HIGH PERFORMANCE FIBERS

1. Introduction

High performance fibers are generally characterized by remarkably high unit tensile strength and modulus as well as resistance to heat, flame, and chemical agents that normally degrade conventional fibers. Applications include uses in the aerospace, biomedical, civil engineering, construction, protective apparel, geotextiles, and electronic areas.

For many years, plastics reinforced with polymer fibers have been utilized in the manufacture of boats and sports cars. More recently, ultrahigh strength, high modulus fibers have been invented and combined into composites whose strength and stiffness on a specific basis are unmatched by conventional construction materials. Composites are now replacing metals in such crucial applications as aircraft and the space shuttle. The polymeric composites contain carbon or aramid fibers several times stiffer, weight for weight, than steel. In composite materials the fibers support the load that is distributed by the plastic that also prevents fatigue and failure (1–4).

In addition to their role in composites, high performance fibers are also found in coated and laminated textile products, three-dimensional fabric structures, multifunctional property improvement, and intelligent or self-adaptive materials.

In this article the preparation and properties of typical high performance fibers are discussed, then their applications are classified and detailed.

Kirk-Othmer Encyclopedia of Chemical Technology.

2. Preparation and Properties

The principal classes of high performance fibers are derived from rigid-rod polymers, gel spun fibers, modified carbon fibers, carbon-nanotube composite fibers, ceramic fibers, and synthetic vitreous fibers.

2.1. Rigid-Rod Polymers.

Rigid-rod polymers are often liquid crystalline polymers classified as lyotropic, such as the aramid Kevlar, or thermotropic liquid crystalline polymers, such as Vectran.

Liquid Crystallinity. The liquid crystalline state is characterized by orientationally ordered molecules. The molecules are characteristically rod or lathe shaped and can exist in three principal structural arrangements: nematic, cholesteric, smectic, and discotic (5,6).

In the nematic phase, within volume elements of the macroscopic sample, the axes of the molecules are oriented on average in a specific direction in various domains. The centers of gravity of the molecules are arranged in a random fashion, and consequently no positional long-range order exists. The molecules are arranged in essentially parallel arrays. Without the presence of an orienting magnetic or physical force, the molecules exist in random parallel arrays. When an orienting force is applied, these domains orient easily. The nematic phase is amenable to translational mobility of constituent molecules.

The cholesteric phase may be considered a modification of the nematic phase since its molecular structure is similar. The cholesteric phase is characterized by a continuous change in the direction of the long axes of the molecules in adjacent layers within the sample. This leads to a twist about an axis perpendicular to the long axes of the molecules. If the pitch of the helical structure is the same as a wavelength of visible light, selective reflection of monochromatic light can be observed in the form of iridescent colors.

In the smectic phase, the centers of gravity of the rod-like molecules are arranged in equidistant planes, ie, the ends of the molecules are correlated. The planes may move perpendicular to the layer normal, and within layers different arrangements of the molecules are possible. The long axes of the molecules may be parallel to the layer normal or tilted with respect to it. A two-dimensional short or long range order may exist within the smectic layers. The smectic modifications are labeled according to the arrangement of the molecules within the layers using the symbols A–K.

In the smectic A phase, the director is perpendicular to the planes, while in the smectic C phase, the director is tilted at an angle $<90^\circ$ to the planes. In the smectic A and C phases, the molecules diffuse randomly and as a result, no positional order exists within the planes (positional order exists only in one dimension). However, other smectic liquid-crystal phases exist in which the molcules have some degree of order within each plane that results in three-dimensional positional order (or quasi-three-dimensional order). In this case, molecules diffusing through the plane spend more time at certain locations than at other locations.

The smectic B phase is a more ordered analogue of the smectic A phase in which the molecules adopt hexagonal order over distances of $\sim$150–600 A (6). The hexagonal S_B phase has two tilted analogues called the smectic I and smectic F phases, in which the hexagonal lattices tilt toward the apex and the side, respectively. In the crystal B phase, the molecules adopt hexagonal order similar to that of the smectic B phase; however, the hexagonal lattices show long range (three-dimensional) positional order. Crystal J and G phases represent hexagonal lattices with long-range positional order that are analogues of S_I and S_F, respectively. The crystal E phase results from contraction of a hexagonal lattice that leads to a herringbone-like structure with restricted rotation. Crystal K and crystal H phases are the respective tilted analogs of the crystal E phase.

In the discotic phase, dislike molecules form liquid-crystal phases in which the axis perpendicular to the planes of the molecules, orients along a specific direction. The nematic discotic phase has orientational order but no positional order. In the columnar discotic phase, the dislike molecules form columns and therefore exhibit orientational and positional order. In a chiral discotic liquid crystal, the director rotates in a helical path throughout the system.

Poly(1,4-benzamide) (PBA) (7) was the first nonpeptide synthetic polymer reported to form a liquid crystalline solution. In order to obtain liquid crystalline solutions of poly(1,4-benzamide), it was first necessary to prepare the polymer in the proper solvent. Preparation of the polymer in *N,N*-dialkylamide solvents at low temperatures from *p*-aminobenzoyl chloride hydrochloride produces tractable PBA polymers with inherent viscosities of as much as 5dL/g. In solvents such as *N,N*-dimethylacetamide [127-19-5] and *N,N,N′,N′*-tetramethylurea [632-22-4] a coupled polymerization-spinning process in liquid crystalline solution has been developed. If polymerization is initiated at temperatures >25°C, lower molecular weight polymer is formed. Above 25°C, chain termination by reaction of acid chloride chain ends with *N,N*-dialkylamide is significant. To obtain high molecular weights, a lithium base such as lithium hydride, lithium carbonate, or lithium hydroxide is added to the polymerization solution after the first 1–2 h of reaction time to neutralize the hydrogen chloride generated. As the reaction proceeds, the polymerization rate decreases because the increasing amounts of hydrogen chloride consequently produce fewer free-terminal amine groups.

When pure needle-like crystals of *p*-aminobenzoyl chloride are polymerized in a high temperature, nonsolvent process, or a low temperature, slurry process, polymer is obtained that maintains the needle-like appearance of monomer. PBA of inherent viscosity, 4.1dL/g, has been obtained in a hexane slurry with pyridine as the acid acceptor. Therefore PBA of fiber-forming molecular weight can be prepared in the solid state.

In 1975, the synthesis of the first main-chain thermotropic polymers, three polyesters of 4,4′-dihydroxy-α,α′-dimethylbenzalazine with 6, 8, and 10 methylene groups in the aliphatic chain, was reported (8). Shortly thereafter, at the Tennessee Eastman Co. thermotropic polyesters were synthesized by the acidolysis of poly(ethylene terephthalate) by *p*-acetoxybenzoic acid (9). Copolymer compositions that contained 40–70 mol% of the oxybenzoyl unit formed anisotropic, turbid melts which were easily oriented.

Polyesters such as poly(*p*-phenylene terephthalate), which would be expected to form liquid crystalline phases, decompose at temperatures below the melting point. Three principal methods have been used for lowering the melting temperatures of thermotropic copolyesters: (*1*) the use of flexible groups as spacers to decouple the mesogenic units and reduce the axial ratio; (*2*) the use of unsymmetrical groups on mesogenic units; and (*3*) the copolymerization of rigid units with nonlinear, bent units which add a “kink” to the rod-like system.

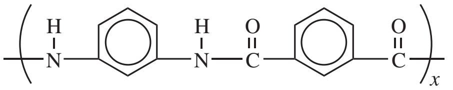
According to patents obtained by Carborundum (10–12), Celanese (13), Du Pont (14–17), and Eastman (9,18) most industrial main-chain thermotropics are prepared by condensation polymerization involving transesterification. Hydroxy-substituted monomers are acetylated before polymerization by acetic anhydride in the presence of a suitable catalyst. The transesterification reactions involve acetylated diol, or monosubstituted hydroxybenzoic or hydroxynaphthoic acids, and diacids. The polymerizations are carried out in an inert atmosphere to prevent oxidation. A stainless steel stirrer is utilized to improve mixing and to accelerate the release of the reaction by-products. The polymerizations are carried out at 50–80°C above the melting point of the highest melting monomer. After a low melt viscosity prepolymer is obtained, a vacuum is applied to remove the additional acetic acid and increase the molecular weight of the polymer. Finally, solid-state polymerization under reduced pressure or in nitrogen at a temperature of 10–30°C below the melting point may be utilized to increase the molecular weight. The heat treatment of spun fibers under these conditions leads to spectacular increases in tensile strength and modulus.

Researchers at Du Pont used hydroquinone asymmetrically substituted with chloro, methyl, or phenyl substituents and swivel or nonlinear bent substituted phenyl molecules such as 3,4- or 4,4′-disubstituted diphenyl ether, sulfide, or ketone monomers. For example, poly(chloro-1,4-phenylene-*trans*-hexahydroterephthalate) and related copolymers were prepared in a melt polymerization process involving the reaction of molar equivalents of the diacetoxy derivatives of diphenols and hexahydroterephthalic acid (19). During polymerization, a phase transition from isotropic to anisotropic occurred soon after the rapid melting of the intermediates to form a clear, colorless liquid.

Also in 1972 (20), Carborundum researchers described a family of aromatic copolyesters that were recognized later to form liquid crystalline melts. The polymers are based on a bisphenol monomer. In 1976, in a patent assigned to Carborundum, a hydroxybenzoic acid–terephthalic acid–bisphenol system, modified and softened with isophthalic acid, was reported to be melt spinnable to produce fiber (21).

Industrial Lyotropic Liquid Crystalline Polymers (Aramid Fibers). The first polyaramid fiber (MPD-1) was based on poly(*m*-phenylene isophthalamide) [24938-60-1]. The fiber was not liquid crystalline but was the first aramid fiber to be commercialized by Du Pont under the trade name Nomex nylon in 1963 and changed to Nomex aramid in 1972 (22). The principal market niche for Nomex was as a heat-resistant material. Teijin also introduced a fiber (trademark Conex) based on MPD-1 in the early 1970s. Fenilon, also based on MPD-1, was produced in the former USSR for civilian, military, and space exploration applications. In 1970, Du Pont introduced an aramid fiber, Fiber B, for use in tires, which was probably based on polybenzamide PBA spun from an organic solvent. Fiber B had high strength and exceptionally high modulus. Another version of Fiber B, based on poly(*p*-phenylene terephthalamide) [24938-64-5] (PPT) was introduced in the 1970s. This version of Fiber B was spun from sulfuric acid and had a tensile strength approximately twice that of the Fiber B based on MPD-1. An even higher modulus fiber based on PPT, in which the modulus was increased by the drawing of the as-spun fiber, was introduced under the name PRD-49 for use in rigid composites. The undrawn and drawn fibers were later announced as Kevlar-29 and Kevlar-49, respectively. In 1975, Akzo of the Netherlands reported the commercialization of an aramid fiber, Twaron, based on PPT.

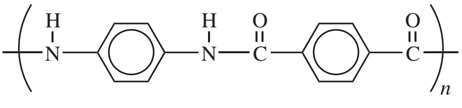
Nomex. This fiber was commercialized for applications requiring unusually high thermal and flame resistance. Nomex fiber retains useful properties at temperatures as high as 370°C. Nomex has low flammability and has been found to be self-extinguishing when removed from the flame. On exposure to a flame, a Nomex fabric hardens, starts to melt, discolors, and chars thereby forming a protective coating (23). Therefore an outstanding characteristic is low smoke generation on burning. The limiting oxygen index (LOI) value (top down) for Nomex fabrics is 26.0 (24). Nomex has a tga weight loss of 10% at 450°C and a use temperature of 370°C. Nomex has good to excellent strength, a tenacity of 0.42–0.51 N /tex (4.8–5.8 gf /den) (25), good extendability, and a modulus greater than that of nylon-6,6. The density is 1.38 g/cm^3 (26). Nomex is more difficult to dye than nylon, but the use of dye carriers allows dyeing to proceed at high temperatures with temperature-resistant basic dyes (27). The structure of Nomex may be represented as follows.



Nomex

MPD-1 fibers may be obtained by the polymerization of isophthaloyl chloride [99-63-8] and *m*-phenylenediamine [108-45-2] in dimethylacetamide with 5% lithium chloride (26). The reactants must be very carefully dried since the presence of water would upset the stoichiometry and lead to low molecular weight products. Temperatures in the range of 0 to -40°C are desirable to avoid such side reactions as transamidation by the amide solvent and acylation of *m*-phenylenediamine by the amide solvent. Both reactions would lead to an imbalance in the stoichiometry and result in forming a low molecular weight polymer. Fibers may be either dry spun or wet spun directly from solution.

Kevlar. In the 1970s, researchers at Du Pont reported that the processing of extended chain all-para aromatic polyamides from liquid crystalline solutions produced ultrahigh strength, ultrahigh modulus fibers. The greatly increased order and the long relaxation times in the liquid crystalline state compared to conventional systems led to fibers with highly oriented domains of polymer molecules. The most common lyotropic aramid fiber is PPT, which is marketed as Kevlar by Du Pont. Aramid fiber is available from Akzo under the trade name Twaron. These fibers are used in body armor, cables, and composites for sports and space applications. Kevlar has the following structure:



Kevlar

PPT of high molecular weight (inherent viscosity of 22 dL/g, corresponding to a molecular weight of 123,000) can be prepared by low temperature polymerization in various solvents (28). The PPT is less soluble in amide solvents than PBA and the most successful polymerization solvents are a mixture of hexamethylphosphoramide [680-31-9] (HMPA) and *N*-methylpyrrolidinone [872-50-4] (NMP) or NMP-containing calcium chloride (29,30). These solvent systems yield fiber-forming polymer. As the molecular weight increases rapidly during the first few seconds of the polymerization, the critical concentration is exceeded and the solution develops the opalescence characteristic of the liquid crystalline state. The critical factors influencing the molecular weight include stoichiometry, solvent composition, temperature, and solids concentration (31). At low monomer concentrations, side reactions can occur between the acid chloride chain ends and the amide solvents. At higher solids concentrations, gelation acts to limit the development of high molecular weights. It is of critical importance to keep the initial temperature low in order to prevent the reaction of the amide solvents with the acid chloride groups.

The preparation of high molecular weight PPT in HMPA/NMP shows a strong dependence of inherent viscosity on reactant concentrations. In 2:1 (by volume) HMPA/NMP, the highest inherent viscosity polymer is obtained when each reactant is present in concentrations of ~0.25 M (32,33); higher and lower concentrations result in the formation of a polymer of lower inherent viscosities. A typical procedure (31) is as follows: 1,4-phenylenediamine [106-50-3], HMPA, and NMP are added to an oven-dried resin kettle equipped with a stirrer and stirred for ~15 min with cooling to -15°C, followed by the addition of powdered terephthaloyl chloride [100-20-9] to the rapidly stirred solution. The reaction mixture changes to a thick, opalescent, paste-like gel in ~5 min.

The manufacturing process utilized (34,35) is continuous polymerization in order to minimize cost. A continuous stream of *p*-phenylenediamine solution is added to a continuous stream of molten terephthaloyl chloride. Volumetric control is easily achieved because both reactants are in the liquid state. Residence time in the mixing apparatus is on the order of 1 s. Next, the reactants enter a high shear, continuous screw mixer, in which the inherent viscosity of the polymer increases to 4–4.5 dL/g. The minimum inherent viscosity required for fiber spinning in sulfuric acid is 4 dL/g. The residence time is <15 s so the polymer solution that enters the third stage is still a fluid. The third stage is a high shear, twin-screw mixer with blades positioned for a number of recycle zones within the mixer, thereby achieving lower temperatures, higher residence times, and higher molecular weights.

An alternative polymerization process utilizes a slurry of calcium chloride in NMP as the polymerization medium (30). The solubility of calcium chloride is only 6% at 20°C; however, the salt continues to dissolve as conversion of monomers to polymer proceeds and calcium chloride–polyamide complexes are formed. Polymer molecular weight is further increased by the addition of *N,N*-dimethylaniline [121-69-7] as an acid acceptor. This solvent system produces fiber-forming polymer of molecular weights comparable to that formed in HMPA/NMP.

Since PPT melts with decomposition at ~560°C (36), melt spinning cannot be employed. Thus, solution spinning techniques (31) must be used to prepare fibers. Although dry, wet, and dry jet-wet spinning methods have all been used to prepare fibers, ordinarily PPT is spun from nematic sulfuric acid solutions using the dry jet-wet spinning process with cold water as the coagulant. In the dry spinning process, a polymer solution is passed through a spinnerette followed by flash evaporation of the solvent in a heated chamber and subsequent winding of the fiber produced on a bobbin. In the wet spinning process, the polymer solution is passed through a spinnerette located in a coagulation bath. The fiber formed is then drawn to increase molecular orientation, tenacity, and modulus. In dry jet-wet spinning, the polymer solution is allowed to flow through a spinnerette into a separated coagulation bath. Therefore the temperatures of the spinnerette and coagulation baths may be independently controlled. The liquid crystalline nature of the PPT dopes and the dry jet-wet spinning technology are principally responsible for the development of commercial high performance Kevlar fibers.

Drawdown of the coagulated fiber is an essential element in high performance fiber technology (31). Under shear, the unoriented domains become oriented in the direction of stretch. In the fiber manufacturing process, the unoriented liquid crystalline domains are oriented in the spinnerette, followed by retention and perfection of the highly ordered nematic phase by the elongational forces in the air gap and further drawdown in the coagulation medium (37). Coagulation sets the high degree of orientational order achieved by stretching. Tenacity increases with increasing drawdown and inherent viscosity as well as decreasing air gap (between the spinnerette and coagulation bath). Modulus increases with increasing drawdown and total spinning strain.

Because of their rigid chain structure, PPT and related *p*-aramids exhibit liquid-crystalline behavior in solution. The rod-like molecules aggregate in nematic, ordered domains. When solutions of these materials are exposed to shear, these ordered domains tend to orient in the direction of flow. On passing through a spinnerette, liquid-crystalline solutions retain the high degree of orientation acquired in the spinning process, leading to as-spun fibers with extraordinary degrees of crystallinity and orientation. As-spun fibers of PPT obtained by spinning a 20% solution of PPT in 100% sulfuric acid have a crystalline orientation angle of $\sim 12^\circ$ (determined from wide-angle X-ray diffraction) and a modulus of ~ 72 GPa (38). Heat treatment increases the degree of crystalline alignment. Correspondingly, heat-treated fibers have an orientation of $\sim 9^\circ$ and a modulus of ~ 120 GPa.

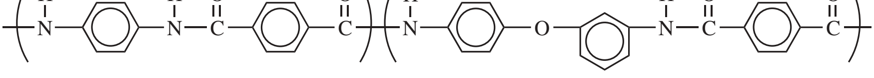
In a typical commercial dry jet-wet spinning process, PPT polymer of inherent viscosity 6.0 dL/g is added to 99.7% sulfuric acid in a water-jacketed commercial mixer in a ratio of 46 g of polymer to 100 mL of acid (39). The mixture is sealed in a vacuum of 68.5–76 mL of mercury. Mixing takes place for 2 h at temperatures of 77–85°C. The dope is then transferred to a glass-lined, water-jacketed kettle at 90°C. Any air or bubbles caused by the transfer are removed under vacuum for ~ 30 min. The dope is then pumped through a heated (90°C) transfer line to an electrically heated spinning block with an associated gear pump. The gear pump then meters the dope through a heated (80°C) 1.25-cm diameter spinnerette containing 100 holes of 51-μm diameter. The dope is extruded from the spinnerette at a velocity of ~ 63 m/min vertically through a 0.5-cm layer of air (air gap) into water at a temperature of 1°C. The yarn is wound on a bobbin under a 50°C water spray. The bobbin is then submerged in 0.1 N $NaHCO_3$ solution and then further extracted with water at 70°C.

Dramatic increases in the mechanical properties of aramid fibers are observed on heat treatment under tension. Tenacity and modulus increase exponentially with increasing temperature (and draw ratios) of wet spun fibers at temperatures of ~360°C (the glass-transition temperature, T_g) to 550°C (the melting temperature). Dry jet-wet spun yarns heat treated under tension show substantial increases in modulus at temperatures >200°C; the already high values of tenacity remain essentially unchanged. An intermediate modulus, high tenacity dry jet-wet spun yarn is thus converted into high modulus, high strength fiber.

Because the inherent viscosities of the heated yarns remain constant, it is postulated that the changes are physical. Yarns with as-spun moduli of 8.8–88 N/tex (100–1000 gf/den) may be obtained directly by dry jet-wet spinning. Yarns with as-spun tenacities of >1.8 N/tex (20 gf/den) are obtained by dry jet-wet spinning. Kevlar-29 has a tenacity of ~2.5 N/tex (28 gf/den) and a specific modulus of ~41 N/tex (464 gf/den) (40). Kevlar-49 has a tenacity of ~2.5 N/tex (28 gf/den) and a specific modulus of ~86 N/tex (980 gf/den). A relatively new fiber, Kevlar-149, is the highest tensile modulus aramid fiber currently available. Its specific modulus is ~126 N/tex (1430 gf/den) and tenacity ~2.3 N/tex (26 gf/den).

The crystal structure of PPT is pseudo-orthorhombic (essentially monoclinic) with $a = 0.785$ nm; $b = 0.515$ nm; c(fiber axis) = 1.28 nm and $\gamma = 90°$ (41). The molecules are arranged in parallel hydrogen-bonded sheets. There are two chains in a unit cell and the theoretical crystal density is 1.48 g/cm^3. The observed fiber density is 1.45 g/cm^3. Based on electron microscopy studies of peeled sections of Kevlar-49, the supramolecular structure consists of radially oriented crystallites. The fiber contains a pleated structure along the fiber axis, with a periodicity of 500–600 nm.

Technora. In 1985, Teijin Ltd. introduced Technora fiber, previously known as HM-50, into the high performance fiber market. Technora is based on the 1:1 copolyterephthalamide of 3,4′-diaminodiphenyl ether and *p*-phenylenediamine (42). Technora is a wholly aromatic copolyamide of PPT, modified with a crankshaft-shaped comonomer, which results in the formation of isotropic solutions that then become anisotropic during the shear alignment during spinning. The polymer is synthesized by the low temperature polymerization of *p*-phenylenediamine, 3,4′-diaminophenyl ether, and terephthaloyl chloride in an amide solvent containing a small amount of an alkali salt. Calcium chloride or lithium chloride is used as the alkali salt. The solvents used are HMPA, NMP, and dimethylacetamide (DMAc). The structure of Technora is as follows:



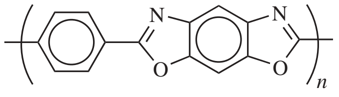
Technora

The polymerization is carried out at temperatures of 0–80°C in 1–5 h at a solids concentration of 6–12%. The polymerization is terminated by neutralizing agents such as calcium hydroxide, calcium oxide, calcium carbonate, or lithium hydroxide. Inherent viscosities of 2–4 dL/g are obtained at 3,4′-diaminodiphenyl ether contents of 35–50 mol%. Because of the introduction of nonlinearity into the PPT chain by the inclusion of 3,4′-diaminodiphenyl ether kinks, the copolymer shows improved tractability and may be wet or dry jet-wet spun from the polymerization solvent. The fibers are best coagulated in an aqueous equilibrium bath containing <50 vol% of polymerization solvent and from 35 to 50% of calcium chloride or magnesium chloride.

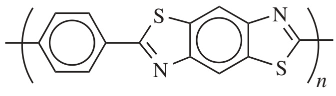
The copolymer fiber shows a high degree of drawability. The spun fibers of the copolymer were highly drawn over a wide range of conditions to produce fibers with tensile properties comparable to PPT fibers spun from liquid crystalline dopes. There is a strong correlation between draw ratio and tenacity. Typical tenacity and tensile modulus values of 2.2 N/tex (25 gf/den) and 50 N/tex (570 gf/den) , respectively, have been reported for Technora fiber (42).

Heterocyclic Rigid-Rod Polymers PBO, PBZ, and PIPD. PBZ, a family of *p*-phenylene-heterocyclic rigid-rod and extended-chain polymers includes poly(*p*-phenylene-2,6-benzobisthiazole) [69794-31-6] (*trans*-PBZT), poly(*p*-phenylene-2,6-benzobisoxazole) [60871-72-9] (*cis*-PBO), and poly[2,6-diimadazo[4,5-b:4′,5′-e]pyridinylene-1,4(2,5-dihydroxy)phenylene (PIPD). Both PBZT and PBO were initially prepared at the Air Force Materials Laboratory at Wright-Patterson Air Force Base, Dayton, Ohio (43). The PBZT was prepared by the reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthalic acid [100-21-0] in polyphosphoric acid (PPA) and PBO by the reaction of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid in PPA. The PIPD was prepared by the reaction of 2,3,5,6-tetraaminopyridine with 2,5-dihydroxyterephthalic acid. PIPD was initially prepared at Akzo Nobel Central Research (44).

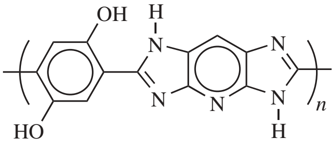
Although the crystal structures of the 2,6-diphenyl- *cis*- and *trans*-benzobisoxazole compounds have colinear exocyclic bonds with the coplanar condensed rings (45), and the phenyl rings coplanar with the heterocycles (46), the central ring of the 2,6-diphenyl-*cis*-benzobisthiazole system is bent (47). The exocyclic bonds of the 2,6-diphenyl-*cis*-benzobisthiazole system are bent out of linearity. The central, condensed ring system of 2,6-diphenyl-*trans*-benzobisthiazole is planar with the exocyclic bonds showing a deviation of only 0.06 nm from colinearity. The phenyl rings of 2,6-diphenyl-*trans*-benzobisthiazole deviate from planarity with a dihedral angle of $\sim 23^\circ$. The phenylene rings in the *trans*-PBZT polymers are coplanar with the central condensed heterocyclic ring system. Wide angle X-ray diffraction studies of PIPD revealed a hydrogen bonding scheme consisting of intramolecular O–H–N hydrogen bonds and intermolecular N–H–O hydrogen bonds. The crystal structure of heat-treated PIPD fiber (M5 fiber) showed monoclinic symmetry (48). Crystal structure analysis showed that the neighboring chains are shifted along the *c* axis (chain axis) relative to one another by 2.0 Å units. Each polymer chain is linked by bidirectional intermolecular hydrogen bonds to it’s four axially shifted neighbors. The presence of bidirectional intermolecular hydrogen bonding in PIPD is considered to be the basis for the exceptionally good compressive properties of PIPD. The relatively high compressive strength of PPT as compared to PBO and PBZT (4) is attributed to interchain hydrogen bonding. The additional bidirectional hydrogen bonding in PIPD compared to PPT would explain the exceptionally high level of compressive strength for PIPD. Sikkema and co-workers (49) reported that while other polymers have compressive strengths between 0.2 and 0.6 GPa, M5 fiber spun from PIPD has a compressive strength of 1.7 GPa. The structures of PBO, PBZT, and PIPD are as follows:



PBO



PBZT



PIPD

The early syntheses of *cis*-PBO and *trans*-PBZT were conducted at polymer concentrations of 3 wt% or less. Since these isotropic solutions had high bulk viscosities, polymerizations had to be carried out at low solids concentrations to maintain tractability. When the concentration of *trans*-PBZT was raised to 5–10 wt%, nematic solutions were formed and polymers with intrinsic viscosities as high as 31 dL/g were obtained. Initially, the formation of *trans*-PBZT solutions of concentrations >10% caused foaming problems during the polymerization and low molecular weights. The discovery of the P_2O_5 adjustment method was the breakthrough that resulted in the production of nematic spinnable dopes.

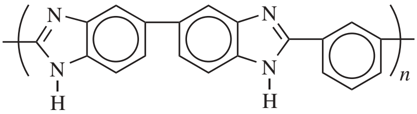
The P_2O_5 adjustment method involves adding P_2O_5 to the PPA polymerization solvent to maintain an effective PPA composition as the PPA acts as solvent, catalyst, and dehydrating agent. The PPA acts as the solvent for monomer, oligomers, and polymer. The PPA also activates the functional groups for polymerization and removes the water of condensation. Also, P_2O_5 is added at the end of the polymerization to achieve the viscosity necessary for spinning. At the end of the polymerization process, the P_2O_5 content must be >82% to keep all the components in solution and <84% to give a solution of the proper viscosity for spinning. The temperatures of the PBO and PBZT polymerizations are raised in steps from 100 to 200°C to avoid decomposition of monomers. The temperature of the PIPD polymerization was raised stepwise from 100 to 180°C.

These rigid-rod polymers are spun using the dry jet-wet spinning technique also used for the spinning of aramid dopes. The solution is extruded under heat and pressure through a single or multihole spinnerette and an air gap into a coagulation bath, followed by washing, drying, and heat setting. Both PBO and PBZT have been spun in PPA and methanesulfonic acid. Water, dilute phosphoric acid, methanol, and ammonia have been used as coagulants. Heat treatment involves temperatures of 500–700°C with residence times on the order of a few seconds to several minutes. The nematic PPA solution formed in the polymerization may be used as the spinning dope. The typical molecular weight range used to spin fibers is 50,000–100,000 Da. PIPD as-polymerized solutions of M_w 60,000–150,000 were air-gap wet spun at 180°C into a water or dilute phosphoric acid bath, followed by washing to a low phosphorus content and drawing at a temperature $>400°C$ to produce the final high modulus M5 fiber.

In thermogravimetric analyses (50) of the ordered polymers, the extrapolated onset of degradation of PBO and PBZT is reported to be 620°C in air. The extrapolated onset of degradation of PBO in helium is over 700°C. In isothermal aging studies in air at 343°C, PBO and PBZT retain ~90% of the weight after 200 h. At 371°C in air, PBO and PBZT retain ~78 and 71% of the original weight, respectively. The PBZ polymers degrade without the observation of crystalline melting points or glass-transition temperatures. The onset of thermal decomposition in air for PIPD was reported to be 530°C.

Toyobo (Zylon) has marketed the PBO fiber and Magellan Systems International has brought M5 fiber to the marketplace. The PBO fibers have the highest reported tensile modulus of any known polymeric fiber, 280–360 GPa(41–52×10^6 psi). Both PBO and PBZT are among the most radiation-resistant polymers. Although the compressive strengths of PBO and PBZT are approximately an order of magnitude less than the tensile strengths, alloys of these fibers with high compressive strength fibers can be produced. The polymers are now being evaluated for other applications such as nonlinear optics. Possible PBO applications include reinforcing fibers in composites, multilayer circuit boards, athletic equipment, marine applications, woven fabrics, and fire-resistant fibers (1). Magellan Systems International reports a tenacity of 5.3 GPa, a modulus of 350 GPa, and a compressive strength of 1.6 GPa for M5 fiber (51). Possible M5 applications include advanced lightweight composites, hard and soft ballistic armour, high strength cables, advanced fabrics and textiles, and high performance fire retardant materials.

Polybenzimidazole (PBI) Fibers. Poly[(2,2′-*m*-phenylene)-5,5′-bisbenzimidazole] [25734-65-0] is a textile fiber originally marketed by the Celanese Corporation (52) that does not form liquid crystalline solutions due to its bent meta backbone monomeric component. The PBI has excellent resistance to high temperature and chemicals.



PBI

PBI is being marketed as a replacement for asbestos and as a high temperature filtration fabric with excellent textile apparel properties. The synthesis of wholly aromatic polybenzimidazoles with improved thermal stabilities was reported in 1961 (53). The Non-Metallic Materials and Manufacturing Technology Division of the U.S. Air Force Materials Laboratory, Wright-Patterson Air

Force Base, awarded a contract to the Narmco Research and Development Division of the Whittaker Corp. for development of these materials into high temperature adhesives and laminates.

Poly[2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole] was chosen as the most promising candidate for further development as a fibrous material. Under the terms of an Air Force contract, Du Pont was able to spin fibers from both dimethyl sulfoxide and dimethylacetamide solutions to form relatively strong, thermally stable fibers. In 1963, an Air Force contract was awarded to Celanese Research Co. for the development of a manufacturing process for the scale-up of PBI production. The PBI fiber of tenacities 0.31–0.44 N/tex (3.5–5.0 gf/den) were produced in sufficient quantity for large-scale evaluation. The fiber was discovered to have a soft hand in addition to possessing a high degree of nonflammability. In the limited oxygen index (LOI) test, the concentration of oxygen required for sustained, steady-state burning was 41%. A new development program was started at Celanese with funding from NASA and the Air Force to develop a flight suit material, fabrics for fatigues worn in space capsules, and utility equipment such as ropes and bungee cords.

Further field tests demonstrated that in spite of the excellent thermal and fire resistance, shrinking of the fabrics occurred above the glass-transition temperature that might expose the wearer to flames. Based on the results obtained in an Air Force contract at Dynatech Co., the Celanese Research Co. developed a two-stage process that reduced the shrinkage from 50 to 6%. The process was also amenable to on-line processing. The sulfonated derivative is the fiber that was marketed by the Celanese Corp. Some end uses include replacement of asbestos, thermal and chemical safety apparel, and stack gas filter bags, airline seat covers, firemen turn coats, and race car driver suits.

Development efforts at Celanese Research Co. established solid-state polymerization as the most practical process for engineering scale-up. Homogeneous solution polymerization of PBI in polyphosphoric acid was eliminated because of the need to work with low solid compositions (in the range of 3–5%) during the precipitation, neutralization, and washing steps required for isolation of the product.

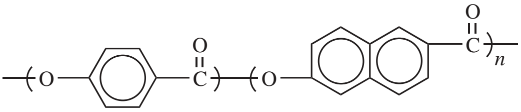
In the first stage of the engineering scale-up process (54), a 189-L oil-jacketed, stainless steel reactor is charged with diphenyl isophthalate [744-45-6] (DPIP) and 3,3′,4,4′-tetraaminobiphenyl (TAB). The reactor is deoxygenated by alternative application of vacuum and filling with nitrogen three times, followed by agitation and heating to 250°C under a stream of nitrogen, followed by heating at 290°C for 1.5–3.0 h in the absence of agitation before cooling. In the second stage of the process, the polymer obtained in three to four runs is ground to 0.84 mm (20 mesh) and charged into a 38-L oil-heated stainless steel reactor for a final heating step with agitation at 370–390°C for 3–4 h. Initially, large amounts of foam were produced in the first stage of the process. Foam reduction involves the addition of 10–20% by weight of an organic additive such as diphenyl ether. At the lower temperature of the first stage, the additive acts to prevent foaming and the additive is then removed at the higher temperatures involved in the second stage. Although the foam volume is significantly reduced, the additive residues are removed only with considerable difficulty.

The spinning process used to produce PBI fibers is dry spinning (55). The preferred solvent for dry spinning of PBI is DMAc. The powdered polymer is dissolved in DMAc at high temperatures (~250°C) to form ~23% wt/wt concentration spinning dopes. The spinning dope is fed by a metering pump through a spinnerette (following filtering) into a countercurrent of hot nitrogen gas in the spinning column. Nitrogen gas is used to prevent oxidation of the oxidatively sensitive filaments formed as the hot gas evaporates the DMAc. The filaments pass to a godet roll and then onto a winder. Washing of the fiber takes place on perforated bobbins to remove lithium chloride stabilizer and residual solvent. The fiber is drawn to achieve improved mechanical properties by passing it from feed rolls to draw rolls through an oven set at temperatures > 400°C while under a positive nitrogen pressure. Acid treatment to minimize shrinkage involves the use of aqueous sulfuric acid to produce an acid salt followed by heat treatment to form sulfonic acid groups. If all the imidazole rings were substituted, the final stabilized product would contain 8% sulfur; however, the level of sulfur ordinarily obtained (~6%) is sufficient for the required improvement in dimensional stability.

Typical properties of stabilized PBI (56) are a tenacity of 0.27 N/tex (3.1 gf/den), a fiber breaking elongation of 30%, an initial modulus of 3.9 N/tex (45 gf/den), a density of 1.43 gf/cm^3, and a moisture regain of 15% (at 21°C and 65% relative humidity).

Solution dyeing of PBI is necessary (57) because the T_g of PBI is >400°C, and as a result dye molecules only slowly diffuse into the PBI fiber structure. Since the pigments are added to the spinning dope, the pigments must be capable of withstanding the high temperatures used in the various fiber-forming processes.

Industrial Thermotropic LCPs. Vectran, poly(6-hydroxy-2-naphthoic acid-*co*-4-hydroxybenzoic acid) [81843-52-9], was the first thermotropic fiber to become commercially available (58). Vectran is synthesized by the melt acidolysis of *p*-acetoxybenzoic acid and 6-acetoxy-2-naphthoic acid.



Vectran

First, *p*-hydroxybenzoic acid (HBA) [99-96-7] and 6-hydroxy-2-naphthoic acid (HNA) [16712-64-4] are acetylated to produce the low melting acetate esters that are molten at 200°C. In an inert gas, the two monomers are melted together at 200°C. The temperature is raised to 250–280°C and acetic acid is collected for 0.5–3 h. The temperature is raised to 280–340°C and additional acetic acid is removed in vacuum for a period of 10–60 min. The opalescent polymer melt produced is extruded through a spinning jet, followed by melt drawdown. The use of the parallel offset monomer, acetylated HNA, results in the formation of a series of random copolyesters of different compositions, many of which fall within the commercially acceptable melting range of 250–310°C. Characteristically, these nematic melts show the persistence of orientational order under the influence of elongational flow fields that results in low melt viscosities under typical fiber formation conditions even at high molecular weights.

Axial orientation develops quickly during melt drawdown with a concomitant increase in fiber modulus. At a drawdown ratio of ~10, the fiber achieves a maximum modulus in the range of 44.1–61.7 N/tex (500–700 gf/den). Neither cold drawing nor annealing led to additional increases in modulus. The high level of mechanical properties is the result of the comparative ease of axial orientation of the nematic phase leading to a highly oriented rod-like fiber structure. This is borne out by X-ray fiber analysis that shows well-defined meridonal maxima characteristic of highly oriented parallel arrays of polymer chains with poor lateral spacing.

Heat treatment of the as-spun fibers results in an increase in tenacity but no attendant increase in modulus. Typically, the as-spun fibers are heat treated in an inert environment at temperatures 10–20°C below the melting point for from 10 min to several hours. There is a corresponding increase in chemical resistance and melting temperatures, presumably due to increases in molecular weight rather than improvements in structural perfection. This is in agreement with X-ray fiber diagram results that show no increase in orientation of mesophases during the heat treatment process. Vectran HS fibers are reported to have typical tensile strength and modulus values of 2 N/tex (23 gf/den) and 46 N/tex (550 gf/den) (59), respectively. The melting point and density are reported to be 330°C and 1.4 g/cm^3. The fibers have excellent chemical resistance except for their resistance to alkali.

2.2. Gel Spun Fibers. In the mid-1970s, it was discovered at the Dutch States Mines Co. (DSM) that through an ingenious new method of gel spinning ultrahigh molecular weight polyethylene it was possible to produce fibers having twice the tenacity of Kevlar, which was then considered to be the strongest known fiber (60). The discovery was important not only because of the exciting 3.8 N/tex (44 gf/den) strengths these new fibers displayed, but also because it clearly demonstrated that factors other than monomer polarity were critical in controlling fiber performance characteristics. These high performance polyethylene fibers (HPPE) produced by the DSM subsidiary company, Stamicarbon, were called Dyneema and those produced by the AlliedSignal Corp. in the United States are sold under the trade name of Spectra 1000. The commercial products have somewhat lower strengths than the laboratory fibers but still are in the high 2.6 N/tex (30 gf/den) range (61).

Process. In the gel spinning process, 1–8% solutions of polyethylene are prepared by dissolving polymer of molecular weights of 1–4 million in hot hydrocarbon liquids such as decalin, melted waxes, or mineral oils at ~150°C. These hot solutions are then screw extruded through spinnerettes having holes of 0.5–2.0-mm diameter and an L/D ratio of 25 to control the viscoelastic flow properties of the fluid. The fibers are spun into a cooling bath that yields disoriented highly crystalline gel fibers of sufficient stability to be wound onto a first godet at several m/min. These gel fibers are then processed in solvents at ~50°C to remove the hydrocarbons. The solvent-free gels are then stretched in progressively hotter zones at temperatures from 120 to 160°C with an overall final windup/extrusion speed of ~1000/L or whatever is required to give the final desired strengths of 1.7–3.5 N/tex (20–40 gf/den) (62).

The patent literature indicates that the Allied Signal process uses lower boiling solvents such as chlorofluorocarbons as the cooling/extraction baths

Table 1. **Properties of Commercial HPPE Fibers**[a]

Fiber	Tenacity, N/tex	Initial modulus, N/tex	Elongation at break, %
dyneema	1.01–3.57	57–128	3–7
spectra 1000	3.4–3.57	162–171	3–7

[a] See Refs. 63 and 64.

(63), whereas the processes of Stamicarbon indicate the use of decalin solvent followed by cooling and slow removal of the decalin in successively hotter chambers while stretching (64).

Properties. Fiber property comparisons for the different products are given in Table 1.

The attributes of HPPE fibers include high strength; high abrasion resistance; high uv stability as compared to other synthetics; high resistance to acids, alkali, organic chemicals, and solvents; and low density. Disadvantages are a low melting point of ~150°C (1), which means performance is limited to no >120°C; difficult processing; and poor surface adhesion properties.

It is difficult to process HPPE staple fibers mechanically because of so-called married fibers, which are bundles of four to six fibers that firmly adhere to each other and resist separation by conventional processing. Although HPPE fibers like to adhere to each other, they exhibit poor adhesion to other materials.

It is possible to modify HPPE to overcome the poor adhesion of the fiber surfaces by using corona discharge in an oxygen atmosphere previously developed for polyolefin films or by the addition of fillers to the polymer solution prior to spinning. The melting point of HPPE fibers embedded in polymer matrices is increased by ~8°C (65,66). Temperature performance can also be enhanced by wrapping the HPPE fibers with other fire-resistant or fire-retardant fibers (67). Other ultrahigh molecular weight polymers have also been spun via the gel spinning process. These include polypropylene, polyacrylonitrile, poly(vinyl alcohol), and nylon-6. However, the property improvements in these cases evidently have not warranted commercialization.

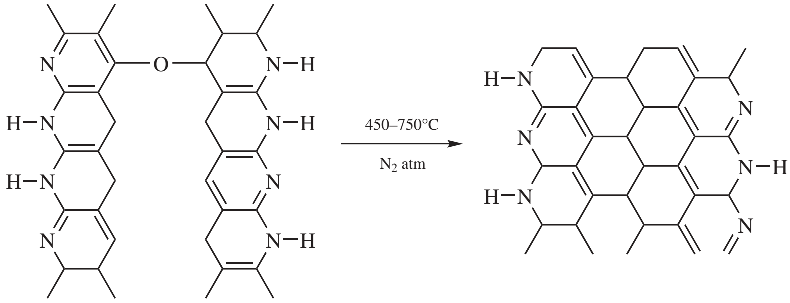
2.3. Modified Carbon Fibers (Elongatable Carbonaceous Fiber).

Carbon fibers are made by the nonoxidative high temperature pyrolysis of fibers originally spun from either rayon, polyacrylonitrile (PAN) [25014-41-9] or mesomorphic hydrocarbon tar (MT or pitch) materials. Of these three staring materials, the most work has been done with rayon because the carbon fibers produced from rayon have the best overall physical and performance characteristics (68).

For example, rayon-based carbon fibers have the lowest density followed by those from PAN, with those from the tar base having the highest density. A similar trend is found in physical strength test results. Of paramount importance for space vehicle use, the carbon fibers from rayon exhibit the best ablative performance with the least loss of weight during reentry into earth's atmosphere. The carbon fibers used in space projects require a special classified type of rayon and special carbonizing conditions to reach peak performance. During the early 1990s such rayon was in short supply due to the closing of the main producer having effluent pollution problems. However, a second new supply was developed with no delay to the space program. Due to their low elongation and resulting high brittleness, essentially all rayon-based carbon fibers are used as reenforcement fibers for laminate structures with polyphenolic and other resins. Carbon fiber cloth can only be woven on special types of textile looms. Acrylonitrile copolymers and terpolymers can be used to make carbon type fibers with higher elongations that are much more applicable for textile operations.

Liquid-crystalline mesophase pitch is employed for high modulus carbon fiber production by stress graphitization. Carbon fibers prepared from this process were commercialized in the early 1980s (1). Petroleum, coal tar, and poly(vinyl chloride) are common sources of the pitch used in the preparation of carbon fibers.

It is difficult to weave or knit regular carbon fiber. For any fiber to be considered as a satisfactory textile fiber it should have an elongation of at least 3% and preferably more in the range of 5–8%. The extreme brittleness, high modulus, and low elongation of standard carbon fibers restrict them to be woven only on a special type of rigid rapier loom. To overcome these drawbacks, an exciting new modification of carbon fiber technology was developed; by using less stringent carbonizing conditions and only partially carbonizing the precursor fibers, improved textile fiber properties have been achieved (69).



OPF EDF

Process. Any standard precursor material can be used, such as oxidized polyacrylonitrile (PAN) fiber (OPF). This OPF is treated in a nitrogen atmosphere at 450–750°C, preferably 525–595°C, to give fibers having between 69–70% C, 19% N; density <2.5 g/mL; and a specific resistivity under 10^{10} cm. If crimp is desired, the fibers are first knit into a sock before heat treating and then de-knit. Controlled carbonization of precursor filaments results in a linear Dow fiber (LDF), whereas controlled carbonization of knit precursor fibers results in a curly carbonaceous fiber (EDF). At higher carbonizing temperatures of 1000–1400°C the fibers become electrically conductive (70).

Properties. Unlike regular carbon fibers, these new products do not conduct electricity, but do exhibit good textile processing properties and possess exceptional ignition-resistant, flame-retardant, and even fire blocking properties. The LOI defines the percentage of oxygen necessary in an oxygen–nitrogen mixture before a material supports combustion. Typical LOI values for various fibers are given in Table 2.

Table 2. **Limiting Oxygen Values of Fibers**[a]

Fiber	LOI, %
polyethylene	17
polystyrene	19
cotton	20
nylon	20
polycarbonate	22
Du Pont Nomex	26
PPO	26
polysulfone	30
polyimide	37
rigid PVC	40–44
oxidized PAN	>40
Hoechst-Celanese PBI	41
Dow EDF	45–55
Phillips PPS	44
graphite	55
PTFE	95

[a] See Refs. 70 and 71.

Previous results with ignition resistant (IR) blends, where such fibers as aramids or PBI are used as the high LOI fibers, show that they need at least 65% and typically 85% fiber content to pass the vertical burn test for lightweight nonwoven batting. In contrast only 7–20% of either the Dow EDF or LDF mixed with flammable natural and synthetic fibers allow the blends to pass such tests while still retaining most of the base natural or synthetic fiber properties. Blends of 50/50 EDF/polyester also passed the stringent FAA airlines ignition resistance tests with zero flame length and no after-burn, whereas other blends of 65% LOI fiber/40% synthetic blends gave burn lengths of 20 cm and 15 s after-burn, clearly demonstrating the superiority of the lower level carbonaceous fiber as a flame blocker (70,71). Such nonwoven batting has exceptional thermal and sound insulation properties and has been successfully tested by the U.S. Navy for pilot's arctic wear.

2.4. Carbon-Nanotube Fibers. In 2000, Poulin and colleagues reported a carbon-nanotube spinning method (72) in which surfactant-dispersed single-walled nanotubes were injected at a rate of 10–100 mL/h into a cylindrical container holding a 5% poly(vinyl alcohol) (PVA) aqueous solution. The cylinder was rotated at speeds of 30–150 rpm. By pumping out the PVA solution, meter-long ribbons were obtained. After the ribbons were washed and rinsed with pure water to remove PVA and surfactant and drying , fibers several tens of centimeters long were made by slowly pulling the ribbons out of water. Young's moduli of the fibers varied between 9 and 15 GPa.

In 2003, Baughman and associates reported that by modifying the Poulin process (73), they were able to spin 100-m lengths of nanotube composite fiber in a continuous process at a rate of more than 70 cm/min. In their process, the spinning gel was injected into a cylindrical pipe in which a a PVA coagulation solution was allowed to flow, resulting in collapse of the spinning solution into nanotube fiber subsequently wound on a mandrel. The second stage of the process involved unwinding the fibers on a series of godets that transport them through an acetone wash-bath, followed by drying and wrapping on a mandrel.

Baughman reported that these composite fibers were tougher than any natural or synthetic fibers descibed to date. The composite fibers were ~50 μm in diameter and contained ~60% single wall nanotubes by weight. They reported a tensile strength of 1.8 GPa (which is comparable to that of spider silk) and an energy-to-break of 570 J/g that is higher than that of spider dragline silk (165 J/g), Kevlar fibers (33 J/g), and graphite fiber (12 J/g). Baughman and colleagues have used the nanotube composite fibers to make nanotube supercapacitors that were woven into textiles. Suggested potential applications for the carbon-nanotube fibers include distributed sensors, electronic interconnects, electromagnetic shields, and attennas and batteries.

2.5. Silicon Carbide Ceramic Fibers. The commercially produced continuous and multifilament Nicalon fiber is produced from polydimethylsilane; however, other organosilicon polymers have been used for the production of silicon carbide fiber. Polydimethylsilane is first distilled to remove the low molecular weight components, and polymer of average molecular weight 1500 is melt spun at 280°C and cured in air at 200°C. The fiber is then heat treated between 800° and 1500°C in nitrogen or vacuum. Optimum mechanical properties are achieved at ~1250°C. Listed properties of the Nicalon fiber are modulus: 200 GPa; and tensile strength: 2.8 GPa (1).

Continuous SiC fibers can also be prepared by using chemical vapor deposition (CVD). For this process, tungsten or a carbon substrate fiber and vapors of CH_3SiHCl_2, $C_2H_5SiCl_3$, or CH_3SiCl_3 have been used. A SiC fiber with a reported modulus of 400 GPa and tensile strength of 3.45 GPa (1) is produced in a tubular glass reactor by a CVD process on a carbon monofilament substrate melt-spun from coal tar pitch. The process is carried out in two steps : (*1*) 1-μm thick pyrolytic graphite is deposited to render the substrate fiber smooth and enhance its electrical conductivity; (*2*) the coated substrate fiber is exposed to the silane vapors. Decomposition at the surface occurs at temperatures of ~1300°C to form β-SiC continuously on the substrate.

Silicon carbide has high thermooxidative stability and good thermal and electrical insulation properties. In composite applications, this fiber can be used to reinforce polymer, metal, and ceramic matrices.

2.6. Vitreous Fibers. Man-made vitreous fibers (MMVF) comprise a number of glass and specialty glass fibers and also refractory ceramic fibers. The vitreous state in glass is somewhat analogous to the amorphous state in polymers. However, unlike organic polymers, it is not desirable to achieve the crystalline state in glass. Glasses are produced from glass-forming compounds such as SiO_2, P_2O_5, etc, which are mixed with other intermediate oxides such as Al_2O_3, TiO_2, or ZnO, and modifiers or fluxes like MgO, Li_2O, BaO, CaO, Na_2O, and K_2O (1).

The purpose of the fluxes is to break down the SiO_2 network so that the molten glass has the proper viscosity characteristics to allow it to cool to the desired vitreous state. Glasses with large fractions of noncross-linking monovalent alkaline fluxes allow the melts to form at lower temperatures but correspondingly have lower chemical resistance. For example, sodium silicate glasses with larger amounts of Na_2O are sold as water solutions (water glass).

A wide range of glass compositions is available to suit many textile fiber needs; the three most common glass compositions are referred to as E, S, and AR glasses. The AR glass is a special glass with higher contents of Zr_2O designed to resist the calcium hydroxide in the cementitious products where it is used. The S glass is a magnesium–aluminum–silicate cross-linked glass used where high mechanical strength or higher application temperatures are desired. The E glass is a member of the calcium–aluminum–silicate family containing $<2\%$ alkali (see composition in ASTM specification D578-89a) and is the predominant glass used to make textile and continuous filament fibers.

Glass fibers <3 μm are to be avoided because these are classified as respirable fibers which can enter and damage lung passages. Most glass fiber products have sufficient fiber lengths to prevent lung entry even if their diameters are <3 μm.

Manufacture. Vitreous fibers are produced by several processes (74).

Continuous Drawing Process. Textile glass filaments are made by a process different from that used for making discontinuous fibers, but literally parallel to a standard organic polymer melt spinning operation that does not employ a screw extruder. Premelted glass or glass marbles are fed into an electrically heated furnace called a bushing which contains platinum nozzles. The exiting glass filaments are drawn down into the desired diameters, water sprayed, coated with a sizing, and the multiple filaments are collected as bundles of strands that are then wound onto a suitable cone.

Rotary Process. This process is much like the making of cotton candy except that molten glass is used in place of molten sugar. The melted glass is dropped into a rotating spinner with sidewall perforations and the exiting glass filaments are drawn to a fine diameter by the centrifugal force. These fibers are collected and coated with a protective spray containing either lubricants, binders, or antistatic and wetting agents. Other versions of the rotary process are (*1*) the wheel centrifugal process where molten glass is cascaded over spinning wheels and the formed fibers are stretched and broken by variations in the wheel speeds prior to being collected, and (*2*) the Downey process where molten glass is dropped onto a centrifuge wheel and then exits into a stream of high velocity air much like the melt blown process for making textile nonwovens.

Flame Attenuation. This process closely resembles the continuous drawing process except that the melted strand is not wound onto a cone. Rather, the exiting strand is blown at right angles with a high velocity gas burner so as to remelt and reform the glass as small fibers, which are collected as a mat onto a moving belt. A modification of this process simply uses the high velocity flame at right angles to a dropping melted stream of glass to fibrillate the mass into minute fibers.

Properties. Glass fibers made from various compositions have softening points in the range 650–970°C. Fiber length and diameter distributions are significant factors in determining thermal and acoustical insulation properties. Slag wool and rock wool fibers are prepared from the slag from pig iron blast furnaces. They contain significant amounts of iron oxides and have a T^s of 760–870°C. Slag and rock wool fibers are used to prevent fires from spreading. At temperatures >850°C, these fibers partially devitrify and form polycrystalline material that melts at 1225–1360°C, which is high enough to contain the fires for several hours. In the United States 70% of the slag wool is used for ceiling tiles.

Refractory Ceramic Fibers (RCF). These MMVF materials constitute only ~1% of the vitreous fiber market but have exceptional high temperature performance characteristics. They are produced by using high percentages of Al_2O_3 ~50:50 with SiO_2 as is or modified with other oxides like ZrO_2 or by using Kaolin clay that has similar high amounts of Al_2O_3. Different compositions result in modifying end use temperatures from ~1050°C or higher for the kaolin-based products to 1425°C and above for the zirconium-containing materials. At temperatures >1000°C these ceramic fibers tend to devitrify and partially crystallize. Specially prepared ceramic fibers are used to protect space vehicles on reentry and can withstand temperatures >1250°C.

3. Applications

Commercial high performance fibers and high technology textile products have become an increasingly important segment of fiber and textile consumption worldwide. Although breakdown of the numerous applications by weight and/or economic value is impractical, one review indicated that high technology textile uses would account for 50% of all worldwide fiber consumption by the year 2000 compared to 10–15% in 1990 (75). In some instances, various technologies and concepts are combined or refined to produce a textile product for the desired application(s). Thus, sophistication and enhancement of properties may be introduced at the fiber, yarn, and/or fabric levels.

3.1. Structure/Property Classification. The relationship between structure and properties of textile or fibrous substrates and their applications is one method of classifying nontraditional or high technology textiles. At the fiber level, the distinguishing high performance characteristics are high tenacity/strength fibers, hollow fibers, very fine or microtex (microdenier) fibers (hollow or nonhollow), fibers with unique porosities, bicomponent and biconstituent fibers, and fibers with superior resistance to extreme heat, flame, and/or chemical agents (Table 3). At the fabric or product level, the classes may be described as coated and laminated fabrics, composites and fiber-reinforced materials, three-dimensional fabric structures, and fabrics containing polymers or structural

Table 3. **Classification of High Performance Fibers and High Technology Fibers by Properties**[a]

Property	Fiber types	Applications
high tenacity and modulus	aramids, gel spun polyethylene, PBO, PIPD, polyarylate	tires, antiballistics, ropes, optical cables
resistant to heat and flame	aramids, PEEK, PBI, polyimides, EDF	protective clothing for various applications
resistance to chemical agents	fluorocarbons, polyolefins	filters, geotextiles, marine applications
microtex and hollow fibers	most synthetics and regenerated fibers	filtration, leisure, insulation, biomedical fashion, fragrances
intricate shapes and porosities	most synthetics and regenerated fibers	antimicrobial, fiber optics, specialty wipes

[a] See Ref. 3.

features that impart multifunctional properties or allow the fibrous substrate to act as an intelligent material. Although some of these fiber and fabric characteristics also apply to conventional textile uses and products, many of these concepts have evolved from the production and use of high performance fibers and products.

Fiber Properties: High Strength Fibers. Super fibers or fibers with very high tenacities and Young's moduli have been defined as those with a tenacity of at least 2.5 GPa (255 kgf/mm^2) and a modulus of at least 55 GPa (5600 kgf/mm^2) (76). Fibers meeting these criteria are glass fibers, aramids such as Kevlar and Twaron, gel spun polyethylene such as Dyneema and Spectra, and various carbon fibers and aromatic liquid–crystalline polyesters such as Vectran. Representative applications are for antiballistic clothing, building materials, aerospace, and as reinforcing material in composites for various applications.

Heat-Resistant Fibers. Inherently flame- and heat-resistant fibers have other criteria for performance in addition to high tenacity and modulus. These fibers must be suitable for protective clothing or for use as a material in a particular application such as firefighters' uniforms, race car drivers apparel for protection from hot metals and gas explosions, and as components in commercial and military aircraft. Dimensional stability and strength retention on exposure to intense heat sources as well as a LOI >30 are essential for most of these applications. Fiber types and blends meeting these criteria are various aramids such as Nomex and Kevlar, polybenzimidazole (PBI), poly(phenylene sulfide) (PPS) such as Ryton, Dow's EDF, and wool blends with these various inherently flame-resistant fibers.

Chemically Resistant Fibers. Fibers with excellent chemical resistance to corrosive and/or chemical warfare agents or extreme pH conditions (eg, very acidic or very alkaline) were initially used for protective clothing. However, applications for filtration of gases and liquids in numerous industrial facilities are now more important. For example, PPS is suitable for use in filter fabrics for coal-fired boilers because of its outstanding chemical and heat resistance to acidic flue gases and its excellent durability under these end use conditions. Many high tenacity fibers are also chemically inert or relatively unaffected under a variety of conditions. Aramids, gel spun polyethylene, polypropylene, fluorocarbon, and carbon fibers meet these criteria and have been used or are being considered for applications where chemical resistance is important.

Fine and Hollow Fibers. Controlling and designing the geometry, fineness or denier, and porosities of fibers (and occasionally of yarns) have led to novel and high technology textile products for diverse applications. Hollow fibers derived from regenerated cellulose or from synthetic fibers have been used in the development of artificial body organs such as the kidney, pancreas, and lung. Hollow fibers have also frequently been employed to increase the insulation value of garments due to the benefits of the air trapped inside the fiber cavity. A variety of ultrafine fibers, ranging in tex (denier) from as little as 0.0011 (0.01) up to 0.011 (0.1) have been commercialized (primarily in Japan) to impart various surface characteristics that change fabric hand and appearance. Because spinning ultrafine fibers directly is technically difficult, such fibers may be produced by spinning bicomponent or biconstituent polymer mixtures, highly stretching them to form ultrafine deniers, and extracting or otherwise removing

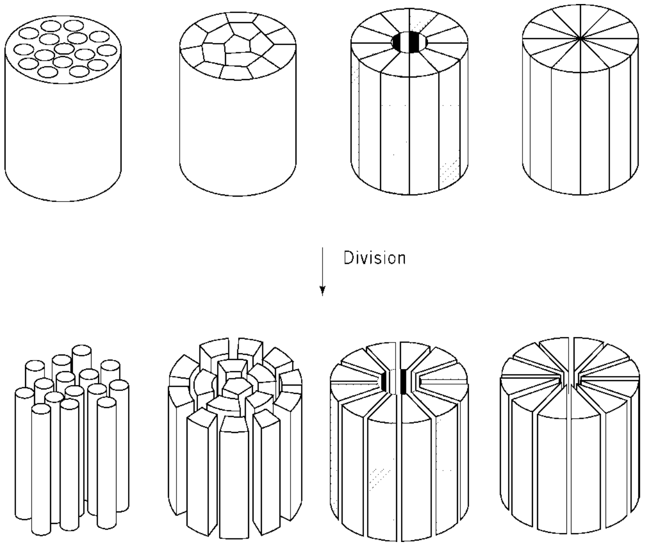


Fig. 1. Ultrafine fibers are produced by spinning bicomponent or biconstituent polymer mixtures, highly stretching such products to ultrafine deniers, and extracting or otherwise removing the undesired matrix carrier to release the desired ultrafine fibers (77). For example, spinning polyester islands in a matrix of polystyrene and then, after stretching, dissolving the polystyrene to leave the polyester fibers; cospinning polyester with polyamides, then stretching, removing the polyester by caustic treatment, leaving 100% nylon ultrafine fibers.

the undesired matrix carrier material to release the desired ultrafine fibers (Fig. 1) (77). Another technique used to prepare ultrafine (nanofibers) fibers is electrospinning (78). Controlling the porosity of fibers has been advantageously used to release antimicrobial agents at different rates for specific applications. Novel core/sheath yarns that control selective distribution of both components are being evaluated for numerous applications.

Product Types: Composites. Various composite materials have evolved over the years as a significant class of high performance textile products. The prototype composite is carbon fiber with an epoxy resin matrix for structural aircraft components and other aerospace and military applications. Carbon fiber composites are also used in various leisure and sporting items such as golf clubs, tennis rackets, and lightweight bicycle frames. However, other types of applications and composites are also entering the marketplace. For example, short cellulose fiber/rubber composites are used for hoses, belting, and pneumatic tire components.

Three-Dimensional Structures. Three-dimensional textile structures have been developed primarily for architectural, civil engineering, and aerospace applications. Such structures fall into four different categories: nonwoven orthogonals (straight, continuous fibers arranged in three directions with no interlacing); multilayer woven (multiple layers interlaced at selected points); multilayer knitted or stitched (multiple layers of yarns stitched in diverse or desired directions); and three-dimensional braids (intertwining of multiple yarns so that a particular yarn follows a path taking it completely across the structure several times) (79).

Multifunctional Materials. Multifunctional property improvement by binding of specific polymers to fibers and fibrous products has been extensively investigated and reviewed (80). With poly(ethylene glycol) as the bound polymer, functional and aesthetic property improvements include thermal comfort, liquid absorbency/repellancy, increased wear life, soil release, resistance to static charge, antimicrobial activity, and resiliency. Numerous applications such as sportswear/ski wear, protective clothing for health care workers, durable and nondurable hygienic items, work uniforms, and space suits are being commercialized and evaluated.

Smart Materials. The field of intelligent or self-adaptive materials is in its infancy, particularly with regard to textile products. Conceptually, any material that is responsive to one or more external stimuli (heat, force, light, moisture, electrical current) and that responds to such exposure by changing shape or related characteristics is classified as an intelligent material. Synthetic gels that act like artificial muscle and fabrics that self-repair to avoid tensile and other forms of mechanical failure are examples of ongoing research and uses (81).

3.2. Classification by Types of Application. Another way to classify high performance fibers and high technology textile materials or products is by types of applications. A scheme of 10 main categories has been adopted (Table 4) and is similar to several classification schemes previously reported (75).

Transportation. High performance fibers and high technology textile products have many applications in the transportation area. Composites are increasingly used as structural materials in aircraft components such as horizontal stabilizers, fins, landing gear doors, fan blades, and nose spin cones. In addition to carbon and glass fibers in composites, aramid and polyimide fibers are also used in conjunction with epoxy resins. Safety requirements by the U.S. Federal Aeronautics Administration (FAA) have led to the development of flame- and heat-resistant seals and structural components in civilian aircraft cabins. Wool blend fabrics containing aramids, poly(phenylene sulfide), EDF, and other inherently flame-resistant fibers and fabrics containing only these highly heat- and flame-resistant fibers are the types most frequently used in these applications.

The introduction of air bags into automobiles represented a new and enormous market for high performance textiles. Polyamide-coated fabrics are primarily used because of the high strength of the polyamide, but there have been marketing and technical studies that indicate the feasibility of using high tenacity polyester as the base fabric. Performance requirements for air bags include tear; tensile, seam, and bursting strength; dimensional stability; resistance to puncture, abrasion, and buckling; flame resistance; and resistance to delamination (82). It has been estimated that by the end of the century $>41 \times 10^6 m^2$ of coated fabrics would be used in the United States alone to make automobile air bags (83).

Manufacturing. The use of advanced textile materials in manufacturing is a diverse and expanding market. Optical fibers are being increasingly used in telecommunications, computers, cable television, and to facilitate process control in the nuclear, petrochemical and chemical, and food industries. Although most optical fibers are glass or of related inorganic composition, there are optical fibers

Table 4. **Classification of High Performance and High Technology Textiles by Types of Applications**[a]

Application class	Subcategories	Examples of specific products
transportation	civilian and military aircraft, traffic	components of aircraft, air bags, seats in planes and cars
manufacturing	electronics, information, and communication	optical fibers for telecommunications and computers, printed circuit boards, industrial filters and belts
agriculture and forestry	horticulture, erosion control, barriers	greenhouse covers, control of drainage, land nets cultivation of plants
civil engineering and construction	geotextiles and geomembranes architectural	road reinforcement, pond liners, and dams, fabric roofs, soil stabilization
fishery and marine	pollution containment, aquatic life, industrial and leisure marine equipment and vehicles	breeding of corrosion resistant composites, conveyers floating backwaters, screens for fish breeding, speedboat components
protective clothing	chemical/environmental/ biological security, heat and flame	firefighters' uniforms, bulletproof vests, protection from toxins and diseases
sports and leisure	sporting goods and vehicles, spas and pools	golf clubs, tennis rackets, snowmobiles, bicycle frames, spa and pool parts, ski wear and Sportswear, luxury apparel
biomedical and health care	devices, artificial organs, sutures, wound care, prostheses	kidneys and artificial limbs, bioimplants, dressings for wounds, hydrogel composites
defense and aerospace	chemical/biological protection, camouflage, components for weapons	chemical/biological warfare protection composites for armour and other weapons, space suits and materials for space travel
energy use and conversion	insulation, containment of hazardous waste, shields from high energy sources	all types of insulation, waste containers, electromagnetic shielding

[a] See Ref. 75.

for special applications comprised of poly(methyl methacrylate), polystyrene, and polycarbonate that are coextruded with fluorinated acrylate polymers. Polyacetal, ie, poly(oxymethylene), fiber has also been used as a reinforcing material for optical fibers. Basic fiber properties required for an optical fiber are (*1*) a structure with a high refractive index core and a low refractive index cladding (sheath bonded to core under high temperature and pressure); (*2*) fiber with a low attenuation or low power loss of light over distance; and (*3*) fiber with low dispersion or pulse broadening as light travels down the fiber (84).

Electronics and electrical insulation are other manufacturing areas in which advanced fibers are extensively used. Manufacturing of computer components such as printed circuit boards and printed wiring boards require use of reinforced fibers that have good dielectric properties, thermal and dimensional stability, chemical resistance, and low moisture regain. For electrical insulation applications, fiber requirements are high dielectric strength, low power loss, and good thermal and chemical resistance. Although inorganic fibers are extensively used for both electronic and electrical applications, aramid fibers are also now used for both types of applications. A variety of natural and synthetic fibers are also used for various electrical applications (85).

A third area that has rapidly expanded in the manufacturing sector is the demand for clean room working garments. The primary electronics and computer industries have the most stringent requirements for cleanliness in their manufacturing environments; clean room garments are also used by personnel in the pharmaceutical, food, precision engineering, and biotechnology–biomedical industries. Requirements for clean room garments and the increasingly stringent standards for both particle size and number of acceptable particles have been critically reviewed and discussed (86). Required properties for garments in clean rooms include fabrics or materials that are dustproof, antistatic, durable to laundering and sterilization procedures, and that are comfortable. Garments have been designed with ability to filter air by mechanical or electrostatic concepts and collect fine particles. Microtex polyester fibers are most frequently used to make these clean room garments. Diameters of particles to be removed have progressed from $\sim 1\ \mu m$ in the early 1970s to only $0.1\ \mu m$ in the 1990s. Industry standards for the corresponding degree of cleanliness (particles/m^3) have decreased from 35,000 to 35 (10,000 to 1 per ft^3). Thermal comfort of many of the garments is unacceptable due to their low moisture content, but some efforts are being made to develop microporous coatings to provide both comfort and function required for this application.

The fourth area of manufacturing for advanced fibrous materials is that of filtration of liquids and gases. Filters have diverse requirements for different industries and environments to which they are exposed. The use of cellulose acetate and aramid hollow fibers to desalinate water by a reverse osmosis process is an example of one of the earlier applications for filtration. Important fiber properties for such filtration are hydrolytic, oxidative, and biological stability over wide pH ranges. Separation of gases by ultrafiltration for a variety of industries is another example of the importance of advanced fibrous substrates. Because of the diversity of exposure to extreme temperature changes and corrosive chemical agents, many of the high temperature, high tenacity, and inert fibers are replacing more conventional types of fibers for such filtration. Poly(phenylene sulfide), polysulfone, aramids, polyimide, polyetheretherketone (PEEK), fluorocarbon, and related fibers are examples of high performance fibers effective for gas and liquid filtration under extreme and rapidly changing environmental conditions.

Agriculture and Forestry. Agricultural and silvicultural applications for high performance textile materials range from geotextile and geomembrane materials to horticultural uses to facilitate the growth, yield, and production of edible and ornamental plants. Geotextile structures, either permanent or biodegradable, are inexpensive alternatives to more expensive, conventional concrete or other materials for prevention and control of gully formation. Also, drainage and soil erosion control on farm acreage have been facilitated by geotextiles. Wind fences and other geotextile barriers have also been advantageously used.

If the geotextile is above ground, it should be stable to sunlight, air pollution, rot, and mildew-producing fungi besides having mechanical integrity and dimensional stability. If the textile is below ground, it should be dimensionally stable and inert to most chemical agents and have good long-term permeability so that it does not become easily clogged with soil particles.

Other examples of agricultural applications are flexible and lightweight silos constructed from geotextiles that hold grain, manure, or any other agricultural commodity of interest. Polypropylene fiber is used primarily in most geotextile (agricultural, civil engineering, and other applications) structures because of its excellent inertness to chemical and biological agents and its dimensional stability over long periods of use. Polyester and glass fibers are also used to some extent in geotextiles.

Horticultural applications include use of greenhouse thermal screens, row-crop and turf covers, conveyer belts to process agricultural products, and other similar items. High performance fibers are not normally used in these applications, but high strength fibers are preferable for conveyer belts. Environmentally inert low cost fibers such as polypropylene are used for many of the outdoor horticultural applications.

Civil Engineering and Construction. These textile applications can be classified as civil engineering applications (also commonly referred to as geotextiles) and architectural applications. High performance fibers are not currently used to any great extent in these applications due to their high unit cost. However, mechanical and environmental requirements for such applications demand that even conventional fibers withstand challenging structural demands and sustained long-term performance outdoors. Polypropylene fibers have captured a sizable portion of the geotextile market because of their excellent dimensional stability and chemical inertness. Polyester and glass fibers are two other types of fibers used in geotextile applications. Reinforcement of highways and roadbeds is by far the principal use of geotextiles. Their primary function is to serve as a soil stabilizer by spreading the impact load of vehicles over a larger area thus prolonging the useful life of roadways. As in agricultural applications, geotextiles are also used to prevent or minimize soil erosion and facilitate drainage. These materials have been utilized in important projects such as reinforcement of dikes in Holland and to construct dams in the United States. Mechanisms for geotextile failure have been critically evaluated and discussed (87). The types of failure must be evaluated relative to the function of the geotextile. Failure modes include piping of soils through or clogging of the geotextile, reduced tensile resisting force, deformation of the fabric, reduced resistance to puncture, and reduced in-plane flow of liquids.

Most architectural fabrics are usually flexible composites comprised of glass fibers coated with fluorocarbons to resist wind, mechanical forces, and outdoor environmental degradation. The airport terminal in Saudi Arabia, and the roofs for the Hubert Humphrey Dome in Minneapolis and the Tokyo Dome Stadium are a few examples of the successful use of architectural fabrics.

Fishery and Marine. Marine applications for textiles include (*1*) those concerned with fishing and fishing industries, (*2*) leisure items and components, and (*3*) industrial, including control of various types of environmental pollution and influences (88,89). The earliest use of textiles in fishery and marine applications were for high strength nets, lines, and ropes. Conventional natural and synthetic fibers are being replaced by high performance fibers such as aramids, gel spun polyethylene, and polyacetal. However, cost is still a factor because the latter fibers are still much more expensive than the conventional fibers. More advanced applications for fishing and marine industries include the construction of artificial seaweed beds comprised of synthetic fiber membranes that facilitate fish breeding.

Advanced composites and fiber-reinforced materials are used in sailcloth, speedboat, and other types of boat components, and leisure and commercial fishing gear. Aramid and polyethylene fibers are currently used in conveyer belts to collect valuable offshore minerals such as cobalt, uranium, and manganese. Construction of oil-adsorbing fences made of high performance fabrics is being evaluated in Japan as well as the construction of other pollution control textile materials for maritime use. For most marine uses, the textile materials must be resistant to biodeterioration and to a variety of aqueous pollutants and environmental conditions.

Protective Clothing. Protection against adverse chemical and biological environments, from heat and/or flame, and antiballistic protection are the principal applications of protective clothing. Several high performance fibers are finding increasing use in many protective clothing applications due to their high strength, resistance to cutting and firearms, and their ability to withstand temperature extremes and corrosive chemical agents. Aramids such as Kevlar and polyethylene fibers such as Spectra are used in many bulletproof vests and other types of security garments. PBI is used in firemen turn coats and race car driver suits.

Aramids are also used in firefighters' uniforms for their excellent flame resistance. The new Dow Curlon EDF fibers have exceptional flame resistance both by themselves and in combination with other flammable fibers. At only 20% by weight, Curlon has been shown to totally prevent the flaming of polyester and other similar flammable materials. This property along with Curlon's good textile processibility will undoubtedly lead to many new applications in the protective garment area (69–71). Garments derived from blends of polybenzimidazole (PBI) and aramid fibers have excellent chemical resistance and a low propensity to severe burns as shown by tests in a gas pit where temperatures could rise as high as 1100°C (90).

There are distinct performance differences for garments that are resistant to flame alone compared to those that are resistant to both heat buildup and flammability. Appropriate tests have been devised that measure the thermal protective performance of fabrics when exposed to a radiant heat source. Sophisticated constructions against biohazards need further development to produce materials that are both thermally comfortable and impermeable to bloodborne pathogens and other deleterious microorganisms. The most promising approaches are materials that are laminated or coated fabrics that are permeable to vapor but impermeable to liquids. Statistics included in recent

OSHA standards for protection against blood-borne pathogens [eg, hepatitis and acquired immune deficiency syndrome (AIDS) viruses] estimate that currently close to 6 million persons in the United States (health care workers and many other occupations) require protective clothing and other types of safeguards against these biohazards (91).

Sports and Leisure. The application of high technology fiber properties and complex structures for sports and leisure are identifiable in three areas: components for sporting goods, boats, and other rigid structures; high technology sportswear and ski wear; and luxury apparel. Although most components for sporting goods (such as tennis rackets, golf clubs, lightweight bicycle frames, spa components, speedboat components) are usually carbon-fiber reinforced composites, the high performance aramids and polyethylene are now being used to manufacture items such as bicycle helmets and other sports items. For these end uses, impact and overall tensile strength, dimensional stability, and resistance to specific environmental agents are required. High technology sportswear and ski wear evolved with the advent of Gore Tex.

Gore Tex. Gore Tex was the first fabric comprised of a microporous polytetrafluoroethylene film laminated to a polyamide fabric. The microporosity of the film allowed the garment to be breathable or allow passage of water vapor yet be waterproof or resistant to liquid penetration. Since that time, a variety of microporous materials or related structures have been developed in the United States and Japan. Another example for high technology sportswear is the latent heat and high water absorbency of a cross-linked poly(ethylene glycol) coating on fabrics that makes it possible for the garment to be thermally adaptable in hot and cold environments (80). Also, microencapsulation of zirconium carbide into polyamide or polyester fibers produces a ski wear garment (called Solar-α) that absorbs sunlight and converts it into heat.

Numerous high touch fibers have been produced and commercialized (primarily in Japan) for luxury apparel. Conceptually, the geometry and fineness of the fibers are carefully modified and controlled to produce fabrics with desirable sensual responses of touch, sight, sound, comfort, and even odor (77,92). There are several techniques for producing ultrafine fibers and this has led to the production and commercialization of materials such as Ultrasuede, artificial leather and silk, fabrics with a peach-fuzz sensation, perfumed hosiery, fabrics that change color due to microencapsulation of cholesteric liquid crystals, and numerous other luxury and novelty textile products.

Biomedical and Health Care. This area is an extremely diverse and expanding market for high performance fiber concepts and their reduction to the desired end use performance. Although the complexity of the human body and its physiological functions are difficult to mimic with artificial materials, significant progress has been made in the introduction of biomaterials and related health care products. The numerous uses of fibers in medicine have been critically and concisely reviewed, including nonimplantable items (such as surgical dressings, gowns, drapes, pressure bandages), extra corporeal devices (components of dialyzers and oxygenators, catheters) and implants (sutures, vascular grafts, artificial organs, fibers and fabrics for surgical reinforcement, optical fibers for medical procedures, and orthopedic devices) (93). In addition to having the desired mechanical and functional integrity for the particular biomedical application, the fibrous product must be nonallergenic, usually nonthrombogenic, noncarcinogenic, sterilizable, and biocompatible. Nonimplant items are usually derived from conventional fibers and fabrics, except for clean room garments. Examples of extra corporeal devices or components are regenerated hollow cellulose fibers for the artificial kidneys or dialyzers and hollow fibers or flatsheet fibrous membranes derived from polypropylene, polytetrafluoroethylene, and various coated fabrics in blood oxygenation devices.

Implants generally can be classified as those that are designed to be bioabsorbable (eg, sutures) and those that are designed for more permanent function (nonabsorbable sutures, vascular grafts, and artificial organs). Bioabsorbable materials have been critically reviewed with emphasis on sutures and related fibrous products (94). Bioabsorbable sutures were originally derived from catgut or collagen, but now a variety of poly(glycolic acid) homo- and copolymers as well as poly(dioxanones) are used. Hydrogel fibrous composites have become important as wound dressings and as implants. Many of these hydrogel composites are poly(ethylene oxide) homopolymers and/or copolymers of poly(acrylic acid), polyacrylamide, or other related structures (95). Nonabsorbable sutures and reinforced structures for vascular grafts and artificial organs are derived from high tenacity polyamide, polypropylene, polyester, polytetrafluoroethylene, and various coated fibers and fabrics. Optical fibers for endoscopy and angioplasty procedures are usually composed of glass or poly(methyl methacrylate). In addition to these classifications, the production of biomimetic fibers, ie, fibrous materials that are specifically designed to mimic physiological and other anatomical functions of living organisms, has been described (96). Applications include artificial cells, nerves and muscles, biosensors, and artificial bones and teeth.

Defense and Aerospace. Military applications for high performance fibers and high technology textiles generally parallel those discussed earlier for civilian aircraft and protective clothing. Protective clothing is usually designed to be impermeable to chemical and biological warfare agents such as nerve and mustard gas. Design of protective clothing for these purposes is usually classified information, but it is reasonable to assume that the clothing assembly consists of microporous membranes and elaborate filtration devices. Another military application is the design of combat uniforms that are dyed in such a manner that they provide effective camouflage and are not detectable by night surveillance devices. Not surprisingly such materials have been adapted to civilian use by hunters to give better camouflage against deer and turkeys, which see uv reflections. Printing of aramid fabrics for this purpose has been described (97).

Requirements for space suits are more complex and frequently involve garments that can circulate water and/or air through the fibrous assembly. Laminated and/or coated garments with specific requirements to pressure, radiation, temperature, and humidity are more structurally complex as a textile product relative to the types of fibers used in this aerospace fabrication.

Fiber composites and three-dimensional textile structures are frequently used in advanced military weapons and aircraft such as extended use armor tracks, materials for engine parts (nose spin cones and fan blades), and primary and secondary structural components of aircraft (main wings, horizontal tail and stabilizer, speed brakes, high performance gaskets, fins, and ailerons). Although many of these materials are carbon fiber—epoxy resin composites or glass fiber—epoxy resin composites, there is an increase in the use of aramid, polyimide, and PEEK fibers because of their excellent strength and thermal/oxidative and chemical stabilities.

Energy Use and Conservation. A variety of materials are needed for high performance thermal insulation, particularly as components of nuclear reactors. Replacements for asbestos fibers are needed for components such as reactor core flooring, plumbing, and packaging. The fibers must be very resistant to high temperatures with outstanding dimensional stability and resistance to compression.

Filters for nuclear fuel reprocessing and replacement of fibrous composites to reduce or prevent radiation leaks are two other areas of application. Advanced fiber composites, aramids, and high tenacity polyethylene for specific applications are types of high performance fibers and structures being considered (3). Metal-coated fibers and fabrics have been effective in electromagnetic shielding applications. High performance fabrics have also been used for containment of hazardous waste in addition to being used for conservation of energy and improving the safety of nuclear power plants (98). The same considerations that apply to geotextiles for other applications also apply to geotextiles used for waste containment. However, there are additional performance requirements such as excellent resistance to municipal waste leachate. Thus, polypropylene and to a lesser extent polyethylene fibers are used in the construction of geotextiles for this type of application.

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