

# Solution Processing of Composite Fibers Containing Rodlike and Thermoplastic Polymers

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## Synopsis

The solution processing and mechanical properties made from blends of the rodlike polymer poly(*p*-phenylene benzobisthiazole) with either poly(ether ether ketone) or nylon 6,6 is described. The concentration dependence of the isotropic–nematic phase transition for solutions of these polymers in methane sulfonic acid is in qualitative agreement with a theory of Flory. The mechanical properties of fibers that were wet spun from isotropic solutions of poly(ether ether ketone) and poly(*p*-phenylene benzobisthiazole) are very sensitive to the concentration of the spinning solution. Fibers spun at concentrations near the isotropic–nematic phase boundary have poor mechanical properties, resulting from phase separation during coagulation. However, when the solution concentration is significantly below the critical value, stiff and strong fibers are produced. In contrast, when nylon 6,6 is used as the thermoplastic component, the mechanical properties are good and are insensitive to the solution concentration. We attribute the solution concentration effects to two factors. The first is the difference in the solubility of poly(ether ether ketone) and nylon 6,6 in methane sulfonic acid–water mixtures. The second is the connectivity of the nematic phase, which also depends on concentration and has a major impact on the mechanical properties of the resulting fiber.

## INTRODUCTION

Extended chain or “rigid rod” polymers have been studied extensively because of their mechanical properties and thermal stability.<sup>1</sup> The major use of such polymers is in fiber-reinforced composites. However, due to weak adhesion at the fiber/matrix interface and stress concentrations at the fiber ends, the ultimate strength is not realized.<sup>2</sup>

It has been suggested that the ultimate properties may be achieved by preparing a composite on the molecular level from blends of rodlike and matrix polymers with similar chemical structures. For example, with sufficient dispersion, improved adhesion and minimization of the stress concentration at the chain ends may be expected. Two such “molecular composite” systems have been studied. The U.S. Air Force has studied the rodlike poly(*p*-phenylene benzobisthiazole) (PPBT) as a reinforcement for a more flexible amorphous matrix such as poly(2-5(6)-benzimidazole).<sup>3</sup> Takayanagi et al.<sup>4</sup> studied polyamide systems of poly(*p*-phenylene terphthalamide) in a matrix of nylon

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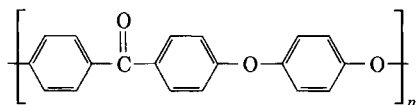
6 or nylon 6,6. It has been suggested that the optimum concentration for spinning molecular composite fibers is slightly below the "critical" value.<sup>5</sup> (The "critical" concentration refers to the total amount of polymer in the ternary mixture for which the isotropic-nematic phase transition is observed.) This concentration depends on the proportion of rodlike and flexible components and can be estimated, at least qualitatively, by the theory of Flory.<sup>6</sup>

In this work, we are interested primarily in the effect(s) of the polymer concentrations on the mechanical and thermal properties of fibers coagulated from solutions of rodlike and thermoplastic polymers. Specifically, we have studied composites of PPBT with either poly(ether ether ketone) (PEEK) or with nylon 6,6 (N66). PEEK was chosen because it is a thermoplastic that may yield a composite that can be melt processed, because it is soluble in methane sulfonic acid<sup>7</sup> (MSA), which is also a solvent for PPBT, and because its mechanical properties, thermal stability, and chemical resistance are superior to many other engineering thermoplastics.<sup>8</sup> We examine the N66/PPBT materials for comparisons with previous studies.<sup>9</sup>

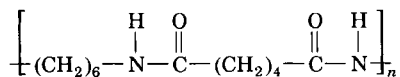
In the next section we describe the materials and the sample preparation. The equilibrium phase behavior for ternary solutions of PEEK and PPBT in MSA is then compared with a theory of Flory. The tensile properties and some microscopy of fibers spun from solutions near the isotropic/nematic phase boundary are reported in the next several sections. Following this, we describe the dramatic effects of polymer concentration in the spinning solution on the mechanical properties. The thermal behavior of PEEK/PPBT fibers is also discussed. Similar mechanical and thermal studies for N66/PPBT fibers are reported for comparison. A final section summarizes the main results and our conclusions.

## MATERIALS AND SAMPLE PREPARATION

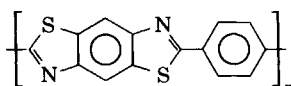
The chemical structure of PEEK is



and the synthesis has been described by Attwood et al.<sup>10</sup> The samples used in this work were obtained from Imperial Chemical Industries and had  $M_n = 13,000$  and  $M_w = 33,000$  as measured by gel permeation chromatography.<sup>11</sup> The structure of N66 is



and we used material with  $M_n = 13,700$  and  $M_w = 27,400$ , obtained from DuPont Co. the structure of PPBT is



We used PPBT synthesized by Wolfe<sup>12</sup> at Stanford Research Institute. The samples had intrinsic viscosities of 25 and 18 dL/g in MSA at 20°C, corresponding to weight average molecular weights of 36,000 (PPBT36) and 30,000 (PPBT30). MSA (98%, Aldrich Chemical Co.) was used as the solvent.

The PPBT36 was extracted into water from a polyphosphoric acid solution; PPBT30 was received in the extracted form. All of the polymers were dried for 1–2 days in a vacuum oven at 70°C and 0.5 torr. The desired amounts of polymer(s) and MSA were mixed at room temperature under a dry nitrogen atmosphere using a magnetic stirrer.

Samples of the solution were prepared for optical microscopy by placing a drop of the solution between a microscope slide and a thin cover glass (sealed with Parafilm to exclude moisture). The transmission of polarized light was then examined using a Vickers no. M70/2/334 optical microscope to test for birefringence which indicates the presence of a nematic phase.

## PROCESSING AND PROPERTY MEASUREMENTS

Fibers were wet spun with very little draw into a water bath at 20°C. A reservoir of solution held in a Teflon barrel was extruded through a 330  $\mu\text{m}$  diameter die at a constant velocity of 100 cm/min into a water bath at 20°C. The fiber was held in water overnight before drying to insure complete removal of the solvent. Two post-processing steps were employed to improve properties. Hot drawing was done by passing an air dried fiber over a Thermolyne type 1900 hot plate set at 265°C, while the fiber was drawn between two rollers. The deformation was characterized by the draw ratio (DR) defined as the ratio of the squared fiber diameter before and after drawing. Heat treatment was done by passing a dried fiber through an oven under a dry nitrogen atmosphere using an apparatus that is described elsewhere.<sup>13</sup>

The fiber diameters were measured by optical microscopy. For mechanical testing, single filaments were mounted with epoxy onto 3-cm gauge length paper tabs. Tensile tests were done on an Instron Universal testing machine using a crosshead speed of 0.1 cm/min. Some of the tensile tested fibers were sputtered with gold using a Polaron E5100 coating unit, and examined with an ETEC Autoscan SEM; a Perkin-Elmer differential scanning calorimeter was used for thermal analysis.

## RESULTS AND DISCUSSION

### PEEK / PPBT Composites

After the initial mixing, the solutions were examined for isotropy by polarized light microscopy; birefringent solutions were diluted with MSA and mixed for 3–4 days and examined again. This procedure was employed to locate the approximate position of the isotropic–nematic phase boundary as shown in Figure 1. The composition of the individual phases were not measured.

Flory<sup>6</sup> derived a statistical thermodynamic theory for the phase behavior in ternary solutions of random coil polymer, rigid rod polymer and solvent; the sole parameters are the aspect ratios of the polymeric components. Figure 1

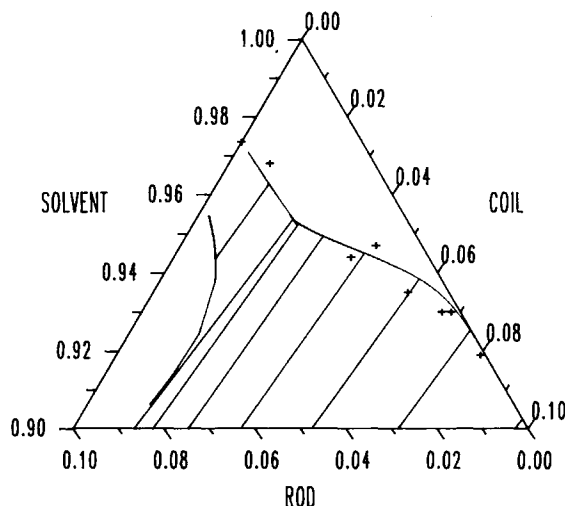


Fig. 1. Phase diagram for PEEK/PPBT/MSA solutions at 20°C showing the isotropic (x) and anisotropic (●) concentrations.

also shows a comparison of this theory with the data. The aspect ratio for PPBT36 was estimated as 300 from the molecular weight,<sup>5</sup> while the aspect ratio of the random coil component was used as a parameter; a value of 10 was chosen in order to describe the data shown in Figure 1. This value is significantly lower than an estimate based on the contour length and dimensions of the PEEK chain, and is thought to be a result of the relatively stiff behavior PEEK in solution.<sup>7</sup>

Composite fibers with proportions of PEEK/PPBT36 ranging from 95/5 to 70/30 (w/w) were wet spun from isotropic solutions in MSA at concentrations close to the critical value. The fibers were too weak to be drawn in the wet state, but were air-dried, hot-drawn, and subsequently tested.

Figure 2(a) shows the behavior of the tensile modulus. The values are unexpectedly low since the modulus for melt processed PEEK is approximately 3 GPa.<sup>14</sup> The effect of solution processing is undoubtedly one important factor, since the as-spun modulus of the PEEK fiber is only 0.17 GPa. In fact, the as-received PEEK and PEEK that was dissolved in MSA and subsequently extracted had intrinsic viscosities of 0.90 and 0.66 dL/g, respectively, indicating some degradation. However, this does not explain the decrease in modulus with increasing PPBT content. Although hot drawing results in a significant enhancement of the modulus, the trend of decreasing modulus with increasing rod content is still evident and the maximum modulus attained is less than 1 GPa. Figure 2(b) shows that the tensile strength is also low compared to a reported value of 100 MPa for melt processed PEEK.<sup>8</sup> The strength also decreases with increasing PPBT content.

After tensile testing, the specimens were examined with the scanning electron microscope. All of the PEEK/PPBT fibers had voids on the fiber surface, such as those that can be seen in Figure 3. Hot drawing resulted in a more fibrillar appearance, but surface voids were still evident. However,

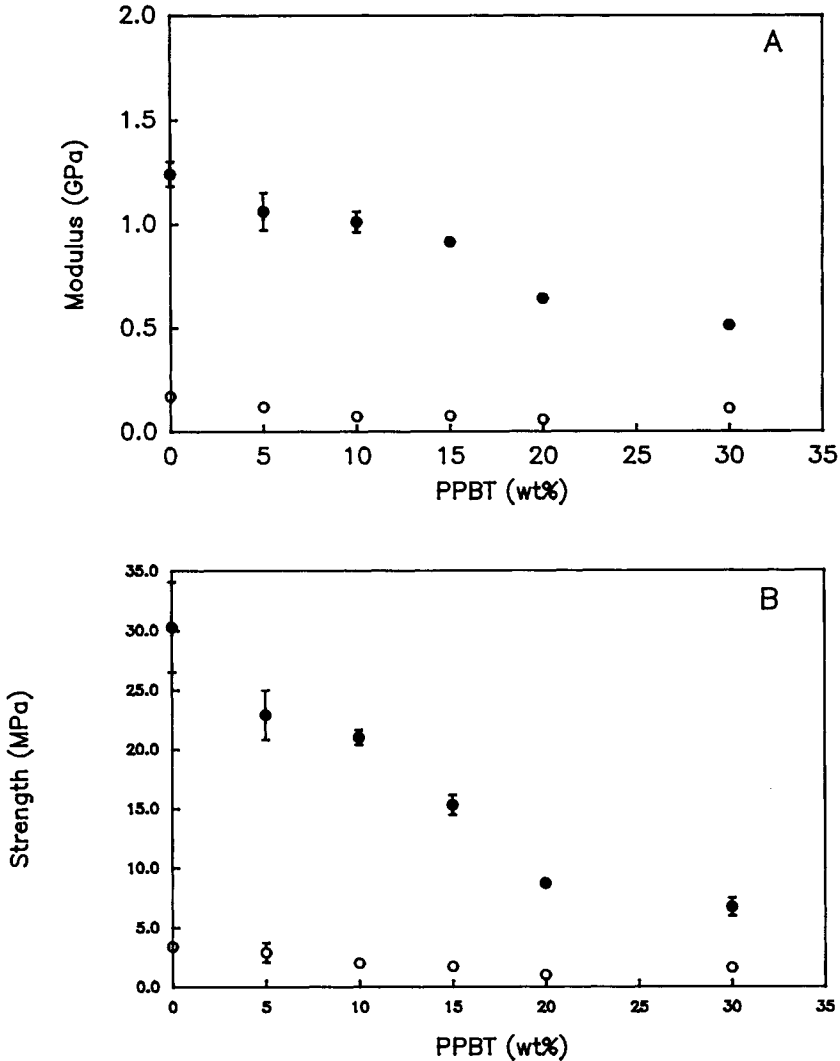


Fig. 2. Tensile modulus (a) and strength (b) for as-spun (○) and hot-drawn (●) PEEK/PPBT fibers, spun close to the critical concentration. (In all of the figures, error bars were estimated from the standard deviation of measurements on at least six samples; they are sometimes smaller than the size of the data point.)

surface voids were not observed on solution spun PEEK fibers as shown in Figure 4.

The microstructure of the PPBT within these composite fibers was examined with a transmission optical microscope, immediately after sulfuric acid (a solvent for PEEK, but a nonsolvent for PPBT) was dripped onto the fiber. Figure 5 shows discontinuous aggregates of PPBT for a 90/10 fiber; these aggregates were typical in the PEEK/PPBT fibers which were spun from solutions near the critical concentration.

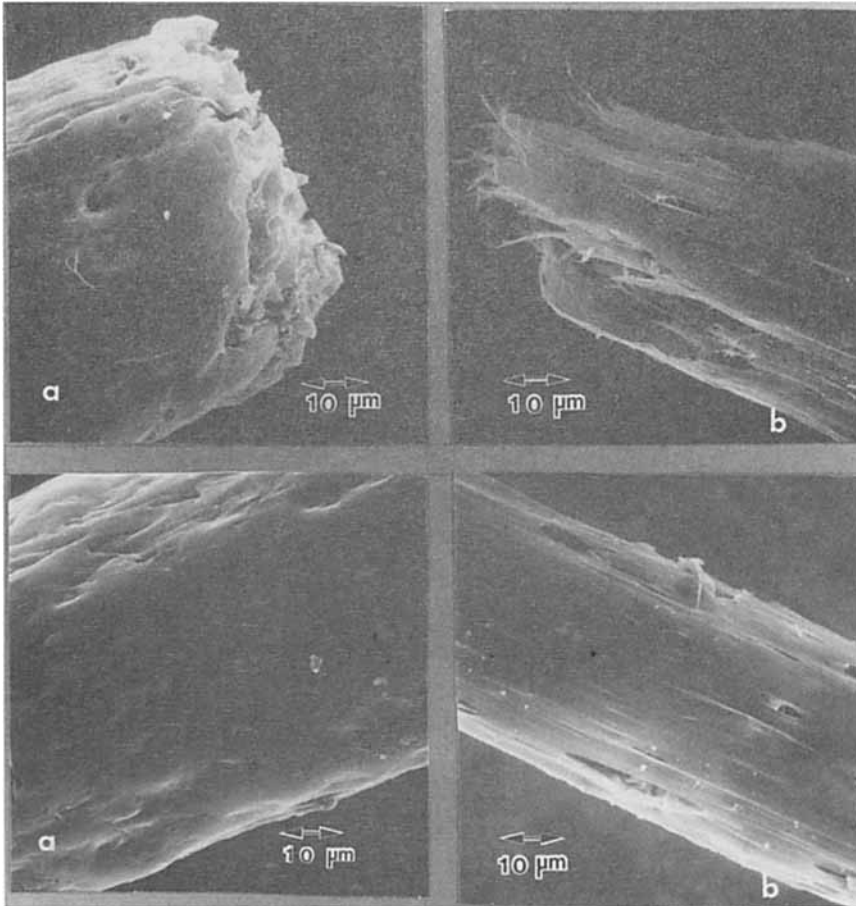


Fig. 3. Scanning electron micrograph of (a) as-spun and (b) hot-drawn 70/30 PEEK/PPBT fiber spun close to the critical concentration.

We recall that these fibers were processed close to the critical concentration with the expectation that the rate of coagulation into the amorphous "molecular composite" phase would be larger than the rate of phase separation into nematic regions of PPBT and isotropic domains consisting primarily of PEEK. However, in light of the mechanical properties and microscopy, it appears that the thermodynamically favored phase separated state has been formed. This suggests that the phase separation occurs on a time scale that is not much slower than that for the formation of an amorphous solid phase when the initial solution concentration is near the critical value.

To study the effects of solution concentration, fibers in a proportion of 75/25 PEEK/PBT30 were spun from solutions with various total polymer concentrations in MSA. The tensile modulus and strength are strong function of concentration as shown in Figure 6. A maximum in the mechanical properties is seen for a concentration near 2% polymer. Scanning electron micrographs of these fibers after tensile testing, as shown in Figure 7, reveal that fibers spun from 1.0, 2.0, and 2.5% solutions have fibrillar surfaces. In contrast,

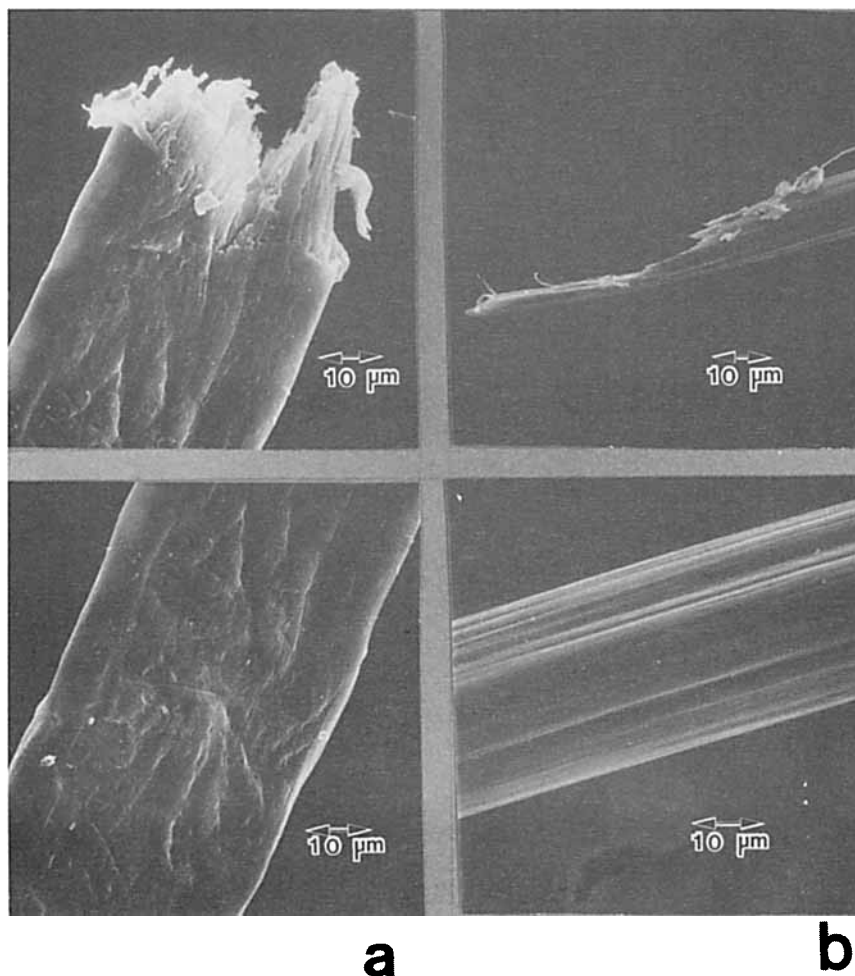


Fig. 4. Scanning electron micrographs of (a) as-spun and (b) hot-drawn PEEK/PPBT fiber.

fibers spun from a 3.0% solution appear almost porous, while voids appear on the surface of the fiber spun at 4.0%. Figure 8 shows the diameters of PEEK/PPBT fibers in comparison with the values expected based on a mass balance for the polymers and assuming that voids are absent. The sharp increase above 3% coincides with the decrease in strength and modulus (cf. Fig. 5) and is due to the presence of voids.

Fibers with various proportions of PEEK/PPBT30 were also wet spun from a 2.0% solution in MSA. Figure 9(a) shows the tensile modulus vs. PPBT fraction. There is nearly an order of magnitude increase in modulus over the values obtained for fibers processed close to the critical concentration and the modulus increases with PPBT content. Heat treatment at 425°C without tension results in a further enhancement of the modulus; we also note the sharp increase of modulus between 10 and 25% PPBT. This may indicate a percolation threshold for the formation of a continuous network of PPBT throughout the fiber. Similar behavior of the tensile strength is seen in Figure

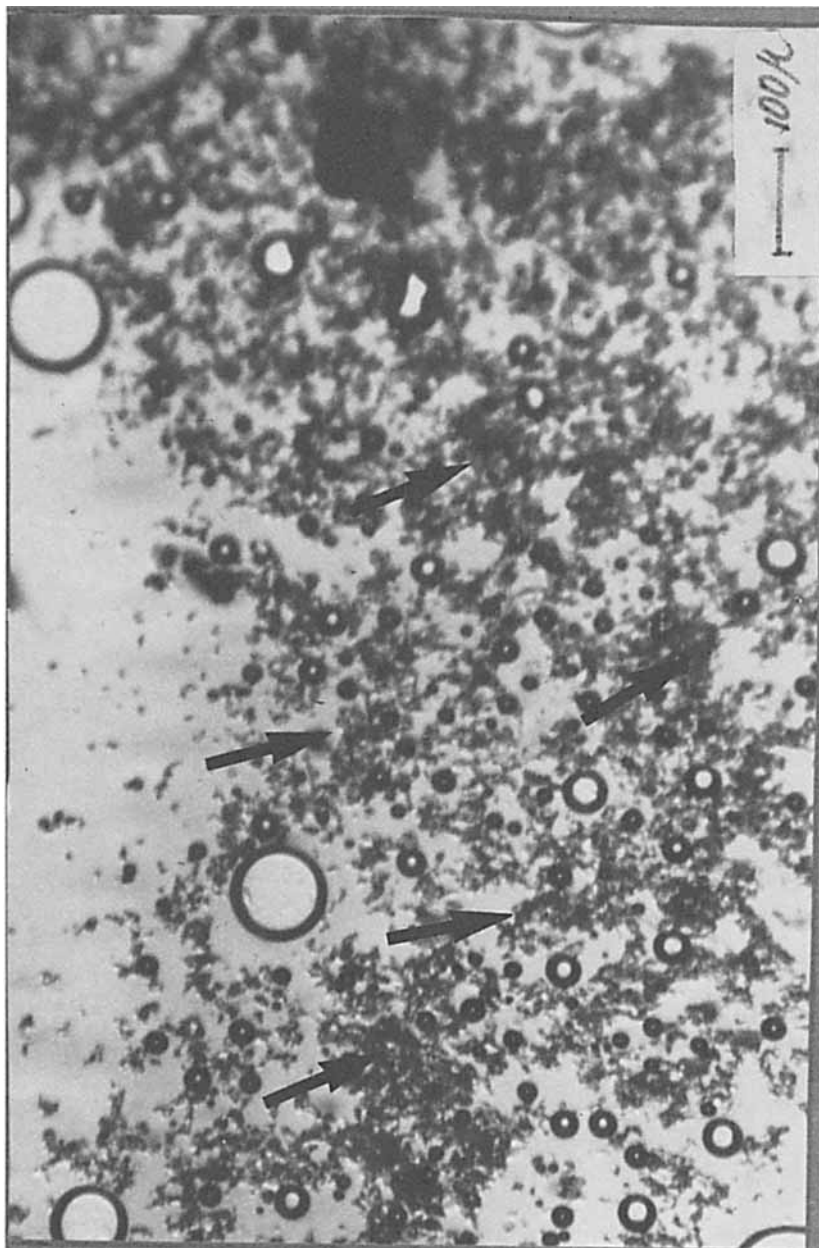


Fig. 5. Optical micrograph of an as-spun 90/10 PEEK/PPBT fiber spun close to the critical concentration, immediately after exposure to sulfuric acid. The PPBT structure is indicated by the arrows; the circles are air bubbles.



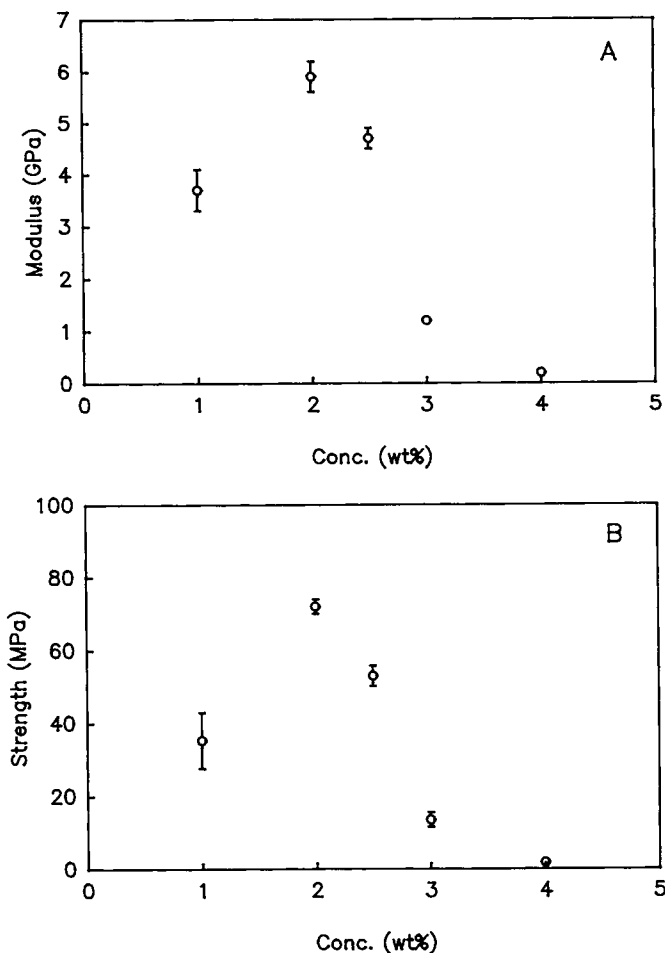


Fig. 6. Tensile modulus (a) and strength (b) for as-spun 75/25 PEEK/PPBT30 fibers as a function of the total polymer concentration in the spinning solution. The error bars were estimated from the standard deviation of measurements on at least six samples.

9(b). Figure 10 shows the strain at break for these fibers. It is interesting that the strain for 5–25% as-spun fibers is less than that for the corresponding heat treated fiber. This is consistent with the presence of a PPBT network that is continuous on the size scale of the fiber. When the fiber is not drawn during spinning, a relatively large strain at break would be expected for the as-spun fibers, and, if such a network is perfected during heat treatment, the strain at break should decrease. Recent mechanical<sup>15</sup> and morphological<sup>16</sup> studies of PPBT fibers spun from anisotropic solutions in poly(phosphoric acid) show a continuous network structure of fibrils with diameters on the order of 70–100 Å.

Fibers processed at 2.0% concentration were soaked in sulfuric acid (a solvent for PEEK, but a nonsolvent for PPBT) for 2 months. An optical micrograph of such a fiber is shown in Figure 11(a). A continuous phase of PPBT propagates throughout the fiber in contrast to the discontinuous

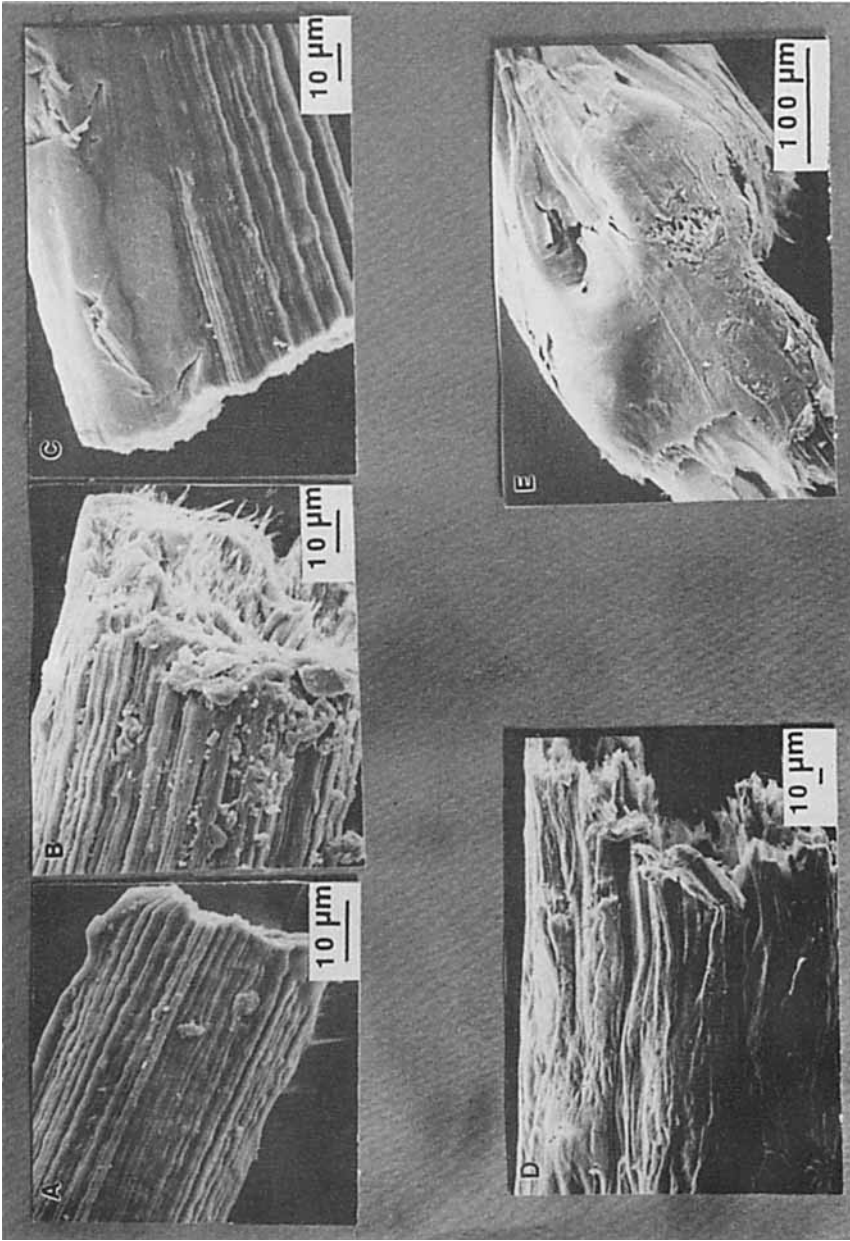


Fig. 7. Scanning electron micrographs of as-spun 75/25 PEEK/PPBT30 fibers spun from (a) 1.0, (b) 2.0, (c) 2.5, (d) 3.0, and (e) 4.0% solutions.

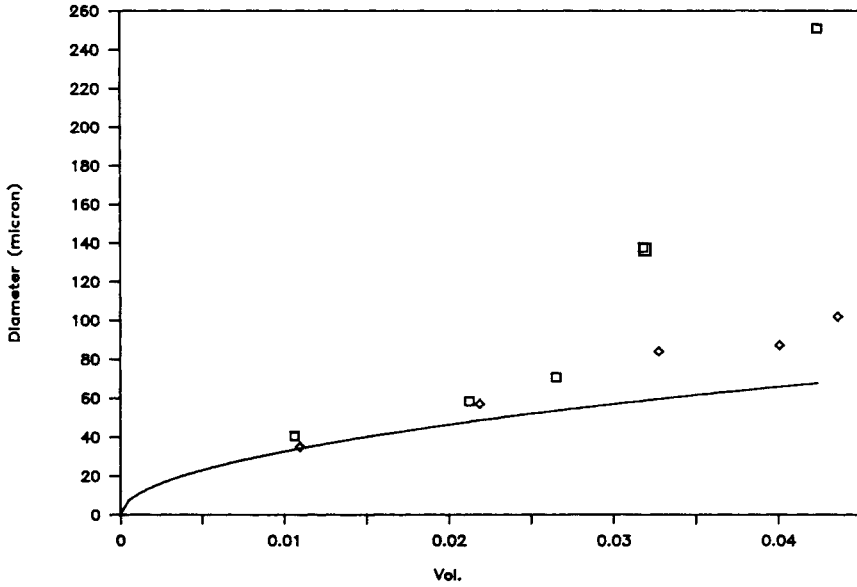


Fig. 8. Dependence of the fiber diameter on the total polymer concentration for 75/25 as-spun PEEK/PPBT30 (□) and N66/PPBT30 (◇) fibers. The solid line is an estimate based on a mass balance assuming complete removal of the solvent and water and the absence of voids.

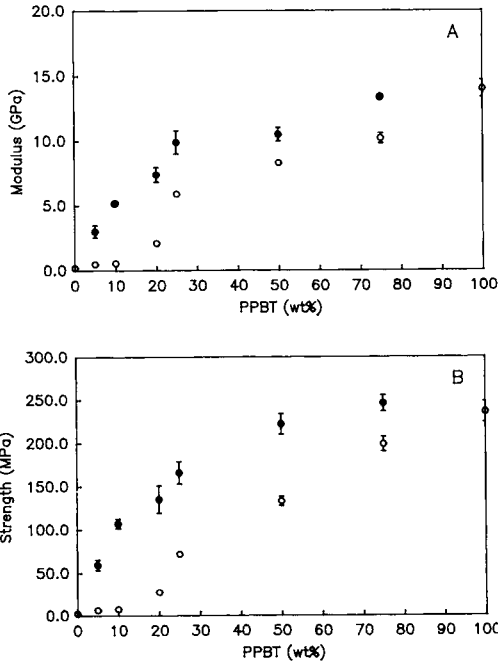


Fig. 9. Tensile modulus (a) and strength (b) for as-spun (○) and heat-treated (●) PEEK/PPBT30 fibers, spun from 2.0% solution in MSA. The error bars were estimated from the standard deviation of measurements on at least six samples.

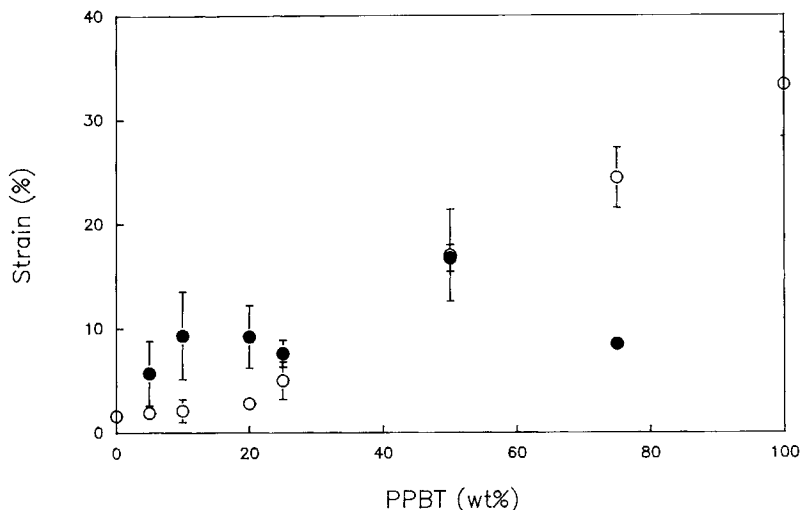


Fig. 10. Tensile strain at break for as-spun (○) and heat-treated (●) PEEK/PPBT30 fibers, spun from 2.0% solutions in MSA. The error bars were estimated from the standard deviation of measurements on at least six samples.

aggregates seen in Figure 5. After heat treatment, the PPBT structure has larger fibrils with a finer structure as shown in Figure 11(b).

The tensile properties are expected to increase further with wet stretching and heat treating under tension and the values reported here can be improved by further post-processing.<sup>17</sup>

Differential scanning calorimetry thermograms for 75/25 PEEK/PPBT fibers spun at various concentrations and for a PEEK fiber spun from a 3.0% solution are shown in Figure 12. The composite fibers have thermal transitions at nearly the same temperatures as the PEEK fiber. After the glass transition at approximately 143°C, a crystallization exotherm is found at approximately 160°C, followed by a melting endotherm at 340–350°C. The crystallization of PEEK apparently occurs at a slightly lower temperature in the presence of PPBT, but these thermal studies indicate the presence of discrete domains of PPBT within the fibers.

### Nylon 6,6 / PPBT Composites

N66/PPBT composite fibers were examined for comparison. Figure 13 shows the tensile properties for 75/25 N66/PPBT30 fibers spun at various concentrations. There is not such a large effect of concentration and, in fact, the fiber spun from a birefringent solution at 4.0% has a modulus of approximately half that of the fibers spun below the critical concentration. There is a similar dependence of the tensile strength on the concentration. The scanning electron micrographs of tensile tested fibers shown in Figure 14 reveal a fibrillar structure. As shown in Figure 8, the fiber diameters increase approximately in proportion to the polymer concentration.

The tensile properties for N66/PPBT fibers are much less sensitive to the solution concentration than those of the PEEK/PPBT fibers, probably because the solubilities of the two blends in MSA/water mixtures are signifi-

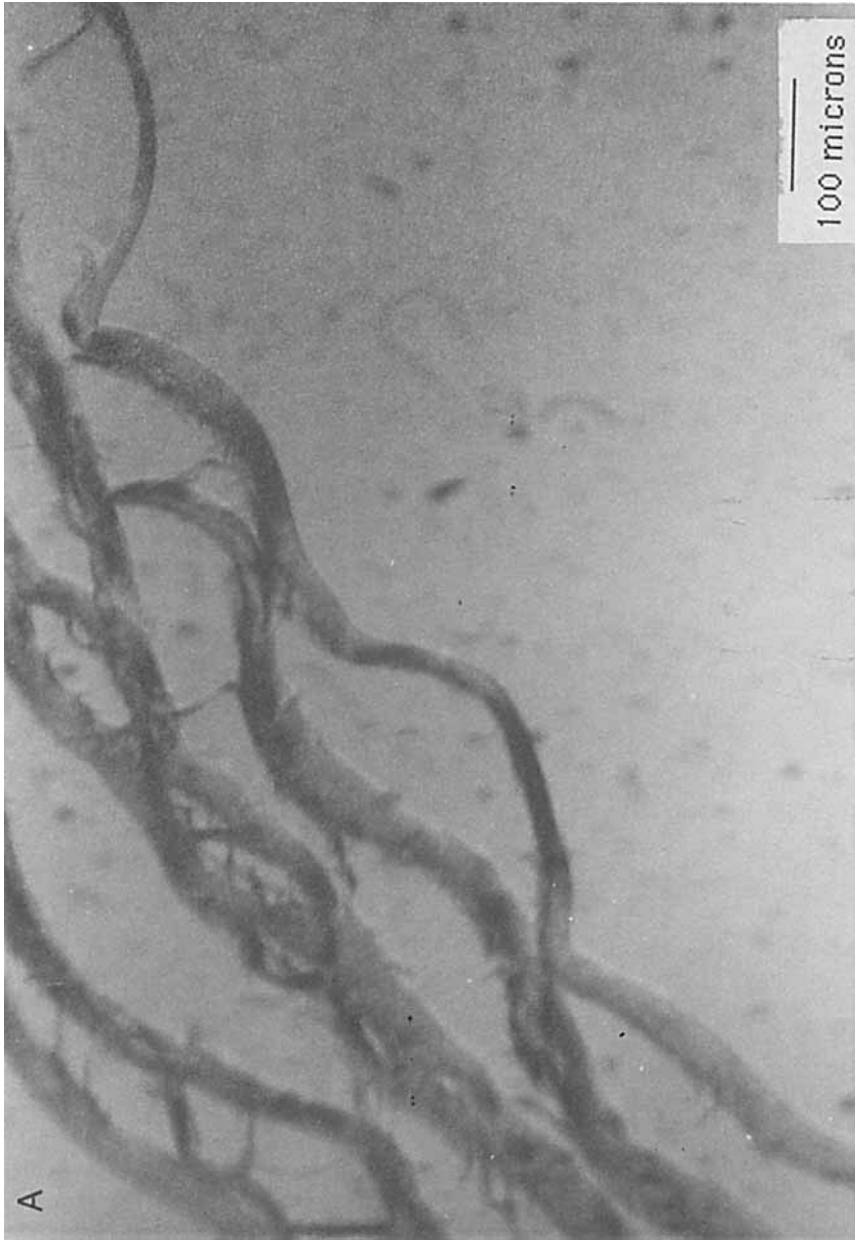


Fig. 11. Optical micrograph of (a) as-spun and (b) heat-treated 90/10 PEEK/PPBT30 fiber spun from a 2.0% solution in MSA after soaking in sulfuric acid for 2 months.

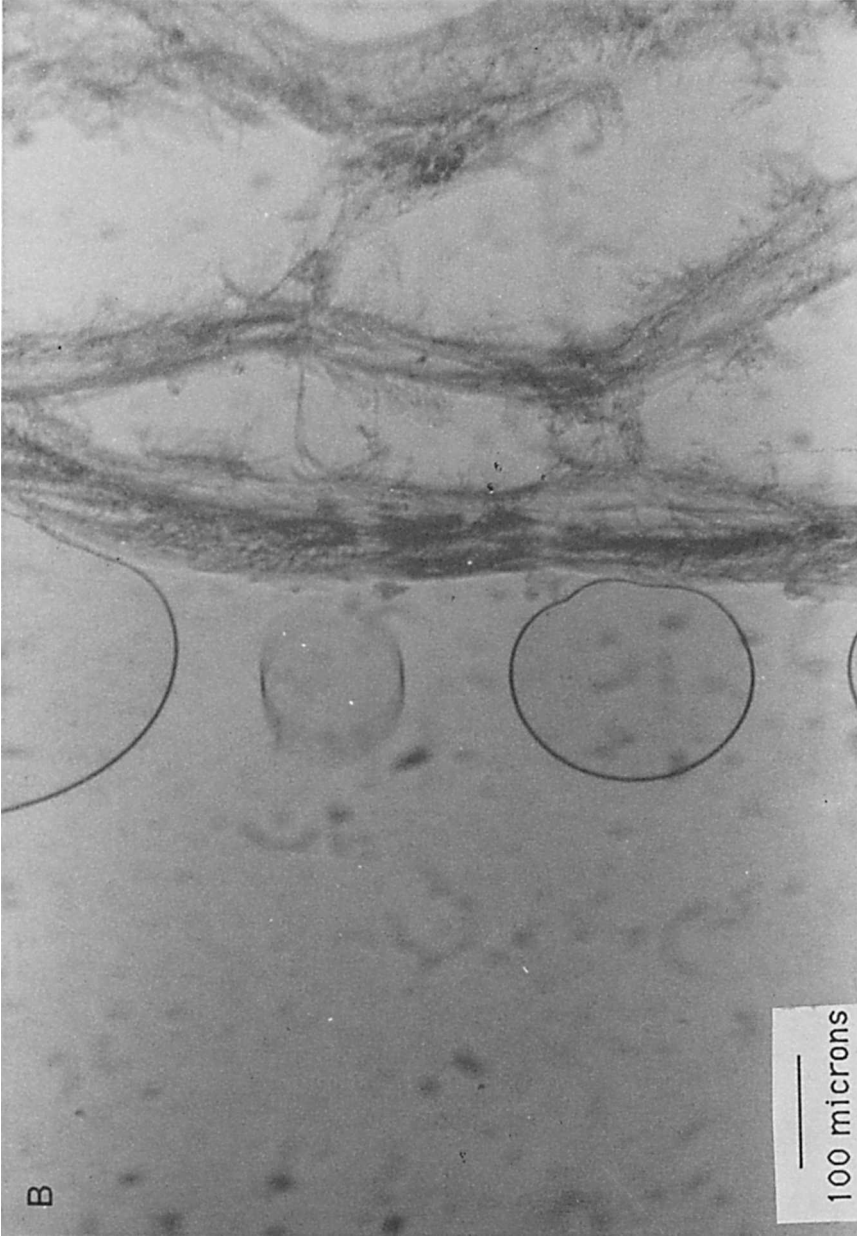


Fig. 11. (Continued from the previous page.)

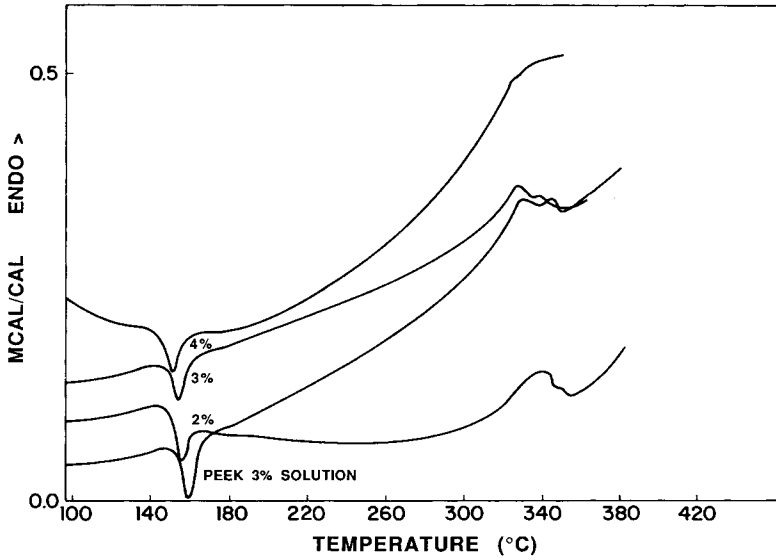


Fig. 12. Differential scanning calorimetry scans for as-spun 75/25 PEEK/PPBT30 fiber spun from 2.0, 3.0, and 4.0% solutions and for as-spun PEEK fiber prepared from a 3% solution.

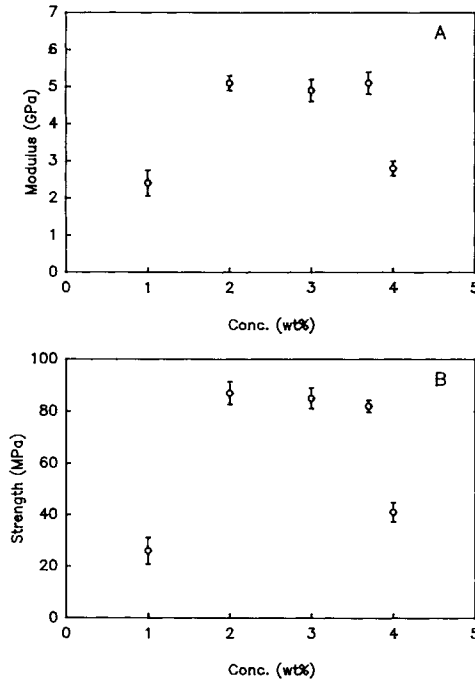


Fig. 13. Tensile modulus (a) and strength (b) for as-spun 75/25 N66/PPBT30 fiber vs. the total polymer concentration in the spinning solution. The error bars were estimated from the standard deviation of measurements on at least six samples.

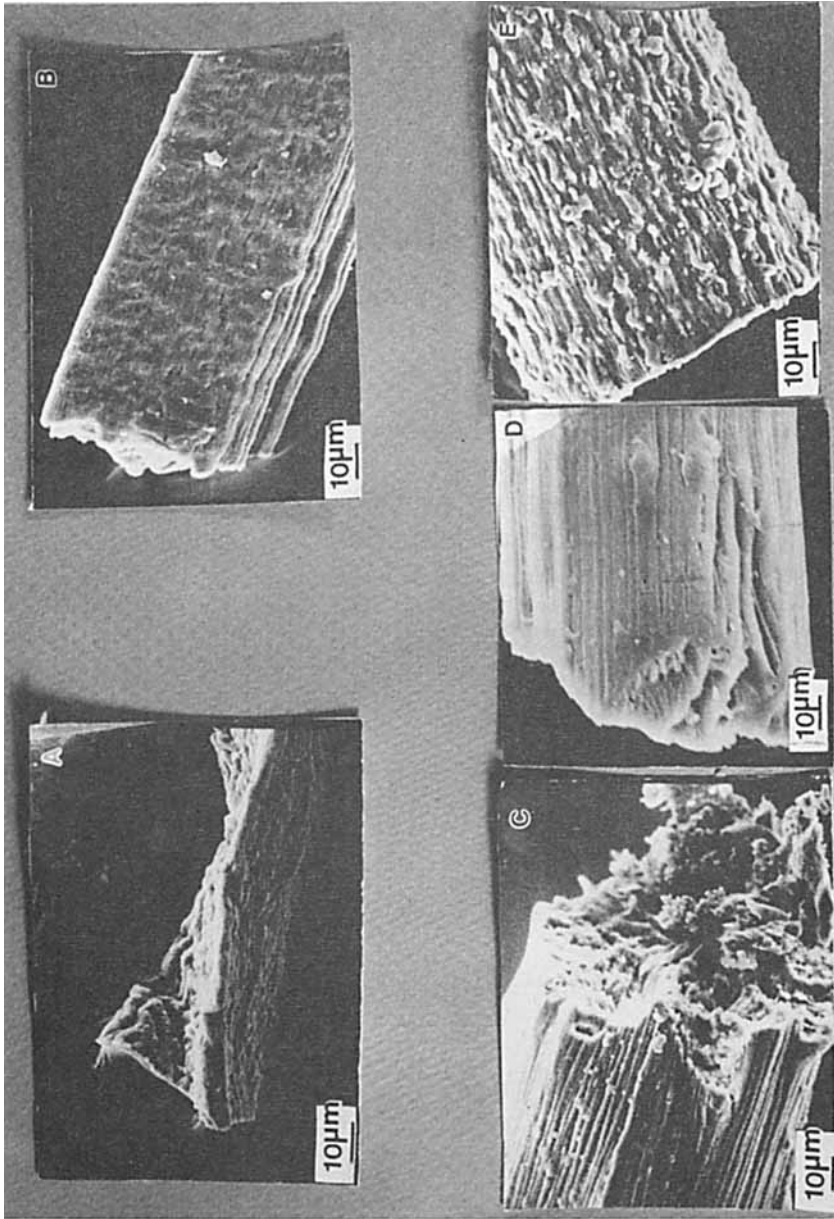


Fig. 14. Scanning electron micrographs of as-spun 75/25 N66/PPBT30 fibers spun from (a) 1.0, (b) 2.0, (c) 3.0, (d) 3.7, and (e) 4.0% solutions.



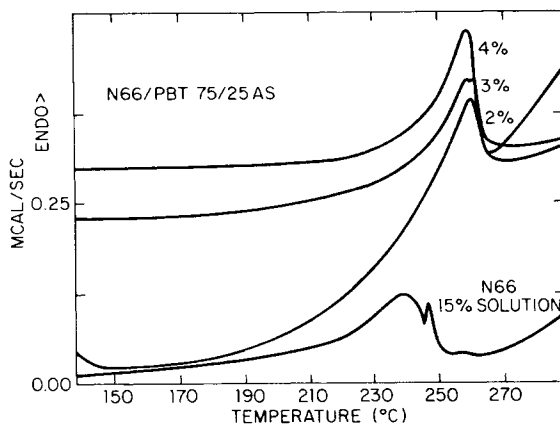


Fig. 15. DSC scans for as-spun 75/25 N66/PPBT30 fiber spun from 2.0, 3.0, and 4.0% solutions and for as-spun N66 fiber spun from 15.0% solution.

cantly different. For example, 3.8 cc of water produces a turbid solution when added to 1.0 cc of a 2.0% solution of N66 in MSA. In contrast, the same effect is produced by the addition of 0.15 and 0.20 cc of water to PEEK/MSA and PPBT/MSA solutions, respectively.

Figure 15 shows DSC scans for as-spun 75/25 N66/PPBT fibers spun at various concentrations and for a N66 fiber spun from a 15% solution in MSA. (N66 cannot be spun into the fiber form at lower concentrations, due to the solubility.) The composite fibers all show approximately the same melting temperature near 267°C, which is 20°C higher than the transition in the N66 fiber. The higher melting point in the composites could be the result of N66 crystallization onto the surface of a PPBT phase.<sup>4</sup> The melt endotherm shows that there are discrete domains of N66 in the composite fibers.

Thus, we expect that there is a network structure of PPBT in the N66/PPBT fibers and that this network can form more effectively than in the PPBT/PEEK fibers due to the greater solubility of nylon in MSA/water mixtures. Further evidence for the presence of a network was found from an extended heat treatment. A 50/50, fiber of N66/PPBT30 as-spun from 2% solution and treated as 425°C for 4 h to remove the nylon matrix. The as-spun fiber diameter was 69  $\mu\text{m}$  compared to 49  $\mu\text{m}$  after heat treatment. The initial values of the tensile modulus, strength, and strain at break were 7.0 GPa, 151 MPa, and 38.4%, compared to values of 16.2 GPa, 224 MPa, and 1.7% after heat treatment.

## CONCLUSIONS

The existence of a continuous, microfibrillar network has recently been demonstrated for pure PPBT fiber spun from nematic solutions in polyphosphoric acid.<sup>15,16</sup> Some evidence for similar network formation in molecular composites is shown here. The tensile modulus and strength have a dramatic increase between 10 and 25 wt % PPBT; this is consistent with a percolation threshold for the formation of a continuous PPBT rich phase. The tensile modulus and the strain at break for composite fibers containing less than 25%

PPBT increase significantly as a result of heat treatment, suggesting that a perfection of the network occurs. A continuous structure of PPBT was observed with optical microscopy for PEEK/PPBT fibers when the PEEK matrix was removed with sulfuric acid. After heat treatment, the PPBT structure had larger denser fibrils.

Differential scanning calorimetry shows that the composite fibers have nearly the same thermal transitions as pure solution processed PEEK, indicating that macroscopic domains of nearly pure PEEK are present in the fiber. Calorimetry studies of the N66/PPBT fibers shows a melting transition that is only slightly higher than pure N66. The rise in the melting point could be the result of N66 crystallizing onto the surface of a PPBT rich phase<sup>4</sup> and is interpreted as indicating the presence of a separate N66 phase. A study of N66/PPBT fibers using transmission electron microscopy and small angle X-ray scattering to provide a more quantitative description of the small scale structure of the PPBT phase will appear elsewhere.<sup>18</sup>

The implications for further studies of molecular composites are as follows. During coagulation, the rodlike component will generally form a network. If there is a slow rate of coagulation of the matrix in comparison to the reinforcement, a fiber spun from a solution close to the critical concentration will not phase separate to form discontinuous domains of PPBT. However, a matrix and reinforcement with little or no interaction and more similar rates of coagulation will result in a phase-separated fiber with poor mechanical properties when processed close to the critical concentration. The solution concentration can be adjusted to inhibit phase separation.

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