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Manufactured Textile Fibers

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TEXTILE BACKGROUND

The first conversion of naturally occurring fibers into threads strong enough to be looped into snares, knit to form nets, or woven into fabrics is lost in prehistory. Unlike stone weapons, such threads, cords, and fabrics—being organic in nature—have in most part disappeared, although in some dry caves traces remain. There is ample evidence to indicate that spindles used to assist in the twisting of fibers together had been developed long before the dawn of recorded history. In that spinning process, fibers such as wool were drawn out of a loose mass, perhaps held in a distaff, and made parallel by human fingers. (A maidservant so spins in Giotto's *The Annunciation to Anne*, ca. A.D. 1306, Arena Chapel, Padua, Italy.[1]) A rod (spindle), hooked to the lengthening thread, was rotated so that the fibers while so held were twisted together to form additional thread. The finished length then was wound by hand around the spindle, which, in becoming the core on which the finished product was accumulated, served the dual role of twisting and storing, and, in so doing, established a principle still in use today. (Even now, a "spindle" is 14,400 yards of coarse linen thread.) Thus, the formation of any threadlike structure became known as spinning, and it followed that a spider spins a web, a silkworm spins a cocoon, and manufactured fibers are spun by extrusion, although no rotation is involved.

It is not surprising that words from this ancient craft still carry specialized meanings within the textile industry and have entered everyday parlance, quite often with very different meanings. Explanations are in order for some of the words used in the following pages. For example, as already indicated, "spinning" describes either the twisting of a bundle of essentially parallel short pieces of wool, cotton, or precut manufactured fibers into thread or the extrusion of continuous long lengths of manufactured fibers. In the former case, the short lengths are known as "staple" fibers, and

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†The author dedicates this chapter to the memory of late Dr. Robert W. Work, Professor Emeritus, a longtime friend and mentor.

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Riegel's Handbook of Industrial Chemistry, 10th Edition
Edited by Kent. Kluwer Academic/Plenum Publishers. New York 2003

TABLE 12.1 Typical (Average) Values of Tensile and Physical Properties of Some Textile Fibers

Fiber	*Breaking Stress (cN/tex)*	*Strain to Fail (%)*	*Moisture Regain (%)*	*Density (g/cc)*
Natural				
Cotton	40	7	8	1.52
Flax	54	3	12	1.52
Silk	38	23	11	1.33
Wool	14	40	14	1.30
Regenerated				
Acetate	13	25	6	1.32
Rayon	25	20	14	1.51
Synthetic				
Acrylic	26	25	1.5	1.18
Modacrylic	28	32	1.5	1.32
Nylon	50	25	4	1.14
Polyester	50	15	0.4	1.38
Polypropylene	53	17	0	0.92

the resulting product is a "spun yarn," whereas the long lengths are called "continuous filament yarn," or merely "filament yarn." Neither is called a "thread," for in the textile industry that term is reserved for sewing thread and rubber or metallic threads. Although to the layperson "yarn" connotes a material used in hand knitting, the term will be used in the textile sense hereinafter.

Before manufactured fibers are discussed, it is necessary to define some terms.* The "denier" of a fiber or a yarn defines its linear density, that is, the mass in grams of a 9000 m length of the material at standard conditions of 70°F and 65 percent relative humidity. Although denier is actually a measure of linear density, in the textile industry, the word connotes the size of the filament or yarn. Fibers usually range from 1 to 15 denier, yarns from 15 to 1650. Single fibers, usually 15 denier or larger, used singly, are termed "monofils." The cross-sectional area of fibers of identical deniers will be inversely related to their densities, which range from 0.92 g/cc for polypropylene to 2.54 g/cc for glass. The approximate densities of some of the other commonly used fibers are given in Table 12.1. Because by definition denier is measured at standard conditions, it describes the amount of "bone-dry" material plus the moisture regain, which ranges from zero for glass and polypropylene to 14 percent for rayon. It should be mentioned that some years ago scientific organizations throughout the world accepted the word "tex," this being the mass (g) of 1 km of the material, as a more useful term than denier. "Tex" is an accepted adjunct to the SI, or International System of Units, but it has received only limited acceptance in commerce, whereas the SI units are being employed increasingly in scientific organizations. Furthermore, the sizes of cotton, wool, and worsted yarns, and yarns containing manufactured fibers but produced by the traditional cotton, wool, or worsted systems, still are expressed in the inverse-count system that has been used for centuries.

The "breaking tenacity" or more commonly, "tenacity," is the breaking strength of a fiber or a yarn expressed in force per unit denier, that is, in grams per denier, calculated from the denier of the original unstretched specimen. "Breaking length" expresses the theoretical length of yarn that would break under its own weight, and is used mostly in Europe. "Elongation" means "breaking elongation" and is expressed in units of increase in length

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*Each year the ASTM publishes in its *Book of Standards*, the most recent and accepted definition and test methods used in the textile and fiber industries.

to break calculated as a percentage of the original specimen length.

Typical force–elongation curves of some manufactured and natural staple fibers and textile-type manufactured filaments are shown in Figs 12.1 and 12.2. Table 12.1 gives the values of some of the physical and tensile properties of textile fibers.

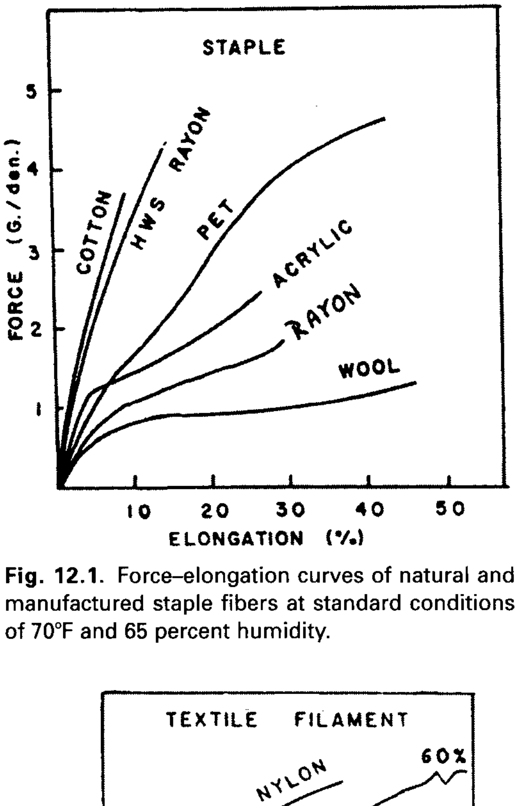


Fig. 12.1. Force–elongation curves of natural and manufactured staple fibers at standard conditions of 70°F and 65 percent humidity.

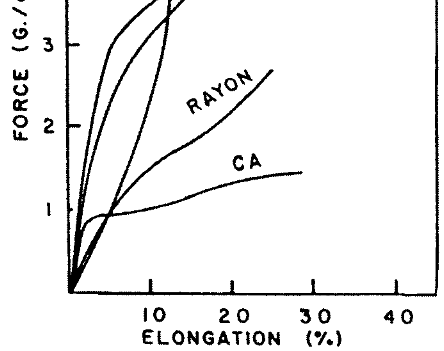


Fig. 12.2. Force–elongation curves of manufactured textile continuous-filament yarns at standard conditions of 70°F and 65 percent relative humidity.

HISTORY

Early humans, over time, became aware of the presence and usefulness of fibrous materials available from such sources as seeds, leaves, stems, animal coverings, and cocoons. They learned to spin, weave, knit, felt, or braid these fibers to protect their bodies and improve their lifestyle. A few hundred years ago, it has been suggested, someone took a clue from a busy worm and thought that it should be possible for humans to make a silk-like fiber that would be of commercial value. Curiosity combined with simple experiments strengthened that premise and much later led to the development of viscose rayon, only partially a manufactured fiber, in the 19th century. Further curiosity, war-time need, and superior commitment by modern researchers led to the synthesis of a totally synthetic fiber in the 1930s. The knowledge gained and the spark thus ignited resulted in the development of other fibers to such an extent that manufactured fibers now dominate the market in the industrialized nations in all major categories of apparel, home furnishing, and industrial end uses.

The story of the development of manufactured fibers is of great historical interest, beginning in 1664 when Robert Hooke, an Englishman, suggested that it should be possible to make a fiber much like silk that could be of value in the market place. Andemars, a Swiss chemist, received the first patent for making silklike fiber in 1855. He drew fibers by dipping a needle and pulling it out from a solution of cellulose nitrate containing some rubber.

The credit for using a spinnerette and forcing a solution through it for producing a fiber, however, goes to the English scientist Sir Joseph W. Swan, in the early 1880s. The first person to put the idea into commercial practice was the French chemist Count Hilaire de Chardonnet, who built the first plant to commercially produce a fiber based on regenerated cellulose, called "artificial silk," at Besançon, France, in 1891. During the last years of the 19th century and the beginning of the 20th century, progress was so rapid that the production of this fiber increased from several thousand pounds in 1891 to over two million in 1910. Commercial production of the fiber in the United States began in 1910 with the opening of the first plant. In 1924, the industry gave the "artificial silk" fiber a new name, rayon.

By the year, 1910, the brothers Camille and Henry Dreyfus had discovered a practical method for producing cellulose acetate polymer and were making plastic film and toilet articles in Basel, Switzerland. During World War I, they built a plant in England to produce acetate dope for painting airplane wings to render them air-impervious. The success of the product led the U.S. government to invite the Dreyfus brothers to build a plant in the United States, which started commercial production in 1924.

The successful manufacture of these two fibers, although based on fibrous materials available in nature, marked the beginning of the development of manufactured fibers in the 1930s. This effort, initiated by a technological breakthrough, was marked by the work of W. H. Carothers, aimed at learning how and why certain molecules joined to form large molecules, or polymers.[2] Fibers were described as being composed of high molecular weight linear polymers; and the first one to be manufactured, nylon 66, was synthesized and produced on a commercial scale in 1939. It was quickly followed by nylon 6, the second most widely used nylon, and modacrylic (1949), olefin (1949), acrylic (1950), polyester (1953), and triacetate (1954). Glass had joined this group of large-production items earlier in 1936.

Several other fibrous materials have been produced, but they are regarded as fibers with special performance characteristics, used either in limited textile or in specialized industrial applications. Some of these worth noting are Spandex (1959), Aramid (1961), polybenzimidazole (PBI) (1983), and Sulfar (1983).

Thus, the period from the 1930s to the 1960s can be considered as a time of discoveries and innovations for manufactured fibers, when the majority of the basic fibers were developed. The years since then may be thought of as a period of modification of performance characteristics. The basic generic materials have been manipulated both chemically and physically to produce a wide variety of different fibers, tailored to secure the desired characteristics for specific end-use products. Thus, fibers can be extruded in different shapes and sizes for special purposes. They can be modified to offer greater comfort, flame resistance, or static-free behavior in apparel; they can offer soil-release and other desirable characteristics for carpets; they can be developed with unique surface characteristics, easier dyeability, or better blending qualities. The industry has begun to discover many possibilities for modifying the behavior of a given fibrous material. It has learned how to produce new fibers with greater strength, greater thermal resistance, or other special qualities.

Essentially, then, no new, large-volume, highly profitable fibers have been developed since the mid-1950s. Instead, the existing ones have become commodities with all the economic impact thereby implied. No major chemical engineering processes have been added, although the previously described ones have been modified to allow for spinning of liquid crystalline polymers or the formation of gel spun fibers. Research activity has been reduced and centered essentially on modifications of fiber size, shape, and properties, and many variants now are successfully marketed. Production volumes have increased enormously for nylon, polyester, and polyolefin.

FIBER CONSUMPTION

Figure 12.3 compares population growth with the production of manufactured fibers and the mill consumption of natural fibers in the United States. Per capita consumption of all fibers, starting at a level in the 1920s of about 30 lb, rose to approximately 40 lb following World War II and reached a level at or about 50 lb in the 1970s. It topped 60 lb in 1973, dropped below 45 lb in 1982, and in 1991 was at 55 lb. But clearly overshadowing the increases resulting from population growth and a higher standard of living are the volumes produced of, first, the cellulosic manufactured

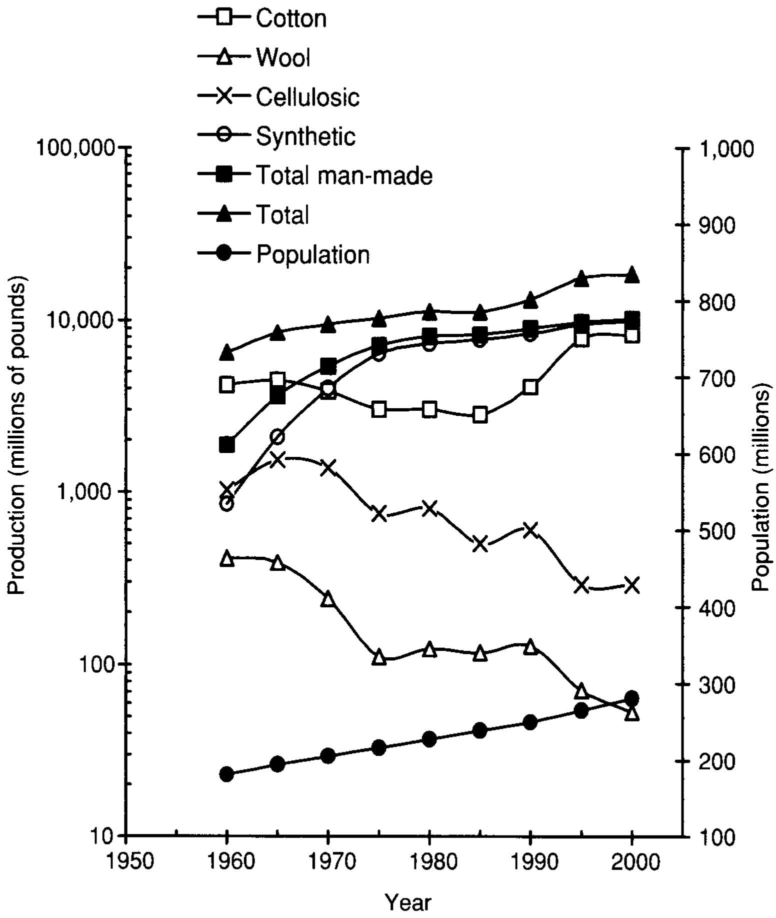


Fig. 12.3. Comparative growth of population and fiber consumption in the United States, 1960–2000.

fibers and, second, the noncellulosic or completely synthetic fibers. The consumption of manufactured fibers increased from about 2 billion lb in 1960 to nearly 9 billion lb in 1990. During the 1980s, the increase was about 11 percent, made up of a decrease in cellulosics of about 200 million lb (25%) and an increase in synthetics of about 1.2 billion lb (17%). Of the 13.2 billion lb of fibers used in the United States in 1990, 4.6 percent was the manufactured cellulosics, 63.3 percent was the synthetics (67.9% manufactured), 31.1 percent was cotton, and less than 1 percent was wool. A significant increase was noted in the use of cotton during the 1980s, from 3.0 billion lb in 1980 to 4.1 billion lb in 1990, believed to be in large measure due to advances in chemical finishes that made caring for the natural fibers easier than it was with the older technology. To some extent, this increase also may have occurred because people were willing to accept a more wrinkled look in order to gain the comfort of hydrophilic fibers. Still, the general figures represent quite a reversal in the consumption of fiber types seen three or more decades ago. For example, in 1960, of the 6.5 billion lb of fibers used, manufactured fibers accounted for only 29 percent of the total, with cotton 65 percent and wool 6 percent.

Major applications of fibers lie in apparel, home furnishing, and industrial products. In each of these, manufactured fibers have made large inroads, and currently their usage dominates. As an illustration, consider the changes that have taken place in the use of the materials required in the manufacture of tire cords. Originally made from cotton, rayon took a commanding position during World War II. But as late as 1951, cotton comprised about 40 percent of the total output of tire cords of approximately half a billion lb, and nylon was at a negligible level of 4 million lb. By 1960, however, cotton had all but disappeared; nylon represented about 37 percent of the total (on a weight basis), even though only about 0.8 lb of nylon is needed to replace 1.0 lb of rayon. Whereas rayon for several years had dominated the so-called original-equipment tire market and nylon had held a corresponding position for replacement tires, more recently, glass and polyester have made heavy inroads into both—especially in belted constructions. The situation continued to change in favor of noncellulosic manufactured fiber usage in tires, so that by 1972, rayon was down to 14 percent, nylon up to 42 percent, polyester up to 32 percent, glass up to 7 percent, and steel at 5 percent, all on a weight basis. By the late 1970s, tire markets were dominated wholly by manufactured fibers with polyester holding over 90 percent of the passenger car original-equipment market and nylon commanding over 90 percent of the truck original-equipment market. This division of markets is a direct result of the performance characteristics of the two fibers. Polyester-containing tires are free of "flat spotting" or cold-morning thump, and so are preferred in passenger cars for their smooth ride. On the other hand, nylon-containing tires are tougher and more durable, and so are the choice for trucks and off-road vehicles.

The production of manufactured fibers throughout the world has developed in a manner that rather parallels the situation in the United States, as may be seen in Fig. 12.4. There are some expected differences, and obviously the data for world usage are strongly influenced by the large components attributable to the United States, which currently accounts for about 23 percent of the manufactured fiber and about 15 percent of the total fiber consumption. The output of the world cellulosics has leveled off, but expansion of the noncellulosics has continued unabated. The use, or at least the recorded use, of the natural fibers, cotton and wool, rose rapidly in the 1950s, as the world economy rebounded at the conclusion of World War II. Since then (1960–1970), a modest increase has continued, essentially parallel to the growth of world population. But, in comparison with population trends, it appears that the great demand has been for manufactured textile fibers. Much of this increase has resulted from an improved standard of living and the absence of major wars.

A detailed economic examination of the processing of fibers and the changes that have taken place during the last half century would show two rather vivid occurrences. The first of these is a rapid decrease in the prices of the newer fibers as they became established, followed by a leveling out and stabilization. The second is the relative stability of prices of the manufactured fibers on short-term and even long-term bases, as compared with fluctuations in the prices for the natural fibers where governmentally imposed stability has not been in effect. Data are not presented about it in this text, but in the first half of the 20th century there was a saying in the textile industry that the person who made or lost money for the company was the one who was responsible for buying cotton and wool "futures."

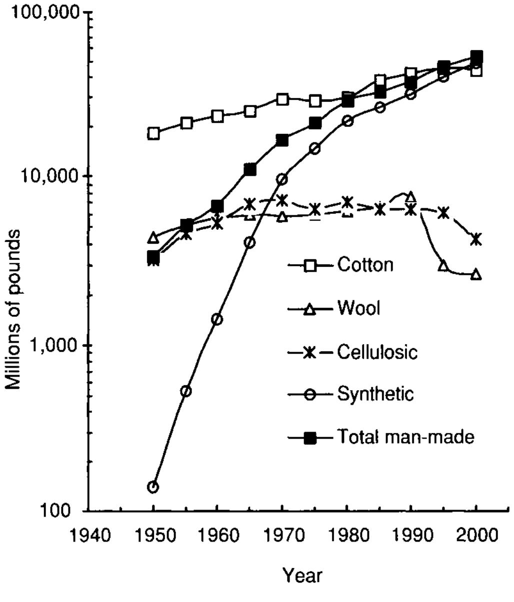


Fig. 12.4. Production of fibers in the world, 1950–2000.

However, it should also be emphasized that list prices of manufactured fibers are ceiling prices and do not reflect the short-term discounts, allowances, and special arrangements that are given in a free marketplace when the demand for any manufactured fiber softens.

A presentation of complete information about the consumption of raw materials, chemical reactions, reagents and catalysts used, and efficiencies of operation in the production of manufactured fibers undoubtedly would contribute to a better understanding of the industrial chemistry involved. Several factors have prevented this, however. In the first half of the 20th century, a historical belief in the efficacy of trade secrets still permeated the chemical industry. Even with the increased mobility of technical and scientific personnel during and following World War II, the idea still prevailed that if nothing other than patents was allowed to become public knowledge, so much the better. The situation has changed considerably since about 1960, as can be noted from the availability of information contained in the list of suggested readings that follows this chapter; yet, secrecy tends to be maintained despite the fact that key employees move from company to company, and the chemical engineering knowledge available in chemical companies that produce large volumes of fibers permits an almost complete appraisal of a competitor's activities.

In general, in the early period of production of a fiber, the cost of the original raw material may have had very little bearing on the selling price of the final fiber. A most important factor is the action of the producer's competitors and the conditions of the market and the demand that can be developed. But the complexity of the processes involved in conversion determines the base cost of the fiber at the point of manufacture. As the process becomes older, research reduces this complexity; with simplification, there may be rapid drops in plant cost. If demand remains high, such reductions will not be expected to be reflected in selling prices; rather, profits are high. As more producers enter the field in order to share in those profits, output capacity surpasses demand, and in accordance with classical economic theory, major selling price reductions result. This was happening, in general, in the 1960s and for cellulose-based manufactured fibers in the 1970s. But beginning in 1973, the cost of petroleum-based products started to rise steeply and erratically. This rise was based not on economic considerations alone but, on political considerations among the oil producing and exporting countries (OPEC) as well. Further upward pressure on manufactured fiber prices has resulted from governmental limitations placed on chemical usage and exposure and on amounts of chemicals that can be discharged into the air and water. To meet these limitations, the manufactured fiber industry has had to supply large infusion of capital. In some instances, such expenditures could not be justified, and plant capacity was shut down permanently. This was particularly true in the case of filament rayon. In recent years, the factors of rapidly rising raw material/energy prices and the costs of meeting environmental regulations have not allowed the prices of manufactured fibers to fall as production experience has been gained and technological advances have been introduced. Instead, selling prices have been continually adjusted upward in an effort to pass along unavoidable cost increases so as to maintain profitability. In areas of application in which a manufactured fiber replaced a natural one because of lower prices and stable availability, swings in fashion and increases in imports sometimes have caused a reduction in fiber utilization. This scenario, combined with environmental concerns, is believed to have particularly applied to acrylic fiber, whose production has decreased recently in both Europe and the United States.

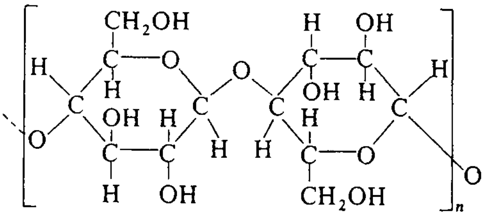
The great importance of manufactured fibers in the chemical industry and in the overall economy of the United States (and, in general, the developed countries) becomes apparent when the volume of production of these materials is considered and compared with the market value of even the least expensive of the raw materials used by them. The amounts of oil and natural gas consumed by the manufactured fiber industry represent around 1 percent of national annual usage.

Of this amount, about one half is used to produce raw materials from petrochemicals, with the other half used for energy to convert trees to wood pulp for cellulose-based fibers and to convert the wood pulp and petrochemical-derived raw materials to fibers.

RAYON

Chemical Manufacture

Rayon, the first of the manufactured fibers produced in large volume, is based on the natural polymer cellulose, a repeat unit of which is shown below:



Two anhydroglucose units

Although in the early days the main source of this raw material was cotton linters, a combination of improved technologies for obtaining alpha cellulose from wood and the shortage of cotton linters used for the manufacture of cellulose nitrate during World War II resulted in a shift in raw material to wood pulp. Only certain trees constitute the most economical supply of dissolving pulp, as the final product is called; the process economics depend upon the cost of logs delivered at the pulping mill and the relative yield of alpha cellulose after the unusable lignin and the other components of the wood are discarded.

A general flow diagram for the manufacture of rayon is given in Fig. 12.5. The dissolving pulp is received by the rayon manufacturer in sheet or roll form. In the manufacturing process, impurities are removed, with special attention being given to removal of traces of such metallic elements as manganese and iron, the former having an effect on the manufacturing process (as will be noted later) and the latter an effect on the color of the final product. The production of dissolving pulp involves drastic chemical action at elevated temperatures, which substantially reduces the originally very high molecular weight of the cellulose. The portion not soluble in 17–18 percent aqueous caustic, known as alpha cellulose, remains, and the lower-molecular-weight beta and gamma fractions are largely soluble and lost. The composition of the pulp is aimed at high alpha content. A typical economic trade-off is involved. The pulp producers can secure an alpha content of up to 98 percent by means of a cold caustic extraction, or, on the other hand, the rayon manufacturer can use a less expensive, lower alpha content pulp (90–96%) and expect to secure a lower yield. The sellers have numerous grades available to meet the specific process needs and end-product requirements of each of the buyers.

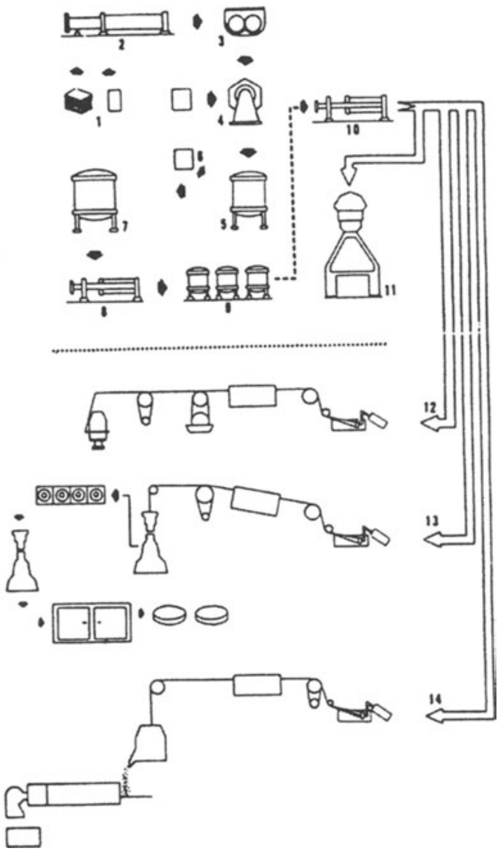


Fig. 12.5. Flow diagram for manufacture of viscose yarn: (1) cellulose sheets and caustic soda; (2) steeping press; (3) shredder; (4) xanthating churn; (5) dissolver; (6) caustic supply; (7) ripener; (8) filtration; (9) deaeration; (10) filtration; (11) continuous process; (12) tire cord; (13) pot spinning; (14) staple spinning.

In the manufacture of rayon, it is the usual practice to begin "blending" at the first step, which involves steeping the pulp. Further blending proceeds throughout successive steps. The warehouse supply of pulp consists of numerous shipments, and in making up the batches for the conventional process, a few sheets are taken from each of several shipments. This serves two purposes. It prevents a slight variation in a single pulp lot from unduly affecting any given volume of production, and it provides a moving average so that changes with time are reduced to a minimum.

The cellulose sheets are loaded vertically, but loosely, into a combination steeping bath and press (Fig. 12.6), which is slowly filled with a solution of 17–19 percent caustic, where they remain for about 1 hr. In the steeping, the alpha cellulose is converted into alkali or "soda" cellulose; at the same time, as already mentioned, the caustic solution removes most of the beta and gamma celluloses (also called hemicelluloses). The exact chemical composition of the soda cellulose is not known, but there is evidence that one molecule of NaOH is associated with two anhydroglucose units in the polymer chain.

$$(C_6H_{10}O_5)_n \text{ (cellulose)} + 18\% \text{ aqueous NaOH} \rightarrow [(C_6H_{10}O_5)_2 \bullet \text{NaOH}]_n \text{ (swollen, insoluble, soda cellulose I)} + \text{soluble soda cellulose from } \beta \text{ and } \gamma \text{ celluloses}$$

The excess caustic solution is drained off for reuse. Additional amounts are removed by forcing the sheets through a press. The sheets are still in a swollen state and retain from 2.7 to 3.0 parts of the alkali solution. The spent steeping solution squeezed out of the pulp is processed for recovering the caustic from the organic materials.

The sheets of soda cellulose are discharged into a shredder. If blending is desired, the charges from two or more steeping presses are mixed in a single shredder, where the already soft sheets are torn into crumbs; cooling is provided to prevent thermal degradation. Shredding is controlled to produce crumbs that are open and fluffy, and that will allow air to penetrate the mass readily; this is essential in aging.

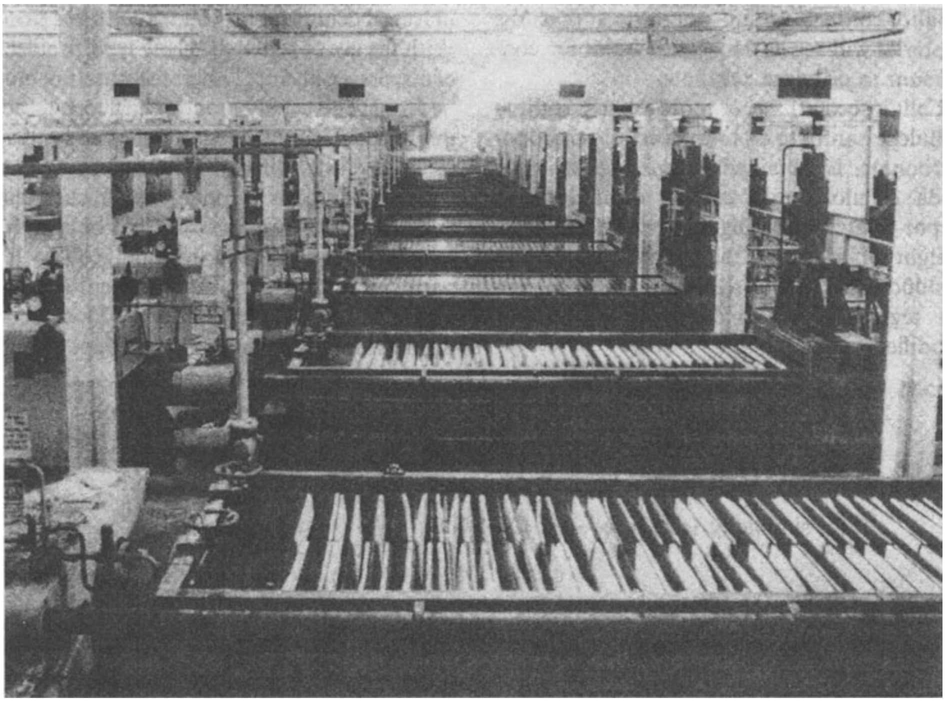
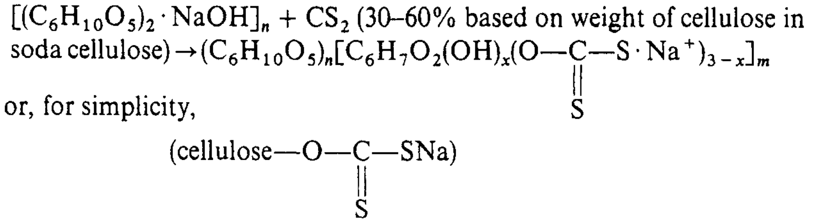


Fig. 12.6. Steeping of cellulose in the manufacture of viscose rayon. (*Courtesy Avtex Fibers, Inc.*)

Soda cellulose is aged by holding it at a constant temperature in perforated containers. The oxygen in the air produces uniform aging accompanied by a reduction in molecular weight and an increase in the number of carboxyl groups present. The target of aging is an average molecular weight high enough to produce satisfactory strength in the final fiber but low enough so that the viscosity of the solution will not be excessively high at the desired concentration for spinning. Each of the various rayon end products has its optimum degree of polymerization or chain length, ranging from about one fourth the original length for regular rayon to one half for certain high-performance fibers. As noted earlier, this optimum size is generally established by effecting a compromise between process economics and desired end-product properties. The aging proceeds for periods of up to two or three days, although the tendency is to speed up the operation by using higher temperatures and traces of metal ions, such as manganese or cobalt, to catalyze the reaction. A combination of experience and constant quality-control testing guarantees that the material will reach the correct point for conversion to cellulose xanthate.

Cellulose xanthate, or more exactly, sodium cellulose xanthate or sodium cellulose dithiocarbonate, is obtained by mixing the aged soda cellulose with carbon disulfide in a vapor-tight xanthating churn. Based upon weight of cellulose, the amount of carbon disulfide used will be in the range of 30 percent for regular rayon to 50–60 percent for modified varieties.



$$[(C_6H_{10}O_5)_2\cdot NaOH]_n + CS_2\ (30\text{–}60\%\ \text{based on weight of cellulose in soda cellulose}) \rightarrow (C_6H_{10}O_5)_n[C_6H_7O_2(OH)_x(O-\underset{\underset{S}{\|}}{C}-S\cdot Na^+)_{3-x}]_m$$

or, for simplicity,

$$(\text{cellulose}-O-\underset{\underset{S}{\|}}{C}-SNa)$$

The xanthate is soluble in a dilute solution of sodium hydroxide—a characteristic discovered by Cross and Bevan in 1892—and this property makes the spinning of rayon possible. It is a yellow solid; when dissolved in a dilute solution of alkali, it becomes a viscous, honey-colored liquid—hence the word "viscose." At this stage, the viscous solution may contain about 7.25 percent cellulose as xanthate in about a 6.5 percent solution of sodium hydroxide, although concentrations of both vary, depending on what end products are desired. The solution is ready for mixing with other batches to promote uniformity, to be followed by filtration, ripening, deaeration, and spinning. The filtration process usually involves several stages so that filters of decreasing pore size may be used to secure a balance of throughput and stepwise particle and gel removal.

Such an operation is a straightforward one for "bright" rayon, but only in the days of "artificial silk" did the shiny fiber alone satisfy the market. After a few years, a dull-appearing fiber also was demanded. At first, fine droplets of oil in the filaments were used to produce dullness until it was discovered that titanium dioxide pigment having a particle size smaller than 1 μm in diameter was even more satisfactory. The latter has since become the universal delustrant for all manufactured fibers. With the use of pigments of any type, problems of dispersion and agglomerate formation must be faced. The usual practice has been to add this pigment when mixing the cellulose xanthate into the dilute solution of caustic.

However, there are many other chemicals and additives that a producer may be required to add to the solution, including: (1) a few parts per million of a tracer element for later identification of the product; (2) coloring pigments for "dope dyed" rayon ("dope dyeing" will be discussed in greater detail under another heading); (3) chemicals for controlling the rate of precipitation and regeneration for obtaining rayon with so-called high performance; and (4) polymers and chemicals to impart specific properties to the fiber. From the standpoint of chemical processing, it is obvious that these additives may also be added when the sodium cellulose xanthate is dissolved in dilute caustic solution, or may be injected into the solution before it enters the spinnerette prior to being extruded. To keep the operations as flexible as possible, the additives should be injected at the last possible moment so that when a changeover is desired, there will be a minimum amount of equipment to be cleaned. On the other hand, the farther along in the operation that additives are placed into the stream, the greater the problem of obtaining uniformity in an extremely viscous medium, and the greater the difficulty in maintaining exact control of proportions before the viscous solution is passed forward and spun. Furthermore, all insoluble additives must be of extremely small particle size, and all injected slurries must be freed of agglomerates by prefiltration; if not, the viscous solution containing the additives must be filtered. Each manufacturer of viscose rayon develops the particular conditions for making additions, depending on a multitude of factors, not the least of which is the existing investment in equipment. All manufacturers must face the universal necessity of filtering the solution with or without pigments or other additives, so that all impurities and agglomerates that might block the tiny holes in the spinnerette are removed.

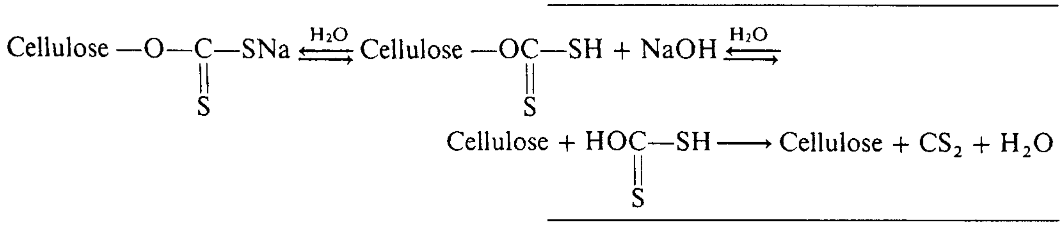
Although it was known in the years following the discovery by Cross and Bevan that a viscose type of solution could be used in the preparation of regenerated cellulose, the conversion of this solution into useful fibers was not possible until the discovery that the solution required aging until "ripe." Ripening is the first part of the actual chemical decomposition of cellulose xanthate, which, if allowed to proceed unhampered, would result in gelation of the viscose solution.

Experience has taught the manufacturer the correct time and conditions for the aging operation, but the requirement of aging itself demands that the entire process be so planned that the viscose solution will arrive at the spinnerette possessing, as nearly as possible, the optimum degree of ripeness, to produce fibers having the desired characteristics. This degree of ripeness is determined by an empirical test made periodically, which is a measurement of the resistance of the solution to precipitation of the soda cellulose when a salt solution is titrated into it. Thus, it is known as the "salt index" or "Hottenroth number" after its originator. An additional step in the overall ripening operation involves the removal of dissolved and mechanically held air by the use of a vacuum on a moving thin film of the viscose solution.

It should be mentioned that so inevitable is decomposition of cellulose xanthate and consequent gelation of the contents of pipes and tanks that all viscose rayon plants must be prepared to pump in-process viscose solutions to other spinning machines or to a waste receiver, purging the entire system with dilute caustic solution, in the event of a long delay in spinning.

Wet Spinning

Spinning a viscose solution into rayon fibers (wet spinning) is the oldest of the three common ways of making manufactured fibers. In this method, the polymer is dissolved in an appropriate solvent, and this solution is forced through fine holes in the face of the spinnerette, which is submerged in a bath of such composition that the polymer precipitates. The pressure necessary for this extrusion is supplied by a gear pump, which also acts as a metering device; the solution is moved through a final or "candle" filter before it emerges



$$\text{Cellulose}-O-\underset{\underset{S}{\|}}{C}-SNa \overset{H_2O}{\rightleftarrows} \text{Cellulose}-O\underset{\underset{S}{\|}}{C}-SH + NaOH \overset{H_2O}{\rightleftarrows}$$

$$\text{Cellulose} + HO\underset{\underset{S}{\|}}{C}-SH \longrightarrow \text{Cellulose} + CS_2 + H_2O$$

from the holes of the spinnerette. There is immediate contact between these tiny streams and the liquid or "wet" bath. As the bath solution makes contact with the material extruded from the holes, chemical or physical changes take place. These changes, whether of lesser or greater complexity, convert the solution of high molecular weight linear polymer first to a gel structure and then to a fiber. As will be observed in what follows, it is an interesting fact that the spinning of viscose rayon, with all of the ramifications made possible by variations in the composition of the solution and the precipitating bath, as well as in the operating conditions, presents the chemist and the chemical engineer with both the oldest and the most complex wet-spinning process.

The formation of rayon fibers from viscose solution is far from being simple, from either a physical or a chemical standpoint. The spinning bath usually contains 1–5 percent zinc sulfate and 7–10 percent sulfuric acid, as well as a surface-active agent, without which minute deposits will form around the holes in the spinnerette. Sodium sulfate (15–22 percent) is present, formed by the reactions, and as sulfuric acid is depleted and sodium sulfate concentration builds up, an appropriate replenishment of the acid is required. There is a coagulation of the organic material as the sulfuric acid in the spinning bath neutralizes the sodium hydroxide in the viscose solution; at the same time, chemical decomposition of the sodium cellulose xanthate takes place to regenerate the cellulose. If zinc ions are present, which is the usual situation in the production of the improved types of rayon, an interchange takes place so that the zinc cellulose xanthate becomes an intermediate. It reacts at a slower rate, causing slower decomposition to cellulose. This provides conditions for more effective stretching or drawing of the fiber. Chemical additives usually are present to repress hydrogen ion action. The gel-like structure, the first state through which the material passes, is not capable of supporting itself outside the spinning bath. As it travels through the bath, however, it quickly becomes transformed into a fiber that can be drawn from the spinning bath and that can support itself in subsequent operation (Fig. 12.7). The reaction between the bath and the fiber that is forming are paramount in determining the characteristics of the final product; it is for this reason that additives (previously mentioned), as well as zinc ions, may be used to control both the rate of coagulation and regeneration. In this manner, the arrangement of the cellulose molecules may be controlled to produce the conformational structure desired. A practical application of this will be discussed later.

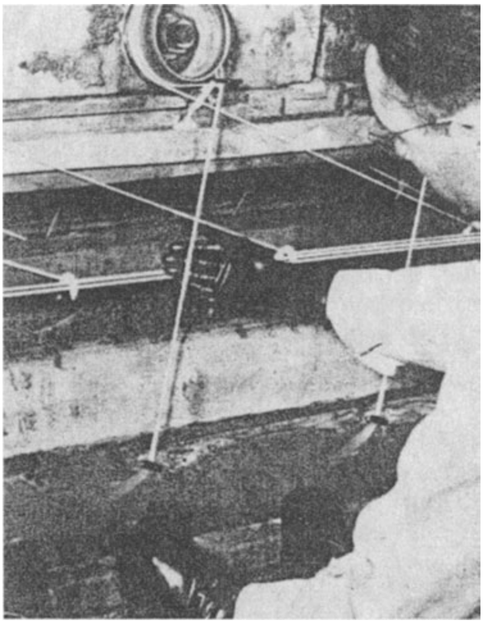
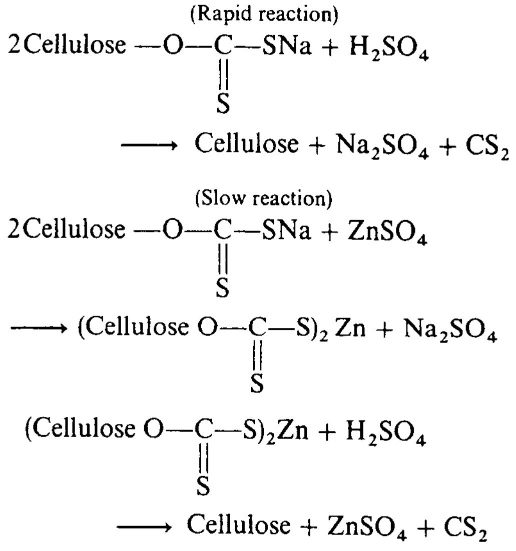


Fig. 12.7. Spinning of viscose rayon. (*Courtesy of Avtex Fibers, Inc.*)



(Rapid reaction)

$$2\text{Cellulose}-\text{O}-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{SNa} + H_2SO_4 \longrightarrow \text{Cellulose} + Na_2SO_4 + CS_2$$

(Slow reaction)

$$2\text{Cellulose}-\text{O}-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{SNa} + ZnSO_4 \longrightarrow (\text{Cellulose O}-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{S})_2\text{Zn} + Na_2SO_4$$

$$(\text{Cellulose O}-\underset{\underset{\text{S}}{\|}}{\text{C}}-\text{S})_2\text{Zn} + H_2SO_4 \longrightarrow \text{Cellulose} + ZnSO_4 + CS_2$$

Because of hydraulic drag, stretching occurs in the bath and also in a separate step after the yarn leaves the bath. In both cases, the linear molecules of cellulose are oriented from random positions to positions more parallel to the fiber axis. If a rayon tire cord is to be the final product, the fibers must be severely stretched to produce a very high orientation of the molecule. This is the basis of the tire cord's high strength and ability to resist stretching, without which growth of the tire body would occur. For regular textile and nonwoven uses, such high strengths are not desired, and the spinning and stretching conditions are controlled to produce rayon of lower strength and greater stretchability under stress.

In order to stretch the yarn uniformly during the manufacturing process, two sets of paired rollers or "godets" are employed, each of the two sets operating at different rotational speeds. The yarn is passed around the first set of godets several times to prevent slippage and is supplied to the stretching area at a constant speed. A second set of godets moves it forward at a more rapid rate, also without slippage. Stretching may range from a few to 100 or more percent. Spinning speeds are of the order of 100 m/min, but may vary with both the size of the yarn and the process used.

Spinning conditions, composition of the spinning bath, and additives to the viscose solution determine the physical characteristics of the rayon—its breaking strength and elongation, modulus, ability to resist swelling in water, and characteristics in the wet state as compared with those of the dry material. Not only must the chemical composition of the spinning bath be carefully controlled, but the temperature must be regulated at a selected point, somewhere in the range of 35–60°C, to ensure those precipitation and regeneration conditions that are essential to the manufacture of any particular viscose rayon having the properties needed for a selected end use.

After precipitation and regeneration of cellulose have been completed and raw rayon fiber has been formed, the subsequent steps must be controlled so that differences in treatment are minimized; otherwise such sensitive properties as "dye acceptance" will be affected, and the appearance of the final product will vary.

Minute traces of suspended sulfur resulting from the chemical decomposition of cellulose xanthate must be removed by washing with a solution of sodium sulfide. It is expedient to bleach the newly formed fibers with hypochlorite to improve their whiteness; an "antichlor" follows. The chemicals originally present and those used to purify the fibers must be removed by washing. As a final step, a small amount of lubricant is placed on the filaments to reduce friction and improve processibility in subsequent operations.

Several different processes are used for the steps involved in spinning and purifying continuous filament rayon. One of the most common involves the formation of packages of yarn, each weighing several pounds, for separate treatment. After it has been passed upward out of the spinning bath and stretched to the desired degree, the yarn is fed downward vertically into a rapidly rotating canlike container called a spinning pot or "Topham" box (after the man who invented it in 1900). It is thrown outward to the wall of the pot by centrifugal force and gradually builds up like a cake, with excess water being removed by the same centrifugal force. This cake is firm, although it must be handled with care, and is sufficiently permeable to aqueous solution to permit purification.

In another method of package-spinning, the yarn is wound onto a mandrel from the side at a uniform peripheral speed. With this process, the yarn may be purified and dried in the package thus formed. In any of these systems, the spinning and stretching, as well as subsequent steps, may involve separate baths.

The continuous process for spinning and purifying textile-grade rayon yarn merits particular mention from the standpoint of industrial chemistry, as it is rather an axiom that a continuous process is to be preferred over a batch or discontinuous operation. This method employs "advancing rolls" or godets that make it possible for the yarn to dwell for a sufficient length of time on each pair, thus allowing the several chemical operations to take place in a relatively small area. Their operation depends on the geometry existing when the shafts of a pair of adjacent cylindrical rolls are oriented slightly askew. Yarn led onto the end of one of these and then around the pair will progress toward the other end of the set with every pass, the rate of traversing, and therefore the number of wraps, being determined by the degree of skewness.

The production of rayon to be converted to staple fiber also is amenable to line operation. Here, the spinnerette has many thousands of holes, and a correspondingly large number of filaments are formed in the precipitation bath. The resulting tow then is stretched to the desired degree and immediately cut in the wet and unpurified condition. The mass of short lengths can be conveyed through the usual chemical treatments, after which it is washed and dried. It is fluffed to prevent matting and is packaged for shipment in large cases.

Cuprammonium, Nitrocellulose, and Cellulose Acetate Processes for Rayon

Cuprammonium Cellulose. Cellulose forms a soluble complex with copper salts and ammonia. Thus, when cellulose is added to an ammoniacal solution of copper sulfate that also contains sodium hydroxide, it dissolves to form a viscous blue solution, and in this form it is known as cuprammonium cellulose. The principles on which the chemical and spinning steps of this process are based are the same as those for the viscose process. Cellulose is dissolved, in this case in a solution containing ammonia, copper sulfate, and sodium hydroxide. Unlike the viscose solution, the cuprammonium solution need not be aged and will not precipitate spontaneously on standing except after long periods. It is, however, sensitive to light and oxygen. It is spun into water and given an acid wash to remove the last traces of ammonia and copper ions. Although this rayon was never manufactured in a volume even approaching that achieved by the viscose process, the smaller individual filaments inherent in it made it useful in certain specialty markets. It no longer is manufactured in the United States but continues to be made abroad.

Nitrocellulose and Cellulose Acetate. Although nitrocellulose and cellulose acetate intermediates have been made and regenerated to form cellulose fibers, neither of these historical processes is still in operation.

Textile Operations

After the filament rayon fiber has been spun and chemically purified, much of it passes through what are known as "textile operations" before it is ready to be knitted or woven. Because these steps of twisting and packaging or beaming are common to the manufacture of all manufactured fibers, it is advisable to review briefly the background and the processes.

Rayon, the first manufactured fiber, not only had to compete in an established field, but also had to break into a conservative industry. Silk was the only continuous filament yarn, and products made from it were expensive and possessed of high prestige, so that they offered a tempting market for rayon. Thus, the new product entered as a competitor to silk and, as already noted, became known as "artificial silk." Under the circumstances, it was necessary for rayon to adapt itself to the then existing silk processing operations and technologies. It was customary to twist several silk filaments together to secure a yarn of the desired size, strength, and abrasion resistance. Because rayon was weaker than silk and its individual filaments were smaller, it required as much twisting as silk or even more.

This twisting could have been carried out in the same plant where the yarn was spun, but the existence of silk "throwsters" (from the Anglo-Saxon *thrawan*, to twist or revolve) made that unnecessary. However, as the rayon industry developed, the amount of yarn twisted in the producing plant or sent forward to throwsters decreased. Over the years, the trend has been to use less twist and to place, instead, several thousand parallel ends directly on a "beam," to form packages weighing as much as 300–400 lb, which are shipped directly to a weaving or knitting mill. The advent of stronger rayons, as well as other strong fibers, and a diminishing market for crepe fabrics which required highly twisted yarns, accelerated the trend away from twisting.

In all twisting and packaging operations, the yarn makes contact with guide surfaces and tensioning devices, often at very high speeds. To reduce friction, it is necessary to add a lubricant as a protective coating for the filaments. This is generally true of all manufactured fibers, and it is customary to apply the lubricant or "spinning finish" or "spinning lubricant" as early in the manufacturing process as possible. For those materials that develop static charges in passing over surfaces, this lubricant also must provide antistatic characteristics.

It is difficult to overstate the importance of fiber lubricants to the successful utilization of manufactured fibers. Few problems can be more damaging to a fiber-handling operation than a lubricant upset. A separate chapter could be written on lubricant usage, but some of its more important aspects will be mentioned here. Obviously, lubricants must reduce friction between the fiber and various surfaces to allow movement without excessive damage to the fiber or the surface contacted, the latter being any one of a variety of metals or ceramics. Similarly, a fiber comes in contact with the surface of other fibers in staple fiber processing and in packaging. The lubricant composition must be stable under a variety of storage conditions, without decomposing or migrating within the package or being lost from the fiber surface by adsorption into the fiber, and must be nontoxic and nondermatitic. It also must be compatible with other materials added during textile processes, such as the protective size coat applied to warp yarns before weaving or the wax coat often applied to yarns before circular knitting. Possible metal corrosion must be evaluated for each lubricant composition. Finally, after having performed its function, the fiber finish or lubricant must be completely scoured from the fabric to permit uniform adsorption of dyes and fabric finishes. The application of sewing lubricants to fabric to be cut and sewn is yet another area requiring attention.

Spun Yarn. After rayon became established in the textile industry, where it could be used as a silklike fiber, and its selling price was greatly reduced, other markets for it were developed. The cotton, wool, worsted, and linen systems of converting short discontinuous fibers to yarns were well established, and their products were universally accepted. Here again it was necessary to make rayon fit the requirements of existing equipment and historically acceptable operations. The first of these was that it be cut into the same lengths as those found in cotton and wool. Fortunately, the viscose rayon process was and is eminently suited to the production of tows containing thousands of filaments. The pressure required to force the solution through the holes is so low that neither thick metal sections nor reinforcement of the surface is necessary to prevent bulging, and large spinnerettes containing several thousand holes can be used. Furthermore, the spinning bath succeeds in making contact with all the filaments uniformly. As a result, the spinning of viscose rayon tow is very similar in principle to the production of the smaller continuous filament yarns.

Because both cotton and wool possess distortions from a straight rodlike structure, machinery for their processing was designed to operate best with such crimped fibers. Thus, it was necessary for rayon staple to possess similar lengths and crimpiness in order to be adapted to existing equipment. The crimp, that is, several distortions from a straight path per inch, is produced in rayon "chemically" by modification of the structure. The precipitation-stretching step in spinning is carried out so that the skin and the core of the individual filaments are radially nonuniform and constantly changing over very short lengths along the filaments. Because the skin and the core differ in sensitivity to moisture, the two components shrink differentially, leading to the development of permanent distortions of the filaments. The latent chemical crimp may be enhanced by a thermomechanical step. In this, the tow is fed between two wheels, which in turn force it into a chamber, called a "stuffer box," heated with steam, in which it is forced against the compacted material ahead of it, causing the straight filaments to collapse immediately. As the mass of material is pressed forward, it becomes tightly compacted, and it tends to remain axially distorted after it escapes through a pressure-loaded door at the opposite end of the chamber.

Modified Viscose Rayon Fibers

The variations of chemical ingredients, their concentrations, and the temperature of the spinning bath determine the rates of coagulation and regeneration, and thus the relative amounts of "skin" and "core" in the cross-section of the fiber. The skin is known to possess a higher degree of order and better mechanical properties than the core, so an increase in its proportion is desired in higher performance fibers. The degree of orientation is determined by the stretch imparted. Inherent in process variations such as these is what may be called the "art" of viscose rayon manufacturing, whereby great diversity in rayon properties can be obtained. The cross-sectional morphologies of some rayons are illustrated in Fig. 12.8.[3,4]

High-Wet-Modulus Rayon. One of the important innovations in the rayon industry has been the development of High-Wet-Modulus (HWM) rayon. For its manufacture, the cellulose molecules require a higher degree of polymerization (DP) than regular rayon; so aging and ripening times are decreased, and the processing temperature is

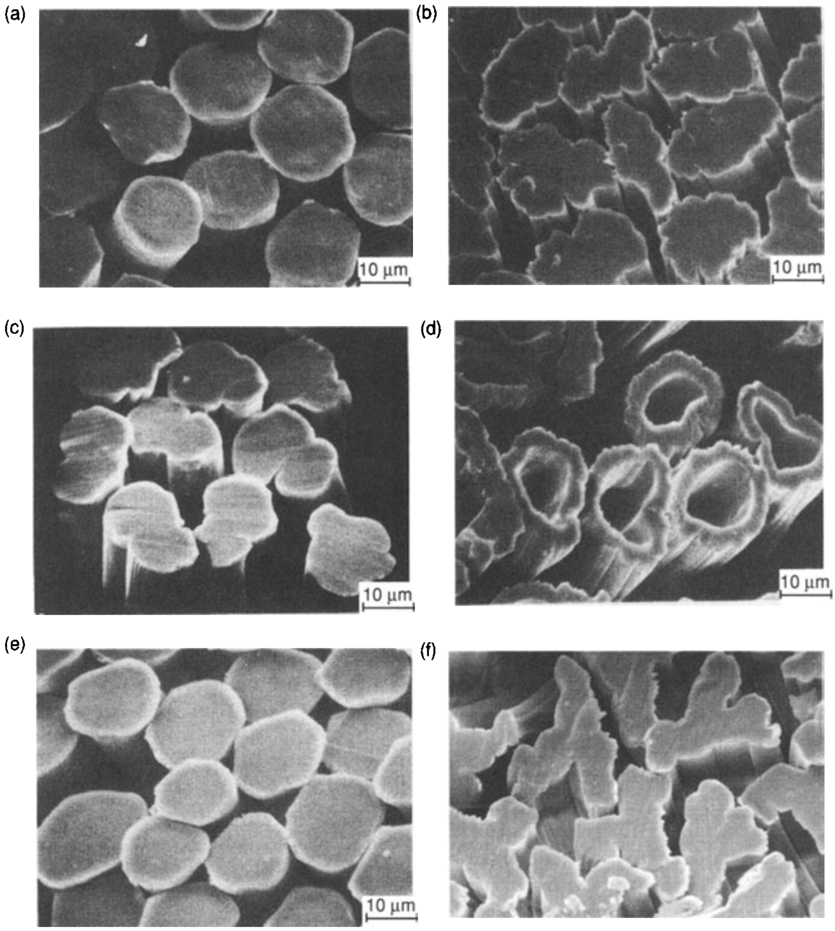


Fig. 12.8. Cross-sectional morphologies of some of the rayon fibers. (a) High wet modulus; (b) regular rayon; (c) crimped HWM; (d) hollow; (e) cuprammonium; (f) trilobal. (Sources: All except *trilobal*: Turbak, A., "Rayon," in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 14, p. 55, copyright John Wiley & Sons, Inc., New York, 1985 and used with permission of the copyright owner; trilobal photo: Gupta, B. S. and Hong, C.T., *INJ*, 7(1), 38 (1995).)

lowered. As the viscose solution flows through the spinnerette into the bath, coagulation takes place to form the needed skin. However, in order for an increase in tenacity to occur, regeneration should proceed slowly; this is aided by using a lower concentration of acid in the spin bath. Also, zinc is added because zinc ions in the bath slow down regeneration by forming zinc cellulose xathate, which is more resistant to acid decomposition than is sodium xanthate. Because of the slow generation process, what is actually formed is nearly an "all-skin" rayon with a round cross-section. Because the structure also is stretched before it crystallizes, a higher stretch is possible; this gives a higher orientation. The fiber thus has significantly higher strength than regular rayon. This higher tenacity exists not only when the material is dry, but also when it is wet; hence the name high-wet-modulus rayon. Because of its high structural orientation and greater order, the fibers have fewer physically accessible sites for water molecules; thus it is less susceptible to swelling and to the adverse effects of basic cleaning solutions, so that the fiber's launderability is improved. The HWM rayons are used extensively for blending with cotton, wool, silk, and all other manufactured fibers.

High Absorbency Rayons. Over the past years, disposable products have become commonplace, especially in the United States and Europe. Cellulosic fibers, particularly rayons, have served the needs of the disposables industry because of their absorbent qualities. The most useful fibers for disposable/absorbent applications are the rayons with crenulations, crimp, and hollow regions, all of which add to the absorbency of the fiber. These characteristics are achieved in varying degrees by physical and chemical alterations in the spinning process. Crenulations, or random irregularities in the shape of the cross-section, typical for most rayon fibers, are caused by the rapid formation of skin before the dehydration is complete. As the fiber interior loses solvent, it collapses in certain areas and produces the crenulated shape. Furthermore, fabricators have learned how to control the cross-sectional shape of filaments by using spinnerettes containing other than round holes. One example is fibers having Y or trilobal-shaped cross-sections, which have been found to be capable of picking up more water and at a faster rate than possible with fibers of round cross-sections.[4]

Hollow viscose fibers contain gas pockets produced by adding "blowing" agents, such as sodium carbonate, to the viscose. When carbon dioxide is released during regeneration, the fibers inflate, leading to the formation of hollow filaments. The added free volume and decrease in molecular order, increase the ability of the fibers to pick up water.

Other New Developments

A number of other developments are taking place in the rayon industry, the target of one being the manufacture of lint-free rayon for use in products such as circuit boards. In another, graphite particles are blended in with the viscose to reduce static buildup. Production of flame-retardant rayon has received increased attention, in one case being achieved by the addition of phosphorus compounds to the spinning dope. The advanced technology now can produce flame-resistant fibers that, when exposed to high temperatures, will not shrink or emit toxic gases. Other developments are in the area of finding better and environmentally safer solvents for the cellulosic raw material. Searches are under way for solvents that may lead to lyotropic liquid crystalline polymer solutions from which ultrahigh-strength and high-modulus fibers can be spun.

Environmentally Friendly High Wet Strength Rayon—Lyocell

Low wet strength of rayon in general has restricted the application of the fiber to disposable and semi-durable materials. Additionally, the environmental concerns associated with its manufacture have resulted in significant curtailment in production of the fiber during the recent past. Search for ways and means to produce a high wet strength fiber using an environmentally acceptable process have occupied much of the research effort during the past two decades. One of the latest additions to the family of rayon fibers is Lyocell. The fiber has wet strength comparable to that of the natural cellulosic fibers and is manufactured with a solvent that is essentially totally recovered and recycled.[5] The solvent used is N-methyl morphine oxide, $O(C_4H_8)NOCH_3$, popularly known as amine oxide. The manufacturing process involves the dissolving of pulp in hot amine oxide, filtration of the solution, and then spinning into a bath containing a dilute solution of the solvent. The bath removes the amine oxide from the fibers, which are washed and dried, and the removed solvent is almost totally reclaimed for further use. The final fiber is said to have a different molecular structure from that of normal rayon, and a smooth surface and a round cross-section. The fiber is noted to be stronger than cotton and normal rayon in both the dry and the wet states.[6]

CELLULOSE ACETATE

Historical

Cellulose acetate was known as a chemical compound long before its potential use as a plastic or fiber-forming material was recognized. The presence of hydroxyl groups had made it possible to prepare cellulose esters from various organic acids, as cellulose consists of a long molecular chain of beta-anhydroglucose units, each of which carries three hydroxyl groups—one primary, the other two secondary. The formula for cellulose (already noted) is $[C_6H_7O_2(OH)_3]_n$; when this is fully esterified, a triester results. It was learned quite early that although cellulose triacetate is soluble only in chlorinated solvents, a product obtained by partial hydrolysis of the triester to a "secondary" ester (having about 2.35–2.40 acetyl groups per anhydroglucose unit) was easily soluble in acetone obtaining a small amount of water. Many other cellulose esters have been prepared, but only the acetate has been commercialized successfully as a manufactured fiber. Propionates and butyrates, and mixed esters of one or both the acetate, have applications as plastics. The first acetate fibers were produced in 1921 in Europe and in 1924 in the United States.

Manufacture of Cellulose Secondary Acetate

Cellulose acetate originally was made from purified cotton linters, but this raw material has been entirely replaced by wood pulp. The other raw materials used are acetic acid and acetic anhydride.

Cellulose acetate is manufactured by a batch process (see Fig. 12.9). There has been mention in the patent literature of a continuous system, but its utilization as a production process has not been announced. The "charge" of cellulose, purified, bleached, and shredded, is of the order of 800–1500 lb. It is pretreated with about one third its weight of acetic acid and a very necessary amount of water, about 6 percent of its weight. If it is too dry at the time of use, more H_2O must be added to the acetic acid. A small amount of sulfuric acid may be used to assist in swelling the cellulose and to make it "accessible" to the esterifying mixture.

Although there has been much discussion of the chemistry of cellulose acetylation, it is now generally agreed that the sulfuric acid is not a "catalyst" in the normal sense of the word, but rather that it reacts with the cellulose to form a sulfo ester. The acetic anhydride is the reactant that provides the acetate groups for esterification. The acetylation mixture consists of the output from the acetic anhydride recovery unit, being about 60 percent acetic acid and 40 percent acetic anhydride, in an amount 5–10 percent above the stoichiometric requirement, to which has been added 10–14 percent sulfuric acid based on the weight of cellulose used. The reaction is exothermic and requires that the heat be dissipated.

In preparing for acetylation, the liquid reactants are cooled to a point (0°C) where the acetic acid crystallizes, the heat of crystallization being removed by an appropriate cooling system. The slush of acetic acid crystals in the acetic anhydride–sulfuric acid mixture is pumped to the acetylizer, a brine-cooled mixer

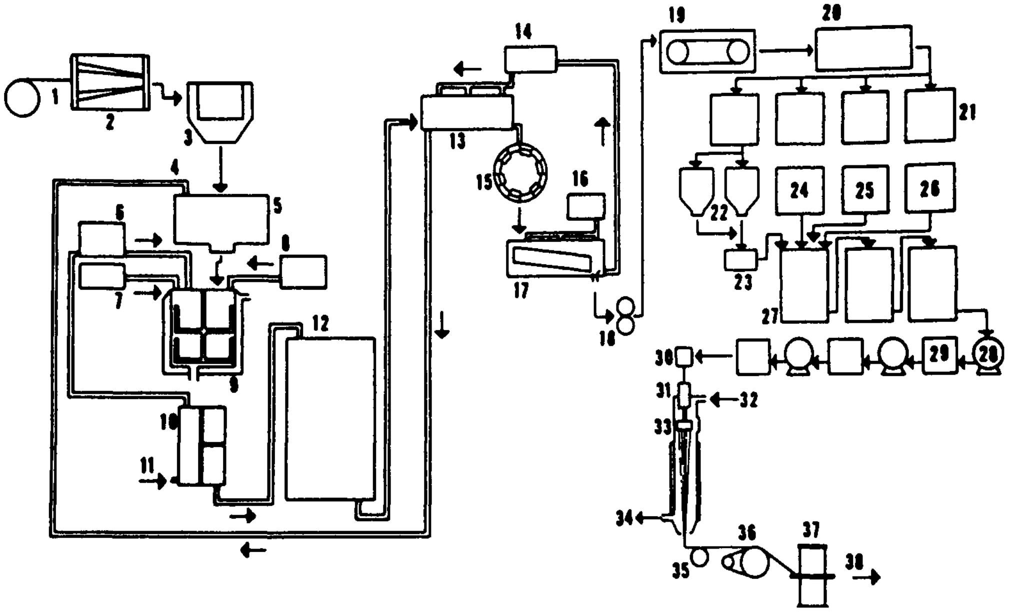


Fig. 12.9. Flow diagram for manufacture of cellulose acetate yarn: (1) wood pulp; (2) attrition mill; (3) cyclone; (4) 35% acetic acid; (5) pretreater; (6) magnesium acetate solution; (7) precooled acetylation mix; (8) sulfuric acid; (9) acetylator; (10) ripener; (11) steam; (12) blender; (13) precipitator; (14) dilute acetic acid; (15) hammer mill; (16) water; (17) rotary screen washer; (18) squeeze rolls; (19) drying oven; (20) blender; (21) storage bins; (22) silos; (23) weight bins; (24) acetone; (25) wood pulp; (26) pigment; (27) mixers; (28) hold tanks; (29) filter press; (30) pump; (31) filter; (32) air; (33) jet; (34) acetone recovery; (35) oiling wheel; (36) feed roll; (37) bobbin; (38) inspection.

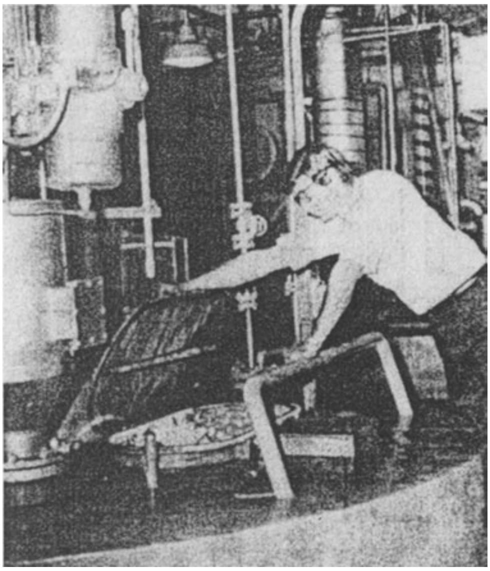


Fig. 12.10. Process vessel for acetylation of cellulose. (*Courtesy Celanese Fibers Co.*)

of heavy construction (see Fig. 12.10). The pretreated cellulose is dropped in from the pretreating unit located above. The reaction is highly exothermic, and at the start large amounts of heat are produced. As the temperature of the reaction mixture rises to the melting point of the acetic acid (16.6°C), its large heat of fusion (45.91 cal/g) prevents a dangerous rise in temperature that would degrade the molecular weight of the cellulose chain. As the reaction proceeds, brine in the jacket of the acetylizer provides additional cooling.

$$\text{Cellulose} + (CH_3CO)_2O + H_2SO_4\ (10\text{–}15\%\ \text{based on weight of cellulose}) \xrightarrow[\text{Anhydrous}]{CH_3COOH} [C_6H_7O_2(OSO_3H)_{0.2}(CH_3COO)_{2.8}]_n$$

The reaction product is soluble in the acetylation mixture; as it is formed and dissolved, new surfaces of the cellulose are presented to the reagents. One variation of this procedure uses methylene chloride, rather than an excess of acetic acid in the reaction mixture. This chemical is used both to dissipate the heat by refluxing (boiling point, 41.2°C) and to dissolve the cellulose ester as it is formed. As the reaction proceeds, the temperature is allowed to rise. Because cellulose is a natural product obtained from many sources, it varies slightly in composition, and at the end of the reaction cannot be predicted exactly; the disappearance of fibers as determined by microscopic examination thus is the usual means of following its progress.

During the acetylation operation, a certain amount of chain fission is allowed to take place in the cellulose molecule. This is to ensure that the viscosity of the cellulose acetate spinning solution will be low enough for ease of handling but high enough to produce fibers with the required strength. The temperature of the reaction controls the rates of both acetylation and degradation of molecular weight.

The next step in the manufacture is “ripening,” whose object is to convert the triester, the “primary” cellulose acetate, to a “secondary” acetate having an average of about 2.35–2.40 acetyl and no sulfo groups (if any sulfuric acid is used in pretreatment) per anhydroglucose unit. While the cellulose sulfo-acetate is still in the acetylizer, sufficient water is added to react with the excess anhydride and start the hydrolysis of the ester. Usually the water is used as a solution of sodium or magnesium acetate, which increases the pH and promotes hydrolysis. The temperature is raised to about 70–80°C, by direct injection of steam to speed up the reaction. Hydrolysis is continued until the desired acetyl content is obtained. When this value is reached, an aqueous solution of magnesium or sodium acetate is added to cool the batch and stop the hydrolysis. It is then ready for precipitation. For example,

$$[C_6H_7O_2(OSO_3H)_{0.2}(CH_3COO)_{2.8}]_n + (CH_3COO)_2Mg \xrightarrow{\text{Aqueous conc. } CH_3COOH} [C_6H_7O_2(OH)_{0.65}(CH_3COO)_{2.35}]_n + MgSO_4$$

The solution is carried to the verge of precipitation by adding dilute acetic acid. Then it is flooded with more dilute acetic acid and mixed vigorously, so that the cellulose acetate comes out as a “flake” rather than a gelatinous mass or fine powder. The flake then is washed by standard countercurrent methods to remove the last traces of acid, and is dried in a suitable dryer.

Manufacture of Cellulose Triacetate

To obtain completely acetylated cellulose, the reaction requires the use of perchloric acid rather than sulfuric acid as the catalyst. In the presence of 1 percent perchloric acid, a mixture of acetic acid and acetic anhydride converts a previously “pretreated” cellulose to triacetate without changing the morphology of the fibers. If methylene chloride rather than an excess of acetic acid is present in the acetylation mixture, a solution is obtained. However, usually a degree of substitution between 92 and 100 percent is acceptable. For obtaining such a triester, it is possible to use about 1 percent sulfuric acid instead of perchloric acid. When the sulfoacetate obtained from such a reaction is hydrolyzed with the objective of removing only the sulfo-ester groups, the resulting product has about 2.94 acetyl groups per anhydroglucose unit. The preparation, hydrolysis, precipitation, and washing of “triacetate” are in all other respects similar to the corresponding steps in the manufacture of the more common secondary acetate. Cellulose triacetate, formerly produced under the trade name Arnel® by Celanese Corporation, is no longer in production in the United States.

Acid Recovery. In the manufacture of every pound of cellulose acetate, about 4 lb of acetic acid is produced in 30–35 percent aqueous solution. The accumulated acid contains a small amount of suspended fines and some dissolved cellulose esters. To remove the suspended material, the acid is passed slowly through settling tanks. Then it is mixed with organic solvents, so that the acid becomes concentrated in an organic layer, which is decanted. Distillation separates the acid from the organic solvent.

To produce the acetic anhydride, the acid is dehydrated to ketene and reacted with acetic acid using a phosphate catalyst at 500°C or higher in a tubular furnace.

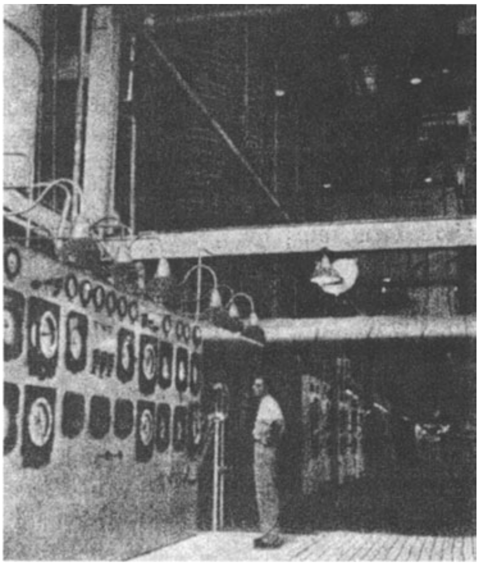


Fig. 12.11. Recovery of acetic acid. (*Courtesy Celanese Fibers Co.*)

$$CH_3COOH \xrightarrow[\text{Catalyst}]{\text{Heat}} H_2O + CH_2{=}C{=}O$$

$$CH_2{=}C{=}O + CH_3COOH \rightarrow (CH_3CO)_2O$$

The mixture of unreacted acid, water, and anhydride is fed to a still, which yields dilute acetic acid overhead and an anhydride–acetic acid mixture at the bottom (see Fig. 12.11). Conditions are controlled in such a way that the raffinate is about 40 percent anhydride and 60 percent acetic acid. As already mentioned, this is the desired ratio for the reaction mixture used for acetylation of cellulose.

Blending of Flake. As in the manufacture of viscose, the products of batch operations are blended to promote uniformity in the manufacture of cellulose acetate. Although a blend of different celluloses is selected in the beginning, the pretreatment, acetylation, and ripening are batch operations with little or no mixing. Before precipitation, a holding tank provides an opportunity for mixing; then precipitation, washing, and drying—all continuous—promote uniformity. The dried cellulose acetate flake moves to holding bins for analysis—the moisture content, acetyl value, and viscosity being especially important. The results of the analyses determine how much further blending is necessary. After blending and mixing of portions of selected batches, the lot is air-conveyed to large storage bins or "silos," which are filled from the center of the top and emptied from the center of the bottom, thus bringing about further mixing.

Spinning Cellulose Acetate

Acetone is metered into a vertical tank equipped with a stirrer, and the cellulose acetate flake and filter aid are weighed in an automatic hopper; all operations are controlled by proportioning methods common to the chemical industry. The ratio of materials is about 25 percent cellulose acetate, 4 percent water, less than 1 percent ground wood pulp as a filter aid, and the remainder acetone. The mixture moves forward through two or three stages at the rate at which it is used, the hold time being determined by experience. After dissolution is completed, filtration is carried out in batteries of plate and frame filter presses in three or even four stages, the passage of the "dope" being through presses of decreasing porosity.

Much of the cellulose acetate is delustered by the addition of titanium dioxide pigment, as with viscose rayon. Between filtrations (and after the last filtration), the dope goes to storage tanks that serve to remove bubbles; in this case, a vacuum is not necessary. From the final storage tank, it is pumped into a header located at the top of each spinning machine; then it is directed to a series of metering gear pumps, one for each spinnerette. Because the holes in the cellulose acetate spinning spinnerette are smaller (0.03–0.05 mm) than those in the corresponding viscose devices, great care must be taken with the final filtration. An additional filter for the removal of any small particles that may have passed through the large filters is placed in the fixture, sometimes called the "candle," to which the spinnerette assembly is fastened. A final filter is placed in the spinnerette-assembly unit over the top of the spinnerette itself.

The method used for spinning cellulose acetate is "dry" spinning. The dope is heated

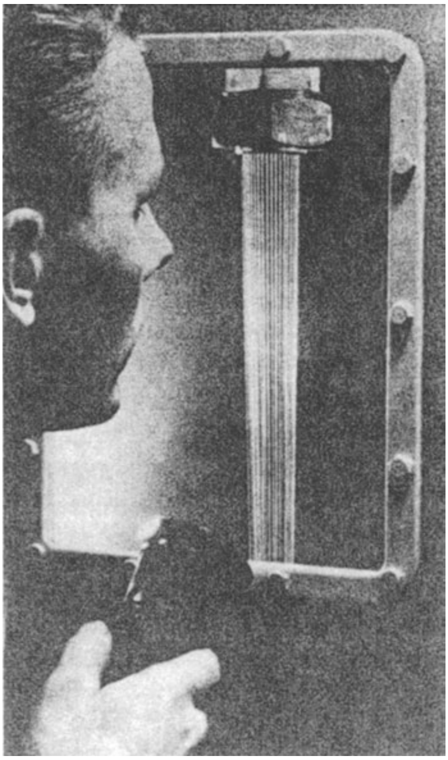


Fig. 12.12. Dry spinning of cellulose acetate. (*Courtesy Tennessee Eastman Co.*)

(in some cases above the boiling point of acetone, 56.5°C) to lower its viscosity and thus reduce the pressure required to extrude it, and to supply some of the heat needed for evaporating the acetone solvent (see Fig. 12.12).

The spinnerette is stainless steel, and because the filaments must be heated and prevented from sticking together, and because space must be allowed for the escape of acetone vapor, the holes must be kept farther apart than those of the spinnerettes used for wet spinning. As the hot solution of cellulose acetate in acetone emerges downward into the spinning cabinet, an instantaneous loss of acetone takes place from the surface of the filaments, which tend to form a solid skin over the still liquid or plastic interior. A current of air, either in the direction the filaments are moving or countercurrent, heats the filaments, and as the acetone is diffused from the center through the more solid skin, each filament collapses to form the indented cross-sectional shape typical of cellulose acetate. The heated air removes the vaporized acetone. Each manufacturer uses a preferred updraft, downdraft, or mixed-draft operation, as needs dictate.

The cabinet through which the yarn passes vertically downward must be long enough to allow sufficient acetone to diffuse outward and evaporate from the surfaces of the filaments so that the latter will not stick to the first surface contacted or fuse to each other. The temperature of the air in the cabinet, the rate of flow, the length of the cabinet, the size and number of filaments, and the rate of travel are all interrelated in the spinning process. Because it is desirable to increase spinning speeds to the limit of the equipment, the tendency has been to construct longer spinning cabinets as each new plant is built. Present spinning speeds are of the order of 600 or more meters per minute, measured as the yarn emerges from the cabinet.

Other dry-spinning operations have followed essentially the same pattern. For example, the dry spinning of cellulose triacetate was identical to that for secondary acetate except that the acetone solvent had been replaced by a chlorinated hydrocarbon such as methylene chloride, the solubility of which was improved by the addition of a small amount of methanol (5–15%).

The acetate yarn emerging from the cabinet makes contact with an applicator that provides the lubricant required to reduce both friction and static formation in subsequent operations. With its surface lubricated, the yarn passes around a "feed" roll that determines the rate of withdrawal from the spinning cabinet, and then to any of several desired packaging devices.

Unlike the packaging of rayon yarn, cellulose acetates are either "ring" spun or wound into a package called a "disc," "zero twist," or "cam wound." In the ring-spun package, the yarn carries a slight twist of less than one turn per inch, but it requires a relatively expensive bobbin. Since the trend is toward less twisting, such acetate yarn is "beamed" in the producer's plant after little or no twisting, the heavy beams being shipped directly to knitters or weavers (see Fig. 12.13).

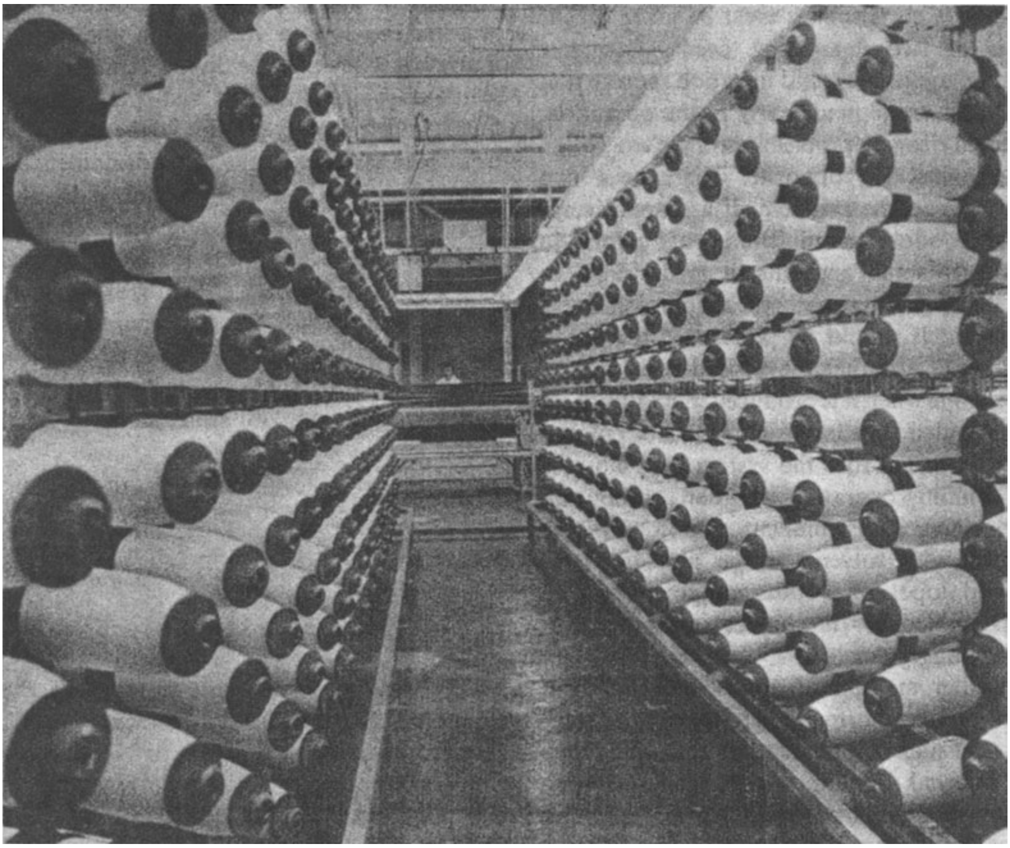


Fig. 12.13. Beaming cellulose acetate yarn from a reel holding about 800 packages of yarn. (*Courtesy Tennessee Eastman Co.*)

Filament yarns are twisted for two reasons. One is to supply certain esthetic characteristics such as touch, drapability, and elasticity. The other more fundamental reason is to provide physical integrity to the filament bundle so that it can be warped, woven, and knitted without excessive breakage or fraying of individual filaments.

The yarn just mentioned as having no twist imparted before beaming may have been subjected to intermingling just prior to windup after extrusion. In the intermingling process, yarn with no twist, and usually under low tension, is passed through a zone where it is impinged upon by a jet stream of compressed air. This causes the filaments to interlace or intermingle with each other, and they can become metastable in this configuration when tension is reapplied. In this condition, the yarn has the integrity of twisted yarn and will pass through several textile processing steps without difficulty; but with each handling, some of the intermingling is worked out.

Solvent Recovery. The air containing the acetone vapor is drawn out of the spinning cabinet and passed through beds of activated carbon that sorb the organic solvent. The acetone is recovered by steaming and then by separating it from the water by distillation. The efficiency of recovery is about 95 percent.

Dope-Dying. As with viscose rayon, colored pigments or dyestuffs may be added to the spinning solution so that the yarn will be colored as it is produced, thus eliminating the need for dyeing the final fabric. As mentioned earlier, even in using titanium dioxide, a compromise must be made on the basis of two competing needs. Complete mixing, uniformity, and filtration require that the addition be made early in the operation; minimal cleaning problems during changeovers require just the opposite. There exist two solutions to the problem. If a manufacturer must produce a multitude of colors in relatively small amounts, it is desirable to premix individual batches of spinning dope. Each batch should be pretested on a small scale to ensure that the desired color will be acceptable when it is produced. Facilities must be provided to allow each batch of colored dope to be cut into the system very close to the spinning operation in order to minimize pipe cleaning. Permanent piping must be flushed with solvent or the new batch of colored dope; some of the equipment may be disassembled for mechanical cleaning after each change of color.

Another method of producing spun-dyed yarn involves using a group of "master" dopes of such color versatility that when they are injected by appropriate proportioning pumps into a mixer located near the spinning operation, they will produce the final desired color. The advantages of such an operation are obvious; the disadvantage lies in the public demand for an infinite number of colors. No small group of known pigments will produce final colors of every desired shade.

PROTEIN FIBERS

As previously mentioned, the use of naturally existing polymers to produce fibers has had a long history. In the case of cellulose the results were fabulous. An initial investment of $930,000 produced net profits of $354,000,000 in 24 years for one rayon company.[7] On the other hand, efforts to use another family of natural polymers—proteins—have thus far resulted in failure or at best very limited production.

These regenerated proteins are obtained from milk (casein), soya beans, corn, and peanuts. More or less complex chemical separation and purification processes are required to isolate them from the parent materials. They may be dissolved in aqueous solutions of caustic, and wet-spun to form fibers, which usually require further chemical treatment as, for example, with formaldehyde. This reduces the tendency to swell or dissolve in subsequent wet-processing operations or final end uses. These fibers are characterized by a wool-like feel, low strength, and ease of dyeing. Nevertheless, for economic and other reasons they have not been able to compete successfully with either wool (after which they were modeled) or with other manufactured fibers.

NYLON

Historical

Nylon was the first direct product of the technological breakthrough achieved by W. H. Carothers of E. I. duPont de Nemours & Co. Until he began his classic research on high polymers, the production of manufactured fibers was based almost completely on natural linear polymers. Such materials included rayon, cellulose acetate, and the proteins. His research showed that chemicals of low molecular weight could be reacted to form polymers of high molecular weight. By selecting reactants that produce linear molecules having great length in comparison with their cross-section, fiber-forming polymers are obtained. With this discovery, the manufactured fiber industry entered a new and dramatic era.

Manufacture

Nylon 66. The word "nylon" was established as a generic name for polyamides, one class of the new high molecular weight linear polymers. The first of these, and the one still produced in the largest volume, was nylon 66 or polyhexamethylene adipamide. Numbers are used following the word "nylon" to indicate the number of carbon atoms contributed by the diamine and dicarboxylic acid constituents, in this case hexamethylenediamine and adipic acid, respectively.

To emphasize the fact that it does not depend on a naturally occurring polymer as a source of raw material, nylon often has been called a "truly synthetic fiber." To start the synthesis, benzene may be hydrogenated to cyclohexane:

$$C_6H_6 + 3H_2 \xrightarrow{\text{Catalyst}} C_6H_{12}$$

or the cyclohexane may be obtained by fractionation of petroleum. The next step is oxidation to a cyclohexanol–cyclohexanone mixture by means of air:

$$xC_6H_{12} + O_2(\text{air}) \xrightarrow{\text{Catalyst}} yC_6H_{11}OH + zC_6H_{10}O$$

In turn, this mixture is oxidized by nitric acid to adipic acid:

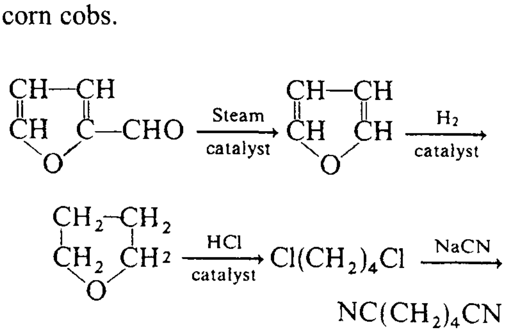
$$C_6H_{11}OH + C_6H_{10}O + HNO_3 \xrightarrow{\text{Catalyst}} (CH_2)_4(COOH)_2$$

Adipic acid so obtained is both a reactant for the production of nylon and the raw material source for hexamethylenediamine, the other reactant. The adipic acid first is converted to adiponitrile by ammonolysis and then to hexamethylenediamine by hydrogenation:

$$(CH_2)_4(COOH)_2 + 2NH_3 \xrightarrow{\text{Catalyst}} (CH_2)_4(CN)_2 + 4H_2O$$

$$(CH_2)_4(CN)_2 + 4H_2 \xrightarrow{\text{Catalyst}} (CH_2)_6(NH_2)_2$$

Another approach is through the series of compounds furfural, furane, cyclotetramethylene oxide, 1,4-dichlorobutane, and adiponitrile, as illustrated below. The furfural is obtained from oat hulls and corn cobs.



Or, 1,4-butadiene obtained from petroleum, may be used as a starting raw material to make the adiponitrile via 1,4-dichloro-2-butene and 1,4-dicyano-2-butene:

$$CH_2{=}CHCH{=}CH_2 \rightarrow ClCH_2CH{=}CHCH_2Cl$$

$$\xrightarrow[\text{Catalyst}]{\text{HCN}} NCCH_2CH{=}CHCH_2CN$$

$$\xrightarrow[\text{Catalyst}]{H_2} NC(CH_2)_4CN$$

When hexamethylenediamine and adipic acid are mixed in solution in a one-to-one molar ratio, the "nylon salt" hexamethylenediammoniumadipate, the direct progenitor of the polymer, is precipitated. After purification, this nylon salt is polymerized to obtain a material of the desired molecular weight. It is heated to about 280°C under vacuum while being stirred in an autoclave for 2–3 h; a shorter holding period follows; and the process is finished off at 300°C. The molecular weight must be raised to a level high enough to provide a fiber-forming material, yet no higher. If it is too high, the corresponding viscosity in the subsequent spinning operation will require extremely high temperatures and pressure to make it flow. Accordingly, a small amount of acetic acid is added to terminate the growth of the long-chain molecules by reaction with the end amino groups.

The polymerized product is an extremely insoluble material and must be melt-spun, as discussed later. Therefore, should a delustered or precolored fiber be desired, it is necessary to add the titanium dioxide or colored pigment to the polymerization batch prior to solidification. For ease of handling, the batch of nylon polymer may be extruded from the autoclave to form a thin ribbon, which is easily broken down into chips after rapid cooling. But, whenever possible, the liquid polymer is pumped directly to the fiber melt spinning operation (see Fig. 12.14).

Nylon 6. Nylon 6 is made from caprolactam and is known as Perlon® in Germany, where it was originally developed by Dr. Paul Schlack.[8] Its production has reached a very large volume in the United States in recent years.

Like nylon 66, nylon 6 uses benzene as raw material, which is converted through previously mentioned steps to cyclohexanone.

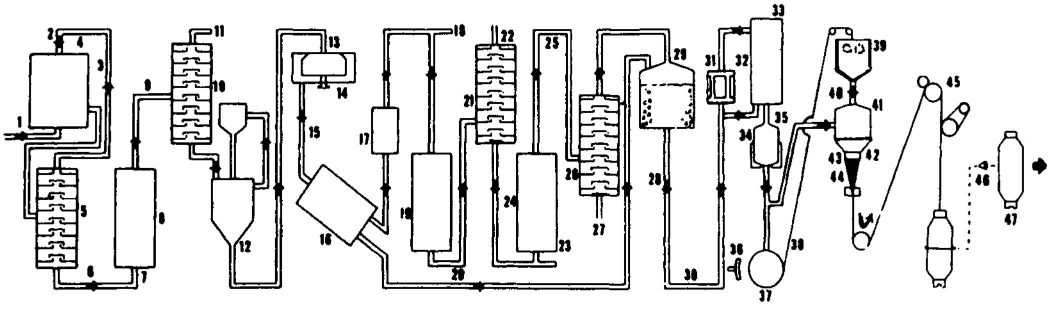
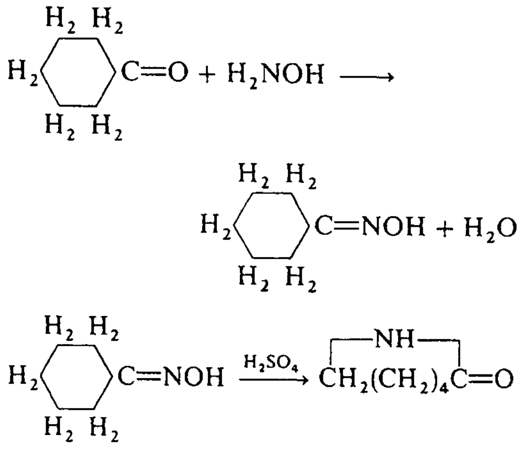


Fig. 12.14. Flow diagram for the manufacture of nylon 66 yarn: (1) air; (2) cyclohexane from petroleum; (3) reactor; (4) recycle cyclohexane; (5) still; (6) cyclohexanol–cyclohexanone; (7) nitric acid; (8) converter; (9) adipic acid solution; (10) still; (11) impurities; (12) crystallizer; (13) centrifuge; (14) impurities; (15) adipic acid crystals; (16) dryer; (17) vaporizer; (18) ammonia; (19) converter; (20) crude adiponitrile; (21) still; (22) impurities; (23) hydrogen; (24) converter; (25) crude diamine; (26) still; (27) impurities; (28) nylon salt solution; (29); reactor; (30) stabilizer; (31) calandria; (32) evaporator; (33) excess water; (34) autoclave; (35) delustrant; (36) water sprays; (37) casting wheel; (38) polymer ribbon; (39) grinder; (40) polymer flake; (41) spinning machine; (42) heating cells; (43) spinnerette; (44) air; (45) draw twisting; (46) inspection; (47) nylon bobbin. (Note: Whenever the demand for liquid polymer at a spinnerette is large, as, for example, in the spinning of tire yarn, it is pumped directly from the autoclave.)

This compound is in turn converted to the corresponding oxime by reaction with hydroxylamine, and cyclohexanone oxime is made into caprolactam by the Beckmann rearrangement.



After purification, the lactam is polymerized by heating at elevated temperatures in an inert atmosphere. During self-condensation, the ring structure of the lactam is opened so that the monomer acts as an epsilon-aminocaproic acid radical. Unlike that of nylon 66, the polymerization of caprolactam is reversible; the polymer remains in equilibrium with a small amount of monomer. As with nylon 66, nylon 6 is extruded in thin strands, quenched, and cut into chips for subsequent spinning, or the molten polymer is pumped directly to the spinning equipment.

Melt spinning

Because of its extremely low solubility in low-boiling and inexpensive organic solvents, nylon 66 required a new technique for converting the solid polymer into fibers; hence the development of "melt" spinning, the third basic method for producing manufactured fibers. The following description refers essentially to nylon 66 because it was the first to use the method, but the process applies, in general, to all melt-spun manufactured fibers.

In the original production of nylon fiber by melt spinning, the chips of predried polymer were fed from a chamber onto a melting grid whose holes were so small that only passage of molten polymer was possible. Both solid and liquid were prevented from contacting oxygen by maintaining an inert nitrogen atmosphere over the polymer supply. The polymer melted in contact with the hot grid and dripped into a pool where it became the supply for the spinning itself. This melting operation has been entirely replaced by delivery of the molten polymer pumped directly from the polymerization stage or by "screw" melting. In the latter process, the solid polymer in chip form is fed into an extrusion-type screw contained in a heated tube. The depth and the helix angle of the grooves are engineered in such a way that melting takes place in the rear section, and the molten polymer is moved forward under increasing pressure to a uniformly heated chamber preceding the metering pump.

Whatever means is used to secure the molten polymer, it is moved forward to a gear-type pump that provides both high pressure and a constant rate of flow to the final filter and spinnerette. The filter consists of either sintered metal candle filters, several metal screens of increasing fineness, or graded sand arranged in such a way that the finest sand is at the bottom. After being filtered, the molten polymer at a pressure of several thousand pounds per square inch is extruded through the small capillaries in the heavily constructed spinnerette. It is necessary to maintain the temperature of the pool, pump, filter, spinnerette assembly, and spinnerette at about 20–30°C above the melting point of the nylon, which is about 264°C for nylon 66 and 220°C for nylon 6. Fibers having desired cross-sectional shapes can be produced by selecting spinnerettes containing holes of appropriate configuration. An example of a trilobal spinnerette capillary and the shape of the resulting trilobal fiber is given in Fig. 12.15.

The nylon production process requires that the extruded fibers emerge from the spinnerette face into a quench chamber where a cross current of relatively cool quench air is provided to promote rapid solidification. The solid filaments then travel down a chimney to cool further, and a lubricant is applied before they make contact with the windup rolls in order to prevent static formation and to reduce friction in subsequent textile operations. The freshly spun yarn from the spinning chamber is taken up by a traversing winder onto a yarn package and "drawn" in a separate operation. In modern high-speed processes, drawing still is required, but in many cases this is combined with spinning in a single operation, as will be described in what follows.

Drawing

It was learned early that the "as-spun" fibers made from nylon 66 could be extended to about four times their original length with very little effort, but that thereafter a marked resistance to extension took place. It was discovered that during this high extension, the entire length of fiber under stress did not extend uniformly. Rather, a "necking down" occurred at one or more points, and when the entire length under tension had passed through this phenomenon, a high-strength fiber was obtained. It also was found that when more than one necking down was allowed to take place in a given length of fiber, a discontinuity occurred at the point where the two came together. Accordingly, the drawing operation was aimed at forcing the drawing to occur at a single point as the yarn advanced from the supply to the takeup package.

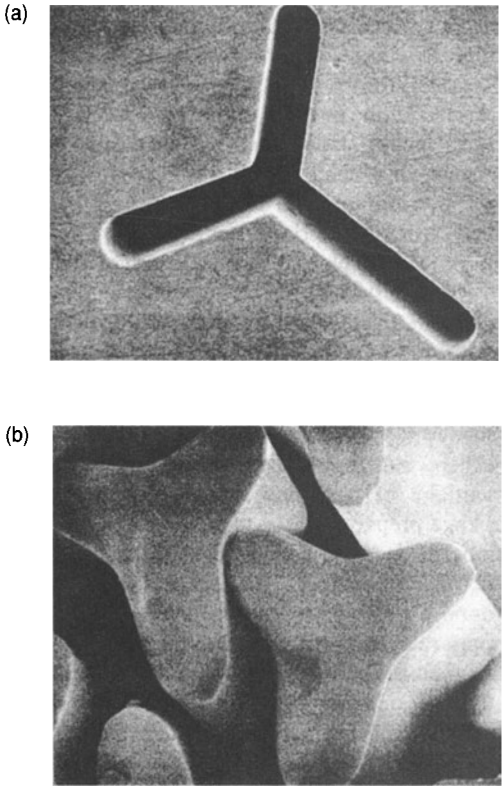


Fig. 12.15. Scanning electron micrographs of: (a) trilobal-shaped spinerette, and (b) resulting cross-sections of nylon fibers. The pictures were taken at different magnifications. (*Courtesy BASF Corporation*)

Where still used, cold drawing consists essentially of removing the yarn from the package prepared in the melt spinning operation and feeding it forward at a uniformly controlled rate under low tension. It is passed around a godet or roller that determines the supply rate and prevents slippage; for nylon 66, it then is wrapped several times around a stationary snubbing pin. From there it goes to a second roller that rotates faster than the supply roller to produce the desired amount of stretch, usually about 400 percent. The necking down occurs at the pin. In the case of nylon 6, drawing may be effected satisfactorily without passing the yarn around such a snubbing pin.

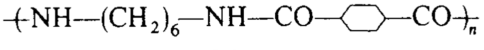
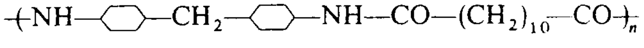
The long molecules of the nylon 66 or 6 polymer, which are randomly positioned in the molten polymer, when extruded from the spinnerette tend to form "crystalline" areas of molecular dimensions as the polymers solidify in the form of freshly spun fibers. In the drawing operation, both these more ordered portions as well as the amorphous areas tend to become oriented so that the lengthwise dimensions of the molecules become parallel to the long axis of the fiber, and additional intermolecular hydrogen bonding is facilitated. It is this orientation that converts the fiber having low resistance to stress into one of high strength.

By controlling the amount of drawing as well as the conditions under which this operation takes place, it is possible to vary the amount of orientation and the degree of crystallization. A minimal amount is preferable in the manufacture of yarns intended for textile applications wherein elongation of considerable magnitude and low modulus or stiffness is required rather than high strength. On the other hand, strength and high modulus are at a premium when fibers are to be used in tire cords and other industrial applications. High resistance to elongation is imperative if the tire is not to grow under conditions of use. In this connection, it should be noted that nylon tire cord that has been produced by twisting the original tire yarn and plying the ends of these twisted yarns together is hot-stretched just before use at the tire plant to increase strength and reduce even further the tendency to elongate under tension.

The separate operations of spinning and drawing nylon presented a challenge whose object was combination of the two operations into a single continuous step. But the problem was obvious, for the operating speeds of the two separate steps already had been pushed as high as was thought to be possible. How then would it be possible to combine them into a continuous spin-draw, wherein a stretching of about 400 percent could take place? The answer lay in the manner in which the cooling air was used and in the development of improved high-speed winding devices. By first cooling the emerging fibers by a concurrent flow of air and then cooling them further by a countercurrent flow, the vertical length of the cooling columns can be kept within reason. In-line drawing may occur in one or two stages, and relaxation may be induced if needed. The final yarn is said to be packaged at speeds of 6000 m/min.

Other Nylons, Modifications, and New Developments

Although nylon 66 and 6 account for most of the polyamide fibers produced, a great many others have been experimentally synthesized and have been developed and manufactured in commercial amounts. Of these, some have been made into fibers, some with limited economic success. These nylons are identified by either the same numbering system used for nylon 66 or 6 or by a combination of numbers and letters, as follows:

Nylon 3	$+NH-(CH_2)_2CO+_n$
Dimethyl nylon 3	$+NH-C(CH_3)_2-CH_2-CO+_n$
Nylon 4	$+NH-(CH_2)_3-CO+_n$
Nylon 6T	
Nylon 7	$+NH-(CH_2)_6-CO+_n$
Nylon 12	$+NH-(CH_2)_{11}-CO+_n$
Nylon PACM-12	
Nylon 46	$+NH-(CH_2)_4-NH-CO-(CH_2)_4-CO+_n$
Nylon 610	$+NH-(CH_2)_6-NH-CO-(CH_2)_8-CO+_n$

Dimethyl nylon 3 is solution-spun because it tends to decompose during melt spinning. Nylon 4 has a moisture regain (mass water per unit mass of dry fiber, under standard atmospheric conditions of 20°C and 65% RH) of 6–9 percent[9] and therefore is superior to other nylons for textile usages, being comparable to cotton. Nylon 11 was developed in France and has been trademarked as Rilsan®. It has a moisture regain of 1.8 percent and density of 1.04 g/cc as compared with 4 percent and 1.14 g/cc, respectively, for nylon 66. Nylon 7 is made in the former Soviet Union and marketed under the name Enant. The fiber has better stability to heat and ultraviolet light than nylon 66 and 6. Nylon 6T, an aromatic polymer, has a much higher melting point (370°C), a higher density (1.21 g/cc), and slightly higher moisture regain (4.5%) than nylon 66. It also has superior resistance to nylon 66 against heat. This fiber has served as a precursor to the development of aramid fibers. Nylon PACM-12, formerly produced under the trade name Qiana® in the United States, is no longer in production.

A *Chemical and Engineering News* report[10] suggests that the most serious competition to nylon 66 and 6 will be provided by a new, still experimental fiber, nylon 46, being developed by DSM in the Netherlands, Trade-named Stanyl®, this fiber results from the interaction of 1,4-diaminobutane and adipic acid. Better order in the structure in the fiber leads to greater crystallinity and, thus, to greater density (1.18 g/cc). The fiber has a melting point of about 300°C, and a breaking stress or tenacity of 9.5 gram force/denier (~1 GPa), modulus at 120°C of 20 gram force/denier (2.1 GPa), and shrinkage in gas at 160°C of 3 percent.

Some of the outstanding characteristics of nylon that are responsible for its many uses in apparel, home furnishing, and industrial products are its high strength and toughness, elastic recovery, resilience, abrasion resistance, and low density. Among many applications of the fiber are such products as intimate apparel and foundation garments, sportswear, carpets, parachutes, tents, sleeping bags, and tire cords.

The world production of nylon has doubled in recent years, increasing from 3.8 billion lb in 1970 to about 7.5 billion lb in 1990. The fiber accounts for about 24 percent of the synthetic fibers produced worldwide. In the United States, the production of the fiber also doubled in two decades, increasing from 1.2 billion lb in 1970 to about 2.4 billion lb in 1990.

The newest activity connected with nylon is the effort at developing a more highly oriented stronger nylon than possible by the current technology. Because of the formation of hydrogen bonds between the chains, the normal polymer is restricted in terms of the maximum draw ratio by which it can be oriented. In the new technique,[11] nylon 66 is dissolved in an agent such as gallium trichloride, which effectively breaks the hydrogen bonds. The solution is spun by the dry-jet wet spinning method. The $GaCl_3$/Nylon 66 complex so obtained can now be stretched to very high draw ratios, levels as high as 40X have been possible. Once drawn, the structure is soaked in water to remove gallium trichloride, which allows the hydrogen bonds to reestablish and link the chains. In preliminary work done thus far, the strength and the modulus obatined exceed the values usually found in nylon 66.

POLYESTERS

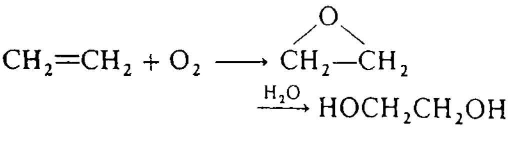
Historical

The stimulus for the development of polyester, as for nylon, was provided by the fundamental work of Carothers. Although his team's initial work was directed toward this material, because of greater promise shown by polyamides at the time, the developmental work on polyesters was temporarily set aside. The polymer, however, attracted interest in Great Britain, where J. T. Dickson and J. R. Whinfield experimented with it and developed a successful polyester fiber.[7] They found that a synthetic linear polymer could be produced by condensing ethylene glycol with terephthalic acid or by an ester-exchange between the glycol and pure dimethyl terephthalate. The polymer thus obtained could be converted to fibers having valuable properties, including the absence of color. Like nylon, this material has been popularized under its generic name, polyester or just "poly." Those persons working with it commonly refer to it as PET. It first appeared under the trade name Terylene® (Imperial Chemical Industries, Ltd.,) in England, and was first commercialized in the

United States in 1953 as Dacron® (E. I. duPont de Nemours & Co).

Manufacture

When the development of polyethylene terephthalate (PET) occurred, ethylene glycol already was being produced in large amounts from ethylene, a by-product of petroleum cracking, by the oxidation of ethylene to ethylene oxide and subsequent hydration to ethylene glycol, which, in a noncatalytic process, uses high pressure and temperature in the presence of excess water.

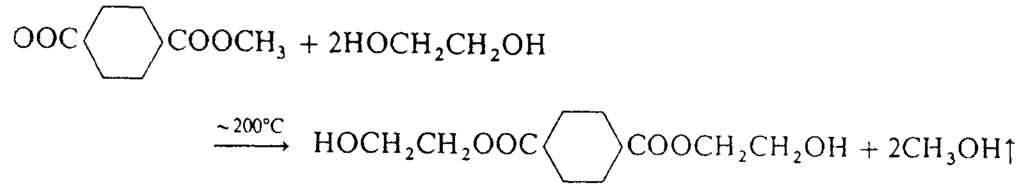


On the other hand, although *o*-phthalic acid, or rather its anhydride, had long been produced in enormous amounts for use in the manufacture of alkyd resins, the *para* derivative was less well known and not available on a large scale. The synthesis is a straightforward one, however, from *p*-xylene, which is oxidized to terephthalic acid, either by means of nitric acid in the older process or by air (catalyzed) in the newer one. In the early years this compound then was converted to the easily purified dimethyl ester in order to obtain a colorless polymer adequate for the manufacture of commercially acceptable fibers.

Several other methods were developed for producing the desired dimethyl terephthalate. The Witten (Hercules) process goes from *p*-xylene to toluic acid by oxidation of one of the methyl groups on the ring, following which the carboxyl group is esterified with methanol. This process then is repeated with the second methyl group to secure the dimethyl ester of terephthalic acid.

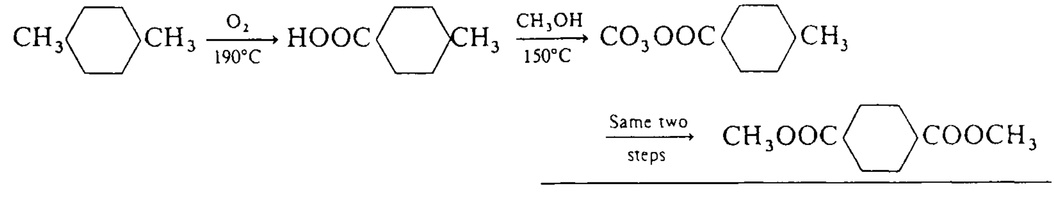
Either phthalic anhydride or toluene, both in ample supply as raw materials, can be used in the Henkel processes. Use of phthalic anhydride depends only upon dry isomerization of the potassium salt of the *ortho* derivative to the *para* form at about 430°C and 20 atmospheric pressure; or toluene is oxidized to benzoic acid, whose potassium salt can be converted to benzene and the potassium salt of terephthalic acid by disporportionation.

The first step in the reaction of dimethylterephthalate and ethylene glycol is transesterification to form bis(*p*-hydroxyethyl) terephthalate (bis-HET) and eliminate methanol.



This product then is polymerized in the presence of a catalyst to a low molecular weight compound and the by-product glycol is eliminated. In a second stage, at a temperature of about 275°C and under a high vacuum, the molecular weight is raised to secure the melt viscosity desired for the particular material involved. Like nylon, this final material may be extruded, cooled, and cut into chips for storage and remelting, or it may be pumped directly to the spinning machines.

From the beginning, it was obvious that there would be considerable progress in industrial chemistry, to say nothing of cost reduction, if the process could be simplified by making it unnecessary to go through the dimethyl derivative to secure a product of adequate purity. This was accomplished in the early 1960s when methods of purifying

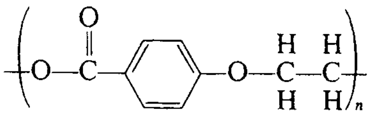


the crude terephthalic acid were developed, and conditions and catalysts were found that made possible the continuous production of a color-free polymer. It is said that the selection of the catalyst is especially aimed at the prevention of ether linkages in the polymer chain due to intracondensation of the glycol end groups.

Two additional rather similar routes are known. Both depend upon the reaction between ethylene oxide, rather than ethylene glycol, and terephthalic acid to form the bis-HET monomer already mentioned. The difference between the two methods lies in the point where purification is done: in one case, it is the crude terephthalic acid; in the other, it is the bis-HET monomer. In both cases this monomer is polymerized by known procedures to form a fiber-grade polyester. The titanium dioxide delustrant is added, as might be expected, early in the polymerizing process.

Another polyester that has reached long-term commercialization is now produced in limited volume as Kodel 200® by Tennessee Eastman Co. and is considered to be 1–4 cyclohexylene dimethylene terephthalate. The glycol that is used instead of ethylene glycol in this process exists in two isomeric forms, one melting at 43°C and the other at 67°C. This makes possible their separation by crystallization, to secure the desired ratio of the two forms for conversion to the polymer. This ratio determines the melting point of the polymer, a most important property for a material that is to be melt-spun. The polymer from the 100 percent *cis* form melts at 275°C, and that from the 100 percent *trans* form at 318°C. Indications are that the commercial product is about 30/70 *cis-trans*.

In 1973, the Federal Trade Commission modified the generic definition of polyester to include in the polyester category materials that previously were polyester ethers or benzoate polyesters. As a result, the fiber known as poly (ethylene oxybenzoate) or PEB and manufactured under the trade name A-Tell in Japan came to be known as polyester. This material is made by reacting parahydroxybenzoic acid and ethylene oxide to give paraoxyethylenebenzoic acid, which is then polymerized to obtain PEB:



The fiber softens at about 200°C and melts at 225°C. It is said to have a silk-like hand and appearance and other properties comparable to those of other polyesters.

Polyesters are melt-spun in equipment essentially the same as that used for nylon, already described. Wherever the volume is large and the stability of demand is adequate, the molten polymer is pumped directly from the final polymerization stage to the melt-spinning machine. The molten polymer is both metered and moved forward at high pressure by use of an extruder coupled with a gear-type pump, through filters to the spinnerette, which contains capillaries of about 9 mils (230 μm) diameter. Great care is taken to eliminate moisture and oxygen from the chips, if they are used, and from the spinning chamber. When the polyester fibers are destined to become staple, the emerging filaments from a number of spinnerettes are combined to form a tow, which can be further processed as a unit. Continuous filament yarn is packaged for further processing such as drawing or texturing. Spin-drawing, described later, has become commonplace today and represents major cost savings to the fiber manufacturer.

Drawing

Unlike nylon, which in the as-spun state contains a high amount of crystalline component, PET fibers are essentially amorphous as spun. In order to secure a usable textile yarn or staple fiber, this product must be drawn under conditions that will result in an increase in both molecular orientation and crystallinity. This is done by drawing at a temperature well above the glass transition point, T_g, which is about 80°C. Conditions of rate and temperature must be selected so that the amorphous areas are oriented, and crystallization will take place as the temperature of the drawn

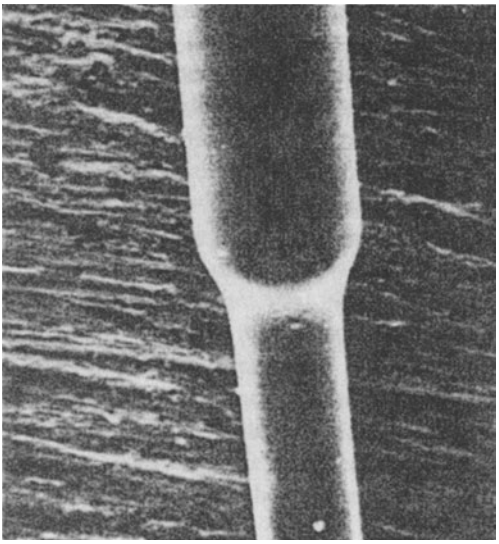


Fig. 12.16. Drawnecking in polyester single filament. (*Courtesy E. I. DuPont de Nemours & Co.*)

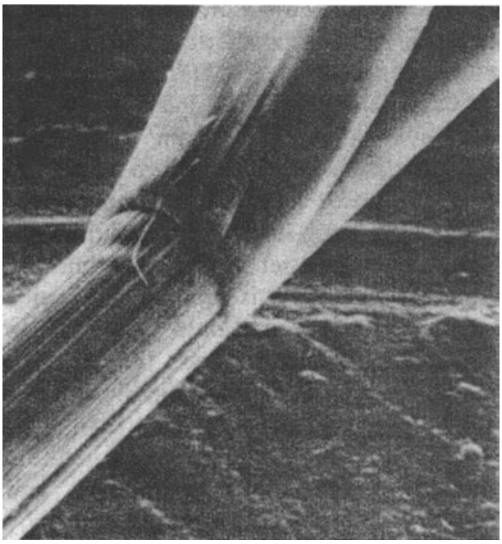


Fig. 12.17. Skin-peeling in polyester showing fibrillar structure. (*Courtesy E. I. DuPont de Nemours & Co.*)

fibers drops to room temperature. An appropriate contact-type hot plate or other device is used, and about 300–400 percent extension is effected.[10] Figure 21.16 shows a filament with drawn and undrawn segments. As with nylon, the conditions of draw, especially the amount, determine the force—elongation properties of the product. Industrial-type yarns, such as those intended to be used as tire cord, are more highly drawn than other yarns and have higher strength with less elongation. The fibers develop the much desired fibrillar morphology for such applications (Figure 12.17).

Heat Setting

The ability of textile fibers to be "set" is not characteristic of manufactured fibers alone. Aided in many cases by the presence of starch, cotton fabrics can be ironed to a smooth and wrinkle-free condition; also, a sharp crease in wool trousers has been commonplace for generations. In other words, these fabrics were exposed to moisture at elevated temperatures while being held or pressed into desired geometrical configurations and then allowed to cool before being released from constraint. Such fabrics tend to remain unchanged while cool and dry, even though the fibers from which they are formed carry internal stresses; but reversion takes place upon washing or exposure to high relative humidity.

With the development of nylon, and especially polyesters, a durable kind of setting has become possible. When fabrics made from these fibers are shaped and then exposed to elevated temperatures either in the dry condition or, in the case of nylon particularly, in the presence of water vapor, thermoplastic relaxation of induced stresses in the fiber takes place and configurations at the molecular level adjust to a new and lower energy level. This depends on not only the temperature used but also the duration of the exposure. Thus a few seconds at 230°C will produce the same results as exposure for a considerably longer period at a temperature 50–75° lower. The permanency of the setting, that is, the ability of a fabric or garment to return to its original configuration after temporary distortion even while exposed to moisture and raised temperatures, is a function of the severity of the heat setting. To impart true permanence, it is essential that the internal crystalline structure be annealed.

It is this property of polyamides and polyesters that has been the main factor contributing to "ease of care" and the "wash and wear" characteristics of garments made from these polymers. In turn, these garments have revolutionized both the textile and the apparel industries.

Textured Yarns

Fundamentally, the manufacture of "textured" yarns is closely related to the heat setting of fabrics, which must be composed of thermoplastic fibers such as nylon or polyester, the difference being that the individual filaments or bundle of filaments in textured yarns are distorted from an essentially straight rodlike form and then heat-set. In some instances, the fibers are distorted in a more or less random way; at other times, a regular pattern is introduced.

The first commercially successful textured yarn was produced by highly twisting nylon 66, heat-setting it as a full package of yarn, and then untwisting it through zero and a small amount of twist in the opposite direction. This process changed yarn from a close-packed structure to one that was voluminous because of mutual interference of distorted filaments. The technique of heat-setting the twisted yarn as a batch-unit operation now has been replaced by a continuous operation, using what is known as a "false twisting" process. This is based upon the principle that if a length of yarn is prevented from rotating at both ends but is rotated on its axis at its center point, the resulting two sections will contain both "Z" and "S" twists in equal amounts. When this occurs with a moving yarn, any element in it will first receive a twist in one direction, but after passing the false twisting point must revert to zero twist. If it is then made to pass over a hot plate while in the twisted state and is heat-set in that configuration, even after returning to the untwisted condition, the individual filaments will tend to remain distorted when lengthwise stress is released. Because of the low mass and diameters of textile yarns or monofilaments, it is possible to false-twist them at extremely high rotational speeds. Yarn forward speeds of about 1000 m/min are currently obtainable by passing the yarn between, and in contact with, high-speed-friction twisting discs. (When attempts are made to secure higher rates, problems of twist control develop.) The same technique is now more commonly applied to unoriented (undrawn) or partially oriented yarn (POY) at the draw-texturing machine. The resulting yarn may be heat-set as part of the same continuous operation by passing it through a second heater under conditions of overfeed or little or no tension in order to secure both thermally stable geometric configurations in the individual distorted filaments that comprise the yarn, and the degree of "stretchiness" and bulk desired in the final product.

Because these yarns are being made in one less step and also within the plants spinning the parent product, this latest development may be said to constitute another advance in the industrial chemical technology of manufactured-textile products. This draw-texturing appears to be especially applicable to polyester yarns intended for fabrics known as "double knits" and "textured wovens."

Yarn can be forced forward by means of "nip" rolls, although this may seem to be quite contrary to the old adage that one cannot push on an end of string. When this is done so that the yarn is jammed into a receiver (stuffer-box) already full of the preceding materials, it collapses with sharp bends between very short lengths of straight sections. In this condition heat is applied, usually in the form of superheated steam, to set it. In practice, the mass of such yarn is pushed through a heated tube until it escapes at the exit past a spring-loaded gate. During this passage it is heat-set in a highly crimped configuration; then it is cooled before being straightened and wound onto a package. In another continuous process, the yarn or monofilament is pulled under tension over a hot sharp edge so that it is bent beyond its elastic limit and is heat-set in that condition. The process is known as "edge crimping," and the result is not unlike that produced by drawing a human hair over the thumbnail. The process is not used much today, but a yarn with similar crimp is produced by bicomponent spinning.

When such yarns are knitted or woven into fabric, the filaments tend to return to the configurations in which they were originally

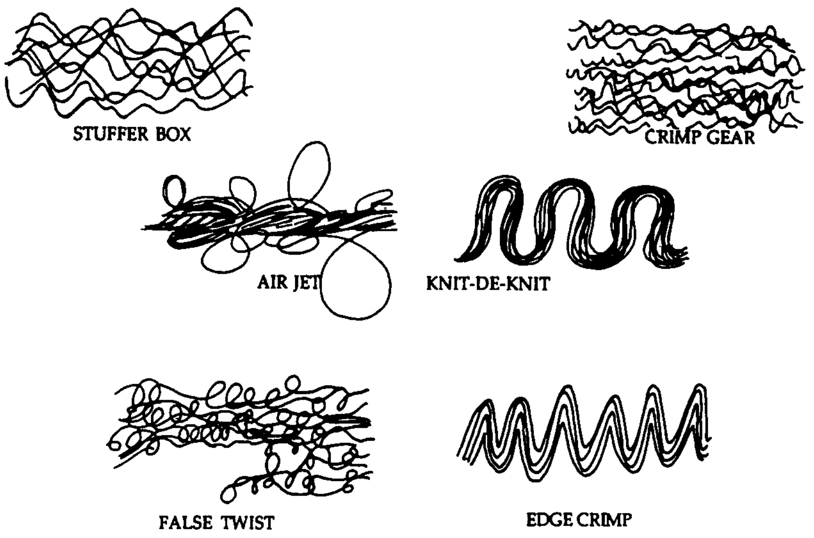


Fig. 12.18. Schematic comparison of the shapes of some textured yarns.

heat-set. Contraction takes place in the direction of the yarn axis, and this in turn converts the smooth flat fabric into a "stretch" fabric and gives the surface a textured appearance. These fabrics or the garments made from them, whatever the process used to produce the yarns, may be given additional heat treatment to secure stability in a desired geometric configuration. A degree of stretch may be retained, or a flat and stable textured surface may be produced. There are a number of variations of the texturing process, which, combined with the many possibilities of heat setting, impart considerable versatility to the final product (see Fig. 12.18). The growth in the use of these products in the 1960s is well known. Carpeting also provides a significant market for them, as texture is one of the most important characteristics of soft floor coverings. Such products have been important to the successful use and expanded development of nylon and polyester yarns.

Staple Process

Unlike nylon, which is used mostly in the form of continuous filament yarn, polyester is utilized both in staple and in continuous filament form in large volumes. For producing staple fiber, the spinning machines consist of a series of packs, 10–30, each with 1000–3000 holes. The extrudates from different packs after solidification and application of finish are combined to form a subtow and collected in a can. Then several such cans are brought together in a creel area, and subtows from these cans are combined to feed a staple drawline. The latter may involve one or more stages of drawing and relaxation, one or more stuffer-box type crimpers, a drying unit, and a cutter. A baling unit following the cutter collects and bales the cut fiber.

Continuous Filament Yarn Process Variants

For producing continuous filament yarn, several process routes are available,[12] each of which involves the basic processes of polymer synthesis, extrusion, quenching, stretching, and winding. In one process, specially meant for textile-type uses, spinnerettes with 20–100 holes typically are used. After solidification and finish application, the filaments may be split into smaller bundles, depending upon end-use applications, for downstream processing. The drawing can also be done in a single integrated process (spin-draw) immediately after finish application to yield a fully oriented yarn (FOY), which having no bulk or texture, is referred to as a flat yarn. Spinning speeds of the order of 1000 m/min or more and winding speeds of about 4000 m/min are used. Similar yarn may be produced on a separate drawing unit, but this process—called draw-twisting because a certain amount of twist is also inserted prior to winding—is less commonly used today. It is more usual to see the separate drawing process done in conjunction with a texturing process—most commonly false twisting, and called draw-texturing—to give a textured yarn. The process leads to orientation and crystallization of the filament structure and bulking of the yarn. The feed yarn for such processes usually is produced at 3000–4000 m/min spinning speed as POY. The latter is designed to be run on draw-texturing machines at speeds ranging from 800 to 1200 m/min.

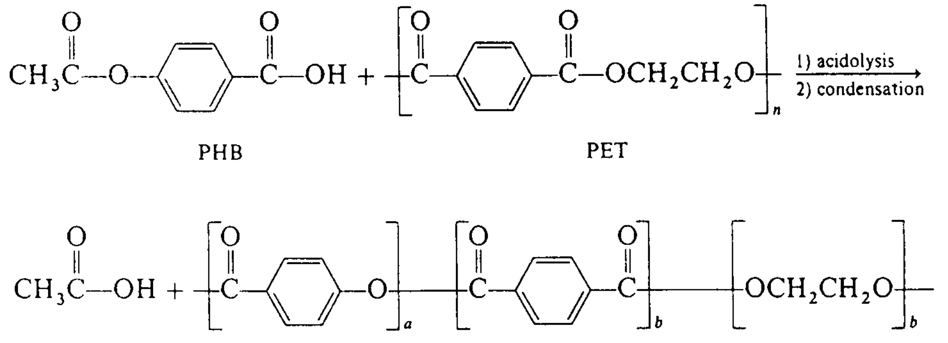
For industrial applications, polyester filaments having high strength low shrinkage (HSLS), low creep properties, and high glass transition temperatures are targeted. To produce such a filament, more severe processing conditions and higher molecular weight polymer are generally used. The filament is spun at low speeds (500–1000 m/min), sometimes with retarded quench, to obtain minimum orientation. The drawing can be achieved in the more common integrated, or spin-draw, process or in a separate draw-twist operation. High strength is achieved by drawing the filament to several times its length over very high-temperature rolls and then heat-setting and relaxing the structure prior to winding. Low shrinkage properties are obtained with a relaxing step at high temperature.

Modifications and New Developments

As was the case with the nylon fibers, the potential polyester fibers offered in apparel, home furnishing, and industrial applications was judged to be enormous. For this potential to be realized in practice, however, some characteristics had to be improved, and others had to be engineered for specific end uses. Thus, fibers of different cross-sectional shapes were developed in order to impart anti-soiling, reflective, and resilient characteristics for rug and carpet applications. A difficulty associated with the early polyester fiber that restricted its applications was its lack of ability to take on dyes through one of many methods available for dyeing. This problem was overcome by introducing chemicals that added sulfonate groups to the molecule and by substituting in some cases isophthalic acid for a small portion of terephthalic acid. These changes allowed fibers to be dyed by cationic and disperse dyes, the dyes most frequently used for polyester. Another area of modification has been the development of inherently flame-resistant fiber. One process involves copolymerizing a derivative of phosphoric acid with PET. An exciting new development in polyester filament yarn for apparel uses is the production of microdenier fiber (denier per filament less than one), discussed later in a separate section. The introduction of finer-denier yarns opened up a whole new field for developing fabrics with special esthetic and performance characteristics that were not possible earlier.

With the use of fibers in conveyor belts, tires, and composites, fibers of greater strength and modulus and lower extensibility have been needed. Much effort was directed in the 1970s, and later, to developing such fibers from polyester. The composition and the properties of wholly aromatic polyamides or aramids are discussed in a later section. When both the diacid and diamine components are *para*-substituted aromatic compounds, the resulting polymer is capable of forming lyotropic liquid–crystalline solutions. These solutions can be dry- or wet-spun into fibers with unusually high tensile strength and tensile modulus. When a similar strategy is tried to make polyester fiber from a homopolymer of a *para*-substituted aromatic diacid and a *para*-substituted aromatic diol, only infusible and intractable materials are obtained. A solution to this problem has been found in the development of polyester copolymers that give thermotropic liquid–crystalline melts over a useful temperature range and have viscosities suitable for melt extrusion into fibers or films having high levels of orientation. Spin-line stretch factors of the order of several hundred percent are used to achieve orientation, and physical properties are developed further by heat treatment at temperatures approaching melting conditions.

The first fibers from a thermotropic liquid crystalline melt whose properties were reported were spun from a copolyester of *para*-hydroxybenzoic acid (PHB) and PET by workers at Tennessee Eastman Co. The preparation of the copolymer proceeds in two stages. First, *para*-acetoxybenzoic acid is reacted with PET in an acidolysis step to give a copolyester prepolymer, which in the second step is condensed further to a higher degree of polymerization suitable for fiber formation.



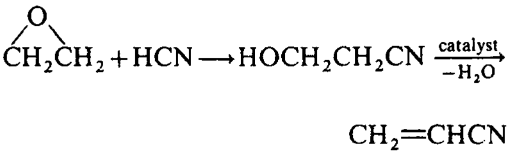
When the mol. percent of PHB in the copolymer exceeds about 30–40 percent, a liquid–crystalline melt is obtained. Up to about 60 mol. percent, order in the melt increases and melt viscosity decreases. Compositions containing about 60 mol. percent PHB can be melt-spun into fibers using standard extrusion techniques. It is the unusual combination of properties that makes this class of materials valuable for the formation of high-strength fibers and plastics.

Among melt-spun fibers, those based on thermotropic liquid–crystalline melts have the highest strength and rigidity reported to date, and appear comparable to polyamides spun from lyotropic liquids–crystalline solutions. This was a very active field of research in the 1970s and later, and many comonomers have been reported. Obviously, these compositions must contain three components at a minimum, but many have four or five components. Some frequently used constituents, in addition to those mentioned above, are 2,6-naphthalene-dicarboxylic acid, hydroquinone, 4,4′-biphenol, isophthalic acid, and 4,4′-dihydroxy-diphenyl ether.

ACRYLICS

Polymer Manufacture

Acrylic fibers are spun from polymers that are made from monomers containing a minimum of 85 percent acrylonitrile. This compound may be made from hydrogen cyanide and ethylene oxide through the intermediate ethylene cyanohydrin:



$$\overset{O}{CH_2CH_2} + HCN \longrightarrow HOCH_2CH_2CN \xrightarrow[-H_2O]{\text{catalyst}} CH_2{=}CHCN$$

It also may be made directly from acetylene and hydrogen cyanide:

$$CH{\equiv}CH + HCN \rightarrow CH_2{=}CHCN$$

But the reaction that currently is preferred uses propylene, ammonia, and air:

$$3CH_2{=}CHCH_3 + 3NH_3 + 7O_2\,(\text{air}) \xrightarrow[<500^{\circ}C]{\text{Catalyst}} CH_2{=}CHCN + 2CO + CO_2 + CH_3CN + HCN + 10H_2O$$

Pure acrylonitrile may polymerize at room temperature to polyacrylonitrile (PAN), a compound that, unlike polyamides and polyesters, does not melt at elevated temperatures but only softens and finally discolors and decomposes. Nor is it soluble in inexpensive low-boiling organic solvents. Because fibers made from it resist the dyeing operations commonly used in the textile industry, the usual practice is to modify it by copolymerization with other monomers, for example, vinyl acetate, styrene, acrylic esters, acrylamide, or vinyl pyridine in amounts up to 15 percent of the total weight (beyond which the final product may not be termed an acrylic fiber). The choice of modifier depends on the characteristics that a given manufacturer considers important in a fiber, the availability and cost of the raw materials in the manufacturer's particular area of production, and the patent situation.

In copolymerizing acrylonitrile with another monomer, conditions must be controlled in such a way that the reaction produces a polymer having the desired chain structure and length. The reaction takes place in the presence of substances capable of producing free radicals. In addition, certain trace metals that have been found to increase reaction rates offer a means of controlling chain length. When polymerization is carried out in solution, after an induction period, the reaction is rapid and liberates a considerable amount of heat. Furthermore, because the polymer is not soluble in the monomer, a thick paste is formed. These facts limit the usefulness of such a process. Carrying out the polymerization in the presence of a large amount of water (water/monomer of 2/1 to 3/1) is a convenient method and the one most generally used. In this case the polymer forms a slurry, and the water provides a means for removing the heat from the site of the reaction. Moreover, most of the common redox-catalyst systems are water-soluble. Polymerization may be carried out batchwise or by a continuous process.

In the batch method, the monomers and catalyst solutions are fed slowly into an agitated vessel containing a quantity of water. The heat of reaction is removed either by circulating cold water through the jacket surrounding the vessel or by operating the reaction mixture at reflux temperature and eliminating the heat through the condenser water. The monomer and catalyst feeds are stopped when the desired amounts have been added, and polymerization is allowed to continue until there is only a small amount of monomer remaining in the reaction mixture. Then the slurry is dumped from the reaction vessel, filtered, washed, and dried (see Fig. 12.19).

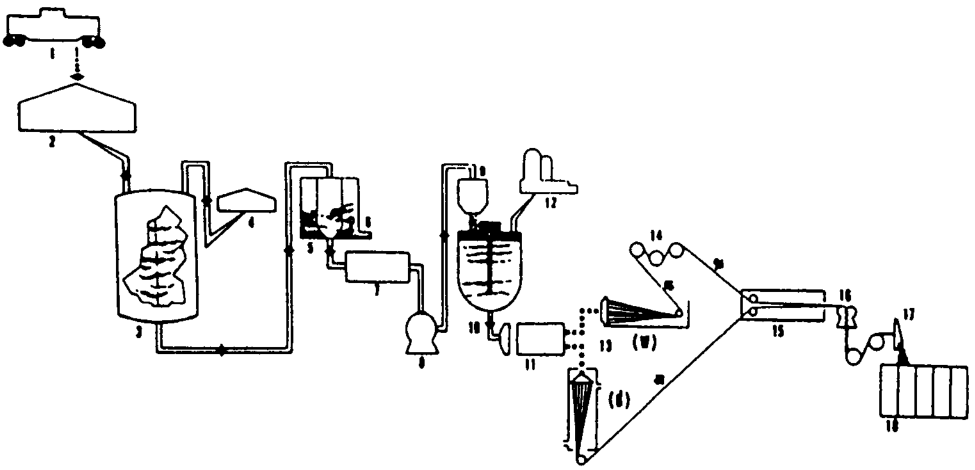


Fig. 12.19. Flow diagram for the manufacture of acrylic fiber: (1) acrylonitrile; (2) tank farm; (3) polymerizer; (4) comonomer and catalyst; (5) centrifuge; (6) waste liquid; (7) dried polymer; (8) grinding; (9) polymer storage; (10) dissolver; (11) filter; (12) solvent plant; (13) spinnerette; (13w) wet spinning; (13d) dry spinning; (14) roller dryer; (15) additional treatment; (16) crimper; (17) cutter; (18) acrylic fiber bale.

In the continuous-overflow method, rather than stopping the monomer and catalyst feed when the reaction vessel is full, the slurry is simply allowed to overflow; the solids are removed by filtration, washed, and dried. The filtrate contains a certain amount of unreacted monomer, which is recovered by steam distillation after the trace metal present has been chelated to stop the redox reaction and thus further polymerization. The dried polymer is the raw material from which fibers are spun.

As mentioned, PAN polymer has two major weaknesses: (1) extremely poor dyeing characteristics due to highly ordered structure, and (2) very low solubility in most of the solvents. To overcome these problems, comonomers are incorporated into the chains. Comonomers have been used to improve hydrophilicity, dyeability, flame retardancy, heat resistance, and so on. For obtaining hydrophilic acrylic fiber, comonomers containing hydrophilic functional groups such as hydroxyl, ester, carboxyl, amide, and substituted amide are used. To make the fiber base-dyeable, comonomer containing carboxylic and sulfonic acid groups is introduced; and to obtain acid-dyeable fiber, comonomers containing pyridine, aliphatic amine, or quaternary ammonium salt are used. Antistatic acrylic fibers can be made by incorporating in the chain polyethylene oxide, polyalkylene derivatives, polyethylene glycol, acrylates, or methacrylates as the comonomers. For improved flame retardancy, halogen-containing vinyl comonomers are used.

Spinning

As already indicated, pure PAN softens at elevated temperatures, and thermal decomposition starts before the molten state is reached. The same is true of the copolymers commonly used to produce fibers. Accordingly, melt spinning is impossible; spinning must be done from a solution of the polymer. Both dry and wet spinning are carried out in current commercial operations.

The operations used to either wet- or dry-spin acrylics are essentially the same as those already described for rayon and acetate, respectively. The polymer must be completely dissolved in solvent and the solution filtered to remove any impurities that would cause spinnerette blockage. Because acrylic polymers are not soluble in common nonpolar solvents, polar substances such as dimethylformamide, dimethylacetamide, or aqueous solutions of inorganic salts such as zinc chloride or sodium thiocyanate are required. Only wet spinning is possible with the latter. Dimethyl formamide boils at 152.8°C and exerts a vapor pressure of 3.7 mm of Hg at 25°C compared with acetone (used in dry spinning of cellulose acetate), which has a vapor pressure of 228.2 mm of Hg at 25°C. It follows that, unlike acetone which requires an activated-carbon system for recovery, dimethylformamide may be condensed directly from the gas stream used to evaporate the solvent from the forming fiber.

In order to obtain the desired characteristics of modulus, rupture tenacity, and rupture elongation, acrylics, like rayon, require stretching which is usually carried out after the fiber has been spun, either as part of the fiber washing operation or after the fiber has been dried. These same properties are influenced by spinning speeds, and the temperature of the drying air, if they are dry-spun, or the temperature and the composition of the bath, if wet-spun. The multitude of combinations made possible by the use of various comonomers and the flexibility of the fiber-forming operations furnish the different manufacturers with versatility and the users with a variety of acrylic fibers. Figure 12.20 shows a wet-spinning operation for acrylic tow.

Acrylic fibers possess a property that made it possible for them in the late 1950s and early 1960s to find immediate, even spectacular, acceptance in the knitted sweater field, until then dominated by wool. When acrylic fibers, normally in the form of a heavy tow, are hot-stretched (e.g., by being drawn over a hot plate and then cooled under tension), they are converted to a labile state. Upon immersion in hot water, such fibers will contract considerably, but not to their prior unstretched length. In practice, this characteristic is used to

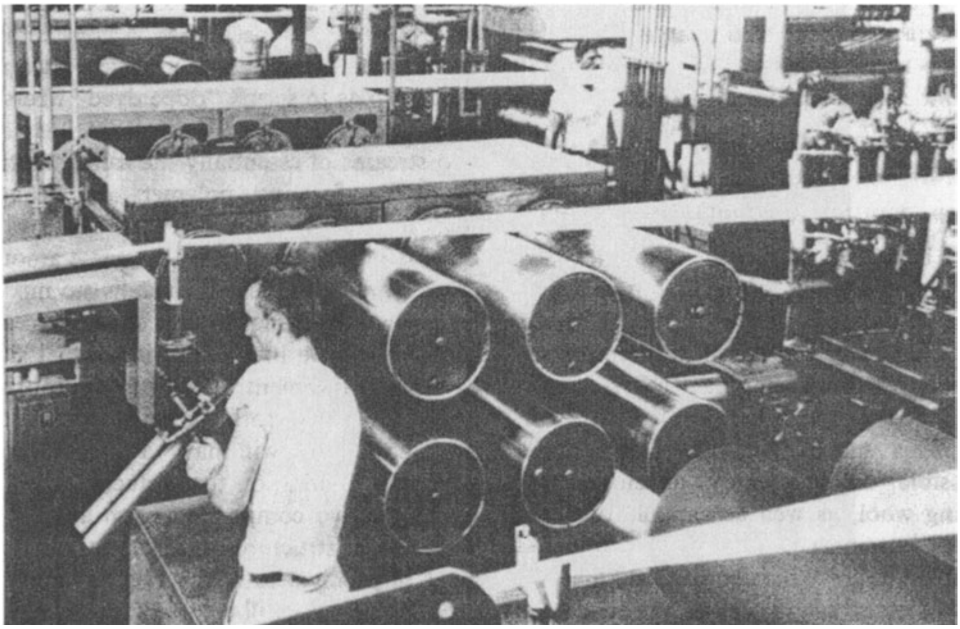


Fig. 12.20. Wet spinning of acrylic tow. (*Courtesy Monsanto Co.*)

produce a bulky yarn resembling the woolen yarns long accepted for use in sweaters. The process is described briefly below.

Using "stretch-break" equipment, the stretched labile fibers are further cold-stretched to the breaking point so that the fiber breaks at different points leading to a distribution of fiber lengths, similar to the lengths found in wool. These are crimped and then mixed with thermally stable acrylic fibers that have been stretched and relaxed and have about the same length and degree of crimp. The blend is converted to a spun yarn by the same process used in making woolen yarns, and in turn this yarn is knitted into sweaters and other similar products. When such garments are dyed in hot water, the labile fibers, intimately blended with stable ones, contract lengthwise individually. In the process, segments of the stable units tend to be carried along physically by entrapment and friction; but because such fibers do not change their overall length, the yarn as a whole decreases in length. Lateral displacement of the large volume of stable fibers results in the formation of a more voluminous structure known as "hi-bulk" yarn.

Bicomponent or Conjugate Spun Fibers

As will be shown, it should be theoretically possible to make any of the common manufactured fibers in bicomponent forms. However, acrylics have received the most attention for quite good reasons. Their general characteristics have tended to make them competitive with wool. This means that they should be processible on machinery developed for handling wool, as well as capable of being accepted into markets previously dominated by an animal hair fiber. It follows that because the natural fiber possesses crimp which produces the cohesion that determines its behavior in processing and in part its appearance and "hand" in usage, a similar crimp was desired for acrylics.

The principle that is the basis for bicomponent fibers usually is likened to that which underlies the bicomponent metal strips often used in temperature controllers. With the latter, differential-thermal expansion of the two joined components results in a bending of the thermal element. With fibers, moisture usually is the agent that acts upon the two side-by-side portions. Differential swelling or shrinkage causes the fiber to be brought into a crimped, or preferably, a spirally distorted condition. As such, the side-by-side structure exists naturally in wool.

The combination of small size and large number of holes in a spinnerette might lead one to conclude that it would be almost impossible to design a spinnerette assembly that could bring two streams of polymer or polymer solutions together at each such hole and extrude them side-by-side to form a single filament. Such designs have, in fact, been made; but solutions of fiber-forming polymers fortunately possess properties that encourage laminar flow and thus make other approaches possible. This phenomenon was remarked upon earlier in connection with dope dyeing; when a suspension of a colored pigment is injected into a dope stream, a considerable problem must be overcome to achieve adequate mixing so as to secure "dope dyed" fibers of a uniform color. Thus, it was known that when two streams of essentially the same solution of a fiber-forming polymer are brought together, side-by-side, and moved forward down a pipe or channel by the same amount of pressure behind each, virtually no mixing takes place. By bringing these streams to each spinnerette hole in such an individual side-by-side arrangement and using appropriate mechanical separators, the extruded filament from each hole will have a bicomponent structure. In addition to producing fibers in which the two components form a bilateral symmetrical structure, an ingenious arrangement of predividers of the two streams can produce from the full complement of holes in a single spinnerette a selected group of fibers wherein the amount and the position of each of the two components are randomly distributed throughout their cross-sections. It follows that curls of uniform or random geometry may be produced to meet the required needs.

The worldwide production of acrylic fiber has declined significantly over the years because of the environmental concerns associated with the solution-spun process. In view of this, scientists have sought over the years a method that could render the high acrylics melt-spinnable. Such a method would not only be economical and environmentally friendly but also allow for engineering the fiber with a wider range of morphologies and properties. In 1997, British Petroleum patented a polymerization process in which the two components usually used in developing spinnable acrylic copolymer were redistributed to allow the resulting material to be melt processable.[13,14] Preliminary findings show that the polymer can be melt-spun into reasonable fine denier fibers with mechanical properties expected of the usual solution-spun material.[15]

VINYL AND MODACRYLIC FIBERS

Vinyls

When nylon 66 was developed, it was described as being "synthetic" or "fully synthetic" in order to differentiate it from rayon and acetate. This was no small act of courage, as the word "synthetic," in that period just following the repeal of Prohibition in the United States, was often associated in the public mind with the least palatable kind of alcoholic beverages. In due time, what is known in the advertising business as "puffing" led it to be known as the "first fully synthetic fiber," which was an anachronism. It so happens that fibers based upon polyvinyl chloride (PVC) predated nylon by several years.

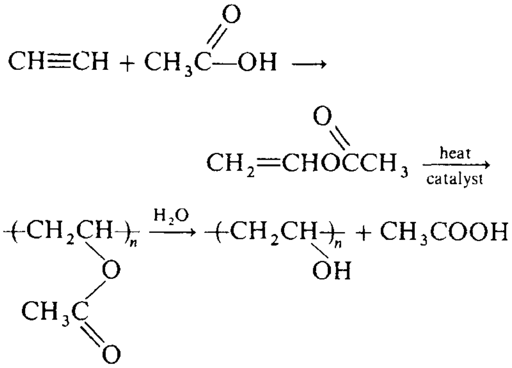
About 1931, the production of fibers from PVC was accomplished by dry spinning from a solution in cyclohexanone. But by chlorinating the polymer, it was possible to secure solubility in acetone, which has the advantage of possessing a boiling point about 100°C lower than that of cyclohexanone. Several million pounds per year of this fiber were produced in Germany during World War II to relieve the shortages of other materials. Unfortunately, PVC begins to soften at about 65°C, and in the fibrous state, it shrinks disastrously upon heating. Because of its low softening point, it cannot be dyed at the temperatures commonly used for this purpose, and, furthermore, it resists dyeing.

Modifications of PVC have been produced by copolymerization with other monomers.

The first successful one consisted of 90 percent vinyl chloride copolymerized with 10 percent vinyl acetate. It was dry-spun from acetone and given the trade name Vinyon by its producer, Union Carbide Corporation. (In 1960, vinyon was accepted as a generic name for fibers containing not less than 85 percent vinyl chloride.) It has never been produced in large volume; it is used for heat-sealable compositions.

A copolymer of vinyl chloride with vinylidene chloride was used for a number of years to produce melt-spun, heavy monofilaments, which found use in heavy fabrics, where the chemical inertness of the polymer was needed, in outdoor furniture, and in upholstery for seats in public-transportation vehicles.

Another vinyl-based fiber, polyvinyl alcohol, or vinal, was developed in Japan but has not been produced or used in the United States. As such, it illustrates the importance of both relative availability of raw materials and differences in markets, in the success of a chemical product. Acetylene made from calcium carbide is converted to vinyl acetate, which, following polymerization, is saponified to polyvinyl alcohol.



$$CH\equiv CH + CH_3\overset{O}{\overset{/\!/}{C}}{-}OH \longrightarrow CH_2{=}CHO\overset{O}{\overset{\backslash\!\backslash}{C}}CH_3 \xrightarrow[\text{catalyst}]{\text{heat}}$$

$$\left(CH_2\underset{\underset{\underset{\underset{O}{\|}}{CH_3C}}{O}}{CH}\right)_n \xrightarrow{H_2O} \left(CH_2\underset{OH}{CH}\right)_n + CH_3COOH$$

The polyvinyl alcohol is soluble in hot water, and the solution is wet-spun into a coagulating bath consisting of a concentrated solution of sodium sulfate. The fibers are heat-treated to provide temporary stability so that they may be converted to the formal derivative by treatment with an aqueous solution of formaldehyde and sulfuric acid. This final product resists hydrolysis up to the boiling point of water. It seems reasonable to assume that it contains hemiacetal groups and some unreacted hydroxyls on the polymer chain as well as cross-linking acetyl groups between the adjacent molecules.

Under the trade name Kuralon® (Kuraray Co., Ltd), it achieved a production level of about 180 million lb in 1970, but production dropped to 16 million lb of continuous filament and 87 million lb of staple in 1980. The former has been mainly used in industrial rubber products, and the latter has been used mostly for uniforms, nonwoven and coated fabrics, and filters.

Modacrylics

In the United States, the modification of PCV has moved in the direction of copolymerizing vinyl chloride with acrylonitrile, or perhaps it should be said that PAN has been modified by copolymerizing the acrylonitrile with chlorine-containing vinyl compounds. In any case, one modacrylic fiber is currently produced in the United States, a modacrylic being defined as containing at least 35 percent but not over 85 percent acrylonitrile.

The first two modacrylic fibers ever introduced in the United States were Dynel® (by Union Carbide) in 1949 and Verel® (by Tennessee Eastman) in 1956. The former was a copolymer of 60 percent vinyl chloride and 40 percent acrylonitrile, and the latter was said to be a 50–50 copolymer of vinylidene chloride and acrylonitrile with perhaps a third component graft-copolymerized onto the primary material to secure dyeability. SEF® and its version for wigs, Elura®, were introduced by Monsanto Fibers in 1972. A few foreign manufacturers are making modacrylic fibers, but the only modacrylic fiber currently in production in the United States is SEF®.

Modacrylic fibers, like acrylic, require after-stretching and heat stabilization in order to develop the necessary properties. It is thought that the stretching is of the order of 900–1300 percent, and that, in a separate operation, shrinkage of about 15–25 percent is allowed during the time that the fibers are heat stabilized.

The modacrylic fibers, like vinyon and unlike the acrylic fibers, have not become general purpose fibers. They can be dyed satisfactorily and thus are acceptable in many normal textile products; but their nonflammability tends to place them in uses where that property is important, even vital. Blended with other fibers, they are used in carpets; but their largest market is in deep-pile products, such as "fake furs," or in doll hair, where a fire hazard cannot be tolerated.

ELASTOMERIC FIBERS

The well-known elastic properties of natural rubber early led to processes for preparing it in forms that could be incorporated into fabrics for garments. One such process uses standard rubber technology. A raw rubber of high quality is compounded with sulfur and other necessary chemicals, calendered as a uniform thin sheet onto a large metal drum, and vulcanized under water. The resulting skin is spirally cut into strips that may be as narrow as they are thick, for example, 0.010 in. by 0.010 in.^2 in cross-section. These strips are desulfurized, washed, dried, and packaged. Larger cross-sections are easier to make. This product, coming out of the rubber rather than the textile industry, is known as a thread.

Another method produces a monofilament known as a latex thread. As the name would indicate, rubber latex is the raw material, and because extrusion through small holes is required, the purity of the material must be of a high order. With proper stabilization, the latex solution may be shipped from the rubber plantation to the plant, where it is compounded with sulfur and other chemicals needed for curing, as well as with pigments, antioxidants, and similar additives. This is followed by "precuring" to convert the latex to a form that will coagulate upon extrusion into a precipitating bath of dilute acetic acid and will form a filament having sufficient strength for subsequent operations. It passes out of the bath and is washed, dried, vulcanized in one or two stages, and packaged.

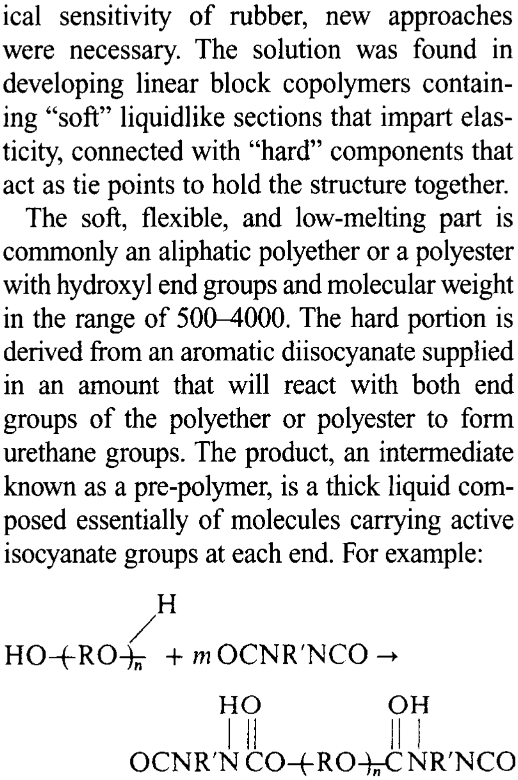
The rubber threads manufactured by either process can be used as such in combination with normal nonelastomeric yarns in fabrics made by weaving or knitting; but most of them, especially those made by a latex process, first are covered by a spiral winding of natural or manufactured yarns. Often two layers are applied in opposite directions to minimize the effects of torque. Such coverings have two purposes. The first is to replace the less desirable "feel" of rubber on human skin by that of the more acceptable "hard" fiber. The second concerns the engineering of desired properties into the product to be woven or knitted into fabric. As an elastomeric material begins to recover from a state of high elongation, it supplies a high stress; but as it approaches its original unstretched condition, the stress drops to a very low order. When wound in an elongated state with a yarn having high initial modulus and strength, the elastomeric component cannot retract completely because its lateral expansion is limited, and jamming of the winding yarn occurs. Thus, the combination of such materials can be made to provide stretch and recovery characteristics needed for a broad spectrum of applications.

The traditional elastomeric threads have been subject to certain inherent limitations, however. The presence of unreacted double bonds makes them sensitive to oxidation, especially with exposure to the ultraviolet radiation of direct sunlight. They also have low resistance to laundry and household bleaches and dry-cleaning fluids.

During recent years, elastomeric yarns or threads have been used to impart comfort, fit, and shape retention to a variety of garments such as women's hosiery and swimwear. Such garments must be thin and highly effective per unit of weight. The materials of which they are composed must be compatible with these requirements. Thus, it was not unexpected that the producers of manufactured fibers, already eminently successful in meeting the needs of the marketplace, should look to the field of elastomeric fibers for new possibilities. Given the limitations of rubbers, both natural and synthetic, as well as the relationships between molecular structure and behavior of fiber-forming linear polymers, the scientists faced new challenges.

As an oversimplification, it can be said that within limits a rubberlike material can be stretched relatively easily but reaches a state where crystallization tends to occur. The structure produced in this manner resists further extension, and the modulus rises sharply. In contrast to the conditions that occur when the manufactured fibers discussed earlier such as nylon or polyester are drawn to form fibers of stable geometry in the crystalline and oriented states, the crystalline state of the elastomeric fibers is labile unless the temperature is lowered materially. Thus, to improve on the chemical sensitivity of rubber, new approaches were necessary. The solution was found in developing linear block copolymers containing “soft” liquidlike sections that impart elasticity, connected with “hard” components that act as tie points to hold the structure together.

The soft, flexible, and low-melting part is commonly an aliphatic polyether or a polyester with hydroxyl end groups and molecular weight in the range of 500–4000. The hard portion is derived from an aromatic diisocyanate supplied in an amount that will react with both end groups of the polyether or polyester to form urethane groups. The product, an intermediate known as a pre-polymer, is a thick liquid composed essentially of molecules carrying active isocyanate groups at each end. For example:



$$\mathrm{HO{-}(RO)_{n}{-}H} + m\,\mathrm{OCNR'NCO} \rightarrow \mathrm{OCNR'\overset{H}{\overset{|}{N}}\overset{O}{\overset{\|}{C}}O{-}(RO)_{n}{-}\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}R'NCO}$$

where—(RO)—is an aliphatic polyether chain, R′ is one of several commonly available ring structures, $n \sim 10$–30, and $m \sim 1.5$–2.

The elastomeric polymer is obtained by “extending” the prepolymer through its reaction with short-chain diols such as butanediol or diamines such as ethylene diamine, thus completing the formation of hard groups between soft, flexible chains. When amines are used, the final step is typically done in a polar solvent such as dimethyl acetamide. The conversion of these polymers into usable fibers may be accomplished by wet-, dry-, or melt-spinning operations, depending on the polymer. Additives to impart whiteness or improve resistance to ultraviolet radiation and oxidation may be incorporated in the spinning solutions or in the melts.

The development of elastomeric fibers has resulted in a variant of wet spinning called “reaction” or “chemical” spinning. In point of fact, rayon, the first wet-spun material, might properly be said to be produced by “reaction wet spinning” or “chemical wet spinning” because complex chemical reactions always have been involved in that operation. In any case, it has been found that the prepolymer of an elastomeric fiber may be extruded into a bath containing a highly reactive diamine so that the chemical conversion from liquid to solid occurs there.

The elastomeric fibers produced in this fashion are based upon segmented polyurethanes and by definition are known generically as spandex yarns. Each manufacturer uses a trade name, for the usual commercial reasons. Perhaps the most noteworthy aspect from the standpoint of industrial chemistry is the multitude of options available to the manufacturer through the ingenious use of various chemicals for soft segments, hard units, chain extenders, and conditions of chemical reaction, followed by numerous possibilities for extrusion and after-treatments. In the United States, there are two main producers of spandex fibers: DuPont (Lycra®) and Globe Rubber Co. (Cleerspan®, Glospan®). There are numerous worldwide producers, including: Bayer, Germany (Dorlastan®); Asahi, Japan (Roica®); Nisshinbo, Japan (Mobilon®); and Tae Kwang, Korea (Acelan®).

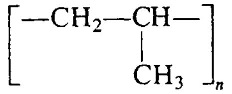
POLYOLEFIN FIBERS

Polypropylene

Although polyethylene was considered a source of useful fibers at an early date, its low melting point (110–120°C) as well as other limitations precluded active development during the period when production of other fibers based upon the petrochemical industry expanded enormously. The higher melting point of high-density polyethylene gave some promise, but it was overshadowed by the introduction of polypropylene (PP) around

1958–1959. Great expectations were held for the latter as a quick competitor with the polyamides and the polyesters, already successful, as well as the acrylics, which then were entering the fiber field in volume. PP was thought to have several advantages. The raw material costs were low, only a few cents a pound; also there was a high level of sophistication in the spinning and processing of fibers, and a presumption that this would readily lead to the development of means for converting the polymer to fibers; and, finally, there was the belief that the American consumer would be ready to accept, and perhaps even demand, something new and different, which this polymer offered. However, the limitations of PP fibers, such as lack of dyeability, low melting temperature, low heat stability, and poor light stability, combined with the lower prices and the greater versatility of the already established fibers, dashed the hopes for quick success. However, all of these deficiencies except the low melting temperature and lack of dyeability now have been overcome. The fiber has found an increasingly important place, and its properties have led to new techniques of manufacture and specialized uses.

The structural formula of PP is as given below, where $100{,}000 < n < 600{,}000$ for chips or granules, and $50{,}000 < n < 250{,}000$ for fibers:



$$\left[-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}- \right]_n$$

The steric configuration is extremely important in the polymer. Only isotactic polypropylene (iPP) has the properties necessary for forming fibers. The molecules are crosslinked only by Van der Waals forces, so it is important that they pack as closely as possible. The isotactic molecules form a 3_1 helix, as shown in Fig. 12.21,[16] and exhibit a high crystallization rate. The atactic molecules, shown in the figure, do not pack well, and although the syndiotactic molecules can pack better and crystallize, this configuration is not a normal product of commonly used catalyst systems. Some properties of isotactic, syndiotactic, and atactic PP are listed in Table 12.2.[17] The insolubility of iPP in hydrocarbon solvents at room temperature often is used to separate iPP from atactic polypropylene (aPP).

Early in the manufacture of PP, a concept was developed for dry spinning directly from the solution obtained in the polymerization operation. Had it been feasible, it would have been the realization of a chemical engineer's dream: the gaseous olefin fed into one end of the equipment, and the packaged fiber, ready for shipment to a textile mill, coming out the other end. But it did not turn out that way, and today melt spinning is the accepted technique for the production of staple fibers, monofilament, and multifilament yarns. To this usual method have been added the fibrillation and the "slit film" procedures for producing yarns.

The PP materials are completely resistant to bacterial attack, are chemically inert, and are unaffected by water. Monofilaments can be produced that possess high strength, low elongation under stress, and dimensional stability at normal atmospheric temperatures.

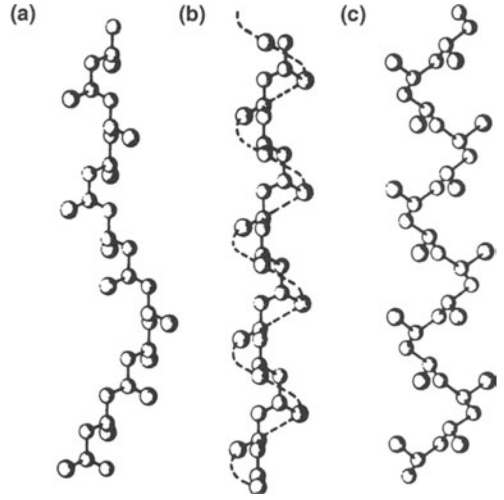


Fig. 12.21. Diagrams showing (a) irregular atactic, (b) stereoregular isotactic, and (c) stereoregular syndiotactic configurations in polypropylene polymer. (Source: Ahmed, M., "Polypropylene Fibers–Science and Technology," *Textile Science and Technology*, **5**, 16, Elsevier Science Publishers SV, Academic Publishing Div., New York, Amsterdam (1982).) Copyright © M. Ahmed. By permission.

TABLE 12.2 Properties of Isotactic, Syndiotactic, and Atactic Polypropylene

Property	*Isotactic*	*Syndiotactic*	*Atactic*
Density, g/cm^3	0.92–0.94	0.89–0.91	0.85–0.90
Melting Point, °C	165	135	
Solubility in hydrocarbons at 20°C	None	Medium	High
Yield strength	High	Medium	Very low

Source: Lieberman, R. B., and Barbe, P. C., "Propylene Polymers," in *Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz (Ed.), p. 916, 1990. Copyright © John Wiley and Sons and reproduced by permission of the copyright owner.

PP monofilaments have found broad application in cordage and fishing nets (which float), and if highly stabilized they are woven into fabrics used for outdoor furniture, tarpaulins, and similar applications. Large filament denier staple is used widely in "indoor–outdoor" carpets. Also, staple fibers have found major applications in tufted indoor carpets and nonwovens used for diaper, filtration, and civil engineering fabrics.

Synthesis. The early PP plants used a slurry process adopted from polyethylene technology. An inert liquid hydrocarbon diluent, such as hexane, was stirred in an autoclave at temperatures and pressures sufficient to keep 10–20 percent of the propylene monomer concentrated in the liquid phase. The traditional catalyst system was the crystalline, violet form of$TiCl_3$ and $AlCl(C_2H_5)_2$. Isotactic polymer particles that were formed remained in suspension and were removed as a 20–40 percent solid slurry while the atactic portion remained as a solution in the liquid hydrocarbon. The catalyst was deactivated and solubilized by adding HCl and alcohol. The iPP was removed by centrifuging, filtration, or aqueous extraction, and the atactic portion was recovered by evaporation of the solvent. The first plants were inefficient because of low catalyst productivity and low crystalline yields. With some modifications to the catalyst system, basically the same process is in use today.

In 1963, liquid polymerization was introduced in which liquid propylene, catalysts, and hydrogen were pumped continuously into the reactor while polypropylene slurry was transferred to a cyclone separator. The unconverted monomer gas was removed, compressed, condensed, and recycled, and the polymer was treated to reduce the catalyst residue. This system also suffered from a poor catalyst yield, and the polymer produced lacked the required stereospecificity, so that it was necessary to remove the atactic portion of the polymer.

In the mid-1960s, a gas phase process was introduced for production of the polymer. The monomer was pumped over adsorbing beds and entered the reactor with the catalyst system. These feed streams of monomer and catalyst, together with a mechanical stirrer, created a turbulent bed of powdered polymer. Periodically the polymer powder was vented off in a carrier gas to extrusion storage hoppers. Meanwhile, the heat of polymerization was removed by condensing the unreacted monomer in a cooling loop and returning it to the reactor, where it immediately vaporized. This process eventually led to the production of highly crystalline products and was adopted by several companies in the United States.

Most processes in use today rely on a combination of these technologies. Montedison's introduction in 1975 of third-generation catalysts gave high yields and allowed polymerization to take place at 60–80°C and 2.5–3.5 MPa (362–507 psi). This was welcome news during the energy crisis, but the resulting polymer was not stereospecific enough to eliminate the need for removal of aPP. Real progress came with the discovery of superactive third-generation catalysts, which gave both the optimal yield and stereospecificity.[18]

Production. Classical melt spinning, which was developed for the production of nylon filaments, is widely used to produce PP fibers today. It involves a high-speed process (2000–3000 m/min) that is particularly suitable for long production runs. The average molecular weight of polypropylene polymer, like that of other addition (olefin) polymers, is relatively high compared to that of other polymers. This results in a high melt viscosity; so, unlike the case of other polymers, its extrusion temperatures are 70–100°C above its melting point. Single-screw extruders are used for melting and homogenizing the polymer. The screw diameters are from 45 to 200 mm and screw lengths are 24, 30, or 36 times the diameter. The polymer granules are fed into the extruder hopper, where they are melted and homogenized. Chips carrying pigments can be fed into and blended with the main charge of the extruder if colored fibers are desired. The molten polymer is forced through the spinnerette via a screen pack to eliminate any contaminant particles. The spinnerette hole determines the shape of the filaments, and the flow rate and the takeup speed determine the size. The polymer has high specific heat and low thermal conductivity, so the cooling zones must be longer than those for polyester and nylon. For filament yarn production, the filaments are drawn at high speed and wound on packages. For staple fiber production, the filaments are collected in the form of tow and then are drawn, crimped, and cut. The multifilament yarns are often textured to improve bulk and appearance. The false twist method is generally used to texture finer yarns, with the stuffer box used for coarser yarns.

The short spinning method used to produce staple fiber is considerably slower than high-speed spinning. The lower spinning speeds (30–150 m/min) would have a negative effect on productivity, but this is counteracted in industry by the use of spinnerettes with a large number of holes (up to 55,000). The required cooling zones are much shorter because of the lower speeds and the use of higher volumes of quench air, which gives this method its name. Because the drawing units can match these low speeds, the two can be fed directly and continuously from the spinning machine to the draw frame to the texturing chamber or the crimper, to produce bulked continuous filament (BCF) yarn or staple fiber, respectively. The short spinning method is used to produce high-tenacity fibers. Many PP yarns are produced using the slit film method. The film extruder is almost identical to a filament extruder. In it, the molten polymer is forced through a film die that converts the melt into film, where the thickness of the film can be controlled by adjusting one of the die lips. The takeoff unit is either a chill roll that removes the film uniformly and cools it below T_m or a water bath followed by nip rolls. The cooled film is slit into separate tapes using a slitter bar that contains a large number of special knives separated by spacers. The film tapes are heated and drawn to their final length.

Several methods are used to produce fibrillated film. They are produced in much the same way as slit film, but these techniques take advantage of the tendency of PP to fibrillate. In one method, a profiled tape is extruded and hot-drawn. It is drawn again to achieve a 10:1 ratio, and the film splits into separate filaments. In another method, called roll embossing, the film is hot-drawn, and then embossed using profiled rollers. The profiled film is drawn again, and fibrillation results. In the pin-roller technique, the film is drawn and cut by knives or pins on a rotating cylinder. This method can produce individual fibers or a controlled web network.

PP nonwovens are created by forming a staple fiberweb and then consolidating it into a fabric. The fibers can be entangled by a needling machine, an air jet, or a water jet. Another method uses a single-stage process in which melt-spun fibers are drawn through an air aspirator jet and deposited randomly on a conveyor. The fibers then are bonded by fusion under heat and pressure to give a "spunbonded" nonwoven fabric (see Fig. 12.22). Yet another method, known as melt blowing, can be used in producing a nonwoven web having special characteristics. The melt-blown (MB) fibers are characterized as ultrafine fibers because of their size relative to other fibers. In the process, molten polymer is forced through a melt blowing die and die tip orifice that are

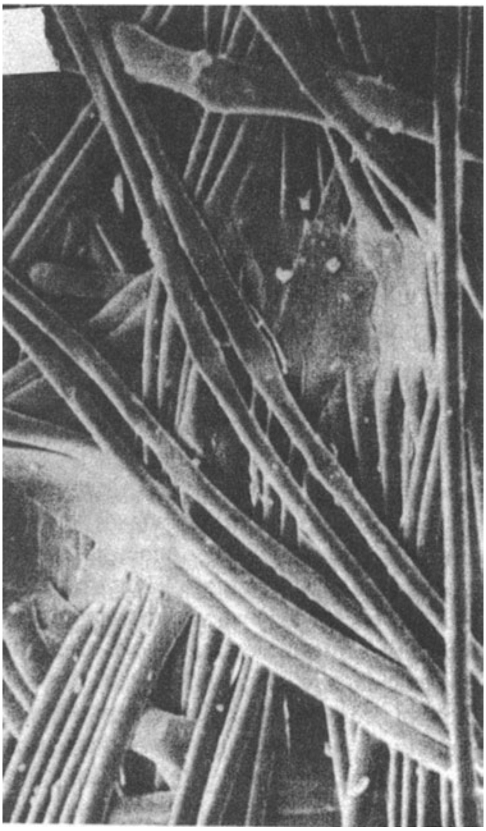


Fig. 12.22. Spunbonded polypropylene showing interfiber bonding, which binds the structure. (*Courtesy E. I. DuPont de Nemours & Co.*)

finer than most orifices used to make manufactured fibers. As the polymer emerges, it is attenuated by a jet of high-velocity hot air. This allows the polymer to stay in a molten state but attenuate until broken. The fibers then come in contact with cool quench air, which causes the former to solidify. The fibers deposit on a collector screen and form a MB web. These webs, composed of very fine size fibers, can be engineered for applications in areas where barrier (such as against bacteria), insulative, and absorptive (such as for oil) characteristics are important.

One of the most recent developments in the use of polyolefin fibers is in composites of spunbond (SB) and melt-blown systems. Some examples of structures being made are SB/MB, known as SM, SB/MB/SB, or SMS, and other combinations of SB and MB. The production and properties of these are particularly enhanced by the use of PP/polyethylene bicomponent fibers in the preparation of the MB layers. Such components are particularly suited for use as light weight coversheets or facings for diapers and sanitary products. The spunbound layers on the top and bottom provide the needed high strength whereas the layers of MB microfibers sandwiched between them provide the greatly enhanced visual uniformity and barrier properties.[19] Figure 12.23 illustrates a low weight (15 g/m^2) SMMS fabric comprised of MB fibers accounting for less than 15 percent of the structure by weight.[20]

The production figures of PP show impressive growth. The volume, which was less than 10 million lb in 1965, reached over 1.5 billion lb in 1990. This included approximately 17 percent filament yarn, 23 percent staple fiber, 18 percent spunbonded fabrics, and 38 percent split film products.

It is recognized that despite its many advantages compared with other synthetic fibers, the use of the fiber is restricted by the fact that most dyestuffs lack affinity for the material. This makes the fiber unsuitable for conventional exhaustion dyeing techniques using disperse or acid dyes. A number of attempts have been made in recent years to improve dyeability of the material.[21] In one of the most recent studies an alloy fiber of polypropylene (PP) and nylon 6 (N6) has been produced by melt spinning. The fiber contained PP grafted with maleic anhydride (MAH) as the third component. The MAH units reacted with the amine end groups of N6 to form block or graft copolymers that acted as a compatibilizer for the blend. Addition of 10% N6 produced a fiber that could be dyed conventionally using disperse dyes.[22]

High Molecular Weight

Polyethylene is probably the material one encounters most abundantly in daily life, such as in the form of grocery bags, shampoo bottles and toys, but now one also finds it as the material in such super high performance products as bullet-proof vests. For such a

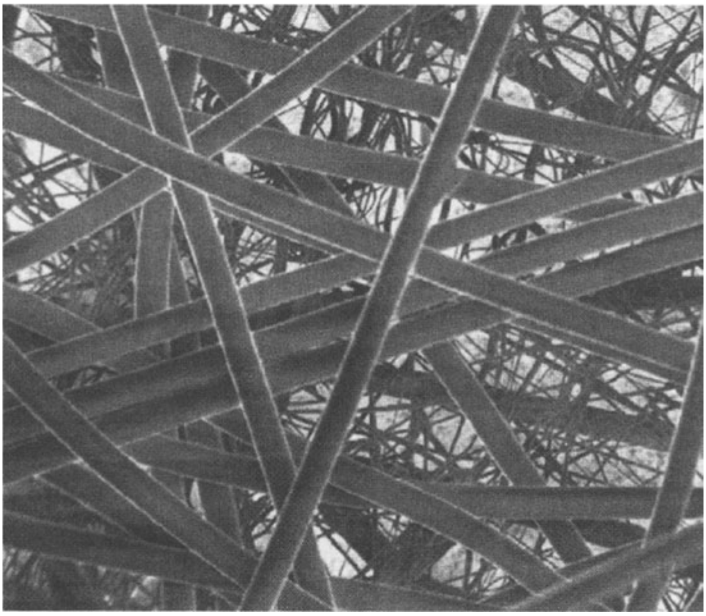
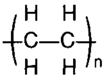


Fig. 12.23. Spunbond/melt-blown composite, SMMS, containing two layers of melt-blown microfibers sandwiched between two layers of spunbonded material and bonded by hot calendaring. (*Source:* Madsen, J. B., *Nonwovens World*, p. 69, 2001, August–September.)

versatile fibrous material, it has the simplest structure of all known polymers:



$$\left(\begin{matrix} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{C} - & \mathrm{C} \\ | & | \\ \mathrm{H} & \mathrm{H} \end{matrix} \right)_n$$

However, during the general addition polymerization process, some of the carbon atoms, instead of having hydrogen attached to them, have segments of polyethylene chains grown on them, leading to a branched or low-density polyethylene (LDPE). If branching is eliminated or greatly minimized, such as found with the use of the Ziegler–Natta polymerization process, utilizing special catalysts, one can get linear chains capable of greater packing. This provides a high-density polyethylene (HDPE) material suitable for fiber use. Molecular weights of the order of one million have been achieved resulting in ultrahigh molecular weight polymer (UHMWPE). Accordingly, a recent addition to the group of high performance fibers is the ultrahigh molecular weight, extended-chain, linear polyethylene. Although fundamental work in the area of developing fully oriented and crystalline structures in polyethylene polymer had been going on since the mid-1960s, it was not until the late 1970s that the possibility of producing such materials on a commercial scale became evident. Presently, three companies worldwide are manufacturing extended-chain polyethylene fibers, which have very high strength and high modulus characteristics.

Routes to High Performance. The achievement of ultimate strength and high modulus in fibers has been a subject of great interest to material scientists and fiber producers. In an attempt to identify the preferred structures for high performance, many theoretical analyses have been conducted to calculate the limiting values. The basis of such calculations is the assumption that in a fiber in which all polymer chains of infinitely long dimensions are extended and oriented parallel to the axis, rupture will occur only when the stress exerted exceeds the intramolecular bond strength. Such calculations show that the limiting values of conventional fibers usually are several times higher than those obtained in actual practice. The reasons for this difference lie in one or more of the following explanations: (1) the molecular weights are not high enough; (2) the chains are not fully extended; (3) the chains are not fully oriented. For a given polymer system and molecular weight, tensile strength and modulus can be enhanced by extending and orienting the chains. Practically, many modern techniques, including zone stretching, multiple-step stretching, and state-of-the-art high-speed extrusion methods, have been adopted to achieve such results.

Still, the results of studies on conventional fibers show that modifications in physical processing alone cannot lead to values that even approach the theoretical maximum within an order of magnitude. Flexible chains, which characterize the bulk of the commercial polymers, tend to conform to a random coil or folded chain structure in an as-spun material, and are very difficult, to reorganize into an extended-chain structure by known methods. Accordingly, in order to achieve ultimate properties, either novel spinning methods are needed, which allow flexible chains to be fully extended, or the chains used must be so configured that they have high intrinsic stiffness and would remain extended in solution or a melt. Both of these goals have been met and are exemplified in the production of (1) high-strength polyethylene fibers, discussed in this section, and (2) aramid fibers, discussed in the next section.

Extended-chain polyethylene fiber became available commercially in 1984 when DSM, a Dutch firm in the Netherlands, introduced Dyneema®, and Mitsui Petrochemicals in Japan announced Tekmilon®. Allied Signal of the United States entered the field in 1985 when it introduced Spectra® fibers. These materials are characterized by very high strength and modulus, which are achieved by the use of ultrahigh molecular weight polyethylene spun by the gel spinning method into fibers having extended-chain structures and near perfect orientation.

Gel Spinning. In general, the purpose for which the gel spinning method is used is to produce an as-spun fiber that contains a loose network of chains with few entanglements, which then can be drawn out to ultrahigh levels to yield a highly oriented structure. The surface-growth method of Pennings,[23] which uses a Couette type apparatus, and the gel spinning method of Smith–Lemstra,[24] which uses a more conventional spinning apparatus, led to the achievement of this goal. In the former method, a polymer solution is stirred between two counterrotating cylinders that provides the elongational flow necessary for initial chain alignment. Essentially the same result is achieved by passing the polymer solution through a constriction prior to spinning in the latter method.

In the surface-growth technique, polymer solution between the inner rotating cylinder and the outer stationary cylinder is maintained within a certain temperature range above the polymer crystallization temperature. A fiber seed is immersed through an opening in the outer cylinder, and its tip is made to attach to the polymer layers absorbed on the inner rotating cylinder. By pulling on the other end of the fiber and winding it onto a bobbin, while at the same time replenishing the solution in the gap between the cylinders, a fiber can be produced continuously. This process results in a fibrous precipitate with a "shish-kebab" morphology (Fig. 12.24). One can conclude, then, that the flow field that is developed extends the chains, which then crystallize in a fibrillar form. Chains that are left unextended, those that are below a certain length for the speed, use the preformed clusters (shishes) as nuclei and crystallize as overgrowths in the form of chain-folded lamellae (kebabs). Fibers formed in this way showed remarkable mechanical properties with modulus in excess of 1200 gram force/denier (102 GPa) and tensile strength in the neighborhood of 30 gram force/denier (2.6 GPa).

Production. Recognition that the shish-kebab fibers produced by the surface-growth procedure result from the deformation of a gel-like entangled network layer at the rotor surface led to the development of gel-spun polyethylene fibers. The fiber is made by the solution spinning method. The polymer is

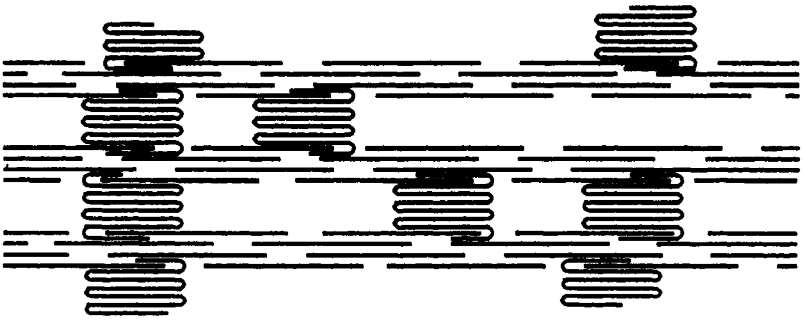


Fig. 12.24. "Shish-kebab" structure showing extended-chain crystals with lamellar overgrowths.

dissolved in a high-temperature solvent, such as decalin, at a low concentration, 10 percent or less, and extruded into cold water. Initially the fiber is formed as a gel that still contains the spinning solvent. It can be oriented by drawing at remarkably high draw ratios of 30 or greater, either before or after solvent removal. A method of spinning polyethylene fiber is described in the patent by Kavesh and Prevorsek.[25] The factors that govern the properties of fibers produced by this method are the polymer molecular weight, the concentration of polymer in the solvent, the type of solvent, the solution temperature, and the stage and the extent of drawing.

The high-performance behavior in these fibers is obtained from their having a very high molecular weight (1–5 million) combined with a very high degree of extended-chain crystal continuity. The fiber can aproach a 100 percent crystalline structure with a theoretical maximum density (~0.97 g/cc). Their use of course, is, limited by the melting point of the polymer, which even in the extended form is only about 150°C. Although higher than that of ordinary polyethylene, it is still much lower (80°C or more) than those of commercial textile and other higher performance industrial fibers. There also has been concern about the creep that occurs in these fibers, although significant improvement has been made in this regard since the introduction of the first fiber. However, these fibers have such a unique combination of strength and lightness that they have proved highly successful in a number of applications, such as sailcloth, body armor, medical implants, fishing net, and sports equipment.

ARAMIDS

Introduction

As pointed out in the preceding section, a second route for developing fibers having properties approaching the ultimate is the use of polymer chains that have high intrinsic stiffness and will remain extended in solution or melt. The development of aramid organic fibers based on aromatic polyamides met these requirements and added another chapter to the history of the development of synthetic fibers. Nomex® aramid, a thermally resistant fiber based on a *meta*-oriented structure, was commercialized by the DuPont company in 1962.

Following the technological breakthroughs which led to the discovery of (1) the liquid crystalline behavior of *para*-oriented aramids[26] and (2) a novel method for spinning anisotropic liquid crystalline polymer solutions,[27] Kevlar® aramid fiber was produced and commercialized by the DuPont company in 1972. Other fibers based on aromatic polyamide compositions, which were produced and commercialized by other companies, were Technora® (Teijin, Japan), Teijinconex® (Teijin, Japan), and Twaron® (Akzo, The Netherlands). Additionally, SVM is a fiber produced in the Former Soviet Union and it was announced in 1990 that a new aramid fiber had been introduced by Hoechst, in Germany.

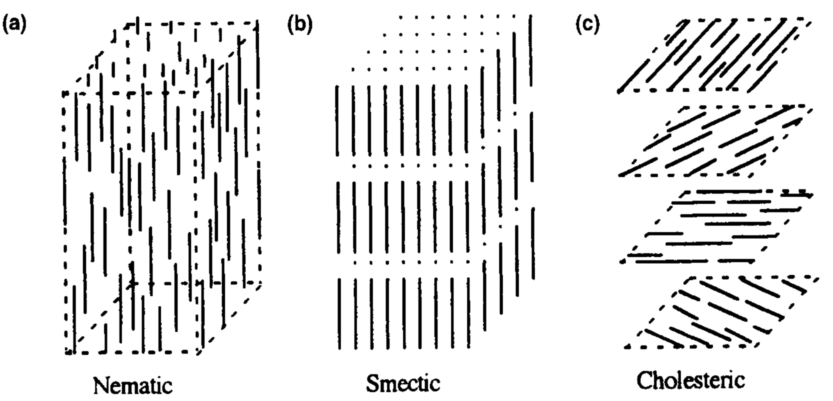


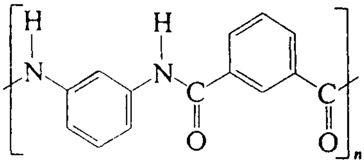
Fig. 12.25. Structure of liquid crystalline polymers showing (a) nematic, (b) smectic, and (c) cholesteric orders.

The rigid rod chains in *para*-aramids tend to form so-called liquid crystals when they are dissolved in polar solvents or heated to certain temperatures. The polymers showing liquid crystalline behavior in melts are called the thermotropic liquid crystalline polymers, and those showing similar properties in solution are called the lyotropic liquid crystalline polymers. These liquid crystals exist in three distinct phases according to their specific structures (Fig. 12.25).

A one-dimensional arrangement of rigid rods is called a nematic structure; a two-dimensional ordered arrangement represents a smectic structure; and the cholesteric structure is formed in terms of rotating oriented sheets so that rigid rods align parallel to each other in every layer, but the directional vectors in each layer are different. The preferential phase considered for fiber spinning is nematic. Nematic solutions or melts are easy to develop into oriented structures through shearing and elongational flow during extrusion because of the rigidity of the polymer chains. Thus high orientation can be obtained in the as-spun fibers without much post-treatment.

Manufacture

In 1973, the Federal Trade Commission recognized aramid as a distinctly different generic material and defined it as "a long-chain synthetic polyamide in which at least 85 percent of the amide linkages are attached directly to two aromatic rings." This distinguishes aramids from nylon, which was redefined as a polyamide with less than 85 percent of the amide linkages attached to two aromatic rings. The first aramid fiber produced in the United States was Nomex®, the reactants being *m*-phenylene diamine and isophthaloyl chloride to give poly(*m*-phenylene-isophthalamide) (MPD-I).



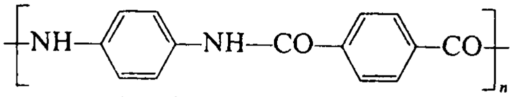
MPD-I

This polymer could not be melted without decomposition, so the preferred fiber formation route was solution spinning. Patent literature suggests that the fiber is spun from a solvent system composed of dimethylformamide and lithium chloride. The final properties are achieved by stretching in steam after washing to remove residual solvent.

The physical and chemical properties of this fiber are not remarkably different from those of other strong polyamides, but it does have excellent heat and flame resistance that makes it particularly suited for use in protective clothing and in specified industrial end uses. Military flight suits, fire-fighter uniforms, and hot gas filtration are a few of its many possible applications.

The other important fiber in this category, which also was first produced commercially in the United States, is Kevlar®, introduced in

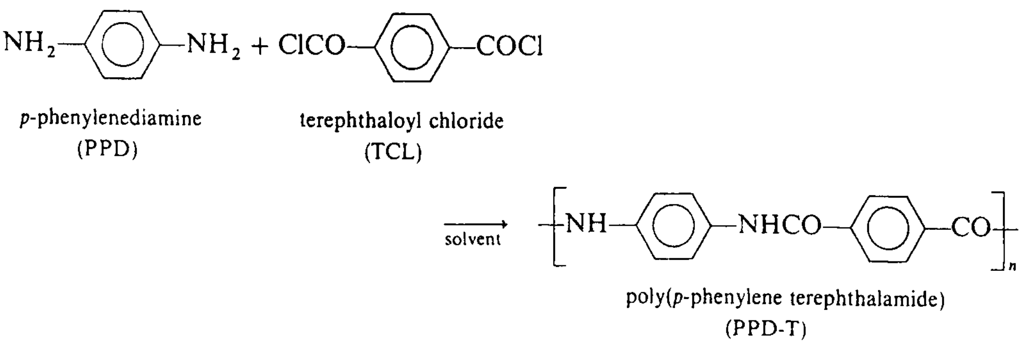
1971 as fiber B and later coded as Kevlar® 29. It was produced from poly(*p*-phenylene terephthalamide).



poly(*p*-phenylene terephthalamide)

Later, a higher modulus version, Kevlar® 49, believed to be made by heat anealing of Kevlar® 29, was introduced.

Poly(*p*-phenylene terephthalamide) PPD-T, also called para-aramid, can be polymerized to a fiber-forming molecular weight by polycondensation of terephthaloyl chloride and 1,4-phenylene diamine.



Poly(1,4-phenylene terephthalamide) (PPD-T) of high molecular weight can be prepared by low-temperature solution polymerization techniques. This polymer is less soluble in amide-type solvents than is poly(*p*-benzamide). The most successful conditions required hexamethylene phosphoramide (HMPA), the original solvent, alone or mixed with N-methyl-2-pyrrolidone (NMP), although other mixtures such as NMP containing $CaCl_2$ also could produce a fiber-forming polymer. During polymerization, the molecular weight increases rapidly within the first few seconds of the reaction. The critical molecular weight or viscosity is exceeded, and the stir opalescence typical of lyotropic solutions is observed. Although gelation of the reaction mixture occurs quickly, polymerization continues, but at a greatly reduced rate. With the choice of a suitable solvent system, gelation can be delayed until the desired higher molecular weight is reached. Large-scale manufacture of a polymer requires continuous polymerization to minimize cost. In the case of PPD-T, special problems that had to be accommodated included the rapid gelation of the reaction solution with increasing molecular weight, the need to control the temperature of a vigorous exothermic reaction, and the handling of solvent HMPA, which is suspected to be a carcinogen.

Although melt-spinning would be preferred from the standpoint of process simplicity and conversion cost, aramids must be spun from solutions, by wet, dry, or dry jet–wet methods because they decompose before or during melting, ruling out melt spinning. Dry-spinning is used to produce Nomex® fiber, where a dope (20%) of the polymer in solvent is converted to yarn. In wet spinning, the polymer dope is extruded into a nonsolvent where the fiber coagulates. The coagulated fiber then is washed and often drawn to develop desired fiber properties. In wet spinning, the spinnerette is in the coagulation bath, hence the dope temperature and the coagulation temperature are the same. In dry jet–wet spinning (Fig. 12.26), as used for Kevlar®, on the other hand, the spinnerette is separated from the coagulation bath, allowing independent control of the dope extrusion and coagulation temperatures. The extrusion jet is placed a small distance above the coagulation bath, and the nascent fibers descend into the liquid, pass under a guide, and proceed in the bath while undergoing stretch; then they are withdrawn from the bath and wound up. A subsequent washing step may be required to

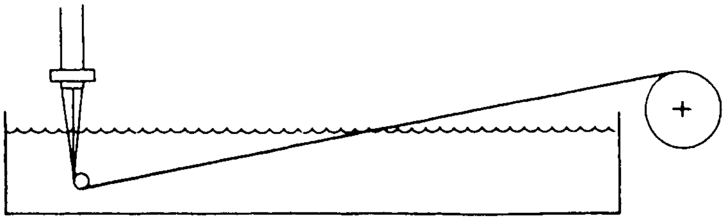


Fig. 12.26. Schematic of dry jet–wet spinning method.

remove residual acid solvent. In systems where the dope must be hot to lower viscosities to extrudable levels, and the bath cold for developing specific structures during coagulation, as is preferred with Kevlar®, dry jet–wet spinning is the option. For production of Kevlar® fibers, a PPD-T/concentrated sulfuric acid solution, containing approximately 20 percent polymer, is extruded at 90°C into a cold water bath (~1°C). Following extrusion, the fiber is washed, dried, and given post-treatment, depending upon the properties desired.

Kevlar® is reported to have about twice the breaking strength (23–27 gram force/denier or 2.9–3.4 GPa) of high-tenacity nylon and polyester, but its most outstanding physical property is its high stiffness (550–1000 gram force/denier or 70–127 GPa), which can range up to an order of magnitude greater than that of standard polyester. This property has led to high-volume usage of the fiber as reinforcement in composite materials such as belts in radial tires and aerospace structures. The world production figure (1999) of this fiber was estimated to be over 60 million lb.

HIGH-TEMPERATURE-RESISTANT FIBERS

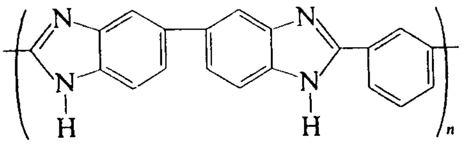
The need for high-temperature-resistance fibers has arisen from demands of a number of industrial applications, as well as applications in aerospace programs. In many of these applications, the usual characteristics of organic-based fibers are desired, but the high temperature resistance of inorganic fibers is required. Thus, the fibers are expected to retain their structural integrity at temperatures of 300°C and above for considerable periods of time, but otherwise their properties should resemble those of the more common manufactured textile fibers. The two leading groups of fibers in this area are the *meta*-aramids and PBI.

Meta-Aramid

The major fibers in this group, based on sales volume, are the products made from poly(*m*-phenylene-isophthalamide), which were introduced by DuPont in 1962 as HT-1 nylon (later known as Nomex®) and by Teijin in 1972 as Conex®. General manufacture of the fiber was described earlier under the heading "Aramids." Other manufacturers now are entering the field with products of similar chemical structure. Although these products are made and spun by different processes, their chemical and physical properties are similar. The fiber is usually utilized in the form of cut staple, which are amenable to conversion on traditional spinning and weaving machinery. Its mechanical properties (tenacity 4–5 gram force/denier, ultimate strain 25–30 percent and initial modulus 90–100 gram force/denier) compare favorably with those of other textile fibers. The main utility of the fiber lies in the resistance it offers to combustion: it has a limiting oxygen index (LOI) of about 0.29, a melting point above decomposition temperature, an ignition point above 600°C and a flash point about 800°C.[28] The LOI gives a relative measure of flame resistance; the higher the number, the lower the flammability. The fiber Kermel® from Rhone Poulenc also is classified as an aramid. It is, chemically, a polyamide-imide fiber and has an LOI of about 0.31. A major application of these fibers is in protective clothing. In order to reduce their cost, they often are blended with other, less expensive, flame-retardant fibers such as those based on cotton, rayon, and wool.

PBI

Poly-2-2′-(*m*-phenylene)-5,5′-bibenzimidazole, commonly called polybenzimidazole (PBI), was developed under the aegis of the U.S. Air Force Materials Laboratory in cooperation with the then-existing Celanese Corporation. The fiber went into commercial production in the United States in 1983. It is a condensation polymer obtained from the reaction of tetra-aminobiphenyl and diphenylisophthalate in a nitrogen atmosphere at temperatures that may reach 400°C in the final stages.[29] The structure of a repeating unit is shown below.



The polymer is dissolved at a high temperature under nitrogen pressure in dimethylacetamide, to which a small amount of lithium chloride may be added to increase the stability of the solution. Then, it is dry-spun in an atmosphere of heated nitrogen (about 200°C), from which the solvent is recovered; next it is stretched slightly in steam and washed. Drawing and relaxing are done in an inert atmosphere, as might be expected, because temperatures up to 250°C or higher are used. The fiber then is given a stabilization treatment in a sequence of steps and made into staple fibers using conventional crimping and cutting techniques. The stabilization treatment involves reaction with sulfuric acid and heating at high temperatures (~475°C) for short periods of time. The process, known as sulfonation, yields a product that has a significantly lower shrinkage than the unstabilized material.

The final yarn is golden yellow, and because this color appears to be an intrinsic property of the polymer, it may have some limitation as far as the civilian market is concerned. This material originally suffered from high shrinkage on exposure to flame; however, further developments including the sulfonation treatment have reduced the shrinkage to only about 5–10 percent at 600°C.[30] The fiber is capable of retaining about one half of its original strength (~3 gram force/denier) upon exposure to air for 18 hr at 350°C or 1 hr at 425°C, it has an LOI of 0.41, which is well above that of the aramids, and it has high resistance to inorganic acids and bases and organic chemicals. Further, with tensile and moisture regain properties comparable to those of many textile fibers, the PBI fiber is well suited for blending with other fibers and conversion into final products using conventional spinning and weaving or non woven equipment. Applications include high-performance protective apparel, flight suits, and aircraft furnishings.

POLYTETRAFLUOROETHYLENE

Historical

Polytetrafluoroethylene (PTFE) was discovered in 1938 when Dr. Roy J. Plunkett and his assistants working on new nontoxic, nonflammable refrigerants at E. I. duPont de Nemours and Co. found that one cylinder, which was supposed to contain tetrafluoroethylene (TFE), ceased to release the gaseous material. Upon opening the cylinder, they discovered that the inside was covered with a white powder. Polymerization of TFE had taken place. The result was PTFE or Teflon®, which is the trade name applied to that polymer by duPont. The company tested the polymer and found that it was virtually inert to all known solvents, acids, and bases, a characteristic that was unique at that time. It also found that this material was resistant to high temperature and had the lowest coefficient of friction of any known solid. The research on PTFE was intensified during World War II because of military demands for improved materials for products such as gaskets, packing, and linings for containers for handling corrosive materials. When the war was over, the release of classified information caused a booming interest in the polymer. Since that time, PTFE has found itself in many different applications.

Manufacture

In one process, the manufacture of the monomer, TFE, involves the following reactions: Hydrogen fluoride is made by reacting calcium fluoride with sulfuric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

Chloroform is reacted with hydrogen fluoride in the presence of antimony trifluoride as the catalyst:

$$CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$$

TFE is obtained by the thermal decomposition of this monochlorodifluoromethane (known as Freon) in a continuous noncatalytic gas-phase reaction, carried out at or below atmospheric pressure at temperatures from 600 to 900°C:

$$2CHClF_2 \rightarrow C_2F_4 + 2HCl$$

Numerous side-products are generated in this process. Many of them are present in trace amounts, but the highly toxic perfluoroisobutylene, $CF_2{=}C(CF_3)_2$, requires special precautions.

TFE also may be manufactured by the reaction of zinc and tetrafluorodichloroethane:

$$ClF_2C\text{–}CF_2Cl + Zn \rightarrow C_2F_4 + ZnCl_2$$

or by the reaction of tetrafluoromethane molecules in an electric arc furnace:

$$2CF_4 \rightarrow C_2F_4 + 2F_2$$

TFE is a colorless, tasteless, odorless, and nontoxic gas. To avoid any undesired reactions during storage, inhibitors must be added. The polymerization is carried out by an addition-type reaction in an aqueous emulsion medium and in the presence of initiators such as benzoyl peroxide, hydrogen peroxide, and persulfates. The monomer is fed into a cooled emulsion medium and then heated to a temperature of 70–80°C, at which the polymerization takes place.

$$CF_2{=}CF_2 \rightarrow (\text{–}CF_2\text{–}CF_2\text{–})$$

The pressure may range from 40 to 100 atmospheres. After removal of the unreacted material, the polymer is washed, pressed, and dried. The degree of polymerization can be quite high, of the order of 50,000. PTFE is manufactured in four different forms: granular, fine powder, aqueous dispersion, and micro powder, and in a variety of grades, each differing in properties. Fillers such as glass fibers, asbestos, graphite, or powdered metals may be added to the granules in order to modify properties.

Fiber Manufacture

Because Teflon® is not soluble, it cannot be wet- or dry-spun, and because it is thermally unstable at its melting point of about 400°C, this combination would seem to pose an impossible problem for the production of fibers. Research into the fundamental characteristics of the polymer, however, revealed that the submicroscopic particles precipitated from the polymerization reaction were about 100 times as long as they were thick.

In one manufacturing process, an aqueous dispersion of PTFE is mixed with a solution of ripened cellulose xanthate, from which a fiber is obtained by a wet-spinning process, after which the cellulose is completely decomposed by heating. The remaining PTFE is sintered into continuous fibers by transporting them over heated metal rolls, followed by stretching to achieve the desired diameters and physical structure. In a process known as “paste extrusion,” the powder is mixed with an organic plasticizer and compressed at 300–500 psi to make a preform or billet. The latter is extruded into filaments which are then dried to evaporate the lubricant. In another process, films are produced that are slit into strips of very small widths, which then are stretched and sintered. In yet another, tapes are extruded, which are converted to fibers by stretching while being twisted to a very small cross-sectional area.

Properties

The unique combination of properties, including chemical resistance, thermal oxidation resistance, high lubricity, electrical and thermal insulation, low flammability and excellent weatherability, are derived primarily from two factors, namely the molecular structure and the molecular weight of PTFE. The structure consists of a core chain of carbon atoms with a fluorine sheath, which essentially completely shields the core. The fluorine atoms are so tightly packed that steric interactions cause a slight rotation of the carbon chain from the normal planar zig-zag to a helical conformation. This dense shield has a low surface energy and a very smooth surface with no side chains or imperfections. As a result, the interchain forces are low and individual molecules are able to slide past each other with relative ease. Compared with other polymers, therefore, creep tends to be high.

The polymer chains pack themselves very closely and regularly to give cylindrical packing which consequently leads to very high crystallinity (~90%). The material has a high melting point which is about 330°C. The smooth surface when combined with low surface energy makes the surface so neutral that it resists sticking to any material. Accordingly, PTFE has the unique property of the lowest coefficient of friction (~0.007), with essentially no stick-slip character. The material has no affinity for water and, therefore, is totally hydrophobic.

The chemical inertness and the thermal stability of this polymer are so great that in spite of its high price ($4–10/lb, depending on the resin type) it is used in chemical operations where drastic conditions exist and no other organic material is suitable. Its low friction allows it to be used as non-stick coating for metals, work surfaces, and cooking utensils. The polymer is regarded as biocompatible and tends to be accepted by the body. This has allowed PTFE to be explored as a material for surgical implants.

Expanded PTFE (ePTFE)

In early 1970s, Dr. Robert W. Gore invented a process by which PTFE could be expanded and gave the trade name of Gore-Tex® to the product obtained. In this process, the specific gravity is reduced by the introduction of micropores but much of the original properties of the polymer are retained. The new material is a hydrophobic but porous membrane of PTFE that is used as a protective layer in a number of applications.

In the process used, in general, a paste is formed of the PTFE polymer and a plasticizer and shaped into an article. It is then expanded by stretching in one or more directions, and while it is held in the stretched form, it is stabilized by heating to high temperature (~327°C) and cooling. The porosity that is produced by the process is retained in the final product.[31] The structure formed by the process consists of "nodes" and "fibrils." The nodes, that vary in size from 5 to 500 μm and are always found perpendicular to the direction of expansion, are interconnected by fibrils. This is seen in Fig. 12.27, which shows a micrograph of Mikrotex®, an ePTFE product.[32] An ePTFE may have as many as a billion or more randomly spaced pores per square centimeter. These pores are unique in size: they are three or more orders of magnitude smaller than the size of a water droplet but two or more orders of magnitude larger than a water vapor molecule. Thus, when used as a rain wear, the product allows the perspiration vapors to escape but blocks out the liquid water from penetrating. The product can likewise serve as a barrier against chemicals and microbes.

GLASS AND CARBON FIBERS

Glass

Among the manufactured inorganic fibers. glass is produced in by far the largest volume. There has been a rapid increase in the use of textile grades of these fibers, and outside the textile field enormous quantities of glass fibers are used in air filters, in thermal insulation (glass wool), and for the reinforcement of plastics.

Glass possesses obvious and well-known characteristics which have largely determined the methods used to form it into large objects. It flows readily when molten and can be

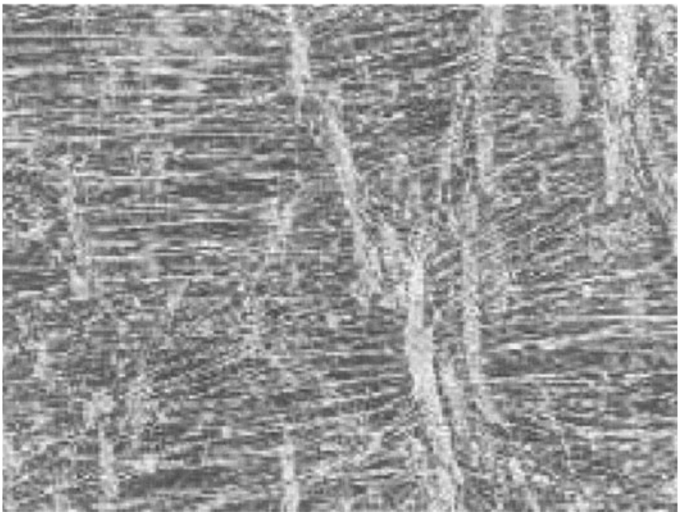


Fig. 12.27. Expanded PTFE micrograph (Microtex® Membrane at 500×) showing a porous structure containing nodes interconnected by fibrils. (*Courtesy Menardi-MikroPul, LLC.*)

drawn into filaments, whose extreme fineness appears to be limited only by the drawing speed. The method used in producing textile-grade glass fibers follows this principle (see Fig. 12.28.)

In the commercial operation, the molten glass, produced either directly from raw materials or by remelting of marbles, is held at a uniform temperature in a vessel, whose bottom carries a bushing containing small uniform holes. The molten glass flows through these holes as tiny streams that are attenuated into filaments at speeds on the order of 3000 m/min; these flaments are coated with a lubricant, gathered into groups to form yarns, and wound up. For a particular glass viscosity,

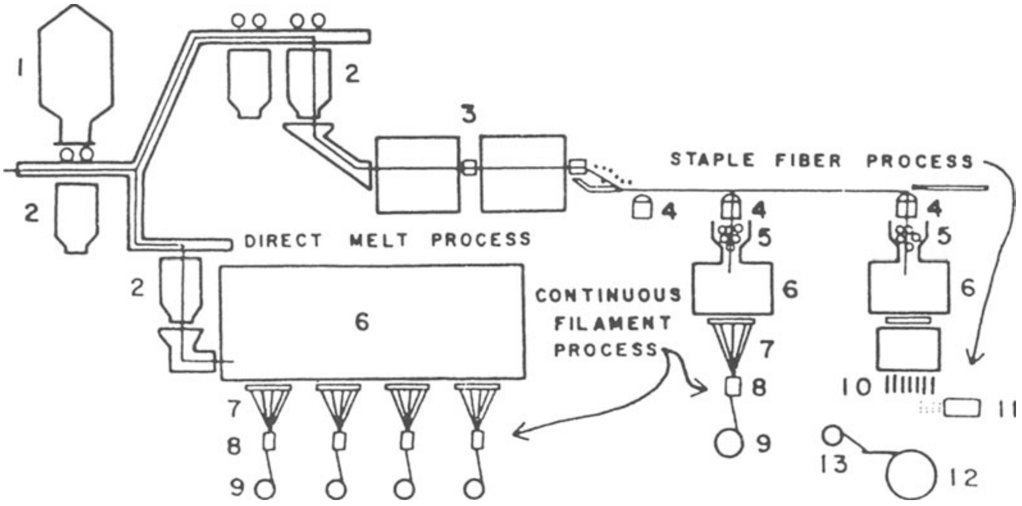


Fig. 12.28. Flow diagram for manufacture of textile glass fiber: (1) glass batch; (2) batch cans; (3) marble forming; (4) cullet cans; (5) marbles; (6) melting furnaces; (7) filament yarn formation; (8) gathering and sizing; (9) yarn packaging; (10) air jets; (11) lubricant spray; (12) collection for staple fibers; (13) staple fiber packaging. (*Courtesy Owens-Corning Fiberglass Corp.*)

the size of the individual filaments is determined by the combination of the hole size and the speed of attenuation.

Because of the inherently high modulus of glass, very fine filaments are required in order to approach the required properties of textile materials. Thus, the diameter of glass filaments falls in the range of 3.8–7.6 μm whereas the average diameter of the finest organic fibers is about twice as great. The fiber and yarn numbering system is based on nomenclature used in the glass industry and differs from the traditional systems accepted in the textile and organic fiber industries.

The method of manufacture of glass staple fibers differs from those used to produce the corresponding organic materials, all of which are based upon cutting the continuous filament product. Air jets, directed in the same line of flow as the emerging streams of glass, attenuate the streams, and break the solid glass into the lengths desired for further processing, which are gathered on an appropriate vacuum drum and delivered as slivers or a matte. To produce fibers that may be coarser and considerably less uniform in length, to be used for the production of filters, paper, or thermal insulation, large streams of molten glass are cross-blown by blasts of hot air, steam, or burning gas.

As might be expected from the nature of glass, the conversion of glass fibers into final products has required the development of new lubricants, finishes, and processing techniques. For example, because glass fabrics cannot be dyed directly or printed with the colors demanded for their acceptance as draperies, the colorant must be applied to a resin coating. But before applying the coating it is necessary to remove the lubricant that was placed on the fibers to permit their conversion into a fabric, which is done by burning. The elevated temperature resulting from this operation also relaxes the internal strains developed in the glass fibers during the steps of the textile operations and sets the yarns in the required geometry. The fabric then is resin-treated, cured, and dyed or printed.

Another inherent property of glass is the tendency of unprotected fiber surfaces to abrade each other to destruction under the action of very little mechanical working. When it was first considered for rubber-reinforcing purposes, its poor adhesion to rubber and the inadequacy of the then-existing bonding agents frustrated attempts by manufacturers to take advantage of the very high tensile strength, completely elastic behavior, high modulus, and lack of moisture sensitivity of glass fibers. However, it has been possible to modify the fiber surfaces so that satisfactory adhesion is achievable, and the impregnant can be applied in such a way that fiber-to-fiber contact is prevented. With the adhesion problems solved, glass in cord form could effectively enter markets in belt-type tire construction and in all kinds of power-transmitting rubber belts. It is estimated that the total glass fiber production in the United States in 2000 was approximately 2.5 billion lb.

Carbon and Graphite Fibers

Following World War II, the development of jet aircraft and rockets created demands for fibers having thermal resistance, strength, and modulus far beyond what could be obtained in existing organic fibers. Much of this need was for reinforcing materials that could be embedded in matrices of one type or another. As a result, techniques have been developed for preparing fibers from a good many metals and refractory inorganic compounds. Although these materials are essential for certain uses, the volume of production still is low, and the prices are correspondigly high (as much as $1000/lb).

Carbon and graphite fibers are made from rayon and acrylic precursors by driving off virtually all of the hydrogen and oxygen contained in them. The principle is essentially the same as that which brought about the formation of coal, or, citing a more recently discovered and dramatic example, the conversion of the original wooden beams of buildings in Herculaneum, buried by a flow of mud from Vesuvius in A.D. 67, to what appears to be charcoal. In the present commercial process, the starting material is selected so as to produce a final product of the desired size and properties. Cotton, bamboo, and other natural fibers were the earliest materials used as precursors. In the

1950s, rayon was used for this purpose, but the first attempts led to fibers with poor strength. Union Carbide, in the mid-1960s, made the first strong carbon fiber from rayon and extended its work to using polyacrylonitrile as the pecursor. The use of mesophase pitch as the starting material began in the 1970s. Carbon fibers may be divided into three types: (1) highly graphitized with a high modulus, (2) heat-treated at a lower temperature to produce fibers with lower modulus but high strength, and (3) randomly oriented crystallites with relatively low modulus, and low strength, but most important, low cost.

The preparation of fibers generally consists of heat-treating the precursor at a low temperature (200–350°C), usually in air, which gives a stable fiber for higher temperature processing. During this step, extensive decomposition occurs, and a percentage of the initial weight is lost, which is related to the cleavage of the C–C and C=O bonds and expulsion of H_2O, CO, and CO_2 (additionally HCN in the case of PAN precursor) as gases. This step is followed by carbonization in an inert atmosphere at 1000–2000°C, which is said to collapse the cyclized structure into a stacked ring carbon fiber structure. Almost all noncarbon elements are evolved as volatiles. This is followed by graphitization, which usually is carried out at temperatures above 2500°C for short periods in argon or nitrogen. The process increases the purity, removes the defects, and further improves the order in the structure. Thus, the difference between the so-called carbon and graphite fibers lies in differences in the ranges of temperatures at which the last step is carried out, the degree of carbon content (97% for carbon and 99.6% for graphite), and the mechanical properties, which are superior in the graphite fibers. In usual discussions, the term "carbon fibers" covers both materials. The majority of carbon fibers produced today are made from a PAN precursor. PAN fibers are fine, and have a higher degree of molecular order and a higher decomposition point than those from rayon. This precursor also leads to a greater carbon yield (45%, as opposed to 24% from rayon), but the fibers are more expensive to produce than those based on rayon. Recent commercial developments have allowed the production of carbon fibers from low-cost petroleum or coal-tar pitch, instead of synthetic fibers. These precursors lead to a higher yield (90%) of carbon, improved lubricity of fiber products, and higher production rates. However, the pitch-based fibers may be more brittle and harder to handle, have a higher specific gravity (2.0, as opposed to 1.8 for those from PAN and 1.66 from rayon) and lower compatibility with some matrix materials.

The fibers have a diversity of applications. One major application is in composites, where they are used for reinforcing resins and metals to provide structural materials with high strength, high modulus, and light weight. The resulting composites are used in the aircraft and aerospace (the largest users), automotive, and sports industries. The fibers also find uses in protective garments, electrical devices, insulation, and filtration. The use of the fibers in the world was about 25 million lb in 2000. The prices dropped significantly during the past decades, but in 2000 the majority remained in the $15–70/lb range. The price of the ultrahigh-modulus carbon fibers, however, can be as high as $1500/lb, or greater.

SULFAR

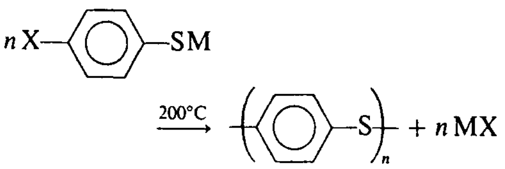
Historical

Sulfar fibers are extruded from poly(phenylene sulfide) or PPS by the melt-spinning process. The first PPS polymer was made in 1897 by the Friedel–Crafts reaction of sulfur and benzene. Researchers at Dow Chemical, in the early 1950s, succeeded in producing high-molecular weight linear PPS by means of the Ullmann condensation of alkali metal salts of *p*-bromothiophenol.

In 1973, Phillips Petroleum Company introduced linear and branched products under the trade name Ryton® by reacting 1,4-dichlorobezene with sodium sulfide in a dipolar aprotic solvent. In 1983, the same company succeeded in stable melt-spinning of PPS. In 1986, the Federal Trade Commission gave the fiber the generic name Sulfar, defined as "a manufactured fiber in which the fiber forming substance is a long chain synthetic polysulfide in which at least 85 percent of the sulfide (–S–) linkages are attached directly to two aromatic rings."

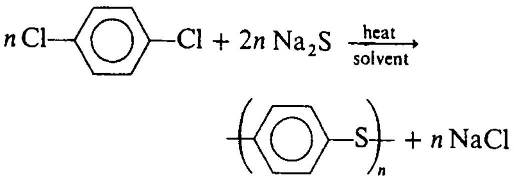
Manufacture

In one process, synthesis was carried out by self-condensation of a metal salt of a *p*-halothiophenol:



where X is a halogen, preferably Br, and M is a metal (Na, Li, K, or Cu, preferably Cu). This reaction was carried out under nitrogen in the solid state or in the presence of materials such as pyridine as reaction media. Considerable difficulty was encountered in removing the by-product, copper bromide, from polymers made by this process. The current commercial synthesis of the polymer is carried out by reaction between *p*-dichlorobenzene and sodium sulfide in a polar solvent.

The process discovered by workers in the laboratories of Phillips Petroleum Co. marked a significant departure from prior processes, and made it possible to prepare a variety of arylene sulfide polymers from the readily available starting materials.[33]



Melt spinning of PPS involves problems such as plugging of the filter and the spinnerette. In order to prevent cross-linking and gel formation during the process of spinning, the company introduced cure retarders comprising Group IIA or Group IIB metal salts of fatty acids, which improved the heat stability of PPS:

$$(\mathrm{CH_3(CH_2)}_n\mathrm{COO})_2M$$

where M is a Group IIA or IIB metal, and n is an integer from 8 to 18. Representative compounds of the type described above include calcium stearate, calcium laurate, calcium caparate, and calcium palmitate. In general, the cure-retardant additives are employed in an amount within the range, of about 0.1–5, preferably about 0.5–2, weight percent based on the weight of the PPS.

Sulfar fibers, sold under the trade name Ryton® in the United States, are characterized by high heat resistance, inherent flame retardancy, excellent chemical resistance, low friction coefficient, good abrasion resistance, and good electrical properties.[34] Physical characteristics include medium tenacity (3.5 gram force/denier or 423 MPa) and elongation (25–40%) and low shrinkage (<5% at 100°C). The fibers find application in a number of industrial products, including filter fabric for coal-fired boiler bag houses, paper maker's felts, materials for electrical insulation, high-performance composites, gaskets, and packings.

Several Japanese and European companies have begun the production of PPS, some with a U.S. partner. The new decade should see the introduction of a number of new fibers and fiber products based on the PPS polymer.

MICRODENIER FIBERS

One of the more important developments in the field of fiber technology in recent years has been the production of fine denier fibers, with worldwide activity in developing new products and outlets for them. Improvements in the quality of polymers, coupled with new technology for extrusion of fibers, have led to the production of fibers with sizes ranging from 1 to 0.1 denier or even lower. Fabrics produced from such fibers have novel and unique properties, and they are finding applications in a wide variety of apparel, and industrial products, including high-fashion fabrics with silk-like texture, synthetic suede, breathable porous but rainproof or bacteria-proof fabrics, wipes for oil and other spills, clean room materials, cloths for cleaning camera, microscope, and spectacle lenses, and for compact discs.

Unfortunately, there is no universally accepted definition for microdenier, and companies have been free to use terms they choose. In general, there seems to be a consensus that the term "fine" may be used for a denier of 1 or less and "micro" for a denier less than 0.5. The production of such fibers is difficult and expensive because the throughput rate must be reduced in order to obtain fine denier filaments, and there is a limit to how fine in denier a regular process could be made to go. Generally, the technology of production of fine and microdenier filaments can be divided into five categories. First, conventional spinning technology can be used, by using fine-size dies and adjusting the throughput rate and quenching and drawing parameters to obtain fine denier polyester filaments. This method has been used by most fiber manufacturers to produce such fibers in limited quantities. In another method, alkali reduction or surface etching is used to dissolve the surface layers, in an effort to reduce the cross-sectional size of filaments in a polyester fabric. A weight loss of as much as 25 percent has been achieved by this process. In the MB process, molten polymer is forced through a melt blowing die and die tip orifices, and the emerging stream is attenuated by a jet of high-velocity hot air until broken. Then the broken fiber is forced into a stream of cold air, where the fiber solidifies. The fiber is collected on a wire screen or apron with other fibers, and a homogeneous MB web is produced. This method is used extensively with PP materials, but other polymers such as nylon, polyester, and polyethylene also have been used. Fibers as fine as 0.5 μm and finer have been produced.

In another approach, filaments containing two polymers that do not adhere to each other are spun and then split. One may, for example, spin a bicomponent fiber of nylon that has several filaments of polyester embedded. After a fabric containing bicomponent filaments has been woven, it is treated to split the components, thus converting the original filament to several smaller filaments. Deniers of the order of 0.1 can be achieved by this ingenious method. In the last method, instead of splitting the two components as in the previous example, one component is dissolved away chemically, leaving bundles of very fine fibers in the fabric.

The majority of the technology for producing fine and microdenier fibers is new and thus expensive; so efforts in the future can be expected to be directed toward optimizing process parameters in existing methods and discovering faster and cheaper methods for manufacturing these esthetically very pleasing and functionally very promising fibers.

NANOFIBERS

An extreme example of the microdenier-size fibers discussed above is the nanofibers that are one or more orders of magnitude smaller in diameter. The fiber with diameter at submicron or nanometer level is spun by a process known as electrospinning, in which the fiber is spun in a field involving high electrostatic forces.[35]

The electrospinning set-up essentially consists of a capillary tube or a needle attached to a syringe filled with a polymer solution or melt, a grounded collector screen, and a high-voltage power supply (Figure 12.29). The collector typically is a metal plate, an aluminum foil or a metal grid. Other forms of the collector, such as a rotating drum, have been used. When the potential (1–30 kV), is applied, the pendant droplet at the end of the needle becomes charged and two opposite forces, namely the surface tension of the droplet itself and the electrostatic force due to applied field, act on it. As the potential is increased, at a certain point, electrostatic force overcomes the surface tension of the droplet and a conelike structure, commonly known as a "Taylor cone," is formed at the tip of the droplet and a jet of polymer solution or melt emanates from it which is accelerated towards the collector.[36] In this process, the polymer jet gets drawn to submicron level while the solvent evaporates or the melt cools down to form the fibers that deposit on the collector and form a nonwoven web.

The electrospun nanofiber webs, with very high surface area to volume ratio and high

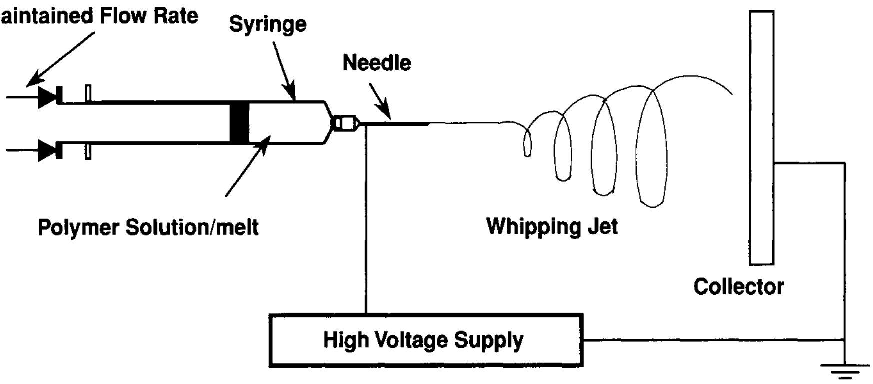


Fig. 12.29. Electrospinning set-up in horizontal configuration.

porosity with interconnected pore networks, have been explored for applications in a number of highly specialized areas such as the scaffolding for tissue engineering, wound dressing, drug delivery, nanosensors, and nanoelectronics. More than 50 different polymers have been electrospun successfully in a solution or melt form that include synthetic nondegradable (polyesters, polyamides, polyurethanes, polycarbonates, etc.), natural (collagen, elastin, chitosan, silk, etc.), and synthetic biodegradable (polyglycolic acid, polycaprolactone, polylactic acid, polylactide-co-glycolide etc.) polymers.[37]

FIBER VARIANTS

Introduction

In a previous section, data and plots were given showing the rapid rise in consumption and production of manufactured fibers at the expense of natural fibers. The principal reason for this has been the wide range of manufactured fiber variants that can be produced from a single fiber-forming polymer. The wide range of polymers available, each with its particular properties, adds yet another dimension. This is not to say that there is only one type of cotton, wool, silk, or asbestos fiber; there are many varieties of natural fibers, but their supply is limited by natural factors such as climate and genetics. The relative availabilities of manufactured fiber types can be altered by controlled chemical-process changes, whereas the amount and the quality of a desired cotton type that can be grown is determined to a great extent by climatic conditions, which humans have not yet learned to control. Another factor that has aided the growth of manufactured fibers is their consistent quality and properties. Again, the grade and the quality of natural fibers are subject to the vagaries of nature.

For the purposes of this discussion, fiber variants will be divided into two types: chemical and physical. Chemical variants will be those involving a small but significant change in composition, whereas physical changes will be those involving a change in either the dimensions of the fiber or its stress/strain or stability features. The definitions of the two variants also could be based on modification of either esthetics or functionality.

Physical Variants

Most manufactured fibers are available as staple, tow, and filament. Natural fibers are available only in the characteristic forms in which they occur, with filament silk and cotton staple as examples. All manufactured fibers are formed initially as filament yarns. The German adjective *endlos* (literally translated "endless") is very descriptive, as filament yarns are continuous strands consisting of one or more members that for most practical purposes are infinite in length. Fine filament yarns (40–100 denier) are used in producing lightweight apparel fabrics, whereas coarse filament yarns (800–1200 denier) are found as reinforcement in tires or conveyor belts. These examples are chosen as extremes to show the range or applicability of manufactured fibers, and represent only a small fraction of the actual range of end uses.

When many filament yarns are collected into a bundle immediately after formation, the resulting structure is called a tow. Tows may range from 10,000 to over a million in total denier. In a next step, the tow may be crimped by the process previously described, which imparts what is usually a sawtooth appearance along the length of all the filaments. For some end uses, the crimped tow itself is provided by the fiber maker, as are, for example, the previously discussed acrylic tows, which are converted to staple as part of the spinning of yarns with a woollike character. Another example is the cellulose acetate tows used to form cigarette filters or the ink reservoirs for marker pens. In the latter case, the compact tow bundle first is treated to separate the individual filaments, giving a voluminous structure, which then is gathered into a continuous rod, wrapped in paper, and cut into appropriate lengths.

In the fiber-making plant, tow may be cut into short lengths of staple, ranging in length from $\frac{1}{16}$ to 6 in., depending upon the end use. For instance, the very short staples are used either in making flocked structures or in the production of papers containing blends of natural cellulose and manufactured fiber. The longest lengths are used in spinning heavy yarns for carpets or cordage. But most staple is $1\frac{1}{2}$–3 in. length and is used to form blends with cotton, rayon, or wool in the yarns employed in standard apparel fabrics. The staple length of the manufactured fiber is chosen to match that of the other blend component; otherwise, uneven yarn of poor quality results.

The size of a manufactured fiber can be altered by changing the size of the hole through which it is extruded and maintaining a constant takeup speed. Commercial fibers range from about 1.25 to 25 denier, corresponding to average diameters of about 5–50 μm. The very large ones would be used to make doll's hair or wigs, but the majority of manufactured fiber staples are made in the 1.5–6.0 denier range, corresponding to cotton blending fiber at the low denier end and coarse wool blending fiber at the high end. Staple and filament yarns used in carpets are in the 12–16 denier range, whereas industrial filament yarns such as tire cord are about 6 denier per filament. The size of a fiber is a determinant of its stiffness, which in turn influences the draping, quality, and the surface feel (often called hand in the textile industry) of a fabric made from it.

Although fibers normally are extruded through circular jet holes, the use of noncircular holes in the jets has led to the availability of a wide variety of cross-sectional shapes. In the case of fibers dry- or wet-spun from solutions, most of the mass exiting from the jet hole is not the polymer. For example, cellulose acetate fiber is made from a 25 percent solution of cellulose acetate in acetone containing a small amount of water. After the fiber leaves the jet face, solvent begins to evaporate, and as a result the area of the fiber cross-section decreases. The final result is a fiber of roughly circular cross-section, but with a serrated edge, and much smaller in area than the parent jet hole. When cellulose acetate is extruded through a triangular jet hole, the end result is a fiber of "Y" cross-section, due to shrinkage from the original triangular shape.

In the melt-spinning process, there is no solvent loss to influence final cross-sectional shape. In the case of a triangular jet hole in melt spinning, the molten fiber leaves the jet face with a triangular cross-section but, being molten, immediately tends to return to a circular cross-section due to surface tension forces. It is necessary, therefore, to quench or cool the fiber as soon as possible in order to maintain the desired cross-sectional definition. Some loss of this definition is unavoidable during the drawing step that normally follows extrusion in a melt-spinning process.

Fibers of noncircular cross-section can modify and change both functional and esthetic properties in textile structures. The triangular cross-section is typical in those respects; its shape leads to a stiffer fiber than circular fiber of the same cross-sectional area, and in a fabric this results in less drapability and a crisper surface feel. Also, the flat surfaces reflect light in a different way than do curved surfaces and can create desirable lustrous effects. These optical effects are subject to many subtle influences having to do with the size of the reflecting surface and the amount of internal reflection that takes place. Triangular or "Y" cross-sectional fibers have greater specific surface areas per unit weight than their circular counterparts, which accounts for their use in aerosol filtration, where surface area is a major factor in efficiency. Yarns made with triangular cross-section fibers are more voluminous than those from round cross-section fibers. Thus when the two types are made into fabrics of equal weight, the variant cross-sectional fabric will transmit less light and be less permeable to air than that made with round cross-section fibers. In the spinning of blended staple yarns, maximum strength is obtained if the blend components have similar load/elongation characteristics. The stiffness of polyester staple fibers can be varied mainly by changing the draw ratio used to orient the fiber after extrusion and thus producing fibers suitable for blending with cotton, rayon, acrylic, or wool fibers, which possess markedly different properties. In many industrial applications, fiber and yarns are used under conditions where they bear a load while hot, as for example in tires and power transmission belts, where it is important that they do not grow or stretch significantly under these conditions. Accordingly, industrial yarns are drawn to a greater extent than other yarns to reduce as much as possible the stretch of the final products. Relatively, these yarns have high strengths, high stiffnesses, and low elongations at rupture.

Although in most instances it is desirable to have fibers that are dimensionally stable, in some structures it is advantageous to use mixtures of fibers that are stable with fibers that do shrink upon exposure to heat or steam. High shrinkage potential usually is built into a fiber by stretching it and not giving it a stabilization treatment. The yarn bulking that occurs with blend yarns of high- and low-shrinkage acrylic staples has already been described, in the section on that fiber. Using the same principle, feltlike structures can be made by heat treatment of nonwoven battings containing low and high-shrink staple.

Chemical Variants

The use of titanium dioxide as an additive in the delustering or dulling of manufactured fibers was discussed in the section on viscose rayon. The addition of pigment particles influences the processing and performance of the fiber, along with changing its appearance. Because of the whiteness of the delustered fiber, it requires more dyestuff to reach a given shade than that needed in the case of a bright fiber. The sliding friction of a delustered fiber is lower because the pigment particles protruding from the fiber surface reduce the contact area between a fiber and the surface it slides against—a guide, for example. By the same token, some pigments can accelerate the wear of contacted surfaces. It has been suggested that the drawing and consequent orientation of delustered fibers proceeds more smoothly because the pigment particles act as nucleation sites where molecular motion is initiated. Unless specially treated, the surface of anatase—one of the crystalline forms of titanium dioxide—can accelerate the ultraviolet light degradation of acetate or nylon fibers. It is postulated that the crystal surface catalyzes the formation of peroxides from the water and oxygen under the influence of ultraviolet light, and that peroxides are the active species in the resulting polymer degradation. For this reason, rutile—the other common crystalline form of titanium dioxide—is used to deluster fibers when improved sunlight resistance is needed.

The degree of polymerization or the molecular weight of the polymers on which manufactured fibers are based can be controlled as part of one of the early steps in the process. The polymer molecular weight chosen for a fiber has a strong influence on process economics, ease of conversion to fiber, and end-use performance. Commercially acceptable fibers are based on the best balance of these factors. However, in fabrics that are open in texture and made from standard polyester staple spun yarns of low twist, a condition known as "pilling" will develop as a result of wearing. The pills are made up of fiber ends that have worked loose from the yarn bundles as a result of surface rubbing and have wrapped around themselves. In the case of fabrics from natural fibers, which are generally less wear-resistant than manufactured fibers, these pills or fiber bundles will be lost by attrition with continuing wear. Because the wear resistance of a manufactured fiber is related to its molecular weight in a general way, the pilling tendency of a polyester staple can be reduced by lowering its degree of polymerization. This compromises the tensile characteristics of the fiber only to a small extent, and all the other desirable properties such as minimum care characteristics are essentially unaffected. When the molecular weight of a polyester or a nylon polymer is increased above the standard, the resultant fibers will have increased tensile properties and fatigue resistance. The filament polyester and the nylon yarns used in end products such as ties and conveyor belts are based on such polymers.

The technology for "dope dyeing" or mass coloration of fiber as part of the fiber manufacturing operation was described in the sections on viscose rayon and cellulose acetate. The use of this technology has decreased, largely because of problems of profitably managing the required inventory of colors in rapidly changing fashion markets, and for this reason it is used extensively only if the fiber cannot be dyed by any other means. PP fiber for use in outdoor carpets is a good example of such a situation. However, if one regards "white" as a color, one finds that a substantial portion of the polyester staple fiber produced for blending with cotton or rayon contains an optical brightener or a fluorescing agent. This is needed to overcome the yellowing tendency of polyester following the absorption of hydrophobic soils. The cotton or rayon fibers in a blend are continually rewhitened by the fluorescing agents added to laundry detergents for that purpose, but these agents are without effect on the polyester blend component. Because the polyester component usually is at least half of the blend, the spun-in optical brightener it contains is vital for the maintenance of overall whiteness.

In the cases of polyester, nylon, and acrylic fibers, their manufacturers have developed fiber variants with a wide range of dyeing behavior, referred to as dye variant fibers. Polyester fibers usually are dyed with what are described as disperse dyes. These dyes are only slightly soluble in boiling water and are used in the form of dispersions. The dye in aqueous solution is assumed to be in monomolecular form, and is absorbed from the dyebath into the polyester fiber by a process often called solid solutioning. As this occurs, more solid dye is dissolved to replenish that entering the fiber. The overall rate of dyeing is a very complex phenomenon but in part is determined by the molecular structure of the fiber through which the dye must diffuse. Generally, the more that the polymer molecules have been organized by drawing and annealing into more geometrically perfect domains or crystallites, the slower is the dyeing rate. The ability of the molecules to be thus organized into compact ordered structures can be reduced by polymerizing a small amount of a foreign dibasic acid or glycol into the polymer. Usually, 5–10 mol. percent is sufficient to prevent this regularity. Adipic acid, isophthalic acid, and polyethylene glycols are used to produce some of the comonomers for fast- or deep-dyeing polyesters. In this way, these fibers are made more economical to dye or print because special dyebath additives, high dyeing temperatures, and high-pressure steam-print fixation usually are not required.

Polyester fibers can be given an additional mechanism for dyeing if an ionic comonomer is added during polymerization. A common additive is an alkali metal salt of dimethyl-5-sulfo-isophthalate, which gives sulfonic (anionic) groups as part of the polymer structure. These groups allow the fiber to absorb basic (cationic) dyes by a specific ionic mechanism. The amount of cationic dye that can be absorbed by the fiber is stoichiometrically related to the number of anionic sites present in the fiber; this is quite distinct from the general solid solutioning that takes place with disperse dyes and polyester. A cationic dyeable polyester is useful for two main reasons in fabric coloration. First, cationic dyes give brighter, clearer shades than disperse dyes, and this can be important for both solid-dyed shades and prints during ever changing fashion cycles. Second, fabrics containing arrangements of unmodified and cationic dyeable polyesters can be dyed in the piece to a variety of color/white combinations by selection of dyestuffs, as day-to-day changes in demand may require. This is more economical than dyeing yarns to different colors, holding them in inventory, and then weaving them into fabrics, if and when they are required.

Nylon 66 can be dyed either with disperse dyes or with acid (anionic) dyes, the former carried out by essentially the same steps as described above for polyester, except that nylon absorbs these dyes much more readily. The ability of nylon to absorb acid (anionic) dyes is the result of a significant number of accessible free amine (cationic) end groups being present in the polymer. The dyeing of nylon with acid dyes is analogous to the dyeing of wool or to the dyeing of modified polyester with basic dyes, except that the polarities of the interacting groups are reversed in the latter case.

For best fastness to light and washing, nylon 66 is dyed with acid dyes, and nylon dye variants thus are based on manipulation of the level of acid dye uptake. By adding a monobasic acid such as acetic acid to the reaction mix near the end of the polymerization process, the amino end groups are converted to amide groups which have no affinity for acid dyes under normal dyeing conditions. This technique creates light acid dyeing or acid reserve dye variants that can have some capacity to absorb basic dyes at the carboxyl end groups. Nylon dye variants with increased acid dye uptake can be made by using a slight excess of diamine in the polymerization. In this way, there are no free carboxylic acid end groups. Nylon dye variants have found the greatest acceptance in floor coverings where attractive patterns can be piece-dyed using controlled dyebath conditions and selected acid dyestuffs.

Acrylic fibers are dyed most frequently with basic dyes. This is made possible by copolymerizing acrylonitrile with an acidic monomer such as styrene-*para*-sulfonic acid. Acrylic fiber suitable for acid dyeing can be made by using a basic comonomer such as a vinyl pyridine or a vinyl pyrrolidone.

Fibers not having inherent flame resistance often can be given this property by incorporation of a suitable additive. This may be done by copolymerization of the additive into the polymer reaction of the additive with the polymer after polymerization, or by applying a polymeric or monomeric noninflammable finish to the surface as a coating. These additives usually contain bromine, nitrogen, or phosphorus, or a combination of these elements. Great care must be taken in choosing the additive and its level of addition in order to prevent loss of other desirable fiber properties and to avoid any harmful effects to processors or ultimate consumers.

A wide variety of special durable surface treatments have been used on manufactured fibers. These include treatments for imparting such characteristics as soil resistance, antistatic behavior, and wearer comfort through moisture wicking and transport. Fiber finishes also have been used successfully in promoting adhesion between two materials, as, for example, between polyester tire cord and rubber, and between glass fiber and polyester resin.

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SUGGESTED READING

The reader is referred to the four encyclopedias listed below for additional information. They contain enormous quantities of information on manufactured fibers as well as comprehensive bibliographies.

Concise Encyclopedia of Polymer Science and Engineering, John Wiley & Sons, New York, 1990.
Encyclopedia of Polymer Science and Engineering, 2nd ed., John Wiley & Sons, New York, 1985. (17 volumes, index volume, and supplement volume.)
Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York. (16 volumes.)
Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Interscience Publishers, New York, (21 volumes and a supplement, 3rd ed.; to date, 16 volumes.)
The following books contain broad discussions of manufactured textile fibers.

Baer, E. and Moet, A. (Eds.), *High Performance Polymers*, Hanser, New York, 1991.
Billmeyer, F. W., *Textbook of Polymer Science*, John Wiley & Sons, New York, 1984.

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