

Fibers from a Soluble, Fluorinated Polyimide

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SYNOPSIS

Polyimide fibers have been produced from both polyamic acid and polyimide resins, derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, by extrusion into various aqueous organic media. Polyimide fibers obtained from polyamic acid fibers after thermal imidization exhibited round or oval cross-sections, while fibers obtained directly from a polyimide resin had dogbone, C-shaped, or oval cross-sections. The effect of polymer inherent viscosity and filament production parameters on the formation of macropores within the filament will be discussed. Tensile properties of fibers, produced under various conditions, are listed and compared. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Previous structure/property relationship studies on aromatic polyimides at NASA Langley Research Center have concentrated on obtaining polymers with high solubility, optical transparency in the 500 nm range, and low dielectric constants.¹⁻³ Such properties have been obtained by reducing the electronic interactions between polymer chains via alterations in the molecular structure and by the incorporation of fluorine atoms into the polymer molecular backbone. One such polyimide, derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4BDAF), yields a film that is highly transparent optically, which has a dielectric constant of 2.5 at 10 GHz. The 6FDA/4BDAF system was selected for this investigation because of these properties and particularly because of the system's solubility in common organic solvents, such as N,N-dimethylacetamide or chloroform.

The present research deals with the production of 6FDA/4BDAF polyimide fibers, from both polyamic acid and polyimide resins, and the comparison of their filament production parameters using var-

ious aqueous organic coagulation media, fiber cross-sectional shape, and fiber tensile properties. Polyimide fibers have been produced by the extrusion of the polyamic acid resin into a coagulation medium, followed by thermal conversion of the polyamic acid fibers to polyimide form (Fig. 1). Because of its enhanced solubility, polyimide fibers of the 6FDA/4BDAF have also been prepared directly by extruding the polyimide resin into a coagulation medium.

EXPERIMENTAL

Materials

The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was obtained from American Hoechst and was used as received. 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4BDAF) was obtained as an experimental material from Ethyl Corporation and was recrystallized from either a dichloromethane/hexane solution or a dichloromethane (acid alumina treated)/hexane solution. N,N-Dimethylacetamide (DMAc), ethylene glycol (EtG), ethanol (EtOH), pyridine, acetic anhydride, acid alumina, dichloromethane, and hexane were obtained from commercial sources and were used as received.

Preparation of Polyamic Acid Resins

Resin synthesis was carried out on a variety of size scales using procedures similar to the one described

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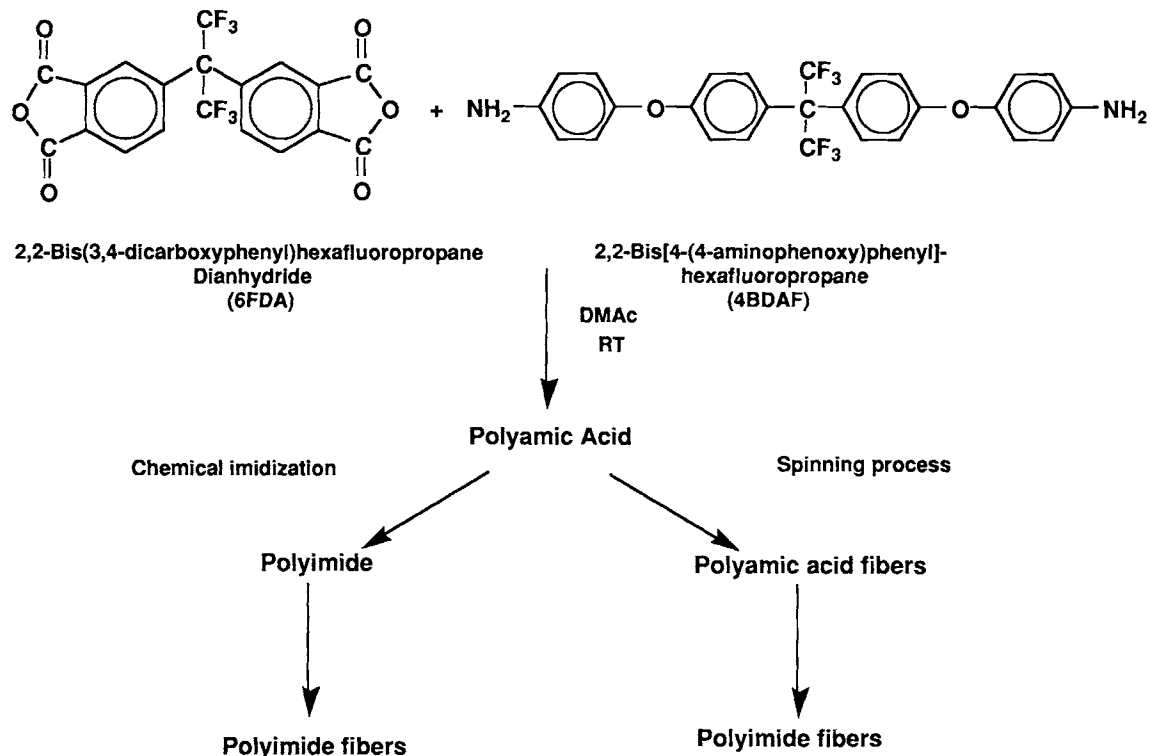


Figure 1 Scheme for producing polyimide fibers.

here. To a 500-mL resin kettle, equipped with an overhead stirrer and nitrogen inlet, were added 32.8703 g (63.400 mmol) of 4BDAF and most of the 345.87 g of DMAc. The kettle was purged with dry nitrogen, and the solution was stirred until all diamine had dissolved. A total of 28.2983 g (63.701 mmol) of 6FDA was added at a steady but moderate rate, with any residual 6FDA being washed into the resin kettle using the remaining DMAc. The resin kettle was purged with dry nitrogen and stirring resumed. A large amount of heat initially evolved and stirring was continued for 4 h under a constant flow of dry nitrogen. The inherent viscosity of the resulting polyamic acid was 1.79 dL/g at 35°C. The 6FDA/4BDAF polyamic acid resin (15.0% solids) was stored in a freezer until it was used. Polyamic acids in this work exhibited inherent viscosities from 1.48 to 2.10 dL/g and resin percent solids of 15.0.

Preparation of Polyimide Resins

The polyimide was obtained by chemical imidization of the polyamic acid under conditions similar to the one described here. The polyamic acid resin was poured into a large stainless steel syringe and was slowly added to a stirred solution of 120.5 mL pyridine and 120.5 mL acetic anhydride in a 500 mL, 3-

necked flask, equipped with a nitrogen inlet. The flask was continuously purged with dry nitrogen during the resin addition. A large bore addition funnel was used in place of the syringe when the viscosity of the resin would allow. The reaction mixture was heated at 65°C for 3 h after completion of the resin addition, and then was allowed to slowly cool to ambient. The solution was poured into a 500-mL separatory funnel and was slowly added to distilled water, stirred by a quart blender, in order to precipitate the polyimide. The precipitate was washed with fresh distilled water several times and was collected by suction filtration using a fitted-glass Buchner funnel. The polyimide solid was vacuum dried at 200°C for 3 h, after which the heat was turned off and the oven was allowed to slowly cool to ambient under vacuum. The resulting polyimide exhibited an inherent viscosity of 1.52 dL/g at 35°C. Polyimides in this work had inherent viscosities ranging from 1.25 to 1.52 dL/g and resin percent solids of 15.0 or 17.5.

Fiber Spinning Equipment

The fiber spinning equipment (Fig. 2) was purchased from Bradford University Research Limited and was modified so as to allow constant temperatures to be

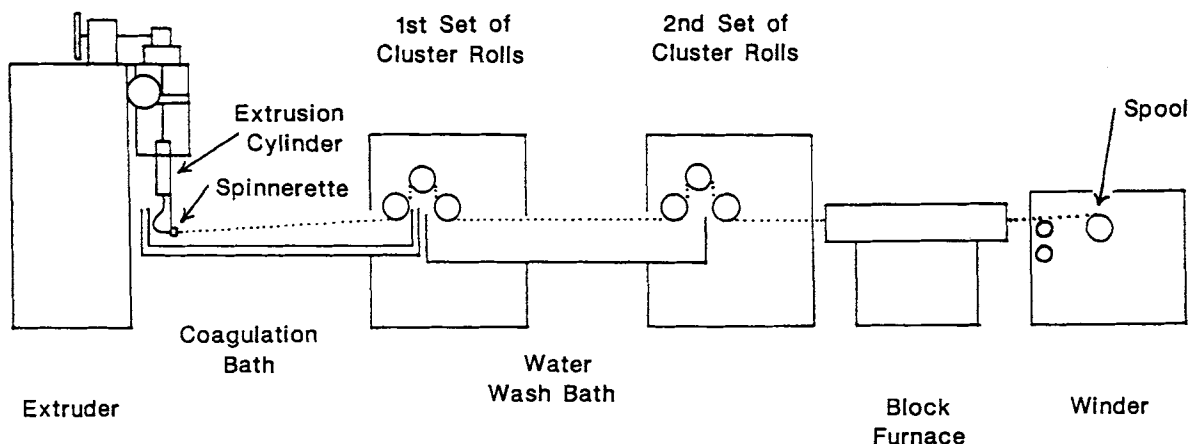


Figure 2 Fiber spinning equipment schematic.

maintained in both coagulation and wash baths using Neslab circulating baths. A 4-liter coagulation bath insert, along with its own circulation/constant temperature system, was also added to reduce the volume of the coagulation medium. Spinnerettes were obtained from Courtaulds Engineering Limited, type SD/50, with a single hole of 100 μm diameter.

Details of the fiber spinning process are described in the previous articles.^{4,5} Resin in the extrusion cylinder was extruded through the spinnerette hole into the liquid coagulation medium. The solidifying filament traveled through the coagulation bath, onto the first set of cluster rolls, through the water wash bath, onto the second set of cluster rolls, and was collected by wrapping around a pyrex spool on the winder. The filament underwent a drawing process, known as the wash bath stretch, as determined by the different surface speeds of the second and first sets of cluster rolls. Polyamic acid filaments were not passed through the channeled block furnace because exposure of the liquid-swollen filament to elevated temperatures may have caused hydrolysis of the amide linkages leading to reductions in polymer molecular weight and ultimately fiber properties. Some of the polyimide wet gel filaments were air stretched at 288–298°C by passing the filament through the block furnace when the spool's surface speed was greater than that of the second set of cluster rolls. The total wet gel stretch was determined by multiplying the wash bath stretch by the air stretch. Both polyamic acid and polyimide wet gel filaments were dried into fibers, using a vacuum oven at approximately 80°C for between 14–18 h. Polyamic acid fibers were converted to polyimide form by heating the spool of fibers in a forced air oven for one hour each at 100°, 200°, and 300°C.

Characterization

Inherent viscosity was determined using an Ubbelohde viscometer and polymer solutions at 0.5% solids (w/w) in DMAc at 35°C.

Fiber diameters, cross-sectional shape, and microscopic features were determined by the visual inspection of at least six fractured fiber ends, using an optical or scanning electron microscope (SEM), Hitachi Model S-510. All fractured fiber ends had an internal structure with a cheesy, granular appearance. Some of these ends also contained various numbers, sizes, and shapes of macropores. Percent solid fiber value corresponded to the number of fiber ends that contained no macropores, divided by the total number of inspected ends ($\times 100$). Noncircular, cross-sectional areas were determined by weighing cross-sectional traces of SEM photos and normalizing to μm^2 .

Fiber tensile properties were measured using a Sintech 2000-2 Computer Integrated Testing System, according to ASTM D 2101-82, at ambient humidity and temperature. Values are reported as the average of at least 15 specimens, along with their percent coefficient of variation (percent COV). The percent COV is calculated by dividing the standard deviation by the arithmetic mean ($\times 100$).⁶

Thermogravimetric analysis (TGA) was performed on polyimide fibers using a Seiko SSC 5040, equipped with a TG/DTA 200 module. An air flow rate of 15.0 mL/min and a 2.50°C/min rate of temperature increase, from 100 to 650°C, were used.

RESULTS AND DISCUSSION

Both polyamic acid and polyimide resins were extruded into 70% aqueous ethylene glycol (EtG) and

Table I Polyamic Acid Fibers Produced From Polyamic Acid Resins

| Coagulation Media | 70% Aqueous EtG | | | 70% Aqueous EtOH | | |
|---|-----------------|-------|-------|------------------|-------|-------|
| Polyamic Acid Inherent Viscosity (dL/g) | 2.06 | 1.79 | 1.48 | 1.79 | 1.65 | 1.48 |
| Resin Extrusion Rate (cc/min) | 0.058 | 0.058 | 0.073 | 0.070 | 0.070 | 0.090 |
| Total Wet Gel Stretch | 1.4 × | 1.3 × | 1.2 × | 1.1 × | 1.1 × | 1.1 × |
| Winder Spool Speed (fpm) | 50–52 | 75–78 | 75–77 | 54–56 | 55–57 | 54–56 |
| Fiber Diameter (μm) | 23 | 21 | 25 | 29 | 28 | 33 |
| % Solid Fibers | 62 | 46 | 0 | 100 | 100 | 93 |

70% aqueous ethanol (EtOH) (w/w). Attempts at extrusion of a polyamic acid resin into pure EtOH failed, due to lack of filament formation, while 80% aqueous EtOH caused a filament to form, but the filament lacked the consistency to be drawn through the coagulation bath, even under no tension. The polyimide resin was also extruded into 80% aqueous EtOH and 20–31% aqueous N,N-dimethyl-acetamide (DMAc). Resin extrusion rates into either aqueous EtG or EtOH were between 0.06 and 0.12

cc/min, while extrusion rates of the polyimide resin into aqueous DMAc varied from 0.18 to 0.20 cc/min. Polyamic acid resin extrusion temperatures, coagulation bath temperatures (18–21°C), and water wash bath temperatures (30–32°C) were kept below 35°C in order to minimize polymer hydrolysis. Similar temperature ranges were used with polyimide resins for comparison purposes. Stretching of the wet gel filament in the water wash bath varied from 1.0 to 1.4 times and from 1.0 to 1.1 times in

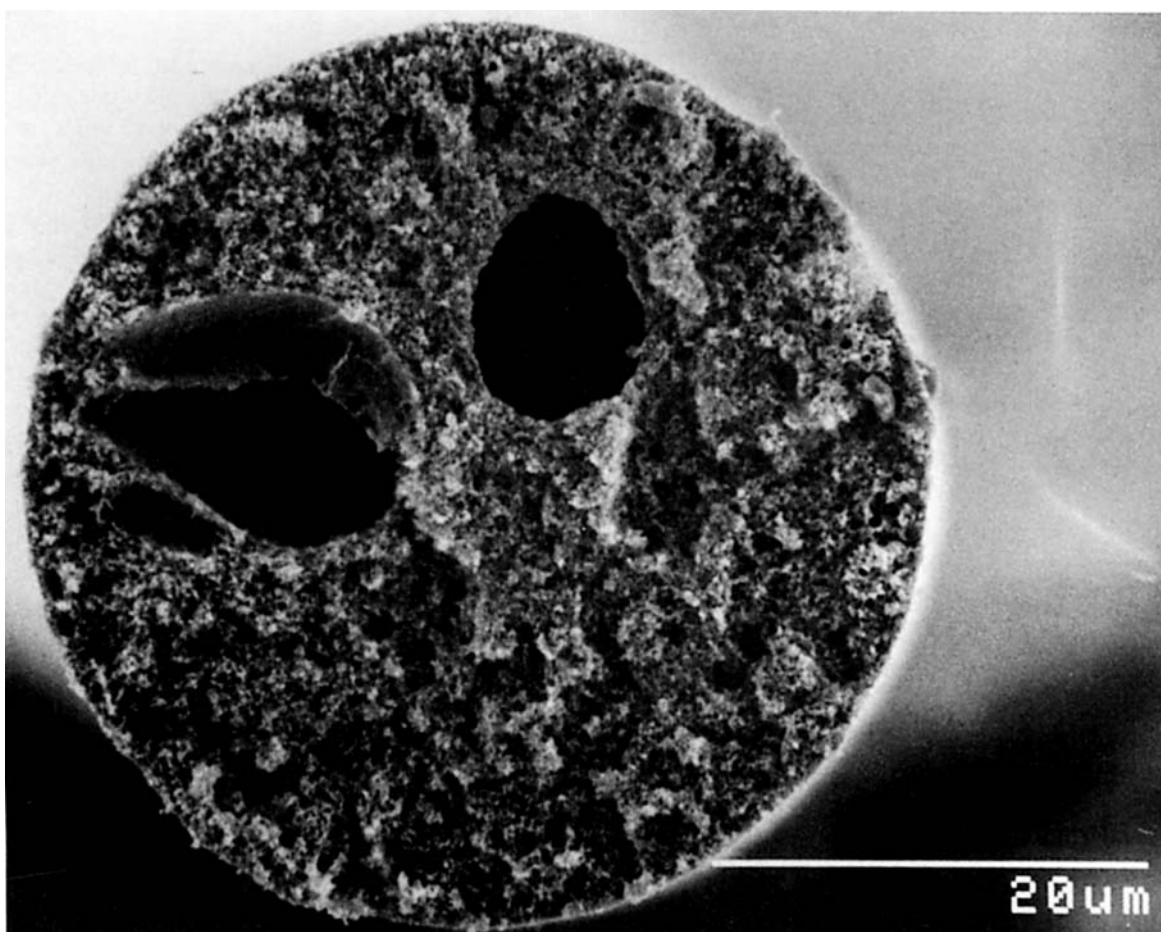
**Figure 3** Fiber produced by extrusion of a polyamic acid resin into 70% aqueous EtG.

Table II Tensile Properties for Fibers Produced From a Polyamic Acid Resin

| Coagulation Media | 70% Aq. EtG | | 70% Aq. EtOH | |
|---|----------------------------|---------------|---------------|---------------|
| Polyamic acid inherent viscosity (dL/g) | 1.79 | 1.79 | 1.79 | 1.65 |
| Fiber Type | Polyamic acid | Polyimide | Polyimide | Polyimide |
| Fiber Diameter (μm) | 21 | 17 | 23 | 24 |
| % Solid Fibers | 46 | 46 | 100 | 100 |
| Breaking Tenacity (ksi) | 12.6 (4.0) ^a | 23.7 (11) | 18.2 (6.3) | 20.8 (9.1) |
| % Elongation to Break | 7.2 (39) | 111 (12) | 113 (6.8) | 106 (8.4) |
| Yield Point (ksi) | 12.4 (3.5) | 15.4 (2.2) | 11.3 (3.7) | 14.5 (3.5) |
| Initial Modulus (ksi) | 488 (3.2) | 434 (3.6) | 311 (3.5) | 379 (3.2) |
| % Elongation at Second Yield | None | 71 (1.8) | 72 (3.3) | 71 (1.2) |
| Stress at Second Yield (ksi) | None | 15.8 (2.3) | 12.8 (2.9) | 14.8 (3.2) |

^a Coefficients of variation in parentheses.

air at ambient temperatures for both systems. Only polyimide wet gel filaments were stretched from 1.0 to 2.3 times at 288–298°C. Wet gel filaments were dried to fiber form at approximately 80°C for 14–18 h, using a vacuum oven. These drying conditions have previously resulted in good consolidation of the wet gel structure and thus have not contributed to macropore formation within the filament in another polyamic acid.⁴ Polyamic acid and polyimide fibers

(from polyimide resin) generally appeared white in color. Thermal conversion of polyamic acid fibers to polyimide fibers was accomplished by heating the fibers while on the spool for one hour each at 100, 200, and 300°C. These conversion conditions are commonly used to transform polyamic acid films to their polyimide form.^{1,3} Polyimide fibers (from polyamic acid) generally appeared slightly yellow in color.

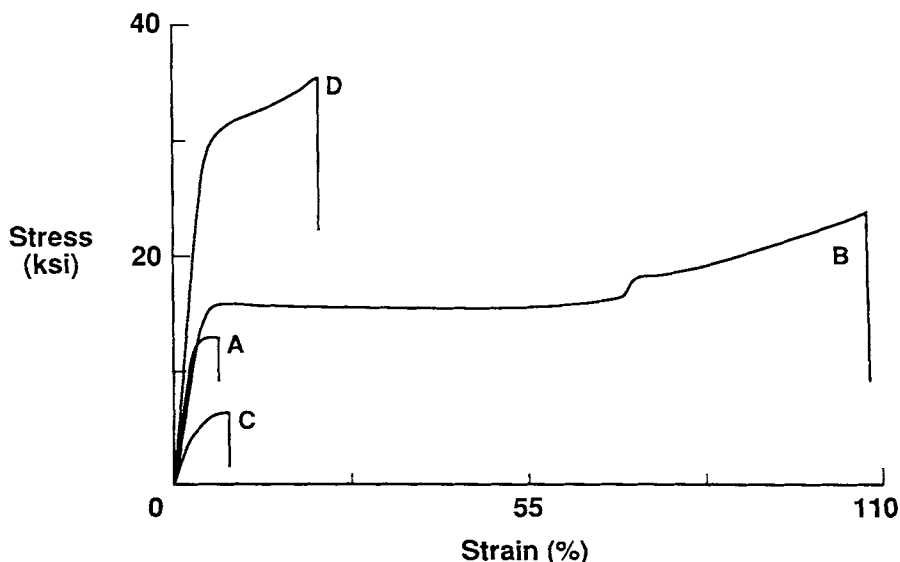


Figure 4 Stress/strain curves for: (A) Polyamic acid fibers, (B) Polyimide fibers from polyamic acid fibers, (C) Polyimide fibers from polyimide resin (unstretched); and (D) Polyimide fibers from polyimide resin air stretched $2.3 \times$ at 289°C.

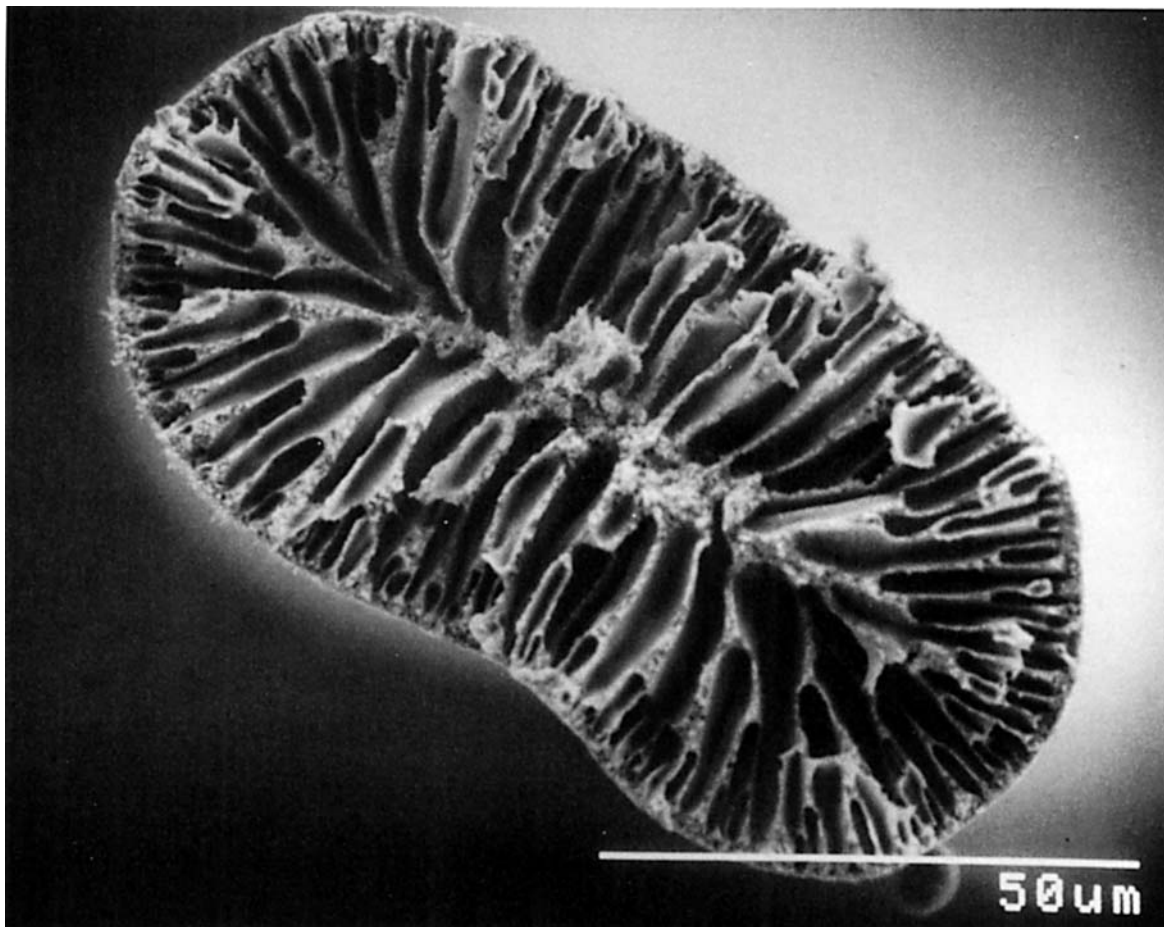


Figure 5 Fibers produced by extrusion of polyimide resins into: (A) 31% aqueous DMAc and (B) 70% aqueous EtG.

Extrusion of Polyamic Acid Resins

Polyamic Acid Fibers

Extrusion of the resin into 70% aqueous EtG or 70% aqueous EtOH, according to the parameters in Table I, resulted in the formation of polyamic acid fibers having a round or oval cross-section. The fiber's

cross-sectional shape is dependent upon the filament formation conditions in the coagulation bath. Circular cross-sections are reported to result: (1) if the outward flux of solvent from the liquid swollen wet gel filament is less than the inward flux of the coagulation agent, or (2) if the outward solvent flux is greater than the inward coagulation agent flux

Table III Fibers Produced From a Polyimide Resin

| Coagulation Media | 31% Aq. DMAc | 70% Aq. EtG | 70% Aq. EtOH | 80% Aq. EtOH | |
|--|--------------|-------------|--------------|--------------|---------------|
| Polyimide Inherent Viscosity (dL/g) | — | 1.25 | 1.52 | 1.25 | 1.49 |
| Resin Extrusion Rate (cc/min) | 0.197 | 0.081 | 0.073 | 0.081 | 0.070 |
| Resin % Solids | 15.0 | 17.5 | 15.0 | 17.5 | 15.0 |
| Total Wet Gel Stretch | 1.2 × | 1.2 × | 1.2 × | 1.2 × | 1.4 × |
| Winder Spool Speed (fpm) | 50 | 65–66 | 60–63 | 59–61 | 45–46 |
| Fiber Cross-sectional Shape | Oval | Dogbone | C-Shape | Dogbone | Dogbone and C |
| Fiber Cross-sectional Area (μm^2) | 4390 | 1120 | 990 | 1180 | 1230 |
| % Solid Fibers | 0 | 0 | 13 | 78 | 76 |

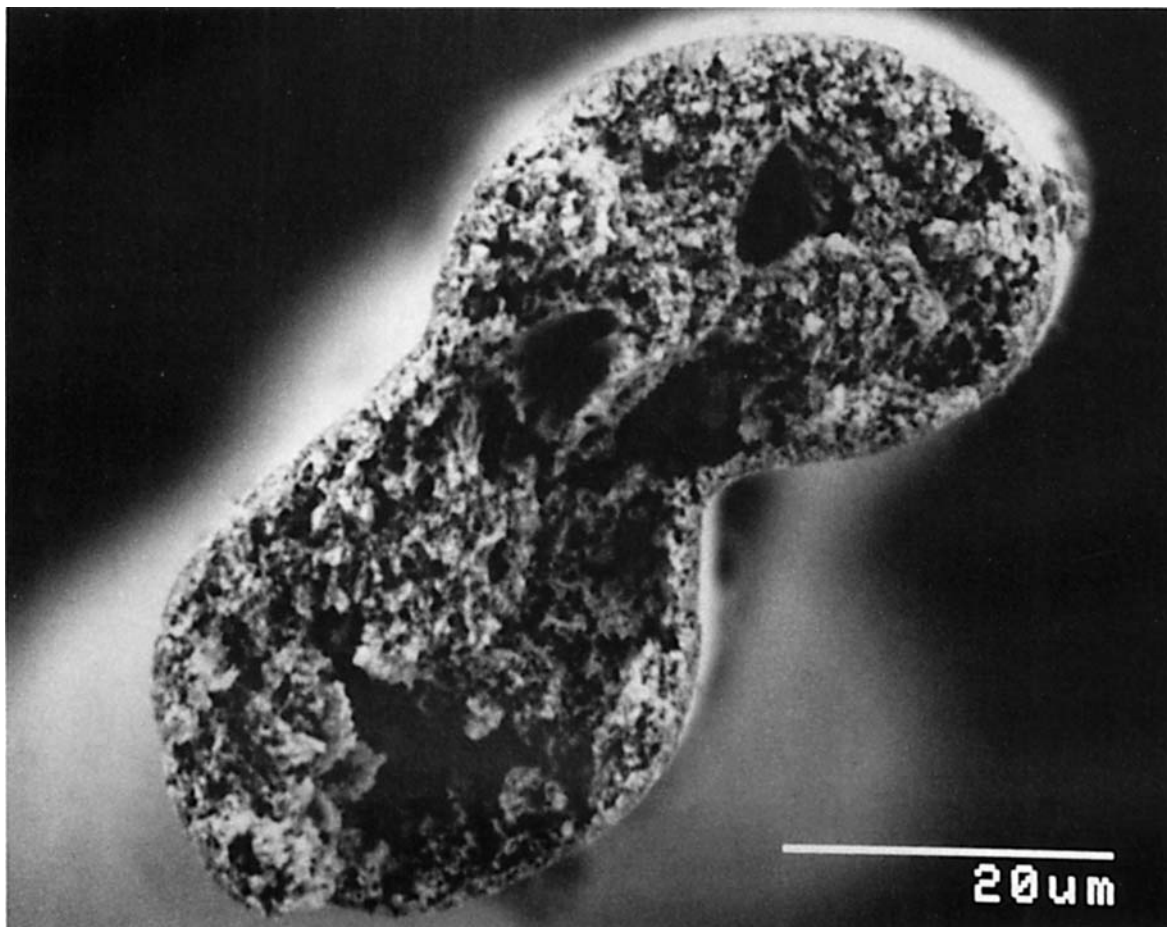


Figure 5 (Continued from the previous page)

and the filament has a soft deformable outer layer (skin).⁷ An SEM photo of a fractured fiber end is displayed in Figure 3, showing the circular cross-section with a cheesy, granular microstructure and two large macropores. Macropore formation depends on the coagulation conditions and may influence the resulting fiber's diameter in conjunction with the resin extrusion rate, resin percent solids, jet stretch, total wet gel stretch, and wet gel drying conditions.

The percent solid fiber value was dependent on the resin inherent viscosity for fibers of a similar diameter. Increasing the resin inherent viscosity from 1.5 to 2.1 dL/g tended to increase the percent solid fiber values. A percent solid fiber value of 60 signifies that one or more macropores were observed in 4 out of 10 fractured fiber ends. A similar trend was observed for another polyamic acid fiber.⁴ Seventy percent aqueous EtOH was found to be a better coagulation medium for this system than 70% aqueous EtG, because extrusion of 6FDA/4BDAF resins with the same inherent viscosity yielded fibers with similar diameters, but with significantly higher

percent solid fiber values. Solid polyamic acid fibers were obtained from resins with inherent viscosities ≥ 1.65 dL/g, using 70% aqueous EtOH as the coagulation medium.

A typical stress/strain curve for polyamic acid fibers produced, using a 70% aqueous EtG coagulation bath, is shown in Figure 4, curve A. A yield point was observed just prior to breaking. These polyamic acid fibers were very fragile, due to their low percent elongation to break of 7.2 and breaking tenacity of 12.6 ksi (Table II).

Polyimide Fibers

Polyimide fibers, obtained by thermal conversion of the aforementioned polyamic acid fibers, while wrapped around a spool, had unique stress/strain behavior, as shown in Figure 4, curve B. The breaking tenacity of these polyimide fibers almost doubled (23.7 ksi), as compared with that of the polyamic acid fibers. The yield point slightly increased to 15.4 ksi, and the initial modulus slightly decreased to

434 ksi. The most dramatic changes occurred in the 15-fold increase in the percent elongation-to-break of 111% and the appearance of a second yield point at a stress of 15.8 ksi and percent elongation of 71. This second yield at ambient is an unusual property. A typical stress/strain curve, obtained during cold-drawing of polymers, showed a yield point, followed by a region of extension at nearly constant stress, in which the neck formed at the yield point traveled along the specimen, a region where the slope of the stress/strain curve increased due to strain-hardening, and finally showed the specimen break.⁸ The second yielding may be attributed to necking of the newly formed material or structure created by the strain-hardening process. Additional research is needed to determine what changes are occurring prior to and at the second yield point.

Tensile properties of polyimide fibers, produced from polyamic acid resins using either 70% aqueous EtG or EtOH as the coagulation medium, were similar even though the fibers significantly differed in their percent solid fiber values (Table II). One would expect the completely solid fibers, spun using aqueous EtOH, to have higher tensile properties than those produced using aqueous EtG, in which half of the fibers contained macropores, but the reverse was observed. This behavior may be due to the fact that the 70% aqueous EtG spun fibers experienced a higher total wet gel stretch (1.3 × as compared to 1.1 ×) than the other fibers, which should result in higher tensile properties.

Extrusion of Polyimide Resins

Extrusion of 6FDA/4BDAF polyimide resin into 31% aqueous DMAc, 70% aqueous EtG, 70% aqueous EtOH, or 80% aqueous EtOH, according to the parameters listed in Table III, resulted in polyimide fibers having noncircular, cross-sectional shapes. Noncircular cross-sections are reported to result if during the coagulation process the outward flux of solvent from the liquid swollen wet gel filament is greater than the inward flux of coagulation agent and the filament has a rigid or nondeformable skin.⁷ Use of 20–31% aqueous DMAc as the coagulation medium produced fibers with an oval cross-sectional shape, containing numerous radially oriented macropores [Fig. 5(A)]. Extrusion of the polyimide resin into aqueous EtG or EtOH yielded fibers with either a "C" or dogbone cross-sectional shape [Fig. 5(B)] and a cheesy, granular microstructure.

Aqueous EtOH was a better coagulation medium than aqueous EtG, based on a higher percent solid

fiber value for polyimides with the same inherent viscosity extruded under similar conditions into fibers of similar cross-sectional areas. The influence of polyimide inherent viscosity on the percent solid fiber value did not appear to be as significant as with the polyamic acids. Extrusion of polyimide resins into the various coagulation media never yielded completely solid fibers. However, one might anticipate the production of solid fibers from polyimides with inherent viscosities ≥ 1.65 dL/g, using 70 or 80% aqueous EtOH as the coagulation medium, with extrusion conditions that would result in fibers with $\leq 700 \mu\text{m}^2$ cross-sectional areas, corresponding to a circular cross-section with a diameter of 30 μm .

A typical stress/strain curve for fibers produced from a polyimide resin, using 70% aqueous EtG as the coagulation medium, is shown in Figure 4, curve C. The corresponding tensile properties are listed in the first column of Table IV. The tensile properties of the unstretched polyimide fibers were less than those of the fibers of Table II and showed a yield point just prior to breaking. However, increasing the air stretch only slightly to 1.1 × and raising the air stretch temperature to 288–289°C, above the polymer's reported glass transition temperature of 263°C,³ dramatically increased the polyimide fibers' mechanical strength, well above values obtained for polyimide fibers derived from polyamic acid fibers. A similar air stretch at elevated temperatures of

Table IV Tensile Properties for Fibers Produced From a Polyimide Resin Using 70% Aqueous EtG^a

| | | | |
|--|---------------------------|---------------|---------------|
| Resin Extrusion Rate (cc/min) | 0.073 | 0.061 | 0.061 |
| Air stretch | — | 1.1 × | 2.3 × |
| Air Stretch Temp. (°C) | Ambient | 288–289 | 289 |
| Winder Spool Speed (fpm) | 60–63 | 39–41 | 79–82 |
| Fiber Cross-section Area (μm^2) | 990 | 370 | 240 |
| % Solid Fibers | 13 | 0 | 0 |
| Breaking Tenacity (ksi) | 6.1 (4.1) ^b | 27.7 (3.9) | 35.7 (3.3) |
| % Elongation to Break | 9.3 (30) | 54 (7.3) | 22 (8.5) |
| Yield Point (ksi) | 5.9 (5.1) | 21.5 (3.0) | 31.1 (2.1) |
| Initial Modulus (ksi) | 183 (2.4) | 672 (3.4) | 766 (2.2) |

^a Polyimide inherent viscosity 1.52 dL/g, wash bath stretch 1.2 ×.

^b % Coefficients of variation in parentheses.

polyamic acid wet gel filaments was not performed, due to concern over the possible hydrolysis of the polyamic acid. Air stretching at 288–289°C of the polyimide wet gel filament also increased the percent elongation to break of the resulting fiber. Increasing the air stretch at 289°C to 2.3 × further raised the breaking tenacity, yield point, and initial modulus, but decreased the percent elongation to break (Fig. 4, curve D). The secondary yielding was never observed in the stress/strain curves for any of these polyimide fibers spun from polyimide resin. Air stretching of polyimide wet gel filaments at elevated temperatures yielded fibers with superior tensile properties, as compared to polyimide fibers from polyamic acid fibers produced under similar conditions. Unsuccessful attempts at stretching the polyimide wet gel 2.9 × at 289°C resulted in the breaking of the filaments.

Tensile properties for polyimide fibers, produced using 70 and 80% aqueous EtOH, are listed in Table V. Fibers having an ambient air stretch exhibited similar tensile properties, which were also lower than those of the fibers of Table II, showing a yield point just prior to or at breaking. Air stretching at elevated temperatures resulted in improved tensile properties that were similar to those observed with 70% aqueous EtG as the coagulation medium. No indication of any secondary yielding in any of these polyimide fibers was found. It is interesting to note that fibers produced under similar conditions, using either aqueous EtG or EtOH, had similar tensile properties, even though the percent solid fiber values of the latter were significantly greater.

A thermogravimetric analysis of those polyimide fibers that were extruded from polyimide resin was performed. These polyimide fibers were extruded according to the parameters in the last column of Table IV, experiencing a 2.3 × air stretch at 289°C. Percent weight losses occurred at the following temperatures: 2% at 408°C, 10% at 478°C, 51% at 528°C, and 67% at 541°C. TGA of a 1 mil thick, 6FDA/4BDAF polyimide film, under similar conditions, showed a 10% weight loss at 497°C and a 50% weight loss at 533°C. The slightly lower thermal stability of the polyimide fibers, as compared to the film, may be a result of exposure of the much larger surface area of the fibers to the heated air. A weight loss of approximately 1% at 350°C indicates the polyimide fibers contained little residual liquid from its formation process or low molecular weight volatile components. These polyimide fibers exhibited good thermal stability in air.

CONCLUSIONS

Polyimide fibers have been produced from a soluble, fluorinated polyimide, derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane. Extrusions of both the polyamic acid and polyimide resins into various aqueous organic media were investigated. Polyamic acid resins were extruded into 70% aqueous EtG or 70% aqueous EtOH and this resulted in fibers with round or oval cross-sections. Polyimide resins, using 20–31% aqueous

Table V Tensile Properties for Fibers Produced From a Polyimide Resin Using Aqueous EtOH

| | | | | |
|---|---------------------------|-----------------|-----------------|-----------------|
| % Aqueous EtOH | 70 ^a | 80 ^b | 80 ^b | 80 ^b |
| Resin Extrusion Rate (cc/min) | 0.081 | 0.070 | 0.070 | 0.070 |
| Air Stretch | 1.1 × | — | — | 2.0 × |
| Air Stretch Temp. (°C) | Ambient | Ambient | 295–298 | 297–298 |
| Winder Spool Speed (fpm) | 59–61 | 45–46 | 40–43 | 80–82 |
| Fiber Cross-sectional Area (μm ²) | 1180 | 1230 | 390 | 260 |
| % Solid Fibers | 78 | 76 | 57 | 79 |
| Breaking Tenacity (ksi) | 6.7 (3.5) ^c | 7.4 (4.3) | 31.8 (5.1) | 33.9 (2.9) |
| % Elongation to Break | 6.9 (19) | 7.7 (25) | 58 (8.1) | 25 (9.1) |
| Yield Point (ksi) | 6.6 (3.0) | 7.4 (4.3) | 21.2 (2.3) | 29.0 (1.6) |
| Initial Modulus (ksi) | 218 (2.3) | 198 (3.0) | 655 (2.5) | 740 (1.4) |

^a Polyimide inherent viscosity 1.25 dL/g, resin % solids 17.5, wash bath stretch 1.1 ×.

^b Polyimide inherent viscosity 1.49 dL/g, resin % solids 15.0, wash bath stretch 1.3 ×.

^c % Coefficients of variation in parentheses.

DMAc, 70% aqueous EtG, 70% aqueous EtOH, or 80% aqueous EtOH as coagulation media, yielded fibers exhibiting oval, C-shaped, or dogbone cross-sections. Aqueous EtOH was a better coagulation medium than aqueous EtG, because polyamic acid or polyimide resins, extruded under similar conditions, yielded fibers having significantly higher percent solid fiber values. Polyimide resins, extruded into aqueous DMAc, always contained numerous radially oriented macropores. Completely solid polyamic acid fibers, with diameters of 28 μm , were obtained using 70% aqueous EtOH as the coagulation medium, with polymers having inherent viscosities ≥ 1.65 dL/g and resin percent solids of 15.0.

An increase in the breaking tenacity, percent elongation to break, and yield point, with a slight decrease in the initial modulus, occurred as a result of thermally curing polyamic acid fibers to polyimide fibers. These polyimide fibers exhibited a secondary yielding at about 71% elongation, which may be due to necking of some newly formed material or structure created during strain-hardening.

Polyimide fibers, produced by extruding polyimide resins into aqueous EtG or EtOH at polyamic acid extrusion conditions, had lower tensile properties than the polyamic acid and its corresponding polyimide fibers. However, thermal treatment at and above 288°C of the polyimide wet gel filament yielded fibers with significantly better tensile properties. These polyimide fibers showed no evidence of any secondary yielding. Stretching at these elevated temperatures caused the breaking tenacity, yield point, and initial modulus to increase significantly, while the percent elongation-to-break de-

creased. The stretched polyimide fibers exhibited good thermal stability in air.

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