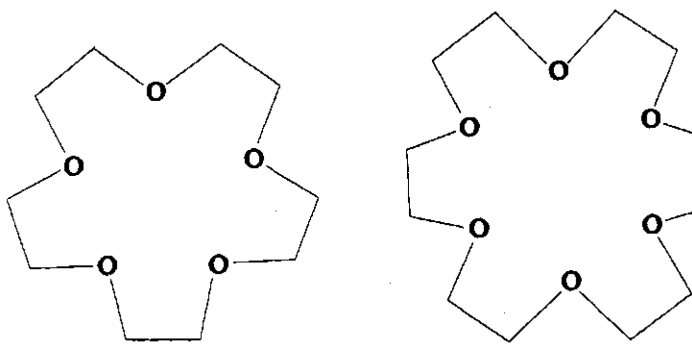
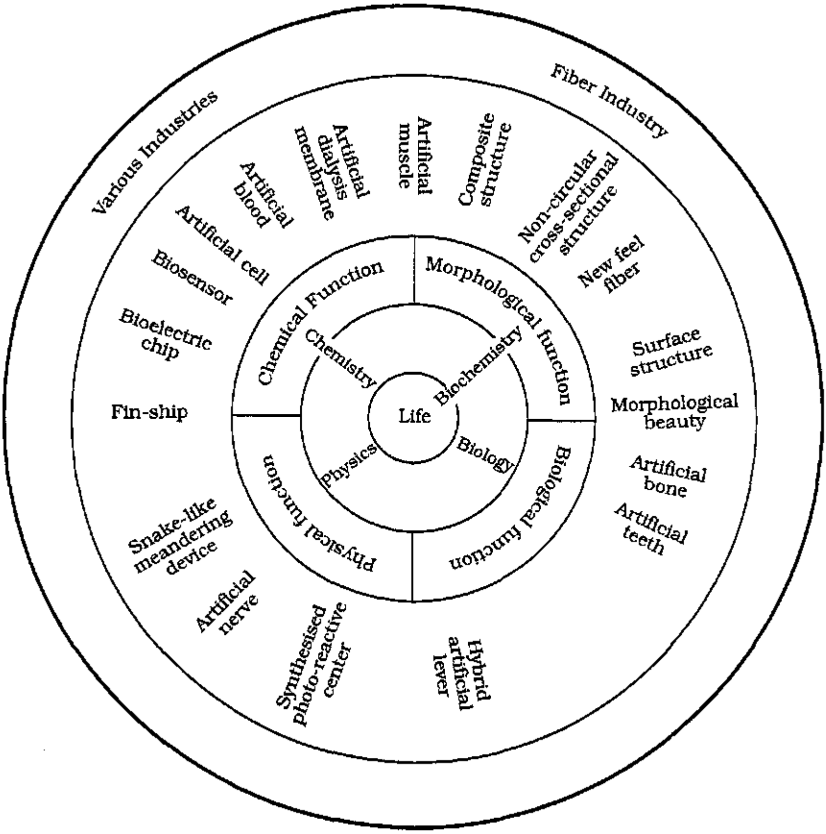
4 Biomimetic chemistry and fibers

The Nobel Prize for Chemistry in 1987 was jointly awarded to Dr Pedersen, formerly of Du Pont, Professor Cram of California University and Professor Lehn of Pasteur University, who pioneered biomimetic chemistry. Dr Pedersen synthesised a large-ring compound designated a "crown ether" (Fig. 4.1) in 1967, which was later theoretically investigated by Professors Cram and Lehn, and resulted in opening up a new field of chemistry. This research showed the potential for producing artificial enzymes and cell membranes. Subsequently, many investigations have been undertaken to mimic biological functions. As a result, not only single but also cooperative biological functions can be realised artificially.

The term "biomimetic chemistry" was proposed by Professor Breslow of Columbia University in 1972 to distinguish this new research field. Here "bio" denotes the living system, and "mimetic" its imitation. Professor Breslow first investigated the enzymic functions of crown ethers, and later developed the synthesis of macromolecules whose functions could be applied practically. Professor Breslow reproduced chemically enzymic reactions by using model systems, and Dr Pedersen synthesised materials that are



4.1 Large ring compound "crown ether".



4.2 Biomimetics in fibers.

analogous with organisms in their ability to react selectively with particular ions or molecules. This field of research and technology is now termed "biomimetics". Since the living organism is too complex and subtle to imitate as a whole, many attempts have been made to reproduce the functions of a part of the living organism with synthesised material. "Functions" here constitute important characteristics of living organisms. Fibers in living systems relate to morphological, biological, chemical and physical functions, as indicated in Fig. 4.2. This chapter outlines the morphological and biological functions, as related to the fiber industry.

4.1 Applications of morphology/structure

The structure and functions of biological materials are precise and subtle. However, if the way in which structure and function are related can be identified, then it might be possible to replicate this molecular design in the service of the fiber industry. For this purpose the fiber industry may conveniently be divided into:

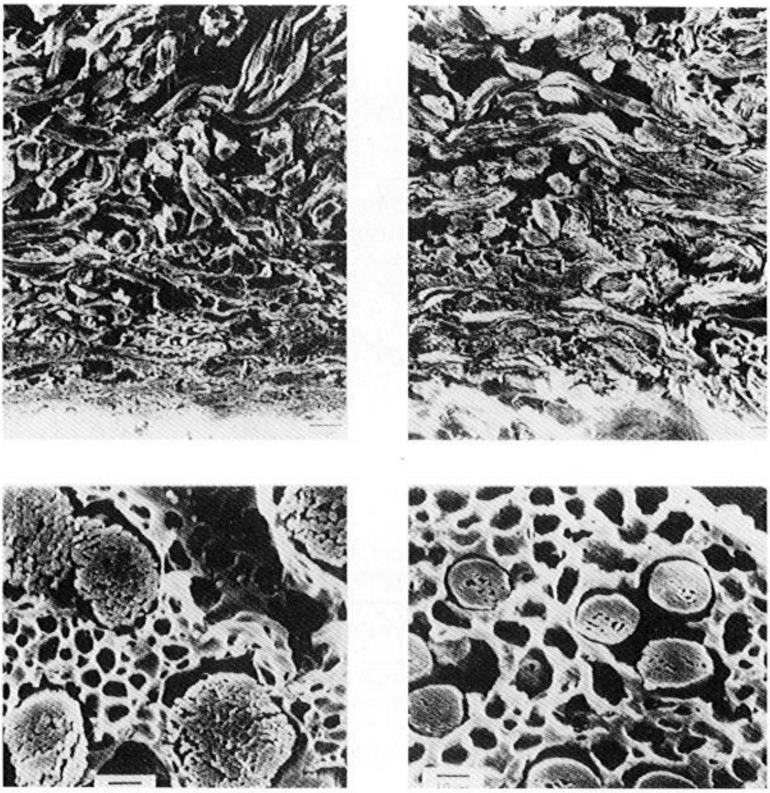
1 The spinning industry of mainly natural fibers such as, cotton, wool and silk.
2 The chemical man-made synthetic fiber industry.

There has been a positive interaction between these two areas. Pioneers, fascinated with silk, made great efforts to produce a silk-like fiber by dissolving cellulose and spinning its solution. The name "rayon" implies that it looked like a "ray". The patents applied for by industry relate the history and trend of the technical developments in this field. Many of the synthetic fibers were developed to imitate the structure and characteristics of natural fibers. For example, a fiber with a silky-lustre and smooth hand-feel was produced by copying the triangular cross-section of silk. A fiber with a deformed cross-section was developed to prepare a cotton-like macaroni-type fiber. This technology was applied to the industrial production of separation films and dialysis membranes for artificial kidneys, which is one of the greatest achievements of present-day high technology.

When comparing the patents applied for by Du Pont with those of Japanese companies, it is evident that Du Pont have placed their emphasis on fundamental research and have been quick to learn from nature. Their Japanese counterparts have been quick to export these ideas to develop the field in a different direction. For example, the silk-like fiber with deformed cross-section produced in Japan has its roots in "Quiana", developed by Du Pont. Many industries in Japan developed silk-like processing technology by combining the spinning of fibers with triangular cross-section and their blending with fibers having a different crimp ratio.

This spinning and processing technology for two components with different characteristics was developed by copying the double layer structure of wool. An extension of these ideas led to the sea–island composite spinning technology described in Chapter 3. This has further been utilised to produce optical and antistatic fibers.

Composite spinning was also applied to produce artificial leather. Natural leather is composed of layers of bundle assemblies, with finer fibers approaching the surface from the inner skin side. At the surface these fine fibers are disbundled and entangled. This structure was successfully imitated by deliberately entangling bundles of fine fibers. Thus, many new artificial leather products have now appeared (Fig. 4.3). Through first imitating natural fibers, natural fibers have now been surpassed. For example, the super-fibers such as carbon, heat-resistant, glass, ceramic and amorphous fiber are now better than the original. It has, therefore, become a biomimetic industry.

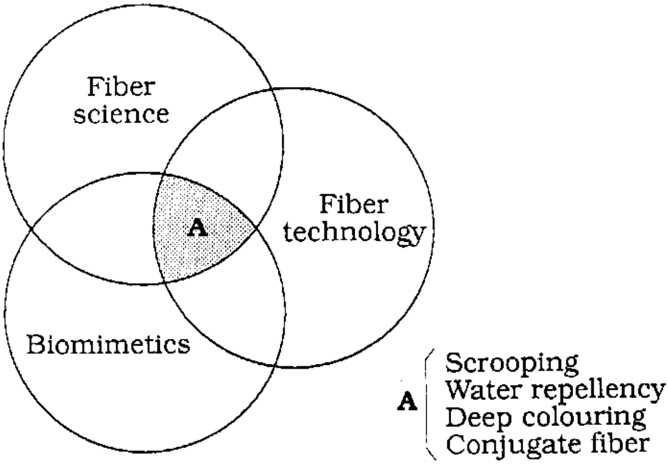


4.3 Which is genuine? The top left and top right show the sectional structure of suede-type leather. *Top left:* natural leather. *Top right:* artificial leather Kuraline F (Kuraray Co.). *Bottom left:* full-grain soft (artificial) leather Kuraline F (Kuraray Co.). *Bottom right:* hard (artificial) leather Kuraline for shoes (Kuraray Co.).

Fiber science and fiber technology can be related to biomimetics, as indicated in Fig. 4.4, where the overlapping part A denotes specific technologies based on three different fields of knowledge. In this way new technologies concerning conjugated fibers, scrooping, water repellency and deep colouring effects were developed. Table 4.1 shows examples of biomimetics in the fiber industry which yielded new products by applying the morphological functions of living organisms. This frontier of fiber technology will now be reviewed.

4.1.1 Composite structure of natural fur

Toray has developed a mink-like artificial fur Furtastic which imitates the composite structure of natural fur, and follows on from its suede-type material



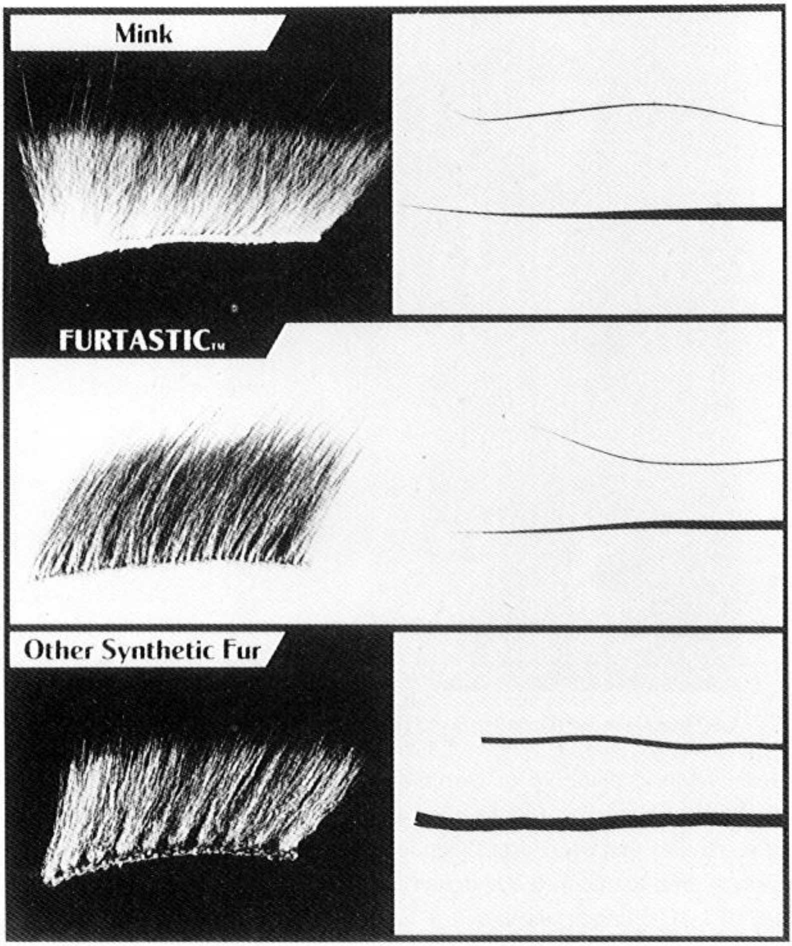
4.4 Interaction of fiber science, fiber technology and biomimetics.

Table 4.1. Examples of biomimetics in fiber industries

Function	Structure	Living system	Biomimetics
	Composite structure	Natural leather	Ecsaine (Toray Industry Inc.)
Morphology	Non-circular cross-sectional structure	Silk, wool	Grasem (Kanebo Ltd.)
	Surface structure	Lotus leaf	Microft-Lectus (Teijin Co.)
	Morphological beauty	Butterfly, moth	Dephorl (Kuraray Co.) Microcrater (Kuraray Co.)

Ecsaine. Observed microscopically, it is seen to consist of piles of extremely fine fibers and "stinging hairs", densely assembled and standing on a skin as in natural mink fur. Furtastic has a double-layer structure composed of "stinging hairs" and "piles" of sharp ends which are densely planted on the skin base as shown in Fig. 4.5 and 4.6.

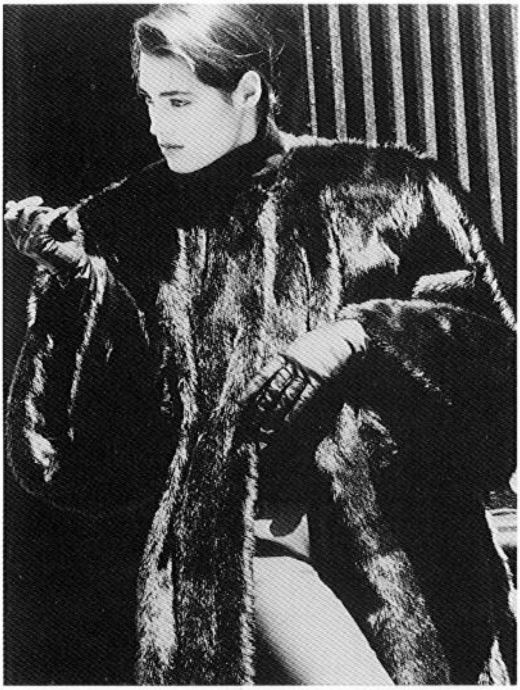
The know-how developed for Ecsaine production was applied to prepare the skin base and the piles of extremely fine fibers. The "stinging hairs" were produced using a newly established technology developed specifically for this purpose. A second technique developed specially for Furtastic is "flocking", to prepare a textile with high raising density. Toray developed flocking technology that could increase the raising density to 17,000 flocks per square centimetre. A patch of natural fur from a single mink is *ca.* 10 cm wide, and the back skins of these patches are stitched together to make the fur broader and bulkier into the coat. Furtastic is produced as a broad sheet, but in a way which looks as though smaller patches had been stitched together. This can be achieved by changing colours carefully. This takes account of the fact that each mink has its specific colour characteristics. Toray has in this way



4.5 Side view of the standing hairs and hair-ends in Furtastic (Toray Industry Co.).

produced more than 36 000 m^2 of artificial fur, which has mainly been employed for sports- and ladies-wear.

Most of the full-grain artificial leathers are produced by nylon-coating PVC leather, or urethane-coating non-woven fabrics. These products are mainly used for making bags or shoes. However, the moisture vapour transmission and hand feel is not as good as full-grain natural leather, because of the polymer-coated surface. Natural leathers can be divided into either (i) the raised suede-type or (ii) the full grain sheep-type. The sheep-type full-grain artificial leather Youest was produced to compensate for the defects in conventional artificial leathers. Ecsaine and Furtastic belong to type (i) and Youest as noted to type (ii). Toray made up the surface of Youest from



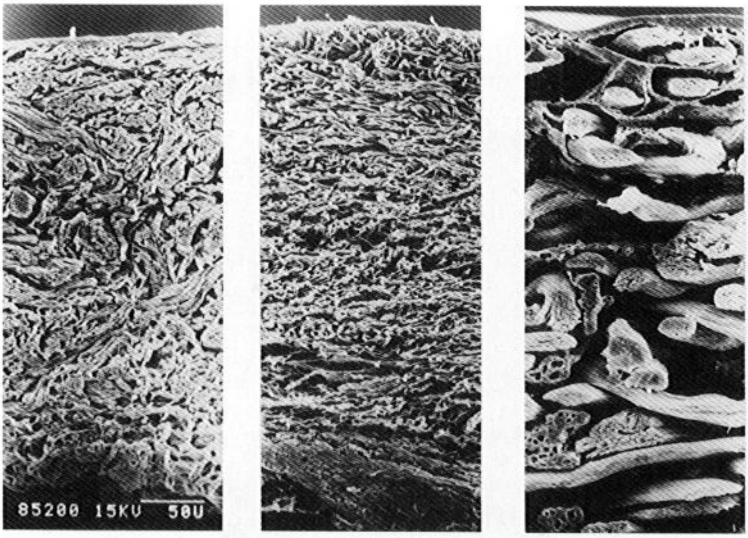
4.6 Three-layered fabric Furtastic (Toray Industry Co.).

high-density fabric made up of extremely fine fibers. When fabric is made from such very fine fibers, it looks like a film to the naked eye but its structure closely resembles that of natural sheep leather (see Fig. 4.7).

Extremely fine filament (0.001 denier) is used for Youest, whereas less fine filament (0.1–0.05 denier) is used for Ecsaine. Youest is thin enough to be used for clothing materials having a soft skin-like feeling.

Toray also developed the micro-pocket fabric Toraysee by applying a new microfiberisation technology. Ecsaine, Furtastic and Youest are non-woven fabrics, but Toraysee is a high-density woven fabric with ultra-fine fibers, which possesses pores containing micro-pockets. Since dust or oil is absorbed by these micro-pockets, Toraysee is well suited for cleaning optical lenses as described in Chapter 3. Some 700 ultra-fine polyester filaments ($\phi = 0.01$ mm) are bundled and woven to make Toraysee without causing fuzzing.

Toray also developed the electrically charged non-woven fabric Toraymicron with a highly oriented polarised structure. Dust or bacteria is charged either positive or negative. Thus these charged micro-particles are caught electrically as well as physically as with conventional filters of non-woven fabrics, when filtered through Toraymicron. This material is made from non-woven fabrics of ultra-fine fibers, using the same techniques as for

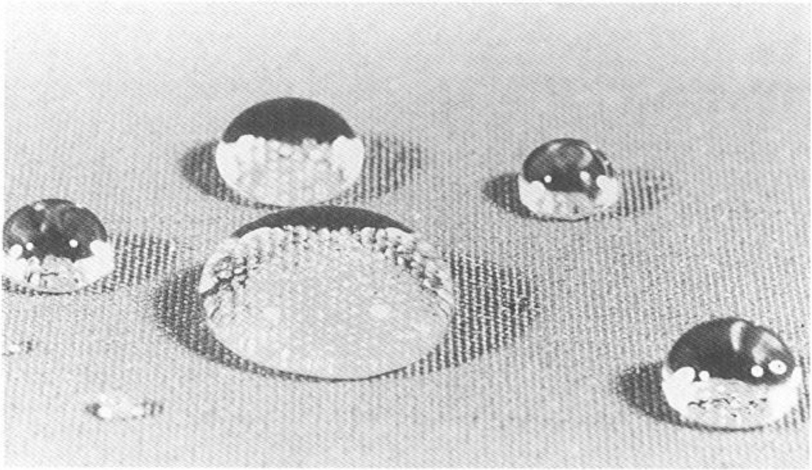


4.7 Cross-sectional view of Youest: *left*, Youest; *centre*, natural leather; *right*, conventional artificial leather (Toray Industry Co.).

Ecsaine. A better filtration efficiency would be expected with a finer-mesh assembly of thin filaments. The filtration efficiency of Toraymicron is further improved by its electrical properties which increase the dust-collecting ability without causing pressure loss. Toraymicron is, therefore, used for the highly efficient filters for clean rooms, masks, machine filters and filters for domestic vacuum cleaners.

4.1.2 Super-Microft based on the structure of a lotus leaf

In 1987 the Technology Prize of the Society of Fiber Science and Technology, Japan, was awarded to the Teijin Co. for its development of fabrics with high water repellency. Super-Microft is one that was designed by emulating the structure of a lotus leaf. Water rolls like mercury from the lotus leaf, whose surface is microscopically rough and covered with a wax-like substance with low surface tension. When water is dropped on to the surface of a lotus leaf; air is trapped in the dents and forms a boundary with water. The contact angle of the water is large, because of the wax-like substance (see Fig. 4.8 and 4.9). The apparent contact angle depends on the evenness and roughness of the surface, and surface tension. When (i) the surface is reasonably even but with



4.8 Super-Microft on which water rolls like mercury (Teijin Ltd).

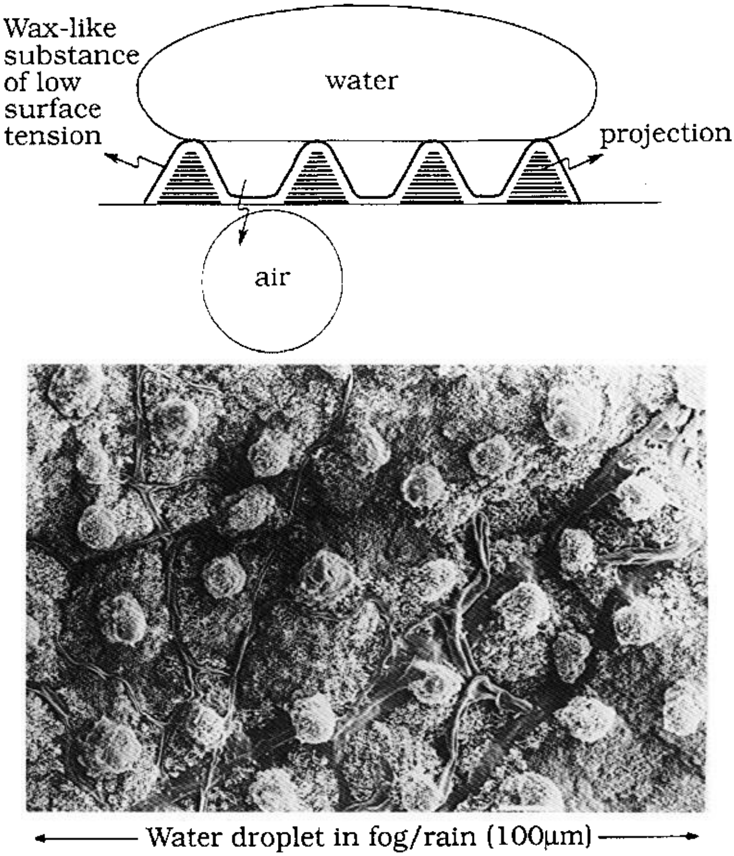
microscopic dents to enlarge the surface area and to trap air, and (ii) the surface tension of fibers is small, then water rolls well on the fabrics. Super-Microft is a highly water-repellent fabric made of polyester fibers, harnessing the water-repellent mechanism of lotus leaves.

The technology of Super-Microft production consists of:

1 The design of the original filaments (to allow air-trapping with high durability, partial crimping, and the potential to give a high bulky filament).
2 The textile design (to give a high density textile with a natural cotton hand-feel and good size stability).
3 A new dyeing process (dyeing in such a way as to produce homogeneous microscopic dents on the textile surface).
4 A new finishing process to reduce the surface tension (by combining water-repellent and wash–wear-resistant processing).

Super-Microft exhibits good water-repellent durability and a high wear resistance. The criterion required for water repellency is to have a "rolling angle" which is extremely small (less than 10°) even after five days of washing in comparison with conventional fabrics (30–40°). This ensures that a water drop rolls well on Super-Microft.

Water-repellent fabrics are widely applied in the production of outdoor sportswear (windbreaker, ski-wear), and general clothing (coat, working clothes) as well as industrial fabrics (tent, bags). So far, only water repellency that relates to the waterproof ability of fabrics has been considered. However, water repellency can also be utilised to evaporate moisture coming from the human body. The new water-repellent fabrics described above are both

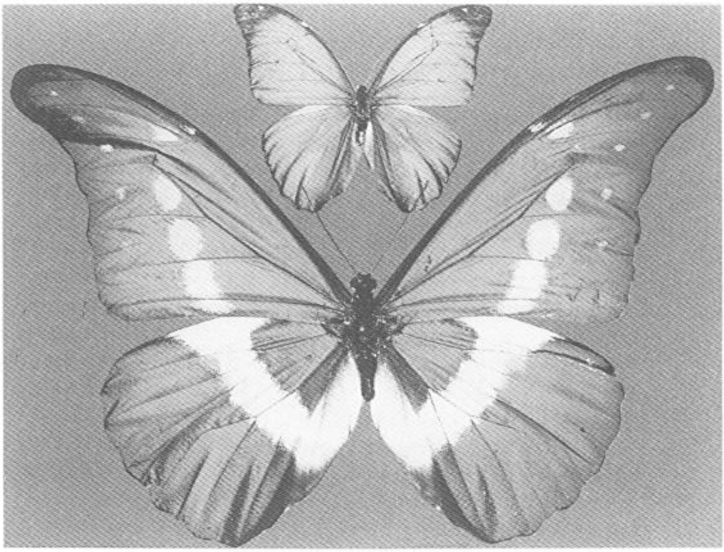


4.9 Surface of lotus leaf (Teijin Ltd).

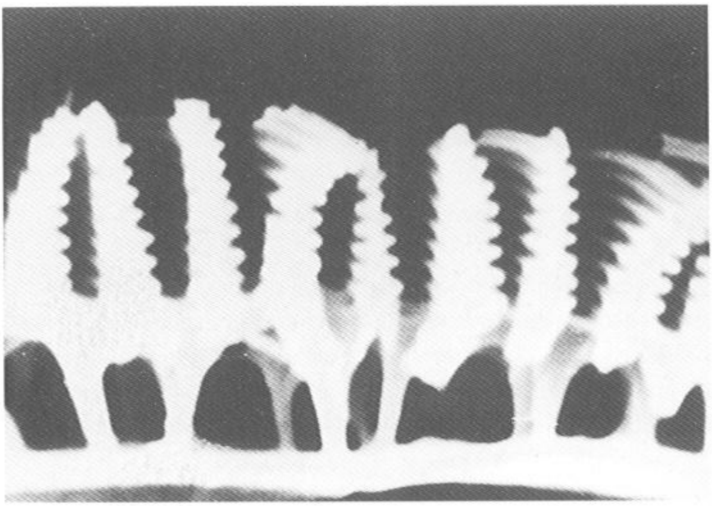
moisture-permeable and waterproof. Therefore, ski-wear from this material does not become stuffy, as does a conventional raincoat. To achieve this, water should form droplets on the surface and not spread evenly over clothes, and thus prevent a water layer forming which could stop moisture permeation. Water repellency must be considered within this overall context.

4.1.3 Morpho-structured fabrics imitate the insect morpho alae

Kuraray developed a new textile Morpho-Structured Fabrics by closely observing and reproducing the structure of the insect *Morpho aloe*. Many insects exhibit various colours according to their natural environment. The colouring mechanism control is so clever that it can teach us more about how to develop materials for clothing. Morphos (Fig. 4.10), which inhabit the



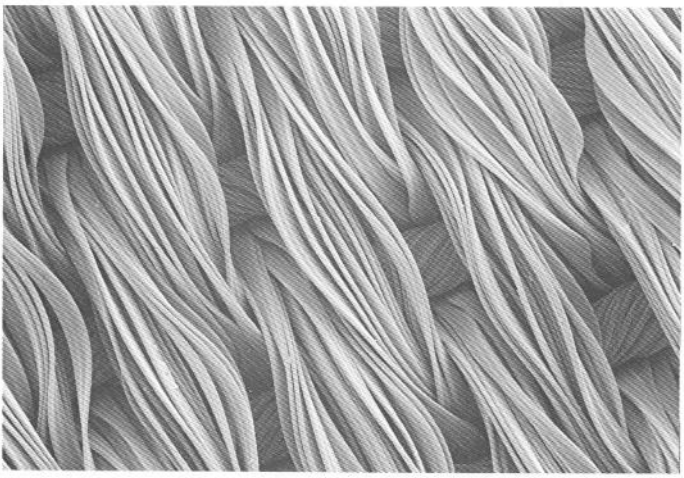
4.10 Morpho ala.



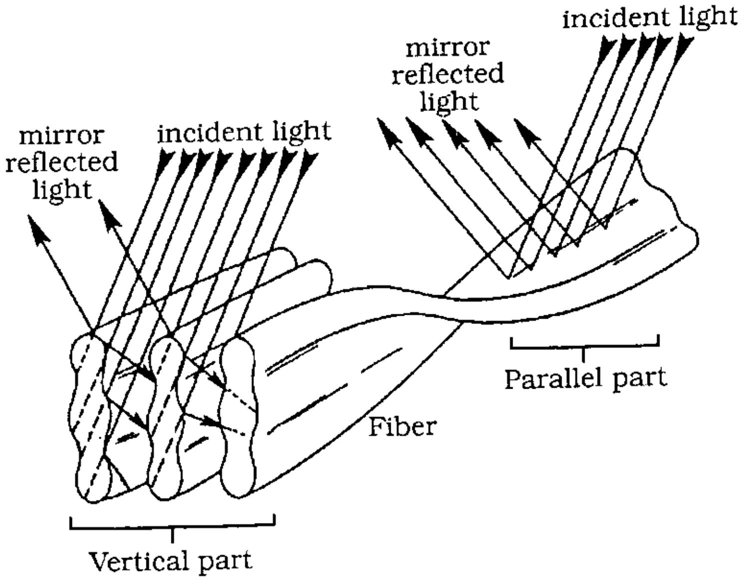
4.11 Scale structure of *morpho alae.*

Amazon valley, are one of the most beautiful genus of butterflies, with a metallic cobalt-blue colour. *Morpho hecuba* is the largest of the species, about 17 cm long. The surface structure of a butterfly alae indicates the fundamental role which the reflection ratio plays in colour appearance as a result of light interference. Since ordinary fibers have a low reflection ratio, they fail to show brilliant colours even when dyed. The colour of *Morpho alae* changes subtly according to the angle of incident light. Its scales are both coloured and non-coloured. The coloured scales are *ca.* 2 μm in height, with flat wall-like appendages with nine or ten pleats running in parallel at regular intervals of *ca.* 0.7 μm as shown in Fig. 4.11. The incident light will reflect/refract/interfere at these appendages, and brilliant metallic colours appear.

Morpho-Structured Fabrics were developed by copying the structure of *Morpho alae*. When bicomponents of different thermal properties are spun, shrinkage will occur, and the resultant fiber is effectively twisted. Morpho-Structured Fabrics are made from a twisted fiber of flat cross-section, with 80–120 twists per inch, which is achieved by thermal processing. When woven and then thermally treated, fibers are twisted and the flat surfaces of the fibers align vertically by reference to the woven fabric plane (see Fig. 4.12). The deep-colouring of Morpho-Structured Fabrics are due to the alternative horizontal/vertical alignment of the flat surfaces of fibers which cause the repeated reflection/absorption of the incident light and reduce the direct reflection (see Fig. 4.13). Thus Morpho-Structured Fabrics exhibit a deep brilliant colour, and also have soft and elegant drape characteristics, suited to dresses and blouses, which imparts a new feeling. The deep slim ditches in the surface of "Diphorl" give rise to a full variety of deep and brilliant colours that conventional fabrics are unable to achieve.



4.12 Morpho-Structured Fabrics: potentially twisted fibers of flat cross-section (Kuraray Co.).

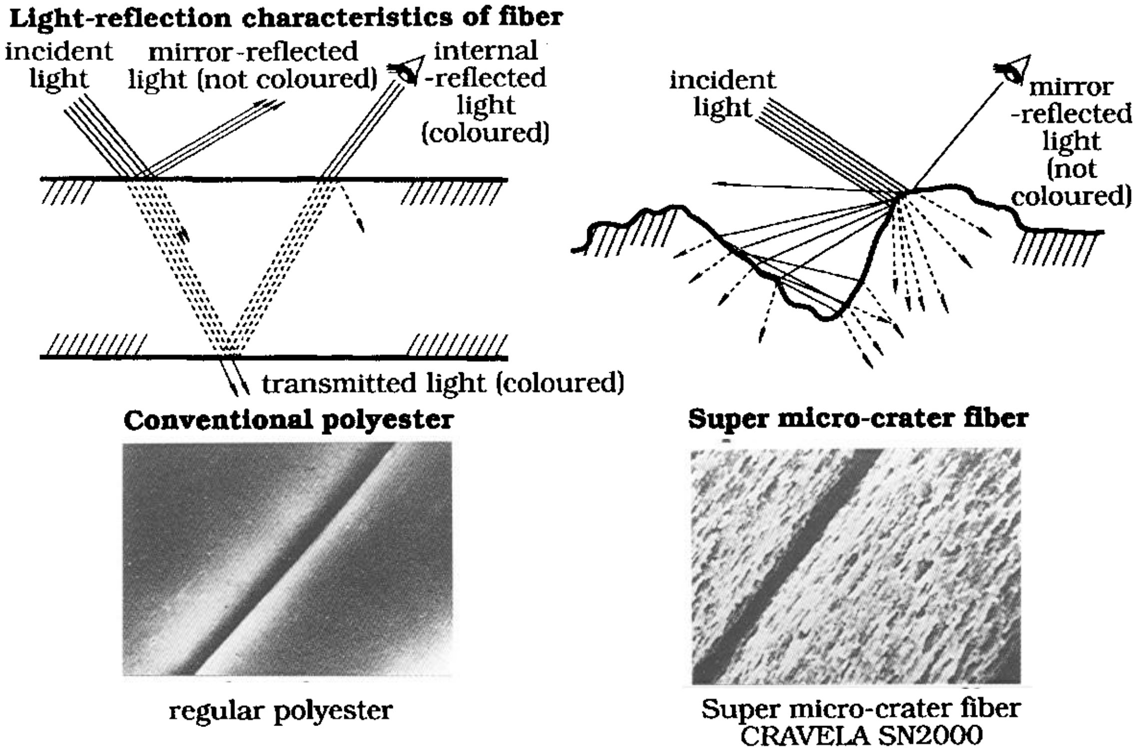


4.13 Deep colouring effect of Diphorl.

4.1.4 Super-Microcrater Fiber: imitating the cornea of the night-moth

Kuraray developed Super-Microcrater Fiber which can achieve a deeper colour effect by emulating the cornea of a nocturnal insect (night-moth). Nocturnal insects have an astonishing natural mechanism that enables them to survive in the dark. Whereas a bat flies freely to catch insects in the dark using its ultrasonic sensor, a night-moth is equipped with a sensor to detect the ultrasonic radiation transmitted from a bat so that it can escape quickly. The cornea of a night-moth when closely observed, has a number of conical projections arranged hexagonally, whereas diurnal insects such as dragonflies and grasshoppers have no such projections. When a billion per cm^2 microcraters are constructed on the fiber surface like the cornea of a night-moth, these craters trap the incident light and consequently the fiber exhibits a deeper colour (see Fig. 4.14). Since the direct reflection of the light at the fiber surface is suppressed, the fiber is able to exhibit brilliant black which conventional fibers cannot achieve. Kuraray has greatly expanded its share of black formal-wear for ladies using Super-Microcrater Fiber.

A highly civilised society promotes individuality in its human life-style by variations in the use of clothing. This requires a variety of colours and forms according to individual sensitivity. We should learn more from the secrets of nature to satisfy the depths of diverse human consciousness.



4.14 Deepening of colour using micro-craters on the surface of the fiber (Kuraray Co.).

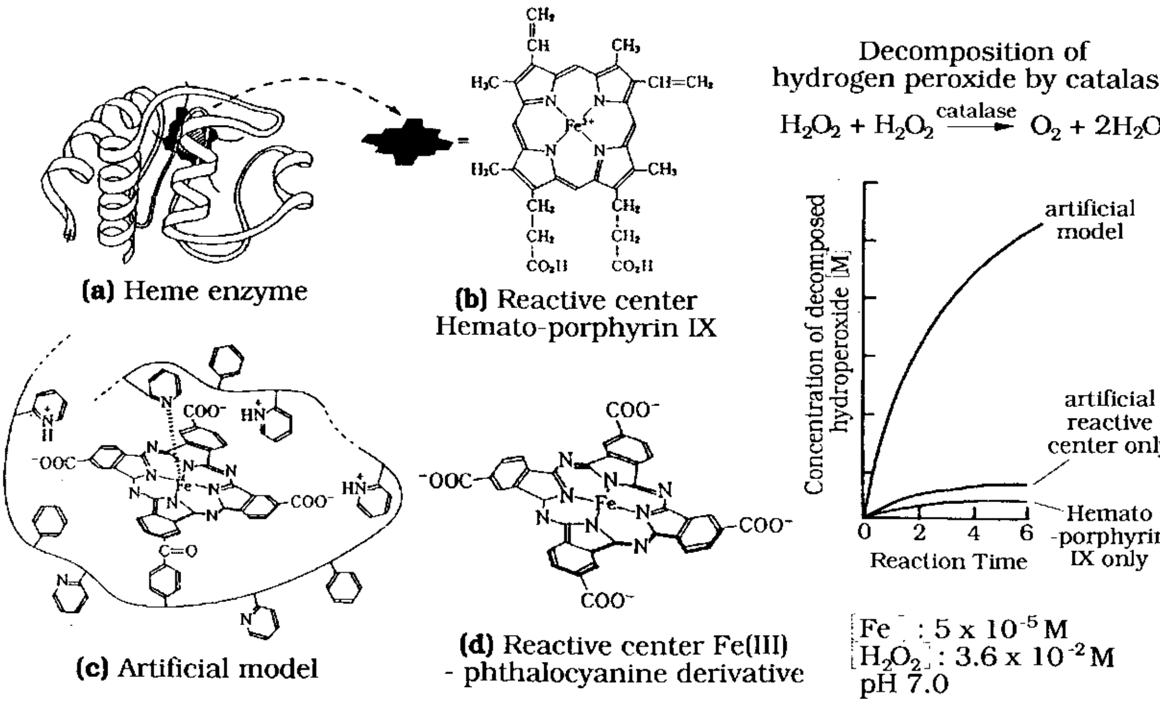
4.1.5 Enzyme-like deodorant fibers

Proteins from meat or soya beans can be decomposed only when cooked with strong acid at high temperatures for long periods, but in the human body, enzymes work as catalysts to decompose proteins into amino acids effectively within a few hours at room temperature. Polymers and other chemicals used in everyday life are produced at high temperatures and pressures in chemical factories, which inevitably cause pollution. Enzymes are capable of producing chemical materials at ambient temperature and pressure without causing any pollution. Although enzymes are highly selective/energy conservative/non-pollution causing catalysts of high efficiency, as materials they are weak and relatively unstable to high temperatures, can be deactivated when contaminated with various bacteria, cannot be used in organic solvents and can be applied only to specific reactions. The development of artificial enzymes will depend on the ability to cope with their vulnerable characteristics. Various artificial enzymes have now been developed and used in everyday life. For example, emulating hematin (ferri (Fe^{3+}) protoporphyrin IX), Professor Shirai at Shinshu University developed a deodorant fiber that has 100 times better efficiency than active carbon. In collaboration with Daiwabo Co., it was harnessed into a commercial product, a deodorant bed "Green Life" which utilises deodorant fiber wool as filling.

Toxic substances taken into a human body are oxidised and detoxified by oxygen in the blood, owing to the catalytic function of a series of oxidising enzymes, including the haem protein. The haem protein contains a reactive centre, which is a flat ring-like ferri-compound called protoporphyrin. The enzyme structure is shown schematically in Fig. 4.15, and consists of a reactive centre, surrounded by the U-shaped part that provides the reactive environment, and supported by the moiety specifying the active site. This U-shaped protein of high molecular weight, which functions with great specificity, can accept or remove electrons, controls the reaction speed within the reactive-environment part, and governs the chemical reactions which occur at the reactive centre. This functional cooperation results in the following:

1 High activity.
2 Energy conservation.
3 High selectivity.
4 High efficiency of the enzyme.

The enzyme loses activity if a structural change accompanies any significant environment change. The enzymes thus function precisely and cleverly within the living body, where hundreds of chemical reactions proceed simultaneously

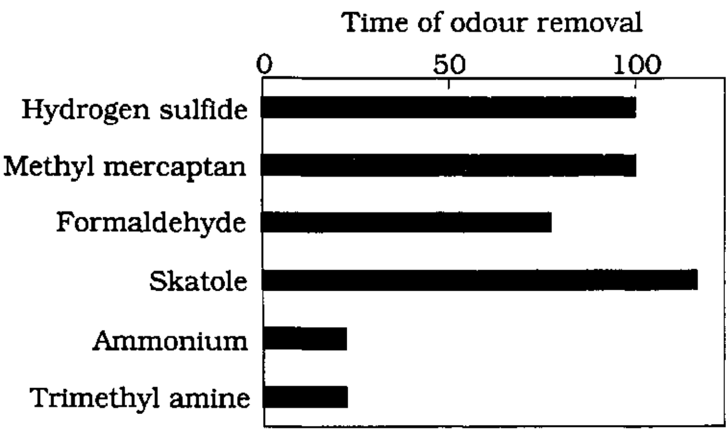


4.15 The performance of an artificial enzyme with an Fe(III)-phthalocyanine derivative reactive centre.

at normal temperature. Animals, including humans could not survive without such enzymes.

Professor Shirai imitated the haem enzyme using polystyrene derivatives coupled with Fe-phthalocyanine. This artificial enzyme has an Fe-phthalocyanine complex as its reactive centre instead of protoporphyrin IX, and although structurally different from the haem enzyme, exhibits a relatively high (1/50th of the enzyme) activity (see Fig. 4.15). In Japan phthalocyanine is widely known as the blue/green paint which forms a complex with copper, and is used for the body colour of the Shinkansen bullet trains.

The reactive centres must be fully exposed and dispersed homogeneously to make efficient contact with reactants to achieve efficient catalytic reactions. For this reason, amorphous rayon was chosen as the supporting material, because this rayon is porous (i.e. it possesses a large surface area) and is amphiphilic. The degree of crystallinity of amorphous rayon (15%) is smaller than conventional rayon (*ca.* 40%). The deodorant fiber consists of amorphous rayon supporting 3 wt% Fe-phthalocyanine type artificial enzyme. This deodorant fiber is capable of destroying an offensive odour by decomposing the foul smelling molecules, such as indole (faeces), hydrogen sulphide (rotten eggs) and mercaptans. The deodorant fiber maintains its activity about 100 times longer than active carbon, but is effective only with a limited range of malodorant sources as shown in Fig. 4.16. The deodorant fiber is used at present in commercial products such as nappies (diapers), an inner sole of a shoe, in refrigerators, and the mat for a toilet seat. Materials other than amorphous rayon are also being examined as a supporting material for artificial enzymes.



4.16 Odour-removal effect of Fe-phthalocyanine-doubled fiber with respect to that of active carbon (which is normalised to 1).

Next page

5 Biopolymer frontiers

Recently, interest has increased considerably in fiber-related biotechnology, and biofiber/biomedical materials, which can be grouped under the heading biopolymers. Here biopolymers denote the polymers that mimic or derive from natural organisms and exhibit similar functions to the natural material. These polymers now find application not only in the traditional areas of food and medical industries, but also in other industries, including information and communication. Biopolymers are thus an important ingredient in the rising generation of high-technology materials.

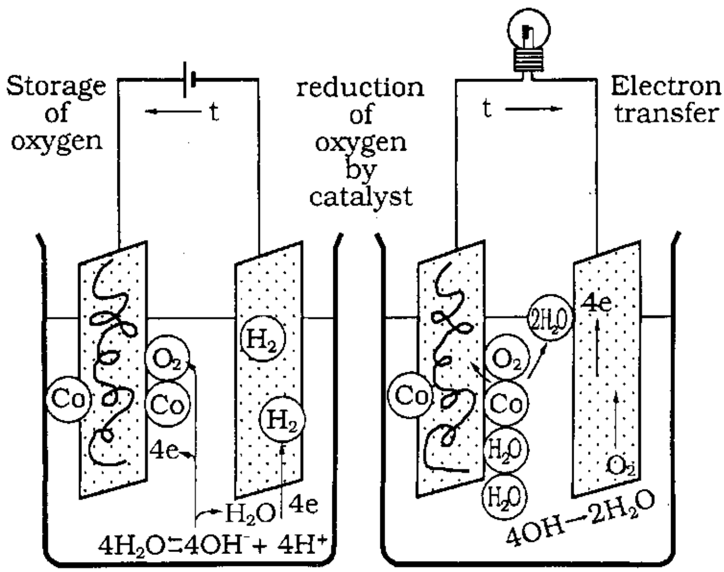
5.1 Mimicking the functions of enzymes and co-enzymes

Enzymes are essential in the fermentation of sake, soya bean paste, soya bean sauce and other foods used extensively in Japan. Life cannot be sustained without the enzymes which occur within the living structures of microorganisms, plants, animals and humans. Many of the chemical reactions of living systems, such as synthesis, decomposition, detoxification and energy supply, are controlled by enzymes. Enzymes are in most instances composed of spherical proteins, which exhibit their activity when bound to a low molecular weight compound, specified as the co-enzyme. The following examples show the particular applications of enzyme/co-enzyme electron transfer mechanisms.

5.1.1 Secondary fuel battery of synthezyme

Enzyme function is essential for the functioning of a stimulus-transferring nerve, a muscle contraction or a heart pulsation. The glow of a firefly is also enzyme-induced. Enzymes cooperate in a well-organised manner to perform a particular function, and often require metal ions such as iron and magnesium or other specific compounds in order to promote their action within the living body.

Cytochrome is a chromoprotein found predominantly in plant and animal cells, and is bound to iron porphorin to facilitate the transfer of electrons. Various attempts have been made to simulate the electron transfer mechanism of cytochrome proteins. A cytochrome film is as electrically conductive as germanium or silicon. Professor H. Shirai, in cooperation with Professor O. Hirabaru of Miyakonojo Technical College, synthesised a cytochrome-like enzyme and used this "synthezyme" to form the electrode for a secondary fuel battery. When an electric current is applied, water is decomposed into hydrogen and oxygen at the electrodes, although each component is seldom separated because of their rapid recombination. Shirai and Hirabaru used cobalt (instead of the iron in natural cytochrome) as the cooperative compound in their synthezyme, which was employed as an electrode on the oxygen side. The electrode operates by electron transfer, and oxygen at the electrode is catalytically reduced and stored by cobalt. This secondary fuel battery, with water as fuel and synthezyme as an electrode, is able to charge and discharge freely, and produce clean energy in the form of hydrogen, as schematically shown in Fig. 5.1. This synthezyme battery system could be developed further to replace lead batteries used in cars, or placed on a roof to harness solar energy to decompose water into



5.1 Secondary battery using synthezyme as electrode and water as fuel.

hydrogen gas, which could be used as a fuel to supply sufficient energy to heat a building, and consequently save natural resources. This synthezyme hydrogen-fuel battery could, therefore, provide a most efficient technology for storing energy by converting water into electric energy.

Biomimetics thus produced this secondary fuel battery, which can now be further improved in terms of energy efficiency and easy handling. The electron transfer mechanism of cytochrome can also be applied for the production of high-precision elements, such as on/off switches or memories operating at a molecular level. These high-precision elements are vital for the development of biocomputers, and are under continued investigation by the Ministry of International Trade and Industry, Japan.

5.1.2 Biobattery: An application of cell current

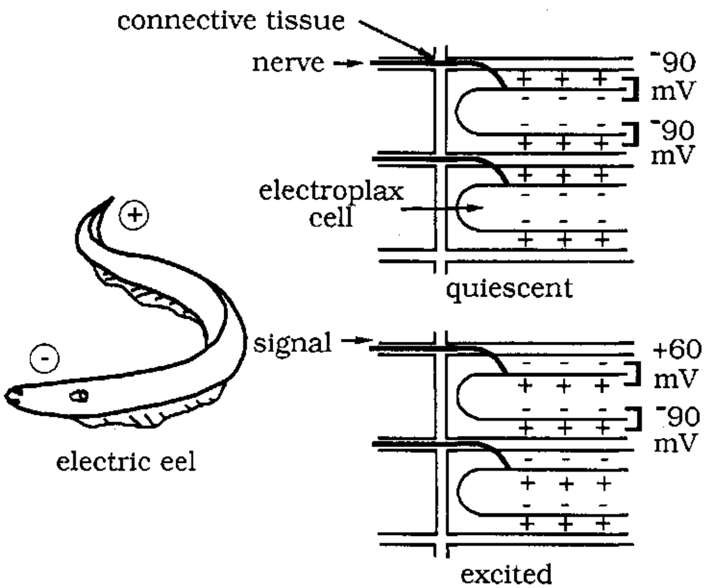
There are certain organisms that emit light or generate electricity. The glowing firefly is a familiar sight at the waterside on an early summer evening. *Cypridina hilgendorfii* glints mysteriously in the sea, and luminous *Armillariella mellea* or *Lampteromyces japonicus* surprises us in the mountains. All these light emissions are attributed to the action of enzymes. For example, a firefly glows when luciferin (a luminescent material) is oxidised by luciferase (a luminescent enzyme), where the heat produced by luciferin oxidation is converted into light energy by luciferase.

In 1791, Galvani observed a contraction of frog legs when joined by two metal pieces. Since then, much effort has been made to harness living organisms to produce electric energy. Advanced technology is necessary to study and harness energy or information stored within the living organisms. A hydrogen-fuelled biobattery is being developed using hydrogen-producing bacteria in the USA for use in the space shuttle.

Natural sources are being screened for suitable biosystems. For example, algae in the sea and lakes produce hydrogen by decomposing water with the aid of light energy. Blue-green algae grow in seawater by absorbing the sun's energy. Since the blue-green algae contain lipids, proteins and hydrocarbons, they can be used as an energy source as well as for the production of new bioactive materials.

An electric fish has a generator in its body. Its electromotive force varies from 30 V (an electric ray in the sea of Japan) or 400–450 V (an electric catfish in Africa) to 650–800 V (an electric eel in South America). The electric fish discharges intermittently as a means of self-defence or to catch food. It generates electricity through an ingenious use of the electroplax cells; its generation mechanism is similar to that of nerve excitation. A signal is transmitted from a synapse (a junction of the nerve fiber terminal to the next nerve cell) to an electroplax cell when the fish is excited. Then a particular side of the electroplax cell membrane depolarises and induces a potential difference on the other side of the membrane (see Fig. 5.2). Since many electroplax cells are stacked upon each other, a large potential is produced. This electric energy can be removed using an electrode, so providing a new way to access biochemical energy.

Electric fish are a special category in having electroplax cells, which are not found in most microorganisms and animals. However, muscle movement or nerve excitation produces a weak electric current, which can be monitored by an electroencephalogram or electrocardiogram. The objective of present research is to take out electric energy directly from the microorganism or animal cells. Although it is known that an electric current is generated when the cell is in contact with an electrode, the mechanism and materials involved in the current generation are not well understood. Recently, Professor T. Matsunaga, Tokyo University of Agriculture and Technology, identified the co-enzyme that transfers electrons from the cell. Electron transfer via this co-enzyme has been observed between an electrode and the cells of yeast, erythrocyte, macrophage and cancer cells. Since the maximum



5.2 Mechanism of generation of electricity by the electric eel.

potential and potential peak shape of the generated current depends on the structure of the cell and cell wall, these can be used to distinguish the cell species, whether in microorganisms or animals. If an efficient method can be found to take out the electric current from the cell, it may be possible to develop a new type of microorganic battery, to interpret the cell information or to suppress the growth of cancer cells selectively.

5.2 Polysaccharides in semiconductors and medicine

Carbohydrates are composed of carbon, hydrogen and oxygen, and are found extensively in nature. Low molecular weight carbohydrates are normally referred to as sugars, and those of high molecular weight as polysaccharides, which can include simple polysaccharides and heteropolysaccharides, depending on the variety of constituent monosaccharide species.

There is a wide variety of monosaccharide species, classified according to the number of constituent carbon atoms they contain and the type of functional groups present. For example, glucose and fructose are monosaccharides found in honey and fruits, and are classified as hexoses, to denote that the monosaccharide contains six carbon atoms. Monosaccharides link together to form successively disaccharides, trisaccharides, tetrasaccharides and eventually polysaccharides. Cane sugar, or sucrose, is probably the most well-known disaccharide since it is consumed every day as a sweetener. Plant cellulose (used as cotton for making clothing) and starch (a food material) are examples of simple polysaccharides found abundantly in nature. Dry plants are made up of 85% polysaccharides and 15% other components. Cellulose makes up more than 90% of the composition of cotton, which is, therefore, referred to as cellulose fiber. Cellulose is produced not only by green plants, but also in large quantities by fungi and certain bacteria and in smaller quantities by sea algae and insects. Such ordinary polysaccharides are used for the physical protection of natural organisms, and in most cases have no specific functionality because they consist of a simple repeating structure.

Table 5.1 describes the simple polysaccharides, heteropolysaccharides and proteins found in nature. Although the heteropolysaccharides are present in small amounts, they can often be physiologically active. The study of the metabolism of polysaccharides was a forgotten subject for a considerable time, despite the fact that such studies could improve our understanding of life phenomena. Only recently have intensive investigations been undertaken in biochemistry, pharmacology, fiber chemistry, polymer chemistry and food chemistry to introduce a specific physiological function into simple polysaccharides.

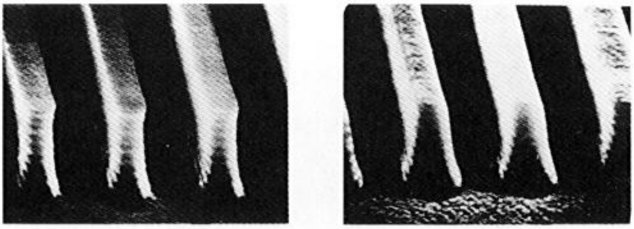
Table 5.1. Polysaccharides and protein biopolymers

Field of science		Fiber science, polymer chemistry, food chemistry	Biology, biochemistry, pharmacology
Polysaccharides	Structure	Simple polysaccharides	Heteropolysaccharides
	Functions	Structural material such as cellulose, starch, pullulan and chitin	Mucopolysaccharides with pharmacological and physiological activities such as heparin and chondroitin sulphate
Proteins	Appearance	Fibrous	Spherical
	Functions	Structural proteins such as silk fibroin, collagen, and wood keratin	Functional proteins such as enzymes
	Properties	Large amounts, lack of physiological functions	Small amounts, high functionality
Reference		Natural fiber	

5.2.1 Improvement of integrated circuits using water-soluble natural polymers

ICs (integrated circuits) can be improved by printing finer circuits on to a silicon base. Matsushita Electric Industry Co. and Hayashibara Biochemical Laboratory developed a new type of photosensitizer to process the fine pattern for circuits of very large-scale integration (VLSI) of the next generation using the water-soluble natural polysaccharide pullulan. Pullulan has a similar structure to the edible polysaccharide starch, and can be removed easily by washing with water; it is not soluble in organic solvents.

The VLSI circuits are produced by photoprinting, that is, by exposing the photosensitive resin coated on the silicon base to ultraviolet radiation. The beam should be as fine as possible to improve the IC capacity. IC integration can be reduced to the submicrometre region when the photosensitive resin is coated with a thin layer of water-soluble photosensitiser. This functions as a filter and prevents beam scattering (see Fig. 5.3). Existing techniques can thus be used to produce 4 Mbit and even 16 Mbit DRAM (dynamic random access memory) by applying such new water-soluble photosensitisers. Additionally, production yields also improve, so that there is no need to introduce new sophisticated systems such as X-ray beams or electron beams. This application illustrates the value of cooperation between two industries in quite different fields, which resulted in a completely new application of natural polymers.



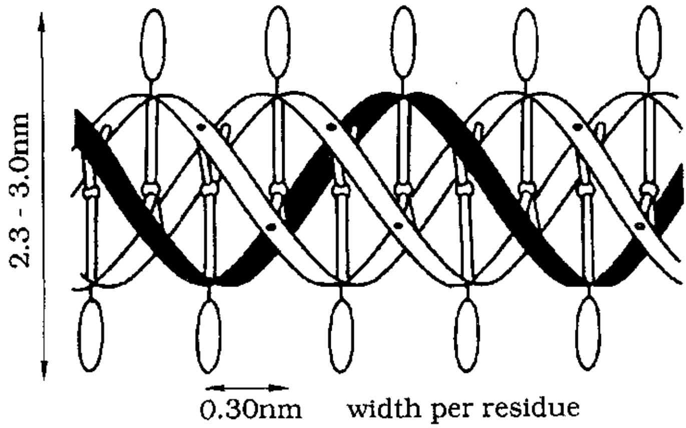
5.3 Scanning electron micrographs showing patterns with line width of 0.6 μm. Conventional photosensitive resin (right) and new water-soluble sensitiser (left).

5.2.2 Antitumour functions of polysaccharides

Plants and animals are provided with built-in mechanisms to survive, which are still beyond our complete understanding. As we discover more about such mechanisms, these find applications in high technology.

Polysaccharides, proteins and nucleic acids are three major biopolymers, which sustain the physiological functions of living organisms. Among them, polysaccharides are known to play an important role in the division of cells and their subsequent growth, while preserving cell characteristics. Mushrooms produce polysaccharides of complicated structure. The Japanese have been aware that mushrooms can be used in an effective anticancer therapy for some time. Two antitumour drugs appeared on the market from this source, namely lentinan and schizophyllan. These are produced from extracts from *Lentinus edodes* (Chinese mushroom) and *Schizophyllum commune*, respectively. Lentinan is a polysaccharide of white powdery appearance with molecular weight about 500,000. Research workers at Ajinomoto Co. Ltd found that lentinan is made up only of β-1, 3-linked glucans. They were found to be physiologically active during the course of the study of structure in relation to anticancer activity using various polysaccharide derivatives. Lentinan has a complicated three-dimensional structure, and exhibits its anticancer activity towards a particular type of cancer as well as exhibiting synergic effects with other chemical anticancer agents. Moreover, it does not show the adverse side-effects that are characteristic of many antitumour chemicals.

The triple-stranded structure of schizophyllan (see Fig. 5.4) is responsible for its antitumour activity. It is a polysaccharide composed solely of glucan bases, and Professor N. Norisue of Osaka University found that antitumour activity is induced when the molecular weight exceeds 50,000 and the triple-stranded structure is formed. Schizophyllan is now commercially available from Taito Co. Ltd. It is extracted from cultivated *Schizophyllum commune*, depolymerised and purified before use by inflection.



5.4 Triple-stranded helix structure of the antitumour medication Schizophyllan.

Taito Co. and Ajinomoto Co. have employed different types of mushrooms to develop antitumour agents, but came to the same conclusion that polysaccharides with β-1,3-linked glucan structures possess the antitumour activity. The anticancer agents derived from mushrooms may not attack cancer cells directly, but increase the immunopotential of the body to suppress cancer cell growth. Activation of the immune response is due to cell-mediated immunity through macrophase, cytotoxic T cells and natural killer cells, rather than by tumoral immunity. The relationship between polysaccharide structure in solution and physiological activity now requires further intensive investigation.

The Mizuno Biohollonics Project (led by Professor D. Mizuno of Teikyo University), within the framework of the Creative Science and Technology programme organised by the Research Development Corporation of Japan, has already identified the potential of activated macrophages in cancer treatment. As yet there have been no clinical use or commercial manufacturing process developed. The Japanese Government has just started a ten-year project in this area to develop new cancer treatments. Considering their physiological role within the cell, polysaccharides need to be investigated more intensively in various fields of medicine, pharmacology, biology, chemistry, physics, and even fiber science and technology. In this context there is a need in Japan for a National Saccharide Research Institute, where researchers with different backgrounds can cooperate.

5.2.3 Polysaccharides as antitumour-agent carriers

The cells making up an organism originate from a single fertilised egg cell, which on repeated division yields cells specific to a particular organ, such as liver, heart, skin or nerve, so differentiating their functions. The polysaccharides on the cell surface are believed to be involved in the mechanism of intercellular interaction.

Although dextran, a polysaccharide produced by a lactic acid bacteria *Leuconostoc mesenteroides*, is pharmacologically inactive, it can be used as a carrier for antitumour drugs, according to the results of Professor M. Hashida of Kyoto University. It is an α-1,6-linked polyglucose. An antitumour drug should remain in the blood at a certain concentration range for a considerable period if it is to work effectively. This is often a problem since the drug concentration usually drops sharply within a short period. If an excess of drug is administered, undesired side-effects can appear. Dextran when used as a carrier of the antitumour drug maintains the drug concentration at a desired level over long periods. This facilitates drug action and suppresses its side-effect.

Professor J. Sunamoto is now investigating the possibility of using *konjak-mannan*-coated liposome as a drug carrier. *Konjak mannan* is a hetero-polysaccharide composed of β-1,4-linked mannose and glucose, and is used regularly in foods in Japan. Since phagocytes tend to encapsulate the *konjak-mannan*-coated liposome which concentrates specifically in the lungs, this system can be applied in the treatment of metastic lung cancer. The

5.5 The sea hare (*Encylopedia on Animals:* Japan Mail Order Co.).

polysaccharide-coated liposome can also be used as a drug delivery system to target particular organs or tissues.

5.2.4 Protective mechanisms of the sea hare (*Aplysia kurodai*)

A sea hare (see Fig. 5.5) grows without a hard shell, and secretes purple sweat to protect its soft body when an enemy approaches. Its egg survives without being infected by bacteria or being eaten by other animals. Professor J. Mizuno of Teikyo University is developing a unique antitumour drug by using a glycoprotein found in the eggs of the sea hare. This protein is believed to participate in its bioprotective mechanism.

The glycoprotein containing 10% saccharide was isolated from sea hare eggs, and was found to destroy cancer cells selectively in mice and humans. This example illustrates that living systems utilise many mysterious materials to achieve survival. Saccharides involved in cell recognition and immunity can surely assist in our own control of physiological functions.

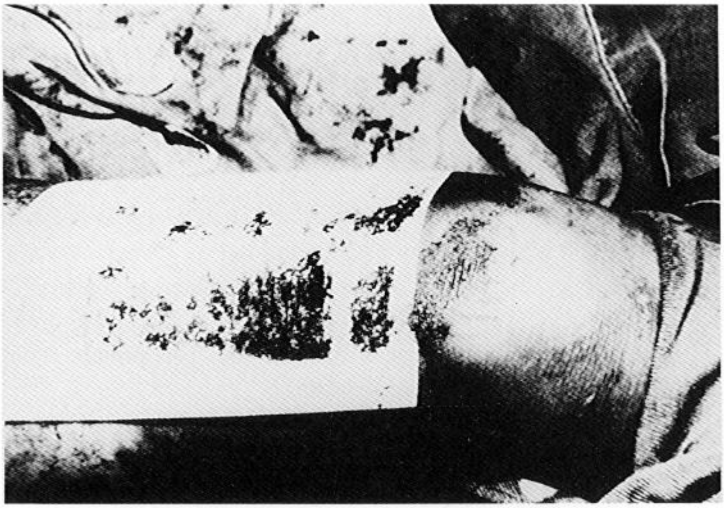
5.3 Biomass of crab and shrimp shells

Chitin, a polysaccharide, is the major component of crab and shrimp shells. Its structure is similar to that of cellulose. Chitin was not considered of value until physiologically active materials were derived from this source. Professor S. Tokura of the Hokkaido University initiated the chitin-utilisation project in 1972, at the request of the Hokkaido Prefectural Office. Professor S. Hirano of Tottori University also started his investigation of the physiological activities of chitin and chitosan in the early 1970s. These two have contributed extensively to this subject since that time.

Chitin has been shown to be physiologically active in relation to an antithrombus effect and adjuvant activity. It can also be used as a food material to control cholesterol levels in blood. The application of its derivative chitosan is now being widely developed: as a slow drug-release membrane; colour adsorbent; antifriction agent for paper; in cosmetics such as the softener/moisture-retainer (conditioner) for hair; drug carrier in the form of porous beads, and as an enzyme immobiliser.

5.3.1 Artificial skin from crab and shrimp shell

Crab meat tastes especially fine in winter, but its shell was simply a disposal problem until recently. Crab and shrimp shells are now considered second only to cellulose as a useful biomass. Since chitin is decomposed and



5.6 Artificial skin derived from chitin (Unitika Ltd).

absorbed in the living organism, it can be used for medical applications. Unitika Ltd developed an artificial dressing, Beschitin-W (see Fig. 5.6), from crab shells. Crabs are extensively fished around Florida and California, USA. Dr Austin, of Delaware University near Florida, holds the basic patent on chitin fiber production. Unitika established an industrial process to produce chitin fibers of various diameters, based on this patent. The choice of solvent is critical and the dissolving conditions must be carefully controlled in the process.

Fibers, fabrics, sutures and non-woven fabrics from chitin are now available. For example, chitin non-woven fabric has excellent characteristics as an artificial skin because of its good adhesion to the human body surface and its value in stimulating new skin formation. It promotes no immune antigen–antibody reaction, and substantially accelerates healing and reduces pain. Unitika started the commercial sale of chitin products in April 1988, in collaboration with Roussel Medica Co. (a subsidiary of the medical marketing company in France). A standard type artificial skin (10 × 12 cm) costs more than $200 at present.

5.3.2 Porous chitosan beads

Alkali treatment of chitin yields chitosan, which is now allowed as a food additive. Since chitosan dissolves easily in acetic acid (vinegar), its processing has been widely investigated for the production of chitosan fiber or film, which can be conveniently applied in the food and biomedical industries.

Professor S. Tokura developed a continuous spinning process for chitosan in 1982. It can be spun in a long filament of a similar strength to rayon, although the present process yields a somewhat thicker filament than cotton. Fuji Spinning Co. Ltd have developed chitosan porous beads, consisting of numerous pores running radially from the surface to the centre. The active surface area, including the interior pores exceeds 200 m^2/g. In other words, the total surface area of 50 g chitosan beads is approximately equal to the ground area of the Korakuen Dome or Wembley Stadium. Because of their good compatibility with living cells, the beads are used for cell culture, and do, in fact, promote cell proliferation. Chitosan porous beads can also be processed into fine beads 10 μm in diameter and the Fuji Spinning Co. now supplies these find beads for HPLC (high-pressure liquid chromatography) in association with Showa Denko Co. Chitosan beads can also be used as a drug carrier, or as a slow drug releaser.

5.4 New applications of silk

Silk has been used as a thread after being spun by silkworms, and in Japan nobody dared, for centuries, to trespass upon the territory of holy silkworms by reprocessing silk threads. As time passed, however, silk lost this aura, and is now used in many forms such as thread, film and powder in order to add to it more commercial value. The raw silk thread produced by a silkworm is composed of fibroid in the core and is covered with sericine. If the sericine is removed by degumming, water-insoluble fibroin remains as a fine silk thread. This thread has a triangular cross-section and, therefore, exhibits a characteristic lustre, pleasant handling and an elegant drape. Silk was also found to be biologically active and Professor T. Asakura specified the structural and reactive regions within silk fibroin molecules. The following examples will demonstrate recent applications of silk in the field of biotechnology.

5.4.1 Stockings of hybrid silk

"Silk" induced a special nostalgia, nobleness and elegance in past generations. It has been the Queen of Fibers ever since the days of Silk Road. The mysterious processes that take place after the silkworms eat mulberry leaves to produce silk fibroid have gradually been unravelled. Recently its good biocompatibility properties opened up new areas of application as a biomaterial for sutures and for enzyme-immobilisation.

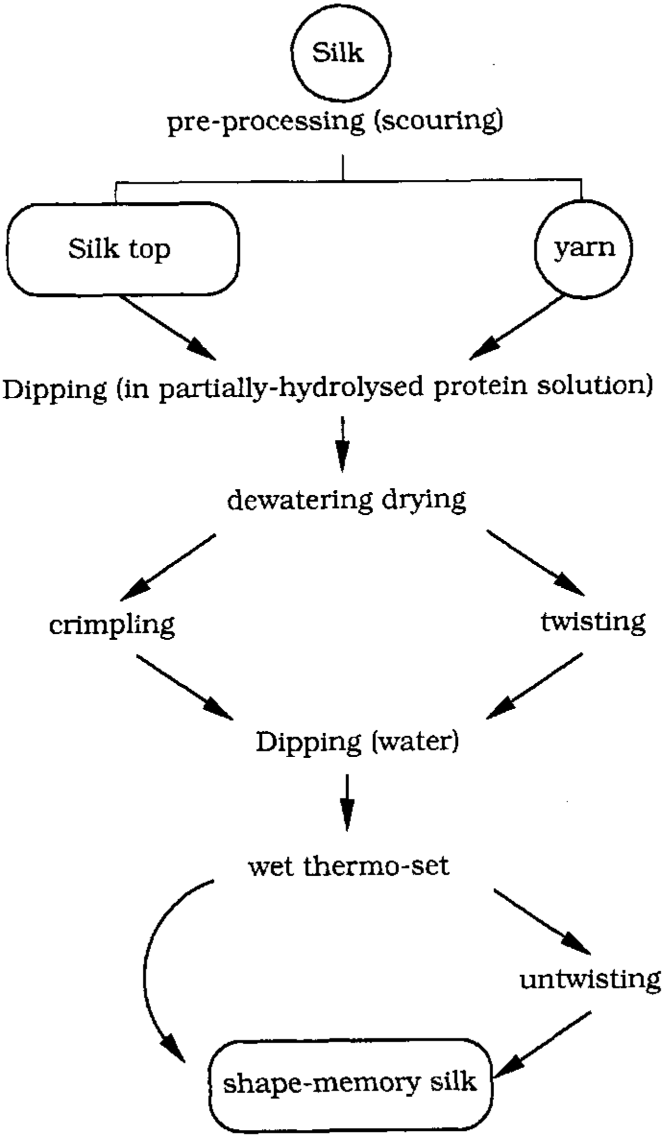
Nylon is the synthetic fiber that was introduced to copy silk, and to replace it for use in ladies stockings in the 1950s and 1960s. Now silkworms can produce finer and longer silk than nylon using biotechnology. The National Institute of Sericultural and Entomological Science, Japan, has succeeded in breeding a new type of silkworm that can produce a fine homogeneous silk filament of about 1,500 m in length. The National Institute has developed the use of this silk in cooperation with the Asahi Chemical Co., Professor A. Shimazaki (Shinshu University) and Professor N. Naruse (Bunka Women's University). This hybrid silk was commercialised under the trade name of Silran in the autumn of 1987. It is produced by extruding silk and nylon together through an air-jet nozzle with nylon filament placed at the centre and five raw silk filaments (2 denier each) twined around the nylon core. Thus the hybrid silk is composed of fine silk at the surface of a synthetic fiber core. It thus retains excellent handling and a good silk lustre as well as having the fiber strength of nylon. When the stockings from this hybrid silk are degummed to remove surface sericine, they show a metallic-silver lustre. The fibroid threads also bulk-up because of the thermal shrinkage of the nylon core. This product is, therefore, a genuine hybrid of silk and nylon, and yields quite different characteristics from the conventional blended yarn of silk and nylon. The wearing test of such hybrid silk stockings demonstrated its good handling, and such products are now commercially available.

5.4.2 Shape-memory silk yarn

A highly elastic silk yarn was developed by S. Mizushima of Mizushima Silk Industry Ltd and commercialised by Daito Spinning and Weaving Co. Ltd. Although both yarns are made of protein, a silk yarn lacks elasticity in comparison with wool because of the difference in internal structure. In the process, silk yarn is chemically treated by dipping in a solution of hydrolysed fibroid keratin and collagen, dried, crimpled, dipped again in water and thermo-set in the wet state under high pressure (2–3 atmospheres; 200–300 kPa) at 110 °C for 10 min, yielding shape-memory silk (see Fig. 5.7). When this product is wet-heated at 60 °C, the silk yarn becomes crimpled and bulky. Since its twisted structure is fixed in the memory even when the silk is untwisted again into uncurled yarn, the silk yarn reversibly recovers its curled shape by steaming. This elastic silk yarn can be applied in various textile products including outer garments, tights and knitted yarns.

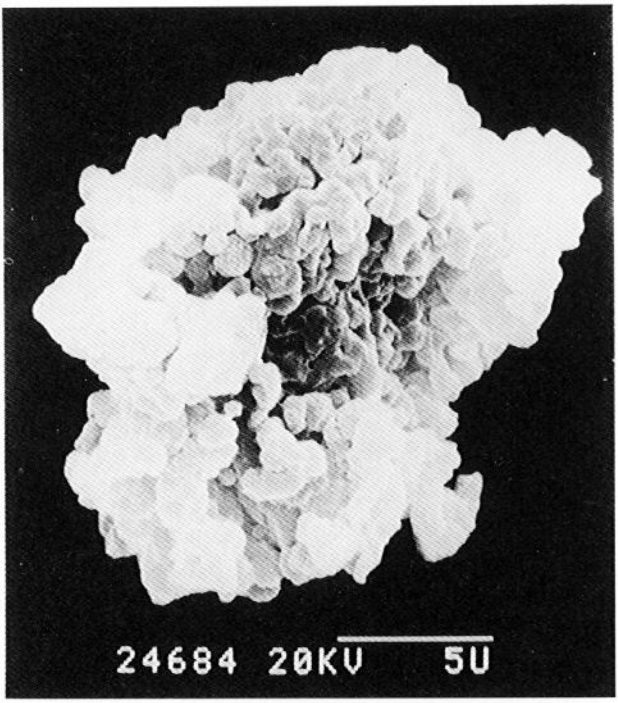
5.4.3 Biocosmetics

Biotechnology has now provided a way to produce new products from silk having specific functions. Kanebo developed the facial treatment cosmetics Fresh-up Powder and Bio-Powder Foam from silk in order to capture the



5.7 Processing of shape-memory silk.

elegant image of silk in the market. Fatty dirts on the skin surface can be removed by washing with soap. Protein dirts from dead skin, however, cannot readily be removed unless they are first hydrolysed with the enzyme proteinase. Certain of the conventional cosmetics contain proteinase, but its hydrolysis activity deteriorates rapidly with time, particularly when left with surfactant in the wet state. Many attempts have been made to maintain the proteinase activity in cosmetics. Kanebo applied an enzyme immobilisation technique for this purpose by encapsulating proteinase in water-insoluble fibroin. The fibroin regenerated from aqueous solution has similar characteristics to liquid silk in the silkworm body. Fibroin will crystallise easily and become water-insoluble when salt or alcohol is added, dried or stirred. Kanebo developed the technology to produce fibroin film, powder, fiber or gel by varying the conditions of crystallisation from aqueous solutions. When processed with added enzyme or antibody in the solution, the fibroid crystallises with the enzyme or antibody trapped inside. This process can be applied to immobilise the enzyme, despite the fact that direct immobilisation of proteinase with fibroin was not possible. The pH value is controlled to suppress the enzymic activity of proteinase, and the proteinase solution is added to the fibroin solution. Fibroin powder containing proteinase is salted out from the mixed solution. The encapsulated proteinase is stable to heat and its hydrolysis activity lasts for a considerable period, since fibroid protects proteinase against heat and moisture. The enzymic activity deteriorates only 10% after 300-day storage at 45 °C in the fibroin. Fresh-up



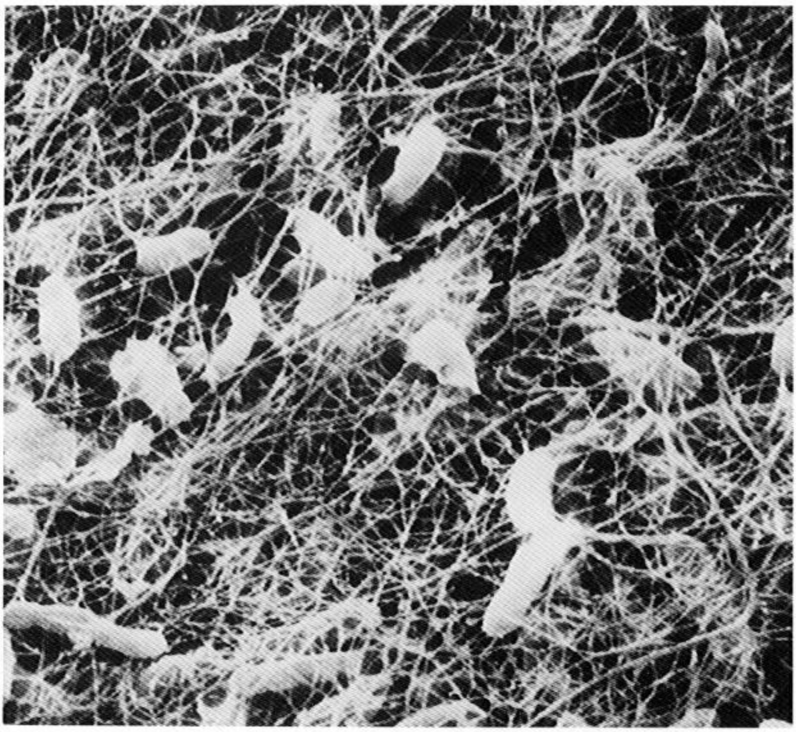
5.8 Scanning electron micrograph of proteinase-encapsulated fibroin powder.

Powder is made of granules of mixed proteinase-encapsulated fibroin powder and detergent (Fig. 5.8). The same know-how can be applied to prepare biosensors, drug carriers and bio-reactors for food.

5.5 Fibers produced by bacteria

5.5.1 Bacterial cellulose

Cellulose, as noted previously, is the main component of cell walls of plants. The cellulose content of wood pulp is 50 to 60%, and as high as 90% in cotton. It has been known for some time that some bacteria, mostly acetic acid producing bacteria, also produce fibrous cellulose without the aid of light. This bacterial fiber is very pure cellulose, and many investigations have been undertaken to identify the bacterial strain and cultivate it effectively. For this Ajinomoto Co. selected *Acetobactor aceti*, the acetic acid bacterium, 1×2 to 1×3 mm in size. When cultivated for seven to ten days in a medium containing 5% sucrose, nitrogen and salts at 30 °C, this bacterial strain



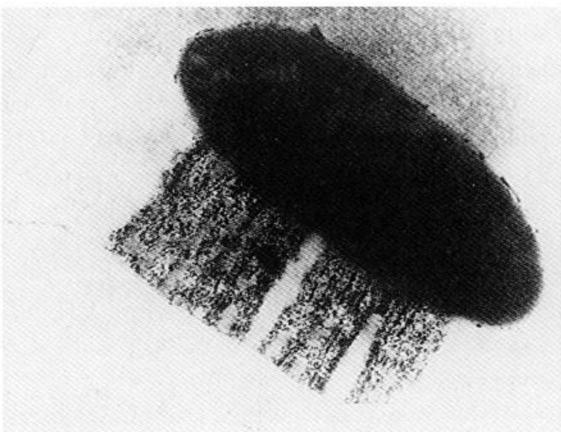
5.9 *Acetobacter aceti*, an acetic acid bacterium, produces cellulose fibers outside the organism (Ajinomoto Co. Inc.).

produces a gel-like material containing fine cellulose fiber, which is too thin (about 20–50 mm in diameter) to classify in terms of the conventional denier unit (see Fig. 5.9). This fiber has great potential for paper, medical and other industrial applications as a new functional material. In 1997 it was introduced in food products by the Kelco–Nutrasweet Company.

It is not yet fully understood how the bacteria produces the fibrous cellulose; the mechanism is of great interest from a scientific viewpoint. Fine gel-like fibers are spun from holes of several nm in diameter on the bacterial cell surface, to form ribbon-like gel sheets outside the cell (see Fig. 5.10). These sheets can be processed into paper of extremely high Young's modulus (30 GPa), which is almost equivalent to that of aluminium. The sheets cannot be torn easily by hand. These unique characteristics of the bacterial cellulose sheet are due to (i) a high degree of cellulose crystallinity; (ii) a high lateral order of the crystallites, (iii) a lamellar alignment of crystallites in several layers; and (iv) a network structure of the sheet.

Ajinomoto, the Research Institute for Polymers and Textiles and Sony are jointly working to develop new applications for the bacterial cellulose sheets. Already Sony has employed these sheets for loudspeaker diaphragms, in order to capitalise on their high specific modulus and high internal loss. The sound reproducibility is outstanding, and Sony has now commercialised high-quality headphones using these bacterial cellulose sheets (see Fig. 5.11).

The extremely fine filament of bacterial cellulose could realise many scientific dreams for textiles. For example, its application is now being extended to produce a new type of artificial leather with a mild touch.



5.10 *Acetobacter aceti* produced ultra-fine cellulose: magnified version of Fig. 5.9 (Dr A. Kai, Tokyo Metropolitan University).

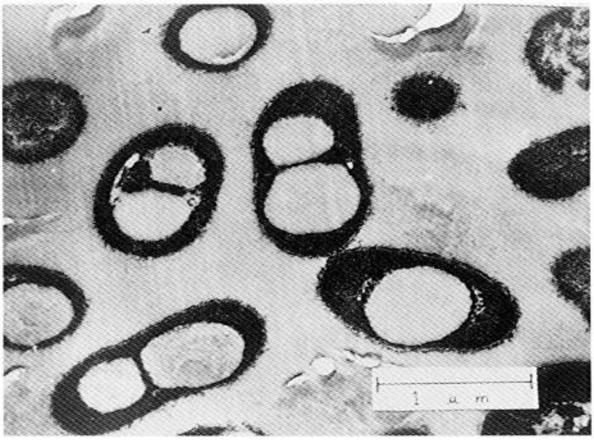
5.11 High-quality headphones of bacteria cellulose (Sony and Ajinomoto).

5.5.2 Bacterial polyester as strong as nylon

As *Acetobacter aceti* produced cellulose, so have bacteria produced polyester for several hundred million years. More than a hundred bacterial species are known to be polyester-producing, which include *Alcaligenes sp.*, *Bacillus sp.*, photosynthetic bacteria and blue-green algae. These microorganisms produce and store polyester, which can be used as an energy source in case of starvation, in the same way as animals and plants store energy in the form of glycogen and amylopectin, respectively (see Fig. 5.12).

The polyester so produced is stored in the bacterial body as particles of 0.5–1.0 μm in diameter, which can be extracted using organic solvents. Natural polymers such as cellulose and fibroid do not melt, but natural polyester is exceptionally thermoplastic and melts at about 180 °C. It can, therefore, be moulded into any shape like any other synthetic polyester.

The polyester-producing bacteria contain both polymerase (an enzyme controlling polymerisation) and depolymerase (an enzyme inducing depolymerisation). Thus, bacterial polyester is biodegradable. Bacterial polyester is, therefore, expected to be used where a natural hazard is created by non-degradable rubbish. It could be an important material in establishing a well-balanced ecosystem. Since the bacterial polyester is composed of highly crystalline D-3-hydroxybutyrate, the product at present is too stiff and brittle for major practical use. Recently a new method was developed to produce bacterial copolymeric polyester efficiently by fermenting a suitable combination of bacteria and food. ICI, UK, has applied this fermentation



5.12 Polyester stored in *Alcaligenes eutrophus* (scanning electron micrograph by Prof. Y. Doi).

technology to produce a random copolyester of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) by feeding these two ester carbon sources to the bacteria. This copolyester can have its 3HV component varying in concentration from 0 to 30% and is now commercially available under the trade name of Bipol. The price will decrease to less than US$6/kg if the annual polymer production exceeds several thousand tonnes.

In 1987 Professor Y. Doi, Research Laboratory of Resources Utilisation, Tokyo Institute of Technology, found another combination of bacteria and food that can produce a copolyester by fermentation. *Alcaligenes eutrophus* produces a copolyester composed of 3-hydroxybutyrate (3HB) and 4-hydroxybutyrate (4HB) when fed with 4-hydroxybutyric acid. The physical characteristics of these bacterial copolyesters vary from elastic rubber-like to hard plastic-like appearance as the proportions of 3HB and 4HB are varied. For example, this bacterial copolyester can be processed into a fiber that is as strong as nylon in terms of tensile strength.

Bioplastics, like the bacterial polyesters, are biodegradable, and these materials can be decomposed by bacteria in sludge and soil. The biodegradability and hydrolysis characteristics can be controlled by changing the copolymer composition and molecular weight. A slow releasing system for agricultural chemicals is now being developed using biodegradable polyester microcapsules containing chemicals. These microcapsules are decomposed in the soil gradually, with the speed controlled by copolymer composition and/or molecular weight, and thus release chemicals over a long period.

Next page

6 Progression of high-tech fibers

High-functional new materials have been developed by combining the expertise of various industrial disciplines, for example, the materials, information, life sciences and energy industries. Unique and high-value-added products can derive from the synergy between these different industries, as shown in Fig. 6.1. Fiber science and technology is a field that is traditionally strong in adding high value to products by controlling the tertiary structures of the materials, for example, by introducing better orientation or higher crystallinity into the fibers. This technical tradition is now being applied to achieve the higher functionalisation of such materials.

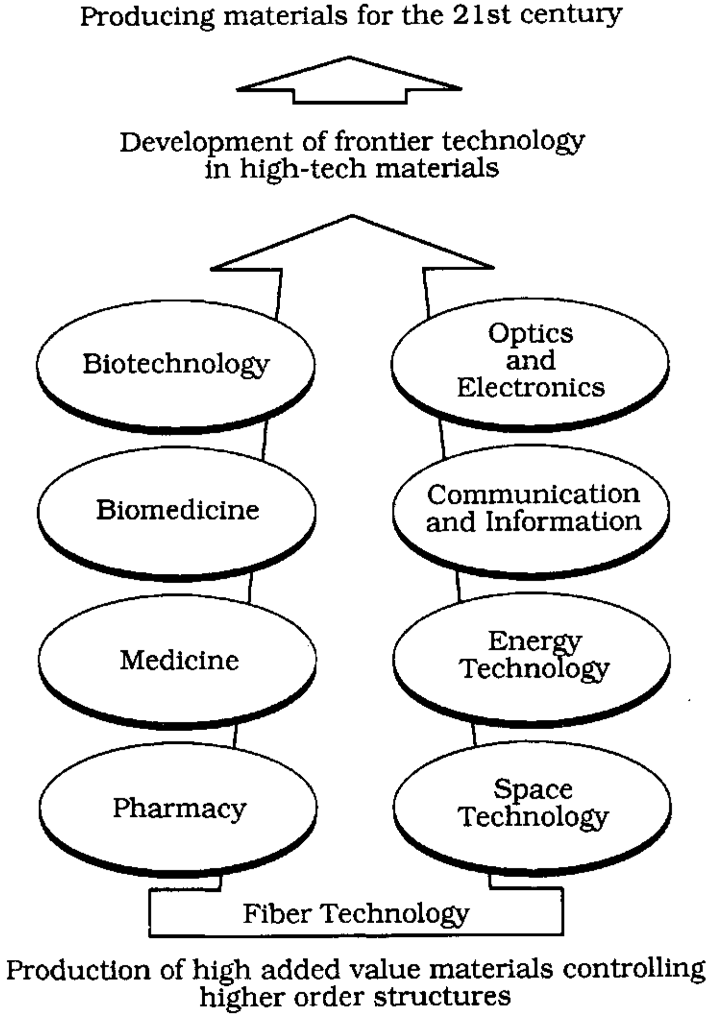
6.1 Utilisation of unused resources

Rayon is produced from alkali-treated wood cellulose, and its fiber can be converted to active carbon fiber. Recently, an investigation was initiated to produce carbon fiber directly from wood as part of a project for the total utilisation of wood.

6.1.1 Carbon fiber from wood

The wood industry is a typical biomass industry, and a variety of research projects is underway to convert wood into more valuable products.

Carbon fiber is produced mostly from PAN at present. Its study was started 30 years ago when it was produced by carbonising rayon derived from cellulose. At one time, lignin, a wood component, was used to produce carbon fiber by mixing it with polyvinylalcohol and combusting. Thus it was natural for the Oji Paper Co. Ltd to consider producing carbon fiber directly from the wood. Wood is composed of several components. The carbonising conditions must, therefore, be carefully controlled to take account of the physical characteristics of the components since each has its own functional qualities.



6.1 Synergies between different industries which can contribute towards providing new materials for the 21st century.

For example, cellulose is characterised by its elongational fibrous property, whereas lignin is responsible for the high carbonisation yield. The different functional groups of wood components control the heterogeneous surface structure of the resulting carbon fiber, which would, therefore, have quite different characteristics from that derived from a single component material, such as PAN or pitch. Most of the attempts to produce carbon fiber from lignin or from various mixed compositions of wood components failed. The appearance of the product was not satisfactory from these attempts.

The Oji Paper Co. found that it was possible to spin wood directly if it was dissolved, in a suitable solvent. They examined the best spinning conditions of the acetylated wood dissolved, for example, in phenol, in cooperation with Kyoto University. A cross-linking agent added to the acetylated wood solution improved its spinning characteristics. The resulting fiber is thermoset for a short time at 250 °C, and then carbonised to yield carbon fiber of better quality than the pitch-type, particularly for general uses. The physical characteristics are somewhat similar to that of Kynol fiber. However, its high production cost, because of the low carbonisation yield, prevents the use of the method on a commercial scale at present.

6.1.2 Fibrous active carbon derived from cellulosics

Toyobo Co. has succeeded in achieving the commercialisation of fibrous active carbon produced from cellulosics. The process incudes both carbonisation and activation. Since cellulosics are flammable, they must first be processed with a flame-retardant, and burnt at a relatively low temperature (200–300 °C) to decompose the organic components into carbon and produce a carbon fiber with sufficient strength for practical applications. The carbon fiber is then activated by treating with carbon dioxide and steam to form fine pores. The temperature and duration of this activation process is critical to produce good fibrous active carbon.

Fibrous active carbon now finds enhanced utilisation as the social demands for pollution prevention and energy conservation increase. The starting material, the cellulosic source, is coconut husks. Compared with conventional granular active carbon, fibrous active carbon exhibits a better adsorption quality owing to its large contact area with air or liquids. The pore size at its surface is approximately 10 Å in diameter, so each pore traps a molecule. The adsorption rate depends on pore size, its position and distribution at the surface. The specific pore surface area is some 1.5–5 times larger than that of granular carbons. Fibrous active carbon can be woven, knitted or converted into a paper sheet. The corrugated cardboard form of fibrous active carbon is now utilised as the base material for the solvent adsorption/desorption devices used in car factories. It is capable of adsorbing various solvents present at low concentrations in exhaust fumes, or arising from the painting process. The system can be regenerated by blowing heated air over the active carbon, which desorbs the material.

Biotechnology has been used for generations in the fermentation processes to produce wine, beer, sake, etc. Alcohol is inevitably released into the air during fermentation, and major brewers are now investigating the recovery of the released alcohol using an adsorption device made from active carbon cardboard. It can then be further used. The released gas during fermentation contains a variety of components. Some, particularly low molecular weight components, such as acetaldehyde and ethyl acetate, produce a foul smell. These noxious components can permeate fibrous absorbents. Only components in the higher molecular weight range can be recovered with this adsorption device. Nevertheless, their recovery can be most useful. Following the fermentation of soya sauce, the recovered liquid is returned to the stock solutions, contributing a considerable resource-saving.

Powdery or granular active carbons of the conventional type have also been used as catalyst carriers, for solvent recovery, the decoloration of sake and sugar, etc. within the chemical and food industries. In view of the new developments, many more applications can be envisaged.

6.2 Biotechnology and fibers

Biotechnology has developed rapidly since 1953 when the gene recombination technique was first established. Now medical/pharmaceutical, foods, fermentation and chemical industries make extensive use of gene recombination, cell fusion, mass cultivation of animal/plant cells and bioreactors.

Now, major fiber-related industries are actively introducing biotechnology, and have invaded the bio-related fields of medical/pharmaceutical, fermentation and foods industries, as summarised in Table 6.1. Japanese cooperation with foreign industries and research institutes has been expanded in the biotechnology field to counter the extreme competition in this field. We should soon see biotechnology widely expanded in the fields of fermentation, foods, resources, energy and agriculture industries. As illustrated in Fig. 6.2, the fiber-related industries are using biotechnology for (i) making changes to production processes; (ii) utilising fibers as biotechnology materials; and (iii) for producing new useful materials.

As an example of (i), biotechnology is now being applied to breed a new type of cotton. Biotechnology has also made possible more efficient energy-saving processes for fiber production and the production of fibers of higher quality and higher functionality. In relation to (ii), fibers are already being used for the making of artificial internal organs and other medical materials. Further applications are imminent in the field of biosensors and bio-electronics. Area (iii) relates to the use of fibrous materials such as fibers, pulp and wood wastes obtained as biomass for producing useful materials by enzymic and microbiological action.

Here we describe the work of Professors Y. Ikada and T. Hayashi of the Research Centre for Medical Polymers and Biomaterials, Kyoto University, in producing medical materials via bioreactors.

Table 6.1. Fibers in biotechnology

Realise a plan	Hardware (raw materials)	Software (examples of utilisation)
	Hollow fiber	Artificial kidney, artificial lung, water deionisation, condensation of alcohol, oxygenator
Short to medium	Antithrombotic or haemolytic fiber	Blood cell exchange, plasmaphoresis
	Carrier fibers for biocatalyst	Drugs, foods, microanalysis
	Resolving fiber	Agricultural and gardening uses
	Slow-release fiber	Drugs, agricultural chemicals
	Biodegradable fibers	Sutures, artificial blood vessels
Medium to long	High-function membrane	High-performance biosensor
	Bacterial fiber	Fuels, chemicals, chemical manure, feed, physiological active materials
	Biomedical material	Artificial heart, artificial muscle, hybrid artificial liver
	Bioelectronics	Biosensor, artificial cell membrane, biocomputer

6.2.1 Fibers for medical uses

There are some 8 million users of contact lenses in Japan, making them the most extensively used items of medical equipment, followed by the artificial kidney where hollow fibers are used for the haemodialysis membrane. There are other major medical use of fibers as shown in Table 6.2. Filaments or threads are used for suture and absorbents (artificial liver). Hollow fibers are applied in blood purification, the artificial kidney and artificial lung. Although small in quantity, knitted or woven fabrics are used for artificial blood vessels. Cotton, non-woven fabrics and gauze are the traditional medical materials for haemostatic dressings and for artificial skin. Table 6.3 summarises such biomedical uses of fiber materials.

6.2.1.1 Sutures

Two types of sutures are currently available: (i) the assimilated type, such as a catgut; (ii) the non-assimilated type such as silk or polyester filament. Inevitably there will be a move to make more use of the readily resorbable type and a greater utilisation of polyester or polypropylene filaments for external use. Catgut, the most widely used assimilated type, is made from collagen, extracted from ox bones. However, it is not particularly suitable for implantation for biocompatible reasons. The human body normally rejects foreign materials, and collagen is not an exception when implanted directly

- **Production Process**
  - Increase of utility factor in process
  - Rationalization
  - Energy saving
  - High quality
  - High functionality
- **Biotechnology**
  - Bioreactors (immobilization of enzymes and microorganisms)
  - Separation, condensation, purification (biomembranes)
  - Medical application (artificial organisms, medical materials)
  - Bioelectronics (biosensors, bioelements, molecular memory, sensors for protein measurement)
- **Useful Materials**
  - Resources, energy (fuel)
  - Foods
  - Useful chemicals
  - Medicine

6.2 Development of biotechnology-related fibers.

into the body. Another weakness of the catgut suture is its strength, which deteriorates by a half after a week in the body, despite the fact that three weeks are required for the recovery of an incision after surgery. Thus active investigations are underway to produce a biocompatible suture of the assimilable type made from synthetic polymers.

A mono-filament is preferable for use as a suture because of its smooth surface. Poly(glycolic acid) is a synthetic polymer currently used for sutures of the assimilable type, but it is too hard a material to make a mono-filament suture. Thus it is now used to make the multifilament or blended type of

Table 6.2. Production of artificial organs

Articles		Total cost (million US$)	Quantity
1	Mechanical lung and heart	24	94,682
2	Pacemaker for heart	61	60,561
3	Artificial valve for heart	18	5,359
4	Haemodialysis	45	7,850
5	Dialyser	344	12,217,250
	(hollow fiber type)	(305)	(11,089,142)
6	Circuit for blood	64	12,596,283
	(for haemodialysis)	(46)	(10,866,672)
7	Instrument to purify blood	11	229,250
8	Artificial pancreas	1	11
9	Artificial blood vessels	6	13,306
10	Artificial joint, artificial bone	38	46,134
11	Suture	27	56,215,209
	(non-absorbable)	(17)	(48,938,311)
	Total	**639**	

suture, and this is commercially available now. To overcome its hardness, and rough surface, it is normally coated with a plasticiser, and in consequence the suture must be knotted several times to ensure that it does not loosen.

The ideal suture is a mono-filament with a smooth surface that can pass through the skin without being caught, and can be tightened with a single knot. The polybutylene teraphthalate (PBT) mono-filament suture is currently the most popular because of its acceptable strength and smooth surface. The poly(glycolic acid) suture is used currently for heart surgery in order to withstand the high pressure within the heart. However, poly(glycolic acid) is not fully assimilable by the body for one to two years. The objective is to reduce this time to less than six months. Johnson and Johnson Inc. have developed the suture with trade name Maxon, which appears to satisfy all the required criteria.

6.2.1.2 Blood purification

Table 6.4 identifies the three major artificial organs related to blood purification. Various fiber materials are now used in the manufacture of these organs.

Artificial kidney

Haemodialysis is indispensable for people suffering from kidney disease, and some have been subjected to this treatment for over 25 years. A complication is that long-term use of the haemodialyser (artificial kidney) can introduce another problem, because some unwanted substances in the blood are not

Table 6.3. Fibers for biomedical uses

Medical use	Examples of fiber materials	Key points for medical use
Fiber materials in hospitals	Cellulose, nylon, polyester	Sterilisable, dust free, easy handling
Suture	Catgut, silk, cotton, polyglycolic acid, polylactic acid, polydioxanone nylon, polypropylene, polyethylene, polyethylene terephthalate	Sterilisable, knotting strength, tissue compatibility, absorbable or non-absorbable, softness, easy handling
Surgical tape, tissue adhesives	Collagen, oxycellulose, fibrin, polyurethane	Ease of preparation, biocompatibility, resorbable, sterilisable
Vascular implant	Dacron, Teflon, biograft, collagen, segmented polyurethane, polyglycolic acid, polyester, urethane	Blood compatibility, porous structure, resorbable, easy for tissue ingrowth, minimise clotting
Artificial skin	Natural skin equivalent (dried pig skin, collagen, chitin), silicon/nylon, polypeptides, silicone/collagen/Glycosamino glycans, hybrid skin equivalents	Adhesive to tissue surface, prevent loss of fluids and infection, resorbable, relief of pain
Soft tissue implant	Silicone, polylactic acid, collagen	Relief of pain, adhesive, resorbable
Joint replacement	Polymethylmethacrylate, high molecular polyethylene, silicone	Mechanical strength, wear durability, must not become loose
Artificial bone	Polyethylene/apatite, polylactide/apatite, polysulphone, carbon fiber, polyethylene terephthalate, glass ceramic	Moderate mechanical strength, adhesion to bone, resorbable
Artificial kidney	Cellulose, polymethylmethacrylate, copolyethylene-vinyl alcohol, polyacrylonitrile, polysulfone, polycarbonate, chitin, chitosan	Moderate mechanical strength and permeability, blood compatibility, suppression of complementary activation
Artificial lung	Silicone, polypropylene, polysulfone polyethylene, Teflon	Gas exchange effect, blood compatibility, suppression of blood plasma leak
Artificial liver	Carbon fiber, cellulose, polyetherurethane, poly(HEMA)	Blood compatibility, adsorptive activity
Carrier for DDS	Polysaccharide, collagen, nylon, polyacrylonitrile, polyvinyl alcohol	Large surface area, porosity, functional group

Table 6.4. Blood purification devices

	Artificial kidney	Artificial liver	Artificial lung
Function	Excretion of waste materials and water. Control of electrolyte concentration	Separation and disposal of patient's plasma and supply the fresh plasma into the patient's blood	Execution of the cardiopulmonary function of the patient
System	Haemodialysis (HD) Haemofiltration (HF) Haemodiafiltration (HDF)	Plasmapheresis (PP) Haemoperfusion (HP)	Haemoperfusion (HP)
Material	Cellulose hollow fibers Polyacrylonitrile Polymethylmethacrylate EVAL	Cellulose hollow fibers Anionic exchange resins Active carbon powder Ceramics	Polypropylene, silicone Silicone hollow fiber Silicone–acrylamide grafts

dialysed out. Also, an immunological reaction can occur with repeated use, since the dialyser is a foreign substance to the human body. When the blood is circulated through the dialyser, the leucocyte count in the blood decreases over the first 20 min of dialysis, but recovers to its original value after 1 h. The haemodialyser is made up from a bundle of hollow fibers through which the blood circulates. The objective is to improve the surface of hollow fibers so that the leucocyte decrease does not occur. Although some materials do not appear to be dialysed from the blood, certain cases of uraemia and other kidney troubles are nevertheless improved on dialysis. There is no definitive explanation for this improvement at present, although there are some hypotheses. Kidney troubles, it is believed, can be caused by proteins of molecular weight between 10,000 to 30,000. The blood also contains substances that must be retained, such as albumin with a molecular weight of about 70,000. Each hollow fiber manufacturer is now developing a suitable membrane, through which the harmful proteins of molecular weight around 20,000 pass but not the proteins of the molecular weight around 70,000. These could have much practical benefit.

Mechanical lung

Silicone or polypropylene hollow fibers are used for the fabrication of the mechanical lung to allow permeation of gases. It ideally should function for at least one to three weeks. However, the present mechanical lung lasts at most one week, because its ability to remove carbon dioxide falls off. The lung is a form of gas exchanger to supply oxygen to the blood and remove carbon dioxide. The mechanical lung was first developed as a device to replace lung function during heart surgery, and is now extensively used for this purpose in the USA (about 250,000 per year) and Japan (20,000 per year). A newer form of mechanical lung can also be used as a supplementary respiratory device over a longer term to assist the breathing of patients suffering from acute lung or heart failure, or older people with weak lung function.

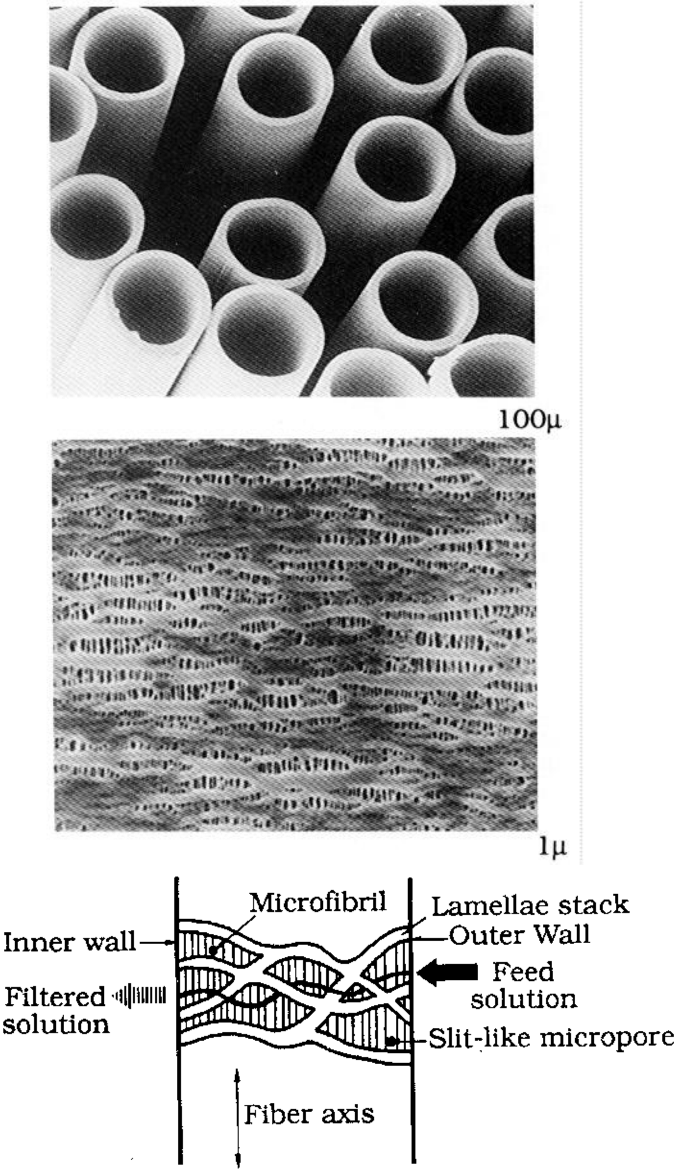
The artificial lung of the micropore membrane type is the presently used system in which oxygen comes into contact with blood via the membrane in the same way as in a natural lung. Mitsubishi Rayon Co. has developed a microporous polypropylene (PP) hollow fiber for the manufacture of an artificial lung (see Fig. 6.3), and is currently supplying the fiber to medical device manufacturers. Here gases freely pass through the pores of PP hollow fibers, but not the blood, because of the hydrophobicity of PP membrane. As a result, the artificial lung of the gas-bubble type is rapidly being replaced with the membrane type, which could soon dominate the artificial lung market, according to the estimates of the Mitsubishi Rayon Co. PP hollow fiber exhibits good compatibility with blood and excellent gas permeability. Its use allows the design of a compact artificial lung that is easy and safe to operate. However, its long-term use causes a leak of blood plasma components, and an investigation is underway to improve the membrane material in order to eliminate this disadvantage.

Artificial blood vessels

Artificial blood vessels are now commercially available, and are made mostly from polyester or Teflon. They are used to replace thick arteries or veins of 6 mm, 8 mm or 1 cm in diameter. Although polyester is biocompatible, its anticoagulant activity is poor. Porous Teflon, on the other hand, exhibits both good biocompatibility and anticoagulant activity. However, thin blood vessels (diameter less than 3 mm) made from Teflon lead to other problems. Consequently, at the present time, the coronary artery or the thin veins in hands or legs are replaced with blood vessels from other parts of the same human body. Thus, research in this field is targeted to produce thin artificial blood vessels of diameter less than 3 mm.

Dr M. Kodama, Research Institute for Polymers and Textiles, Japan, has developed an artificial blood vessel of inner diameter 1.5 mm, which has a three-layered structure made up of collagen, heparin and Teflon. The inner layer of collagen and heparin imparts good anticoagulant activity, whereas the porous Teflon tube which makes up the middle layer provides the mechanical strength. It is coated with collagen to form an outer biocompatible layer.

The task of producing an artificial substitute for the bile duct can be approached in a similar manner to blood vessels. However, the bile duct exhibits two contradictory physical properties, in being extremely soft but also very tough. The bile duct cannot be cut using a thread, whereas a soft synthetic polymer tube slices easily this way. A synthetic polymer material



6.3 Schematic structure of microporous polypropylene membrane (longitudinal cross-section).

which resists thread tightening, is generally too hard and causes other problems during surgery. The race is now on to develop a soft but tough synthetic polymer material suitable both for artificial blood vessels and bile ducts.

6.2.2 Bioreactors

Biotechnology is often regarded as one of the most advanced modern technologies. Yet fermentation technology is traditional in Japan, and much recent biotechnology has been developed on this traditional basis. Newer developments use more recent technologies, such as gene recombination, cell fusion, large-scale cell cultivation and bioreactors.

The bioreactor utilises the specific function of biocatalysts to produce new and useful fine chemical materials effectively, to generate energy, for use in quantitative and qualitative analysis and to remove pollutants. In effect, it is a type of immobilised biocatalyst, utilising enzymes. Over 2,000 enzymes have been found suitable for use in a bioreactor, but few are in commercial use at present. If, however, organelles, microorganisms or cells could be immobilised, the bioreactor's efficiency would increase sufficiently to allow practical use.

Enzymic reactions proceed under extremely mild conditions compared with the usual type of chemical reaction. Thus effective use of enzymes in chemical processes leads to energy conservation. They are also characterised by substrate specificity; the reaction yield is high, and there is no by-product, so the process can be economically favourable.

How then can fibers be applied as carriers for immobilisation processes and what are the advantages? Bead-like, spherical or membrane-type carriers are conventionally used to immobilise biocatalysts. However, a fibrous carrier is capable of providing an infinitely extended surface area. Porous, non-circular cross-sections, fine and/or hollow fibers can offer a large specific surface area without break. Such a fibrous carrier can be processed in the form of a thread, braid, cloth, net or a non-woven fabric, according to its applicational environment. Porous fibers can be made in the form of filter paper or non-woven fabric and used as a biosensor. With recent technology, pores of homogeneous size can be produced on the fiber surface to entrap relatively large substances such as enzymes (over 4 μm) or bacteria (a few tens of μm).

Various methods are currently employed to immobilise biocatalysts. The most popular is to wet-spin the mixture of biocatalyst and carrier in order to entrap the enzyme or bacteria within the fiber. Many pores can be formed on the fiber surface by wet-spinning in such a way that substrates and reaction products freely pass through, but biocatalysts of relatively large size remain entrapped. Biocatalysts can be immobilised by simple adsorption on to the porous fiber surface. If biocatalysts need to be fixed more firmly, they can be covalently or ionically bound to the fiber. For example, penicillinacylase can be immobilised on a reduced porous polyacrylonitrile fiber by covalent linkage to produce 6-amino penicillin, which serves as a raw material for reactive penicillin. Several thousand tonnes of 6-amino penicillin are produced annually in this way. Enzyme-immobilisation by covalent linkage is currently a most active research field.

With the advent of more old people in society, clinical analysis will increase in importance as a support for preventive medicine. Efficient biosensors need to be developed to ensure rapid, economic and effective analysis. Biosensors using immobilised biocatalysts of the covalent linkage type are very suitable for quantitative analysis, since no biocatalyst is lost after the reaction. Moreover, this type has another advantage because the biocatalyst is immobilised on the carrier surface and can contact the substrate without hindrance. Such a device is now being utilised in the food industry with amylase, in the pharmaceutical industry with penicillinamylase, and in the medical industry with urease (to detect urea in blood).

In some instances, enzyme-immobilisation by adsorption is favoured. Since the enzyme here is loosely linked on the fiber surface, its activity is high but it is desorbed easily. Consequently, the carrier can be regenerated by replacing the original enzyme with a replacement, after the enzyme has lost its activity after repeated use. This type of the bioreactor is used in acetic acid production, by utilising acetobacter adsorbed on to cotton-like polypropylene fiber.

Bioreactor design is also important if an immobilised enzyme is to be harnessed effectively. The choice depends on the application. There are many types available, for example, the integrated type which mixes the substrate and immobilised enzyme, or the flux-flow type, where the substrate flows through uniformly packed beads of immobilised enzyme. The beads can be replaced with a bundle of hollow fibers with the immobilised enzyme on the surface, and the substrate is transported either in the fiber hollow or along the outer surface of the fibers.

Although bioreactors are generally recognised as extremely useful, their practical application has not yet been fully realised.

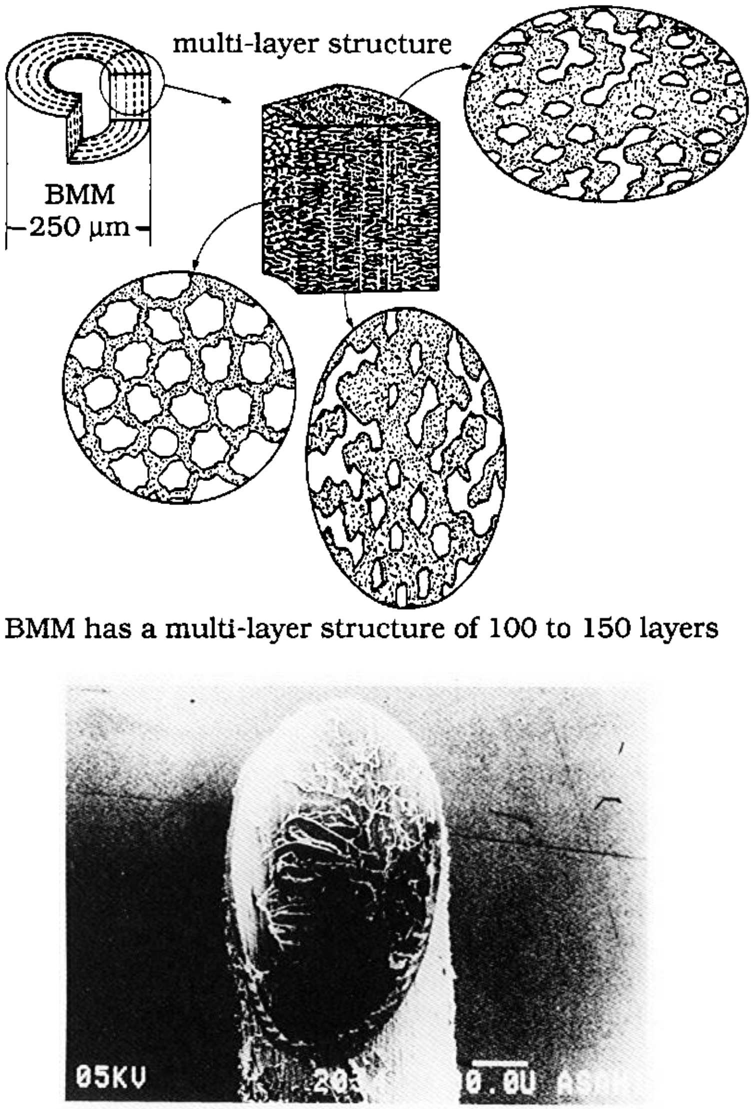
6.2.3 Magic fiber for AIDS diagnosis and treatment

The Asahi Chemical Industry Co. has developed a porous hollow fiber membrane Bemberg Microporous Membrane (BMM) to filter out and isolate the AIDS virus and hepatitis type B in blood. BMM is made from cellulose fiber (Bemberg) regenerated from cuprammonium solutions of cotton linters.

Synthetic polymers are known to cause blood clotting as a result of protein adsorption. However, regenerated cellulose is free from this problem, and for this reason is used for the artificial kidney in the form of hollow fiber. In order to allow proteins to permeate, but to isolate viruses using the same membrane, it is necessary to have homogeneous pores in the membrane that are larger than proteins but smaller than viruses. The Asahi Chemical Industry Co. has established the technology to produce such cellulose membranes having homogeneously distributed pores of predetermined diameter. Spherical B-type hepatitis virus and the AIDS virus have a diameter of 42 nm and 90–100 nm, respectively. Thus the membrane needs to have pores of 30–40 or 40–75 nm in diameter, respectively, to isolate these viruses. A single layer of membrane is not sufficient to isolate such viruses completely; consequently BMM has a multi-layer structure of 100–150 layers. This multi-layer hollow fiber membrane is produced by wet-spinning from cuprammonium solution of cotton linter mixed with an organic solvent. The solution undergoes phase separation and is composed of two phase made up of a concentrated and a dilute organic solvent. The concentrated phase forms a continuous organic solvent layer, and the dilute phase is made up of small organic solvent holes of a uniform size in the cotton linter solution. When spun, the resulting hollow fiber is made of 100–150 layers of cellulose membrane, with pores of a predetermined diameter (see Fig. 6.4). The pore size and the degree of crystallinity of BMM depends on many external factors such as temperature, solvent composition, component purity and time. Usually BMM is 300–400 μm in outer diameter, 250–350 μm in inner diameter, and is composed of 100–150 layers of membrane of 25–40 μm in thickness. The actual module is made of 300 BMM hollow fibers which together are 3 cm in diameter and 15 cm in length. Each layer of BMM has over a billion pores which enables complete filtration and isolation of the viruses.

Yamaguchi University and the Hokkaido Red Cross Blood Centre have cooperated with the Asahi Chemical Industry Co. to use BMM for the isolation of AIDS and hepatitis B virus. They first reported the work at Third International AIDS Conference held in Washington, USA, in 1987. Professor N. Yamamoto, School of Medicine, Yamaguchi University, demonstrated that he was able to isolate the AIDS virus completely from a culture solution of human AIDS virus.

BMM is now expected to be applied to the diagnosis and treatment of AIDS. At present, AIDS is diagnosed by using the antigen–antibody reaction, but using this method the result is negative until an antigen is formed. Since BMM isolates the AIDS virus itself, AIDS diagnosis by BMM is possible even in the early stage of virus infection, even before the antigen is formed. Although BMM does not influence directly the AIDS virus, it is capable of removing virus from plasma and so suppresses its multiplication. AIDS virus immersed into lymphocytes grows there, and then overflows into plasma. If the isolation rate of virus from plasma is fast, the clinical progress of AIDS can be suppressed. This suppression of the AIDS virus can allow the



6.4 BMM is made from cellulose fiber (Bemberg) (Asahi Chemical Industry Co.).

reactivation of the metabolic functions of the human body, so that treatment efficiency will improve when combined with other medical treatments.

Other applications of BMM are found, for example, in the complete isolation of virus during plasma medicines manufacture, the administration of fractionated plasma-producing medicines for haemophiliacs, and the prevention of virus infection during ordinal plasma transfusion. BMM is also useful for the isolation of hepatitis non-A non-B virus and in the study of unknown viruses or other physiologically active substances.

6.3 Electronics and fibers

Clean rooms are indispensable for the production of VLSI circuits, which herald the sub-micrometre age in the fields of semiconductors and biotechnology. The degree of required cleanliness is continually increasing as the scale of integration and precision in the VLSI industry improves. The demand for cleanliness is increasing also in other production areas, such as that of magnetic discs and cathode-ray tubes. Indeed, no high technology can develop to its extreme without even stricter cleanliness.

The production yield in a clean room falls in to the presence of dust, which mostly (40–50%) comes from workers in the room. Thus synthetic fiber manufacturers are working energetically on the development of dust-free garments of high performance to meet this demand, by improving the dust-proof and electrostatic-proof characteristics of the materials. Functionalities such as safety, thermal insulation, wear comfort and working efficiency are primary requisites for working clothes. Although the design of working clothes for the clean room is constrained by the specific environment involved, a fashionable element needs to be introduced to add mental comfort to the functionalities required. Working clothes must be free from electric charges when used in a clean room for the production of semiconductor devices to avoid static electricity, but should also be durable against repeated washing and steaming necessary for sterilisation against bacterial contamination.

The main criteria for working clothes suitable for the clean room are; (i) the dust generated from underwear must not leak through the working clothes; (ii) no dust must escape from the clothing material itself; (iii) the clothes must be antistatic and dust-proof; (iv) they should be moisture-permeable and comfortable; and (v) the clothing should be durable against washing (see Table 6.5).

Polyester is probably the best synthetic material currently available for clean room working clothes. Carbon is mixed into the polyester resin to make it electrically conductive. These conducting fibers can be woven into high-density fabrics and eliminate static electricity induced by the low humidity atmosphere of the clean room. Aramid fiber is used when high fire-resistance is required. Natural fibers such as cotton or wool are not applicable for this purpose because of the dust they generate.

The degree of cleanliness is evaluated in terms of the number of dust particles per unit volume atmosphere. The highest degree is denoted as Class 1, where a unit cubic foot (0.028 m^3) of air contains less than one dust particle

Table 6.5. Properties required for garments for use in clean rooms

Required property	Contents	Remarks
Dust-proof	Garments should not cause dust. Ravellings and processing agents must not be released	Dust should not come out from inside of garment, especially from nape and cuff
	Cloth for clean garments should have ability to filter dust from human body and underwear	
	Surface of clean garment should not adsorb dust	
Charge-proof	Garments should not adsorb dust	Destruction of semiconductor and explosion of flammable gas should not be caused by spark discharge due to garments
	Cloth for clean room must not induce static electricity	
Durability	Garments should be easy to wash and no need for ironing	Durability for 100 washings is necessary
	Garments should have durability to washing, steam sterilisation	Water and tetrachloroethylene are used for washings
	Garments should be durable to chemicals	Steam sterilisations are carried out at 120–130 °C for 20–30 min
Wearability	Easy to work in the garments	The garment design must allow ease of work
	Cloth is not stuffy and has good handling	
	Cloth is not "see-through"	
Others	Cloth is suitable for sewing	

of maximum 5 μm in diameter. The degree of cleanliness is graded down as Class 10 (less than 10 dust particles), Class 100 (less than 100 dust particles), Class 1000 (less than 1000 dust particles), and so on. A clean room meeting Class 1 to Class 10 criteria can only be achieved by strict control of the air conditioning and filtration systems.

The total demand for clean room working clothes was some 1.6 million items in 1996 in Japan, with 54% used in the electronics industry, 13% in the pharmaceutical industry, 11% in the food industry, 9% in the precision engineering industry and 13.7% in biotechnology, medical research and printing. Although the required degree of cleanliness depends on the type of industry, 66% require a degree between Class 10,000 and Class 1,000, 20% Class 100,000, 12.5% Class 100 and 1.5% Class 10. Each year a higher degree

Table 6.6. Development of clean rooms for industry with the required degree of cleanliness

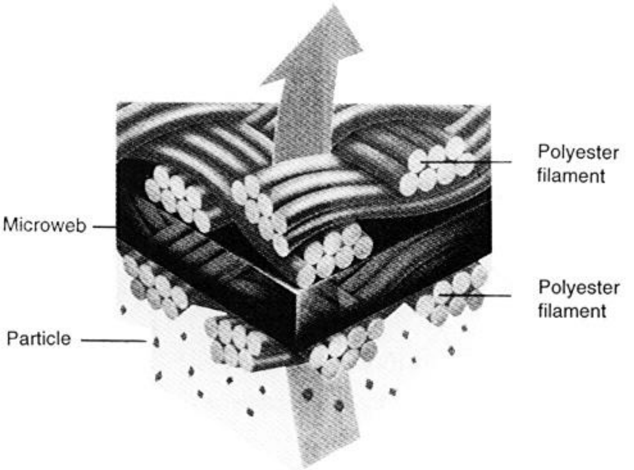
	(1970)	→	(1980)	→	(1985)	Frontier at present	
Integrated circuit	1 kbit	4 kbit	16 kbit	64 kbit	256 kbit	1 Mbit	4 Mbit
Minimum pattern dimension (μm)	8	5	3	2		1	
Diameter of particle to be removed (μm)	1	0.8	0.5	0.3	0.2		0.1
Degree of cleanliness (particle/ft^3)	10,000	1,000		100		10	1
				←	ultra-clean room		→

of cleanliness is required by the semiconductor industry. Classes 1,000 to 10,000 were sufficient a few years ago, but now Classes 0 to 1 are called for to accommodate the increase in IC capacity of semiconductors. IC capacity is expressed in terms of bits. A few years ago, 256 kbit was the most integrated circuit available, but now a 1 Mbit IC is commonly used (see Table 6.6). The line width of the 1 Mbit IC pattern is 1 μm, so that a dust particle of 1 μm damages the pattern. The maximum dust size allowed in a clean room is 1/10th of the pattern line width. The IC capacity is now increasing from 4 Mbit to 16 Mbit, and as a consequence Class 0 or Class 1 is required for the degree of cleanliness in the production of these high-density semiconductors. Humans must be regarded as a major dust source, so that it is unlikely that any human can enter a clean room of Class 0 or Class 1. A robot replaces a human worker in this situation. Even so, a robot also generates dust due to abrasion between its moving parts, and consequently this too must be reduced to a minimum.

Humans foul clean room air by dropping dandruff, old skin and dust from underwear. Each apparel maker is now developing dust-free working clothes which envelop a person completely and ensure that there is no leak of dust from the seam or neck areas. For example, Toray, in cooperation with Professor T. Ohnishi of Tohoku University, developed the Toray-type dust-free working clothing. The neck is made of Spandex, the edge of the sleeve is double to prevent dust release, the fastener is positioned at the side, and it is fitted with an integrated cap having a knitted interior to envelop the hair.

Kanebo cooperated with Shimizu Construction Co. and Sharp Corporation to develop the sucking-type of dust-free working clothing. This system is fitted with a small electric vacuum cleaner (weighing 1 kg) attached to the waist with a sucking vest which filters the air inside the clothing and exhausts clean air into the atmosphere.

The Asahi Chemical Industry Co. is now selling the M-bit clean suit



6.5 Structure of Hepa Cloth (Asahi Chemical Industry Co.).

Hepawear. This is dust-proof working clothing made from Hepa Cloth (see Fig. 6.5), which was developed as Hepa (high-efficiency particulate air filter) in the USA for military and high-technology purposes. Hepa Cloth is able to filter the air and collect fine particles of 0.3–0.5 μm in diameter. The material has a three-layered structure composed of a dust-proof non-woven fabric, made from a fine polyester filament of 1–2 μm in diameter, sandwiched with polyester clothing material. It has a dust filtration capacity of 0.3 μm (according to JIS Z-8901). Such Hepa Cloth has a low pressure loss, good dust-proof ability (over 80%), and air permeability of about 10 cm^3/cm^2 s. Hepawear partly employs Hepa Cloth, and is designed to ensure free body movement, comfort and good moisture permeability.

Teijin has developed the antistatic and dust-proof clothing Selguard C, which is a two-layer polyester fabric laminated with a moisture-permeable antistatic carbon-containing film 25–30 μm thick. Up to 2000 V is allowed for static electricity generated during wearing dust-proof clothes, but Selguard C generates less than 50 V static electricity. It is, therefore, ideal for use in the production of semiconductors and prevents the damage caused by electric discharge. For this purpose 0.6 μq per suit is acceptable in a clean room working to JIS standards, but it is often necessary to reduce below 0.3 μq. Selguard C achieves less than 0.1 μq in terms of the charge generated per suit.

Elitron, developed by Toyobo (see Fig. 6.6), is an electrostatic air filter made of electret fibers having a high dust filtration efficiency and low pressure loss. These electret fibers retain positive and negative charges, and collect dust

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