

POLYAMIDES, FIBERS

1. Introduction

Polyamide fibers are spun from linear thermoplastic polymers having recurring amide groups made from diamines and dicarboxylic acids $(\text{CONH}-\text{R}-\text{NHCO}-\text{R}')_n$ or lactams $(\text{RCONH})_n$. Polyamides are generally referred to as nylons when R and R' are essentially aliphatic, alicyclic, and less than 85% of the amide linkages are attached directly to two aromatic rings. When these linkages are equal to or greater than 85% aromatic, the fibers are referred to as aramids. Polyamides from the condensation of diamines and dicarboxylic acids are termed AABB type, and those from lactams, AB type. Aliphatic polyamides are identified by numerals that indicate the number of carbon atoms in the monomer. One number is used for the AB type and two numbers, the first designating the diamine, for the AABB type. For example, the polyamide made from caprolactam (six carbons) is nylon-6 [25038-54-4], and those from hexamethylenediamine and adipic acid, nylon-6,6 [9011-56-6]. Monomers containing ring structures are coded by either a single letter such as T for terephthalic acid (nylon-6,T) or an abbreviated form such as PACM for bis(*p*-aminocyclohexyl)-methane, eg, PACM-12. In designating a random copolyamide, the components are named in order of decreasing percentages, followed by their weight percentages in parentheses. For example, if hexamethylenediamine adipic acid, sebacic acid, and dodecanedioic acid are copolymerized to give 50% nylon-6,6, 40% nylon-6,10, and 10% nylon-6,12, the product can be designated as nylon-6,6/6,10/6,12 (50/40/10). A block copolyamide, which is made by melt-blending two polyamides or a yarn consisting of fibers spun from two different polymer melt streams such as nylon-6,6 and nylon-6,10, can be designated as nylon-6,6/6,10 (50/50).

Wallace H. Carothers and his research team at DuPont discovered nylon-6,6, which is covered in his patents issued in 1937 and 1938. Diamines from C₂ to C₁₈ were synthesized and reacted with aliphatic and aromatic dicarboxylic acids to make polyamides, which were then melt spun and evaluated as fibers. Nylon-6,6 was ultimately selected for scale-up and development because of its favorable melting point ($\sim 260^\circ\text{C}$), best balance of properties, and lower manufacturing cost. DuPont announced nylon-6,6 as the first synthetic fiber on Oct. 27, 1938, completed the pilot plant in Wilmington, Delaware, in July 1938, and introduced nylon to the market as Exton bristles for Dr. West's toothbrushes (1). The first nylon filament plant was built in 1939 at Seaford, Delaware, and nylon stockings went on sale nationally on May 15, 1940.

In 1929, while employed at the Agfa Film Factory near Leipzig, Germany, Paul Schlack discovered caprolactam, the intermediate for nylon-6 (2). He polymerized caprolactam to nylon-6 and was granted a patent in 1941 assigned to I. G. Farbenindustrie (3). Nylon-6 was developed and commercially introduced as Perlon in 1940 (4,5). I. G. Farbenindustrie had evaluated many polyamide constituents without finding an improvement over nylon-6 and nylon-6,6 (6). In Italy, Societa Rhodiaceta started making nylon-6,6 in 1939. In the United Kingdom, ICI and Coutaulds formed British Nylon Spinners in 1940 and started to manufacture nylon-6,6 in 1941. In the United States, Chemstrand started spinning nylon-6,6 in 1952, and by 1955 Allied Chemical, American Enka, and Industriale Rayon started spinning nylon-6 fibers.

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Approximately 4×10^6 t of nylon fiber is produced annually worldwide; nylon-6 and nylon-6,6 account for about 98% of the total production. Nylon fibers are used in the flooring, apparel, industrial and transportation industries. The advantages of nylon fibers over other synthetic fibers are high strength, durability, resilience, ease of dyeability, and low specific gravity.

In 1998, the worldwide nylon fibers market was shared by DuPont with 27%; BASF, 9%; Rhodia, 9%; Solutia, formerly Monsanto fibers, 7%; AlliedSignal, 7%; and the remaining 41% by many smaller manufacturers (7). The downturn in the fiber business, worldwide recession, overcapacity, and competition from polyester fibers in the late 1980s led to acquisitions and merges. Some mills started to melt spin their own fibers, notably nylon-6, during this period (8,9).

2. Properties of Nylon-6 and Nylon-6,6

Both the inherent properties and those that can be engineered into the fiber and ultimately into the fabricated article account for the diverse end uses of nylon. For every end use, the fiber must offer performance and/or a perceived market value, meet mill acceptance standards, and have favorable economics.

The properties of textile fibers can be divided into three categories—geometric, physical, and chemical—which can be measured with available methods (10–12). Perceived values such as tactile aesthetics, style appearance of apparel fabrics, comfort of hosiery, as well as color, luster, and plushness of carpets are difficult to quantify and are not always associated with the properties of the fiber, but rather with the method of fabric construction and finishing.

The most useful synthetic fibers for textile applications are linear, semi-crystalline, oriented polymers, whose properties are defined by molecular structure and molecular organization. The first level of molecular organization is the chemical structure that defines the structure of the repeating unit in the base polymer and the nature of the polymeric link. This relates directly to chemical reactivity, dyeability, moisture absorption, and swelling characteristics, and indirectly to all physical properties. Macromolecular structure, the second level, describes the family of polymer molecules in terms of chain length, chain-length distribution, chain stiffness, molecular size, and molecular shape. The third level, supermolecular organization, describes the arrangement of the polymer chains in three-dimensional space. Levels two and three are directly related to the physical properties of textile fibers and have a significant bearing on some of their chemical characteristics. The chemical and macromolecular structures of polyamide fibers can be determined by chemical and instrumental analysis (13). The supermolecular organization of nylon-6 and nylon-6,6 have been defined in terms of crystallinity, crystalline and amorphous orientation, and chain folds by xrd, fiber density, dsc, and nmr methods (10,14–18).

Molecular chains in a polyamide fiber are held in specific structural configurations by weak van der Waal and strong intermolecular hydrogen-bonding forces between amide groups. An increase in the number of amide bonds raises the melting point in a homologous series, with the AABB type having the higher melting points T_m in the series (Fig. 1). AABB polymers have a more symmetrical

repeating unit than AB. Other things being equal, the more symmetrical the repeating unit, the higher the T_m .

Nylon-6 and nylon-6,6 are isomers that share the same empirical formula, $C_6H_{11}NO$; density, 1.14 gm/cm^3 ; refractive index n_D , 1.530 (unoriented fiber); and many other properties (19). However, they differ in melting point by 40°C because of differences in the alignment of molecular chains and crystallization behavior (18). These parameters are important in fiber formation in melt spinning, but are not as significant as the glass-transition temperature T_g in the downstream processing of the fiber into a specific end-use article (20). The T_g which signifies a transition from a glassy to a rubbery state, plays a role in the drawing, texturing, and dyeing of a fiber. By controlling melt spinning and downstream processing, the fiber properties of both nylon types can be adjusted to accommodate a variety of end-use performance requirements.

2.1. Tensile Properties. Tensile properties of nylon-6 and nylon-6,6 yarns, shown in Table 1, are a function of polymer molecular weight, fiber spinning speed, quenching rate, and draw ratio. The degree of crystallinity and crystal and amorphous orientation obtained by modifying elements of the melt-spinning process have been related to the tenacity of nylon fiber (18).

Tensile properties of synthetic and natural fibers (or yarn) are measured from stress-strain curves as shown in Figure 2. These measurements are not only important in determining the suitability of a nylon fiber for a specific end use, but also in comparing it to other fiber types. Nylon staple generally has higher elongation but similar tenacity to regular nylon filament because of differences in melt-spinning conditions, such as draw ratio and quench rate, and because it is usually a crimped product. Both nylon fiber forms have a lower modulus than polyester, cotton, silk, Nomex and Kevlar; the last two are aramids produced by DuPont. Increasing the tenacity increases the modulus of nylon, but it is still lower than polyester and Kevlar. The toughness of nylon is approximately 20% higher than polyester and much higher than silk, cotton, wool, Nomex and Kevlar.

Definitions of the commonly measured tensile properties are as follows: *Linear density* (tex) is the weight in grams of 1000 m of yarn. *Tenacity* (N/tex) is the tensile stress at break and is expressed in force-per-unit linear density of unstrained specimen. *Knot tenacity* is the tensile stress required to rupture a single strand of yarn with an overhand knot tied in the segment of sample between the testing clamps. It is expressed as force-per-unit linear density and is an approximate measure of the brittleness of the yarn. *Loop tenacity* is the tensile stress required to rupture yarn when one strand of yarn is looped through another and broken. It is expressed as force-per-unit linear density. Loop tenacity is an indication of brittleness, but is not considered as sensitive as the knot test. Reported values are one-half the actual test values.

Breaking strength is the maximum load required to rupture a fiber. It is expressed in grams. *Tensile strength* is the maximum stress or load per unit area in units of Pascal ($1 \text{ MPa} = 145 \text{ psi}$). Tensile strength (MPa) = tenacity (N/tex) \times specific gravity $\times 1005$. *Elongation at break* is the increase in sample length during a tensile test and is expressed as a percentage of original length. *Tensile modulus*, ie, Young's modulus, also called *initial modulus* or *elastic modulus*, is the load required to stretch a specimen of unit cross-sectional area by a

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unit amount. It is expressed as the ratio of the tensile stress divided by the tensile strain in the initial straight-line portion of the stress–strain curve, extrapolated to 100% sample elongation. *Work-to-break* is the actual work required to rupture the material. It is proportional to the total area under the stress–strain curve. *Yield point*, or *elastic limit*, is the point on the stress–strain curve where the load and elongation cease to be directly proportional. It is the point at which the stress–strain curve deviates from the tangent drawn to the initial straight-line portion of the curve, as in tensile modulus determinations.

Creep is the change in shape of a material while subject to a stress; it is time-dependent. *Elasticity*, the ability of a fiber to return to its original dimensions upon release of a deformation stress, is described by the tenacity of the yield point on the stress–strain curve. *Toughness*, the ability of a fiber to absorb work before it ruptures, is evaluated from the area under the total stress–strain curve. The toughness index is defined as one-half the product of the stress and strain at break and is also in units of gram-per-unit linear density. *Creep and recovery* define the plasticity or plastic flow of a fiber in relation to load and time (21). At a critical applied load above the yield point, the fiber extends very rapidly and continues to extend at a much slower rate as time progresses, spanning from a few seconds to over a month. When the load is removed, the reverse process occurs. The fiber recovers part of its extension very rapidly and then begins to contract over a period of time (delayed recovery). The recovery is a relaxational phenomenon where the stress that generated the deformation is dissipated as a function of time, which in effect is complimentary to creep. The quantification of the plastic flow of a fiber resulting from molecular motions induced by the deformation and recovery processes is dependent on load, time, and temperature (22).

Elastic recovery is the ability of a fiber to regain its original form after being stretched at a specified percentage of its length. Shrinkage induced by hot–wet treatment of a fiber is also a form of stress relaxation. Compared to other fibers, nylon fibers have an outstanding degree of elasticity, recovering well from high loads and extension.

2.2. Temperature and Moisture Properties. Thermal treatment and moisture affinity significantly influence the physical properties of nylon fibers and fabrics. The absorption of water causes the fiber to swell, which alters its dimensions and in turn changes the size, shape, stiffness, and permeability of yarns and fabrics. It also alters the frictional and static behavior of yarns in mill processing as well as the performance of fabrics during use. Water, a powerful plasticizer for nylon, preferentially penetrates the amorphous regions, readily hydrogen-bonds to the amide, and increases molecular chain mobility (23–28). As a result, the absorbed water lowers tensile modulus, the work to elongate and work recovery (29–30), and the glass-transition temperature (31). The crystallinity of nylon also increases as it absorbs water (32), which breaks up intermolecular hydrogen bonding and allows the hydrocarbon chain segments to pack better. Water also affects the heat setting properties of nylon yarns and fabrics (33,34). The moisture regain of nylon-6 and nylon-6,6 is shown in Table 1. For comparison, polyester has a moisture regain of approximately 0.4%, acrylic 1.5%, cotton 8%, and wool 16%.

Because of water's plasticizing effect, the water content of nylon fibers and fabrics must be known and controlled when measuring physical properties. Prior to the measurement, samples are conditioned at a specified temperature and relative humidity (rH) for at least 24 h.

Nylon-6 softens at 170°C and melts at 215–220°C. Nylon-6,6 softens at 234°C and melts at 255–260°C. Nylons also have thermal behavior properties between the melting and glass-transition temperatures that are important in fiber melt spinning and drawing and in fiber-to-fabric processing. These behavior properties are the result of relaxational phenomena due to the onset of mobility of the aliphatic chain segments in the amorphous and crystalline regions and occur between 70 and 180°C (28,35). Typical unrestrained nylon-6,6 fibers begin to shrink as the temperature increases from 25 to 70°C with the application of dry heat. At 70°C the fiber undergoes crystallization that tends to reduce chain mobility. From 70 to 115°C the fiber continues to shrink and at 115–125°C loses absorbed and bonded water. The crystal structure also changes from the triclinic to the hexagonal form. At 170–180°C, the hexagonal crystals begin to break up and the polymer chains take on a fluid-like mobility. Because of its higher temperature profile, nylon-6,6 requires higher fiber melt processing, texturing, heat setting (36), and end-use application temperatures (eg, thermal bonding) than nylon-6.

2.3. Electrical Properties. Nylon has low electrical conductivity (high electrical resistivity) and behaves like an insulator. Nylon-6 has a resistivity of $6 \times 10^{14} \Omega\text{-cm}$ when dry and a resistivity of $2 \times 10^8 \Omega\text{-cm}$ when conditioned at 100% (RH) at 20°C (37); nylon-6,6 responds similarly.

Because of its insulating nature, nylon can accumulate positive or negative electrical charges on its surface when rubbed or in contact with other substances, followed by separation. These charges do not dissipate readily and can cause problems in fiber processing and certain end-use applications. Consequently, anti-static agents are added to spin finishes to facilitate fiber processing, conductive fibers are added to carpets to prevent static shock, and antistats are added to the fibers to prevent static cling of women's slips.

The dielectric constant of nylon-6,6 (at 1000 Hz) is 4.0 at 22°C and 18% (rH), and increases to 20.0 when wet (38).

2.4. Optical Properties. When light falls on a nylon fiber, it can be partially transmitted, absorbed, or reflected, depending on the cross-section shape and the nature of any second substance added during polymerization or melt spinning. Additive-free nylon with a standard round cross section has a translucent high sheen luster. The inherent luster of the fiber and the color introduced in dyeing are important optical properties that relate to a fabric's visual quality and its acceptance by the customer. Fibers that need to be opaque or to cover well in certain applications such as apparel are melt spun from polymer containing TiO_2 delusterant.

Optical properties also provide useful structure information about chemically similar fibers. The orientation of the molecular chains of a fiber can be estimated from differences in the refractive indexes measured with the optical microscope, using light polarized in the parallel and perpendicular directions relative to the fiber axis (39,40). The difference of the principal refractive indexes is called the *birefringence*, which is generally used to monitor the orientation of

nylon filament in melt spinning (43). Birefringence can also be used to distinguish nylon from other chemically dissimilar fiber types as illustrated:

| Refractive index | | | Birefringence |
|------------------|-------|-------|-----------------|
| Nylon | 1.578 | 1.522 | 0.056 (Strong) |
| Polyester | 1.706 | 1.546 | 0.160 (Intense) |
| Acrylic | 1.511 | 1.514 | -0.003 (Weak) |

2.5. Chemical Properties. The chemical reactivity of nylon is a function of the amide groups and the amine and carboxyl ends. The aliphatic segment of the chain is relatively stable.

Solvolysis and Reactivity. Generally, nylon is insoluble in organic solvents, but soluble in formic acid, some phenolic solvents, and fluorinated alcohols such as hexafluoro-2-propanol. Nylon is relatively inert to alkalis. Dilute solutions of strong mineral acids, such as sulfuric and hydrochloric, weaken nylon fibers and hydrolyze them at high concentration and elevated temperature. Strong oxidizing agents and mineral acids such as potassium permanganate solution and nitric acid degrade nylon. Nylon, however, can be bleached in most bleaching solutions common to household and commercial mill applications. Nylon can be hydrolyzed by water under pressure at 150°C and above. The amine end group of a nylon fiber can undergo the same reactions as primary amines, such as neutralization, acylation, and dehydrohalogenation of alkylbromides at elevated temperatures (41).

The amine ends also react with atmospheric contaminants, such as SO₂ and oxides of nitrogen and ozone, under ambient storage conditions (42). This phenomenon is referred to as aging and results in reduced acid-dye affinity.

Thermochemical Properties. Thermal oxidation of nylon-6 and nylon-6,6 starts to occur at 120–140°C, ultimately leading to product yellowing and strength loss. Prolonged exposure at 50–60°C above the melting point will cause cross-linking and the formation of gel, and in the case of nylon-6, depolymerization emitting caprolactam. Thermal degradation of polyamides involves complex chemical reaction paths that are a function of the chemical structure, temperature, length of time exposed, and levels of moisture and oxygen.

The preferred and also the most effective thermal stabilizers for nylon subjected to hot-stretching in tire cord manufacturing are salts and organic derivatives of copper (43–47). The copper salt is added before polymerization at concentrations that give 30- to 70-ppm Cu in the spun yarn. Alkali metal iodides or bromides are also added at 0.1–0.3% for synergism and stabilization of the cuprous/cupric moieties during melt processing (48). Organic antioxidants such as hindered phenols alone and in combination with organic phosphites are moderately effective.

Photolytic Properties. The extent of photodegradation of nylon-6 and nylon-6,6 depends on the intensity and spectral distribution of the light source, the length of time exposed, humidity, air quality, and the presence of photosensitizers on and below the fiber surface. Photosensitizers include the degradation

products created during melt spinning and high temperature fiber processing, TiO_2 (the standard fiber delusterant), iron salt contamination, as well as certain dyes and dye bath chemicals. The chemistry of the photodegradation of nylon is as complex as thermal degradation and has also been studied extensively (49,51–53).

Nylon-6 and nylon-6,6 fibers degrade when exposed directly to sunlight outdoors and under glass or to a source of uv radiation in the 300- to 400-nm wavelength range, resulting in the formation of hydroperoxides, chain scission, yellowing, and strength loss (53). In contrast, polyester, if shielded by glass, and acrylic fibers have outstanding resistance to direct sunlight. Polyester is therefore preferred for window curtain fabric and acrylic for outdoor furniture.

The prepolymer copper-based antioxidants described earlier are also effective photostabilizers for nylon and are used in yarns for parachutes. Soluble copper salts (eg, CuSO_4) can also be applied to fibers as part of the finish or to fabrics as post-treatments to protect against uv exposure.

The TiO_2 delusterant is photostabilized by adding manganese salts of pyrophosphorous acids, phosphites, and phosphates (54,56,57) in the prepolymer, or by using TiO_2 coated with a manganese compound (57,58).

2.6. Staple Properties. In contrast to continuous filament, spun nylon staple yarns have a softer, warmer tactile hand and a more natural appearance. Nylon staple is used as the pile material in plush carpets and woven velour automotive upholstery fabrics because of its high strength, abrasion resistance, and ease of recovery from pile crush and distortion. It is also used in blends with natural fibers and regenerated cellulose and acrylics primarily to add strength in yarn spinning of both coarse and fine count yarns and for weaving apparel greige goods.

To accommodate the various uses in 100% form and in blends, the tenacities and elongations of the nylon staple offerings range from 0.3 to 0.6 N/tex (3–7 g/denier) and from 50 to 100% elongation. Most other fiber properties of nylon staple differ little from those of the continuous filament; property characteristics of nylon-6 and nylon-6,6 are similar.

The multiplicity of nylon blends, processing systems, and uses requires a large variety of staple types. Tex per filament may be 0.1–2 (1–20 denier), the cross section may be round or modified, the luster may be bright or dull, crimp may be present or absent, and the fiber may be heat-set or not, depending on its use. The staple length is about 4 cm for cotton system processing, 5–7 cm for the woolen system, 8–10 cm for the worsted system, and about 18–20 cm for carpet staple.

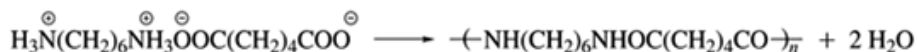
3. Preparation of Nylon-6 and Nylon-6,6 Polymer

Fiber quality polymer requires that ingredients have optimum purity; are protected from exposure to oxygen; the equipment be maintained, cleaned, and purged; and new additives be pretested for melt stability and polymer reactivity.

Hexamethylenediamine [124-09-4] and adipic acid [124-04-9] are used in the commercial production of nylon-6,6, and ϵ -caprolactam [105-60-2] is used for nylon-6.

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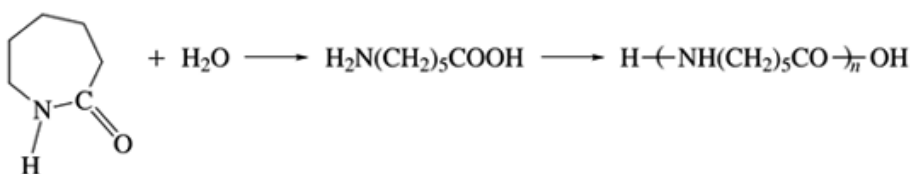
Nylon-6,6 is made by the polycondensation of hexamethylene diamonium adipate salt with removal of water.



The diamine and diacid react in equimolar quantities to form a salt having a pH of 7–7.5 and stored as a 50–60% aqueous solution. Nylon-6,6 can be polymerized in either a batch or continuous process. In the batch process, the salt is transferred to an evaporator where it is heated at 150–160°C and concentrated to 80–85% by the removal of water. Additives such as chain terminators, dye modifiers, and antioxidants are introduced. The mixture is pumped into an autoclave purged with nitrogen and heated under pressure from 210 to 275°C until prepolymer having about 4000 molecular weight is formed. At this point, TiO₂ delusterant can be added. The pressure is gradually released and the temperature is maintained to remove more water in order to increase the degree of polymerization. After the molten polymer has equilibrated to the desired molecular weight, it is extruded under pressure in the form of a ribbon, which is quenched on a water-cooled casting wheel and cut into flakes of a specified size. The flake is dried in a flake conditioner and packaged.

The number-average molecular weight is adjusted in the 12,000–15,000 range for apparel fibers, >20,000 for high strength yarns for tires and industrial end uses.

Nylon-6 is the polyamide formed by the ring-opening polymerization of ε-caprolactam. The polymerization of ε-caprolactam can be initiated by acids, bases, or water. Hydrolytic polymerization initiated by water is often used in industry. The polymerization is carried out commercially in both batch and continuous processes by heating the monomer in the presence of 5–10% water to temperatures of 250–280°C for periods of 12 to more than 24 h. The chemistry of the polymerization is shown by the following reaction sequence.



Depending on the final polymerization conditions, an equilibrium concentration of monomers (ca 8%) and short-chain oligomers (ca 2%) remains (59). Prior to fiber spinning, most of the residual monomer is removed. In the conventional process, the molten polymer is extruded as a strand, solidified, cut into chip, washed with water to remove residual monomer, and dried. In some newer continuous processes, the excess monomer is removed from the molten polymer by vacuum stripping.

The addition of small, but specific, amounts of a monofunctional acid to the polymerization is often used to control molecular weights and catalyze reactions.

The polymerization is controlled to produce a number-average molecular weight of 18,000–30,000, depending on the end use.

Nylon-6 can be easily polymerized at atmospheric pressure. A continuous process was developed in 1940, called the VK process, which in German stands for *vereinfacht kontinuierlich*, or simplified continuous (60). The VK process is widely used in industry in the 1990s, whereas batch processes, being less economical, are gradually phased out of use. Procedures are also available for making gram quantities of nylon-6 and nylon-6,6 in the laboratory (61).

4. Manufacture of Nylon-6 and Nylon-6,6 Fibers and Yarns

All commercial linear polyamides that melt at or below 280°C are melt—rather than solution—spun into fiber because melt spinning is more economical.

Polyamide fibers are manufactured by melt spinning (or extrusion), followed by drawing (or stretching). In spinning, the molten polymer is delivered from an extruder or a metal-grid melter, or directly from continuous polymerization located upstream of the spinning machine. The molten polymer passes through a filter and a spinnerette. The emerging molten filaments are quenched by cross-flow air in a vertical chimney, attenuated partially in the molten state to achieve the desired spun tex and partially in the solid state to develop some degree of orientation. The filaments are converged and a finish preparation is applied to the yarn to provide lubrication and static protection prior to winding on a bobbin. In a two-step process, the spun yarn packages are first lagged in a conditioned area to facilitate drawing and to maintain package integrity. The yarns are then drawn to approximately 130% (draw ratio of 1.3) up to 600% (draw ratio of 6.0) of their original length, resulting in higher tensile strength, lower elongation, and oriented crystallization. The drawing process is controlled and modified to achieve the yarn properties for specific end use. Conventional drawing is used for moderate tenacity apparel straight (flat) yarns and heat is applied, followed by a heat-relaxation step for the high tenacity, low shrinkage tire yarns. For carpets and some apparel applications, flat yarns are textured (crimped) to impart softness and fabric cover (bulk).

Combinations of two or more of the above steps into consecutive processes, such as spin–draw or spin–draw–texture, reduce manufacturing costs. In addition to continuous-filament yarn, nylon is also offered in staple, tow, and flock forms. Staple is made by cutting crimped continuous-filament yarn into 3- to 20-cm lengths. In manufacturing, tow is made by combining many yarn ends, either flat or crimped, to give a total tow size of 6–111 ktex. Flock is made by precision-cutting tow into 0.5- to 3-mm fiber lengths.

5. Spinning Continuous-Filament Yarns

In the first commercial process for melt-spinning nylon, polymer chips were stored under nitrogen pressure in a sealed hopper from which they flowed by gravity to a pancake coil heated by a central Dowtherm system (62). The nitrogen pressure moved the molten polymer to a gear pump that forced the metered poly-

mer stream through a sand-filled filter pack and a spinneret, both maintained at the desired temperature by the single Dowtherm system for the entire machine. The molten filaments were quenched by a cross flow of air at ambient temperature in a chimney with side panels to prevent outside air disturbances. The quenched filaments were converged over a ceramic guide to form the single threadline per spinnerette. Finish was applied by a roll and the threadline wound on friction-driven bobbins at speeds of a few hundred meters per minute. The spun yarn was taken to another machine, the draw twister, where it was drawn, given twist for coherence, and wound on shipping packages containing about 0.5 kg of yarn.

Over the years, fiber producers have improved on the basic design and developed more efficient spinning machines that have lowered manufacturing costs and improved yarn quality. In the early 1950s, the continuous polymerization (CP) process for nylon was combined directly with the spinning machine to eliminate the use of polymer chips. The capacity of a CP direct-spinning machine can be as high as 70,000 t/year and the machine is used in the production of apparel, carpet, industrial yarn, and staple. Extruders are also used to melt polymer chips. They can be horizontal or vertical, vented or unvented, having capacities up to 5000–7000 t/year.

Molten polymer must be delivered to the spinnerette in precisely metered amounts or the filaments will vary in size and give unacceptable products. A metering pump is installed after the extruder to discharge exact volumes of molten polymer per unit time against pressures as high as 70 MPa (10,000 psi) at temperatures in the 300°C range. The molten polymer is also filtered under high shear to remove gel particles and particulate matter that can clog spinnerette holes. A filtration-shear device is attached directly to the distribution plate and spinneret. The typical pack for spinning low tex yarns is a cylindrical cavity about 3.7 cm in diameter and 3.7 cm in height, filled with layers of sand, the finest on the bottom and the coarsest on top. Fine-mesh screens in the bottom and top of the cavity keep the sand in place. Specially designed screens and sintered metal are replacing the sand. Pack designs must avoid stagnant spots where polymer can be trapped and thermally degrade, thus increasing the pressure drop through the pack and shortening its life.

Early spinnerettes were 316-stainless steel disks, ~5 cm in diameter, 0.5 cm in thickness, and with 13 round holes. Over the years, the increased productivity demands have led to as many as 500 holes for larger disk spinnerettes and 4000 holes for rectangular shape spinnerettes.

The molten filaments are extruded through the spinnerette down a vertical chimney where they are air-quenched. The filaments are then converged to form the threadline in the V shape formed by crossed ceramic pins or other similar devices. The threadline passes to the floor below where finish is applied and is wound up on the spin bobbins.

In earlier years, the windup speed was 275–375 m/min with 0.5 kg of yarn per bobbin. In the 1990s, winders are designed for 10- to 25-kg bobbins, two or more bobbins per winder, operating at speeds up to 6000 mpm, and equipped with automatic bobbin changers.

A conventional spinning apparatus is shown in Figure 3 (63). Polymer chips are melted in a larger extruder, which, in turn, feeds a manifold spinning line.

The feed lines are made as short as possible and the polymer is distributed to a series of spin packs and chimneys where the yarn is quenched. The yarn passes to the tube conditioner, over finish rolls and take-up godet rolls, and then to winders. Spare winders switch over rapidly to a new roll during the doffing operation to avoid yarn loss. The yarns then pass on monorail conveyors to the drawing areas. In plant production, multiple yarns are spun simultaneously, each with many filaments. Efforts must be taken from polymer makeup through spinning to control the uniformity of each end of yarn and to minimize defects that can result in breaks and down time. A significant design trend in spinning has been toward modern short and ultrashort compact machines (64,65). The concept is to have one floor spinning where the maximum distance between spin die and winder is 1.3–2 m compared to conventional processes having up to 5 m between spinnerette plate and winder.

5.1. Draw-Twist Process. This is a two-step split process where yarn spun onto bobbins at 300–3000 m/min is lagged and then taken to a draw-twisting operation (Fig. 4a). The degree of drawing or stretching is accomplished by adjusting the speed of the draw rolls, which run faster than the feed rolls. The drawn yarn is then twisted for coherence and wound on a pirn with a standard ring-and-traveler mechanism. Yarns for apparel, hosiery, and industrial end uses have been made by this process.

5.2. Spin-Draw Process. In the early 1960s, a single-step process was commercialized in which the spinning and drawing steps were combined (Figs. 4b and 4c). This required the development of high speed drawing, winding technology, and air jet interlacing to tangle instead of twisting the yarn. For apparel and carpet yarn end uses, the process utilizes the conventional cold draw; for tire and high strength industrial yarn applications, heated-draw assists such as jets, rotating pins, shoes, roll chests, and yarn relaxation steps are added (66). The spin-draw process has also been combined with continuous polymerization. The double-sided unit in Figure 3 is commonly used where the stretch godets and draw assists are installed before the windup (67,68).

In the coupled process (Fig. 4c), the draw ratio, which affects the tenacity and elongation, lowers with increasing spinning speed. As draw ratio is increased, tenacity and initial modulus increase and elongation decreases.

5.3. New Developments in Spinning and Drawing. The continual effort by the fiber producers to increase production, lower manufacturing costs, and improve quality has led to a better understanding of the effects of the spinning and drawing process on physical and molecular structure of fibers (69–77). The polymer factors that affect melt spinning are molecular weight and polydispersity index, which is the ratio of weight-average molecular weight M_w to number-average molecular weight M_n . M_w is determined by solution viscosity and M_n by end-group analysis. In spinning, the tensile stress of the extruded fiber is affected by the polymer melt viscosity, spinning speed, cooling rate, and its degree of structural orientation.

The earlier work cited was in the 100- to 2400-m/min spinning speed range, but the later effort is focused at 4000–6000 m/min (78,79). The effect of spinning speed on residual drawing was classified by the degree of fiber orientation (80). Low orientation yarns (LOY) have a high residual drawing, low crystallinity, and limited storage stability. These yarns are subsequently processed through the

draw-twisting process. Medium oriented yarns (MOY) processed at 1800–2800 m/min are slightly more crystalline, but still have limited storage stability. Partially oriented yarns (POY) processed at 3000–4000 m/min are partially drawn (70–100% elongation) with some residual drawing, but still have low crystallinity. Partially or spin-oriented nylon feed yarns were developed in the early 1970s to meet the needs of increased false-twist texturing speeds (81). In processing, the drawing step is eliminated and the orientation required for draw texturing is controlled in spinning. POY yarns have also been used in the 1990s in the process of draw warping to make flat yarn warps for weaving and knitting (81–84). A process has been defined for making feed yarns that impart excellent uniformity with structure-sensitive large acid dye molecules in dyeing fabrics from warp-drawn yarns (85). Highly oriented yarns (HOY) spun at 4000–6000 m/min are not fully drawn (50–60% elongation). Fully oriented yarns (FOY) with elongations of 20–30% require spinning speeds of well over 6000 m/min.

Molecular weight has a strong effect on the properties of high speed melt-spun nylon. Generally, higher molecular weight leads to higher modulus and filament tenacity and lower elongation to break (86). In spinning POY nylon, the yarn bundle can be transferred directly to winders capable of 4500–6500 m/min, (which is referred to as godetless spinning), or through a set of driven godets (87). Improvements in the processing and properties of nylon-6,6 have been made by modifying quench and windup hardware (64,88), using higher than usual molecular weights (86,89), adding a trifunctional branching agent to increase melt viscosity (90), incorporating minor amounts of hydrogen-bonding agents in high molecular weight polymer (87), and adding pyrogenic silica to the polymer (91). The hydrogen-bonding agents include nylon-6 monomer or 2-methylpentamethylene diamine.

5.4. Texturing Processes. Texturing is the conversion of flat continuous-filament yarns to crimped ones so as to simulate properties inherent in natural and synthetic spun staple yarns, such as thermal insulation, fullness, cover (bulk), softness, and moisture transport. In texturing, the geometry and, to a degree, the surface of the filaments are mechanically deformed by bending, twisting, or compressing to introduce permanent wavy (crimp) loops and coils. Prior to the texturing step, heat is applied in the range of 100–190°C to soften the filaments. After texturing, the yarn is cooled to set the crimp and the mechanical deformation is removed by tensioning the yarn during package windup. Texturing affects the tensile properties, dyeability, and the macromolecular structure of the fibers in a nonuniform way that can cause dye structure and barré problems in dyeing fabrics. Depending on how the filaments have been mechanically deformed and the temperature used, differential stresses and random disoriented molecular chains are set in specific configurations to give one of three classifications of textured yarns: stretch, modified stretch–bulk, or bulk. The textured stretch or bulk is developed when the yarn experiences a stress-relaxing environment under low or no tension, as in steaming hot air, or dyeing. Stretch yarns have high extensibility and good recovery, but only moderate bulk compared to modified stretch and high bulk-textured yarns.

Descriptions of the various texturing processes and latest machine modifications to increase quality, speed, and efficiency have been the subject of numerous reviews (92–96). In air jet or Taslan texturing, the yarn is introduced into a

venturi tube in the air jet where the turbulence from a stream of compressed air cause the filaments to entangle and form surface loops. The product has bulk, but no stretch, and the process can be varied to give a range of bulk and novelty effects (97). In false-twist texturing, a specially made yarn is heated by a radiant or contact heater just below the melting point, twisted as high as 30–40 turns/cm, then untwisted and packaged at windup speeds as high as 1200 m/min. Draw-texturing is a continuous process where partially oriented yarns are drawn and false-twist-textured. A continuous high speed spin–draw–false-twist-texturing process for nylon has also been developed (98). False-twist-textured filaments are coiled, have good bulk, but are regarded primarily as stretch yarns.

In another form, bulked continuous-filament (BCF) yarns are spin-drawn and textured with a fluid jet in a continuous one-step process. After drawing, the yarn is heated over rolls in a hot chest and passed through a hot air or superheated steam jet under controlled conditions. In some designs, texturing is achieved by impinging the yarn onto a baffle plate, a screen, or the walls of a specially shaped chamber (99–102). BCF yarns have bulk with some stretch and each filament has a random, three-dimensional curvilinear crimp form. Edge crimping is accomplished by drawing a heated yarn over a knife edge that compresses (flattens) the edge side and stretches the outside of the filament. The metastable stresses so imposed are relaxed during heating, causing the yarn to crimp and coil to give a stretch yarn (103–105). Gear crimping is adaptable to draw-twisting or spin–draw–texture operation and generally used to texture high tex yarns. Stuffer-box crimping is used for both low and high tex yarns and for crimping tow for staple. Most of the crimped nylon made in the United States is stuffer-boxed, gear, false-twist, and air- or fluid-jet-crimped.

Commercial textured yarns cover a range of yarn sizes and end uses. The 1.7- to 3.3-tex (15- to 30-denier) yarns for hosiery are false-twist-textured, as is the 4.4- to 22.2-tex (40- to 200-denier) yarns for apparel. The 56- to 333-tex (500- to 3000-denier) yarns for carpets, upholstery, and soft-sided luggage are air- and fluid-jet-textured.

Most of the textured apparel and industrial yarns are woven or knitted directly into fabric. The carpet BCF yarns can be tufted directly off package into loop pile or velvet constructions. For the textured saxony constructions, the BCF and the spun staple yarns must be ply-twisted and heat-set. The heat-setting temperature for nylon-6 and nylon-6,6 is 180–220°C in hot–dry atmosphere, and 120–140°C in saturated steam. The yarns are twist-set in pressurized autoclaves or continuously on the Superba and Suessen machines (106). Before setting the twist, the yarn is heated and relaxed for predevelopment of the bulk.

5.5. Staple Fiber. Staple manufacturing consists of spinning, drawing, crimping, cutting, and baling (107). The spun yarn from individual spinnerettes, ranging from several hundred to a few thousand filaments, are piddled into a can, lagged, the ends of which combined into a tow, and drawn. Finish is applied in spinning to help drawing, and is usually applied again after drawing to assist in the crimping and cutting operations. In crimping, multiple tow ends are forced continuously into a constricted stuffer box by preset feed rolls. The box is sealed by an adjustable hinged and weighted gate. The tow ends filling the chamber are

arranged in uniform folds by compression. When the pressure in the stuffer box exceeds the pressure of the hinged gate, the gate rises to permit discharge of the crimped tow, and then falls, thereby repeating the process (108). Prior to cutting, water is applied to the crimped tow to reduce static and maintain wear life of the knives. The compact spinning systems, approximately 6 m high by 6 m wide and developed for nylon, polyester, and polypropylene, can be integrated into accommodating, designed downstream staple process operations (crimping, heat-setting, cutting, baling) to reduce space and cost as well as to expand product flexibility and improve quality (109). This process is a spin-draw type where tow is fed directly to drawing and then through the staple-making operations. The spinning and drawing speeds must be coordinated for proper performance. When utilizing the conventional low speed staple process, the spinning and drawing speeds must be reduced substantially. To compensate for the loss in throughput capacity per position, spinnerets having high number of holes (8000–75,000) are used. In another process where spinning and drawing are maintained close to conventional spinning, the stuffer-box crimper must be designed to process large tow titers, and to prevent the sticking of filaments on the roller and escaping of filaments that break loose from the bundle. Developed by Takehara, Japan, a high speed crimper capable of 6000 m/min avoids the problems encountered with the conventional roller (110). The Takehara Type T-K-K has a large-diameter ring roller that rotates in one direction, and an inner roller that lies on the inner surface of the ring roller and rotates with it in the same direction and with the same speed while holding the tow to be crimped (111).

Staple is used directly in the manufacturing of nonwoven fabrics and spun into yarn through the cotton, worsted, and woolen systems in 100% form or in blends with other synthetic or natural fibers.

5.6. Flock. *Flocking* is the mechanical and/or electrostatic application of finer fiber particles to adhesive-coated fabrics, paper, yarns, plastic, or metal objects (112). Flocking offers a soft, velvety surface for decorative and visual appeal and has a wide variety of functions: sound dampening, thermal insulation, friction reduction of sliding surfaces, increased surface exposure for evaporation and filtering, buffing and polishing, liquid retention or dispersal, cushioning of heavy objects, and even preventing the settling of barnacles on boat hulls (113).

Flock is made by precision-cutting drawn, uncrimped tow using a rotary or guillotine cutter into 0.3- to 6-mm lengths, depending on the denier per filament. The higher the denier per filament, the longer the tolerable length before curvature of the cut fiber becomes a problem in flock preparation. The tow presented to the cutter can be a combination of tow with lower total tow ktex creeled directly out of shipping boxes or a tow that had been scoured, pad-dyed, rinsed, and treated with special finish on a continuous range. The tow size can be from 111 to 3889 ktex (1,000,000–35,000,000 denier) at the cutter.

Whether the process is continuous or batch, the flock must be similarly treated for electrostatic application. The spin finish is removed by scouring and then a finish mixture is applied to impart the following properties to the flock (114): (1) good siftability; (2) low interfiber adhesion needed for proper coverage, (3) good movement and orientation in the electrostatic field needed to get the flock to go straight into the adhesive coating, (4) correct level of conductivity

appropriate to the strength of the field and compatible with an ac- or dc-applied voltage, and (5) good wetting-out properties in the adhesive. Fiber length has a great effect on flock properties; increasing the fiber length decreases the number of fibers sifted, the number of fibers flocked, and the percentage of maximum flock density (115).

Nylon is the preferred fiber for flocking because of its good chemical bonding to a wide range of adhesives, its toughness, and its ease of dyeability and printability. Nevertheless, the tow must be manufactured with the proper ktex, cohesion, and spin finish to be readily converted to flock.

5.7. Finishes. Fiber finishes are designed to provide fiber cohesion, lubricity, and static-free operability at low and high traverse speeds over a variety of metallic and ceramic surfaces encountered in fiber plant and mill operations (116–118). Fiber cohesion is important in that loose or protruding filaments can catch on processing equipment and cause snags and breaks, or become entrapped within a windup package, causing unevenness in texturing, knitting, and weaving. Finishes, consisting primarily of lubricants, emulsifiers, and antistatic agents, are generally applied as aqueous emulsions at concentrations giving a finish-on-yarn level of 0.3–1% after the evaporation of water.

In application, the aqueous-finish emulsion is pumped to a holding or storage tank from which it is circulated through a system that feeds the spinning machine. The finish is applied by passing the yarn either through the circulating finish across a constantly revolving “kiss” roll that is partially immersed in the emulsion, or through a slotted pin or guide in which the emulsion stream is metered through an orifice.

5.8. Modified Cross Sections. Nylon filaments are spun in a variety of cross-section shapes that include the conventional round to irregular solid and hollow shapes (Fig. 5). The cross-section shape is an important variant in designing the functionality and luster of fibers. The round cross section is used for strength in industrial applications and for subdued luster in apparel and upholstery. The multilobal cross sections are used to enhance bulk and for bright luster in both BCF and spun staple yarns for carpets and upholstery. The grooves in the multilobal shapes also enhance moisture transport by wicking water through capillary action. Flat-sided ribbon-like cross sections provide cover in apparel applications.

Bright (no delusterant) round and hollow fiber cross sections have a smooth sheen-like luster, whereas multilobal cross sections vary from bright sheen to bright glitter luster, depending on how they are designed to converge and transmit internally reflected light (119).

In spinning the different fiber cross sections, spinnerette orifice shape and dimensions must be made to exacting tolerances, and changes in polymer melt viscosity, block temperature, and air quenching conditions must be anticipated to assure the desired shape, spinning continuity, and quality yarn. In spinnerette manufacture, the final orifice is produced after counterboring all but the thin sections of the spinnerette blank. Noncircular spinnerette orifice shapes are made by electron-beam milling and electrodischarge machining. For the solid, nonround shapes, a single orifice design is used. Various specific orifice shapes have been developed and fiber cross sections have been defined using mathematical relationships (120,121).

In making hollow fibers, both pre- and post-coalescent spinnerettes and spinning techniques can be used. The former requires injection of a gas through the capillary to create the void (122,123), whereas the latter involves entrapment of gas (air, nitrogen) by coalescence of the molten polymer spun exiting from a segmented orifice designed to give the desired number of cross-section holes, shape, and percent void (124,125).

The open hollow-fiber shape shown in Figure 5 is made by a unique process requiring bicomponent yarn technology (169). A yarn is spun with a water-soluble copolyester core and nylon sheath where the core is dissolved out with an alkali treatment in fabric dyeing.

5.9. Additives. Additives can be introduced in salt preparation, polymerization, or the molten polymer stream prior to extrusion of the filaments. Additives are used to alter the basic characteristics and performance of the fiber and can be classified by function.

Delusterants reduce the transparency, increase the whiteness, and alter the fiber's reflectance of light. TiO_2 is the delusterant of choice for all melt-spun fiber types because of its high cover, whiteness, and chemical and thermal stability. The anatase, not the rutile form of TiO_2 , is preferred because it is softer and contributes less to abrasion wear of machine guides and rolls. Nylon is translucent and requires TiO_2 in most textile and home furnishing applications for the cover and to reduce objectionable sheen and gloss in fabrics. Semidull nylon yarns contain ca TiO_2 , 0.3%; middull, ca 1.0%; and fulldull, ca 1.5–2.0%.

TiO_2 requires careful slurry preparation and introduction to the nylon to minimize the formation of agglomerates and to maintain an average particle size of 0.1–0.5 μm in fiber. Otherwise, filter packs will clog and require frequent replacement. TiO_2 is added as an aqueous dispersion to the prepolymer in the manufacturing of nylon-6,6, and to the caprolactam in the manufacturing of nylon-6, frequently as a master batch containing up to 30% TiO_2 in low molecular weight polymer (127). Nonmelt-compatible polymeric materials such as poly(ox-ethylenes), polystyrene (128), and poly(methyl pentene) (129) have also been used as delusterants.

Colorants can be introduced into the fiber by adding dyes and pigments in salt preparation, during polymerization, or into the molten polymer just before spinning (130). Pigmented fibers are referred to as mass-dyed, dope-dyed, solution-dyed, or producer-colored. Inorganic pigments are used more than the organics, especially where high color, light, and crock fastness are required, such as in upholstery and carpet for automotive interiors. The organic pigments have higher chroma, but are not as colorfast to heat and light. Nylon-6 can accommodate more pigments than nylon-6,6 because of its lower melt-processing temperatures. Like TiO_2 , the pigments must be dispersible and heat stable in polymer and fiber manufacturing. A common and efficient approach to adding pigment to the base polymer in spinning is first to disperse the pigment as a concentrate in a carrier polymer, usually a lower melting copolymer. The concentrates range from 25 to 50% pigment content and are offered as a single color or a compounded color blend in pellet or flake form. The flake can be blended with the base polymer flake at a specified loading and charged to the feed hopper of the spinning process or remelted in a vessel that allows it to be metered directly into the molten polymer prior to spinning. Quality pigmented fibers

are spun with processes equipped with mixing screws and volumetric or gravimetric automatic feeders. Typical pigments for nylon are carbon black, red iron oxide, aluminum cobalt blue, and phthalocyanine blue and green. Carbon black enhances nylon's resistance to photodegradation. A number of light-stable pigments that are also environmentally friendly are available (131).

Antioxidants are used to prevent thermal and oxidative degradation of nylon in manufacturing, post-fiber and fabric processing, and final use.

Antistats such as polyoxyethylenes (132,133) and *N*-alkyl polycarbonamide (134) are added to nylon to reduce static charge and improve moisture transport and soil release in fabrics. These additives also alter the luster of fiber spun from bright polymer. Static reduction in carpets is achieved primarily by the use of fibers modified with conductive carbon black.

Antimicrobial agents are used where there is a need to inhibit bacterial and fungal growth. The additives can consist of copper, germanium, zinc and zinc compounds, metal oxides or sulfides, metal zeolites, as well as silver and copper oxide coated inorganic core particles (135–140).

Flame retardants designated for nylon plastics, such as halogenated organic and phosphorous derivatives, are difficult to spin into fiber because of the high loading required for effectiveness and their adverse effects on melt viscosity and fiber physical properties.

Both fiber producers and fabric mills have realized that many of the performance variants that are difficult to incorporate into fiber melt spinning can be accomplished by post-treating yarns or fabrics. Mills can apply flame retardants, softeners, dye-fade inhibitors, and stain- and soil-resisting agents as part of the finishing of a fabric.

6. Dyeability

Nylon is atmospherically dyed using established trade procedures for staple (stock dyed), yarn (yarn dyed), fabric (piece dyed) for batch dyeing systems (becks, jets, kettles), for continuous dyeing systems [pad – dye, steam (fixation), rinse], and for printing systems (flatbed, rotary screen, roller and transfer) (141–143). Because of their physical and chemical structure, nylon-6 and nylon-6,6, unlike the principal synthetic and natural fibers, have an affinity for every dye class as summarized in Table 2 (144).

Commonly used dyes are the disperse, acid, and premetallized. Disperse dyes are easy to apply, but have marginal wash and lightfastness on nylon. Acid dyes, unlike the disperse dyes, are water soluble, interact with the amine ends, and, as expected, have better wash and lightfastness than the disperse dyes. There are two categories of acid dyes. Those containing one sulfonate group on the dye molecule are referred to as leveling acid dyes and those containing two or more sulfonates, nonleveling or critical acid dyes. Premetallized dyes are large metal complex molecules that respond like critical acid dyes. They have the best wash and lightfastness and are used for high uv-exposure end uses such as automotive upholstery. Leveling acid dyes are used in piece dyeing and wet roller and screen printing of carpets, upholstery, and apparel. Disperse dyes are used to dye carpets and for transfer printing primarily of flocked upholstery

and carpets. In transfer printing, dyes printed on special papers are transferred to the fabric under heat and pressure.

6.1. Effect of Fiber Properties. Acid dyes are attracted to the accessible amine ends of the nylon chains located in the amorphous regions of the fiber. Acid dye affinity of nylon can be adjusted by adding excess diamine or diacid to the polymer salt or by changing the molecular weight in polymerization. A light acid-dyeable nylon-6,6 is spun with 15–20 amine ends, expressed in terms of gram equivalents per 10^6 grams of polymer. A medium or regular acid-dyeable nylon has 35–45 and a deep acid-dyeable nylon has 60–70 amine ends. Ultra-deep acid-dyeable nylons have 80 amine ends or more and are made by adding basic compounds such as *N*-(2-aminoethyl)piperazine in polymerization to enhance the total available dye sites (145). Nylon-6,6 can also be made base-dyeable by increasing the level of carboxyl ends (146) or by introducing sulfonic acid groups through the addition of a copolymerizable dicarboxylic acid derivative to a polymer salt, such as the sodium salt of 3,5-dicarboxybenzene sulfonate (147). By using the proper dyes, dye-bath auxiliaries, and pH control, light, medium, and deep acid- and base-dyeable yarns can be dyed in combination in a single bath to give multitonal and two-color styling effects. This concept of differential-dyeing yarns is unique to nylon and is used extensively in the piece dyeing of carpet, apparel, and upholstery fabrics.

Macromolecular structure and supermolecular organization also affect dye affinity. Drawn (oriented) nylon-6 has more of a random open structure than nylon-6,6 (148). Nylon-6, therefore, dyes more rapidly than nylon-6,6, but is also more susceptible to color crocking, especially with disperse dyes. High dye rates can be achieved with nylon-6,6 by adding a minor random copolyamide component in polymerization. Also, any melt-spinning process adjustment or post-fiber and fabric treatment that decreases orientation in the amorphous domain increases dyeability. Examples are lowering the draw ratio, applying steam or swelling chemicals (eg, phenol), and texturing particularly with pre- or post-heat relaxation (149,150). Nonuniform drawing or heat application can cause streaks with structure-sensitive nonleveling and premetallized dyes. Variations in fiber geometry and cross-section shape and yarn crimp level in texturing cause optically related color streaks. The streaks are caused by a single yarn or groups of yarns that appear to take up dye differently from neighboring groups of yarns. The yarns differing in heat history, amine-end sites, and/or processing tensions will cause streaks.

The appearance of streaks with leveling or nonleveling acid and premetallized dye can be subdued by increasing the dye-bath pH, at a sacrifice in dye exhaust, by adding chemical agents that retard the dye strike or, more effectively, by metering all or a portion of the dye in a concentrated solution at or near the dyeing temperature of the fiber (87.8–104.4°C) instead of at the usual 26.7–48.9°C practiced by the trade (151).

For end uses demanding high dye lightfastness such as automotive interior fabrics, select premetallized dyes and uv inhibitors are applied through the dye bath (152,153). Nylon can also be co-dyed with polyurethane elastomeric fibers, wool, acrylics, polyesters, and cellulotics (154).

7. Modified Nylon-6 and Nylon-6,6 Fibers

7.1. Bicomponent and Biconstituent Fibers. Bicomponent fibers consist of two polymers of the same generic class, eg, nylon-6 and nylon-6,10; biconstituent fibers consist of two dissimilar generic polymers, eg, nylon-6,6 and polyester. Both fiber types are made separately by melt-spinning the two different polymers through a common, specially designed spinneret such as the one in Figure 6 (155). The spinneret hole and block channels can be designed so that the two polymers emerge side by side, as sheath–core or conjugate fibers. The fibers are processed through conventional drawing or spin–draw operations. The original intent of the side-by-side bicomponent yarn was to impart stretch in tricot knit and hosiery applications. Nylon-6 and nylon-6,6 homopolymers were paired to a copolyamide on the basis of shrinkage difference as measured on the individually spun polymers. Depending on the differential shrinkage, the bicomponent yarn would assume a level of helical crimp in dyeing or steaming.

Examples of earlier bicomponent stretch yarns were spun with a nylon-6,6 sheath and core compositions of nylon-6,6/6,10 (50/50) and nylon-6,6/6 (80/20). Stretch was also achieved by spinning side-by-side two nylon-6,6 polymers having a relative viscosity difference of at least 15 units (156), and by spinning nylon-6 with a melt-spinnable polyurethane (157).

Most of the stretch hosiery today are made from textured POY and with elastomeric spandex fibers.

Bicomponent technology has been used to introduce functional and novelty effects other than stretch to nylon fibers. For instance, antistatic yarns are made by spinning a conductive carbon-black polymer dispersion as a core with a sheath of nylon (158) and as a side-by-side configuration (159). At 0.1–1.0% implants, these conductive filaments give durable static resistance to nylon carpets without interfering with dye coloration.

Dye selectivity can be altered by spinning a high amine-end nylon core with a sulfonate-containing nylon sheath (160). In standard dyeing conditions, the core accepts leveling acid dyes, but not critical or basic dyes; the sheath accepts basic dyes. The effect creates a third color when dyed in combination with acid- and base-dyeable yarns.

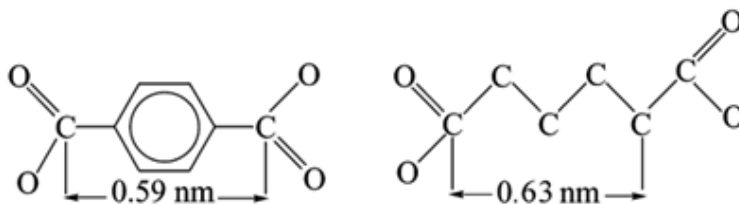
Microdenier fibers, ie, very fine fibers, can be made by spinning biconstituent conjugate fibers such as those illustrated in Figure 7. The technology was developed by Kanebo and marketed under the fabric names Belseta and Glacem. The concept, referred to as alkalization, is to spin a readily alkali-soluble copolyester with nylon and then to dissolve away the polyester in the fabric stage. For example, the wedge-like nylon portion of the round 1.7-decitetex (1.5 denier) filament in Figure 7 can split into eight components, each 0.20 decitetex (0.18 denier) (161). The hexagonal cross-section fiber is of the “islands-in-the-sea” type where the orange wedge-shaped nylon “islands” in the copolyester “sea” connect slightly at the matrix center (162).

Microdenier nylon and polyester were a significant spinning breakthrough when demonstrated in 1985. The finer-than-silk fibers added a new dimension to fabric aesthetics, comfort, and performance. Microdenier nylons are used in

weaving, warp knits, and weft knits for sports-, leisure-, and fashion-wear. Polyester can be melt spun at 0.55 decitex/filament, but the finest nylon is spun at 1.1 decitex/filament. The ultramicro staple nylons made by the polyester alkalization procedure are used to manufacture suede and water-resistant fabrics.

7.2. Copolymers. There are two forms of copolymers: block and random. A nylon block copolymer can be made by combining two or more homopolymers in the melt. The composition of the melt is a function of temperature and more so of time. Two homopolyamides in a moisture-equilibrated molten state undergo amide interchange where amine ends react with the amide groups. As time progresses, the two homopolyamides in the melt form a block and eventually a random copolymer as a result of amide interchange. Block copolymerization is a way of introducing a new variant into a base polymer without grossly affecting the spinning performance and physical properties of the yarn. The process requires careful control, however, to maintain the desired composition in order to ensure uniform product and spinning continuity. Examples of this technology are the block copolymers of poly(4,7-dioxadecamethyleneadipamide) and poly(dioxaarylamide) with nylon-6 (163–164) for hydrophilic nylons.

Random copolymers are made by combining two or more monomers in the polymerization process. The melting temperature of random copolymers are lowered as the regularity with which the monomer groups are spaced along the backbone is reduced. Hydrogen bonding between the amides is also reduced. This is illustrated in the melting point–composition relationship for nylon-6,6/6 and nylon-6,6/6,10 in Figure 8. Crystallinity and orientation are also reduced with increasing randomization. However, in the case of nylon-6,6/6,T, the crystallinity is not reduced because the copolyamide segment is similar in size to that which is replaced. Such monomers which can be exchanged or replace each other in the crystal lattice are often termed *isomorphic monomers*.



Random copolyamides that melt below 200°C are difficult to process through melt spinning because they are difficult to crystallize and consequently remain tacky through the windup. Copolyamides that melt above 300–310°C are also difficult to process because of their higher melt viscosities and greater susceptibility to thermal oxidation.

The general properties of random copolyamides are high dyeability (especially with nonleveling large dye molecules), lower melting and softening points, reduced dry and wet strength properties, high creep failure, and high shrinkage. The last property led to the use of the copolyamides in bicomponent self-crimping yarns. Copolyamides are also suitable for thermal bonding of fiber and fabrics because of their low softening temperature. Random copolyamides are also

used to modify the dyeability of nylon-6,6. The addition of 0.5–2% comonomer increases the dyeing rate to almost that of nylon-6. Comonomers are also used as assists in the high speed godetless spinning of draw-texturing feed yarns. Nylon-6,6 copolyamides with ethyltetramethyleneadipamide, pentamethyleneadipamide, or 2-methylpentamethyleneadipamide units lower the gelation rate of nylon-6,6 at the spinning temperature of nylon-6,6 (165–167).

7.3. Graft Polymers. The grafting of polymers on nylon fiber surfaces as a means of altering chemical or physical properties has been explored and demonstrated over the years. However, a process has not yet been found that is safe, economical, and efficient for grafting yarns at conventional spinning speeds. Nevertheless, efforts continue because the property changes are dramatic and permanent, and because the process is more conducive to slower speed fabric-finishing processes. Vinyl monomers can be grafted to almost any nylon by ionizing radiation usually from a Co-60 source, high energy uv radiation, or chemical means. Radiation grafting of acrylonitrile on nylon-6 gives basic dyeability, and that of styrene, hydrophobicity (168). Nylon-6,6 can also be made basic-dyeable by chemically grafting acrylic or methacrylic acid with a water-soluble formaldehyde sulfoxylate salt (169). The friction of nylon fibers can be changed by grafting poly(dimethylsiloxane) macromolecules to the surface (170).

Nylon carpet fibers can be made to resist stain from certain acidic artificial and natural colorants found in soft drinks, juices, coffee, and red wines, by grafting a phenyl–vinyl and ether–maleic anhydride copolymer to the fiber surface using uv light and a photoactivator in the solution (171). However, there are other techniques for blocking the stain-sensitive amine ends that are more commercially applicable and efficient. They include (1) the post-treatment of nylon carpets with an alkali metal silicate in a phenol–formaldehyde product (172) or with a sulfonated naphthol or sulfonated phenol–formaldehyde product at a specific pH (173), (2) manufacturing of carpets with only cation-dyeable nylon yarn and dyeing or printing them to shade and acceptable lightfastness with pre-metallized or acid dyes (177), and (3) melt-spinning of fibers–pigmented or producer-colored fibers—from nylon polymer containing a high level of a sulfonated derivative (174,175).

8. Other Nylons

Poly(tetramethylenediamine-*co*-adipic acid), nylon-4,6 [24936-71-8], polymer introduced as Stanyl by Dutch State Mines is spun into a high-temperature-resistant, high-tenacity filament yarn, Stanylenka 460 HRST, by Akzo Nobel Faser AG in Wuppertal, Germany. Stanylenka is intended for industrial applications including tire cord and automotive airbags because of its enhanced heat capacity, improved chemical resistance, better dimensional stability, and higher modulus than nylon-6,6 (176). The fiber melts at 285°C and has a density of 1.18 g/cm³.

Poly(bis-*[p*-aminocyclohexyl]methane-*co*-dodecanedioic acid), PACM-12 [24936-74-1], introduced by DuPont as Qiana in 1968 was later withdrawn from the market. This diamine exists in several *cis*–*trans* and *trans*–*trans* iso-

meric forms that influence fiber properties, such as shrinkage and tenacity. The product offered silk-like hand and luster, dimensional stability, and wrinkle resistance similar to polyester. The yarn melted at 280°C, had a high wet glass-transition temperature of ~85°C, and a density of 1.03 g/cm³; the last was lower than that of nylon-6 and nylon-6,6. Qiana required a carrier for effective dyeing.

Poly(hexamethylenediamine-co-dodecanedioic acid), nylon-6,12 [24936-74-1], melts at 212°C, has a density of 1.06 g/cm³, and has a lower moisture regain than that of nylon-6,6. Nylon-6,12 is used primarily for fishing lines and tooth-brush bristles. It has a good apparel fiber properties, but is not as readily dyeable as nylon-6,6.

Poly(butyrolactam), nylon-4 [24938-566-27], melts at 268°C, has a density of 1.25 g/cm³, and has a moisture regain of 6–9%, which is similar to cotton at 60% RH. It is easier to dye than nylon-6 and cotton, but is difficult to manufacture (177).

9. Applications

World production of nylon fibers is expected to reach 4×10^6 t in the year 2000 (178). Just under 50% of this volume will be produced in the United States and Western Europe, while future production growth will be predominantly in developing regions of China and southeast Asia (179). Production by polyamide type is about 70% nylon-6 and 30% nylon-6,6 (180).

Nylon and polyester make up almost 75% of world's synthetic fiber production (178). As the various market segments and end-use technologies have developed over the years for these maturing synthetic fibers, nylon has moved specifically into higher value applications where its unique properties justify the higher price. Nylon has grown more slowly than polyester, and now nylon filament production volume is one-third of polyester (179). Nylon filament prices are generally higher than those of polyester filament, for example, ranging from around 25% higher for tire reinforcement to over twice as much for some apparel yarns (181).

Principal market segments for nylon are carpet face yarns, which in the United States account for 70% share of nylon consumption; knit and woven apparel at 18% share; industrial end uses such as tires and reinforced rubber products at 7%; and all other uses at 5% (182).

Nylon is the preferred fiber for carpets because of its excellent wear resistance, appearance retention, and ease of coloration. For a given appearance retention and wear life, particularly in plushes, less nylon (in terms of weight per unit area) is required than for polyester or polypropylene. Technical innovations such as soil and stain resistance and antistatic carpeting have contributed significantly to the growth of nylon in this industry. Branding or certification programs, including DuPont's Stainmaster*, Solutia's Wear-Dated*, Allied's Anso*, and BASF's Zeftron*, and others, have been used to grow volume and market share. In the 1990s, the industry also saw much push toward lower cost, nonbranded offerings, and significant industry integration, mergers, and reorganization. Nylon filament and staple have 60% share of carpet face fiber

usage in the United States, exceeding 2 billion pounds per year; polypropylene filament has grown to almost 30% share, while staple fibers of polyester and other materials make up the rest (182).

Recycling of carpet components, especially the face fiber, has received much attention during the 1990s because over 4 billion pounds of post-consumer and manufacturing carpet-related waste is discarded annually, usually to landfills (183). The industry and major nylon fiber and carpet producers have demonstrated and are implementing collection methods, material management methods, and technologies to recycle waste carpet materials in a variety of bulk composites, re-formed plastics via component separation and remelt, and recovered base polymer ingredients for both nylon-6 and nylon-6,6. Less than 1% of the discarded material is currently being recycled (183), but significant growth in recycled volume is expected during the next 5 years (184).

Two largest segments of industrial nylon applications are (1) reinforcing yarns in tires and (2) woven fabrics for airbags in automobiles. Because of its excellent strength, adhesion to rubber, and fatigue resistance, nylon is the preferred fiber in bias-ply industrial/commercial tires (eg, for short-distance trucks, construction/agricultural equipment, racing cars, and airplanes), in mini-spacer passenger car tires, and in off-road vehicles tires. Polyester is the dominant fiber used in the carcass of radial passenger car tires because of its relative cost and higher modulus versus nylon. Nearly all high performance radial passenger car tires have nylon cap plies (above steel belts) to improve high speed durability.

In 1984 the U.S. Department of Transportation ruled that all new cars sold in the United States must be equipped with automatic crash-restraints for driver and front-seat passenger by 1990. This led to the adoption of the airbag concept, which created a new fabric opportunity for nylon industrial yarns. Airbag usage in light vehicles grew to over 110 million units by the year 2000, as frontal airbag installations for drivers and passengers reached 100% in the United States and approached 70% in Europe and Japan (185). Significant additional growth is expected as other regions adopt this concept, and adoptions of side-impact airbags increase. The air bag fabric is woven with high tenacity nylon industrial yarns, generally nylon-6,6, ranging from 47 to 94 tex (420–840 denier), in plain or rip-stop construction, and then scoured, heat-set, and coated with a neoprene formulation to protect the fabric from environmental pollutants and changes in temperature and humidity.

Other applications for the heavier denier, industrial grade nylon yarns include cordage, hose, webbing, sport goods, coated fabrics, belting, printer ribbon tapes, personal flotation devices, luggage, upholstery (automotive, contract), home furnishings, and papermaker felts (staple).

In apparel applications, nylon is preferred over polyester in warp knit fabrics for lingerie because of nylon's relatively fine denier, low weight, and softness; and in circular knit fabrics for sheer hosiery and pantyhose for these same reasons plus its superior textured yarn properties (especially stretch/recovery). Nylon is also the companion yarn of choice in stretch knit and woven constructions that incorporate elastane fibers, such as Dupont's Lycra* or Bayer's Dorlastan*, because of textile processing compatibility (especially dyeing) versus polyester and elastane, in addition to nylon's preferred tactile aesthetics. Volume

growth of nylon in apparel is expected to continue at relatively low rates, around 2.0% per year (186), but higher growth in value is expected as the recent consumer/retailer demands for high value, branded fabrics and garments continue (187). Examples of these specialty offerings are the stretch fabrics with elastane yarn, typically 5–20% of the composition; and branded offerings differentiated by aesthetics or functional performance, like Dupont's Tactel*, Nylstar's Meryl*, and BASF's Ultra Touch*. Because of their softness, drape, and comfort, one denier per filament and microdenier yarns (less than 1 denier/filament) continue to gain popularity as compared to the workhorse 3 denier/filament yarns in previous years.

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ANTHONY Anton

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Table 1. Tensile Properties of Nylon-6 and Nylon-6,6^a Continuous-Filament Yarns^b

| Property | Nylon-6 | | Nylon-6,6 | |
|---|------------------|----------------|------------------|---------------|
| | Regular tenacity | High tenacity | Regular tenacity | High tenacity |
| Breaking tenacity, N/tex ^c | | | | |
| Standard | 0.35–0.64 | 0.57–0.79 | 0.20–0.53 | 0.52–0.86 |
| Wet | 0.33–0.55 | 0.51–0.72 | 0.18–0.48 | 0.45–0.71 |
| Loop | 0.34–0.49 | 0.45–0.89 | 0.18–0.45 | 0.44–0.67 |
| Knot | 0.34–0.48 | 0.42–0.59 | 0.18–0.45 | 0.44–0.67 |
| Tensile strength, MPa ^d | 503–690 | 703–862 | 275–731 | 593–924 |
| Breaking elongation, % | | | | |
| Standard | 17–45 | 16–20 | 25–65 | 15–28 |
| Wet | 20–47 | 19–33 | 30–70 | 18–32 |
| Average modulus (stiffness), N/tex ^c | 1.6–2.0 | 2.6–4.2 | 0.44–2.1 | 1.9–5.1 |
| Average toughness, N/tex ^c | 0.06–0.08 | 0.06–0.8 | 0.07–0.11 | 0.07–0.11 |
| Elastic recovery, % | 98–100 at 1–10% | 99–100 at 2–8% | 88 at 3% | 89 at 3% |
| Moisture regain at 21°C, % | | | | |
| 65% RH | 2.8–5.0 | 2.8–5.0 | 4.0–4.5 | 4.0–4.5 |
| 95% RH | 3.5–8.5 | 3.5–8.5 | 6.1–8.0 | 6.1–8.0 |

^aConditioned at 65% RH and 21°C.^bRef. 21.^cTo convert N/tex to g/den, multiply by 11.33.^dTo convert MPa to psi, multiply by 145.

Table 2. **Dye Affinity of Major Textile Fibers^a**

| Fiber types | Dye types | | | | | | | |
|----------------|-----------|-----|----------|--------|------|--------|----------|----------|
| | Direct | Vat | Reactive | Sulfur | Acid | Premet | Cationic | Disperse |
| Cellulose | D | D | D | D | S | S | — | — |
| Wool | S | SS | HS | S | D | D | — | D |
| Nylon | S | HS | HS/D | HS | D | D | D | D |
| Acetate | S | S | S | S | — | — | — | D |
| Acrylic | — | — | — | — | — | — | D | D |
| Polyester, 2GT | — | — | — | — | — | — | D | D |
| Polypropylene | — | — | — | — | — | — | — | — |

^aFrom Ref. 147, reprinted with permission from AATCC.^bD = dyes; S = stains; HS = heavy stain; SS = slight stain; D = requires special polymer; Requires carrier or high pressure and temperature.

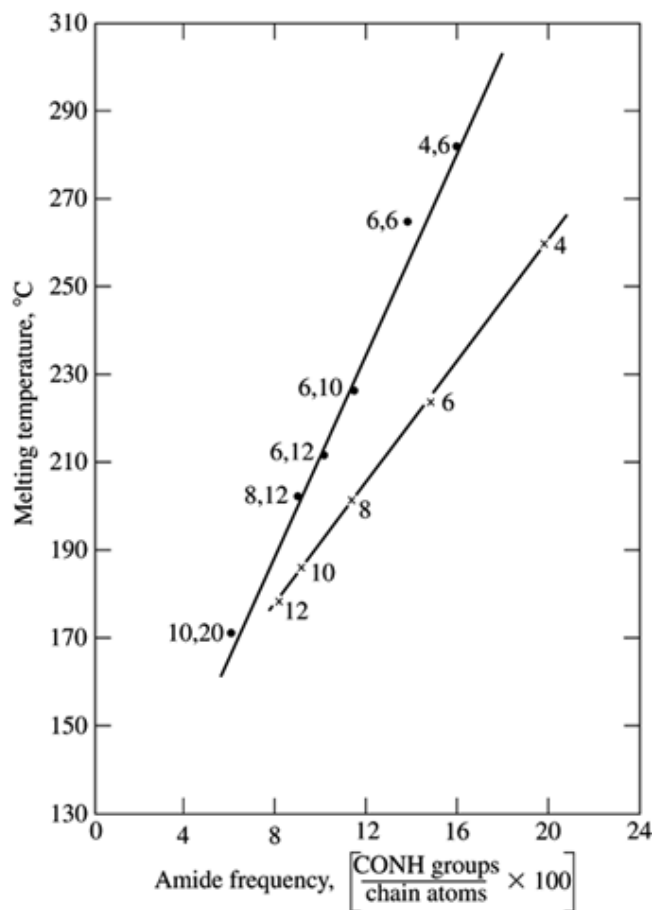


Fig. 1. Effect of amide frequency on the melting points of AB-type (x) and AABB-type (•) polyamides. The number on the curves indicate the specific nylon.

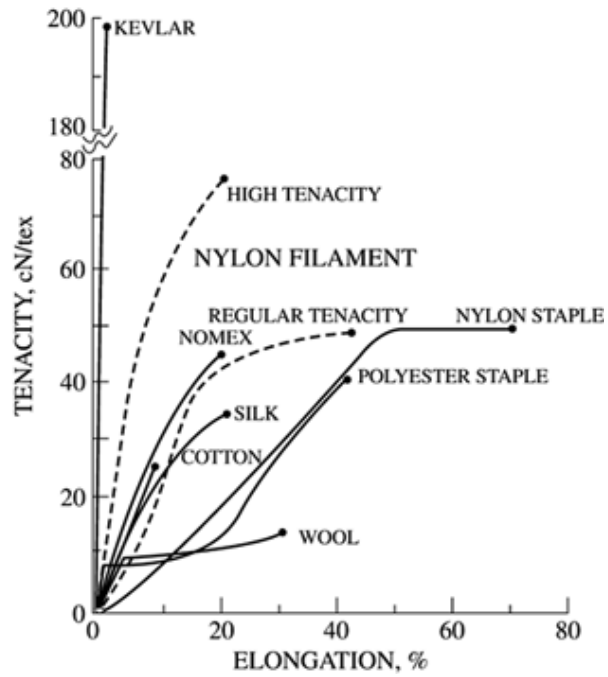


Fig. 2. Stress-strain curves of some textile fibers (22). To convert cN/tex to N-tex, divide by 100.

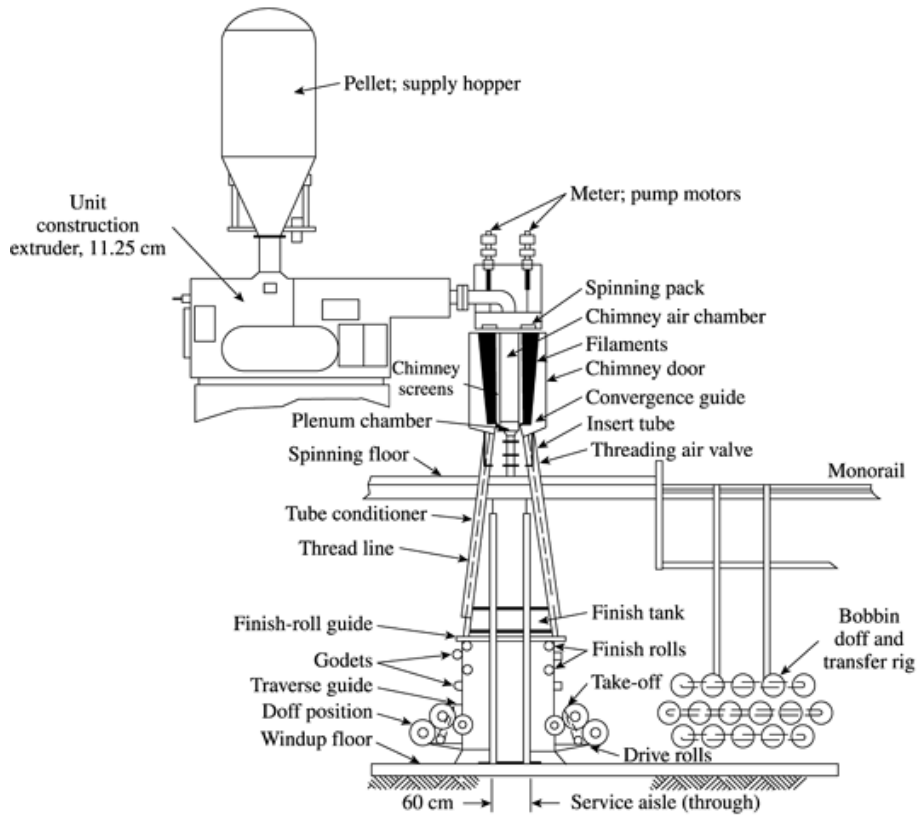


Fig. 3. Conventional melt spinning apparatus. Reproduced with permission from Ref. 66. Copyright © 1966 Noyes Publications.

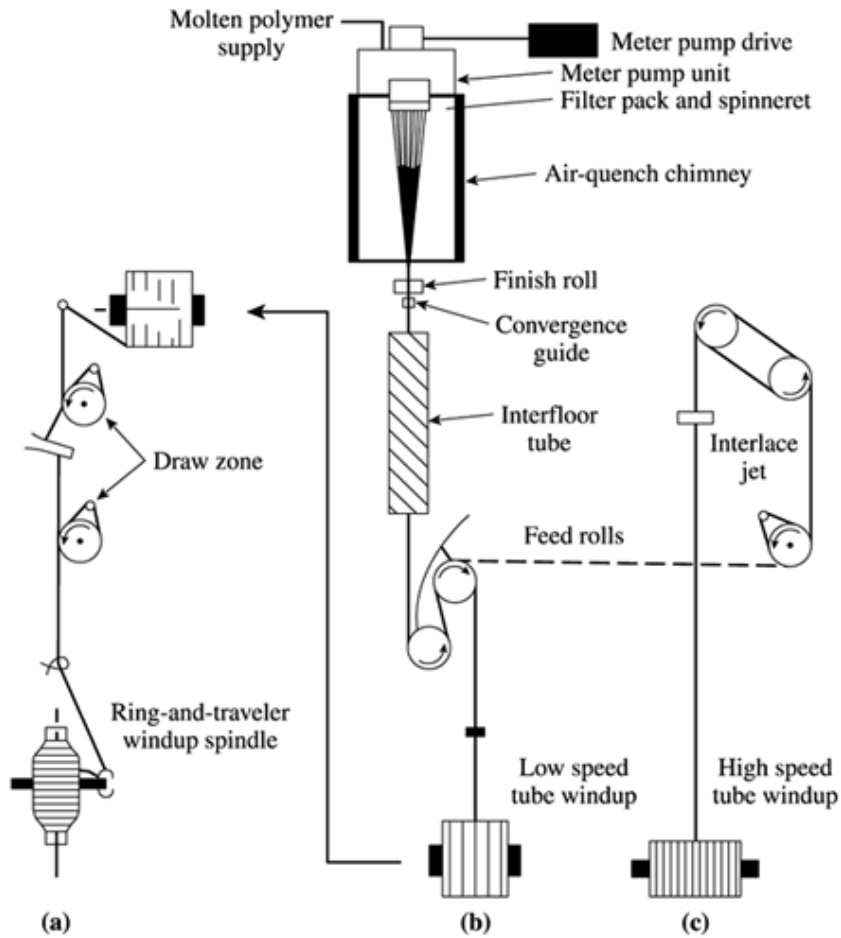


Fig. 4. Melt spin–draw processes for nylon yarn (a) draw–twist process, (b) conventional spinning process, and (c) coupled process.

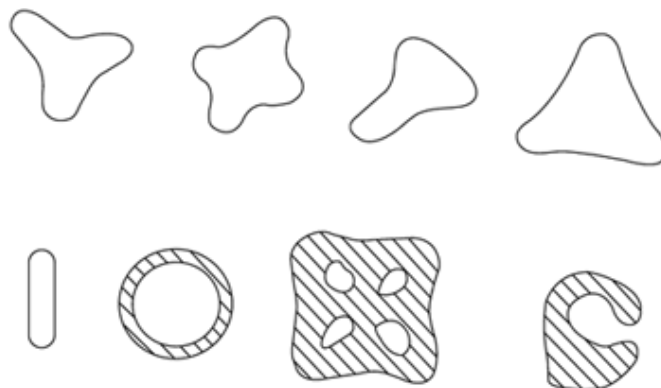


Fig. 5. Typical nylon fiber cross-section shapes.

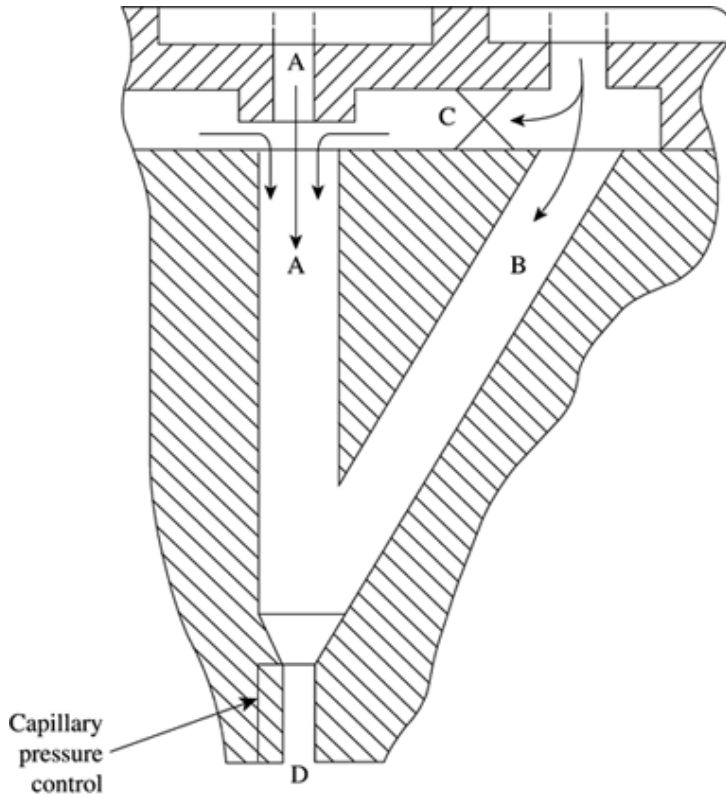


Fig. 6. Bicomponent spinneret for sheath-core fiber where A represents copolymer; B, homopolymer; and D, bicomponent fiber capillary exit. If side-by-side fiber is desired, the interconnecting channel C is sealed at X.

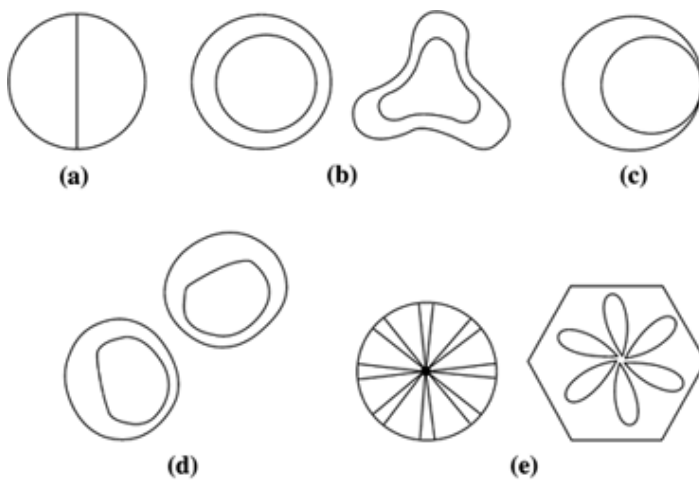


Fig. 7. Bicomponent cross-section forms: (a) side by side, (b) concentric sheath core, (c) eccentric sheath core, (d) kidney-shaped sheath core, and (e) conjugate.

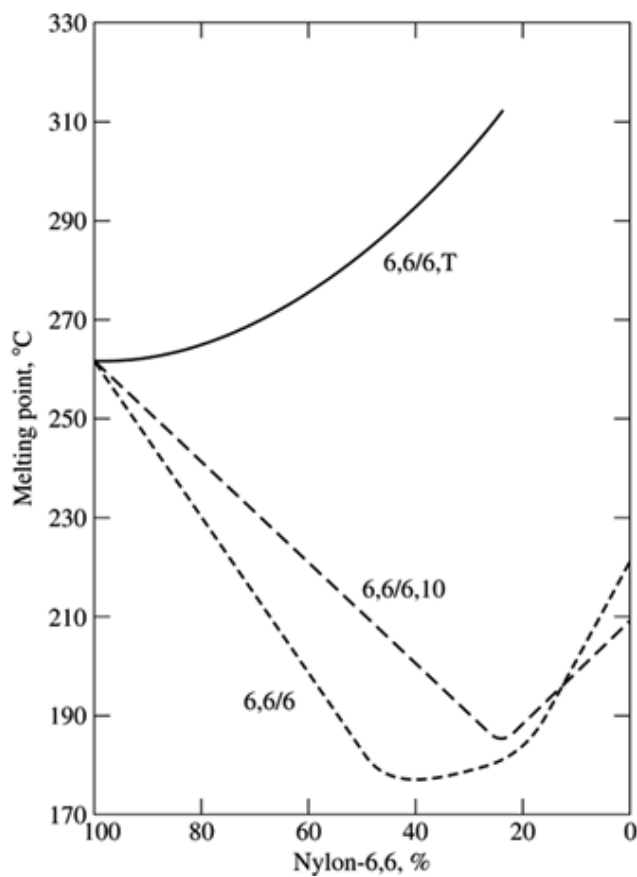


Fig. 8. Melting point–composition curves for random copolyamides of nylon-6, 6.