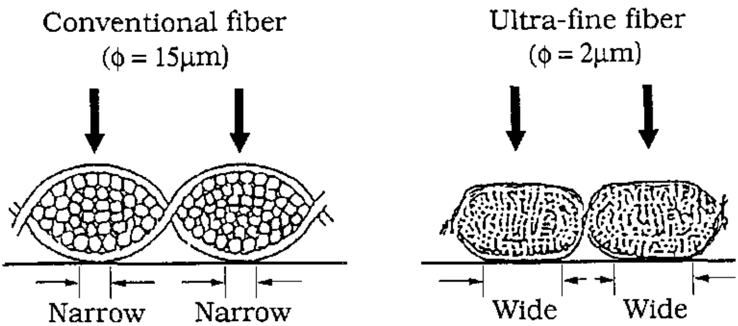


3.8 Multi- and sharp-shaving effect.

is covered. When the wiping cloth is made of ultra-fine fibers, the fatty dirts are removed and drawn into the micro-pockets (see Fig. 3.8).

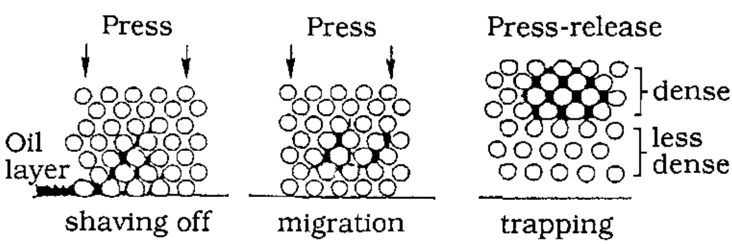
2 *Multi-shaving effect.* The contact frequency with the glass surface is much higher for ultra-fine fibers than for a single fiber before it is split into 70 ultra-fine fibers. As a two-blade razor is more effective in shaving than a single-blade razor, so a wiping cloth of ultra-fine fibers removes dirt more effectively than a single fiber. The ultra-fine fibers are thin and soft, and no scratch is left on the glass surface (see Fig. 3.8).

3 *Wide-contact effect.* A wiping cloth of ultra-fine fibers contacts over a wider area with the glass surface than a conventional wiping cloth. Thus the effective wiping area increases in comparison (see Fig. 3.9).



3.9 Wide-contact effect.

4 *Inner trap effect.* A wiping cloth made of ultra-fine fiber contains micro-pockets. As the cloth is pressed by the finger wiping the spectacles, the fatty dirt on the glass is adsorbed by the micro-pockets. When the pressure is released, the fatty dirt migrates into the inner part of the cloth where the fiber density is higher. After migration, there is less dirt on the surface area of the cloth, and the cleaning efficiency recovers (see Fig. 3.10).



3.10 Inner trap effect.

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