Textbook of Fiber Formation Technology

By Qing Shen
沈青 编著

纤维成型技术教程

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内容提要

《纤维成型技术教程》是一本以英文编写的教材，在每一章的结束附有相应的习题，主要面向高分子材料专业的本科生、研究生，也适合其他读者阅读参考。

本书的内容分成7个部分，第1章介绍纤维的历史；第2章介绍纤维的定义、结构和分类；第3章介绍16种根据应用命名的纤维，如工业纤维、复杂纤维、军用纤维、智能纤维等等；第4章介绍主要的纤维及其来源，如天然纤维、合成纤维等；第5章主要介绍23种纺丝技术，如熔融纺丝、湿法纺丝、干法纺丝、凝胶纺丝等；第6章主要介绍伯测试与表征技术；第7章主要通过实例介绍不同的纤维成型技术，涉及11个例子，如一步法合成技术直接制备纳米纤维等。

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Preface

Fiber plays a key role in many areas and the past century has witnessed a huge increase of research interest in the study of fiber products and quantity development. Now, the properties of various fibers in synthetic, chemical and natural all are very importantly applied elsewhere.

This book provides a brief introduction of fiber knowledge and various fiber technologies as well as related cases on fiber formation. The fiber types represent their applications which we met in life and somewhere covering main aspects of cutting edge in research and development.

This book is organized by seven chapters with total not more pages to fit the course study for students in China. Chapter 1 introduced the fiber history. Chapter 2 consists of five parts and deals with fundamental aspects of fiber knowledge such as fiber definition, structure and classification. Chapter 3 described various fiber types in relation to their possible application. Chapter 4 contains main fiber resources, e.g. from natural and synthetic polymers or from inorganic materials, respectively. Chapter 5 introduced main fiber formation techniques and related equipment, where the melt spinning was in detail described. Chapter 6 deals with main methods for fiber measurement and characterization where the fiber morphology, structure, properties and surface wetting were introduced. Chapter 7 presented several detailed cases on fiber formation which was considered to help students to direct understand fiber formation.

Of this textbook, the recommended reading was arranged in each chapter and this was expected to fit the further reading for students. In some chapters, problems were also appeared in the final to lead students to think some novel question on development of fiber techniques. Also, it is greatly wished that this textbook can help students to start advanced study internationally.

I would like to thank my family for their friendly and courteous assistance.

Qing Shen

Contents 目录

Chapter 1

Fiber History

Fiber is defined as a solid material with stable thin shape and long size as well as certain level of tensile strength. As has been consistently recognized that the fiber science and technology were learnt from silkworm and spider since their fiber producing processes are good examples of the biosynthetic and biospinning techniques because they convert non-fiber foods by enzymes into proteins in body then spun fibers as a cocoon or net. In addition to animal fibers, plants-based fibers are generally synthesized in natural conditions, e. g. by photo, carbon dioxide and water.

The use of fiber in human history can back to the Paleolithic times by observing the ancient people used cordage in fishing, trapping and transport, as well as the fabrics for clothing using palm leaf, jute, flax, ramie, sedges, rushes and reeds as raw materials. The first true paper is made in southeastern China in the second century AD from old rags, hemp and ramie and later from the fiber of the mulberry tree.

For thousands of years, the fiber use was limited by the inherent qualities available in the natural world, e. g. cotton and linen wrinkled from wear and washings, silk required delicate handling, and wool shrank irritating to the touch and eaten by moths. A mere century ago, the first manufactured fiber, rayon, was developed and soon applied to people's life. The secrets of fiber chemistry for countless applications must be emerged.

Man manufactured fibers now are put to work in modern apparel, home furnishings, medicine, aeronautics, energy and various industry areas, and these lead fiber engineers to combine or modify fibers in some ways far beyond the performance limits of fiber drawn from the silkworm cocoon, grown in the fields, or spun from the fleece of animals.

The earliest published record of an attempt to create an artificial fiber took place in 1664 when the English naturalist *Robert Hooke* suggested the possibility of producing a fiber that would be "if not fully as good, nay better" as compared with the silk.

The first patent for "artificial silk" was granted in England in 1855 contributed by a Swiss chemist, *Audemars*. He dissolved the fibrous inner bark of a mulberry tree; to chemical modify it to produce cellulose. He formed threads by dipping needles into this solution and drawing them out, however, it never lead him to emulate the silkworm by extruding the cellulosic liquid through a small hole.

In the early 1880's, an English chemist and electrician, Sir *Joseph W. Swan*, was spurred to action by *Thomas Edison*'s new incandescent electric lamp. He experimented with forcing a liquid similar to *Audemars's* solution through fine holes into a coagulating bath, obtained fibers worked like carbon filament.

It also occurred to *Swan* that his filament could be used to make textiles. In 1885 he exhibited some fabrics crocheted by his wife from his new fiber in London.

The first commercial scale production of manufactured fiber was achieved by French chemist, *Count Hilaire de Chardonnet*, in 1889, when his fabrics of "artificial silk" caused a sensation at the Paris Exhibition. After that about two years, he built the first commercial rayon plant at Besancon, France. On the basis of this great contribution, he has fame as the "father of the rayon industry".

In United States, several attempts have been made to produce "artificial silk" during the early 1900's but none were commercially successful until the American Viscose Company formed by Samuel Courtaulds Co., Ltd. to produce rayon in 1910.

In 1893, *Arthur D. Little* of Boston, invented another cellulosic product, acetate, and developed it as a film. By 1910, *Camille* and *Henry Dreyfus* made acetate motion picture film and toilet articles in Basel, Switzerland. During the World War Ⅰ, they built a plant in England to produce cellulose acetate dope for airplane wings and other commercial products. Upon entering the War, the United States government invited the Dreyfus brothers to build a plant in Maryland to make the product for American warplanes. The first commercial textile uses for acetate in fiber form were developed by the Celanese Company in 1924.

In the meantime, U.S. rayon production was growing to meet increasing request, and by the mid of 1920's, textile manufacturers could purchased the fiber for half the price of raw silk.

In 1931, American chemist, *Wallace Carothers*, reported their research results carried out in the laboratory of the DuPont Company on "giant" molecules called polymers. He focused his work on a fiber referred to simply as "66", a number derived from its molecular structure. Nylon, the "miracle fiber", was born. The Chemical Heritage Foundation is currently featuring an exhibit on the history of nylon.

In 1938, a scientist, *Paul Schlack*, worked at the I. G. Farben Company in Germany, polymerized the caprolactam and created a different form of the polymer, which was identified simply as nylon "6".

Nylon's coming created a revolution in the fiber industry because rayon and acetate have been derived from plant cellulose, while nylon was synthesized completely from petrochemicals to establish the basis for the ensuing discovery of an entire new world of manufactured fibers *via* human synthesis.

DuPont began commercial producing nylon in 1939, when the first experimental testing used nylon as sewing thread, in parachute fabric, and in women's hosiery. Nylon stockings were shown in February 1939 at the San Francisco Exposition, and since then most excited fashion innovations of the age were underway.

During the World War Ⅱ, nylon replaced Asian silk in parachutes and used in tires, tents, ropes, ponchos, and other military supplies, and even was used in the production of a high-grade paper for U.S. currency. At the outset of the War, cotton was king of fibers, accounting for more than 80% of all fibers used. Manufactured and wool fibers shared the remaining 20%. By the end of the War in August 1945, cotton stood at 75% of the fiber market. Manufactured fibers had risen to 15%.

After the War, GI's came home, families were reunited, industrial America gathered its peacetime forces, and economic growth surged. The conversion of nylon production to civilian uses started and when the first small quantities of postwar nylon stockings were advertised, leading thousands of frenzied women lined up at New York department stores to buy.

In the immediate post-war period, most nylon production was used to satisfy this enormous pent up demand for hosiery. But by the end of the 1940's, it was also being used in carpeting and automobile upholstery. At the same time, three new generic manufactured fibers started production at Dow Badische Company (today, BASF Corporation), e. g. the metalized fibers; at Union Carbide Corporation, e. g. the modacrylic fiber; and at Hercules, Inc. e. g. the olefin fiber. Since that period, the man-made fibers continued their steady march.

By the 1950's, the industry was supplying more than 20% of the fiber needs of textile mills. A new wool-like fiber, "acrylic", was developed at DuPont.

Meanwhile, polyester, first examined as part of the Wallace Carothers in early researches, was attracting new interest at the Calico Printers Association in Great Britain. There, *J. T. Dickson* and *J. R. Whinfield* produced a polyester fiber by condensation polymerization of ethylene glycol with terephthalic acid. DuPont subsequently acquired the patent rights for the United States and Imperial Chemical Industries for the rest of the world. A host of other producers soon joined in.

In the summer of 1952, "wash and wear" was coined to describe a new blend of cotton and acrylic, and this term was eventually applied to a wide variety of manufactured fiber blends including the polyester fiber leading a revolution in textile product performance.

Polyester was commercialized in 1953 by the introduction of triacetate. In the 1960's and 1970's, consumers bought more and more clothing made with polyester. Clotheslines were replaced by electric dryers, and the "wash and wear" garments they dried emerged wrinkle free. Ironing began to shrink away on the daily list of household chores. Fabrics became more durable and color more permanent. New dyeing effects were being achieved and shape-retaining knits offered new comfort and style.

In fact, in the 1960's, the manufactured fiber production was accelerated by continuous fiber innovation. The revolutionary new fibers were modified to offer greater comfort, provide flame resistance, reduce clinging, release soil, achieve greater whiteness, special dullness or luster, easier dyeability, and better blending qualities. New fiber shapes and thicknesses were introduced to meet special needs. Of which, the Spandex, a stretchable fiber; aramid, a high-temperature-resistant polyamide; and para-aramid, with outstanding strength-to-weight properties, were introduced into the marketplace.

One dramatic new set of uses for manufactured fibers came with the establishment of the U. S. space program. The industry provided special fiber for uses ranging from clothing for the astronauts to spaceship nose cones. When Neil Armstrong took "One small step for man, one giant leap for mankind", on the moon on July 20, 1969, his lunar space suit included multi-layers of nylon and aramid fabrics. The flag he planted was made of nylon.

Today, the exhaust nozzles of the two large booster rockets that lift the space shuttle into orbit contain 30 000 pounds of carbonized rayon. Carbon fiber composites are broadly used as structural components in the latest commercial aircraft, adding strength and lowering weight and fuel costs.

Innovation is the hallmark of the manufactured fiber industry. More numerous and diverse fibers than any found in nature are now routinely created in the laboratories of industry.

Nylon variants, polyester, and olefin are used to produce carpets that easily can be rinsed clean-even 24 hours after they've been stained. Stretchable Spandex and machine-washable, silk-like polyesters occupy solid places in the U.S. apparel market. The finest microfibers are remaking the world of fashion.

For industrial uses, manufactured fibers relentlessly replace traditional materials in applications from super-absorbent diapers, to artificial organs, to construction materials for moon-based space stations. Engineered non-woven products of manufactured fibers are found in applications from surgical gowns and apparel interfacing to roofing materials, road bed stabilizers, and floppy disk envelopes and liners. Non-woven fabrics, stiff as paper or as soft and comfortable as limp cloth, are made without knitting or weaving.

Below we listed the innovation history for each man-made fiber. The first man-made cellulose fiber was reported by *Nicolaus de Chardonnet* in 1884. The first cooper silk filaments was reported in 1898 in Oberbruch near Aachen of Germany, by *Paul Fremery*, *Bromert* and *Urban*. The first polyvinyl chloride, PVC, was produced by *Klatte* in 1913. In 1927 *Staudinger* first spun the fully synthetic fiber from polyoxymethylene and later from polyethylenoxide by melting spinning. In 1934, the first semitechnical production of polyaerylonitrile fibers (PAN) was reported in Germany. The polyurethane, PU, fiber was developed in 1937 by *O. Bayer* et al. In

1938, *Carothers* reported the first polycondensation fiber, Nylon, in DuPont de Nemours & Co. Following, *Schlack* produced the lactam-based fiber, Perlon®, in 1939 in Berlin-Lichtenberg, Germany. The commercial polyester fibers were reported around 1950 developed by *Whinefield*. The first polypropylene, PP, fiber was reported around 1958 developed by *NaUa*. The high performance fiber, e.g. Nomex® and Kevlar®, both were developed by DuPont in 1963 and 1970, respectively. The development of high-grade carbon fibers was in 1966 with the oxidation and carbonization of PAN filaments. The novel biodegradable fiber, poly(lactic acid), PLA, was developed by Cargill Dow Chemical Company in 1997.

Among above periods, a lot of developed fibers without commercialized, e.g., polyaminotriazoles fiber, polyamides 4 and 7, PA 4 and PA 7, due to spinning difficult or cost reasons.

Recommending reading

[1] M. Harris, ed.. *Handbook of Textile Fibers*. Harris Research Laboratories, Inc., Washington, D. C., 1954.

[2] J. G. Cook. *Handbook of Textile Fibers. Vol. I: Natural Fibers*. 5th ed.. Merrow Publishing, Durham, N.C., 1984.

[3] T. Hongu, G. O. Phillips, M. Takigami. *New Millennium Fibers*. CRC Press, Woodhead Publishing Limited, 2005.

Chapter 2

Fiber Definition, Structure and Classification

2.1 Fiber definition

Fiber is defined as a solid material with stable thin shape and long size as well as certain level of tensile strength.

2.2 Fiber morphology and structure

The morphologies of some fibers are showed in Figure 2-1. It is clearly that the plant-based fibers, e.g. flax and cotton, with pore structure, while the animal-based fibers, e.g. wool and silk, having solid structure.

The fiber structure is generally known in micro- and macro-state as Figures 2-2 and 2-3 described, respectively.

Basically, it was known that the fiber consists of three distinct phases, i.e. the oriented crystalline regions, the amorphous regions also with preferential orientation along the fiber axis which contain tie molecules connecting crystallites, and the highly extended non-crystalline molecules which was called the interfibrillar phase. In these three phases, the interfibrillar phase plays a key role in the tensile properties of the fiber.

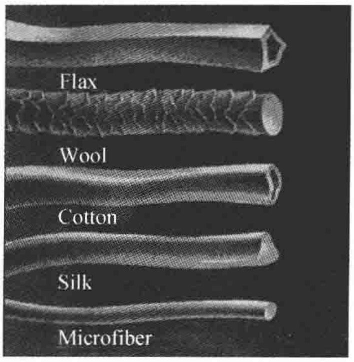


Figure 2-1 Morphologies of several fibers

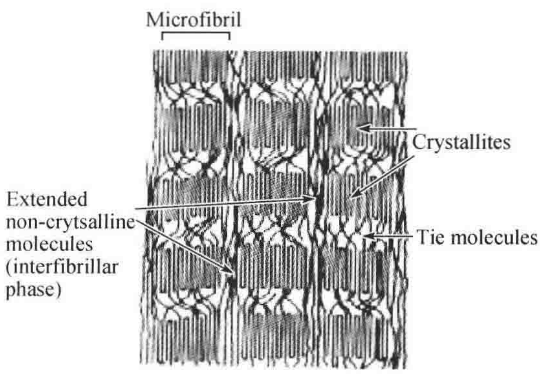
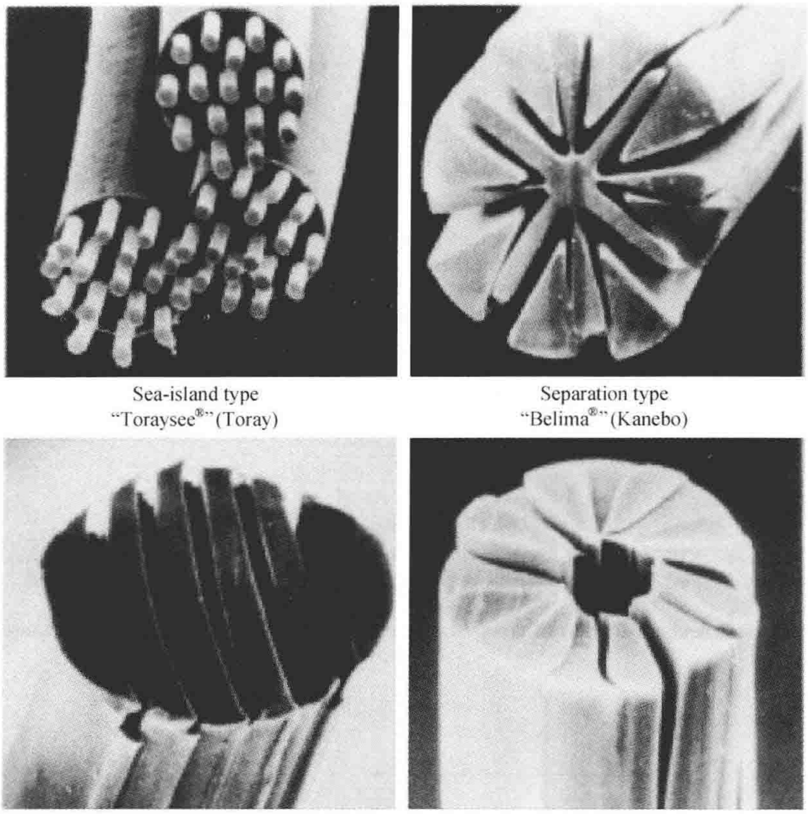


Figure 2-2 A scheme of the micro structure of fiber



Sea-island type "Toraysee®" (Toray)

Separation type "Belima®" (Kanebo)

Multi-layer type "WRAMP®" (Kurarag)

Separation type "Micro Star®" (Teijin)

Figure 2-3 The macro-structure of fiber

2.3 Fiber classification

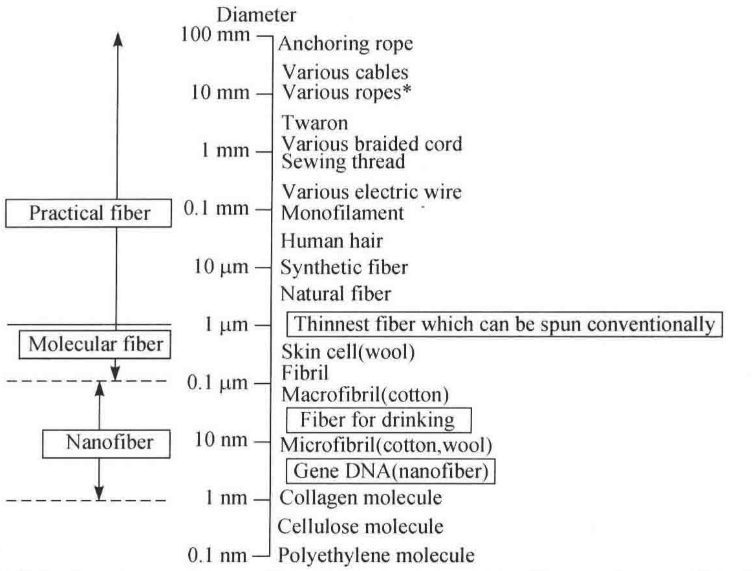
The classification of fiber has been defined by many people while yet without a standard agreed with all scientists and engineers.

Man-made fibers are probably classified into three classes according to the raw materials, e. g. the natural polymeric fiber, the synthetic polymeric fiber and the inorganic material-based fiber.

2.4 Fiber diameter and cross-sections

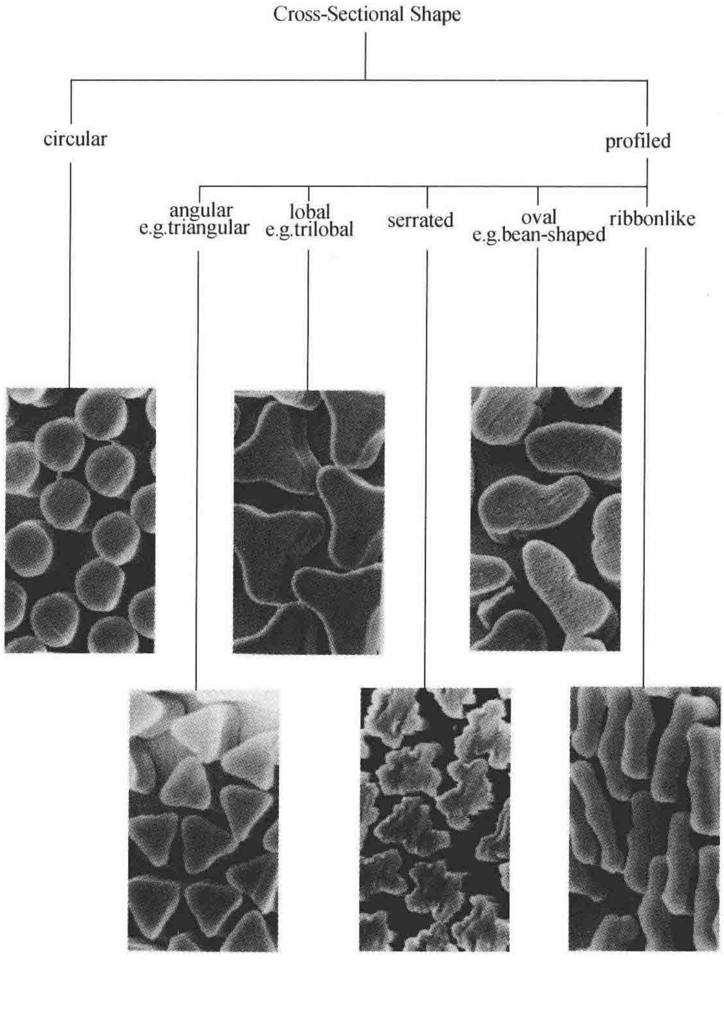
The fiber diameter-based classification can be understood from Figure 2-4, where the material kind related information appeared correspondingly. Of which it must be addressed that the nanofibers are also produced available by people using different methods, and here presented examples only for those in their initial size.

The common shape of fibers defined according to the cross-section morphology was described in below (Figure 2-5).



*: Distinction of fiber and assembly of fibers is necessary(Possible to make rope thicker)

Figure 2-4　A classification of fiber based on diameter in relation to different materials



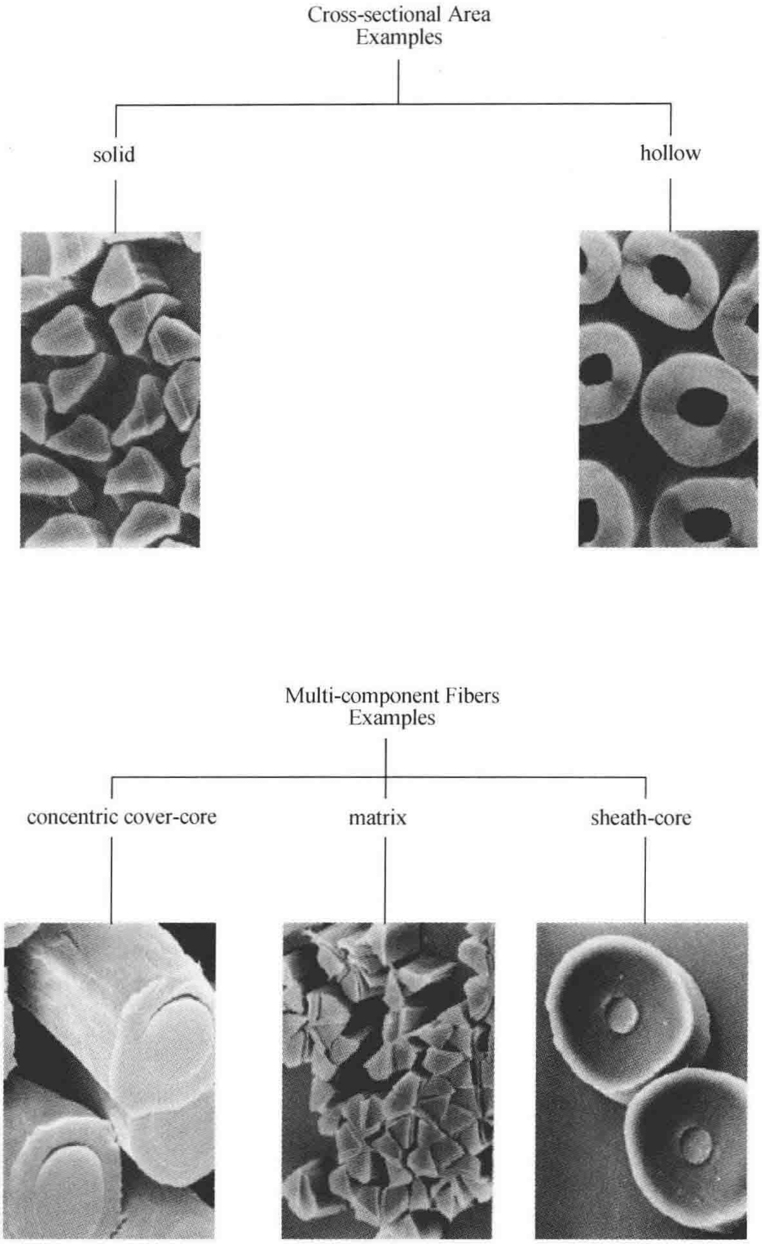


Figure 2-5 Cross-section of several fibers (Franz Fourne. *Synthetic Fibers, Machines and Equipment, Manufactory, Properties.* Hanser Publisher, Germany, 1998)

2.5 Importance of fiber technology

Below is a summarization of the fiber importance on the basis of the application.

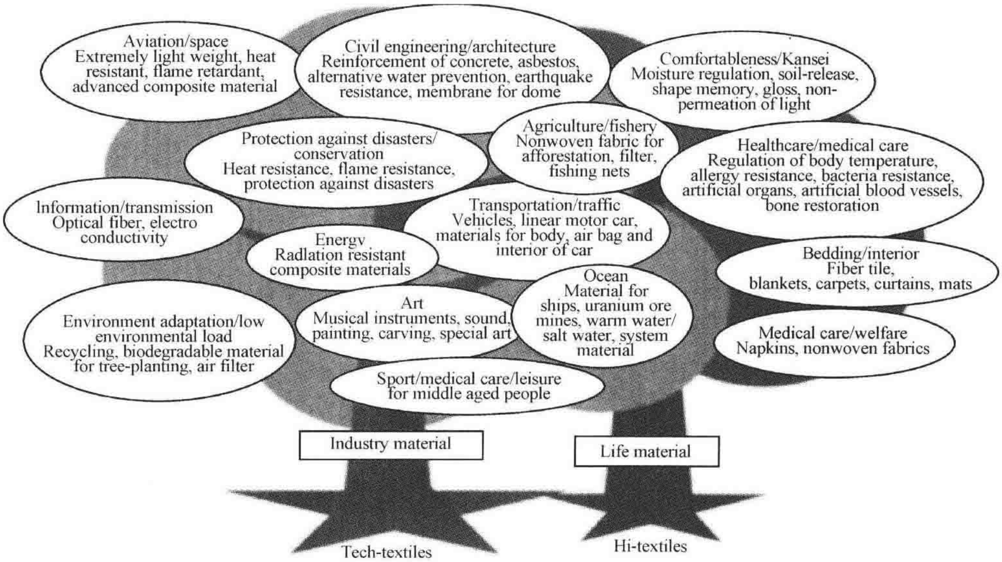


Figure 2-6 A summary of the use of fibers in today (T. Hongu, G. O. Phillips, M. Takigami. *New Millennium Fibers*. CRC Press, Woodhead Publishing Limited, 2005)

Recommending reading

[1] M. Harris, ed.. *Handbook of Textile Fibers*. Harris Research Laboratories, Inc., Washington, D. C., 1954.

[2] J. G. Cook. *Handbook of Textile Fibers*. 5th ed.. Merrow Publishing, Durham, N.C., 1984.

Problems

1. In terms of the fiber definition, does the steel needle or steel tube can be defined as a fiber respectively?