FIBERS, ACRYLIC

1. Introduction

The first reported synthesis of acrylonitrile [107-13-1] and polyacrylonitrile (PAN) [25014-41-9] was in the 1890s (1). The polymer received little attention for a number of years, until shortly before World War II, because there were no known solvents and the polymer decomposes before reaching its melting point. The first breakthrough in developing solvents for PAN occurred at I. G. Farben in Germany where fibers made from the polymer were dissolved in aqueous solutions of quaternary ammonium compounds, such as benzylpyridinium chloride, or of metal salts, such as lithium bromide, ammonium thiocyanate, and zinc chloride (2). In the United States, duPont discovered an organic solvent for PAN, *N,N*-dimethylformamide (DMF) (3). The same solvent was discovered independently by I. G. Farben at about the same time (4).

Using DMF as the spinning solvent, DuPont produced the first commercial acrylic fiber under the trade name Orlon in 1950. Orlon was spun using a "dry spinning" process at a plant in Camden S.C. Shortly afterward, Chemstrand, a joint venture of Monsanto and American Viscose (now Solutia.) introduced Acrilan acrylic, produced using Monsanto polymer technology and American Viscose wet spinning technology with *N,N*-dimethylacetamide (DMAc) solvent. As is common with new technologies, both products got off to rocky starts, Orlon with poor dyeing performance, Acrilan with fibrillation, but by the late 1950s each had solved the initial problems and established viable markets.

Modacrylic fibers (defined in the United States as those with 35–85% by weight acrylonitrile units) can be dissolved by more conventional solvents, such as acetone, and so were earlier on the market. Union Carbide introduced the first flame-resistant modacrylic fiber in 1948 under the trade names "Vinyon N" and "Dynel". Vinyon N was a continuous filament yarn; Dynel was the staple form. Both were based on 60% vinyl chloride–40% acrylonitrile copolymer.

During the 1950s, at least 18 companies began production of acrylic fibers. Because acrylic fibers require a spinning solvent, and newly discovered solvents received patent protection, the range of technology used commercially is far greater for acrylics than for any other fiber. The most significant were American

Cyanamid's aqueous sodium thiocyanate wet spinning process, and Asahi's nitric acid wet spinning process. In the 1950s and 1960s world production was concentrated in western Europe, Japan, and the United States. By 1960 annual worldwide production had risen to >100 million kilograms. Once staple processes were developed, acrylic fibers became a significant competitor in markets held primarily by woolen fibers. By 1963 the carpet and sweater markets accounted for almost 50% of the total acrylic production. In the 1970s, the growth rate in the United States and western Europe decreased sharply due to the maturing of the wool replacement market and loss of market to nylon in carpeting and to polyester in many apparel applications. In the 1970s, there was rapid growth of acrylic fiber production capacity in Japan, eastern Europe, and developing countries. By 1981, an estimated overcapacity of ~21% had developed. The 1990s saw significant shrinkage of acrylic production in the United States as DuPont and Mann Industries (formerly Badische) exited the business. Significant change has continued into the new century. In 2002, Sterling (formerly Cytec) significantly reduced production of commodity acrylics at their Pace FL plant. These changes have left Solutia as the principal U.S. supplier. In Europe, the changes have been mainly swaps of ownership, with Acordis now having both the Courtaulds and Hoechst businesses and Fraver, an Italian firm, taking over Bayer's business. Aksa in Turkey, with the world's largest acrylic fiber plant, has become an important supplier to Europe. Explosive industry growth has taken place in the Far East, particularly China, where plants based on DuPont and Sterling (Cytec) processes have proliferated. China now has 22% of world capacity, versus 9% 10 years earlier. Japan has reduced capacity, with Asahi Chemical being the latest to announce closure (March 2003) of their business. Modacrylics have all but disappeared from the marketplace, as demand for flame retardant textiles have been met by treated cotton or other synthetics at lower cost. A few new markets have emerged, such as carbon fiber precursors and asbestos replacement fibers, but the volume is small compared to that of the markets lost. For acrylic producers, profit will continue to be sparse.

2. Physical Properties

Acrylic fibers are sold mainly as staple and tow. Staple lengths may vary from 25 to 150 mm, depending on the end use. Fiber fineness may vary from 1.0 to 22 dtex (0.9 to 20 dpf); 2.2 dtex (2.0 dpf) and 1.3 dtex (1.2 dpf) are the most common forms. Tow is sold as a bundle of up to 2.2 million ktex (2.0 million total denier).

The fiber cross-section under microscopic examination is generally one of three shapes (Fig. 1)—round (wet-spun, slow coagulation), bean (wet spun fast coagulation), or dogbone-shaped (dry spun). It is also possible to produce acrylics with special shapes such as ribbon or mushroom by use of shaped or bicomponent spinnerettes. The cross-section may show particles such as TiO_2 added to reduce luster or other pigment to provide coloration. The surface of acrylic fibers is fibrillar, with the fibril size dependent on the spinning process (Fig 2).

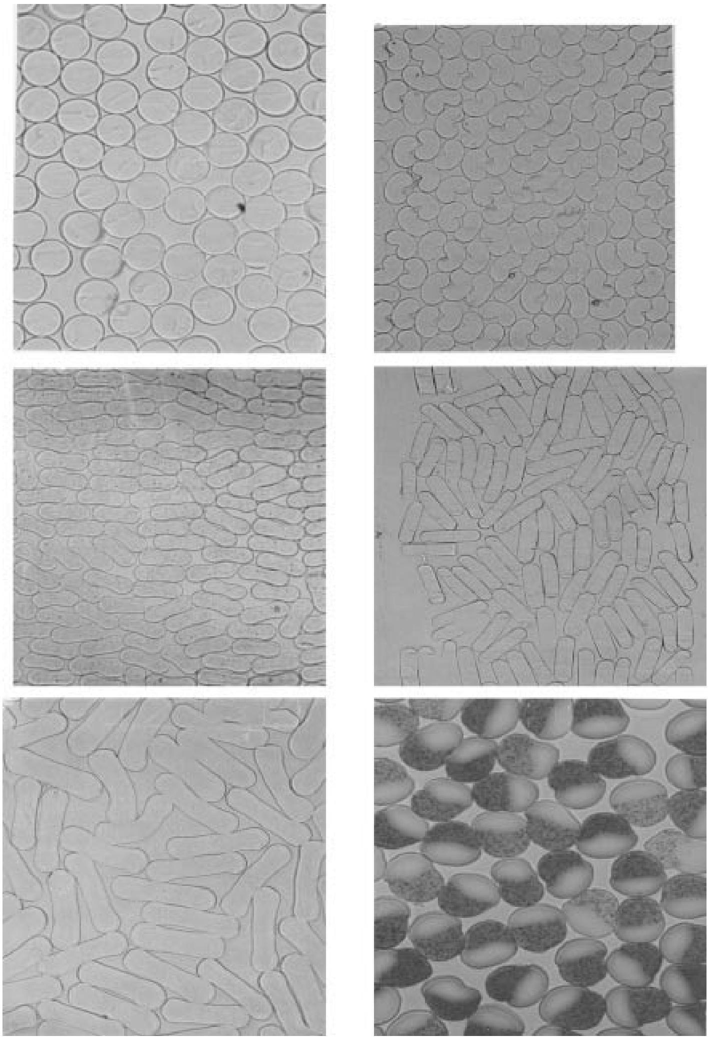
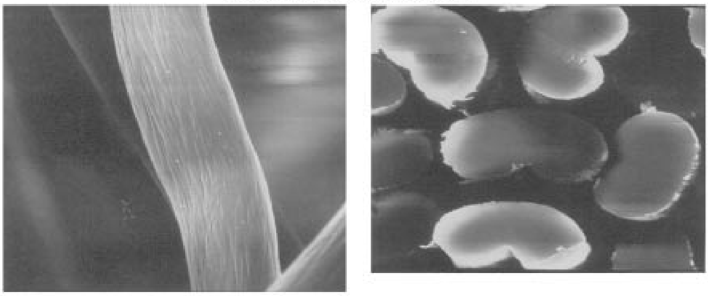


Fig. 1. Acrylic fiber cross-sections. (Scale: 1 mm = 10 μm.)

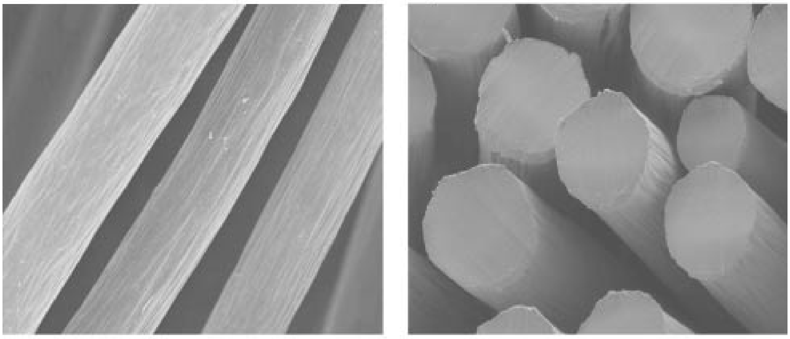
The physical properties of these fibers are compared with those of natural fibers and other synthetic fibers in Table 1.

The elastic properties of these fibers can be characterized as wool-like, with high elongation and elastic recovery. The tensile strength of acrylics and modacrylics is about the same, both considerably lower than other synthetics but higher than wool and about the same as cotton. These elastic properties rank acrylics and wool as compliant fibers, yielding fabric with a characteristically soft handle. Acrylics with tenacities as high as 80 cN/tex (9 gf/den) can be produced (7), but these are usually from higher molecular weight polymers, with low comonomer content and higher stretch orientation. Specialty products such as carbon–fiber precursor and cement-reinforcing fiber are produced using this technology.

Organic solvent wet spun



Salt solvent wet spun



Organic solvent dry spun

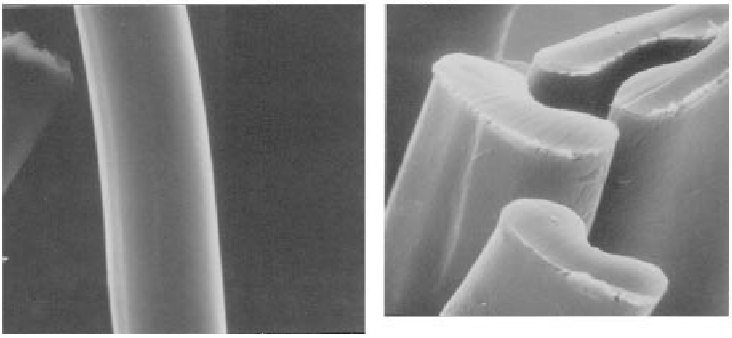


Fig. 2. Acrylic fiber structure comparisons. (Scale: 1 mm = 0.5 μm.)

The mechanical properties of acrylic fiber are deficient under hot-wet conditions. This is primarily due to the fact that the wet T_g of acrylonitrile copolymers is lower than the boiling point of water. Textile wet-processing must be carried out in such a way as to minimize yarn or fabric distortion. Shape retention and maintenance of original bulk under the lower temperatures in home laundering cycles are acceptable. Typical stress–strain curves for acrylic fiber in air and in wet conditions are shown in Figure 3.

Moisture regain, a property that has a great effect on wear comfort, at ~2%, is reasonably good though not as high as that of cotton (7%) or wool (14%). This property can be enhanced by adding hydrophilic comonomers or by generating a porous internal structure in the fiber. Dunova, an acrylic formerly marketed

Table 1. **Physical Properties of Staple Fibers**[a]

Property	Acrylic	Modacrylic	Nylon-6,6	Polyester	Polyolefin	Cotton	Wool
sp gr	1.14–1.19	1.28–1.37	1.14	1.38	0.90–1.0	1.54	1.28–1.32
tenacity, N/tex[b]a							
dry	0.09–0.33	0.13–0.25	0.26–0.64	0.31–0.53	0.31–0.40	0.18–0.44	0.09–0.15
wet	0.14–0.24	0.11–0.23	0.22–0.54	0.31–0.53	0.31–0.40	0.21–0.53	0.07–0.14
loop/knot tenacity	0.09–0.3	0.11–0.19	0.33–0.52	0.11–0.50	0.27–0.35		
breaking elongation, %							
dry	35–55	45–60	16–75	18–60	30–150	<10	25–35
wet	40–60	45–65	18–78	18–60	30–150	25–50	
average modulus, N/tex[a]a dry	0.44–0.62	0.34	0.88–0.40	0.62–2.75	1.8–2.65		
elastic recovery, %							
2% stretch	99	99–100		67–86		74	99
10% stretch		95	99	57–74	96		
20% stretch							65
electrical resistance	high	high	very high	high	high	low	low
static buildup	moderate	moderate	very high	high	high	low	low
flammability	moderate	low	self-extinguishing	moderate	moderate	spontaneous ignition at 360°C	self-extinguishing
limiting oxygen index	0.18	0.27	0.20	0.21		0.18	0.25
char/melt	melts	melts	melts, drips	melts, drips	melts	chars	chars
resistance to sunlight	excellent	excellent	poor; must be stabilized	good	poor; must be stabilized	fair; degrades	fair; degrades
resistance to chemical attack	excellent	excellent	good	good	excellent	attacked by acids	attacked by alkalies, oxidizing, and reducing agents
abrasion resistance	moderate	moderate	very good	very good	excellent	good	moderate
index of birefringence	0.1		0.6	0.16			0.01
moisture regain, 65% rh, 21°C, %	1.5–2.5	1.5–3.5	4–5	0.1–0.2	0	7–8	13–15

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[a] Ref. 6.

[b] To convert cN/tex to gf/den, multiple by 0.113.

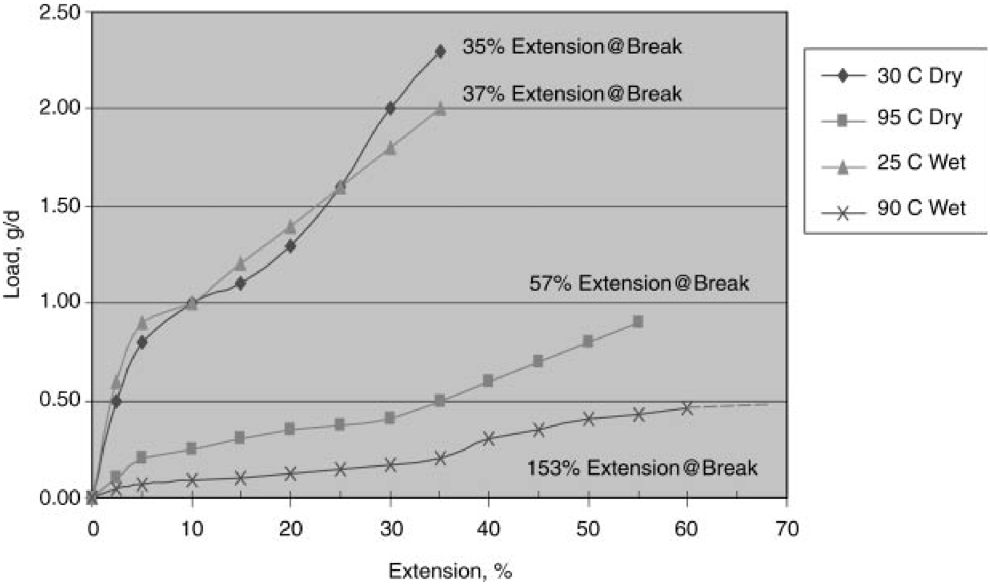

Fig. 3. Acrylic fiber stress–strain behavior. Copolymer at wet and dry conditions.

by Bayer, achieved moisture absorption and transport by internal porosity. The adequate regain plus their high compliancy make acrylics competitive in the wear-comfort markets. However, acrylics cannot match the wrinkle resistance and crease retention of polyester.

3. Chemical Properties

Among the outstanding properties of acrylic fibers is their very strong resistance to sunlight. One study (8), found that the acrylic fibers resisted degradation eight times longer than olefin fibers, over five times longer than either cotton or wool, and almost four times longer than nylon. This property makes the acrylics particularly useful for outdoor applications, such as in awnings, tents, and sandbags, as well as for upholstery for autos and outdoor furniture. Pigmented acrylic or modacrylic fibers with lightfast colors are particularly useful for outdoor applications.

Acrylic fibers are also resistant to all biological and most chemical agents. Weak acids or bases, organic solvents, and oxidizing agents affect acrylics very little. They are attacked by strong bases and highly polar organic solvents such as DMAc, DMF, and dimethyl sulfoxide (DMSO). Acrylic fibers tend to be much more susceptible to chemical attack by alkali than by acid. For example, acrylic fibers are stable for up to 24 h at 100°C in 50% sulfuric acid: these same fibers begin degrading with <0.5% sodium hydroxide at the same exposure time and temperature (9).

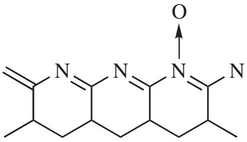

Fig. 4. Structure of air oxidized pan.

In resistance of fibers to oxidizing agents, Orlon acrylic (former DuPont product) was compared to cotton, and acetate yarns (9). The acrylic yarn is far superior in strength retention. After 6-h exposure to bleach the cotton and acetate yarns had completely deteriorated, whereas the acrylic retained ~92% of its original strength.

The excellent chemical resistance of acrylic fiber stems from its laterally bonded structure. Dipole bonds, formed between nitrile groups of adjacent chains, must be broken before chemical attack, melting, or solvation can occur. In addition, the repulsive forces between adjacent nitriles in one chain result in a very stiff polymer backbone which yields very little entropy gain when the bonds between adjacent chains are broken in solvation or melting. Therefore, relatively high temperatures are required for solvation and melting.

Acrylic fibers discolor and decompose rather than melt when heated. The discoloration process involves formation of a ladder structure containing conjugated C=N double bonds. Some color formation accompanies fiber production; commercial acrylics often contain low levels of blue dye or pigment to mask the yellow tinge. In comparison to polyester, acrylic fiber whiteness stability in sublimation dyeing is deficient; this limits acrylic utility in fleece and sheeting markets. Extensive heating in air leads to a color progression ending in a black fiber having the structure shown in Figure 4. This product, termed “Panox”, is useful as a flame resistant textile. Conversion of acrylic fiber to Panox is the first step in carbon fiber production.

3.1. Flammability. Most apparel uses either do not have any flammability standard, or only a modest one which serves to eliminate “torch” fabrics. More rigorous standards are applied for end uses such as carpet, children’s sleepwear, drapery, and bedding. Fibers for these applications must be self-extinguishing after removal from the ignition source. Cotton, rayon, and acrylics burn with the formation of a char. The char acts as a wick that feeds additional fuel to the flame. Nylon and polyester meet some flammability tests by melting away from the ignition source. Modacrylics self-extinguish by generation of chlorine radicals which interfere with the flame-propogation mechanism. This is generally achieved by incorporating vinylidene chloride or vinyl chloride comonomers. Blends of a char-forming fiber with a meltable one require incorporation of an active fire-retardant to meet any stringent flammability test.

A measurement used to compare the flammability of textile fibers is the limiting oxygen index (LOI). This quantity describes the minimum oxygen content (%) in nitrogen necessary to sustain candle-like burning. Values of LOI, considered a measure of the intrinsic flammability of a fiber, are listed in Table 2 in order of decreasing flammability.

Table 2. **Limiting Oxygen Index of Textile Fibers (10) in Order of Decreasing Flammability**

Fiber	LOI Ignition	Temperature, °C
cotton	18.0	400
acrylic	18.2	560
rayon	19.7	420
nylon	20.1	530
polyester	21.0	450
wool	25.0	600
modacrylic	27.0	690
verel modacrylic	33.0	self-extinguishing
100% polyvinyl chloride (PVC)	37.0	self-extinguishing

4. Polymer Analysis

Many techniques are available for characterizing acrylic and modacrylic materials in order to establish the dyesite content, molecular weight, and chemical composition. The dye-site content of the polymer may be determined by dyeing a polymer suspension with a cationic dye of known molecular weight and either measuring directly the dye-on-fiber or indirectly by measuring the unincorporated dye. The dye sites themselves, in most acrylics and modacrylics, are sulfonate and sulfate end groups derived from the free-radical initiator used in polymerization. Therefore, the dye site content of the polymer can be measured by potentiometric titration of the strong acid groups or by determining the sulfur content of the polymer. The low levels of sulfur normally required for fiber dyeability can be measured accurately by X-ray fluorescence. Some acrylics have added "dye receptors"—acidic monomers such as sodium *p*-vinylbenzene sulfonate (SSS) or itaconic acid (IA). This sulfonate can be determined directly using ultraviolet (uv) spectroscopy. Sulfur analysis will yield a total dye-site value including the end groups and the SSS. Potentiometric titration of a polymer containing IA will yield two breaks, one for the sulfonate/sulfate end groups, and a second for one of the IA carboxyls. Dyeing of polymers containing weak-acid dye receptors such as IA does not give an accurate value for total sites, as the dyeing of the IA is incomplete.

The weight-average molecular weight of the polymer can be measured using gel-permeation chromatography with low angle light scattering detection. Solvent systems such as DMF−LiCl are employed to eliminate ionic effects (11). Osmometry may be used to obtain number-average molecular weight (12). These methods are useful to provide absolute values and to determine changes in molecular weight distribution. However, methods based on solution viscosity are the most popular in commercial practice. The simplest method is to measure the viscosity of a solution of the polymer at a specified concentration and temperature. This may be done using a capillary viscometer. For quality assurance purposes, usually a single point (specific viscosity) determination is sufficient. The viscosity-average molecular weight may be obtained by extrapolating specific viscosities at several concentrations to zero concentration. The intrinsic viscosity thus derived is then used in the Staudinger equation (13) or Cleland-Stockmayer equation (14) to give the viscosity-average molecular weight.

Typical acrylic polymers have number-average molecular weights in the 30,000–40,000 range, or roughly 700 repeat units. The weight-average molecular weight is typically in the range 90,000–120,000, with a polydispersity index (M_w/M_n) between 2.0 and 3.5. Fiber producers favor the lowest molecular weight and broadest distribution that is consistent with acceptable fiber physical properties, as that will result in the highest number of sulfate and sulfonate dye-sites.

Analytical methods for identifying and quantifying the chemical composition of acrylic and modacrylic materials are numerous. The usual comonomers found in acrylics–vinyl acetate, methyl acrylate, and methyl methacrylate—can be identified using nuclear magnetic resonance (NMR). They may be quantified using infrared (ir) spectroscopy by the absorbance of the carbonyl group; calibration of the method is sometimes accomplished by preparation of ^{14}C tagged polymer standards. Sulfonated monomers, such as SSS or sodium *p*-(sulfophenyl) methallyl ether, can be detected by strong uv absorbance due to the phenyl group. Halogen monomers can be quantitatively measured by pyrolyzing the polymer and analyzing the pyrolysis products by halide titration. X-ray fluorescence may also be used to determine the concentration of specific halogens. Comonomer content may also be quantified by differential scanning calorimetry of a water–polymer slurry. The mole fraction of comonomer depresses the melting point linearly (15).

5. Fiber Characterization

To establish if a fiber or fabric is acrylic or a blend containing acrylic, a portion should be separated into the individual filaments and introduced in a density gradient column (16). Acrylic fibers have a density of 1.17 ± 0.01. An ir scan of a KBr pellet of ground fiber can be used to identify the presence of nitrile groups. It is more difficult to establish the fiber supplier. A library of cross-sections, known comonomer type and other specific information is required. Since many producers now use almost identical technology, it may not be possible to achieve positive identification unless the fiber contains a marker.

In addition to characterizing the properties introduced by the choice of comonomers and the polymerization process itself, further characterization is required to describe the properties imparted by spinning and subsequent downstream processing. These properties relate to the order and microstructure of the fibers, and the resultant performance characteristics, such as crimp retention, abrasion resistance and mechanical properties. Mechanical testing, to determine breaking elongation, tenacity, and modulus of elasticity, is carried out using devices such as the Instron. Dry-heat shrinkage and shrinkage in boiling water are measured by determining the difference in the length of a section of fiber after treatment at specified conditions. Other properties important to ease of processing or the end use include finish level, crimp frequency and amplitude, whiteness and dyeing rate.

6. Acrylonitrile Polymerization

Virtually all acrylic fibers are made from acrylonitrile combined with at least one other monomer. The comonomers most commonly used are neutral comonomers, such as methyl acrylate [96-33-3] and vinyl acetate [108-05-4] to increase the solubility of the polymer in spinning solvents, modify the fiber morphology, and improve the rate of diffusion of dyes into the fiber. Sulfonated monomers, such as sodium *p*-(vinylbenzene)sulfonate [27457-28-9] (SSS), sodium methallyl sulfonate [1561-92-8] (SMAS), and sodium *p*-(sulfophenyl) methallyl ether [1208-67-9] (SPME) are used to provide additional dye sites or to provide a hydrophilic component in water-reversible-crimp bicomponent fibers. Halogenated monomers, usually vinylidene chloride [75-35-4] or vinyl chloride [75-01-4], impart flame resistance to fibers used in the home furnishings, awning, and sleepwear markets.

6.1. Polymerization Methods. Acrylonitrile and its comonomers can be polymerized by any free-radical method. Bulk polymerization is the most fundamental of these, but its practical use is limited by its autocatalytic nature. Aqueous dispersion polymerization is the most common commercial method; solution polymerization, where the spin solvent serves as the polymerization medium, is the other commercial process. Emulsion polymerization is used for certain modacrylic compositions.

Aqueous Dispersion Polymerization. By far, the most widely used method of polymerization in the acrylic fibers industry is aqueous dispersion (also called suspension). When inorganic compounds such as persulfates, chlorates, or hydrogen peroxide are used as radical generators, the initiation and primary radical growth steps occur mainly in the aqueous phase. Chain growth is limited in the aqueous phase, however, because the monomer concentration is normally low and the polymer is insoluble in water. Nucleation occurs when aqueous chains aggregate or collapse after reaching a threshold molecular weight. If many polymer particles are present, as is the case in commercial continuous polymerizations, the dissolved radicals are likely to be captured on the particle surface by a sorption mechanism. The particle surface is swollen with monomer. Therefore, the polymerization continues in the swollen layer and the sorption becomes irreversible as the chain end grows into the particle.

Since polymer swelling is minimal and the aqueous solubility of acrylonitrile is relatively high, the tendency for radical capture is limited. Consequently, the rate of particle nucleation is high throughout the course of the polymerization, and particle growth occurs predominantly by a process of agglomeration of primary particles. Unlike emulsion particles of a readily swollen polymer, such as polystyrene, the acrylonitrile aqueous dispersion polymer particles are massive agglomerates of primary particles which are $\sim$100 nm in diameter.

Redox initiation is normally used in commercial production of polymers for acrylic fibers. This type of initiator can generate free radicals in an aqueous medium efficiently at relatively low temperatures. The most common redox system consists of ammonium or potassium persulfate (oxidizer), sodium bisulfite (reducing agent), and ferric or ferrous ion (catalyst). The mechanism is shown in Figure 5. This redox system works at pH 2.0–3.5 where the bisulfite ion

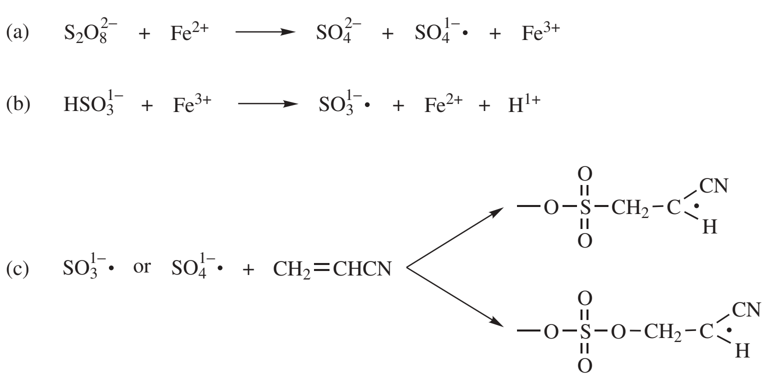

Fig. 5. Persulfate redox initiation mechanism.

predominates and the ferric ion is soluble. The sulfate- and sulfonate ion-radicals react with monomer to initiate rapid chain growth. Termination occurs by radical recombination or by chain transfer. Bisulfite ion is both a reducing agent and chain-transfer agent; it reacts by transferring a hydrogen radical to terminate the chain, thus producing a bisulfite radical to initiate a new chain. The bisulfite concentration has a pronounced effect on polymer molecular weight with virtually no effect on the overall rate of polymerization (17). The ratio of bisulfite to persulfate in the reaction mixture has a strong effect on the dye-site content of the polymer (17,18). Bisulfite chain transfer increases the total dye-site content of the polymer by reducing the polymer molecular weight but at the same time produces chains with just one dyesite. At a given molecular weight the dye site content of the polymer can, in theory, vary from two per chain at low bisulfite levels to one per chain at very high bisulfite levels.

In commercial practice, excess reducing agent to oxidizing agent ratios are used, eg, molar ratios of bisulfite to persulfate ranging from 5 to 15. These high ratios give narrower molecular weight distributions and, for a given molecular weight, relatively low conversion to polymer. Low conversion is an effective means of minimizing branching and color producing side reactions.

A comprehensive review of aqueous polymerization has been published (19). Many reviews of acrylonitrile polymerization have been published (20–23).

In commercial practice, polymerization is effected in a continuous-stirred-tank–reactor (CSTR), a system in which all components are fed continuously and mixed, and the product is continuously discharged. For start-up, the reactor is charged with a certain amount of pH adjusted water or the reactor is filled with overflow from another reactor already operating at steady state. The reactor feeds are metered in at a constant rate for the entire course of the production run, which normally continues until equipment cleaning or maintenance is needed. A steady state is established by taking an overflow stream at the same mass flow rate as the combined feed streams. The reaction vessel is normally an aluminum alloy; this minimizes scale build-up as the wall provides a sacrificial surface. The reactor is jacketed; steam may be introduced to heat the contents for start-up, but once the polymerization is initiated, water is circulated in the jacket to remove the heat of polymerization and maintain a constant temperature—usually 50–60°C.

An example of a continuous aqueous dispersion process is shown in Figure 6 (24). A monomer mixture composed of acrylonitrile and up to 10% of a neutral comonomer, such as methyl acrylate or vinyl acetate, is fed continuously. Polymerization is initiated by feeding aqueous solutions of potassium persulfate (oxidizer), sulfur dioxide (reducing agent), ferrous iron (promoter), and sodium bicarbonate (buffering agent). Alternately the system may employ a sodium bisulfite–sulfur dioxide or a sodium bisulfite–sulfuric acid buffer. The aqueous and monomer feed streams are fed at rates that give a reactor dwell time of 40–120 min and a feed ratio of water to monomer in the range from 2 to 5. The reactor overflow, an aqueous slurry of polymer particles, is mixed with an iron chelating agent or the pH is raised to stop the polymerization. The slurry is then fed to the top section of a baffled monomer-separation column. The separation of unreacted monomer is effected by contacting the slurry with a countercurrent flow of steam introduced at the bottom of the column. Monomer plus water is condensed from the overheads stream and the monomer separated using a decanter, the water phase being returned to the column. The stripped slurry is taken from the column bottoms stream and the polymer separated using a continuous vacuum filter. After filtration and washing, the polymer is pelletized, dried, ground, and then stored for later spinning.

A less desirable recovery process is to filter or centrifuge the slurry (with washing) to recover the polymer and then pass the filtrate plus wash water through a conventional distillation tower to recover the monomers. Delaying monomer removal may increase operator exposure, results in monomer in drier emissions and reduces acrylonitrile yield through emissions and a side reaction. The need for monomer recovery may be minimized by using two-stage filtration with the first stage filtrate recycled to the reactor. Nonvolatile monomers, such

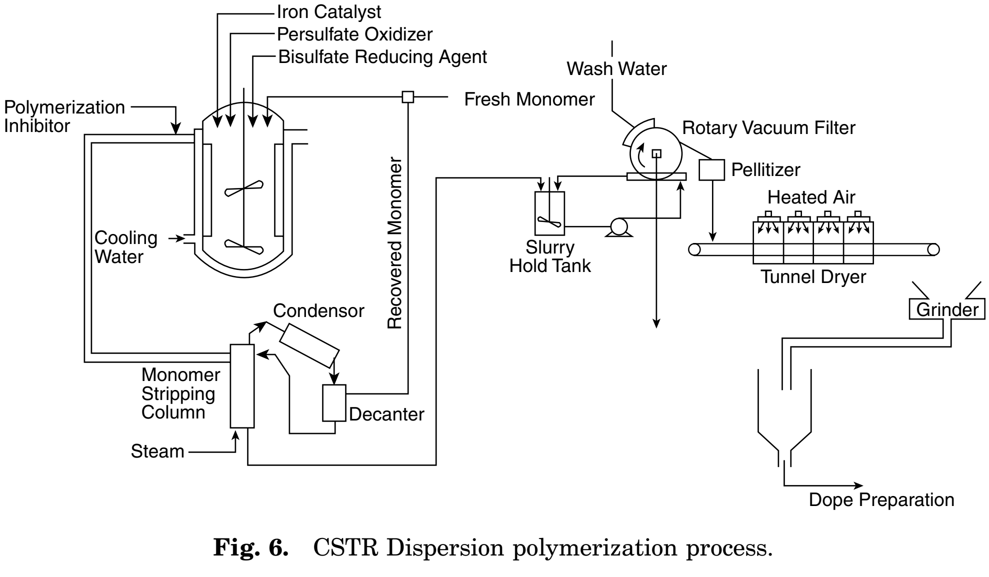

Fig. 6. CSTR Dispersion polymerization process.

as sodium *p*-vinylbenzene sulfonate, can be partially recovered in this manner. This makes process control more difficult because some reaction by-products can affect the rate of polymerization and the concentration of the recycle stream may vary.

Cost reduction has been a focus of fiber producers since the overall market for acrylic fibers in developed countries has not grown. A significant savings is realized by operating continuous aqueous dispersion processes at very low water/monomer ratios. Mitsubishi Rayon, eg, has reported ratios as low as 1.75 (25,26). This compares to ratios of 4–5 widely used in the 1970s. The low water/monomer ratios produce a change in the nucleation and particle growth mechanisms that yields denser polymer particles. The dense particles yield a fluid reaction mass, so long as conversion is relatively high. Removal of the heat of polymerization is more difficult in low water/monomer polymerizations as there is more heat generated per unit volume. The cost reduction comes in the drying step. While conventional water/monomer ratios give wet cake moisture levels of 200% (dry basis) the modified process yields wet cake moisture levels of 100% or less. Thus a savings in drying cost is realized. The low water/monomer process has the added advantage of increased reactor productivity.

After monomer removal by slurry distillation, salts are removed from the polymer by washing, either on a rotary vacuum filter or centrifuge. In the case of aqueous salt spin solvents such as NaSCN, the polymer cake may be used without drying to make a spin dope. With organic solvents, a drying step is required. Both belt dryers (with a pretreatment of pelletizing the polymer) and cyclone dryers are used; the former is most common. After drying, the pellets are again reduced to a powder and sent to bin storage. To ensure uniformity, the contents of several bins may be fed to the dope preparation area simultaneously.

Solution Polymerization. Solution polymerization is used by a few producers in the acrylic fiber industry. The reaction is carried out in a homogeneous medium by using a solvent for the polymer. Suitable solvents are sodium thiocyanate (NaSCN) used by Acordis, and (DMSO) [67-68-5] used by Toray. The homogeneous solution polymerization of acrylonitrile follows the conventional kinetic scheme developed for vinyl monomers (27).

Thermally activated initiators such as azobisisobutyronitrile (AIBN), ammonium persulfate, or benzoyl peroxide can be used in solution polymerization, but these initiators are slow acting at temperatures required for fiber-grade polymer processes. Half-lives for this type of initiator are in the range of 10–20 h at 50–60°C (28). Therefore, these initiators are used mainly in batch processes where the reaction is carried out over an extended time. Redox initiators, such as the ammonium persulfate–sodium bisulfite–copper system, have much higher initiation rates and are reported to be employed in the Acordis NaSCN process. A typical continuous solution polymerization equipment diagram is shown in Figure 7.

Chain transfer is an important consideration in solution polymerization. Chain transfer to solvent may reduce the rate of polymerization as well as the molecular weight of the polymer. Other chain-transfer reactions may introduce dye-sites, branching, and structural defects which reduce thermal stability. The organic solvents used for acrylonitrile polymerization are active in chain transfer. Both DMSO and DMF have chain-transfer constants of

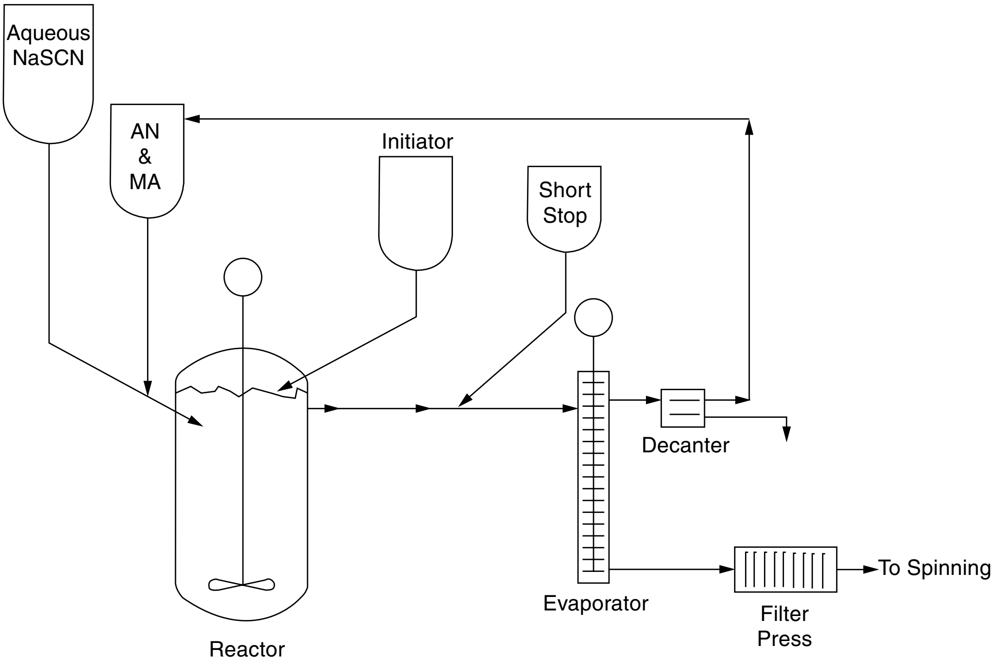

Fig. 7. CSTR NaSCN Solution polymerization process.

$0.1–0.8 \times 10^{-4}$ and $2.7–2.8 \times 10^{-4}$, respectively—high when compared to a value of only 0.05×10^{-4} for acrylonitrile itself and 0.006×10^{-4} for aqueous zinc chloride.

Of the two common comonomers incorporated in textile-grade acrylics, methyl acrylate is the least active in chain transfer whereas vinyl acetate is as active in chain transfer as DMF. Vinyl acetate is also known to participate in the chain transfer-to-polymer reaction (28). This occurs primarily at high conversion, where the concentration of polymer is high and monomer is scarce.

The advantage of solution polymerization is that the polymer solution can be converted directly to spin dope by removing the unreacted monomer. Incorporation of nonvolatile monomers, such as the sulfonated monomers can be a problem. The sulfonated monomers must be converted to a soluble form such as the amine salt. Nonvolatile monomers are difficult to recover or purge from the reaction medium. Monomer recovery systems based on carbon adsorption have been developed. However, the usual practice is to maximize the single-pass conversion of these monomers.

Subsequent to the polymer reactor, acrylonitrile and volatile comonomers are removed in a thin-film evaporator. Additives such as pigments or stabilizers may be incorporated using a static or active mixer before the dope is transferred to the spinning area.

Bulk Polymerization. The idea of bulk polymerization is attractive, since the polymer would not require water removal and the process would not have the low propagation rates and high-chain transfer rates of solution processes. But bulk polymerization of acrylonitrile is complex. Even after many investigations into the kinetics of the polymerization, it is still not completely understood.

The complexity arises because the polymer precipitates from the reaction mixture barely swollen by its monomer. The heterogeneity leads to kinetics that deviate from normal.

When initiator is first added, the reaction medium remains clear while particles 10–20 nm in diameter are formed. As the polymerization proceeds, the particle size increases, giving the reaction medium a white milky appearance. When a thermal initiator, such as AIBN or benzoyl peroxide, is used the reaction is autocatalytic. This contrasts sharply with normal homogeneous polymerizations in which the rate of polymerization decreases monotonically with time. With acrylonitrile bulk polymerization, *three* propagation reactions occur simultaneously accounting for the anomalous auto-acceleration (30). These are chain growth in the continuous monomer phase; chain growth of radicals that have precipitated from solution onto the particle surface; and chain growth of radicals within the polymer particles (28,31).

Bulk polymerization is not used commercially because the autocatalytic nature of the reaction makes control difficult. This, combined with the fact that the heat generated per unit volume is very high, makes commercial operations difficult to engineer. Last, the viscosity of the medium becomes very high at conversion levels $>$ 40–50%. Therefore commercial operation at low conversion would require an extensive monomer recovery operation. A bulk process was developed (32) by MEF, which limited conversion to ~50%; it reportedly reached pilot plant stage but was not commercialized.

Emulsion Polymerization. The use of emulsion polymerization in the acrylic fiber industry is limited to the manufacture of modacrylic compositions. One notable example of an emulsion process was the former Union Carbide process for Dynel (33,34). The mechanism of emulsion polymerization was first developed qualitatively (35) and later quantitatively (36,37). It was shown that the emulsifier disperses a small portion of the monomer in aggregates of 50–100 molecules ~5 nm in diameter called micelles. The majority of the monomer stays suspended in droplet form. These droplets are typically 1000 nm in diameter, much larger than the micelles. Since a water-soluble radical initiator is used, polymerization begins in the aqueous phase. The micelle concentration is normally so high that the aqueous radicals are rapidly captured (38). The micelle is essentially a tiny reservoir of monomer; therefore polymerization proceeds rapidly, converting the micelle to a polymer particle nucleus. Since the halogen-containing monomers have little water solubility, the micelle promotes their ability to react. The ability of emulsion polymerization to segregate radicals from one another is of great importance commercially. The effect is to minimize the rate of radical recombination, allowing high rates of polymerization to be achieved along with high molecular weight. This is important in modacrylic polymerizations where chain-transfer constants of the halogen monomers are high. Comprehensive reviews of emulsion polymerization technology have been published (39,40), and emulsion polymerization reactor modeling has been reviewed (41). The polymer for Kanekaron modacrylic is reported to be prepared by emulsion polymerization.

6.2. Copolymerization. *Homogeneous Copolymerization.* Virtually all acrylic fibers are made from acrylonitrile copolymers containing one or more additional monomers that modify the properties of the fiber. Thus copolymerization kinetics is a key technical area in the acrylic fiber industry. When carried out in a homogeneous solution, the copolymerization of acrylonitrile follows the normal kinetic rate laws of copolymerization. Comprehensive treatments of this general subject have been published (42–46). The more specific subject of acrylonitrile copolymerization has been reviewed (47). The general subject of the reactivity of polymer radicals has been treated in depth (48).

For textile end-use acrylics, the most common comonomer is vinyl acetate, followed by methyl acrylate. The monomer pair acrylonitrile—methyl acrylate is close to being an ideal monomer pair. Both monomers are similar in resonance, polarity, and steric characteristics. The acrylonitrile radical shows approximately equal reactivity with both monomers, and the methyl acrylate radical shows only a slight preference for reacting with acrylonitrile monomer. Many acrylonitrile monomer pairs fall into the nonideal category, eg, acrylonitrile–vinyl acetate. This example is of a nonideality sometimes referred to as kinetic incompatibility. A third type of monomer pair is that which shows an alternating tendency. This tendency is related to the polarity properties of the monomer substituents (49). Monomers that are dissimilar in polarity tend to form alternating monomer sequences in the polymer chain. An example is the monomer pair acrylonitrile–styrene. Styrene, with its pendent phenyl group, has a relatively electronegative double bond whereas acrylonitrile, with its electron-withdrawing nitrile group, tends to be electropositive.

Copolymer composition can be predicted for copolymerizations with two or more components, such as those employing acrylonitrile plus a neutral monomer and an ionic dye receptor. These equations are derived by assuming that the component reactions involve only the terminal monomer unit of the chain radical. The theory of multicomponent polymerization kinetics has been treated (42,43).

Heterogeneous Copolymerization. When copolymer is prepared in a homogeneous solution, kinetic expressions can be used to predict copolymer composition. Bulk and dispersion polymerization are somewhat different since the reaction medium is heterogeneous and polymerization occurs simultaneously in separate loci. In bulk polymerization, eg, the monomer-swollen polymer particles support polymerization within the particle core as well as on the particle surface. In aqueous dispersion or emulsion polymerization, the monomer is actually dispersed in two or three distinct phases: a continuous aqueous phase, a monomer droplet phase, and a phase consisting of polymer particles swollen at the surface with monomer. This affects the ultimate polymer composition because the monomers are partitioned such that the monomer mixture in the aqueous phase is richer in the more water-soluble monomers than the two organic phases. Where polymerization occurs predominantly in the organic phases these relatively water-soluble monomers may incorporate into the copolymer at lower levels than expected. For example, in studies of the emulsion copolymerization of acrylonitrile and styrene, the copolymer was richer in styrene than copolymer made by bulk polymerization, using the same initial monomer composition (50–52). Analysis of the reaction mixtures (53) showed that nearly all of the styrene was concentrated in the droplet and swollen particle phases. The acrylonitrile, on the other hand, was distributed between both the aqueous and organic phases. The monomer compositions in the droplet and particle phase were found to be essentially the same. The effect of monomer partitioning on copolymer composition is strongest with the ionic monomers since this type of monomer is usually soluble in water and nearly insoluble in the other monomers. Reviews of emulsion copolymerization kinetics and the effects of reaction heterogeneity on reaction locus have been published (54,55).

In a CSTR dispersion process, the percentage of the less reactive monomer increases until steady state is reached. For example, if a reactor is fed monomer composed of 91% acrylonitrile and 9% vinyl acetate and the process is carried to 75% conversion, the polymer will contain 7.4% vinyl acetate. The unreacted monomer composition will be 86.2% acrylonitrile and 13.8% vinyl acetate.

7. Solution Spinning

As the acrylic fiber industry has matured, the wide range of spin solvents that were commercialized in the 1950–1960s has narrowed. Dimethyl sulfoxide and zinc chloride are each limited to one producer; no processes based on ethylene carbonate solvent remain in operation. Most newer plants are based on either dimethylacetamide or sodium thiocyanate wet spinning. Table 3 shows commercial solvents and the dissolved polymer concentration range for a spin solution.

For dry polymer, the dope-making process may use chilled solvent to form a slurry and wet out the polymer particles before they begin to dissolve, or may use hot solvent so that the solutioning process occurs immediately. Additives such as thermal stabilizers and delusterant (TiO_2) are added at this time. In both cases, active mixing is required. Subsequently, the suspension is pumped through a shell-tube heat exchanger to complete dissolution. The resulting dope is degassed and filtered (plate and frame) before being pumped to the spin area.

7.1. Dry Spinning. This was the process first employed commercially by DuPont in 1950. It is shown schematically in Figure 8. For acrylic fibers, the only dry spinning solvent used commercially is DMF. The DMF spin dope coming from the dope preparation unit is filtered and then heated to approximately 140°C. It is pumped through spinnerets of up to 2800 holes placed at the top of a solvent removal tower. The DMF is evaporated by circulating an inert gas through the tower at 300–350°C. The tower walls are also heated to prevent any solvent condensation. With such a high boiling solvent (b.p. 153°C) it is not possible (or desirable) to remove all solvent in the tower. Consequently, the fiber from the bottom of the tower contains 10-25% solvent. In discontinuous

Table 3. **Polymer Concentrations Suitable for Solution Spinning**

Solvent	% in Water	Polymer, %
dimethylformamide (DMF)		20–32
dimethylacetamide (DMAc)		20–27
dimethyl sulfoxide (DMSO)		20–30
ethylene carbonate (EC)		15–18
sodium thiocyanate (NaSCN)	45–55	10–15
zinc chloride ($ZnCl_2$)	55–65	8–12
nitric acid (HNO_3)	65–75	8–12

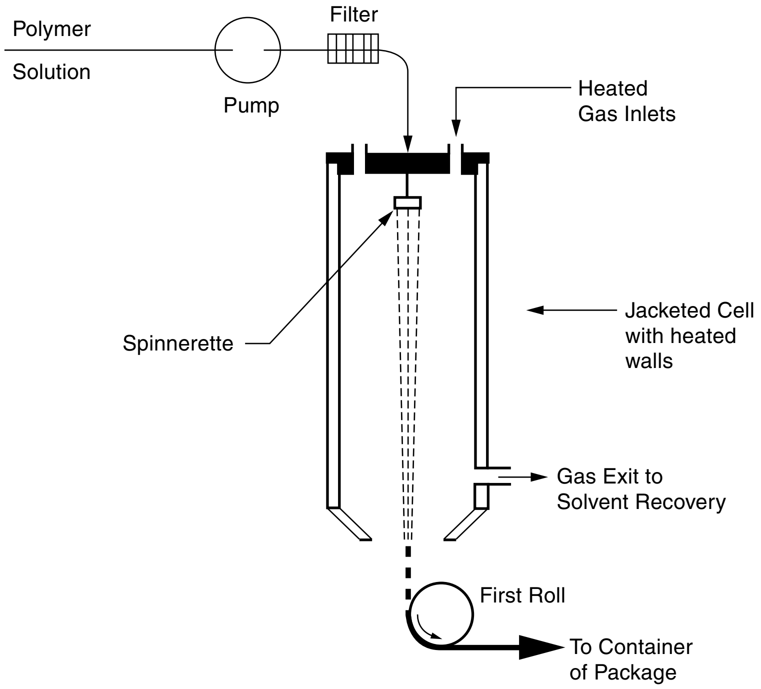

Fig. 8. Dry spinning tower.

processes, the fiber exiting the tower is wet with water and combined with the product from other threadlines into a rope; the rope is plaited into a can. The residual DMF is removed in a second step by passing the rope via roll sets through a series of hot water baths. A more modern process, introduced by Bayer, washes the fiber by sprays while passing on a belt. The as-spun fiber has little orientation, so it is stretched 3–6X either before or concurrent with the washing step. The fiber is crimped to improve bulk and textile processing, then dried by heated air on a moving belt. During drying the fiber structure collapses to the same density as solid polymer and the length decreases as the structure relaxes. A "finish" comprising an antistatic agent and a lubricant are applied by spray or kiss rolls and the product is either cut to staple or packaged directly as tow. Figure 9 shows the subsequent process steps.

The filament microstructure in dry spinning is derived from gelation exclusively. As evaporation proceeds, the polymer concentration in the filament increases until gelation occurs. This may happen within a few centimeters of the spinneret face. Since no nonsolvent is used, precipitation does not occur during solvent removal. Fiber densities from wet and dry spinning have been compared

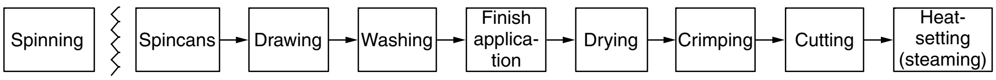

Fig. 9. Conventional wash-draw-dry-relax fiber process.

(56); density of as-spun fiber is much higher in dry spun fiber. The fiber cross-section shape is typically a "dogbone" (Fig. 2). Very little fibrillar structure, characteristic of wet spun fibers, is observed in the dry spun filaments. During stretching, however, the dry spun fibers develop a fibrillar network similar to that of the wet spun fibers but finer in diameter. This mode of fiber formation is economical for commodity fibers of 1–5 dtex but has severe limitations for other products. (*1*) Solvent removal is not fast enough to produce fibers of 12–20 dtex suitable for the carpet industry; (*2*) the limitation on the number of holes per spinneret makes production of fine filaments (<1 dtex) expensive, as unlike the wet spinning process, the number of holes per spinneret is limited; (*3*) the compact structure makes producer dyeing of fiber more difficult; (*4*) the gelation process does not work well to produce special-shaped filaments; the dogbone cross-section is not suitable as a carbon fiber precursor; and it is not possible to produce a fibrillated product for the asbestos-replacement market.

7.2. Wet Spinning.

Wet spinning differs from dry spinning primarily in the way solvent is removed from the extruded filaments. Instead of evaporating the solvent in a drying tower, the fiber is spun into a liquid bath containing a solvent–nonsolvent mixture called the coagulant, as shown in Figures 10 and 11. The solvent is the same as the dope solvent and the nonsolvent is usually water. Filament fusion is less of a problem in wet spinning so the number of capillaries in wet spinning spinnerets is much larger than in dry spinning. The spinnerets in commercial processes may have anywhere from 3000 to 100,000+ capillaries, which may range in diameter from 0.05 to 0.25 mm; it is common to use multiple spinnerets in a single spinbath.

Because the fiber microstructure is established in the spinbath, the coagulation conditions employed are the result of extensive optimization. The critical part of this process is the transition from a liquid to a solid phase within the filaments. Two liquid/solid phase transitions are possible. The first is precipitation of the polymer to form a microporous solid phase. In extreme cases, precipitation produces a structure with macrovoids which must be "healed" in later processing or the fiber lateral properties will suffer. Precipitation is favored when the solvent is organic and the nonsolvent is water as the solubility of

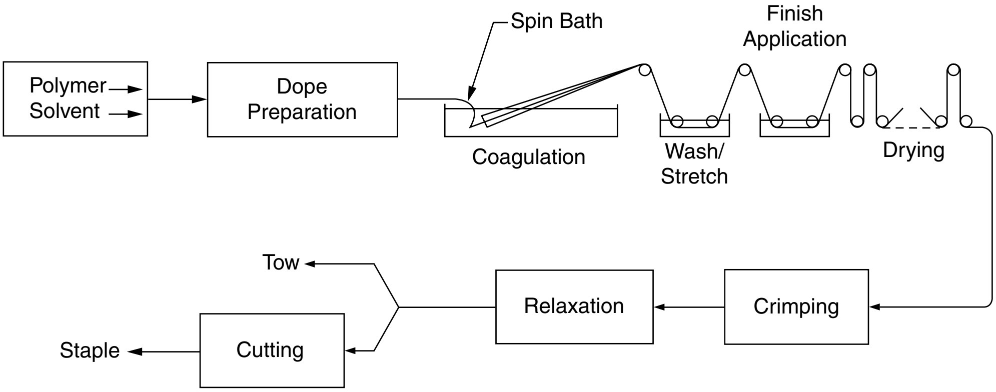

Fig. 10. Wet spinning organic solvent process.

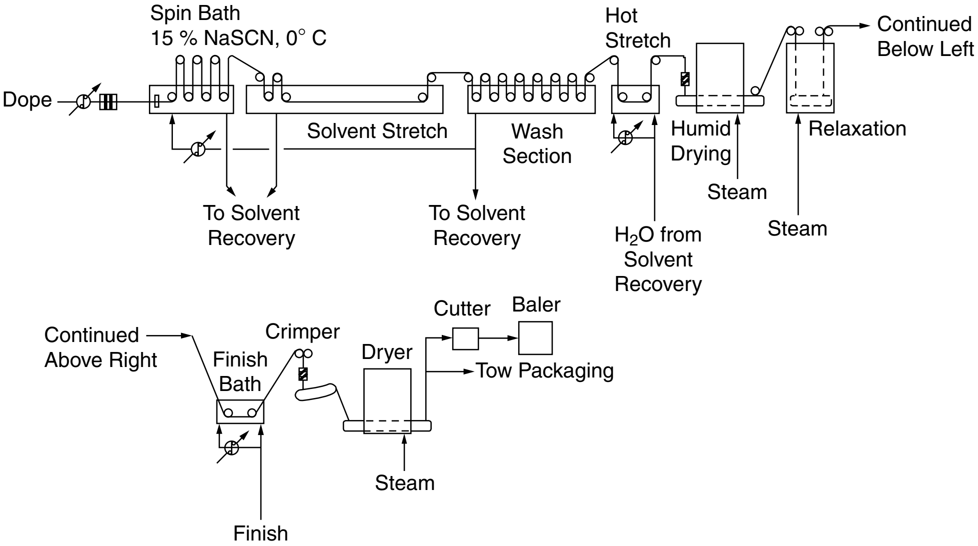

Fig. 11. Wet spinning NaSCN salt process.

polymer decreases abruptly with water concentrations of only a few percent. The second and more desirable solid phase is the gel state, characterized by hydrogen and dipole bonding between the polymer and solvent. The gel state is desirable because it gives rise to a finer microstructure once the solvent is removed. Thus the conditions in the spinbath should be optimized so that gelation of the polymer precedes precipitation. Studies (57) have shown that gelation occurs more rapidly at high dope solids and lower spinbath temperatures.

Low spinbath solvent concentration promotes initial rapid solvent extraction but also produces a thicker filament skin that ultimately reduces the rate of solvent extraction and may lead to the formation of macrovoids. High spinbath solvent concentration gives a denser microstructure, but solvent extraction is slow and filament-to-filament fusion may occur. Other spinbath conditions that affect coagulation and microstructure are dope solids, spinbath temperature, jet stretch (the ratio of actual filament speed to theoretical speed in the capillary) and immersion time.

The fiber emerging from the spinbath is a highly swollen gel containing both solvent and nonsolvent from the spinbath. The fibers are essentially unoriented except at the fiber skin. The microstructure consists of a fibrillar network. The spaces between fibrils are called microvoids. Depending on the conditions of coagulation the filaments may also contain large voids radiating out from the center of the fiber. The best combination of tensile properties, abrasion resistance, and fatigue life is realized when the coagulated fiber has a homogeneous, dense structure with small fibrils and no macrovoids (58).

Fiber cross-sectional shape is determined by the coagulation conditions. A thick skin characteristic of most organic solvent-spun fibers will generate a bean-shaped cross-section as the solvent is removed from the interior. The thinner skin characteristic of inorganic solvent-spun fibers can contract with solvent removal and retain the round shape. It is possible, however, to produce the opposite shape in either system. Examples of these shapes were shown in Figure 1. Special cross-sections, such as rectangular or oval can be made from nonround capillaries by controlling coagulation conditions. Control of die swell is of critical importance. Die swell occurs because most spin dopes are viscoelasic in nature. After undergoing stretching deformation during extrusion through the small spinneratte hole, the dope partially rebounds to a larger, preextrusion diameter. To maintain a nonround shape the tension on the filament at the spinneret face must be great enough to counterbalance die-swell.

After the spinbath or spin-tower step the tow processing is similar for both wet- and dry-, spun yarns. Wet spun tows however, may contain 100–300% of solvent–nonsolvent, while dry-spun tows generally hold only 10–30% solvent. Therefore, the initial washing steps differ in their details. The key wet spinning steps are washing, stretching, finish application, collapse, drying, crimping, and relaxing. The washing step consists of several countercurrent stages with the effluent being recycled to a solvent recovery process. Various wash units are employed including baths, sprays, and proprietary devices (59); washing efficiency is a key aspect of cost, as it impacts recovery of solvent from the effluent. The wash step may also be combined with stretching. In one variation of this method, the tow is drawn between sets of godets and passed through a series of solvent extraction baths at the same time.

The washing step may be followed by additional stretching. The porous fibrillar structure of wet-spun fibers increases in density with stretching. In-line dyeing of fiber using cationic dyes is usually carried out after almost all solvent is removed. Due to the open structure of wet-spun fiber, dye penetration and fixation is rapid. An additional wash step removes auxiliaries and unfixed dye. After the fiber is washed, stretched and optionally dyed, finish may be applied using a bath or similar device. If drying is accomplished on heated rolls (Fig. 10), a predrying finish is required to prevent fiber fusion. In other processes (Fig. 11) finish application may be postponed until the fiber is dried and collapsed.

The collapsing–drying step can be accomplished with the tow held at constant length by contacting the tow on heated rolls or by passing the tow through an in-line oven using a conveyor belt. For fiber that contains a large void structure, roll drying is necessary to effect collapse of the voids. After collapse, boiling water shrinkage is reduced and higher temperatures are required for subsequent relaxation.

After drying–collapsing, the tow is relaxed. Relaxation is essential because it reduces the tendency for fibrillation and increases the dimensional stability of the fiber. Relaxation also increases fiber elongation while reducing strength and increases dye diffusion rate. Relaxation can be done in-line or in batches in an autoclave. For fiber that has been belt dried, relaxation can be accomplished by an atmospheric process (Fig. 11). However, for roll dried fiber, saturated steam is used because the moisture reduces the process temperatures required. This process can be accomplished in-line, but more commonly it is done batchwise in an autoclave. Fiber shrinkage during relaxation ranges from 10 to 40% depending on the temperature, the polymer composition, and the amount of prior orientation. The amount of relaxation is tailored to the intended application of the product.

Fiber crimping using a stuffer box device may be done before in-line relaxation or before autoclaving. The relaxation process tends to "set" the crimp. In some autoclave processes, a second crimping step is employed subsequent to relaxation. Fiber may be cut to staple at the machine end for in-line relax processes or batch-wise for autoclave processes. Tow can be produced from either process type, although large packages of one ton or more are produced more readily from the in-line relax process.

Process speeds for wet spinning vary from ~55–260 m/min. The limitations are the speed at which the fiber can move through the spinbath without filament breakage and the equipment line length required to complete the washing and drying processes. A single machine may have up to 48 spinnerets (6 rows of 8) with a total productivity of 50 tons/day.

7.3. Air Gap Spinning. This process, also termed dry-jet wet spinning, is used to provide filament yarn either for textile use or as a carbon fiber precursor. It is suitable for producing the small bundles required for these end uses because the filament has been drawn before it enters the bath, so drag forces are less likely to cause breakage; thus much higher line speeds can be achieved. In theory any acrylic solvent can be used in air gap spinning. Commercial examples are known from DMAc, NaSCN, and DMSO.

The dope solids for air gap spinning are higher than for wet spinning, the intent being to achieve quick gelation on extrusion. The spinneret is positioned a short distance above the bath, which is a solvent nonsolvent mixture, typically at low temperature. The fiber is spun vertically into the bath, then rerouted out via a tube or pulley as shown in Figure 12. Spinnerets may be <1000 holes for a textile product or as many as 4000 for a carbon fiber precursor. The remainder of the process resembles the wet spinning process except that there are many small bundles that must be kept separate and the final product is taken up on bobbins. Final line speeds may be up to 500 m/min, but because of the small bundle size, machine productivity may be only 5 tons/day.

7.4. Solvent Recovery. Efficient use of solvent and water are key elements in an economic process. With most spinning processes practiced on a

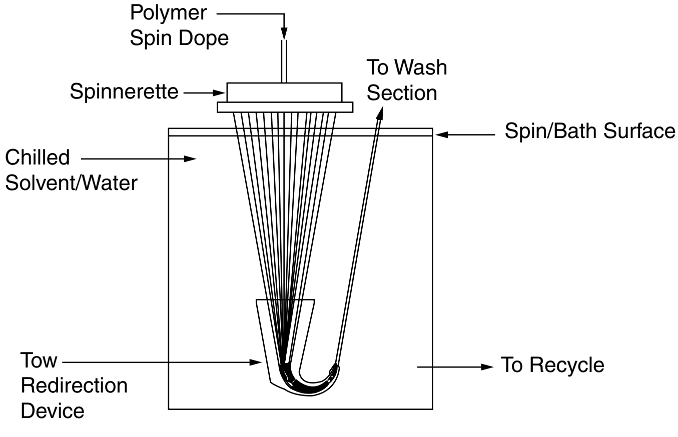

Fig. 12. Air gap coagulation.

large scale, <1% solvent is not recycled, based on fiber produced. Since the ratio of solvent to fiber is in the range of 4:1, this means <0.25% of the solvent employed is expended per pass. Solvent loss is of several types: (*1*) solvent remaining in final fiber; (*2*) solvent lost as vapor; (*3*) solvent decomposed; (*4*) solvent lost in reprocessing or maintenance.

The main means of solvent recycling is distillation, either atmospheric or vacuum. With the organic solvents, the water is distilled, perhaps in several steps, then the higher boiling solvent is distilled, leaving behind dissolved salts and low molecular weight polymer. Amide solvents such as DMF and DMAc are subject to hydrolysis and may require a step to remove the acid generated; the recovered water may require removal of dimethyl amine before reuse. Figure 13 shows a DMF recovery train (60). Salt solvents such as NaSCN are concentrated by water removal in multieffect evaporators, then may have an ion exchange and/or crystallization step to remove impurities. Recycled water may have the pH adjusted by addition of acid or base to assure neutralization of the fiber in the washing step.

7.5. Melt Spinning. Compared to most other synthetic fibers, acrylics have always had the disadvantage of extra process steps and cost incurred because they could not be melt spun. Several approaches to eliminating this limitation have been proposed. Plasticization of the polymer with DMSO was proposed (61) as this lowered the melting point. This only reduced the amount of solvent to be recovered but did not eliminate the washing and solvent recovery steps. A more promising approach was plastization with water (62). This eliminated the process steps, but it was necessary to heat the plasticised mass to 200°C under pressure. The fiber had to be extruded into a chamber also under pressure or the result would be a foam structure as the water vapor flashed.

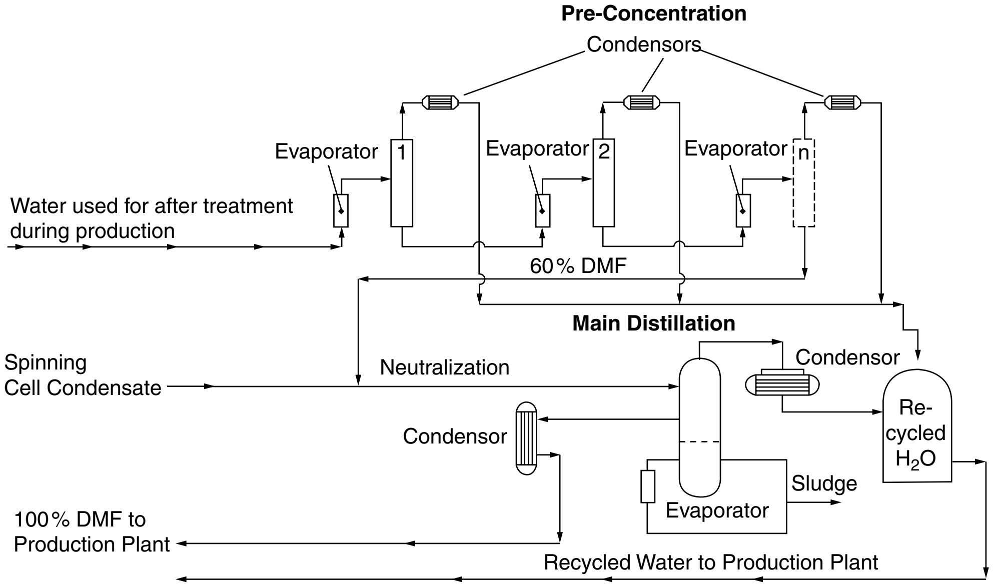

Fig. 13. Diagram of DMF recovery unit.

A true melt spinning process has been developed by a group at Standard Oil (63). Their approach was to make a polymer containing substantial comonomer content by a process which minimized "blocking" of AN groups. The resultant polymer was melt processible without degradation. Possible limitations of this approach are that the high comonomer content leads to high relaxation shrinkage, lower softening and sticking temperatures. These are disadvantages in modern textile processes. No commercial applications of this technology have appeared.

7.6. Modifications of Properties.

Reduced Pilling. Staple fabrics, in general, develop small balls of fiber or pills on the fabric surface as a result of abrasive action on the fabric surface. However, the pills build up more on acrylic fabrics than on comparable woolens. Pilling can be reduced by increasing the likelihood that the pills will break or wear off. Thus the most effective approaches include reducing fiber strength, incorporating defects in the fiber, increasing fiber brittleness, and reducing shear strength. Using the same polymer base, wet spinning processes can be modified by using low solvent concentration in the spinbath and high spinbath temperature to give more brittle fibers with high void content. Other possible approaches are lower draw ratios, which result in low tensile strength, and less complete relaxation which reduces fiber elongation to break. Commercial examples include Dralon L930 (Fraver), Super Camelon (Mitsubishi Rayon) and Acrilan Pil-Trol (Solutia).

Improved Abrasion Resistance. Abrasion resistance is generally improved by reducing the microvoid size and increasing the initial fiber density. Abrasion-resistant fibers have been produced by incorporating hydrophilic comonomers or comonomers with small molar volumes. Sulfonated monomers, acrylamide derivatives, and *N*-vinylpyrrolidinone are some of the hydrophilic comonomers that can be used to slow coagulation thus reducing the void content. Vinylidene chloride, with its relatively small molar volume, is effective in increasing fiber density. The spinning process itself has a significant effect on initial fiber density and abrasion resistance. Dry spinning, eg, produces a denser initial fiber structure than conventional wet spinning. Wet spinning techniques used to improve abrasion resistance generally do so by promoting gelation. Examples include high spinbath that concentration, low spinbath temperature, and additives to the dope or spinbath that slow coagulation. Spinbath additives include nondiffusing nonsolvents, such as poly(ethylene glycol) or high molecular weight alcohols, such as *tert*-butyl alcohol in place of water.

8. Commercial Products

The majority of acrylic fiber production is 1.0–5.6 dtex (0.9–5 den) staple and tow furnished, undyed, in either bright or semidull ($\sim$0.5% TiO_2) luster. The principal markets are in apparel and home furnishings. Within the apparel sector these fibers are used in sweaters and in single jersey, double-knit, and warp-knit fabrics for a variety of knitted outerwear garments such as dresses, suits, and children's wear. Other markets for acrylics in the knit goods area are hand-knitting yarns, deep-pile fabrics, circular knits, fleece fabrics and half-hose. Acrylics also find uses in broadwoven fabric categories such as blankets, drapery and upholstery. Minor tufted end uses include area rugs and carpets.

8.1. Acrylic Tow.

A significant proportion of acrylic fiber, perhaps 25% in the United States and >50% in Europe, is sold as tow for conversion to yarn through stretch-breaking using the Superba, Seydel or similar equipment. Tow packages may be as large as one ton with no break in the bundle. The larger the tow package, the higher the tow customer's productivity. Ability to offer a large tow package implies that a producer has a highly stable process, as no knots are allowed. Producers with continuous relaxation have no limit on the package size they can offer; the only limits are those arising in package handling. In Europe, many fiber producers convert tow to "tops"—stretch broken product that is ready for yarn spinning.

8.2. Acrylic Filament Yarns.

Continuous filament acrylic yarns face stiff competition from nylon and polyester. Since they are more costly, acrylics have penetrated only those markets where they have a clear advantage in a critical property. In Japan continuous filament yarns in very fine deniers are valued as a silk replacement. In this market, the yarn is a premium product used in high fashion dress fabrics, satins, and poplins or to produce a cloth suitable for surface raising to give a suede or fine velour effect.

8.3. Producer Dyed Fiber.

The largest volume "specialty" product offered by acrylic producers is producer-dyed fiber (PDF). Producer dyeing decreases systems cost by elimination of a process step for the customer, but it complicates the inventory. PDF is usually made in an on-line process as shown in Figure 14 (64). The dye is applied using a device which promotes rapid penetration of the fiber mass, as acrylics have a high strike rate and very poor leveling qualities. The process is automated to maintain constant color (shade and depth) by real-time color analysis and correction. Since the final color is influenced by relaxation and crimp, further monitoring and testing may be required. Alternately, the dyes are premixed and a mixed stream is injected into the dyeing device. If the shade is right, then only depth needs adjustment. PDF fiber spun using this dyeing technology is usually sold as "lots", as color from one production run to the next may not match sufficiently for critical end-uses. Dry-spun

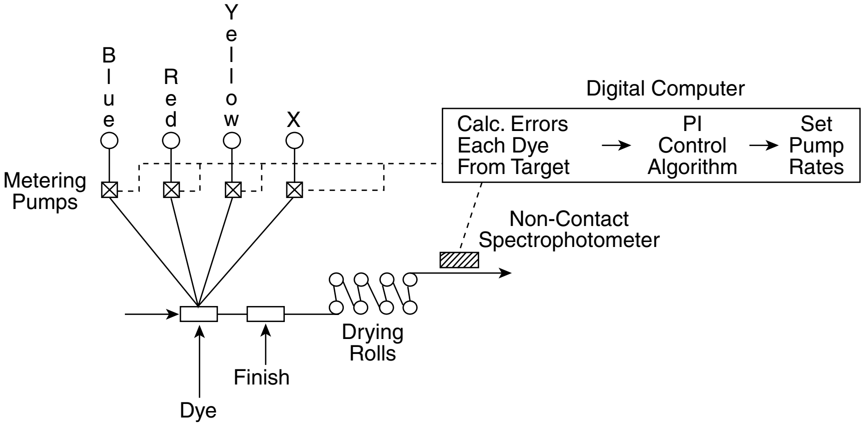

Fig. 14. Color control in a producer-dyed fiber process.

fibers are difficult to dye in-line as their compact structure makes dyeing too slow to be compatible with the required process speeds. For dry-spun acrylic, the only practical process is dope dyeing. For colors with only a low demand, some producers may use postproduction dyeing with a device such as a Serricant Tow-Fix-R. More than 20 producers worldwide offer PDF acrylic.

8.4. Pigmented Fiber. Pigmented acrylic and a small amount of modacrylic are used in outdoor applications where outstanding light stability provides a competitive advantage. Pigmentation provides more stable coloration than dyeing through the lifetime of the fabric. End uses include awnings, tents and lawn furniture. Modacrylic is used where local codes require a flame-retardant fabric. The technology involves mixing of the pigments with the spin dope prior to extrusion. The same feedback mechanism of color control described for PDF may be used with pigmented fiber. About a dozen producers offer pigmented fiber; however some only sell one color: black. Generally, pigmented fiber commands a higher price than PDF owing to the high cost of organic pigments. This coupled with the decreased luster of the pigmented products means they do not usually compete in the same end-uses.

8.5. Fibers with High Bulk and Pile Properties. High-bulk acrylic fibers are commonly made by blending high shrinkage and low shrinkage staple fibers or by blending relaxed and unrelaxed sliver from tow. The two staple products are made by variation in the fiber stabilization process. When the resulting yarn is allowed to relax, the high-shrink component causes the low shrinkage (relaxed) fiber to buckle and add bulk to the yarns.

Another method of producing high bulk yarns is the use of bicomponent fibers. Bicomponent fibers have developed from a desire to match the bulkiness and handle of wool. The three-dimensional crimp of animal fibers in general comes from the presence of two components on the fiber surface. Acrylic bicomponent fibers achieve three dimensional crimp by spinning two copolymer dopes into a single fiber. If the two streams are present in the same proportion in each spinneret hole, the process is “true” bicomponent; if the proportion varies from filament to filament, then it is a “random” bicomponent. To generate the spiral crimp, the two polymers must have different responses to heat or moisture. For example, if one polymer is more moisture-absorbent than the other, a crimp develops when the fiber is dried. The copolymers for this type of bicomponent may be acrylonitrile–vinyl acetate and acrylonitrile–vinyl acetate–sodium *p*-(vinylbenzene) sulfonate. In this combination, the copolymer containing the sulfonate moiety is the more moisture absorbent, and therefore shrinks the most on drying. This type of crimp is reversible because it can be renewed by wetting and redrying. Solutia’s A-21 and B-21 are examples of commercial water-reversible-crimp fibers. Crimp can also be imparted by using polymers that react differently to heat. By using copolymers of different compositions the crimp is imparted permanently when the fiber is heated. The copolymers for this type of bicomponent have a single comonomer, such as vinyl acetate or methyl acrylate, incorporated at two different levels.

True bicomponents require special spinnerets that provide the required dopes to each hole. In random-bicomponent technology, the second component is incorporated through a layering device prior to the spinneret. This concept is based on the fact that the viscous spinning solutions can be merged without complete mixing (65). When passed through a standard spinneret, bicomponent fibers are produced ranging in composition from 100% component A to 100% component B. For many years, this was the only bicomponent technology available to wet spinners.

8.6. Flame-Resistant Fibers. Acrylics have relatively low flame resistance, comparable to cotton and regenerated cellulose fibers. Additional flame resistance is required for certain end uses, such as children's sleepwear, blankets, carpets, outdoor awnings, and drapery fabrics. The only feasible route is copolymerization of acrylonitrile with halogen-containing monomers such as vinyl chloride, vinyl bromide, or vinylidene chloride. Modacrylics were developed for uses where a high resistance to burning is required. In such fibers, the level of halogen-containing units was up to 60%, as in Dynel, one of the earliest modacrylics. This fiber, no longer produced, was 40–60 acrylonitrile–vinyl chloride copolymer. Tennessee Eastman's Verel, an acrylonitrile-vinylidene chloride copolymer, has also been discontinued. Solutia's SEF modacrylic is the only remaining U.S. produced modacrylic flame-resistant fiber. It is produced solely in pigmented form as SEF FR for the commercial awning business. Kanekaron, another AN-vinyl chloride composition produced in Japan by Kanegafuchi, finds use in wigs, toys, pile and industrial filter fabrics.

There have been reviews of flammability (66–70), methods that can be used to enhance the flame resistance of acrylic and modacrylic fibers (71), and the mechanism of flame-retardant additives (72).

8.7. High Strength Fibers by Conventional Solution Spinning. As a reinforcing material for ambient-cured cement building products, acrylics offer three key properties: high elastic modulus, good adhesion, and good alkali resistance (73). The high modulus requires an unusually high stretch orientation. This can be accomplished by stretching the fiber 8 to 14X above its glass-transition temperature, T_g. Normally, this is done in boiling water or steam to give moduli of 8.8 to 13 N/tex (100–150 gf/den) (74,75). Alternatively, the stretch orientation can be achieved by a combination of wet stretch at 100°C and plastic stretch on hot rolls or in a heat-transfer fluid such as glycerol. This technique is reported to give moduli as high as 17.6 N/tex (200 gf/den) (76,77). Mitsubishi Rayon Co. reported an acrylic asbestos-replacement fiber with a tensile strength of almost 600 MPa (87,000 psi) (78). Many patents have been obtained for acrylic reinforcing fibers (79–82). The Acordis fiber, marketed under the trade name Dolanit, is offered in several forms (Table 4).

Acrylic fibers such as Dolanit (83) are blended in ambient-cured cement at a rate of 1–3%, compared with 9–15% by weight for asbestos. The flexural strength of cement sheets of acrylic-reinforced cement is equivalent to asbestos-reinforced cement and nearly double that of untreated cement (84). Two factors limiting the rapid development of acrylic asbestos-replacement fibers are a high manufacturing cost (compared to asbestos) and uncertainty as to the long-term stability of the acrylic fiber. Loss of modulus and chemical degradation may be significant over a period of decades. Other studies of acrylic fibers for concrete reinforcement have been carried out (85).

8.8. Carbon Fiber. Carbon fibers are valued for their unique combination of extremely high modulus and strength and low specific gravity. Precursors for carbon fiber can be pitch, rayon or acrylic fiber. Rayon offers a very low yield of

Table 4. **Properties of Dolanite Asbestos Replacement Fibers (7)**

	Dolanite type 10	Dolanite type 12			
filament fineness, dtex	1.5	0.7	1.7	2.2	8.2
staple length, mm	6, 12	40	50	60, 80	80
tenacity, cN/tex	80–87	65–70	65–70	54–58	43–47
elongation to break, %	8–12	15–20	15–20	13–16	14–17
boiling water shrink, %			1.5		
hot air shrink, % @ 150°C			1–2		
same, yam form @ 200°C			3–4		
hydrolysis resistance	Very good—after 350 h @ 130°C—93% tenacity remains				
resistance to acids	Very good—after 8 weeks @ 20°C in 50% sulfuric acid—85% tenacity remains				
heat resistance	Good—200 h @ 150°C 75% tenacity remains	Good—permanent operating temp, up to 125°C, peaks up to 140°C			

carbon fiber and is no longer used as a precursor. Pitch is useful for generating carbon fiber of exceptionally high modulus, but the predominant precursor is acrylic. Precursors are converted into carbon fibers in a two-stage thermal treatment—a medium temperature "oxidation" stage in air that renders the fiber infusible, and a high temperature "carbonization" treatment in an inert atmosphere, where the fiber is converted into nearly pure carbon. The polymer composition generally has about 98% AN and 2% of a weak acid such as itaconic or acrylic acid. The function of the acid is to provide a site to initiate the "ladder" formation in the oxidation step and thus lower the temperature at which the reaction occurs and reduce the exotherm. Acrylic precursors are usually made by air-gap spinning, as it allows higher line speed and the small bundle size is not a serious drawback. One exception is the Courtaulds (now Acordis) process which uses wet-spinning to produce a splittable tow; Toray is reported to use both wet- and air-gap processes to produce precursor. Increased stretch orientation is required to generate the high tenacity and modulus required in a precursor. It has been shown that precursor properties translate directly to carbon fiber properties (86). Precursor fiber is roll dried and not relaxed subsequent to drying. Special attention must be paid to the electrolyte content of the fiber and to drying conditions in order to produce a precursor which will perform well in oxidation and carbonization. The use of PAN as a carbon-fiber precursor has been reviewed (87,88).

8.9. Other Specialty Fibers. *Microdenier.* In the late 1980s, producers of polyester introduced "microdenier" products that offered softer, more luxuriant handle to fabrics. Some acrylic producers have followed. There are no appreciable technical hurdles to producing a fiber with a denier of 0.6–0.9 (0.66–1.00 dtex), but unless commensurate changes are made in line speed or the number of spinneret holes, productivity will suffer. Acrylic microfibers on the market are all staple products, with Sterling in the United States producing a 0.8 dpf acrylic staple product named MicroSupreme and Solutia a 0.95 dpf product called Ginny. Mitsubishi Rayon offers H-129 (1.0 dtex).

Antimicrobial. For certain end-uses such as half-hose, the ability to inhibit the growth of bacteria and fungi provides a marketing advantage. Several

Table 5. **World Acryfic Fiber Production 2003**

Country	Company	Location	Process	Capacity kMT	Comments
Belarus	Novepolosk Polimir	Novopolotskos	susp NaSCN wet	25	10 mod. (acetone)
	Novepolosk Polimir	Novopolotskos	sol DMF wet	35	
Bulgaria	Dimilar Dimov	Burgas	susp DMF wet	15	
Germany	Fraver	Dormagen	susp DMF dry	115	
		Lingen	susp DMAc wet	60	
	Acordis	Kelheim	susp DMF wet	11	
	Markische Faser	Premnitz	susp DMF wet	shut	capacity 48
Hungary	Zottek	Nyergesujfalu	susp DMF wet	35	5 precursor
Italy	Montefibre	Porto Marghera	susp DMAc wet	150	
		Ottana	susp DMAc wet	90	
Macedonia	OHIS	Skopje	sol NaSCN wet	60	operates intermittently
Portugal	Fisipe	Lisbon	susp DMAc wet	50	
Romania	Melana	Savintsa	emul acetone wet	46	modacrylic
Spain	Fisipe	Prat de Liobroget	sol NaSCN wet	70	
	Montefibra	Miranda del Ebro	susp DMAc wet	85	
Russia	JS Nitron	Saratov	sol NaSCN wet	23	
Uzbekistan	Navolazot Production Assn.	Navol	sol NaSCN wet	23	
United Kingdom	Acordis	Grimsby	sol NaSCN wet	80	
total Europe				*973*	
Argentina	Noy Valesina	Varnedero	sol DMF wet	20	
Brazil	Sudamericas de Fibras	Camacari	susp DMF dry	shut	capacity 25
	Crylor Industria	San Jose Dos Campos	susp DMF wet	25	
Maxico	CYDSA	El Salto, Jalisco	susp DMF wet	100	
	Fibras Sinteticas	Cotaxia, Verscruz	susp HNO_3 wet	28	
	Fibras Nationales de Acrilica	Attamira, Tarrautipes	sol DMF wet	50	
Peru	Fibras Sudamericanas	Lima	susp DMF dry	36	
USA	Hexcel	Decatur AL	susp NaSCN air	4	
	Solutia	Decatur AL	susp DMAc wet	145	
	Sterling	Pace FL	susp NaSCN wet	40	

total Americas				*428*	
Japan	Asahi	Fuji	susp HNO_3 wet	shut	capacity 96
	Japan Exlan	Saldalji	susp NaSCN wet	59	
	Kanebo	Hofu	susp DMF wet	38	
	Kanegafuohl	Takasago	emul acetone wet	56	
	Mitsubishi Rayon	Otake	susp DMAc wet	119	
	Mitsubishi Rayon	Otake	susp DMF dry	5	
	Toho Rayon	Mishima	sol $ZnCl_2$ wet	50	
	Toray	Ehima	sol DMSO wet	44	
total Japan				*370*	
China	Anqing Petrochemical	Anqing. Anhul Prov.	susp NaSCN wet	70	
	Deqing Petrochem Acry. Fiber	Deqing, Helionggijang P.	susp NaSCN wet	54	
	Dequing Petrochem Chem Fiber	Deqing, Helionggijang P.	susp NaSCN wet	10	
	Deqing Refin-chem Acry. Fiber	Deqing, Helionggijang P.	susp NaSCN wet	30	
	Fushun Petrochem. Acryfic	Fushun, Liaoning Prov.	susp DMF dry	30	
	Fushon Flame-retard. Acry.	Fushun, Liaoning Prov.	susp acetone dry	5	
	Gaoglao No. 2 Chemical Plant	Shanghai	sol NaSCN wet	7.5	
	Jllin Chemical Fiber	Jllin, Jllin Prov.	susp DMAc wet	70	
	Jinyong Acrylic Fiber Co.	Zhejiang Prov.	susp DMF dry	30	
	Lanzhou Chemical Fiber Plant	Lanzhou, Gansu Prov.	susp NaSCN wet	20	
	Maoming Acrylic Fiber Co.	Maoming, Guangdong P	susp DMF dry	30	
	Qinghuangdao Acrylic Fibre	Cinghuangdao, Hebel P.	susp DMF dry	50	
	Qilu Petrochem. Acry. Fiber	Zibo, Shandong Prov.	susp DMF dry	54	
	Shanghai Petrochemical	Shanghai	susp DMF dry	120	
	Xunyin Chemical Fiber Co.	Zibo, Shandong Prov.	sol NaSCN wet	28	
total China				*608.5*	
Indonesia	Golden Key	Serang	susp DMF dry	shut	capacity 40
India	Consolidated Fibres	Haldia W. Bengal	susp NaSCN wet	shut	capacity 12
	Indian Acrylics	Sangrur Punjab	susp DMAc wet	36	
	J. K. Synthetics	Kota Rajasthan	susp DMAc wet	shut	
	Indian Petrochemicals	Baroda Gujarat	susp HNO_3 wet	15	
	Indian Petrochemicals	Baroda Gujarat	susp DMF dry	12	

Table 5 (*Continued*)

Country	Company	Location	Process	Capacity kMT	Comments
	Pasupati Acrylon	Thakurdwada, Uttar Pradesh	susp DMF wet	20	
	Vardhman	Gujarat	susp NaSCN wet	17	
Pakistan	Dewan Saiman	Hattar, North-west Frontier		25	
South Korea	Hanil	Masan, Kyongsangnam-do	susp HNO_3 wet	90	
	Tae Kwang Idustrial Co.	Ulsan, Kyongsangnam-do	susp NaSCN wet	92	
Taiwan	Tong Hwa Synthetic Fiber	Chupel City, Hsinchu Halen	susp NaSCN wet	54	
	Formosa Plastic	Jenwu, Kaoshlung Hslen	susp HNO_3 wet	95	
Thailand	Thal Acrylic Fiber	Sara Buri	susp NaSCN wet	57	
total Other Asia				*513*	15.9%
Iran	Polyacryl Iran	Isfahan	susp DMF dry	39	
South Africa	Sasol Industries	Durban	sol NaSCN wet	shut	capacity 40
Turkey	Aksa	Yalova	susp DMAc wet	255	
	Yalova Elyaf	Yalova	susp DMF wet	35	
total Middle East				*329*	
total World				*3221.5*	

producers offer acrylics which have this characteristic. The antimicrobial effect is achieved by incorporating an additive such as chitosan (from chitan, a polysaccharide from the exoskeleton of crusteations), metal ions or chlorinated phenols. Commercial examples are New Tafel and Parclean from Mitsubishi Rayon and BioFresh from Sterling.

Fibrillated Fibers. Acrylic fibers are sold in the form of fibrillated pulps for use as highly efficient binders. These fibrillated fibers have a tree-like structure with "limbs" (fibrils) attached to the main "trunk" (fiber). The trunk is 20–50-μ diameter and the limbs range from a few microns to submicron. The product is generated from a special precursor fiber by intense mechanical action. Commercial examples are CCF from Sterling Fibers, Acri-Pulp from Solutia and Dolanit 10D from Acordis.

Dry pulps are used in dry mix compounding applications such as nonasbestos friction materials. In these applications the product provides green strength for friction material performs. As little as a few percent pulp is required.

Wet pulps are used in specialty paper applications such as speaker cones, filtration, and specialty papers. These pulps have been successfully processed on cylinder, rotoformer and Fourdrinier paper machines. As little as 15% of a highly fibrillated pulp can interlock other fibers or powders without the need for resin binders.

Conductive Fibers. Acrylic conductive fibers are used in areas where electrostatic discharge is a problem such as electronic device manufacture. Here the applications include dissipative clothing, flooring and work surfaces. Another application is solids–air filtration where discharge has the potential to trigger an explosion. Sterling Fibers manufactures Contructrol, which utilizes a combination of condutive carbon in the fiber and a conductive polymer attached to the fiber surface. Tex-Stat markets Thunderon, which uses a chemically bonded copper sulfide technology.

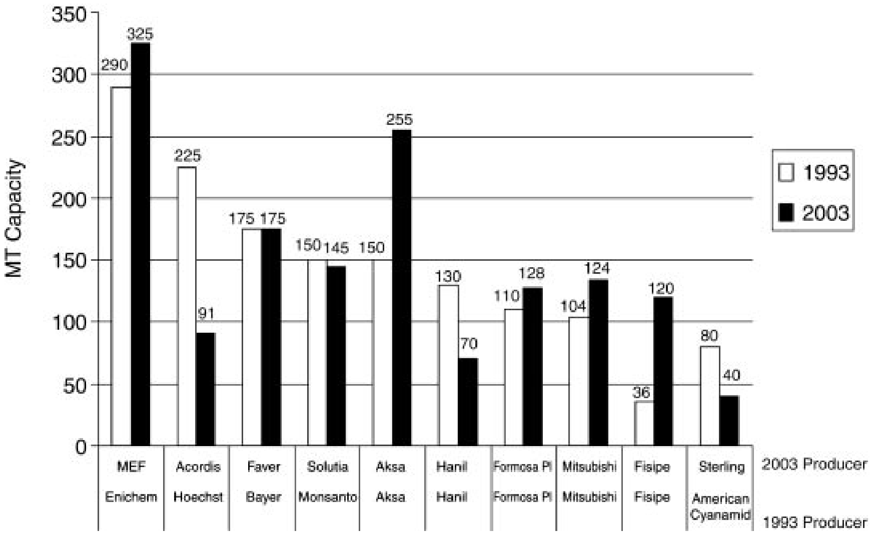

Fig. 15. Leading acrylic producers.

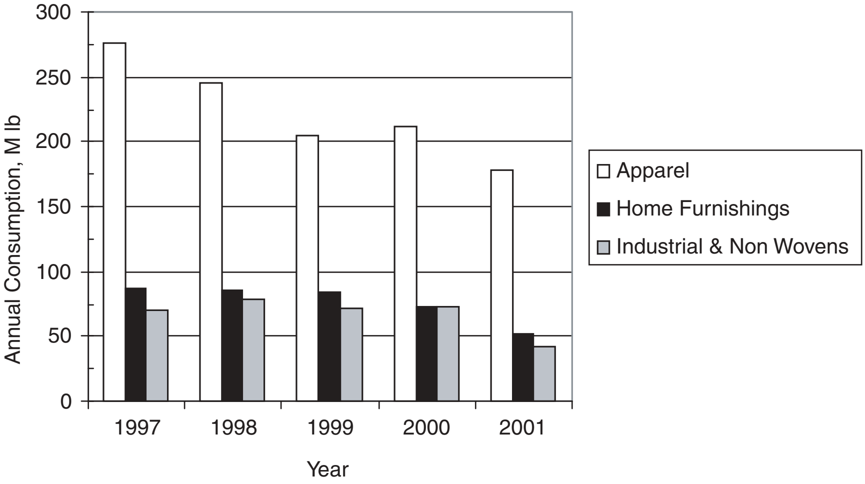

Fig. 16. U.S. acrylic fiber consumption (excluding carbon fibers).

9. Economic Aspects

As has been mentioned earlier, the focus of acrylic production has moved to Asia, which now accounts for 46% of world capacity. The most recent information on world acrylic capacity is listed in Table 5 (89). China leads in building new acrylic capacity with 16 plants as of 2000 and 19% of world capacity versus 8 plants and 9% of world capacity only seven years earlier (90). Conversely, Europe, which had 38% of capacity in 1993, now has 29%. The changes in capacity and ownership of the major producers are shown graphically in Figure 15.

Markets for acrylic fiber in developed countries have been stagnant or declining as shown in the example for the United States in Figure 16. Many acrylic articles such as sweaters come into the U.S. as finished goods from Asia. The volumes consumed in U.S. apparel markets are shown in Table 6. All developed countries face a similar situation due to the disparity of labor costs. Losses of volume in western Europe in the late 1990s have been less severe than in the United States, but still ominous as shown in Table 7 (91). The next decade will likely continue the exodus of capacity from the United States, Europe, and Japan.

Table 6. **U.S. Shipments of Acrylic and Modacrylic for Apparel Markets (k MT)**

Year	Sweaters	Socks	Craft	Pile	Fleece
1995	24.1	9.5	11.8	6.4	28.6
1996	25.0	9.1	11.8	6.4	33.6
1997	30.0	10.0	10.0	8.2	27.3
1998	22.3	10.5	9.1	8.6	21.8
1999	14.1	8.6	9.1	7.7	15.9

Table 7. **Western European Consumption of Acrylic Fiber (k MT)**

Year	Weaving	Knitting	Carpet	Others	Total
1995	77	201	12	12	302
1996	76	225	10	12	323
1997	52	280	7	7	346
1998	48	248	7	7	310
1999	48	244	11	7	310
2000	43	245	6	7	301

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