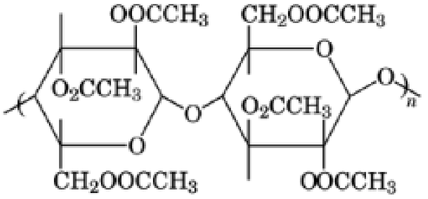
Kirk-Othmer Encyclopedia of Chemical Technology.

FIBERS, CELLULOSE ESTERS

The predominant cellulose ester fiber is cellulose acetate, a partially acetylated cellulose, also called acetate or secondary acetate. It is widely used in textiles because of its attractive economics, bright color, styling versatility, and other favorable aesthetic properties. However, its largest commercial application is as the fibrous material in cigarette filters, where its smoke removal properties and contribution to taste make it the standard for the cigarette industry. Cellulose triacetate fiber, also known as primary cellulose acetate, is an almost completely acetylated cellulose. Although it has fiber properties that are different, and in many ways better than cellulose acetate, it is of lower commercial significance primarily because of environmental considerations in fiber preparation.

1. Polymer Characteristics

Cellulose triacetate is obtained by the esterification of cellulose(qv) with acetic anhydride (see Cellulose esters). Commercial triacetate is not quite the precise chemical entity depicted as **1** because acetylation does not quite reach the maximum 3.0 acetyl groups per glucose unit. Secondary cellulose acetate is obtained by hydrolysis of the triacetate to an average degree of substitution (DS) of 2.4 acetyl groups per glucose unit. There is no satisfactory commercial means to acetylate directly to the 2.4 acetyl level and obtain a secondary acetate that has the desired solubility needed for fiber preparation.



(1)

The degree of acetylation is specified by two separate terms: acetyl value (%) and combined acetic acid (%). The ratio of these two values is always 43:60, reflective of the molecular-weight ratio of the acetyl group to acetic acid. Acetyl and combined acetic acid values over the possible range of acetyl contents are shown in Figure 1. Commercial cellulose triacetate [9012-09-3] has a combined acetic acid content of 61.5%, corresponding to 2.92 acetyl groups per glucose unit. Cellulose acetate [9004-35-7], with 2.4 acetyl groups per glucose unit, has a combined acetic acid content of approximately 55%.

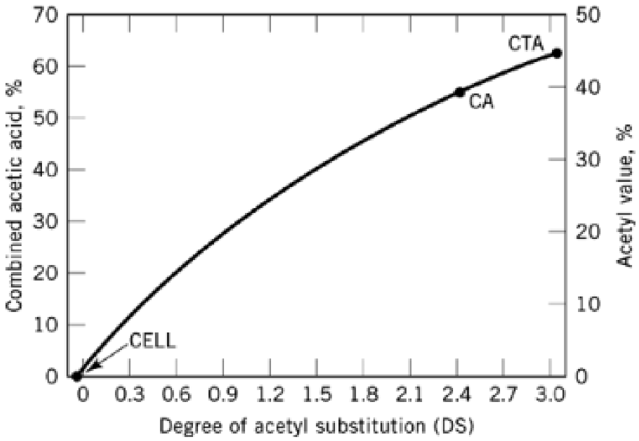


Fig. 1. Acetyl value and combined acetic acid for acetate esters of cellulose. Designations are as follows: CA=acetate(DS=2.4); CELL=cellulose(DS=0); CTA=triacetate(DS=3.0). Combined acetic acid (%)=6005(DS)/(159.1+43.04(DS)); acetyl value (%)=4304(DS/(159.1+43.04(DS)).

2. Fiber Properties

The performance of a textile fabric is characterized by terms such as strength, hand, drape, flexibility, moisture transport, and wrinkle resistance. Although the interactions among fibers in a fabric array are complex, its properties reflect in part the inherent properties of the fiber as well as how the fibers are assembled.

2.1. Mechanical Properties

The mechanical properties of a fiber are characterized by classical stress–strain and recovery behavior under conditions of tensile, torsional, bending, and shear loading. Typical stress–strain curves indicative of most commercial acetate and triacetate yarns are shown in Figures 2 and 3. It is common to use the ultimate stress or breaking strength to characterize the fibers' tensile properties. The units of tensile stress, or tenacity, are Newtons/tex (gram force/denier) and the strain is given as a percentage of elongation. Temperature and moisture content of the fiber affect viscous behavior and hence modify the stress–strain relationship. Most stress–strain data are reported under standard conditions of 21°C and 65% rh.

Acetate and triacetate have a tenacity in the range of 0.10–0.12 N/tex (1.1–1.4 gf/den) with a breaking elongation of about 25–30%. Compared to other common textile fibers, acetate and triacetate are relatively weak, eg, 20–25% the tenacity of polyester. This is not necessarily a disadvantage because fabric construction can be used to obtain the desired fabric performance targets. Pilling, the accumulation of fuzz balls on the fabric with wear, is not a problem as it is with the higher tenacity fibers. Figures 4 and 5 also show that moisture or heat can significantly impact the stress–strain behavior.

The ratio of stress to strain in the initial linear portion of the stress–strain curve indicates the ability of a material to resist deformation and return to its original form. This modulus of elasticity, or Young's modulus, is related to many of the mechanical performance characteristics of textile products. The modulus of elasticity can be affected by drawing, ie, elongating the fiber; environment, ie, wet or dry, temperature; or other procedures. Values for commercial acetate and triacetate fibers are generally in the 2.2–4.0 N/tex (25–45 gf/den) range.

The wet modulus of fibers at various temperatures influences the creasing and mussiness caused by laundering. Figure 6 shows the change with temperature of the wet modulus of acetate and triacetate, and

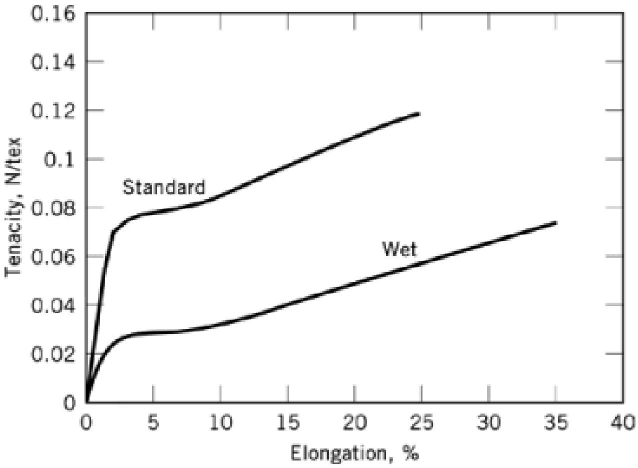


Fig. 2. Cellulose acetate stress–strain properties at standard and wet conditions, tested at 60% min extension rate, 3.9 cm gauge length. Sample conditions: standard, 21°C, 65% rh; wet, 21°C, water wet. To convert N/tex to gf/den, multiply by 11.33.

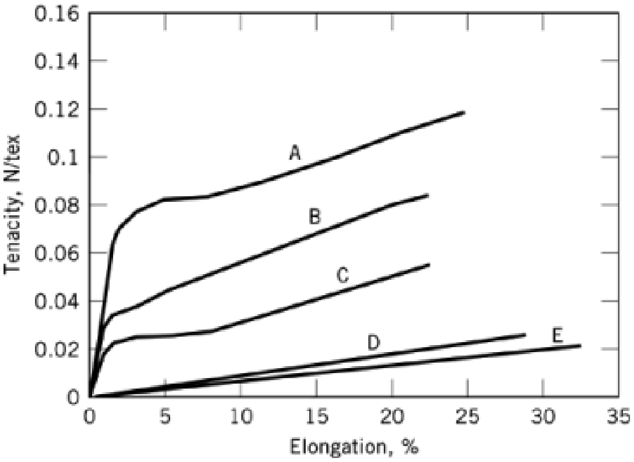


Fig. 3. Cellulose triacetate stress–strain properties at different temperatures (1). A, 21°C, 65% rh; B, 100°C, 150°C; D, 175°C; and E, 205°C. Tested at 60% min extension rate, 3.9 cm gauge length. To convert N/tex to gf/den, multiply by 11.33.

compares them with a number of other fibers (2). Acetate, triacetate, and rayon behave quite similarly, with a lower sensitivity than acrylic.

The ability of a fiber to absorb energy during straining is measured by the area under the stress–strain curve. Within the proportional limit, ie, the linear region, this property is defined as toughness or work of rupture. For acetate and triacetate the work of rupture is essentially the same at 0.022 N/tex (0.25 gf/den). This is higher than for cotton (0.010 N/tex = 0.113 gf/den), similar to rayon and wool, but less than for nylon (0.076 N/tex = 0.86 gf/den) and silk (0.072 N/tex = 0.81 gf/den) (3).

A fiber that is strained and allowed to recover releases a portion of the work absorbed during straining. The ratio of the work recovered to the total work absorbed, measured by the respective areas under the stress–strain and stress–recovery curves, is designated as resilience.

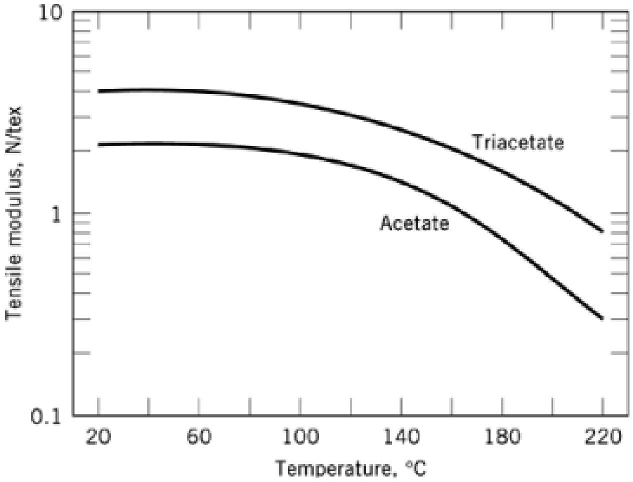


Fig. 4. Tensile modulus as a function of temperature. To convert N/tex to gf/den, multiply by 11.33.

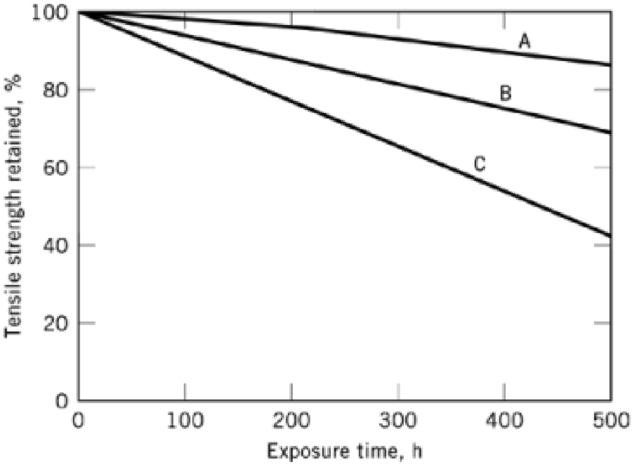


Fig. 5. The effect of dry heat exposure on acetate and triacetate fibers. Tested at 65% rh, 21°C after exposure. A, acetate, 100°C; B, triacetate, 130°C; and C, acetate, 120°C.

The elongation of a stretched fiber is best described as a combination of instantaneous extension and a time-dependent extension or creep. This viscoelastic behavior is common to many textile fibers, including acetate. Conversely, recovery of viscoelastic fibers is typically described as a combination of immediate elastic recovery, delayed recovery, and permanent set or secondary creep. The permanent set is the residual extension that is not recoverable. These three components of recovery for acetate are given in Table 1 (4). The elastic recovery of acetate fibers alone and in blends has also been reported (5). In textile processing strains of more than 10% are avoided in order to produce a fabric of acceptable dimensional or shape stability.

The bending properties of a fiber generally depend on the viscoelastic behavior of the material. In most textile applications, the radius of curvature of bending is relatively large, and the imposed strains are of a low order of magnitude. As a first approximation, the bending stiffness or flexural rigidity of a fiber is the product of the bending modulus and the moment of inertia of the cross section. For fibers of round cross section and

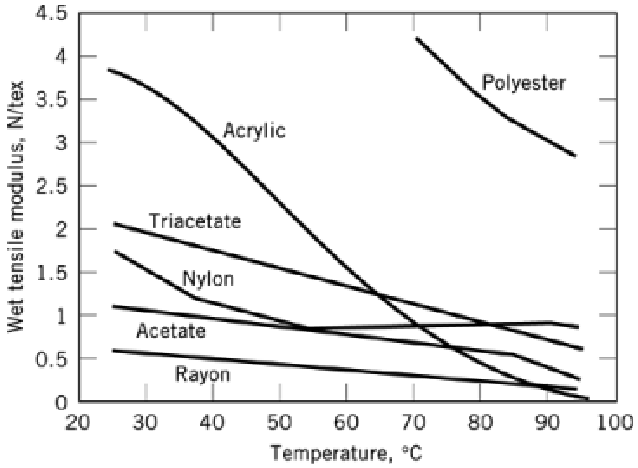


Fig. 6. The effect of water temperature on the wet modulus of fibers. To convert N/tex to gf/den, multiply by 11.33.

Table 1. Elongation Recovery of Acetate Fibers[a]

Fiber	Immediate elastic recovery, %	Delayed recovery, %	Permanent set, %
acetate multifilament			
at 50% of breaking tenacity	74	26	0
at breaking point	14	16	70
acetate staple yarn			
at 50% of breaking tenacity	58	42	0
at breaking point	12	18	70

[a] Ref. 4.

constant modulus, the flexural rigidity varies directly with the square of the tex. Torsional and shear properties of acetate and other fibers are discussed in Reference 6. Table 2 shows some additional mechanical properties characteristic of commercial acetate and triacetate fibers.

2.2. Absorption and Swelling Behavior

The absorption of moisture by acetate and triacetate fibers generally depends on the relative humidity and whether equilibrium is approached from the dry or wet side. This hysteresis effect is noted over the entire range of relative humidities, as shown in Figure 7 (7). The percentage of moisture regain of commercial fibers (ASTM D1909-68), taken at 65% relative humidity for the absorption cycle, is 6.5 for acetate fiber and 3.5 for triacetate (8). Heat treatment can lower the moisture regain of triacetate fiber, and values of 2.5–3.2% have been observed (9, 10). Sorption isotherms have been analyzed in terms of the BET adsorption isotherms (11).

Percentage of water imbibition is an important property in ease-of-care and quick-drying fabrics. This value is determined by measuring the moisture remaining in a fiber in equilibrium with air at 100% rh while the fiber is being centrifuged at forces up to 1000 g. The average recorded value for acetate is 24%; triacetate not heat-treated, 16%; and heat-treated triacetate, 10%.

Absorption of water by fibers generally causes swelling roughly proportional to the moisture content. The average increase in length of acetate fibers due to water absorption is ca 1%, and the average cross-sectional

Table 2. Tenacity and Elongation of Commercial Acetate and Triacetate Fibers

Properties	Value
Tenacity, N/tex[a]	
standard conditions[b]	0.10–0.12
knot	0.09–0.10
loop	0.09–0.10
wet	0.07–0.09
bone dry	0.12–0.14
Elongation at break, %	
standard conditions[b]	25–45
wet	35–50

[a] To convert N/tex to gf/den, multiply by 11.33.
[b] Standard conditions are 65% relative humidity, 21°C.

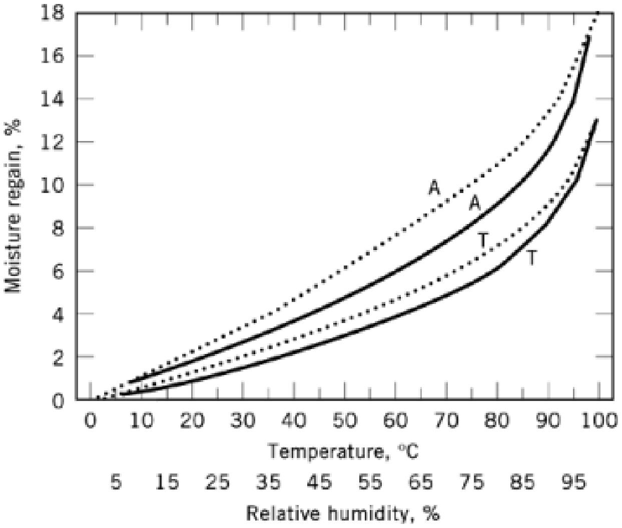


Fig. 7. Moisture regains of cellulose acetate (A) and triacetate (T) fibers. Moisture content on a bone-dry basis, measured at 22°C: (___), absorption cycle; (....), desorption cycle.

increase is ca 10%. The corresponding values for triacetate fiber are lower, ie, a 1.5% increase in cross-sectional area for heat-treated triacetate fiber and a 4.0% increase for fiber not heat-treated (12). Increasing the relative humidity from 0 to 100% causes acetate to elongate about 2% as compared to 3.4% for rayon, 2.4% for nylon, and less than 0.3% for acrylics and polyester.

2.3. Specific Gravity

Fiber cross sections are often irregular and specific gravity is measured by an immersion technique. The values of 1.32 for acetate and 1.30 for triacetate are accepted for fibers of combined acetic acid contents of 55 and 61.5%, respectively (13–15).

2.4. Refractive Index

The refractive index parallel to the fiber axis (ϵ) is 1.478 for acetate and 1.472 for triacetate. The index perpendicular to the axis (ω) is 1.473 for acetate and 1.471 for triacetate. The birefringence, ie, the difference between ϵ and ω, is very low for acetate fiber and practically undetectable for triacetate.

2.5. Thermal Behavior

As with most thermoplastic fibers, acetate sticks, softens, and melts. Sticking and softening temperatures depend on geometric factors, eg, yarn diameter and fabric construction, and are not necessarily directly related to the fiber melting point. Acetate softens and sticks in the 190–205°C range, and fuses at ca 260°C. The apparent shining or glazing temperature is usually lower than the sticking temperature. The sole-plate temperature of an iron should not exceed 170–180°C when used on acetate fabrics. The sticking and glazing temperatures of untreated triacetate fiber are in the same range as those of acetate, whereas those exhibited by heat-treated triacetate fibers are considerably higher. Fabrics made of the latter can be ironed at temperatures as high as 240°C. The melting point of triacetate is ca 300°C.

Acetate and triacetate exhibit moderate changes in mechanical properties as a function of temperature. As the temperature is raised, the tensile modulus of acetate and triacetate fibers is reduced, and the fibers extend more readily under stress (see Fig. 4). Acetate and triacetate are weakened by prolonged exposure to elevated temperatures in air (see Fig. 5).

2.6. Light Stability

The resistance of textile fibers to sunlight degradation depends on the wavelength of the incident light, relative humidity, and atmospheric fumes. Acetate and triacetate fibers have essentially the same light-absorption characteristics in the visible spectrum; absorption in the uv region is slightly higher. Both fibers, when exposed under glass, behave similarly to cotton and rayon, ie, they are somewhat more resistant than unstabilized pigmented nylon and silk and appreciably less resistant than acrylic and polyester fibers. When acetate and triacetate are exposed to weathering, their resistance is lower than when exposed under glass. Certain pigments, eg, carbon black or the rutile form of titanium dioxide, offer some increased protection from sunlight exposure.

2.7. Electrical Behavior

The resistivity of acetate varies significantly with humidity with typical values ranging from $10^{12}\ \mathrm{ohm{\cdot}cm}$ at 45% rh to $10^{7}\ \mathrm{ohm{\cdot}cm}$ at 95% rh (16). Because of the high resistivity both acetate and triacetate yarns readily develop static charges and an antistatic finish is usually applied to aid in fiber processing. Both yarns have also been used for electrical insulation after lubricants and other finishing agents are removed.

2.8. Dyeing Characteristics

Disperse dyes, high melting crystalline compounds with low solubility in the dye bath, are most frequently used for cellulose acetate and triacetate fibers. They are milled to very small particle size, permitting effective dispersion without agglomeration in the dye bath, and diffuse into the fiber to give a uniform color. Dyebath temperature and fiber composition affect the diffusion-controlled dyeing rate. Triacetate fibers are dyed more slowly than acetate fibers; dye carriers accelerate the rate (1, 17–22). Selection of the appropriate azo, anthraquinone, or diphenylamine disperse dye ensures good colorfastness. Fading inhibitors are used to counteract the effects of nitrogen oxides and ozone. Dyed triacetate fabrics, which are subsequently heat-treated

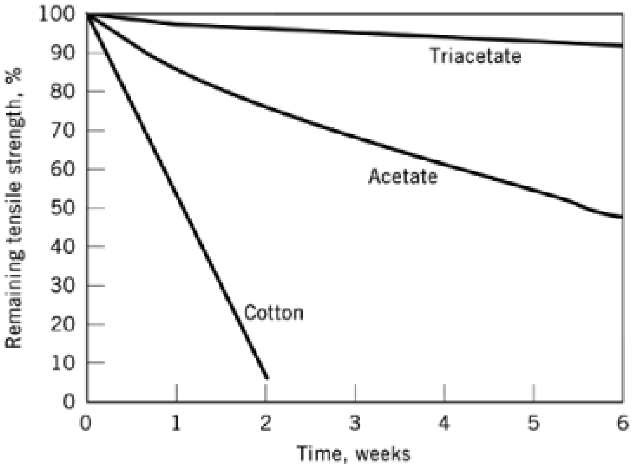


Fig. 8. The resistance of cellulose fibers to biological attack via soil-burial testing.

to raise the safe ironing temperature, drive the dye further into the fiber to increase fading resistance and improve colorfastness (see Dyes, application and evaluation).

Colored acetate and triacetate yarns are produced by incorporating colored pigments (inorganic or organic), soluble dyes, or carbon in the polymer solution before extrusion. Solution-dyed acetate and triacetate yarns are extremely colorfast to washing, dry cleaning, sunlight, perspiration, seawater, and crocking, and usually surpass the performance of vat-dyed yarns. In addition, acetate and triacetate dyed by conventional methods are susceptible to gases or fumes and fade; such fading is absent in solution-spun, pigment-dyed yarn.

2.9. Chemical Properties

Under slightly acidic or basic conditions at room temperature, acetate and triacetate fibers are resistant to chlorine bleach at the concentrations normally used in laundering.

Triacetate fiber is significantly more resistant than acetate to alkalies encountered in normal textile operations. Temperatures no higher than 85°C and pH no more than 9.5 are recommended for dyeing. Under normal scouring and dyeing conditions, alkalies up to pH 9.5 and temperatures up to 96°C may be used with triacetate with little saponification or delustering. Heat-treated triacetate fiber exhibits even higher alkali resistance (23). Strong alkalies and boiling temperatures saponify triacetate as well as acetate fiber.

Acetate and triacetate are essentially unaffected by dilute solutions of weak acids, but strong mineral acids cause serious degradation. The results of exposure of heat-treated and untreated triacetate taffeta fabrics to various chemical reagents have been reported (9). Acetate and triacetate fibers are not affected by the perchloroethylene dry-cleaning solutions normally used in the United States and Canada. Trichloroethylene, employed to a limited extent in the UK and Europe, softens triacetate.

2.10. Resistance to Microorganisms and Insects

Resistance of triacetate to microorganisms, based on soil-burial tests, is high, approaching that of polyester, acrylic, and nylon fibers. Soil-burial test results on acetate, triacetate, and cotton are shown in Figure 8. Neither acetate nor triacetate fiber is readily attacked by moths or carpet beetles.

3. Manufacture

3.1. Cellulose Acetate and Triacetate Polymer

The production of acetate and triacetate polymer is accomplished by the esterification of high purity chemical cellulose with acetic anhydride (24–26); wood pulp is the principal source of the chemical cellulose, except for special plastic-grade acetates requiring low color and high clarity, where cotton linters are used. A high degree of cellulose purity is needed to assure complete polymer solubility for the preparation of fibers, since the hemicellulose impurities form undesirable gels (27). Acetylation-grade wood pulp ideally has a 95–98% alpha-cellulose content, but strong economic incentives have led to the commercialization of 92–93% alpha-cellulose wood pulps. The other raw materials, ie, acetic acid, acetic anhydride, and sulfuric acid, are commercially available in high purity grades.

3.2. Secondary Acetate Processes

There is no commercial process to directly produce secondary cellulose acetate sufficiently soluble in acetone to produce fiber. Hence, the cellulose is completely acetylated to the triacetate during the dissolution step and then hydrolyzed to the required acetyl value.

Most cellulose acetate is manufactured by a solution process, ie, the cellulose acetate dissolves as it is produced. The cellulose is acetylated with acetic anhydride; acetic acid is the solvent and sulfuric acid the catalyst. The latter can be present at 10–15 wt % based on cellulose (high catalyst process) or at ca 7 wt % (low catalyst process). In the second most common process, the solvent process, methylene chloride replaces the acetic acid as solvent, and perchloric acid is frequently the catalyst. There is also a seldom used heterogeneous process that employs an organic solvent as the medium, and the cellulose acetate produced never dissolves. More detailed information on these processes can be found in Reference 28.

The solution process consists of four steps: preparation of cellulose for acetylation, acetylation, hydrolysis, and recovery of cellulose acetate polymer and solvents. A schematic of the total acetate process is shown in Figure 9.

3.3. Preparation for Acetylation

Wood pulp is customarily supplied in rolls weighing up to 300 kg, but can also be obtained in bales of individual sheets. The pulp sheet must be dispersed without damaging individual fibers to generate sufficient surface area for complete acetylation. Some manufacturers use a disk refiner, others use wet methods. In one example, to further increase accessibility the fluffed pulp is agitated with an acetic acid–water mixture for ca 1 h at 25–40°C. An activation stage is generally included in the low catalyst process using an acetic acid–sulfuric acid mixture with a sulfuric acid concentration of ca 1–2% of the pulp weight. The activation may last for 1–2 h, during which the degree of polymerization of the cellulose is reduced. A controlled combination of activation time and temperature achieves the desired degree of polymerization. A separate activation step is usually not included in the high catalyst procedure. The degree of polymerization is further controlled by the conditions selected during acetylation and hydrolysis. The pulp is subsequently charged to the acetylation reactor after pretreatment and activation.

3.4. Acetylation

The esterification of cellulose with acetic anhydride liberates 1.03 kJ/g (246 cal/g) of cellulose, and the reaction of acetic anhydride with water from the pretreatment generates 3.30 kJ/g (789 cal/g) of water. Hence, a heat sink is needed for the two exothermic reactions that occur in the acetylation process. In high catalyst acetylation, heat is generated quickly, and a jacketed vessel does not provide the necessary cooling capacity for the viscous

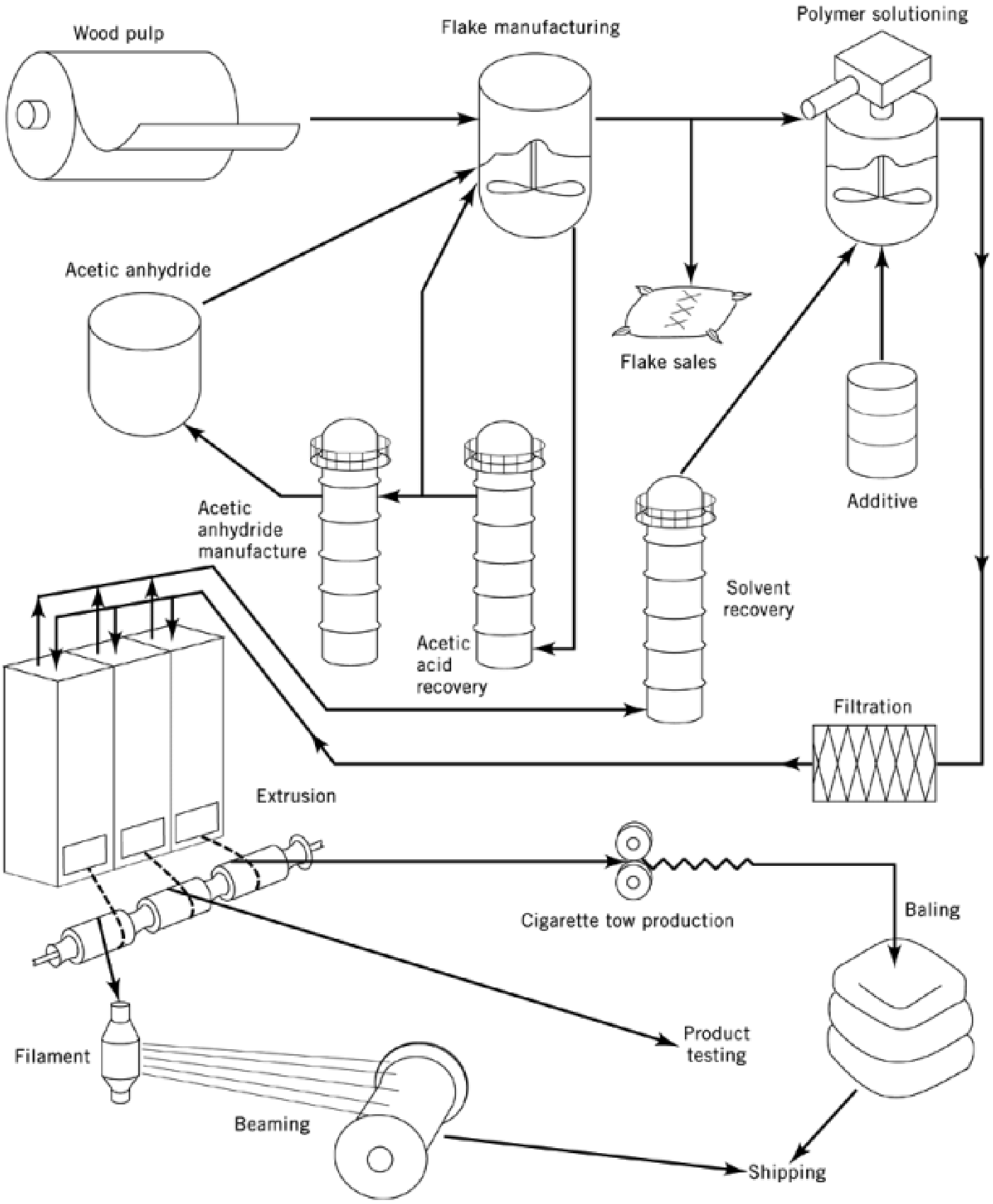


Fig. 9. Cellulose acetate process.

mixture. Hence, the acetylation mixture is prechilled in a separate vessel called a crystallizer, and some of the acetic acid freezes and provides a readily accessible heat sink. This is particularly important in the early stages of acetylation, in which a rapid temperature rise would uncontrollably reduce the degree of polymerization. To improve process economics, attempts are made to acetylate at the highest possible temperature (29). In the low catalyst process, heat is generated more slowly, and cooling in a jacketed vessel is satisfactory. In the methylene chloride process, the required heat transfer is provided by refluxing the solvent. In either process, a 5–15 wt % excess of acetic anhydride ensures complete reaction. A series of simultaneous, complex reactions occurs during acetylation (24–26).

When the acetylation is completed, microscopic examination of the solution should reveal no undissolved residues. The reaction is terminated by adding water to destroy the excess anhydride and provide a water concentration of 5–10% for hydrolysis. A 10–25% cellulose acetate concentration is typical.

All commercial acetylation processes are essentially heterogeneous, even though the final polymer is soluble in the solvent. Much of the original cellulose crystalline structure is retained in the acetate or triacetate (30). A truly homogeneous process, although not commercial, is attractive from a technical standpoint. Several solvents permit nondegradative dissolution of the cellulose, eg, dimethylformamide–dinitrogen tetroxide, dimethyl sulfoxide–formaldehyde, dimethylacetamide–lithium chloride, and *N*-methylmorpholine oxide (31–38). Cellulose in solution can be esterified uniformly and directly to the desired degree of substitution; hydrolysis to obtain solubility in acetone is not necessary. Homogeneous acetylation with acetyl chloride in dimethylformamide–chloralpyridine reportedly produces a chloral-containing cellulose acetate (39). Dissolution of cellulose in dimethylformamide–dinitrogen tetroxide followed by sulfuric acid treatment produces an acetic acid-soluble cellulose sulfate which is directly acetylated to an acetone-soluble cellulose acetate (40). The homogeneous process offers the advantage of good quality acetate flake from lower purity wood pulps. The disadvantage is the cost of solvent recovery.

3.5. Hydrolysis

The number of acetyl groups present on each anhydroglucose unit at the completion of the acetylation is slightly less than 3.0 and must be reduced to ca 2.4 to prepare secondary cellulose acetate soluble in acetone. The number of acetyl groups is reduced and the combined sulfate groups are minimized by acid hydrolysis under controlled time, temperature, and acidity. The sulfate groups, which are hydrolyzed more easily than the acetyl groups, increase the acidity of the reaction. In high catalyst acetylation, for example, a portion of the sulfuric acid is neutralized, eg, by the addition of sodium acetate or magnesium acetate, to prevent excessive depolymerization of the cellulose acetate. The hydrolysis temperature is normally 50–100°C and the reaction time varies from 1 to 24 h. Hydrolysis can also be conducted at other conditions. For example, when conducted at higher temperatures (41) there is polymer degradation and reduced yield.

3.6. Polymer Recovery

Precipitation, washing, and drying are the final steps in polymer preparation. Precipitation is initiated by treating the hydrolyzed cellulose acetate solution with a stream of dilute (10–15%) acetic acid to the point of incipient precipitation. More dilute acetic acid is rapidly added and the solution vigorously agitated. To obtain a powder precipitate, the agitated solution is slowly diluted until precipitation occurs. Another process involves extrusion of the hydrolyzed solution through small holes into a precipitating acid bath; this produces fine strands which are cut into pellets.

The precipitated cellulose acetate is filtered from the dilute (25–36%) acetic acid. The acetic acid and salts remaining from the sulfuric acid neutralization are removed by washing. The wet polymer is typically dried to a moisture content of 1–5%. The dilute acetic acid obtained from the washing and precipitation steps cannot be used in other stages of the process. Its efficient recovery and recycle are an economic necessity.

If thermal stability and absence of yellowing upon heating are critical, for example in thermoplastic molding applications, any remaining sulfate group must be removed. This is accomplished by heating the acetate polymer in deionized water at 1.4 MPa (200 psi) for ca 1 h and is called pressure stabilization.

Acetate and triacetate polymers are white amorphous solids produced in granular, flake, powder, or fibrous form. They are used as raw materials in the preparation of fibers, films, and plastics. Polymer density varies and ranges from 100 kg/m^3 for the fibrous form to 500 kg/m^3 for granules. Acetate polymer is shipped by trailer truck, railroad freight car, or multiwall bags.

3.7. Acid Recovery

Approximately 4.0–4.5 kg of acetic acid per kg of cellulose acetate is used in the solution process; ca 0.5 kg is consumed by the product and the remaining 3.5–4.0 kg is recovered as an aqueous solution of 25–35% acetic acid. This solution may also contain dissolved salts from sulfuric acid neutralization, and dissolved and suspended low molecular weight cellulose and hemicellulose acetates. Acetic acid is recovered from the clarified weak acid stream by solvent extraction with solvents such as ethyl acetate or methyl ethyl ketone. Benzene, also formerly used, is being phased out because of carcinogenic concerns. The organic extract is sent to a distillation column, and the aqueous raffinate phase, containing most of the inorganic salts, is discarded. The extraction solvent is distilled off, leaving glacial acetic acid. The energy requirements for acid recovery depend on the organic solvent used and may be in the 4.2–10.5 kJ/g (1–2.5 kcal/g) range of acid recovered. A portion of the acetic acid may be subsequently converted to acetic anhydride by catalytic pyrolysis in good yield and at low cost. A new acetic anhydride process uses synthesis gas obtained from coal as feedstock (42, 43).

3.8. Processes for Triacetate

There are both batch and continuous process for triacetate. Many of the considerations and support facilities for producing acetate apply to triacetate; however, no acetyl hydrolysis is required. In the batch triacetate sulfuric acid process, however, a sulfate hydrolysis step (or desulfonation) is necessary. This is carried out by slow addition of a dilute aqueous acetic acid solution containing sodium or magnesium acetate (44, 45) or triethanolamine (46) to neutralize the liberated sulfuric acid. The cellulose triacetate product has a combined acetic acid content of 61.5%.

In the batch methylene chloride process, the sulfuric acid concentration can be as low as 1% and only limited desulfonation is required to reach a combined acetic acid content of 62.0%. With perchloric acid catalyst, the nearly theoretical value of 62.5% combined acetic acid is obtained.

A lesser employed batch heterogeneous process employs a liquid that does not dissolve the triacetate and gives products of nearly theoretically combined acetic acid.

The continuous triacetate process has been described in detail (9); the economic impact of triacetate has significantly diminished recently, particularly in the United States (47–50).

4. Cellulose Acetate and Triacetate Fibers

4.1. Extrusion Processes

Polymer solutions are converted into fibers by extrusion. The dry-extrusion process, also called dry spinning, is primarily used for acetate and triacetate. In this operation, a solution of polymer in a volatile solvent is forced through a number of parallel orifices (spinneret) into a cabinet of warm air; the fibers are formed by evaporation of the solvent. In wet extrusion, a polymer solution is forced through a spinneret into a liquid that coagulates the filaments and removes the solvent. In melt extrusion, molten polymer is forced through a multihole die (pack) into air, which cools the strands into filaments.

The dry-extrusion process consists of four operations: dissolution of the polymer in a volatile solvent; filtration of the solution to remove insoluble matter; extrusion of the solution to form fibers; and lubrication, yarn formation, and packaging.

4.1.1. Polymer Dissolution

Acetone is the universal solvent for cellulose acetate in dry extrusion. Although methylene chloride is a better solvent (39), it is more expensive and there are more environmental concerns. The optimum concentration for an acetate spinning solution depends on a balance between the highest possible solids concentration and the resulting high solution viscosity. Though high concentrations of solids produce fibers with better properties and reduce the relative amount of solvent to be recovered, practical limits of viscosity are quickly reached. Solutions in aqueous acetone exhibit minimum viscosity at an acetone–water ratio of ca 9:1. A cellulose solvent, N-methylmorpholine oxide, reportedly reduces the solution viscosity (51). Typical solvent composition is ca 95% acetone and 5% water, with a typical polymer solids concentration of 20–30%, depending on the polymer molecular weight. The viscosity of the solution at room temperature is ca $100 - 300$ Pa·s (1000–3000 P). The solubility of acetates of different combined acetic acid content in acetone–water and acetic acid–water solution has been well-studied (52).

Cellulose triacetate is insoluble in acetone, and other solvent systems are used for dry extrusion, such as chlorinated hydrocarbons (eg, methylene chloride), methyl acetate, acetic acid, dimethylformamide, and dimethyl sulfoxide. Methylene chloride containing 5–15% methanol or ethanol is most often employed. Concerns with the oral toxicity of methylene chloride have led to the recent termination of the only triacetate fiber preparation facility in the United States, although manufacture still exists elsewhere in the world (49).

Acetate or triacetate polymer is charged to heavy-duty mixers along with the solvent and a filter aid such as wood-pulp fibers. Concentration, temperature, and mixing uniformity are closely controlled. For a delustered or dull fiber, 1–2% of a finely ground titanium dioxide pigment may be added in the mixing process or by injection of a pigment slurry after filtration. The polymer concentration and the composition of the extrusion solvent strongly affect the uniformity and tensile properties of the acetate fiber and must be closely controlled.

4.1.2. Solution Filtration

The polymer solution, free of unacetylated cellulose, rigid particle contaminants, and dirt, must pass through spinnerets with holes of 30–80 μm diameter. Multistage filtration, usually through plate-and-frame filter presses with fabric and paper filter media, removes the extraneous matter before extrusion. Undesirable gelatinous particles, such as the hemicellulose acetates from cellulose impurities, tend to be sheared into smaller particles rather than removed. The solution is also allowed to degas in holding tanks after each state of filtration.

4.1.3. Extrusion

The filtered, preheated polymer solution is delivered to the spinneret for extrusion at constant volume by accurate metering pumps. The spinnerets are of stainless steel or another suitable metal and may contain from thirteen to several hundred precision-made holes to provide a fiber of desired size and shape. Auxiliary filters are inserted in front of the fixture that holds the spinneret and in the spinneret itself to remove any residual particulate matter in the extrusion solution.

Before entering the spinneret, the extrusion solution, also called a dope, is heated to reduce the viscosity and provide some of the heat necessary to flash the solvent from the extruded filament. A thermostatically controlled heat exchanger may be used to heat the dope, or the filter–spinneret assembly may be located inside the heated extrusion cabinet.

The heated polymer solution emerges as filaments from the spinneret into a column of warm air. Instantaneous loss of solvent from the surface of the filament causes a solid skin to form over the still-liquid interior. As the filament is heated by the warm air, more solvent evaporates. More than 80% of the solvent can be removed during a brief residence time of less than 1 s in the hot air column. The air column or cabinet height is 2–8 m, depending on the extent of drying required and the extrusion speed. The air flow may be concurrent or countercurrent to the direction of fiber movement. The fiber properties are contingent on the solvent-removal rate, and precise air flow and temperature control are necessary.

A feed roll applies tension to the bundle of fibers to withdraw them from the extrusion cabinet. The product of one extrusion position is called a continuous-filament yarn, as distinguished from staple. Cellulose acetate yarns are generally produced in a weight range of 5–100 tex (45–900 den). Feed-roll speed, metering pump output, and column conditions are carefully balanced to produce a yarn of specified and uniform tex (denier).

Only a small quantity of triacetate yarn is made by wet extrusion because extrusion speeds are much lower than for dry extrusion and the process is not attractive for producing filament yarns. Melt extrusion is only used for the production of a small quantity of triacetate yarn.

The solvent used to form the dope is evaporated during the extrusion process and must be recovered. This is usually done by adsorption on activated carbon or condensation by refrigeration. For final purification, the solvent is distilled. Approximately 3 kg of acetone, over 99%, is recovered per kg of acetate yarn produced. Recovery of solvent from triacetate extrusion is similar, but ca 4 kg of methylene chloride solvent is needed per kg of triacetate yarn extruded.

4.1.4. Finish

A finish or lubricant gives the extruded yarn the frictional and antistatic properties required for further processing. The finish, applied at concentrations of 1–5% as the yarn leaves the cabinet, depends on the intended use of the yarn; proprietary formulations are generally used. The lubricated yarn, containing only a small amount of residual solvent, can be taken up on a ring twister, which imparts just enough twist to prevent the handling difficulties of untwisted yarn, or with no twist by being wound on a cylindrical tube. In addition, the yarn filaments may be entangled, ie, compacted, by passing the yarn through a device which intermingles the filaments with air jets (53–55).

5. Anisotropic Solutions

Many cellulosic derivatives form anisotropic, ie, liquid crystalline, solutions, and cellulose acetate and triacetate are no exception. Various cellulose acetate anisotropic solutions have been made using a variety of solvents (56, 57). The nature of the polymer–solvent interaction determines the concentration at which liquid crystalline behavior is initiated. The better the interaction, the lower the concentration needed to form the anisotropic, birefringent polymer solution. Strong organic acids, eg, trifluoroacetic acid are most effective and can produce an anisotropic phase with concentrations as low as 28% (58). Trifluoroacetic acid has been studied with cellulose triacetate alone or in combination with other solvents (59–64); concentrations of 30–42% (wt vol) triacetate were common.

Ternary-phase diagrams for cellulose triacetate, trifluoroacetic acid, and either water, methylene chloride, or formic acid demonstrate the narrow concentration region over which the solutions are anisotropic (65). Cellulose triacetate in a nitric acid–water solution is reported to give very high strength fiber, eg, a tenacity of 0.7–0.9 N/tex (8–10 gf/den) (66). It has been demonstrated that the inclusion of a low concentration of a flexible polymer, eg, poly(ethylene terephthalate), in a trifluoroacetic acid–methylene chloride solution of cellulose triacetate enhances the ordering of the triacetate, reducing the concentration of triacetate needed to form an anisotropic solution. The viscosity of the solution is also lowered (67, 68). Subdenier triacetate fibers were prepared from a trifluoroacetic acid solution by attenuating the fibers with a pressurized gas stream (69). Another study characterized the crystal structure of deacetylated triacetate produced from a lyotropic solution (70). Anisotropic solutions were not limited to just acetate esters. Formate and formate–acetate esters from anisotropic solutions have been described (71). Although fiber has been prepared experimentally from almost all these liquid crystalline polymeric solutions, no significant commercial products exist.

6. Products

6.1. Yarns and Fibers

Many different acetate and triacetate continuous filament yarns, staples, and tows are manufactured. The variable properties are tex (wt in g of a 1000-m filament) or denier (wt in g of a 9000-m filament), cross-sectional shape, and number of filaments. Individual filament fineness (tex per filament or denier per filament, dpf) is usually in the range of 0.2–0.4 tex per filament (2–4 dpf). Common continuous filament yarns have 6.1, 6.7, 8.3, and 16.7 tex (55, 60, 75, and 150 den, respectively). However, different fabric properties can be obtained by varying the filament count (tex per filament or dpf) to reach the total tex (denier).

Although the cross-sectional shape of the spinneret hole directly affects the cross-sectional shape of the fiber, the shapes are not identical. Round holes produce filaments with an approximately round cross section, but with crenelated edges; triangular holes produce filaments in the form of a "Y." Different cross sections are responsible for a variety of properties, eg, hand, luster, or cover, in the finished fabric. Some fibers may contain chemical additives to provide light-fastness and impart fire retardancy. These are usually added to the acetate solution before spinning.

A metier is an array of individual extrusion positions on one machine. The yarn is collected as a package, eg, bobbin, tube, pirn, at each metier position and removed from the machine at regular intervals to maintain a constant supply of yarn on each package. The package may contain 0.5–7.0 kg of yarn. Bobbin yarn may contain a slight twist, ie, ca 0.08 turns per cm, whereas yarn taken up on tubes may have zero twist. The yarn is transferred from bobbins to different packages for sale. The product may contain a twist of 0.3–8.0 turns per cm. At present, compacted yarn is more popular than low twist yarn.

6.2. Yarn Packages

The principal package types used by the textile industry are tubes, cones, and beams. Tubes are wrapped with 1.0–7.0 kg of yarn. The package is built on winders to provide package integrity and easy removal. Some packages are provided with a magazine wrap at the start of winding so that packages can be changed automatically.

Cones contain 0.6–4.0 kg of yarn. The tip of the cone tube must have a smooth finish to prevent damage to the yarn, which is drawn over the top. Again, a magazine wrap may be provided for automatic package transfer. Both compacted and twisted yarns are packaged on cones.

Beams, ie, large spools, are usually constructed of an aluminum alloy and vary from 50 to 170 cm in length and from 50 to 90 cm in flange diameter. A beam holds 100–700 kg of yarn. The beam most commonly used by the warp knitting trade is 107 cm long and 53–76 cm in diameter. Section beams for weaving are usually 137 cm long and 76 cm in diameter. Both types are parallel wound with a large number (up to 2400) of individual yarn ends. The length of yarn on beams varies with yarn denier, beam capacity, and intended use. Lengths are ordinarily 11,000–78,000 m. When beam winding is complete, the ends are taped in position and the beam is wrapped with a protective cover.

6.3. Staple and Tow

The same extrusion technology that produces continuous filament yarn also produces staple and tow. The principal difference is that spinnerets with more holes are used, and instead of winding the output of each spinneret on an individual package, the filaments from a number of spinnerets are gathered together into a

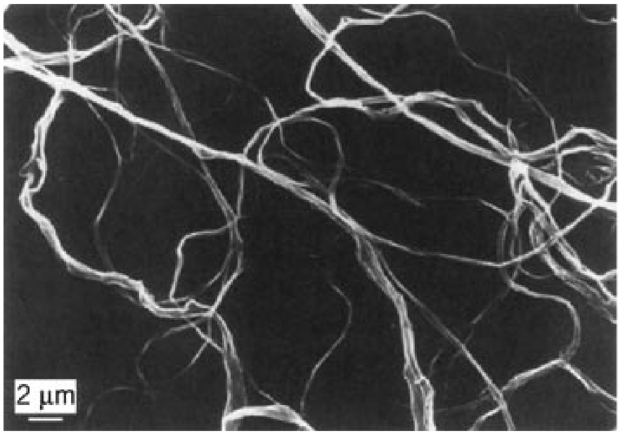


Fig. 10. Cellulose acetate fibrets.

ribbon-like strand, or tow. A mechanical device uniformly plaits the tow into a carton from which it can be continuously withdrawn without tangling.

Staple is produced by cutting a crimped tow into short lengths (usually 4–5 cm) resembling short, natural fibers. Acetate and triacetate staple are shipped in 180–366 kg bales, but production is quite limited. Conventional staple-processing technology applied to natural fibers is used to process acetate and triacetate staple into spun yarn.

6.4. Fibrillated Fibers

Instead of extruding cellulose acetate into a continuous fiber, discrete, pulp-like agglomerates of fine, individual fibrils, called fibrets or fibrids, can be produced by rapid precipitation with an attenuating coagulation fluid. The individual fibers have diameters of 0.5 to 5.0 μm and lengths of 20 to 200 μm (Fig. 10). The surface area of the fibrillated fibers are about 20 m^2/g, about 60–80 times that of standard textile fibers. These materials are very hydrophilic; an 85% moisture content has the appearance of a dry solid (72). One application is in a paper structure where their fine fiber size and branched structure allows mechanical entrapment of small particles. The fibers can also be loaded with particles to enhance some desired performance such as enhanced opacity for papers. When filled with metal particles it was suggested they be used as a radar screen in aerial warfare (73).

7. Economic Aspects

Cellulose acetate, the second oldest synthetic fiber, is an important factor in the textile and tobacco industries; 731,000 metric tons were produced worldwide in 1991 (Fig. 11) (74). Acetate belongs to the group of less expensive fibers; triacetate is slightly more expensive. An annual listing of worldwide fiber producers, locations, and fiber types is published by the Fiber Economics Bureau, Inc. (74).

The principal textile applications of both acetate and triacetate fibers are in women's apparel and home-furnishing fabrics. Although the use of acetate fiber for textile applications has generally declined (Fig. 11), the total worldwide production of cellulose acetate increased owing to tow for cigarette filters, which rose from 335,000 to 481,000 t between 1980 and 1991 (Table 3) (74). Much of the increase in cigarette filter tow production came from the conversion of textile acetate capacity. A new cigarette tow facility in the People's Republic of China was commissioned in 1989 (10,000 tons), and there are other announced plans for additional

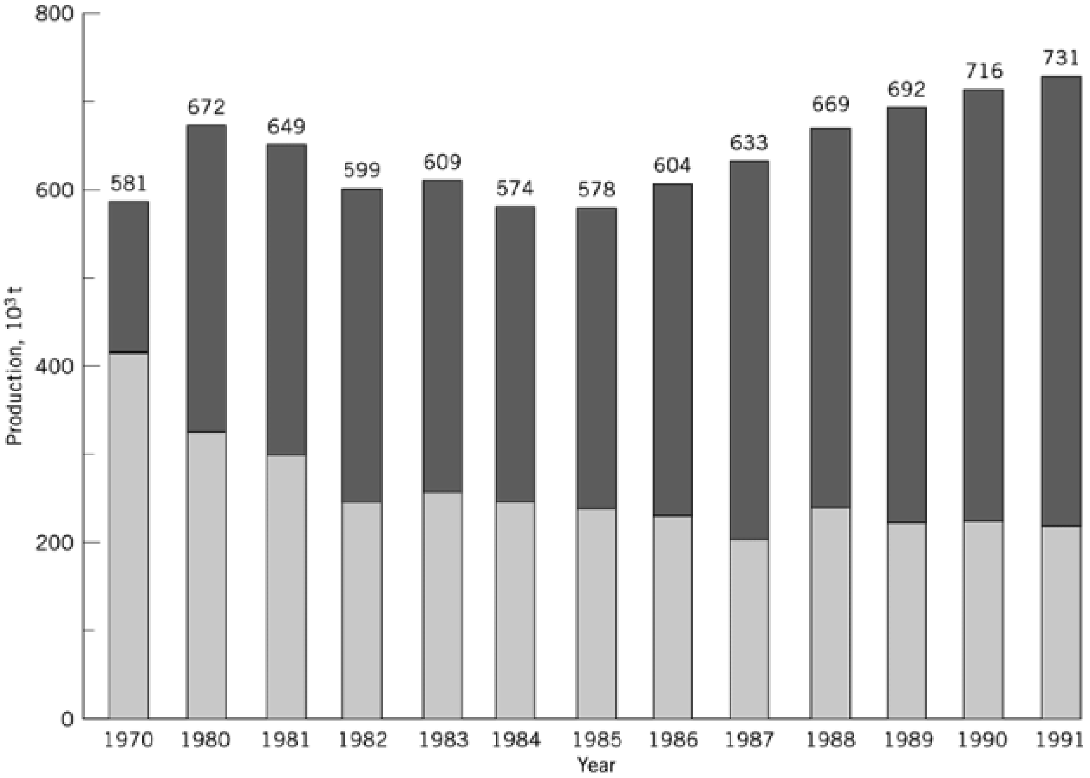


Fig. 11. World production of cellulose acetate and triacetate fibers: ■, cigarette tow; ▨, textile (74).

capacity by Hoechst Celanese, Eastman/Rhône-Poulenc, and Daicel/Mitsui (75–78). Because of its superior filtration, effect on cigarette taste, and low cost, acetate is expected to supply over 90% of the filter-cigarette market.

A list of world acetate and triacetate producers is given in Reference 74. The combined annual world acetate production (filament, staple, and tow) peaked in 1980 with 672,000 t, dropped to 574,000 t in 1984, and rose to 731,000 t in 1991. The United States accounted for ca 45% of the world total. Other principal acetate producing countries include the UK, Japan, Canada, Italy, and the former USSR.

8. Uses

The two principal markets for cellulose acetate are textiles and cigarette filters.

8.1. Textiles

A unique combination of desirable qualities and low cost accounts for the demand for acetate in textiles. In the United States, acetate and triacetate fibers are used in tricot-knitting and woven constructions, with each accounting for approximately half the total volume. This distribution changes slightly according to market trends. The main markets are women's apparel, eg, dresses, blouses, lingerie, robes, housecoats, ribbons,

Table 3. World Production of Cellulose Acetate Cigarette Filter Tow,[a] 10^3 t

Year	Americas[b]	Europe[c]	Asia[d]	China	Totals
1970	99	35	20		154
1980	220	74	41		335
1981	226	81	42		349
1982	216	81	42		339
1983	211	80	43		334
1984	187	80	47		314
1985	210	83	44		337
1986	216	104	42		362
1987	248	107	46		401
1988	250	114	49		413
1989	265	118	55	5	443
1990	275	120	58	12	465
1991	280	120	69	12	481

[a] Ref. 74.
[b] United States, Brazil, Canada, Colombia, Mexico, and Venezuela.
[c] UK, Belgium, Germany, and the former USSR.
[d] Japan and the Republic of Korea.

and decorative household applications, eg, draperies, bedspreads, and ensembles. Acetate has replaced rayon filament in liner fabrics for men's suits and has been evaluated for nonwoven fabrics (79–81).

Acetate and triacetate fibers have lower strength and abrasion resistance than most other synthetic fibers and are frequently combined with nylon or polyester in yarns or specific fabric constructions. This permits them to be used in applications not suitable for 100% acetate fabrics, eg, men's shirts. Combination yarns can be prepared by twisting or air-entanglement and bulking. Yarns prepared by air-entanglement and bulking have unique characteristics and aesthetic properties that allow their use in casement and upholstery fabric markets. With chemical additives, both acetate and triacetate fibers can pass U.S. government flame-retardant fabric regulations, eg, DOC FF 3-71. The flammability of acetate and triacetate is compared to that of other textiles in Reference 82.

Triacetate offers better ease-of-care properties than secondary acetate in many apparel applications. Of particular importance are surface-finished fabrics, eg, fleece, velour, and suede for robes and dresses. These fabrics offer superb aesthetic qualities at reasonable cost. Triacetate is also desirable for print fabrics, where it produces bright, sharp colors. The recent discontinuance of triacetate fiber in the United States has led to the use of acetate with fibers such as polyester (47–50).

8.2. Cigarette Tow

Acetate fiber used in the production of cigarette filters is supplied in the form of tow (83). Tow is a continuous band composed of several thousand filaments held loosely together by crimp, a wave configuration set into the band during manufacture (Fig. 12**a**). A tow is formed by combining the output of a large number of spinnerets and crimping the combined filaments to create an integrated band of continuous fibers. The tow is dried and baled. The wide range of available acetate filter tow products permits control of properties in the finished cigarette-filter rod.

A tow product is characterized by cross section, tex (denier), and crimp. The shape of the cross section is related to the shape of the minute orifices in the spinneret used to form the filament (Fig. 13).

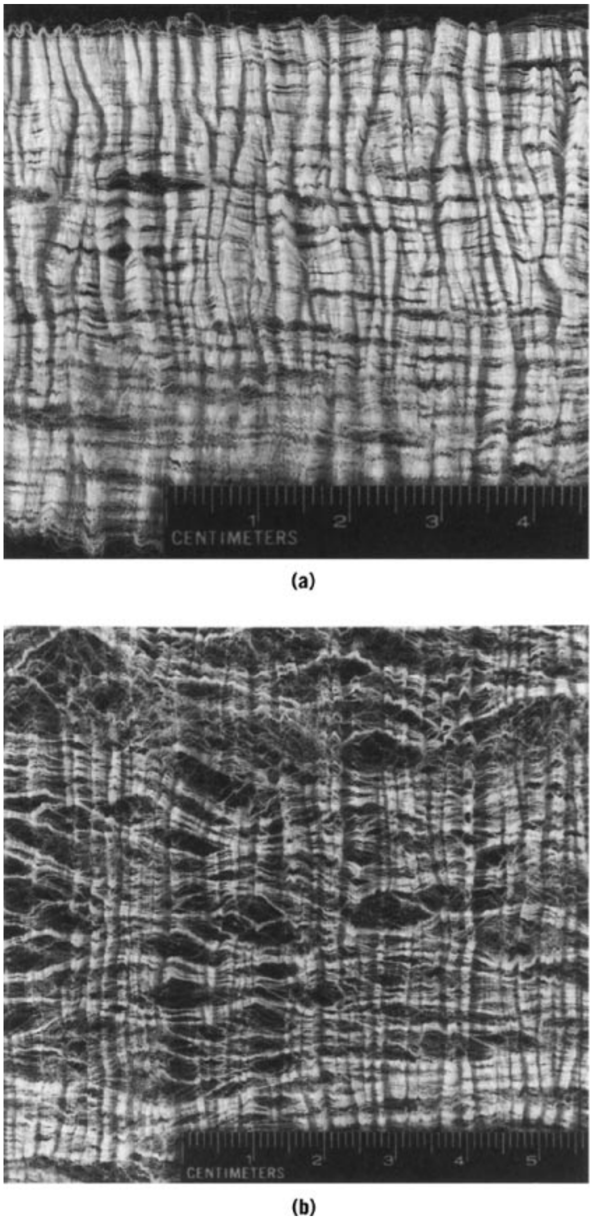


Fig. 12. Cellulose acetate cigarette filter tow (**a**) as supplied and (**b**) “opened” for cigarette-filter rod preparation.

Several tex terms are important in filter-tow processing: tex (denier) per filament, total tex (denier) of the uncrimped tow (the product of the tex per filament multiplied by the number of filaments in the tow band), and crimped total tex (denier), which is somewhat higher than the total tex (denier).

A tow product described as 0.9 tex, 5000 total tex, may therefore be interpreted as an uncrimped tow band that weighs 5000 g for each kilometer of length and that is composed of 5555 individual filaments (5000/0.9) each weighing 0.9 g for each kilometer of length.

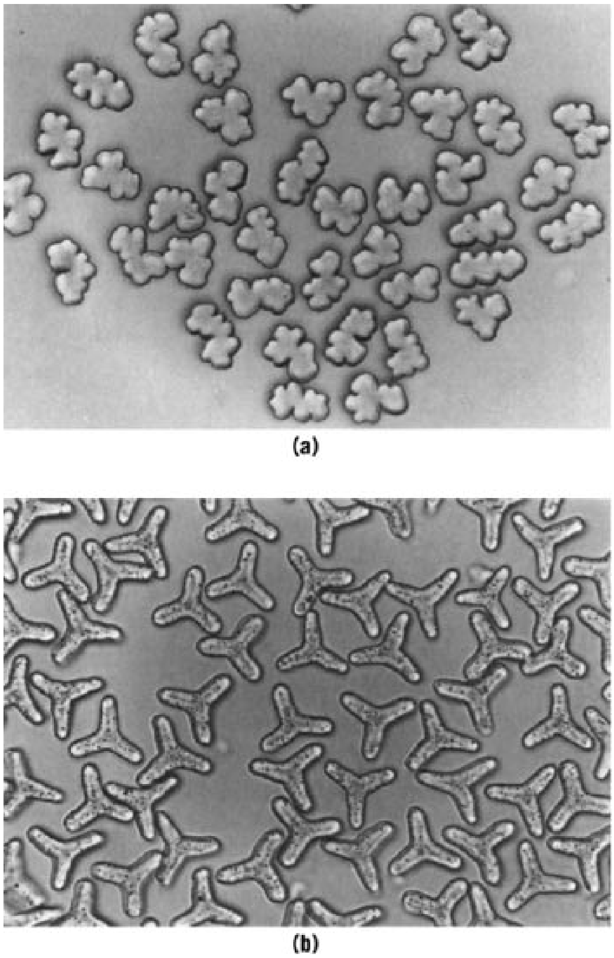


Fig. 13. Cross sections of cellulose acetate fiber from (**a**) circular and (**b**) triangular spinneret holes.

The crimp imparted to the tow has a sawtooth or sinusoidal wave shape. Because the filaments are usually crimped as a group, the crimp in parallel fibers is in lateral registry, ie, with the ridges and troughs of the waves aligned, as shown in Figure 14.

The presence of crimp in the tow is necessary to ensure that the tow can be packaged, processed, and handled easily and to impart bulk to the finished filter. To achieve the latter in the production of the filters, it is necessary to open the tow band (Fig. 12**b**) to the desired bulk so that the fibers completely fill the paper wrap without voids and soft spots.

A linear relationship, constant for any given tow item, exists between the weight of tow in a cigarette-filter rod and certain of its properties, such as pressure drop and smoke-removal efficiency. By preparing filter rods over a range of rod weights and testing the rods for pressure drop, a linear curve characteristic of the specific tow item is obtained. This characterization provides a means of designing the required cigarette-filter characteristics. For example, a typical linear plot shows that to achieve a certain target pressure drop, either a 3.0- or 3.9-denier (tex) per filament of the same total denier can be selected. However, the latter will produce a heavier filter rod. At the same denier per filament, increasing the total denier can give the same pressure drop,

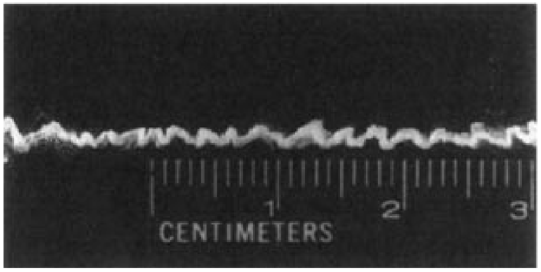


Fig. 14. Section of cellulose acetate cigarette filter tow showing crimp configuration.

but this also gives heavier rods and shifts the pressure drop range upward. Other factors such as economics, rod firmness, and rod diameter affect the final selection of the tow product used.

8.3. Other Applications

Other large-volume, nontextile, or cigarette-filter tow applications for cellulose acetate are filament fibers for decorative packaging ribbons and tows which are converted into ink dispensers for felt-tip pens. Additional commercial and development applications for acetate and triacetate polymers and fibers continue to be pursued. Cellulose acetate has been a beneficial membrane material in film or hollow fiber form (84–97). Water-soluble acetate polymers and fibers (98–101) can be produced by selecting a combined acetic value in the range of 20–27%. A technique for producing them directly, rather than by hydrolysis of the triacetate, was recently described (102, 103). Techniques for improving the antistatic characteristics of acetate fiber have been evaluated (104–110). Other references describe work aimed at improved water and solvent resistance (111–114), abrasion resistance (115–118), grafting (119), selective adsorption (120), timed release of additives (121), microporous fiber (122), reinforcing fiber (123), absorbent (124), blends with polyester (125), photochromic fibers (126), irrigation system (127), odor adsorbing (128), blood filtration (129–131), immobilizing substrate (132–135), hygroscopic additive for polyester fibers (136), and makeup applicators (137) and offer potential for future applications.

BIBLIOGRAPHY

"Acetate Fibers" treated in *ECT* 1st ed., under "Rayon and Acetate Fibers," Vol. 11, pp. 552–569, by G. W. Seymour and B. S. Sprague, Celanese Corp. of America; "Acetate and Triacetate Fibers" in *ECT* 2nd ed., Vol. 1, pp. 109—138, by L. I. Horner and A. F. Tesi, Celanese Fibers Co., Division of Celanese Corp. of America; "Cellulose Acetate and Triacetate Fibers" in *ECT* 3rd ed., Vol. 5, pp. 89–117, by G. A. Serad and J. R. Sanders, Celanese Fibers Co.

Cited Publications

1. T. Vickerstaff and E. Water, Jr., *J. Soc. Dyers Colour.* **58**, 116 (1942).
2. J. C. Guthrie, *J. Text. Inst.* **46**(6), T193 (1957).
3. R. Meredith, *J. Text. Inst.* **37**, T107 (1945).
4. G. Susich and S. Backer, *Text. Res. J.* **21**, 482 (1951).
5. W. Zurek, I. Sobieraj, and T. Trzesowska, *Text. Res. J.* **49**(8), 438 (1979).
6. E. R. Kaswell, *Textile Fibers, Yarns, and Fabrics*, Reinhold Publishing Corp., New York, 1953, p. 57.
7. D. K. Beever and L. Valentine, *J. Text. Inst.* **49**, T95 (1958).

8. *ASTM Standards, ASTM D1909-E1*, Vol. **17.01**, American Society for Testing and Materials, Philadelphia, Pa., 1992, 500–501.
9. G. A. Serad, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **3**, 2nd ed. Wiley-Interscience, New York, 1985, 200–226.
10. A. Mellor and H. C. Olpin, *J. Soc. Dyers Colour.* **71**, 817 (1955).
11. K. Kohata, M. Miyagawa, A. Takaoka, and H. Kawai, *Proceedings of the International Symposium on Fiber Science and Technology, Hakone, Japan, August 24–25, 1985*, Society of Fiber Science and Technology, Tokyo, p. 270.
12. A. F. Tesi, *Am. Dyest. Rep.* **45**, 512 (1956).
13. F. Fortess, *Text. Res. J.* **19**, 23 (1949).
14. P. M. Heertjes, W. Colthof, and H. I. Waterman, *Rec. Trav. Chim.* **52**, 305 (1933).
15. C. J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.* **34**, 430 (1942).
16. *Effect of Conditioning Humidity on the Electrical Resistance of Rayon Yarns*, British Cotton Industry Research Association, London, 1945.
17. C. L. Bird and co-workers, *J. Soc. Dyers Colour.* **70**, 68 (1964).
18. R. K. Fourness, *J. Soc. Dyers Colour.* **72**, 513 (1956).
19. F. Fortess and V. S. Salvin, *Text. Res. J.* **28**, 1009 (1958).
20. F. Fortess, *Am. Dyest. Rep.* **44**, 524 (1955).
21. R. J. Mann, *J. Soc. Dyers Colour.* **76**, 665 (1960).
22. J. Boulton, *J. Soc. Dyers Colour.* **71**, 451 (1955).
23. L. G. Ray, Jr., *Text. Res. J.* **22**, 144 (1952).
24. L. Segal, in N. M. Bikales and L. Segal, eds., *Cellulose and Cellulose Derivatives*, High Polymers Series, Vol. **V**, Wiley-Interscience, New York, 1971, Chapt XVII-A.
25. G. D. Hiatt and W. J. Rebel in Ref. 24, Chapt. VI1-B.
26. C. L. Smart and C. N. Zellner in Ref. 24, Chapt. XIX-C.
27. W. B. Russo and G. A. Serad, in A. L. Turbak, ed., *Solvent Spun Rayon, Modified Cellulose Fibers and Derivatives*, ACS Symposium Series 58, American Chemical Society, Washington, D.C., 1977, p. 96.
28. C. J. Maim and G. D. Hiatt, in E. Ott, H. M. Spurlin, and M. W. Graffin, eds., *Cellulose and Cellulose Derivatives*, High Polymers Series, 2nd ed., Vol. **V**, Wiley-Interscience, New York, 1954, Pt. II.
29. U.S. Pat. 4,306,060 (Dec. 15, 1981), Y. Ikemoto (to Daicel Chemical Industries, Ltd.).
30. S. E. Doyle and R. A. Pethrick, *J. Appl. Polym. Sci.* **33**(1), 95–106 (1987).
31. B. Philipp, H. Schleicher, and W. Wagenknecht, *Chem. Tech. Leipzig* **7**(11), 79 (1977).
32. A. F. Turbak, R. B. Hammer, R. E. Davis, and H. L. Hergert, *Chem. Tech. Leipzig* **10**(1), 51 (1980).
33. S. M. Hudson and J. A. Cuculo, *J. Macromol. Sci. Chem.* **18**(1), 1 (1980).
34. U.S. Pat. 4,302,252 (Nov. 24, 1981), A. L. Turbak, A. El-Kafrawy, T. W. Snyder, Jr., and A. B. Auerbach (to International Telephone and Telegraph Corp.).
35. U.S. Pat. 4,324,593 (Apr. 13, 1982), J. K. Varga (to Akzona, Inc.).
36. C. L. McCormick and T. C. Chen, preprint, *American Chemical Society National Meeting*, Division of Organic Coatings and Plastics, New York, Aug. 1981.
37. Brit. Pat. Appl. GB 2,055,107 (Feb. 25, 1981), A. L. Turbak, A. El-Kafrawy, T. W. Snyder, Jr., and A. B. Auerbach (to International Telephone and Telegraph Corp.).
38. U.S. Pat. 4,265,675 (May 5, 1981), G. T. Tsno, B. E. Dale, and M. R. Ladisch (to Purdue Research Foundation).
39. A. Isogai, A. Ishizu, and J. Kanako, *Cellul. Chem. Technol.* **17**, 123 (1983).
40. W. B. Russo and G. A. Serad in Ref. 27, p. 115.
41. Brit. Pat. 2,105,725 (Mar. 30, 1983), H. Yabune and M. Uchida (to Daicel Chemical Industries Ltd.).
42. *Chem. Eng. News*, 6 (Jan. 14, 1980).
43. *Chem. Week*, 40 (Jan. 16, 1980).
44. U.S. Pat. 2,259,462 (Oct. 21, 1941), C. L. Fletcher (to Eastman Kodak Co.).
45. Brit. Pat. 566,863 (Feb. 26, 1945), H. Dreyfus (to Celanese Corp.).
46. U.S. Pat. 3,525,734 (Aug. 25, 1970), A. Rajon (to Societé Rhodiaceta).
47. *Daily News Record*, 7 (Jan. 10, 1986).
48. *Women's Wear Daily*, 38 (Jan. 22, 1986).
49. *Text. Marketing*, 5 (June 1986).

50. *Women's Wear Daily*, 6 (July 14, 1986).
51. U.S. Pat. 4,118,350 (Oct. 3, 1978), A. F. Turbak and co-workers (to International Telephone and Telegraph Corp.).
52. C. J. Maim and co-workers, *Ind. Eng. Chem.* **49**, 79 (1957).
53. U.S. Pat. 2,985,995 (May 30, 1961), W. W. Bunting, Jr., and T. L. Nelson (to E. I. du Pont de Nemours & Co., Inc.).
54. U.S. Pat. 3,110,151 (Nov. 12, 1963), W. W. Bunting, Jr., and T. L. Nelson (to E. I. du Pont de Nemours & Co., Inc.).
55. U.S. Pat. 3,364,537 (Jan. 23, 1968), W. W. Bunting, Jr., and T. L. Nelson (to E. I. du Pont de Nemours & Co., Inc.).
56. U.S. Pat. Appl. 656,359 (Feb. 9, 1976), M. Panar and O. Willcox (to E. I. du Pont de Nemours & Co., Inc.).
57. J. Takahashi, A. Kiyose, S. Nomura, and M. Kurijawa, in Ref. 11, 20–24.
58. S. M. Aharoni, *Mol. Cryst. Liq. Cryst. Lett.* **56**, 237 (1980).
59. J. LeMatre, S. Dayan, and P. Sixou, *Mol. Cryst. Liq. Cryst.* **84**, 267 (1982).
60. P. Navard. J. M. Haudin, S. Dayan, and P. Sixou, *J. Polym. Sci. Part B* **19**, 379 (1981).
61. G. H. Meeten and P. Navard, *Polymer* **23**, 177 (1982).
62. S. Dayan, P. Maissa, M. J. Vellutini, and P. Sixou, *J. Polym. Sci. Part B* **20**, 33 (1982).
63. G. H. Meeten and P. Navard, *J. Polym. Sci. Part B* **24**(7), 815 (1983).
64. D. L. Patel and R. D. Gilbert, *J. Polym. Sci. Part A-2* **21**, 1079 (1983).
65. U.S. Pat. 4,501,886 (Feb. 26, 1985) John P. O'Brien, (to E. I. du Pont de Nemours & Co., Inc.)
66. U.S. Pat. 4,725,394 (Feb. 16, 1988) John P. O'Brien, (to E. I. du Pont de Nemours & Co., Inc.)
67. R. D. Gilbert, R. E. Fornes, and Y. K. Hong, *Tappai Nonwoven Conference*, Tappi, Norcross, Ga., 1986, 231–236.
68. Y. K. Hong and co-workers, *Polymer Associated Structures: Microemulsions and Liquid Crystals*, ACS Symposium Series, 384, American Chemical Society, Washington, D.C., 1989, 184–203.
69. U.S. Pat. 4,963,298 (Oct. 16, 1990) S. R. Allen, A. A. Mian, and S. L. Samuels (to E. I. du Pont de Nemours & Co., Inc).
70. E. J. Roche and J. P. O'Brien in Ref. 11, p. 281.
71. U.S. Pat. 4,839,113 (June 13, 1989) (to Michelin Recherche et Technique SA).
72. J. E. Smith, *Nonwovens World* **3**(6), 40–42 (1989).
73. Eur. Pat. 0,390,580 (Mar. 30, 1990) J. C. Hornsby (to E. I. du Pont de Nemours & Co., Inc.).
74. *Data of Fiber Economics Bureau*, as published in *Text. Organon*, 112–113, and 115 (June 1986) *Fiber Organon*, 138–139 and 144 (July 1992); and author information.
75. *Chem. Mark. Rep.*, 52 (July 23, 1990).
76. *Chem. Week* **150**, 13 (Feb. 12, 1992).
77. *Chem. Week* **150**, 30 (March 18, 1992).
78. *Chem. Week* **150**, 6 (April 8, 1992).
79. A. A. Lukoshaitis and co-workers, *Fibre Chem. USSR* **6**, 441 (1974) Y. A. Matskevichene and co-workers, *Fibre Chem. USSR* **6**, 446 (1974).
80. R. R. Rhinehart, *Symposium Papers, March 1975*, Miami Beach Meeting, International Nonwovens and Disposables Association, New York, p. 25.
81. Ger. Pat. 2,502,519 (July 31, 1975), C. K. Arisaka and co-workers (to Daicel, Ltd.).
82. B. Miller, J. R. Martin, and R. Turner, *J. Appl. Polym. Sci.* **28**(1), 45 (1983).
83. *Acetate Tow Production and Characterization*, Filter Products Division, Technical Bulletin FPB-4, Hoechst Celanese Corp., Charlotte, N.C., 1989.
84. G. Rakhmanberdiev and co-workers, *Zh. Prikl. Khim. Leningrad* **46**(2), 416 (1973).
85. U.S. Pat. 3,763,299 (Oct. 2, 1973), W. S. Stephen (to FMC Co.).
86. G. Rakhmanberdiev and co-workers, *Fibre Chem. USSR* **6**, 219 (1974).
87. Brit. Pat. 1,418,115 (Dec. 17, 1975), R. L. Leonard (to Monsanto Co.).
88. G. Tanny, *Appl. Polym. Symp.* **31**, 407 (1977).
89. U.S. Pat. 4,127,625 (Nov. 28, 1978), K. Arisaka, K. Watanabe, and K. Sasazima (to Daicel, Ltd.).
90. Brit. Pat. 2,001,899 (Feb. 14, 1979), M. Mishiro and S. Kasai (to Asahi).
91. Brit. Pat. 2,000,722 (Jan. 17, 1979), M. J. Kell and R. D. Mahoney (to Cordis Dow Corp.)
92. Brit. Pat. 2,002,679 (Feb. 28, 1979), M. Mishiro and K. Nakata (to Asahi).
93. Brit. Pat. 2,035,197 (June 18, 1980), K. Hamada, Z. Takade, and K. Numata (to Toyobo Co., Ltd.).
94. U.S. Pat. 4,219,517 (Aug. 26, 1980), R. E. Kesting (to Puropore, Inc.).
95. Brit. Pat. 2,065,546 (July 1, 1981), D. T. Chen and R. D. Mahoney (to Cordis Dow Corp.).
96. U.S. Pat. 4,276,173 (June 30, 1981), M. J. Kell and R. D. Mahoney (to Cordis Dow Corp.).

97. S. Kim, J. Cha, J. Kim, and U. Kim, *J. Membrane Sci.* **37**(2), 113–129 (1988).
98. U.S. Pat. 3,482,011 (Dec. 2, 1969), T. C. Bohrer (to Celanese Corp.).
99. G. Rakhmanberdiev, G. A. Petrotpsavlovskii, and K. U. Usmanov, *Cellul. Chem. Technol.* **12**(2), 153 (Mar.–Apr. 1978).
100. C. Rakhmanberdiev, K. Dustmukhamedov, M. Mukhamedzhanov, and K. U. Usmanov, *3rd Mezhdunar. Simpoz. PO Khim. Voloknam* **5**, 281 (1981).
101. A. K. Mukherjee, R. K. Agarwal, H. K. Chaturvedi, and B. D. Gupta, *Indian J. Text. Res.* **6**, 120 (1981).
102. C. M. Buchanan, K. J. Edgar, J. A. Hyatt, and A. K. Wilson, *Macromolecules* **24**, 3050–3059 (1991).
103. C. M. Buchanan, K. J. Edgar, and A. K. Wilson, *Macromolecules* **24**, 3060–3064 (1991).
104. O. G. Pikovskaya and Z. G. Serebryakova, *Fibre Chem. USSR* **2**, 378 (1970).
105. F. A. Ismailov and co-workers, *Fibre Chem. UUSR* **4**, 584 (1972).
106. P. A. Chakhoya and co-workers, *Fibre Chem. UUSR* **5**, 184 (1973).
107. A. V. Kuchmenko, *Fibre Chem. USSR* **5**, 210 (1973).
108. Brit. Pat. 1,381,334 (May 31, 1973), W. Ueno, H. Kawaguchi, and N. Minagawa (to Fuji Photo Film Co., Ltd.).
109. A. P. Fedotov and co-workers, *Fibre Chem. USSR* **6**, 87 (1974).
110. M. N. Skarnlite and Y. Y. Shlyazhas, *Fibre Chem. USSR* **6**, 557 (1974).
111. *Text. World* **123**(9), 37 (1973).
112. U.S. Pat. 3,816,150 (June 11, 1974), K. Ishii and co-workers (to Daicel, Ltd.).
113. U.S. Pat. 3,839,617 (Oct. 1, 1974), A. F. Turbak and J. R. Thelman (to International Telephone and Telegraph Corp.-Rayonier).
114. U.S. Pat. 3,839,528 (Oct. 1, 1974), A. F. Turbak and J. R. Thelman (to International Telephone and Telegraph Corp.-Rayonier).
115. C. F. Kiseleva and co-workers, *Fibre Chem. USSR* **4**, 257 (1972).
116. M. Papikyan and co-workers, *Fibre Chem. USSR* **4**, 441 (1972).
117. M. Mirzaev and co-workers, *Khim. Volokna* **3**, 21 (1975).
118. Brit. Pat. 1,414,395 (Nov. 19, 1975), N. V. Mikhailov and co-workers (to USSR).
119. M. A. Siahkolah and W. K. Walsh, *Text. Res. J.* **44**(11), 895 (1974).
120. Ger. Pat. 2,507,551 (Feb. 28, 1975), B. V. Chandler and R. L. Johnson (to Commonwealth Scientific Organization).
121. U.S. Pat. 3,846,404 (Nov. 5, 1974), L. D. Nichols (to Moleculon Research Corp.).
122. Brit. Pat. 2,009,667 (June 20, 1979), R. Noguchi, S. Suzuki, Y. Meede, and R. Minami (to Mitsubishi Acetate Co.).
123. Brit. Pat. 2,040,956 (Sept. 3, 1980), D. William and P. Grey (to Wycombe Marsh Paper Mills, Ltd.).
124. U.S. Pat. 4,289,130 (Sept. 15, 1981), A. Usami, T. Uebayashi, K. Sato, and T. Goda (to Daicel Ltd.).
125. U.S. Pat. 4,770,931 (Sep. 13, 1988), M. A. Pollock, W. J. Stowell, and J. J. Krutak (to Eastman Kodak Co.).
126. Eur. Pat. 0,328,320 (Feb. 3, 1989), P. Wright (to Courtaulds).
127. U.S. Pat. 4,928,427 (May 29, 1990)
128. Brit. Pat. 2 229 364 A (Sept. 26, 1990) H. Nakel and S. Edagawa (to O.K. Trading Co. Ltd.).
129. U.S. Pat. 4,919,823 (Apr. 24, 1990), L. A. Wisdom (to Miles Inc.).
130. U.S. Pat. 4,767,541 (Aug. 30, 1988), L. A. Wisdom (to Miles Laboratories, Inc.).
131. U.S. Pat. 4,596,657 (Jun. 24, 1986), L. A. Wisdom (to Miles Laboratories, Inc.).
132. A. A. Sedov, *Fibre Chem. USSR* **9**(3), 281 (May–June 1977).

133. A. A. Sedov, *Fibre Chem. USSR* **9**(4), 367 (July–Aug. 1977).
134. A. V. Matveev and co-workers, *Fibre Chem.* **21**(1), 29–33 (1989).
135. K. G. Raghavan, T. P. A. Devasagayam, and V. Ramakrishnan, *Analyt. Lett.* **19**(1&2), 163–176 (1986).
136. Jpn. Pat. 2,221,413 (Feb. 17, 1989), O. Kimihiro and Y. Hironori (to Teijin Ltd.).
137. Jpn. Pat. 1,119,203 (Nov. 2, 1987), N. Kenji.

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