AFWAL-TR-87-4048

ADA 184458

Molecular Composites: Processing, Post-Treatment and Mechanics

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July 1987

Final Report for the Period May 1983 - September 1986
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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFWAL-TR-87-4048

6a. NAME OF PERFORMING ORGANIZATION
University of Massachusetts

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
Air Force Wright Aeronautical Laboratories
Materials Laboratory (AFWAL/MLBC)

6c. ADDRESS *(City, State and ZIP Code)*
Chemical Engineering Department
Goessmann Laboratory
Amherst MA 01003-0011

7b. ADDRESS *(City, State and ZIP Code)*
Wright-Patterson AFB, OHIO 45433-6533

8a. NAME OF FUNDING/SPONSORING ORGANIZATION

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F 33615-83-K-5001

8c. ADDRESS *(City, State and ZIP Code)*

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
62102F	2419	01	40

11. TITLE *(Include Security Classification)* Molecular Composites: Processing, Post-Treatment and Mechanics

12. PERSONAL AUTHOR(S)
M. F. Malone, C. F. Hwang, C. A. Gabriel, O.A. Nehme, R. J. Farris

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 5/83 TO 9/86

14. DATE OF REPORT *(Yr., Mo., Day)*
July 1987

15. PAGE COUNT
96

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.
11	04	
11	09	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Ordered polymer, molecular composite, fiber, film, PBT, Nylon, PEEK

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Composites of poly(p-phenylene benzobisthiazole) (PBT) with nylons and with poly (ether ether ketone) (PEEK) were prepared in fiber and film form. Fiber and film spinning from dilute solutions in methane sulfonic acid (MSA) along with compression molding and sheet spinning were used to prepare materials for testing. Composite fibers of PBT and nylons exhibit tensile properties comparable to those previously reported for nylon/PBT materials. The mechanical and thermomechanical properties can be dramatically improved by post-treatment under tension at temperatures exceeding the melting point of the nylon. The torsional modulus is decreased somewhat by such post-processing and is in the range of 700 to 1000 GPa. Films of nylon/PBT material can be compression molded into larger articles, but the strength can be attributed to behavior of nylon alone.

Composite fibers of PEEK and PBT prepared from MSA solutions exhibit tensile properties that are very sensitive to the solution concentration; processing near the isotropic-nematic phase boundary results in poor mechanical properties over a wide range of compositions. Decreasing the solution concentration or increasing the amount of PBT

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22c. OFFICE SYMBOL
AFWAL/MLBC

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

19 (continued)

in solution leads to an increase in the tensile properties until, at very low concentrations, there is another decrease in properties.

The mechanical behavior of all of these materials is consistent with the existence of a microfibrillar network of PBT embedded in a nylon matrix. The stiff PEEK material, if present in sufficient amounts, prevents large domains that contain the microfibrillar PBT network from connecting, resulting in poor mechanical properties. In contrast, nylons do not interfere significantly with the formation on connected domains; this is principally due the higher solubility and lower rate of phase separation of nylon in mixtures of MSA and water.

Preliminary microstructural studies show the presence of separate nylon and PBT phases. The PBT phase appears to be microfibrillar with a characteristic size that is comparable to that previously reported for single-component PBT fibers spun from poly(phosphoric) acid solutions.

Foreword

This report was prepared in the Departments of Chemical Engineering and Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, 01003, under Contract F33615-83-K-5001. The contract was administered by the AFWAL Materials Laboratory, Wright-Patterson AFB, Ohio 45433. The program monitor was Dr. Charles Lee.

This report describes work conducted from May 1983 through September 1986 and was submitted in February 1987. The authors are M. F. Malone, co-principal investigator, R. J. Farris, principal investigator, O. A. Néhmé, post-doctoral research associate, and C. A. Gabriel and C. F. Hwang, graduate students. We acknowledge the assistance of S. M. Wickliffe in the preparation of the materials in Section 2, and the assistance in fiber spinning and mechanical property measurements of S. Connelly and P. Pierce. We also thank Professor E. L. Thomas and Dr. Y. Cohen for assistance with the microstructural investigations is gratefully acknowledged.

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1. Introduction

Poly(p-phenylene benzobisthiazole) (PBT) is a high performance rodlike polymer, with excellent mechanical and thermal properties. For example, a modulus of 330 GPa and tensile strength of 3 GPa have been reported for a heat-treated PBT fiber[1] and weight retention of 50% after 200 hours at 371°C in air has been observed.[2] Unfortunately, PBT is relatively difficult to process, since it degrades before it melts, and it is soluble only in strong acids; the compressive strength and shear properties of PBT are also low in comparison to the tensile properties. Some of these difficulties may be circumvented by preparing a blend of PBT with a thermoplastic polymer where the resulting "molecular composite" would be analogous to a macroscopic fiber-reinforced composites.[3] Due to the strong intermolecular forces between rigid rod molecules, it is difficult to disperse rodlike molecules finely and uniformly in the matrix.

The processing, properties and mechanics of molecular composites of rodlike polymers, primarily poly(*p*-phenylene benzobisthiazole) (PBT) with nylons and with poly(ether ether ketone) (PEEK) are described in this report.

The report is organized into five sections. The post-processing and properties of Nylon/PBT fibers are discussed in the first section, primarily with respect to the effects of wet-stretching and heat-treatment on the tensile properties, although some data on the mechanical behavior of these fibers in shear is also discussed. In the next section, the behavior of fibers made with several matrix materials are summarized. The following section describes the processing and the thermomechanical properties of nylon/PBT composite films. Following this, an investigation of alternative processing techniques for the preparation of larger shapes is described. The final section describes the techniques and results of microstructural investigations.

---

[1] S. R. Allen, R. J. Farris, and E. L. Thomas, *J. Mater. Sci.*, *20*, 2727 (1985).

[2] T. E. Helminiak, *ACS Div. Org. Coat. Plast. Chem. Papers*, *40*, 475 (1979).

[3] T. E. Helminiak *et al.*, U.S. Pat. 4,207,407 (1980).

2. Post-Processing and Mechanical Properties of Nylon/PBT Fibers

2.1 Introduction

The preparation and mechanical properties of nylon 6,6/PBT fibers at a 30/70 (w/w) composition has been described elsewhere in some detail[4] but a brief summary of the results is presented here to motivate the subsequent sections of the report.

The tensile properties of a polymeric material improve with the addition of reinforcing fibers; increasing the aspect ratio of the reinforcing fibers at constant concentration also improves tensile properties.[5] The influence of reinforcing fibers on the matrix also depends on the strength of the interfacial bond between the fiber and the matrix. At a critical aspect ratio, the load on the composite will be shared equally between the fiber and the matrix, and the force required to pull the fiber out of the matrix will be greater than the strength of the reinforcing fiber. Below this critical aspect ratio, the fiber contributes little to the composite strength and failure occurs when the fiber is pulled from the matrix. Finally, long fibers reduce the stress concentration, and increase the probability of deflecting crack growth. A highly desirable reinforcing fiber, therefore, would seem to be a single, extended, rodlike polymer molecule. This is the basis of the "molecular composite" concept.

The theory of Halpin and Tsai[6] has been used to estimate the composite tensile modulus from the properties of the components. For large aspect ratios, the composite modulus in a highly oriented sample is predicted to follow a linear "rule of mixtures," i.e., the composite modulus is a linear combination of the rod and the matrix properties weighted by volume fraction. Such reinforcement has been reported for composites of PBT in aromatic, heterocyclic matrix polymers[7] and there has been

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[4] S.M. Wickliffe, AFWAL-TR-86-4126 (1986). Also see "Processing and Properties of Poly(*p*-phenylene benzobisthiazole)/Nylon Fibers," *J. Appl. Polym. Sci.*, to appear (1987).

[5] See S.W. Tsai, J.C. Halpin and N.J. Pagano, Editors, *Composite Materials Workshop*, Technomic Publishing Co., Connecticut (1968); G.S. Holster and C. Thomas, *Fibre Reinforced Materials*, Elsevier Publishing Co., Ltd. (1966); D.M. Bigg, *Polym. Eng. Sci., 19*(16), 1188 (1979); and J.L. Kardos and J. Raisoni, *Polym. Eng. Sci., 15*(3), 183 (1975).

[6] J.E. Ashton, J.C. Halpin and P.H. Petite, *Primer on Composite Materials: Analysis, Progress in Materials Science,* Volume III, Technomic Publishing Co., Connecticut (1969); J.C. Halpin and R.L. Thomas, "Ribbon Reinforcement of Composites," *J. Comp. Mater., 2*(4), 488 (1968).

[7] W.-F. Hwang, D.R. Wiff, C.L. Benner and T.E. Helminiak, *J. Macromol. Sci. - Phys., B22*(2), 231 (1983)

a recent effort to achieve this with thermoplastic matrix materials.[8] Of course, such reinforcement is a necessary but not sufficient test for the existence of a composite on a molecular level.

We report here on the tensile properties and processing of composite fibers made from nylons and PBT. In the next section, we describe the particular materials used for this study, the processing conditions and the techniques used for post treatment and mechanical property measurements. The following section summarizes typical tensile properties and the effects of wet-stretching and heat-treating the composite fibers after spinning. Following this, we report some of the variations of properties with the matrix molecular weight and the effects of more extensive heat-treatment. The shear properties of selected fibers are reported in the next section and we interpret the results in a final section, pointing out the evidence for a structure other than the molecular composite in the PBT/nylon materials.

2.2 Experimental

Poly(*p*-phenylene benzobisthiazole), PBT, was prepared by SRI and had an intrinsic viscosity of 25 dl/g in methane sulfonic acid solution, corresponding to a weight average molecular weight of 36,400 according to the correlation developed by Berry *et al.*[9]. The PBT was received as an anisotropic solution in polyphosphoric acid and was extracted in water, washed with methanol and thoroughly dried. Nylon 6 and 6,6 were obtained from Polysciences and DuPont. Two samples of nylon 6 with number average molecular weights of 14,500 and 20,000 and of nylon 6,6 with number average molecular weights of 13,700 and 17,500 were used. Except for drying, the nylons were used as received.

The proportions of polymer were 30 wt% PBT and 70 wt% nylon in the work reported here. The concentration of polymer in the methane sulfonic acid (98%, Aldrich Chemical Co.) solution was 3.5 wt% for nylon 6 and 3.7 wt% for nylon 6,6. These concentrations were close to but slightly less than the critical values for the isotropic-nematic transition, as determined by optical microscopy.

Fibers were spun through a die with a single 330 micron diameter hole into a water bath at approximately 20°C . All solutions were filtered during the spinning process with a 7X Dynalloy micromesh filter. A constant extrusion rate was used,

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[8] T.T. Tsai and F.E. Arnold, *Polym. Preps., ACS Div. Polym. Chem.*, *23*(1), 1 (1982).

[9] G.C. Berry, E.F. Casassa, P. Metzger and S. Venkatramen, "Physical - Chemical Properties of Complex Aromatic Heterocyclic Polymers," AFML-TR-78-164 (1979).

corresponding to a fiber velocity of 13 cm/minute. No tension was applied during take-up, but after coagulation the fibers were wet-stretched between corotating rollers at draw ratios of 1.1 to 2.0. Heat-treatment was done under dry nitrogen at 215, 255 or 295°C for residence times of 0.5, 1 and 2 minutes. Tensions in the range of 10 to 100 MPa were applied during heat-treating with the highest value corresponding to fiber breakage.

Composite fibers of nylon 6/PBT (nylon molecular weight 14,500) and nylon 6,6/PBT (nylon molecular weight 13,700) and solution-spun fibers of the corresponding pure nylons were used for extended heat-treatment studies. The composite fibers were solution-spun, wet-stretched and heat-treated under tension before being exposed to extended heat-treatment. The nylon fibers were tested without additional stretching or heat-treatment. Nylon 6 and 6,6 pellets that had not been dissolved in acid were also subjected to the extended heat-treatment. Temperatures of 170 and 220°C were used for the nylon 6,6 samples; nylon 6 was treated at 160 and 225°C . The nylon 6,6 and composite fibers were placed in an oven under vacuum for 12 hours while the nylon 6 and composite fibers were treated for 17 to 19 hours. Intrinsic viscosities in formic acid were measured after the extended heat-treatment.

Fibers of nylon 6 (20,000) / PBT that were heat-treated for one minute were soaked in sulfuric acid. The two samples had been heat-treated at tensions of 86 and 55 MPa and the sulfuric acid was 98% (Fisher Chemical Co.), a solvent for nylons but not for PBT. The composite fiber (heat treated at 86 MPa) was placed loosely in a beaker of sulfuric acid, and allowed to remain for 12 days. The fiber was then held at constant length, washed in water for 2 days and then dried in air. The fiber which had been heat-treated at 55 MPa was held under tension during extraction for 7 days, in contrast to the first sample. The fiber was then washed without tension, held at constant length and dried in air.

Fiber samples with a gauge length of 3.0 cm were tested on an Instron Universal Testing Machine at a crosshead speed of 0.1 cm/min, under ambient conditions. Samples were mounted on paper tabs with Devcon 5 Minute Epoxy and then cured overnight. Diameters were measured with an optical microscope under 200× magnification. The mechanical properties reported are the average of seven samples.

2.3 Results

The influence of wet-stretching, heat-treatment time, heat-treatment tension and temperature on the mechanical properties were investigated. The effect of matrix

Table 1: The Effect of Wet-stretching on the Tensile Properties of PBT/Nylon Fibers

	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain at break (%)
Nylon 6,6 (13,700) / PBT			
As Spun	5.3	102.3	30.8
Wet-stretched, 40% draw	7.0	156.0	21.4
Nylon 6,6 (17,500) / PBT			
As Spun	6.1	113.5	23.3
Wet-stretched, 10% draw	8.4	150.2	20.2
Nylon 6 (14,500) / PBT			
As Spun	3.2	64.5	2.6
Wet-stretched, 10% draw	5.2	127.5	37.9
Nylon 6 (20,000) / PBT			
As Spun	2.9	63.5	2.9
Wet-stretched, 100% draw	5.9	141.2	17.0

molecular weight on the tensile properties was also studied.

The solutions lacked sufficient viscosity to allow stable drawing during the spinning process, and no stretching was applied the wet-spinning process. Wet-spun fibers generally exhibit low mechanical properties compared with dry-jet wet-spun fibers or with melt-spun fibers and this would be expected in the PBT/nylon system due primarily to a lack of orientation. However, wet-stretching after coagulation provides an orienting step in these composites.

Table 1 shows substantial increases in the tensile modulus and strength as a result of wet-stretching. The nylon 6,6/PBT fibers were subjected to a low degree of wet-stretching, yet increases of 32 to 38% are seen in the moduli and 32 to 53% in the tensile strengths. The elongation at break drops by 10 to 30% as a result of wet-stretching, indicating a greater orientation in the fibers. Nylon 6/PBT fibers were subjected to a higher degree of wet-stretching (as measured by a decrease in the cross sectional area to one half the original). Increases of 63 to 123% in the moduli and tensile strengths were found. The as-spun nylon 6/PBT fibers are brittle compared to the nylon 6,6/PBT fibers, but the strength and strain at break increased dramatically by wet-stretching.

Composite fibers were also heat-treated under tension at 215, 255 and 295°C for 0.5, 1.0 and 2.0 minutes. Tension was applied at values increasing from 10 to at most 100 MPa, until the limiting value for fiber breakage was reached. The standard deviation of the data was approximately 6%.

The tensile properties as a function of heat-treatment time and tension for nylon 6,6/PBT are shown in Figure 1. The fibers containing lower molecular weight nylon (13,700) and heat-treated at 255°C show some sensitivity to the residence time as seen in Figure 1. Heat-treatment for 0.5 minute results in a 25 to 30% improvement in modulus over heat-treatment for 1 or 2 minutes. However, the longer times result in 5 to 10% higher tensile strength values. The tensile properties for the fibers containing a higher molecular weight nylon (17,500) and heat-treated at 295°C showed a diminished sensitivity to oven residence time. In fact, the moduli and tensile strengths are identical within the experimental error at the three residence times studied.

The tensile properties of nylon 6/PBT fibers are shown as a function of heat-treatment tension and temperature in Figures 2 and 3. The lower molecular weight nylon (14,500) and heat-treatment at 215°C gives a 5 to 10% higher modulus at the 2 minute residence time and a 5 to 10% higher tensile strength at the 1 minute time, indicating some sensitivity to residence time. The high molecular weight nylon (20,000) yields composite fibers that are slightly less sensitive to oven residence time. From Figure 4, the modulus is 5 to 15% higher at the 0.5 minute time, while the tensile strengths are 5 to 15% higher at the 1 and 2 minute times.

Tension applied during heat-treatment drastically improves the modulus and, less dramatically, the tensile strength. Also, the rate of increase of modulus and tensile strength diminishes with increasing heat-treatment tension and appears to reach an upper limiting value. The tensile properties are not as strong a function of residence time for the high molecular weight nylons. However, the highest tensile strengths are achieved with the higher tensions during heat-treatment that can be applied at the lower residence times.

Temperatures of 255 and 295°C were chosen for heat-treatment of fibers containing nylon 6,6; for nylon 6, 215 and 255°C were used. Typical tensile property results are shown in Figures 4 and 5. The composite mechanical properties are not a strong function of heat treatment temperature for the residence times and the oven temperatures studied, although the properties increased somewhat at the higher temperatures. This is perhaps unexpected because these temperatures are approximately 40°C higher than the melting point of the nylons.

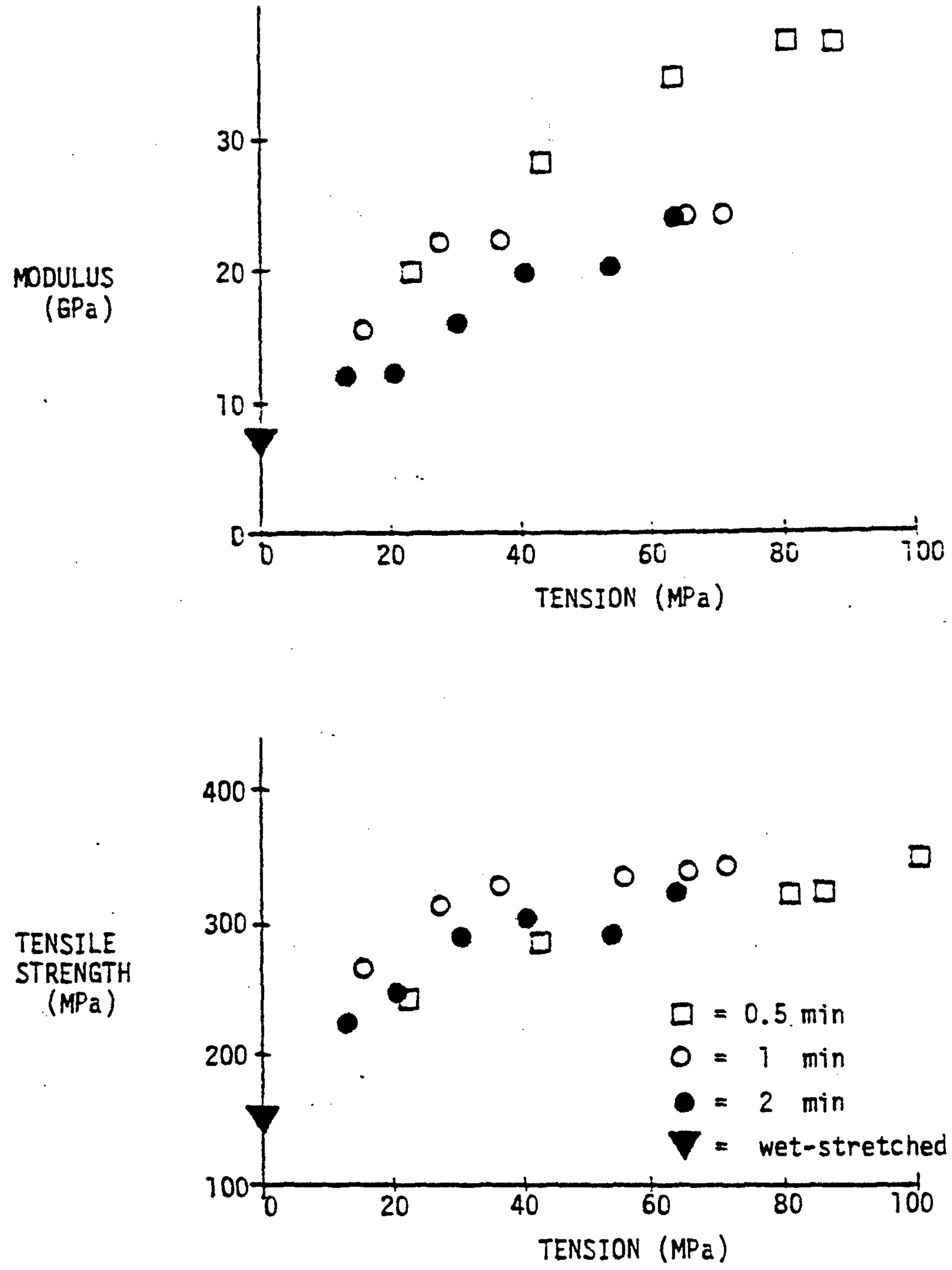

Figure 1: Tensile properties as a function of treatment time and tension for Nylon 6,6 (13,700) / PBT fibers heat-treated at 255°C .

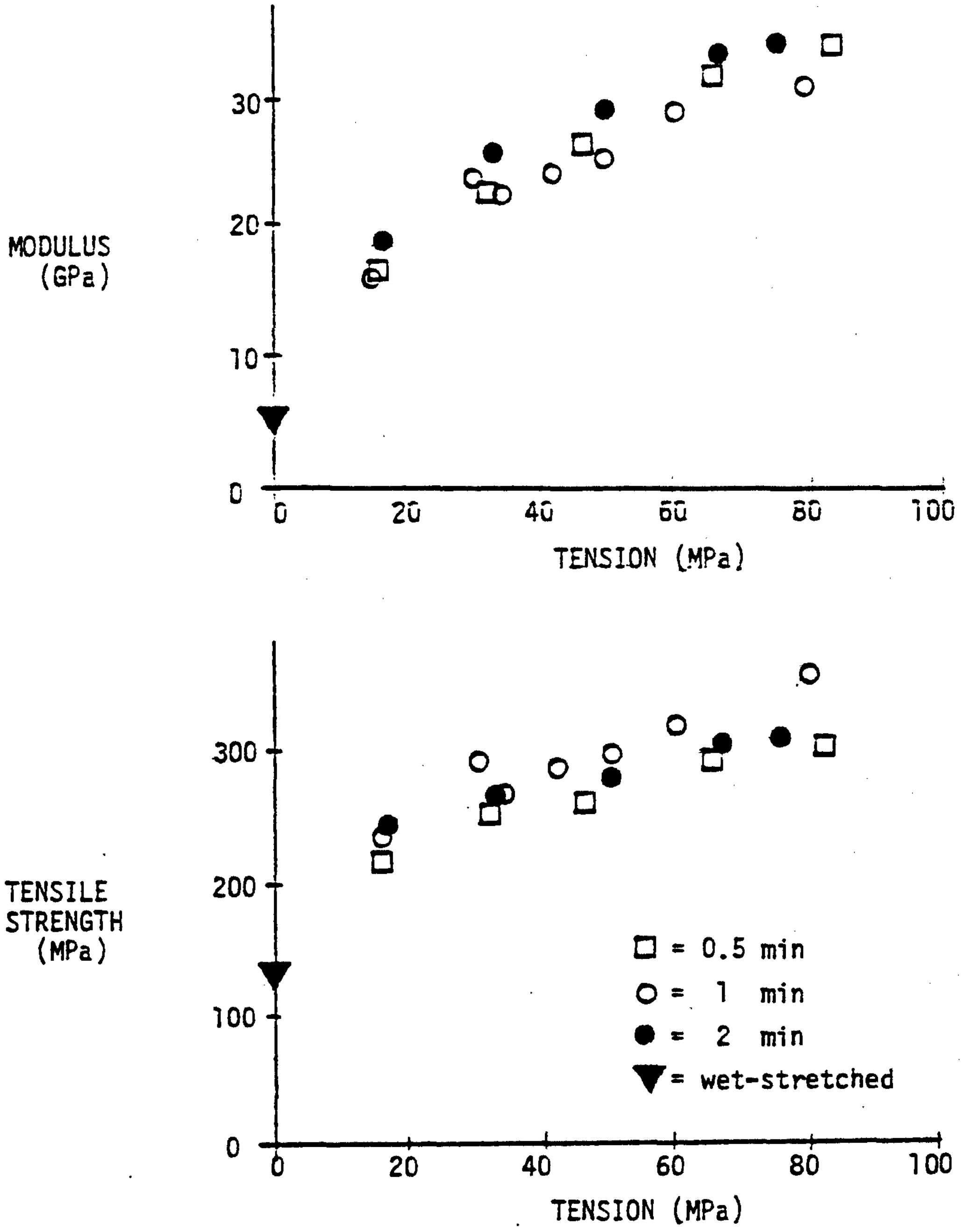

Figure 2: Tensile properties as a function of the treatment time and tension for Nylon 6 (14,500) / PBT fibers heat-treated at 215°C .

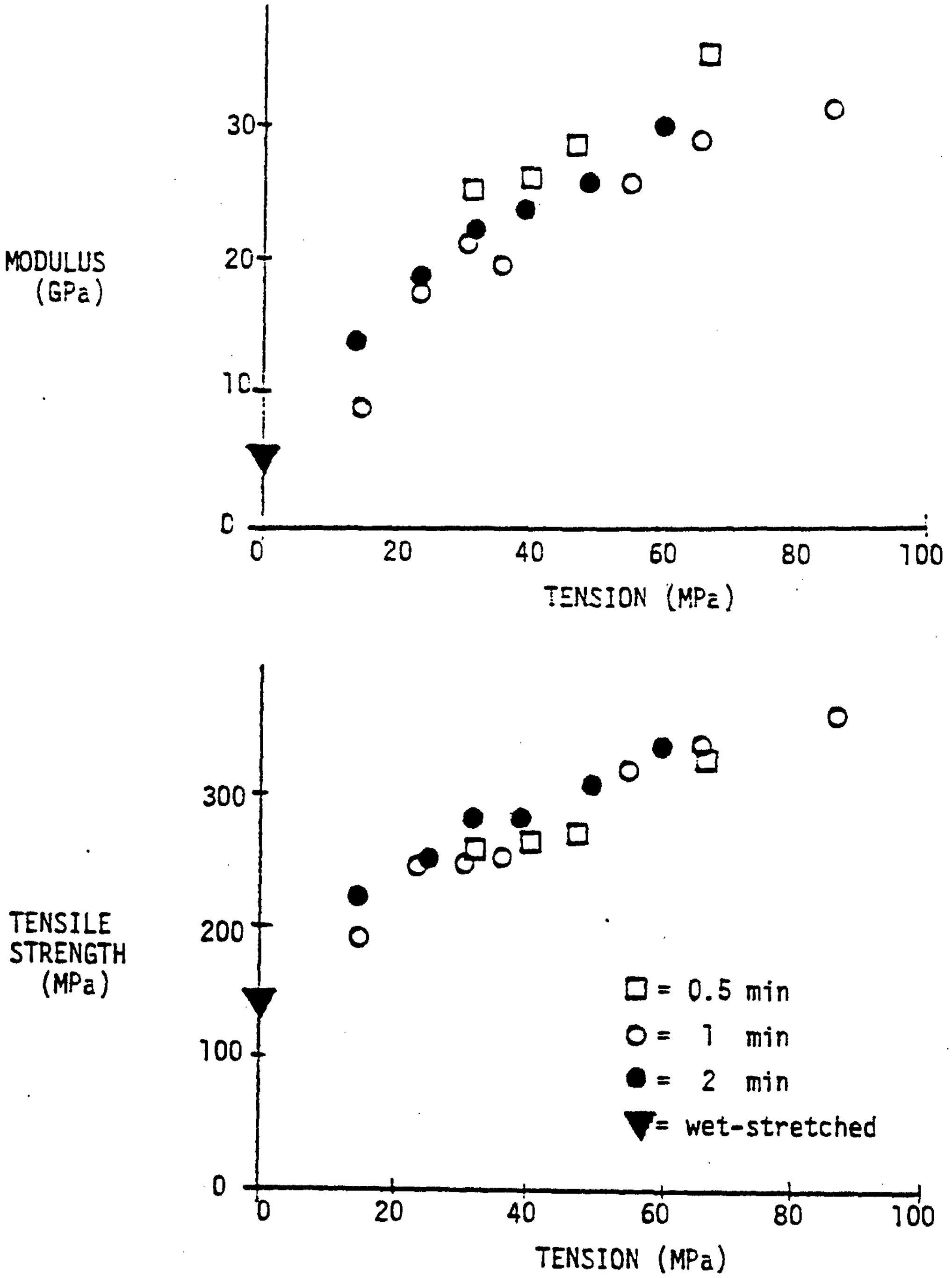

Figure 3: Tensile properties as a function of the treatment time and tension for Nylon 6 (20,000)/PBT fibers heat-treated at 255°C .

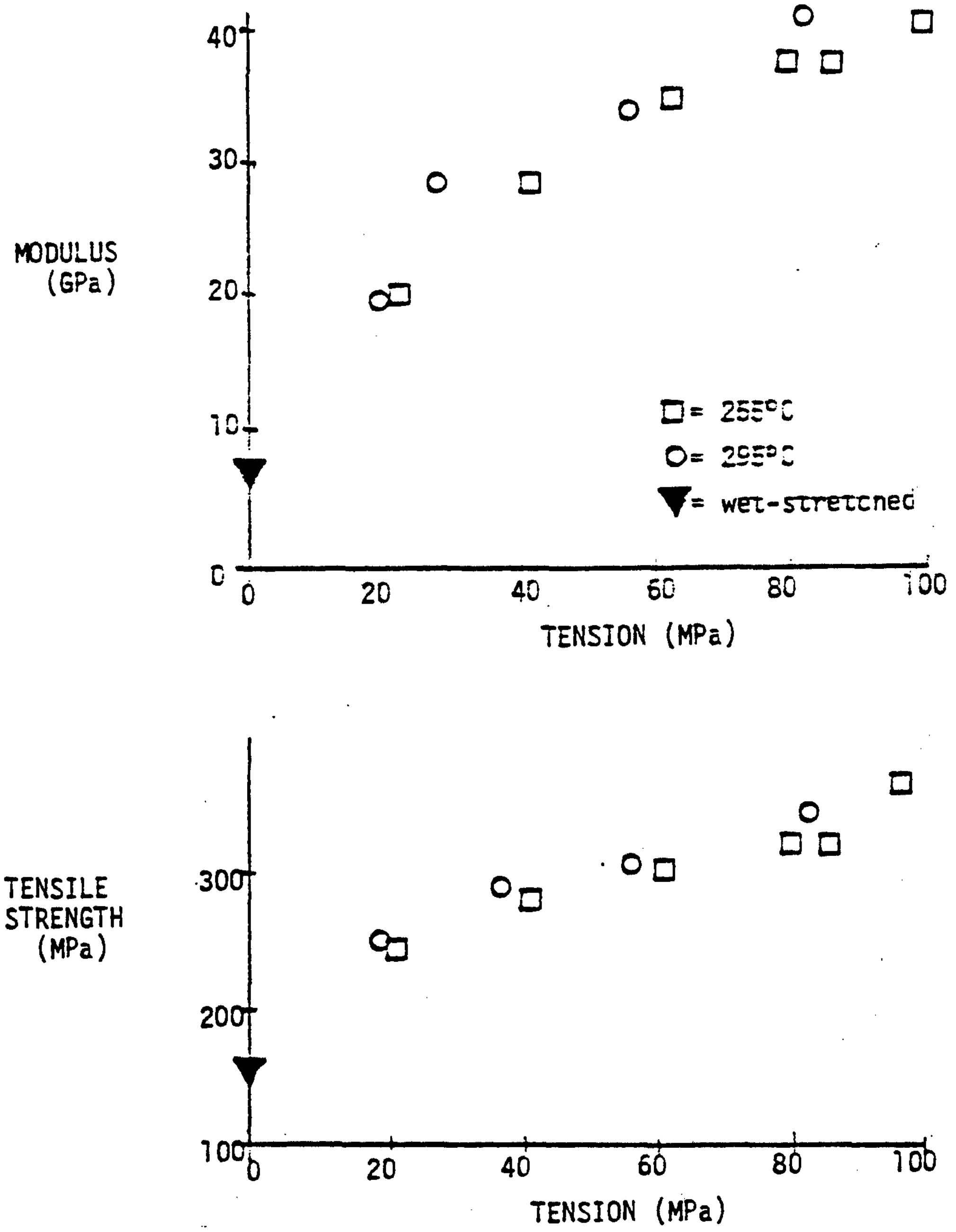

Figure 4: Tensile properties as a function of the heat-treatment temperature and tension for Nylon 6,6 (13,700) /PBT fibers heat-treated for 0.5 minute.

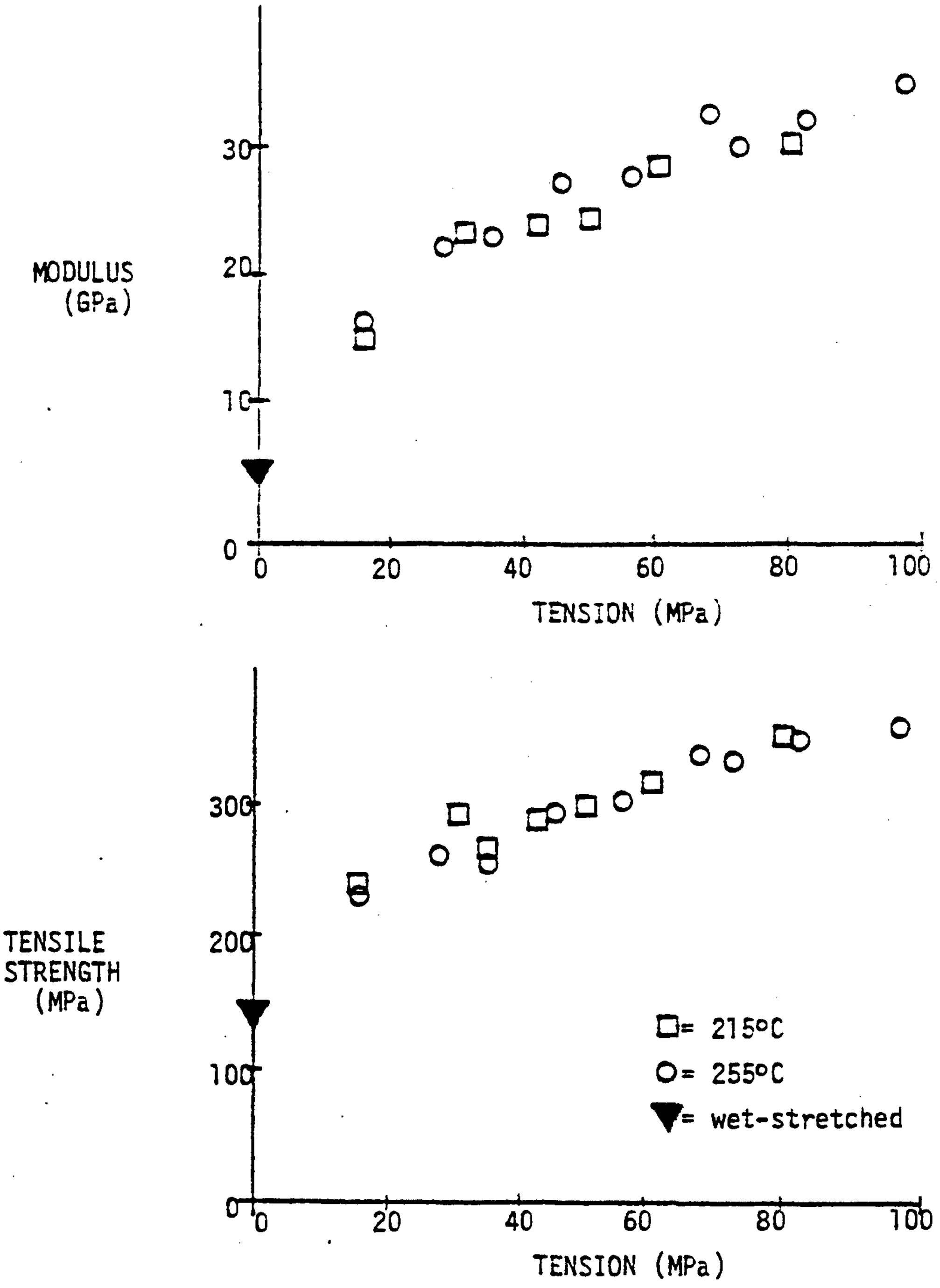

Figure 5: Tensile properties as a function of the heat-treatment temperature and tension for Nylon 6 (14,500)/PBT fibers heat-treated for 1.0 minute.

Table 2: The Effect of Extended Heat-Treatment.

	Intrinsic Viscosity at 25°C in 88% Formic Acid (dl/g) BEFORE	AFTER
Nylon 6, treated for 16 hr		
at 160°C	1.10	1.32
at 220°C	1.14	2.07
Nylon 6,6, treated for 12 hr		
at 170°C	0.99	1.11
at 220°C	0.95	1.96

The tensile strength and modulus of nylon 6/PBT and nylon 6,6/PBT fibers are shown as a function of matrix molecular weight and heat-treatment tension in Figures 6 and 7. The results are surprising because the properties of the fibers containing lower molecular weight nylon are equivalent or slightly higher than for the high molecular weight nylon at any tension. However, the lower molecular weight nylon fibers can be treated at higher tensions and thereby achieve the highest properties. The rate of increase of the modulus and tensile strength diminishes with increasing applied tension.

Extended heat-treatment results in a 23 to 49% higher modulus and a tensile strength increase of 1 to 29% without significant changes in the elongation at break. The lower temperature of 170°C results in higher tensile properties as compared to the fibers treated at 220 °C or for those not heat-treated for the extended period.

Increased crystallinity or solid state polymerization of the matrix could be important factors in the extended heat-treatment, and a sample of nylon pellets was heat-treated along with the fibers for comparison. The intrinsic viscosity of the untreated nylon pellets (measured in 88% formic acid, Fisher Chemical Co.) was compared to the value for the pellets which had undergone extended heat-treatment, with the results shown in Table 2. The nylon treated at 220°C shows an intrinsic viscosity that is nearly double that of the untreated material, while the pellets treated at 170°C show a smaller increase in viscosity. We interpret this as evidence for a solid state polymerization of the nylon. These results are also consistent with the finding that

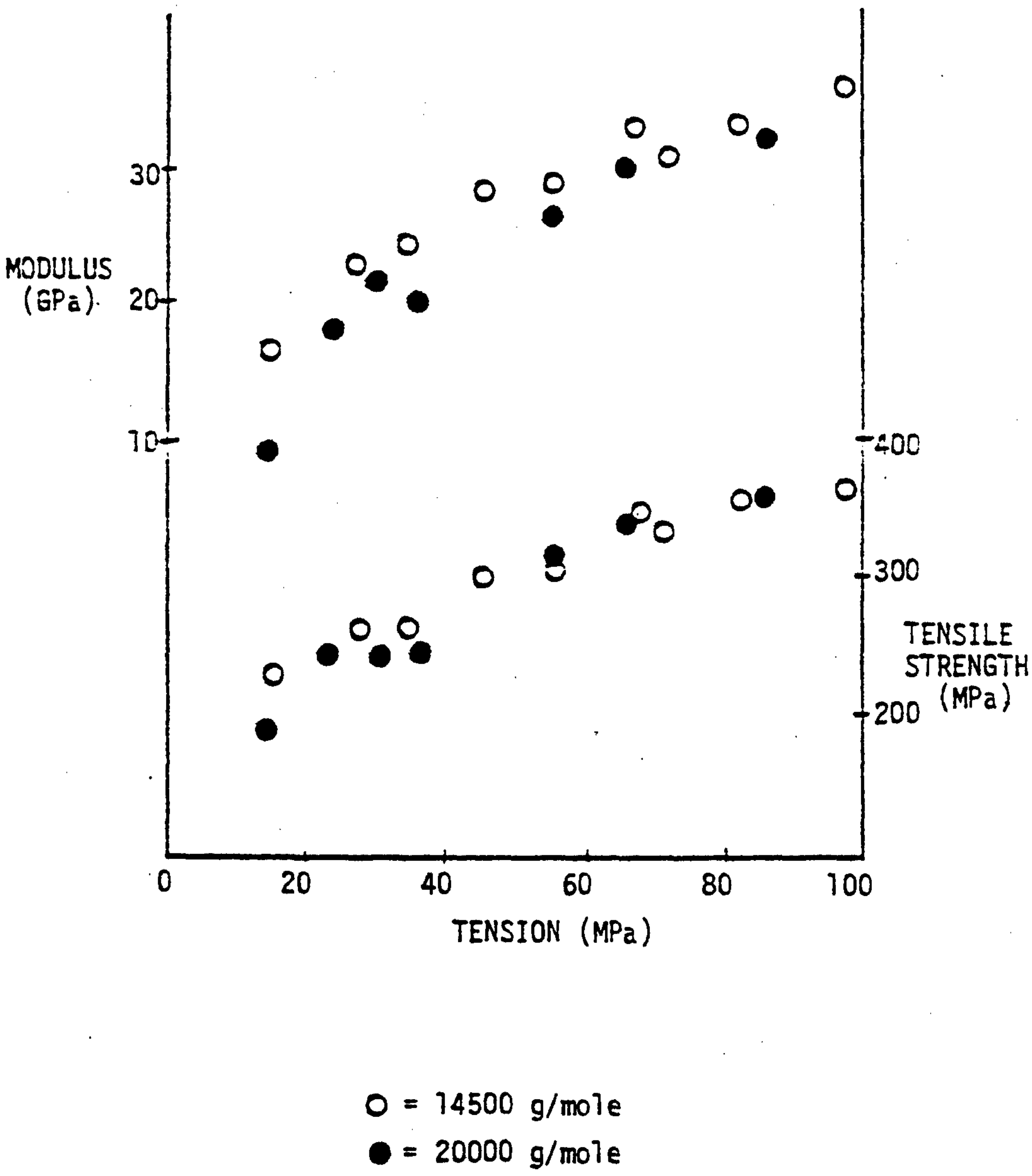

Figure 6: Tensile properties of Nylon 6/PBT fibers as a function of the nylon molecular weight and the applied tension. The fibers were heat-treated at 255°C for 2 minutes.

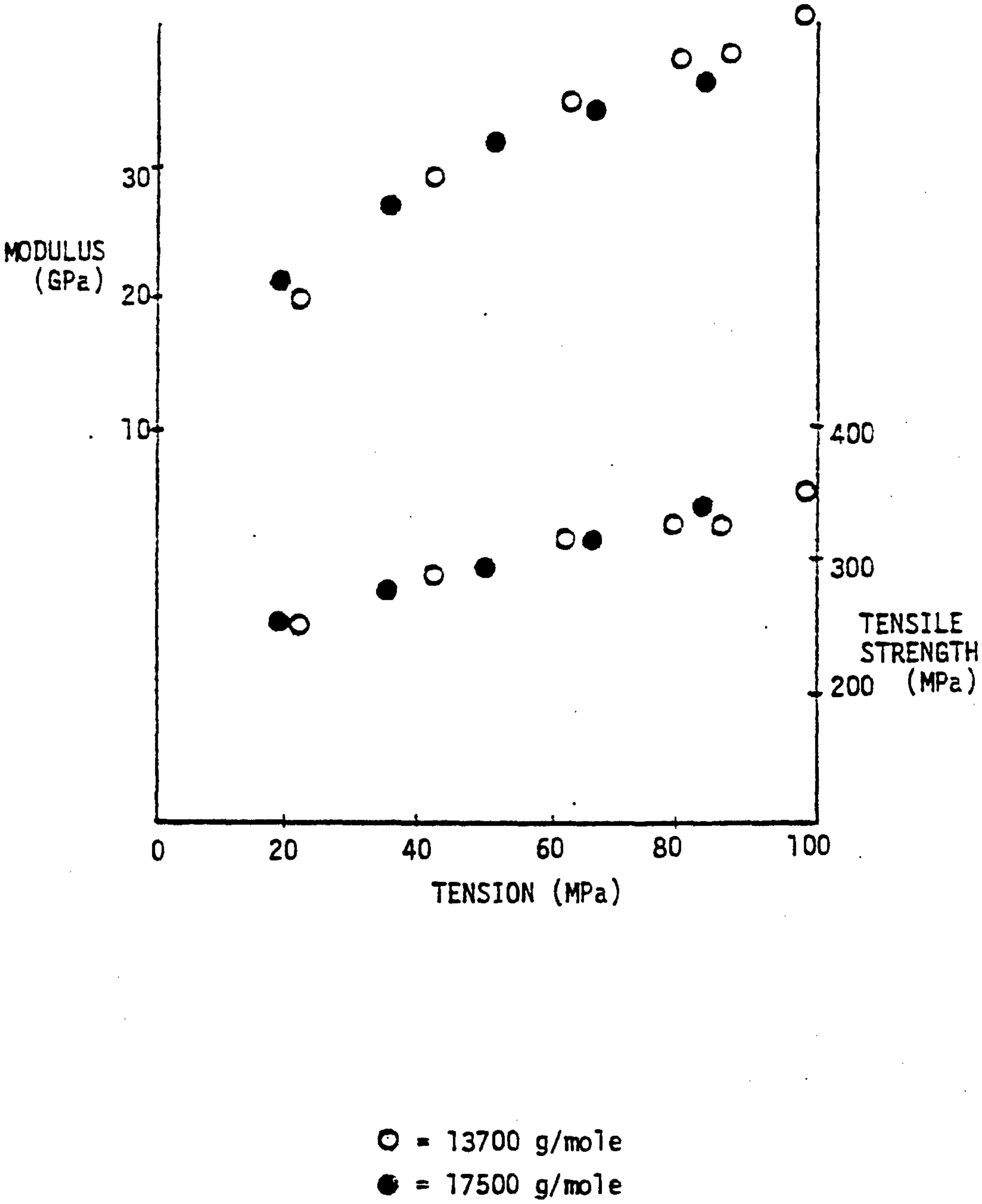

Figure 7: Tensile properties of Nylon 6,6/PBT fibers as a function of the nylon molecular weight and the applied tension. The fibers were heat-treated at 255°C for 0.5 minute.

Table 3: The Effect of Extraction with Sulfuric Acid.

	Diameter Modulus (micron)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain at break (%)
Extracted Without Tension Heat-treatment at 86 MPa				
Before Extraction	62.9	31.2	354.9	1.2
After Extraction	43.3	25.2	467.4	7.1
Extracted Under Tension Heat-treatment at 55 MPa				
Before Extraction	67.2	26.0	314.2	1.4
After Extraction	41.8	39.3	418.6	1.4

the lower molecular weight matrix polymer has the better tensile properties. Apparently, the higher temperature results in a higher matrix molecular weight, although these fibers exhibit lower moduli and tensile strengths than those treated at 170°C .

The nylon 6/PBT fibers, when soaked for extended periods in sulfuric acid, did not disintegrate as might be expected for a molecular composite of PBT in nylon. The fibers remained intact, presenting evidence for the existence of a network of PBT within the nylon matrix. A yellow color was noted in the sulfuric acid bath which can be attributed to the dissolution of nylon, as can the reduction of 30 to 40% in fiber diameter that occurred as a result of extraction of the nylon.

The extracted fibers were also tensile tested; the results are compared in Table 3. The modulus decreased for the fibers heat-treated at 86 MPa tension, while the tensile strength increased. The lower modulus may be explained by the fact that the fiber was not held in tension during the extraction and washing process, allowing the PBT to become less oriented as the nylon was removed. This is further supported by a much larger elongation at break after extraction, indicating a less oriented fiber. In contrast, the fiber treated at 55 MPa tension was held in tension during extraction, and both the modulus and the tensile strength were increased. The values reported in in Table 3 support this interpretation.

2.4 Shear and Compressive Properties

We have also examined some of the nylon/PBT fibers in shear and compression. A simple torsion pendulum apparatus was used to determine the torsional moduli, while the compressive properties were studied by beam-bending. Both of these techniques were described by DeTeresa and others[10]

Fiber samples with a gauge length of 20 mm were mounted onto cardboard tabs with Devcon 5 Minute Epoxy. Figures 8 and 9 show the effects of heat-treatment time and tension on the torsional moduli of the Nylon 6,6/PBT fibers. The torsional modulus is in the range of 700 to 1200 MPa and decreases with increasing applied tension, in contrast to the tensile modulus. The effect of oven residence time can be eliminated by treatment at high enough temperatures for sufficiently long times. A microfibrillar microstructure should be strengthened in shear by adhesion of the miscrofibrils to the matrix material. These results can be interpreted as evidence of decreased interaction and adhesion after melting and recrystallization of a separate nylon 6,6 phase. In contrast, the torsional modulus of Nylon 6/PBT fibers is essentially constant at approximately 775 MPa and is independent of the applied tension and of the molecular weight as shown in Figure 10.

Table 4 shows the results of the compression test for the nylon 6,6/PBT fibers (nylon M_n=13,700) that were heat-treated at 255°C . The strengths are approximately 0.1 to 0.17 GPa and are insensitive to the heat treatment time and tension within the accuracy of this measurement.[11] The compressive measurements for a nylon 6 matrix are quite similar to the results for nylon 6,6 and do not depend significantly on the matrix molecular weight in either case.

2.5 Discussion and Conclusions

The tensile modulus and strength of nylon/PBT fibers can be increased by more than 100% by wet-stretching; the tensile modulus of wet-stretched fibers increases by a factor of seven and the tensile strength increases by a factor of three as a result of heat-treatment under tension. The tensile properties are not a strong function of heat-treatment time in the range 0.5 to 2 minutes, although the modulus tends to be slightly higher at shorter residence times and the tensile strength higher at

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[10] S.J. DeTeresa, S.R. Allen, R.J. Farris and R.S. Porter, *J. Mater. Sci.*, *19*, 57 (1984).

[11] It is significantly more difficult to observe the formation of kink bands in the composite fibers than in the neat PBT system due to the presence of the matrix.

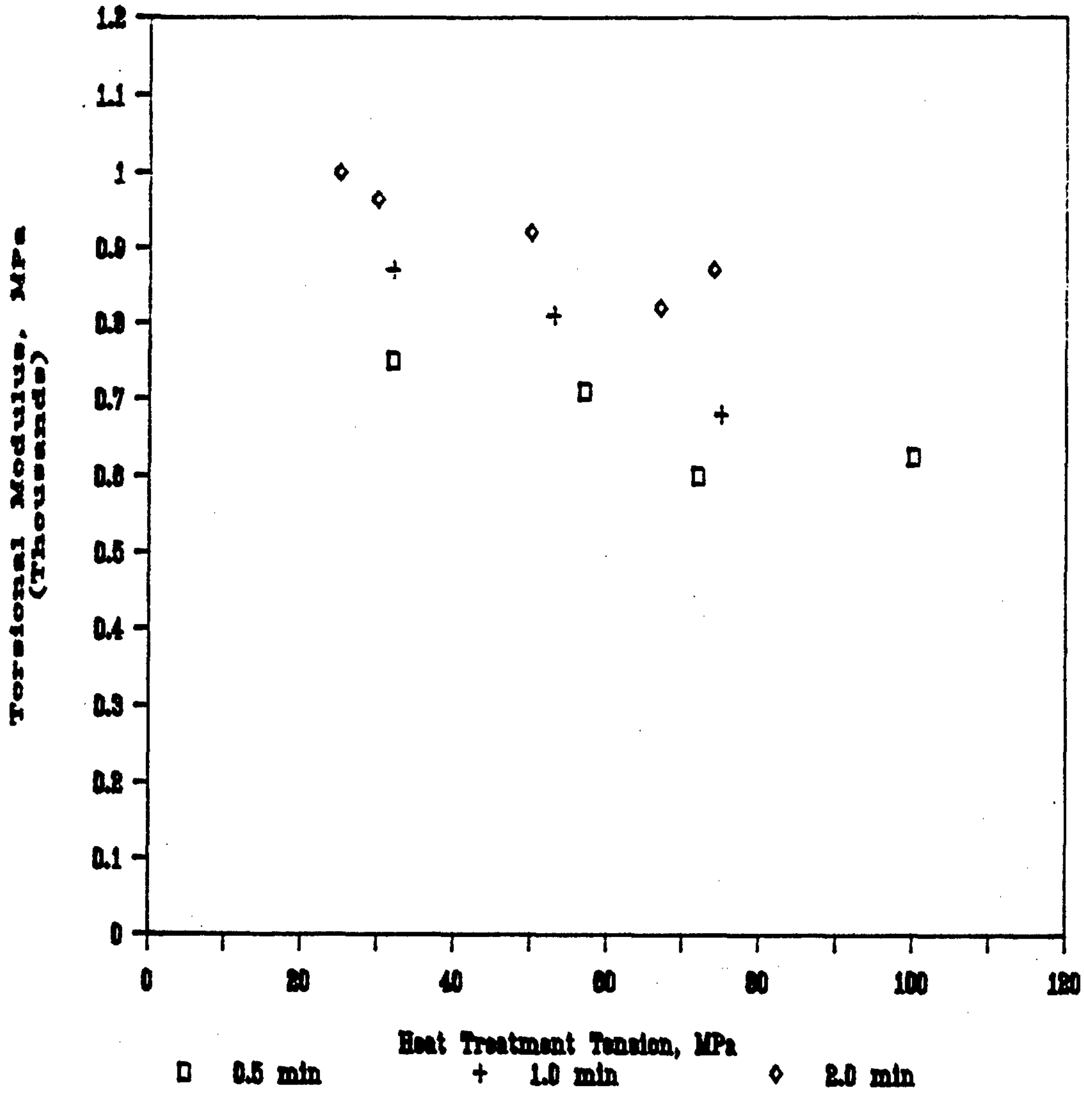

Figure 8: Torsional modulus of Nylon 6,6/PBT fibers heat-treated at 255°C .

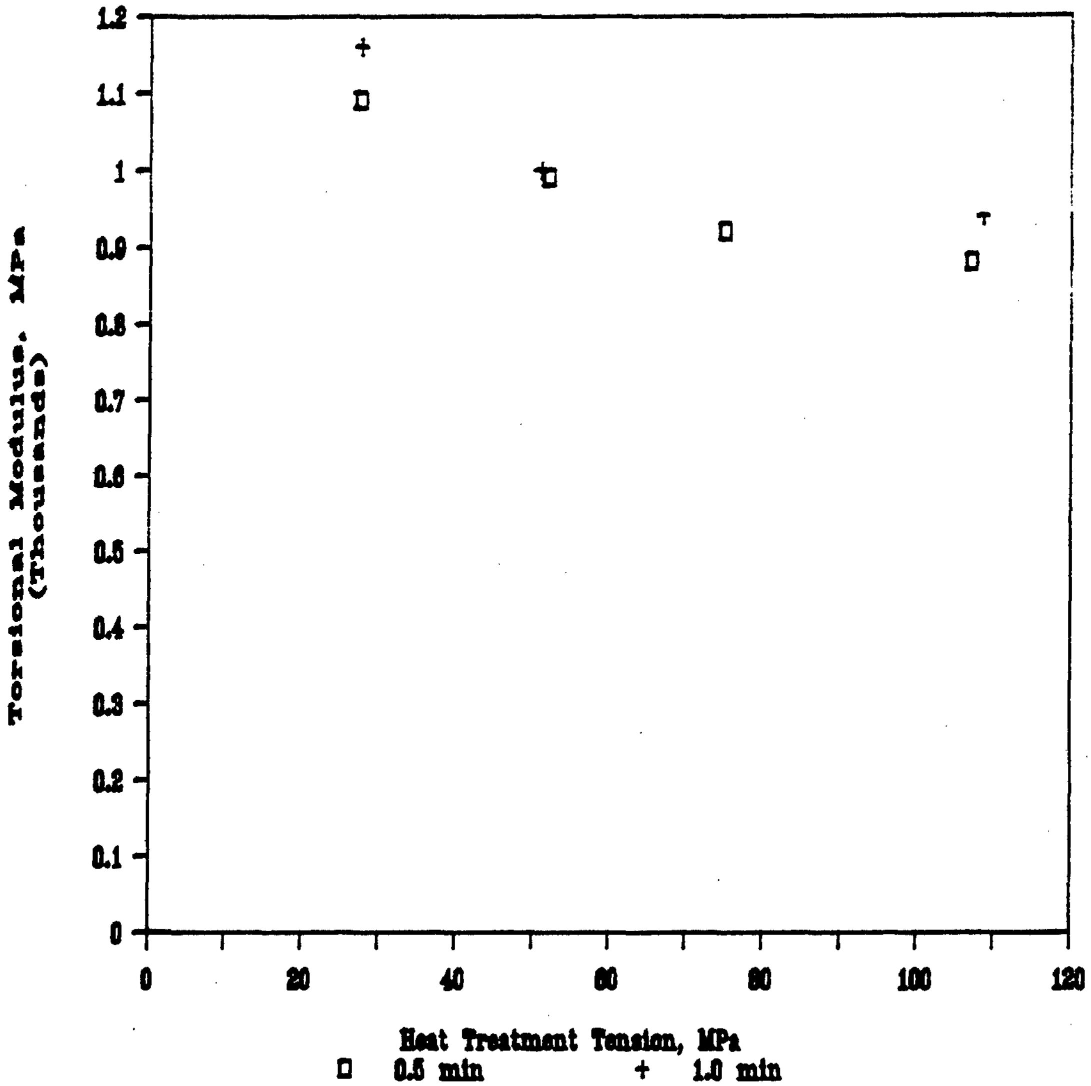

Figure 9: Torsional modulus of Nylon 6,6/PBT fibers heat-treated at 295°C .

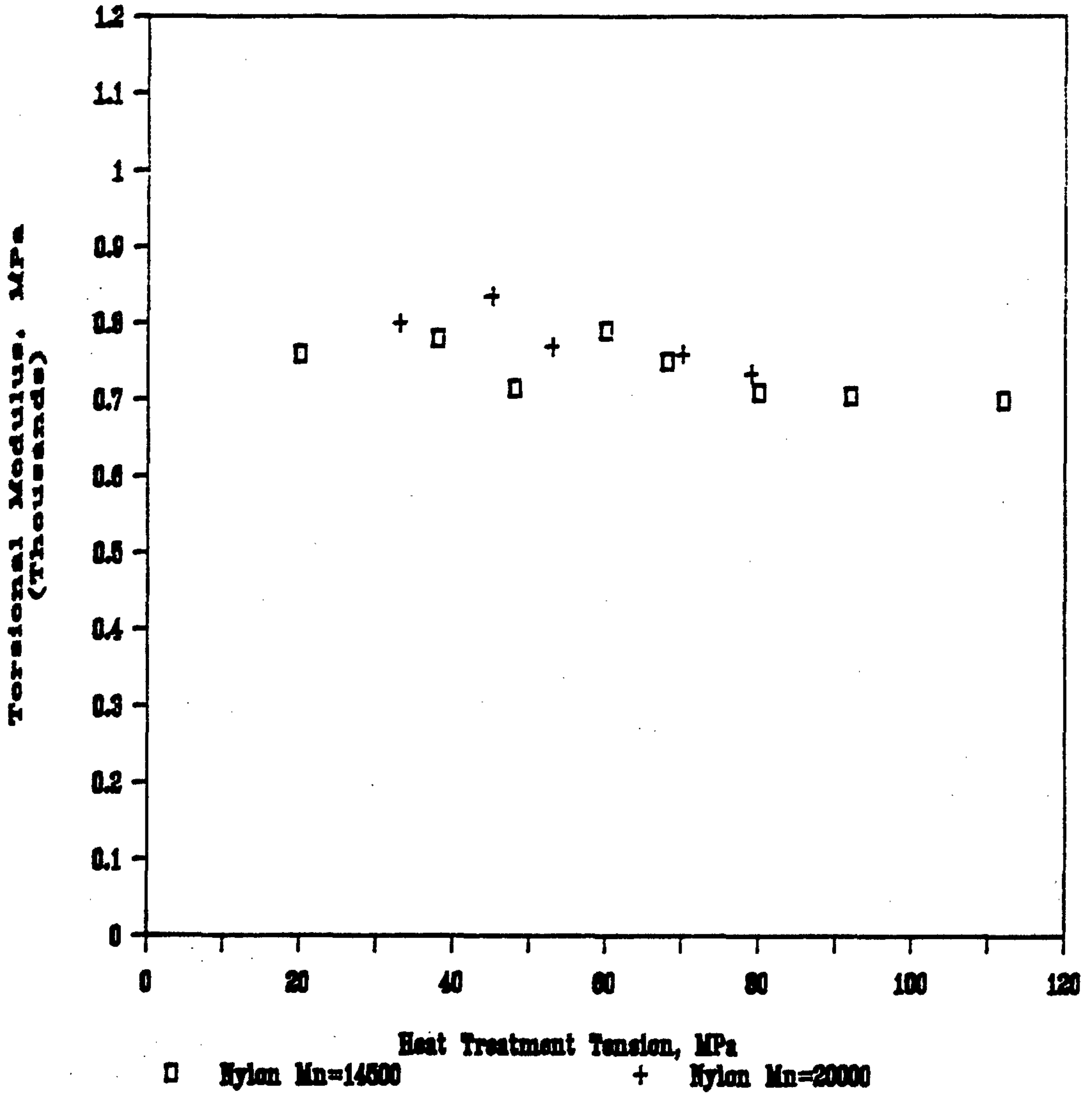

Figure 10: Torsional modulus of Nylon 6/PBT fibers heat-treated for 2 minutes at 255°C .

Table 4: Compressive Properties of Nylon 6,6/PBT Fibers Heat-Treated at 255°C .

Residence Time (min)	Treatment Tension (MPa)	Strain (%)	Strength (GPa)
0.5	46.0	0.53	0.16
	71.0	0.43	0.16
1.0	19.3	0.98	0.19
	29.8	0.77	0.17
	29.8	0.78	0.17
	52.4	0.65	0.12
	52.4	0.83	0.16
	92.1	0.56	0.14
	92.1	0.69	0.18
2.0	43.0	0.51	0.11
	68.0	0.52	0.14

longer residence times. The highest tensile strengths are achieved with high tension which is possible at the low residence times. Similarly, the mechanical properties are not a strong function of heat-treatment temperature (up to 295°C) or of the nylon molecular weight. However, a higher heat-treatment temperature increases the tensile strength and modulus as does a lower molecular weight matrix material. The initial increase in strength with applied tension is more rapid than that of the modulus, but at higher tensions, this trend is reversed, e.g., Figure 1. This trend would be expected if the strain energy corresponding to tensile failure were approximately constant. For geometrically similar samples in the linearly elastic region, this energy is proportional to the ratio of strength squared to twice the tensile modulus — for the samples heat-treated for 2 minutes shown in Figure 1, this ratio varies from 1.3 to 1.6 Pa.

Heat-treatment for an extended period also improves the tensile properties, most notably the modulus. The modulus of fibers that were heat-treated for an extended period increased by 20 to 50% and the tensile strength improved by 3 to 15%. This process also increased the melting point above the value for the matrix by 5 to 10°C. Bulk nylons subjected to extended heat-treatment show an increase in solution viscosity, probably due to solid state polymerization. Fibers that were heat-treated for the same extended periods but at a lower temperature have a smaller increase in intrinsic viscosity, yet have better properties. This is consistent with the result that the lower molecular weight nylons also yield superior tensile properties. The torsional moduli appear to be decreased somewhat for the nylon 6,6 matrix as the applied tension is increased, while the values for nylon 6 are insensitive to the tension. The compressive strengths are approximately 0.1 to 0.17 GPa and appear to be insensitive to the matrix material and to post-processing.

It appears that a structure different than the "molecular composite" of PBT in nylon was present. For example, the rule of mixtures estimate for the modulus of the composite fibers is 81 GPa[12]; only about half of this value could be obtained in this study, in spite of the orienting effect of wet-stretching, or the use of heat-treatment. In addition, when the composite fibers are soaked in sulfuric acid, a solvent for nylon, the fibers remain intact and differential scanning calorimetry indicates that the remaining fiber contains little or no nylon.

The results of this study are consistent with the hypothesis that a network of PBT can be formed during solution-spinning of fibers from PBT/nylon/MSA solutions. In fact, a microfibrillar structure in single-component PBT fibers has recently been reported.[13] In the composite materials, a lower molecular weight nylon, with a lower viscosity, may allow the network to form more completely than in the higher molecular weight matrix. Likewise, higher heat-treatment temperatures give rise to a more perfect network. In addition, the fibers remain intact at heat-treatment temperatures which are above the nylon melting point and although DSC studies show a melting transition for the material, the composites do not flow. Further support for the presence of the network is found in the tensile property data. The modulus does not follow the "rule of mixtures" and both the modulus and the tensile strength appear to reach an upper limiting value as increasing tension is applied during heat-treatment. Although it may be that the molecular composite can be attained with other matrix materials or alternative processes, it appears that a network structure of PBT in a separate nylon phase is more stable and consistent with the results of this study.

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[12] Densities of 1.56 and 1.14 g/cc for PBT and nylon 6,6 were used to estimate the volume fractions as 24 and 26 %, respectively. The tensile modulus for nylon 6,6 was estimated as 2.9 GPa and a value of 330 GPa was used for PBT. The latter was taken from S.R. Allen, R.J. Farris and E.L. Thomas, *J. Mat. Sci., 20,* 2727 (1985).

[13] Y. Cohen and E.L. Thomas, *Polym. Eng. Sci., 25,* 1093 (1985).

3. Fiber Processing and Properties

3.1 Materials and Sample Preparation

PBT was obtained from SRI[14]. The samples had intrinsic viscosities of 25 dl/g and 18 dl/g in MSA, corresponding to weight-average molecular weights of 36,000 (PBT36) and 30,000 (PBT30). PBT36 was extracted into water from a polyphosphoric acid solution; PBT30 was received in the extracted form. We have also examined poly(*p*-phenylene benzobisoxazole) (PBO) as a reinforcement. The PBO used was also synthesized at SRI and had an intrinsic viscosity of 20.4 dl/g in methane sulfonic acid (MSA), corresponding to a weight-average molecular weight of 24,000. The PBO was extracted using the same procedure as for PBT36.

Several thermoplastic matrix materials were examined. Two aromatic, heterocyclic, semi-flexible matrix polymers were obtained from SRI. The first was poly(2-5(6)benzimidazole) (ABPBI) which was received in extracted form and had an intrinsic viscosity of 16 dl/g in MSA, corresponding to number average molecular weight of approximately 100,000. The second articulated matrix polymer was poly(2-5(6)-benzothiazole) (ABPBT) which was received as a 17.9 % solution in poly(phosphoric acid) (PPA) and which had an intrinsic viscosity in MSA of 20.5 dl/g.

Several more flexible thermoplastics were also examined. Nylon 6,6 was chosen as the primary polyamide, based on the fiber properties described in the last section. We also examined a matrix polymer with superior mechanical properties, poly(ether ether ketone) (PEEK) which was obtained from Imperial Chemical Industries[15] The PEEK sample had number- and weight-average molecular weights of $M_n = 13{,}000$ and $M_w = 33{,}000$.

The solvent used was methane sulfonic acid (98% pure, Aldrich Chemical Co.).[16] All of the polymers were dried for 1 to 2 days in a vacuum oven at 70°C and 0.5 torr. The desired amounts of polymer(s) and MSA were mixed in a sample jar at room temperature under dry nitrogen using a magnetic stirrer.

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[14] The synthesis was described by J.F. Wolfe and F.E. Arnold, *Macromolecules, 14*, 909 (1981)

[15] T.E. Attwood, P.C. Dawson, J.L. Freeeman, L.R.J. Hoy, J.B. Rose, and P.A. Staniland, *Polymer, 22*, 1096 (1981).

[16] Distilled MSA and occasionally the addition of chlorosulfonic acid in small amounts have been used in previous studies of molecular composites. We have found no significant differences in the mechanical properties of fibers or films prepared using 98% MSA, provided that care was taken to prevent water adsorption during the solution preparation.

It has been reported that the optimum concentration[17] for spinning molecular composite fibers is slightly below the "critical" value,[18] for which the isotropic-nematic phase transition occurs. By processing from such a solution, it is thought that the kinetics of the coagulation into a molecular composite phase will be fast enough to dominate the rate of phase separation which is thermodynamically favored.[19] This critical concentration depends on the solution composition of rodlike and flexible components and can be described, at least qualitatively, by the theory of Flory.[20] The phase behavior of the solutions used here was investigated by placing a drop of the solution between a microscope slide and a thin coverglass and sealed to exclude moisture. The slide was examined under polarized light with a Vickers No. M70/2/334 optical microscope for the appearance of birefringence, which indicates the presence of a nematic phase.

Fibers were wet-spun into a water bath at approximately 21°C . Due to the low viscosity, very little draw was applied during the spinning. A 330 micron diameter die and a Teflon barrel and ram were used to extrude fiber at a velocity of 100 cm/min. The fibers were allowed to coagulate in water overnight. Three post-processing steps were employed to improve properties. Wet-stretching was done by winding the fiber under water from one roller onto another. Hot-drawing was done by passing an air-dried fiber over a Thermolyne Type 1900 hot plate set at 230°C , while the fiber was drawn between two rollers. These post-processing steps are both characterized by a draw ratio, DR, defined as the ratio of the squared fiber diameter before and after drawing. Finally, heat-treatment was done by passing an air-dried fiber through an oven containing a dry nitrogen atmosphere; the apparatus is described elsewhere.[21]

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 testing of other dried fibers was done on an Instron Universal Testing Machine using

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[17] We use "concentration" to refer to the weight fraction of total polymer in solution, while "composition" denotes the ratio (w/w) of rodlike polymer to matrix material.

[18] W.F. Hwang, D. Wiff, T.E. Helminiak, G. Price, and W.W Adams, *Polymer Eng. Sci.*, *23*, 784 (1983).

[19] W.W. Adams, *et al.*, AFWAL-TR-85-4108 demonstrated that the morphology of PBT/ABPBI films prepared slightly above the critical concentration was substantially different from that in a material prepared from an isotropic solution near the phase boundary. Use of the phase-separated solution resulted in a film with markedly inferior mechanical properties.

[20] P.J. Flory, *Macromolecules*, *11*, 1130 (1978).

[21] S.R. Allen, PhD. Thesis, Polymer Science and Engineering, University of Massachusetts (1983).

Table 5: The Tensile Properties of 70/30 PBT/ABPBI Composite Fibers Spun from MSA Solutions.

	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain at Break (%)	Draw Ratio
PBT IV=31 dl/g				
As-Spun, 3%	5.9	400	12.7	1
Work-Hardened	28.9	570	11.7	2
PBT IV=25 dl/g				
As-Spun, 2.5%	18.5	425	3.9	4
Heat-Treated, 510°C	23.8	496	2.4	4
Heat-Treated, 550°C	23.7	470	2.1	4
PBT IV=25 dl/g				
As-Spun, 3.2%	5.6	170	58.0	1
	35.4	720	5.3	4

a crosshead speed of 0.1 cm/min. The wet fibers were tested while under water on a Toyo Testing Machine.

After tensile-testing, some of the fibers were sputtered with gold using a Polaron E5100 coating unit, and examined with an ETEC Autoscan SEM. For thermal analysis, a Perkin Elmer Differential Scanning Calorimeter was employed. Also, a Perkin Elmer Thermal Mechanical Analyzer was used.

3.2 Articulated Matricies

Several isotropic solutions (2.5, 3.0, and 3.2 wt%) were made from PBT36 and ABPBI in MSA at a fixed composition of 70/30 (ABPBI/PBT). These solutions were spun using a 130 micron die and a one inch air gap. These initial spinning studies produced fibers of comparable stiffness and strength to those reported in the literature, as shown in Table 3.2. The MSA solutions lack the integrity to allow drawing during the spinning process and the orientation of the rod like component must be induced by post-processing techniques such as wet-stretching and heat-treatment under tension. To have a viscous molecular composite solution, poly(phosphoric acid)

(PPA) was considered as a solvent. Two anisotropic dopes, one of PBT36 and one of ABPBT in PPA were diluted with PPA and mixed together at 90°C ; due to the high viscosity, the solutions required long mixing times (2-3 months). The high viscosity of the solution caused air to be trapped and an apparatus for degassing under vacuum was built to address this problem. [22]

3.3 Thermoplastic Matricies

Thermoplastic matrix molecular composites could potentially be melt processed. This would provide obvious advantages over PBT which is, of course, limited to solution processing. Several candidates were considered for matricies. The only requirement being that the thermoplastic be soluble in methane sulfonic acid. We chose to focus on PEEK and nylons, since these materials were readily available and soluble in MSA.

3.3.1 PEEK/PBT Fibers

The phase behavior of the solutions was examined to determine the location of the isotropic-nematic phase boundary. Before spinning, the solutions were examined under crossed polars. Birefringent solutions were diluted with MSA and mixed for 3-4 days. This process was repeated until the birefringence disappeared, resulting in an isotropic solution. The approximate position of the phase boundary was thus located as shown in Figure 11.

Flory[23] derived a statistical thermodynamic theory for the phase behavior in ternary solutions of a random coil polymer, a rigid rod polymer and a solvent; the sole parameters are the aspect ratios of the polymeric components. The solid line in Figure 11 represents the prediction of this theory. The aspect ratio for PBT30 was estimated to be 300.[24] The aspect ratio of the random coil component was used as a fitting parameter; a value of 30 was found to fit the data shown in Figure 11. This value is significantly lower than the estimate of 120, based on the contour length the PEEK chain (828 Å) and is somewhat closer to the value of 7.8 estimated from

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[22] In an attempt to avoid the long mixing times, yet produce solutions with enough integrity to be drawn on line, mixtures of MSA/PPA were investigated as possible solvents. This approach seemed quite promising, but was not continued due to the lack of materials.

[23] P.J. Flory, *Macromolecules, 11,* 1130 (1978).

[24] W.F. Hwang, D. Wiff, T.E. Helminiak, G. Price, and W.W Adams, *Polymer Eng. Sci., 23,* 784 (1983).

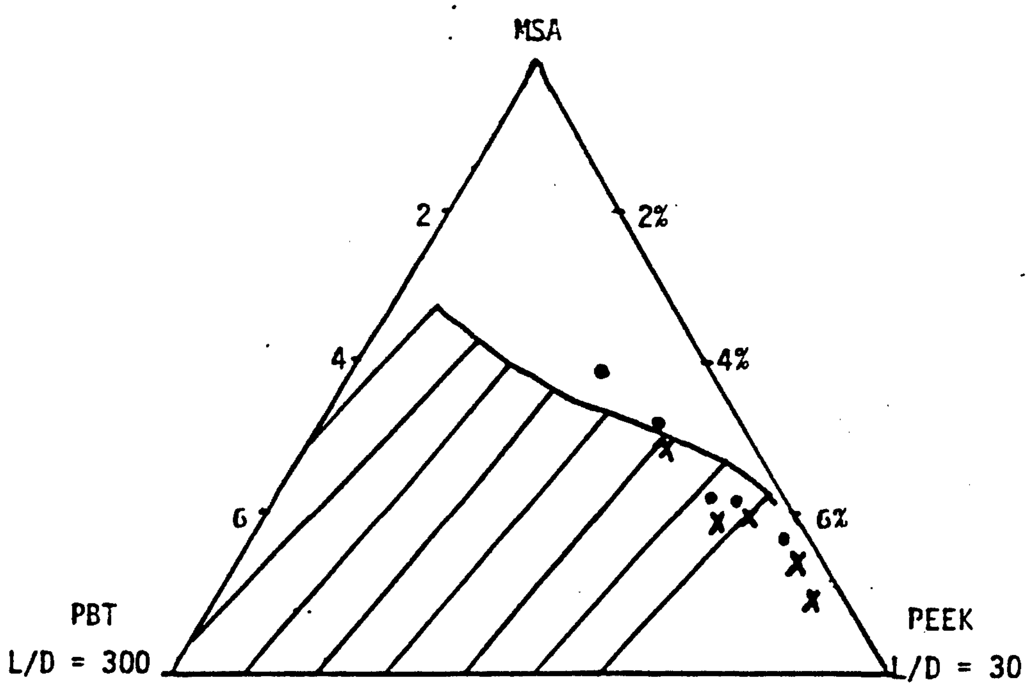

Figure 11: The phase diagram for PEEK, PBT36, MSA solutions. The solid line is the theory of Flory; the points are the observed isotropic (•) and anisotropic (×) concentrations.

the persistence length of the PEEK (54 Å in H_2SO_4.[25] It is also reported here that PEEK is completely soluble in MSA at 25°C .). This is thought to be a result of stiff behavior of PEEK in solution. Such solution behavior was previously noted for ABPBI/PBT/MSA and PPQ/PBT/MSA.[26] Both ABPBI and PPQ are some what stiff in solution. Although the thermodynamic theory for mixtures of rigid and semi-flexible chains in a solvent is not available, Flory's prediction for the system of two rigid rods in a solvent[27] indicates the rigid rod polymer is more tolerant of a rigid second component than a flexible one. It is not suprising, therefore, that the predictions for a rigid rod/flexible coil/solvent underestimates the critical concentration for the PBT/PEEK/MSA system.

Composite fibers with proportions of PEEK/PBT36 ranging from 95/5 to 70/30 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 tensile tested. Figure 12a shows the behavior of the tensile modulus. The values are unexpectedly low since the modulus reported for melt-processed PEEK is approximately 3 GPa.[28] 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 extracted from MSA had intrinsic viscosities of 0.90 and 0.66 dl/g, in H_2SO_4 indicating some degradation. However, this does not explain the decrease in modulus with increasing PBT content. Although hot-drawing enhances the modulus, a decrease in modulus with increasing rod content is still evident and the maxium modulus is less than 1 GPa. Figure 12b shows the tensile strength of these fibers, which are low in comparison to 100 MPa reported for melt-processed PEEK and which also decrease with increasing PBT content.

Tensile tested specimens were examined with the scanning electron microscope. All of these PEEK/PBT36 fibers spun from solutions slightly below C_{cr} were observed to have voids on the fiber surface, which are evident on the 70/30 PEEK/PBT shown in Figure 13. Hot-drawing resulted in a more fibrillar appearance, but surface voids were still evident. However, surface voids were not observed on the solution-spun PEEK fiber shown in Figure 14. The hot drawn PEEK fiber appears very fibrillar.

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[25] M.T. Bishop, F.E. Karasz, and P.S. Russo, *Macromolecules, 18* ,86 (1985).

[26] W.F. Hwang, D.R. Wiff and C. Vershore, *Polym. Eng. Sci., 23,* 789 (1982). PPQ is poly (2,2'-(1-4-phenylene)-6,6'-bis(3-phenylquinoxaline)).

[27] A. Abe and P.J. Flory, *Macromolecules, 11,* 1122 (1978).

[28] D.P. Jones, D.C. Leach and D.R. Moore, *Polymer, 26,* 1385 (1985).

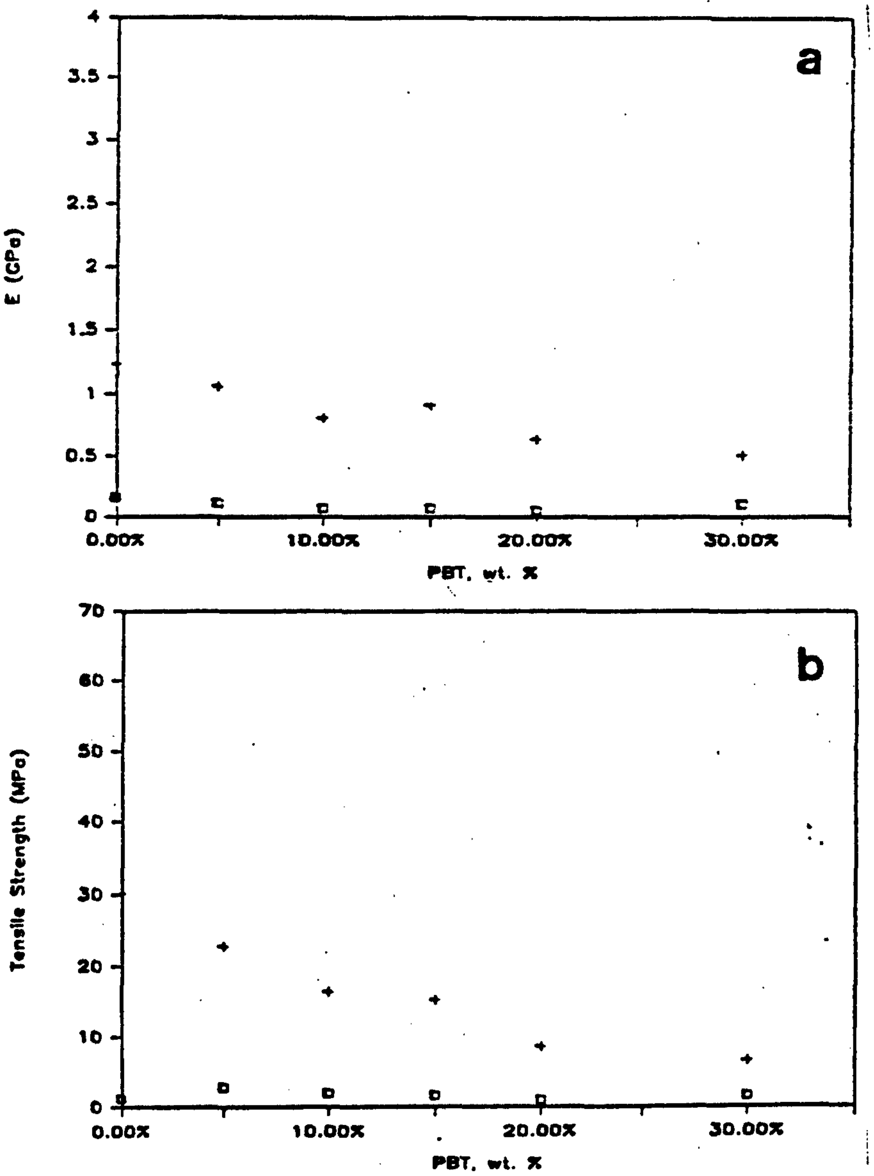

Figure 12: Tensile properties for PEEK / PBT fibers, as-spun (□) and hot-drawn (+), spun close to the critical concentration, (a) modulus, (b) strength.

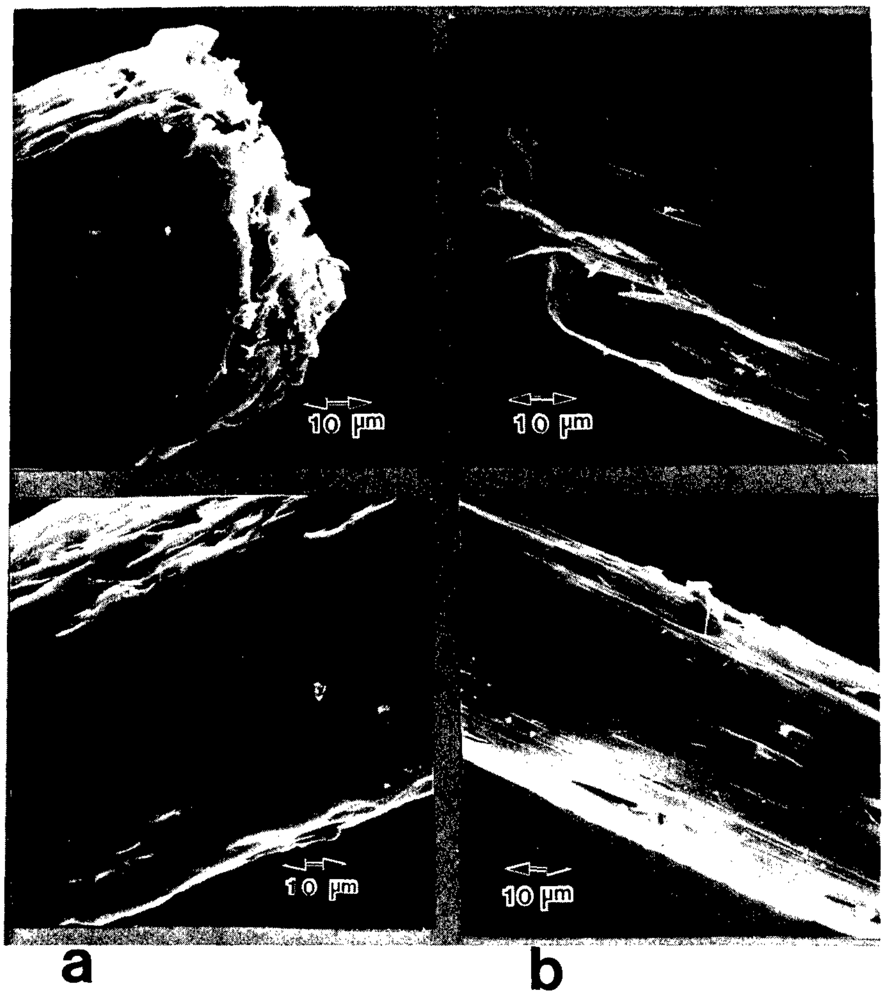

Figure 13: Scanning electron micrographs of (a) as-spun and (b) hot-drawn 70/30 PEEK / PBT fiber spun close to the critical concentration.

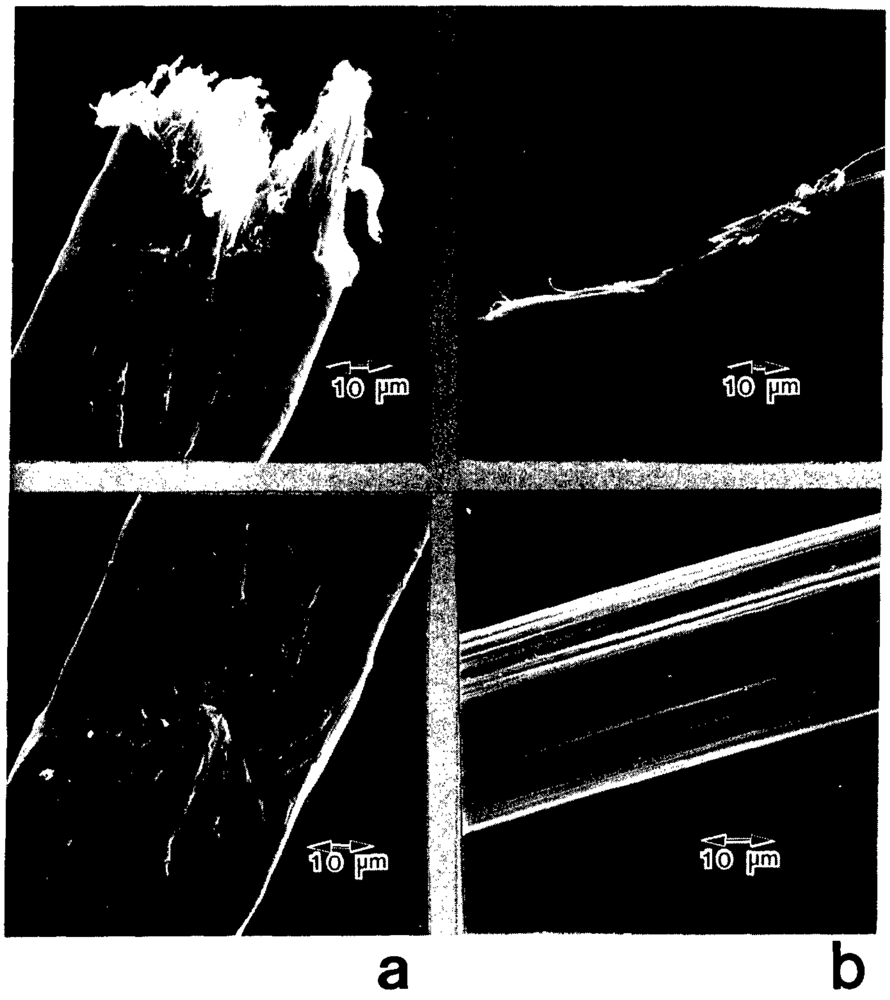

Figure 14: Scanning electron micrographs of an (a) as-spun and (b) hot-drawn PEEK fiber spun from a 4% solution in MSA.

We recall that these fibers were processed close to the critical concentration with the expectation that the rate of coagulation would be fast enough to "freeze" in the isotropic molecular distribution of the rods present in solution, thus resulting in the formation of the non-equilbruim structure defined as a "molecular composite". In light of the mechanical properties and microscopy, it apppears that the thermodynamically favored phase-separated product has resulted. This suggests that the phase separation has occured on a time scale comparable to the coagulation. One way to increase the time required for a phase-separated structure to form would be to decrease the total amount of polymer in the processing solution, which is discussed in the next section.

Fibers with a 75/25 PEEK/PBT30 composition were spun from solutions at various concentrations in MSA. Figure 15 shows that the tensile modulus and strength are strong functions of the solution concentration. A maxium in the mechanical properties is seen for a concentration near 2.0 wt %. Scanning electron micrographs of these tensile tested fibers are shown in Figure 16. The dramatic increase in fiber diameter (Table 1) above 3.0% for PEEK/PBT30 fibers coincides with the decline in strength and stiffness, e.g. Figure 15, and is due to the presence of voids, which are evident on the surface of the fiber spun from a 4.0% solution.

These fibers were also soaked in H_2SO_4 for several weeks, to remove the PEEK; the residual fibers were analyzed using a Perkin Elmer Thermogravimetric Analyzer, and no degradation of residual PEEK could be detected and we conclude that the PEEK was effectively removed. The residual PBT was observed with an optical microscope; a typical result is shown in Figure 17. Only the fiber spun from the 4.0% solution, slightly below the critical concentration, did not remain intact upon exposure to sulfuric acid because the PBT is distributed in a discontinuous structure. The fiber spun from the 3.0% solution has a continuous phase of PBT reinforcing it that appears to be an open, network-like structure. The fiber spun from a 2.0% solution has a denser structure, almost rope-like in appearance. The structure fiber spun from a 1.0% solution is continuous only for short lengths. It is evident that for a 75/25 PEEK/PBT material, the optimium processing concentration is approximately 2%. This PEEK/PBT fiber has good as-spun stiffness and strength, and is apparently reinforced by a continuous structure of PBT.

Fibers of different PEEK/PBT30 compostions were wet-spun from a 2.0% solution in MSA. Figure 18 shows the tensile modulus, strength and strain at break. There is nearly an order of magnitude increase in modulus over that obtained for fibers processed close to the critical concentration; furthermore, the modulus and the

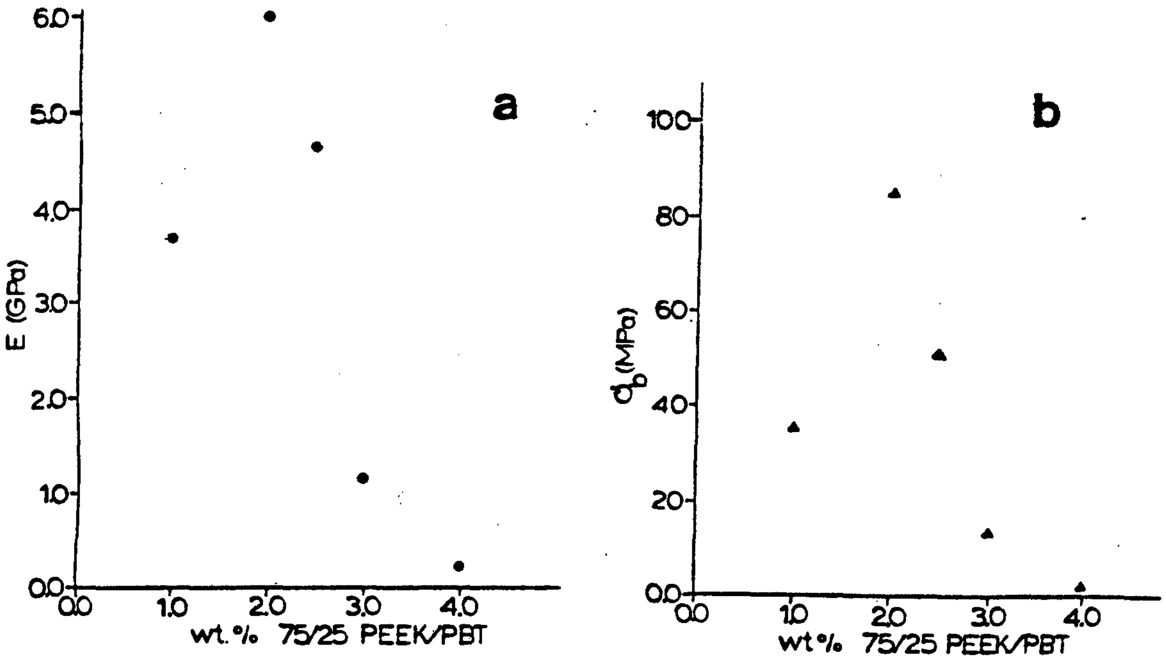

Figure 15: Tensile properties for as-spun 75/25 PEEK / PBT30 fiber vs. the total polymer concentration in the spinning solution, (a) modulus, (b) strength.

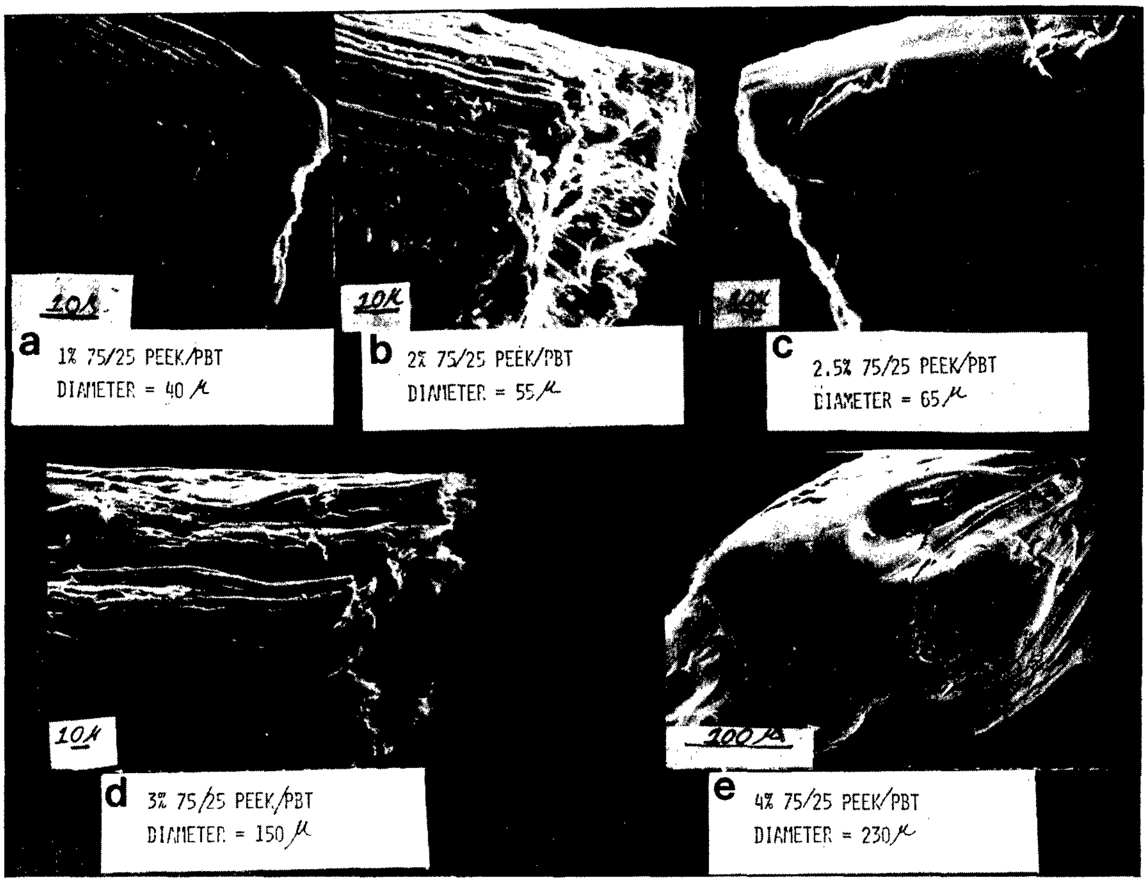

Figure 16: Scanning electron micrographs of as-spun 75/25 PEE / PBT30 fibers spun from (a) 1.0% solution, (b) 2.0% solution, (c) 2.5% solution, (d) 3.0% solution, (e) 4.0% solution.

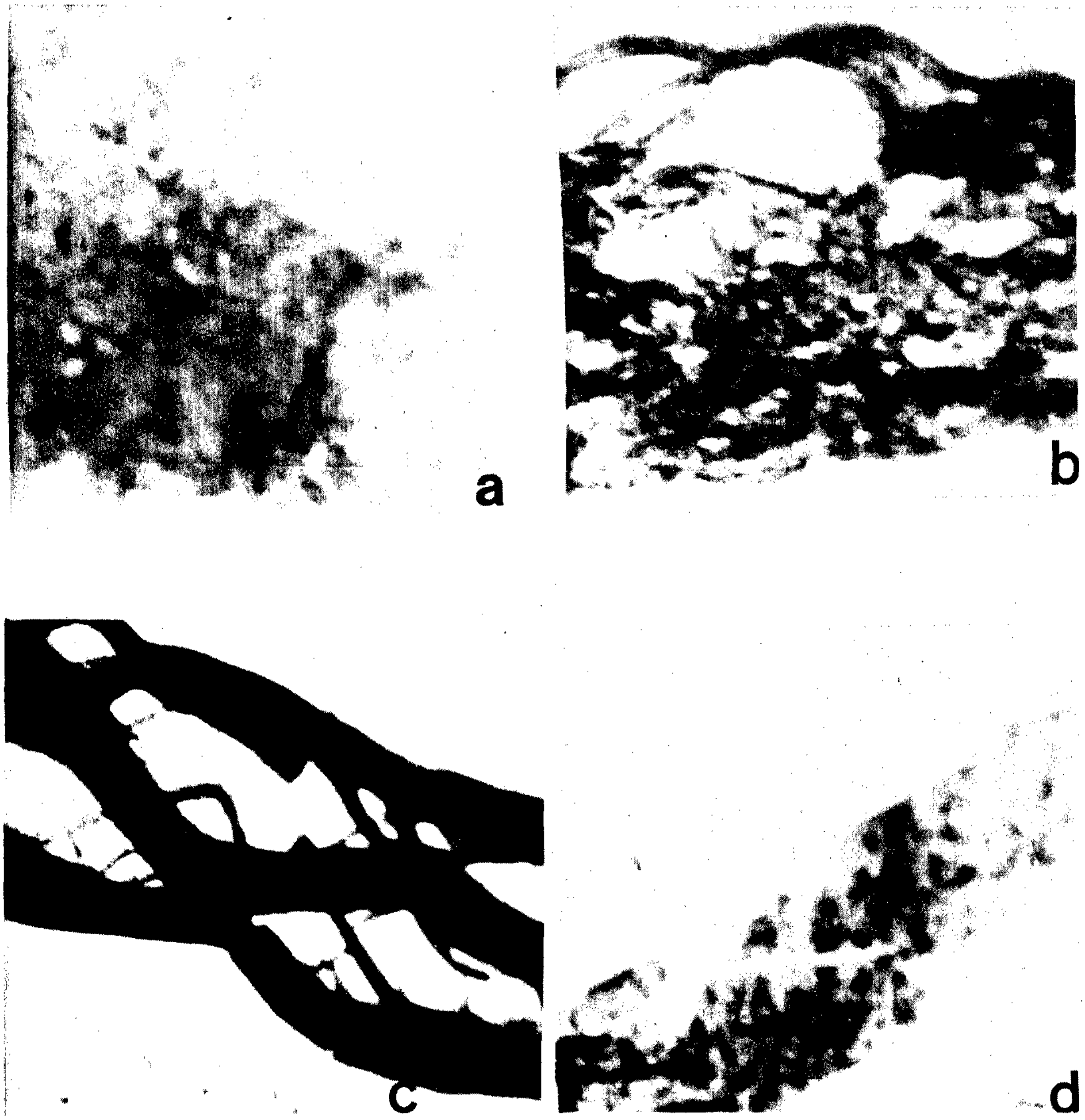

Figure 17: Optical micrographs of an as-spun, 75/25 PEEK / PBT fiber soaked in H_2SO_4 for several weeks (a) spun from a 4.0% solution, (b) spun from a 3.0% solution, (c) spun from a 2.0% solution, (d) spun from a 1.0% solution.

strength increase with PBT content and with heat-treatment. We also note the sharp increase in the as-spun fiber modulus and strength between 20 and 25% PBT. This may indicate a percolation threshold above which a continuous PBT phase is present throughout the fiber. Heat-treatment at 425°C with no tension increases the modulus and strength significantly. Figure 18c shows the strain at break for these fibers. An interesting result is that the strain for the as-spun, fibers with less than 25% PBT is lower than the strain for the corresponding heat-treated fiber. We can interpret this as evidence for the presence of disconnected or loosely connected PBT domains in the as-spun fibers that are perfected into a sample-spanning network by heat-treatment. The tensile properties can be expected to increase further with wet- stretching and heat-treating of the fibers under tension.

A marked dependence of mechanical properties of PEEK/PBT fibers on solution concentration has been demonstrated for a compostion of 25% PBT. The effect of solution concentration on mechanical properties for higher PBT composition fibers was also investigated. Figure 19 shows the tensile strength and modulus for PEEK/PBT fibers containing 25, 50, and 75% PBT spun from various solution concentrations. In contrast to the behavior of the 25% PBT fiber, the stiffness and strength of the 50 and 75% fibers are relatively insensitive to the solution concentration. Apparently, PBT forms a continuous phase for higher compositions regardless of the solution concentration. In fact, for the 75% PBT fiber, spun from a 3.0% solution (which is above the critical concentration) the stiffness and strength are approximately half those of a fiber spun from an isotropic solution.

The rapid increase of the tensile properties with the amount of PBT suggests an interpretation of the mechanical property data in terms of percolation concepts. A statistical theory of chain formation predicts that a continuous path along rods with an aspect ratio of 300 will appear at a concentration of 0.265 vol % rods in a medium where they are allowed to randomize their configurations.[29] The stiffness and strength of the 75/25 PEEK/PBT fiber spun from a 1.0% solution are low and continuous short lengths of PBT are observed in Figure 17. In this solution, the PBT concentration is 0.23 vol. % and we can interpret the decline in properties at very low concentrations as a consequence of a microstructure that consists of disconnected PBT domains that each contain microfibrillar networks on a much smaller scale. This interpretation is also consistent with the low strains at break in as-spun fibers containing less than 25% PBT.

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[29] D.E. Davenport, *Polym.-Plast. Tech. Eng.*, *17* (2), 211 (1981).

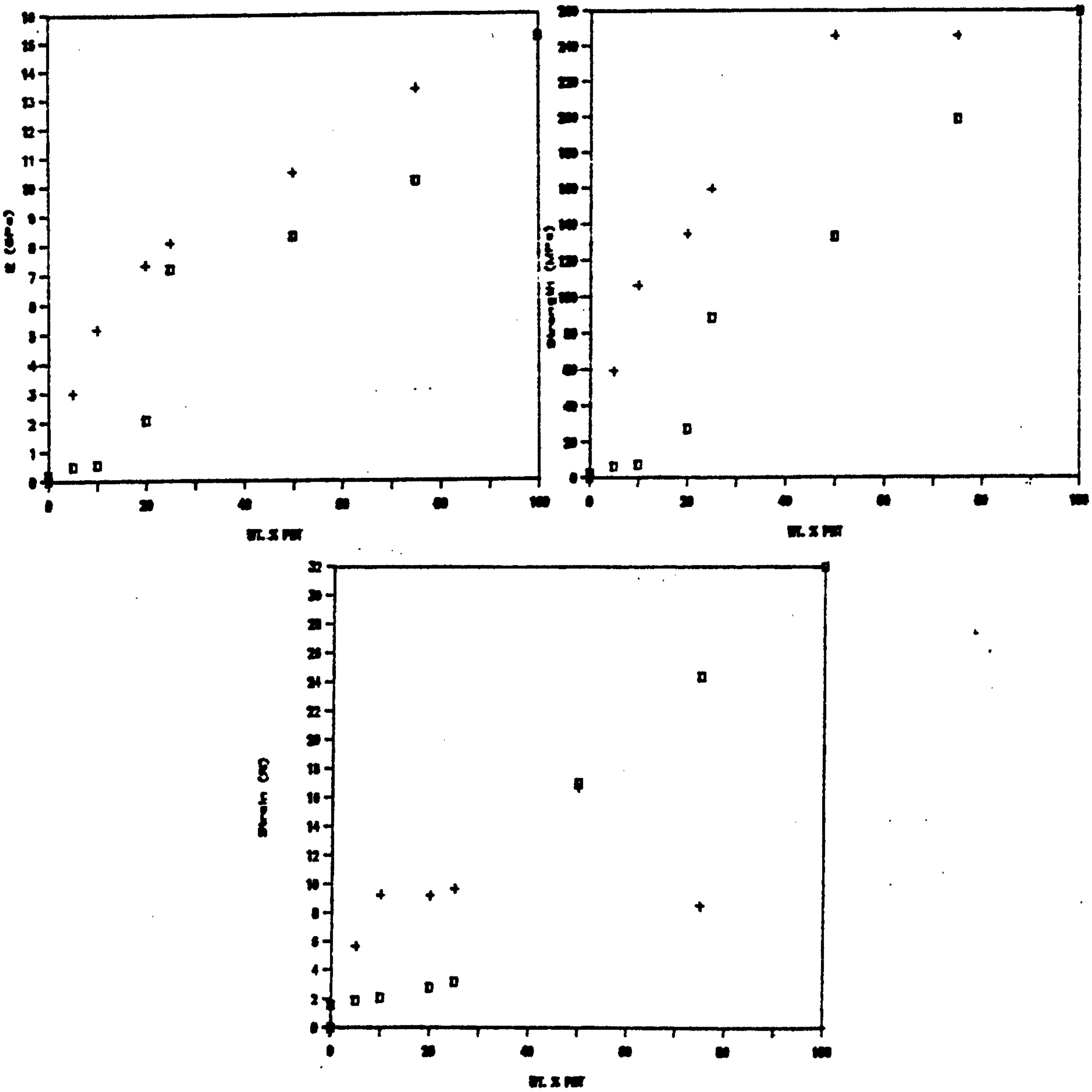

Figure 18: Tensile properties for PEEK/PBT30 fibers prepared from 2.0% solution in MSA. As-spun (□) and heat-treated at 425°C (+), (a) modulus, (b) strength, (c) strain at break.

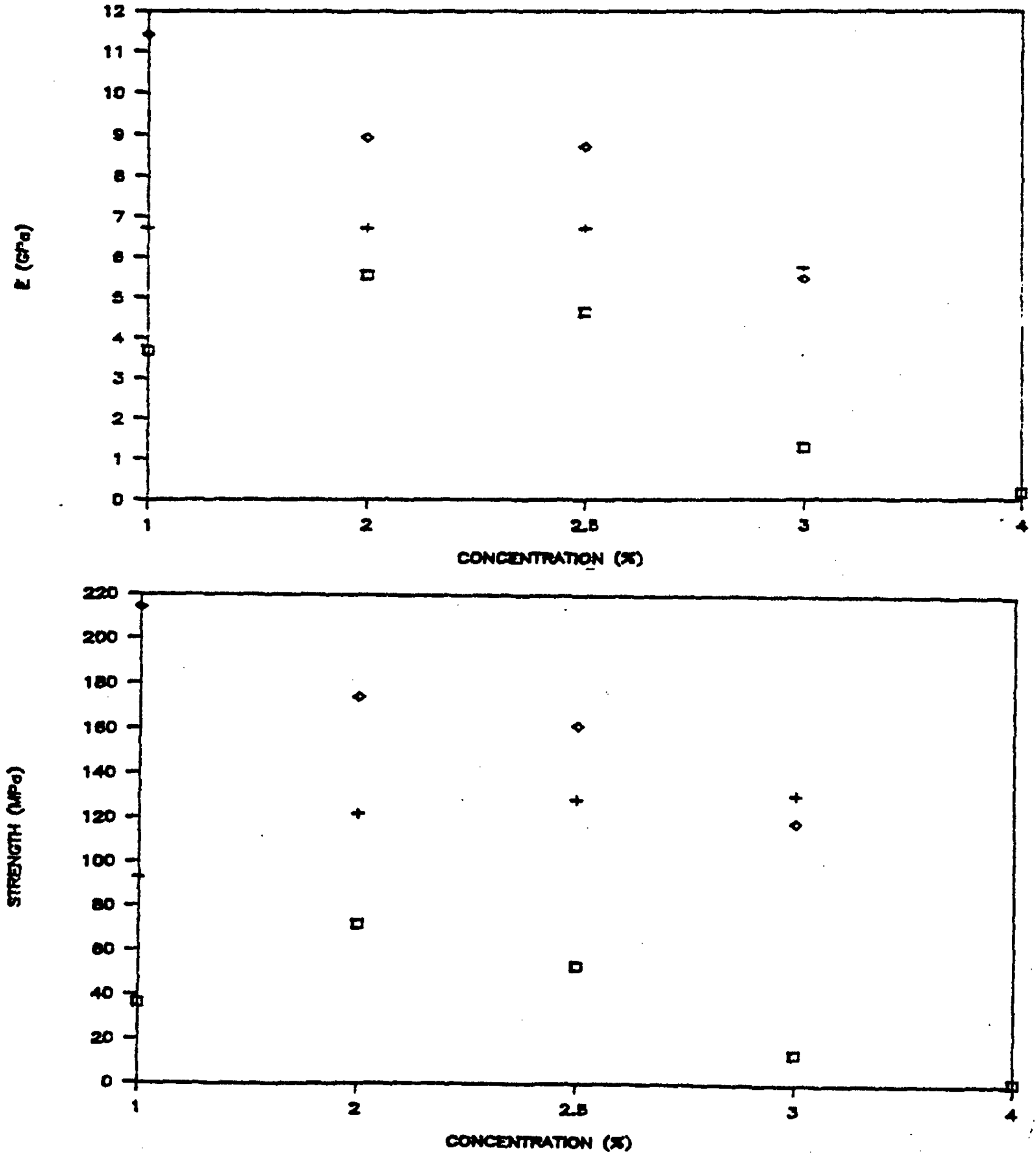

Figure 19: Tensile properties for as-spun 75/25 (□), 50/50 (+), and 25/75 (◇) PEEK/PBT30 fibers vs. the total polymer concentration in the spinning solution, (a) modulus, (b) strength.

Since the rate of coagulation is apparently an important processing parameter, PEEK fibers were spun from a 5.0 wt.% MSA solution into various coagualtion baths. Figure 20 shows the effect of the MSA concentration in the coagulation bath on the fiber tensile modulus and the fiber diameter (used as a measure of the void content in the fiber). Coagulation in a bath of 5.0 wt% MSA in distilled water ($pH = 0.99$) produces the optium PEEK fiber having a modulus approximately twice that of fibers coagulated in distilled water. The fibers also have the smallest diameter, indicating the lowest void content. These results indicate that the coagulation conditions can be used to some extent to improve the properties of PEEK fibers. We would expect a similar effect in the composites, although the effect is probably less important than the concentration of the spinning solution.

Figure 21 shows DSC scans of 75/25 PEEK/PBT fibers spun from 2.0, 3.0, and 4.0% solutions in MSA along with the scan for an as- spun PEEK fiber prepared from a 3.0% solution. All of the composite fibers have the same thermal transitions as the pure PEEK fiber, indicating phase separation.

The thermal expansion of these fibers was investigated using a thermal mechanical analyzer (TMA). A fiber was placed under constant tension, of approximately 20 MPa and heated from 50°C to 300°C at 10°C per minute while the displacement of the fiber was monitored. Figure 22a shows the elongation vs. temperature curve for an as-spun PBT fiber prepared from a 2.0% solution. The fiber elongates when heated to 200°C; cooling to 50°C and reheating to 300°C reveals that the fiber is dimensionally stable at temperatures to which it has previously been exposed. The fiber exhibits a negative thermal expansion coeffecient, which is consistent with previous studies of the force-temperature behavior of PBT.[30] Figure 22b show the elongation vs. temperature curve for an as-spun, 75/25 PEEK/PBT fiber prepared from a 2.0% solution. The composite fiber also has a memory of its thermal history similar to the as-spun PBT fiber. The first heating through the T_g of PEEK (approximately 140°C) results in elongation of the fiber. The second scan through the 140°C , shows the fiber to be dimensionally stable up to the highest temperature it has previously encountered, even above the T_g of the matrix. The final scan from 50°C to 300°C shows that the thermal expansion behavior of the PBT dominates the behavior of the composite. This behavior is consistent with the concept of a continuous phase of PBT spanning the entire composite fiber.

Evidence for a continuous network microstructure in PBT fibers spun from anisotropic

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[30] L.A. Pottick, S.R. Allen and R.J. Farris, *J. Appl. Polym. Sci.*, *29*, 3915 (1984).

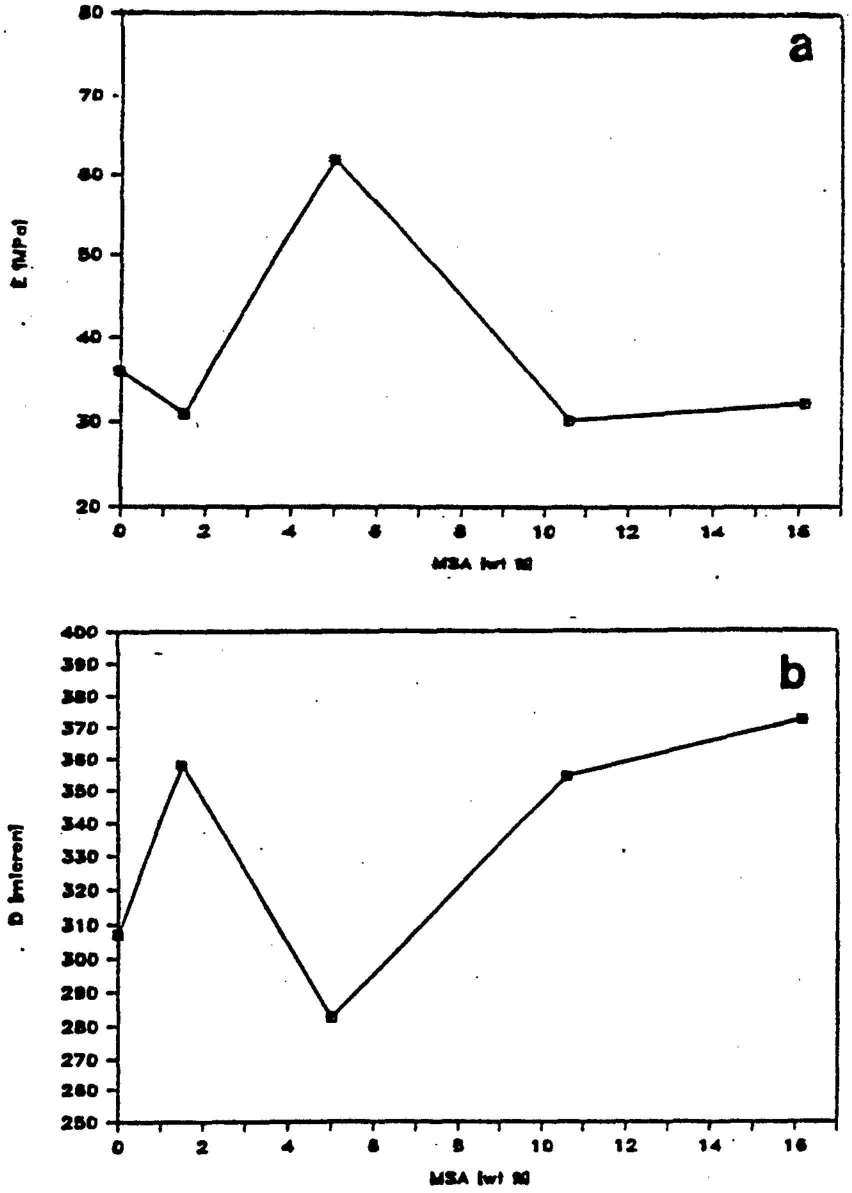

Figure 20: Properties for as-spun PEEK spun from a 5.0% solution vs. the wt.% MSA in the coagulation bath, (a) tensile modulus, (b) diameter.

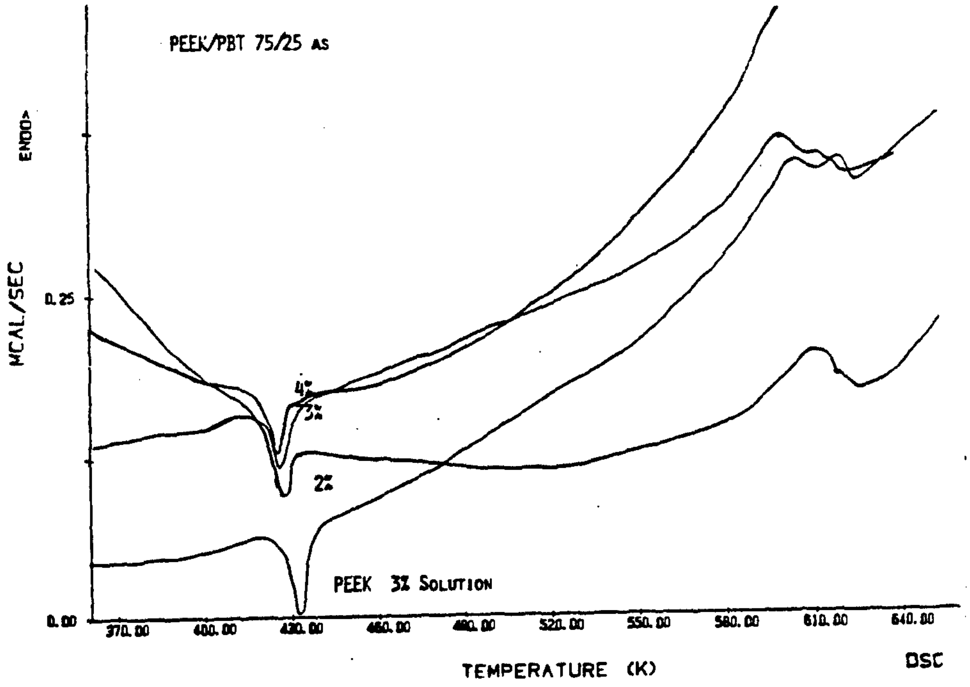

Figure 21: DSC scans for as-spun 75/25 PEEK/PBT30 fiber prepared from 2.0, 3.0, and 4.0% solutions in MSA and for an as-spun PEEK fiber prepared from a 3.0% solution.

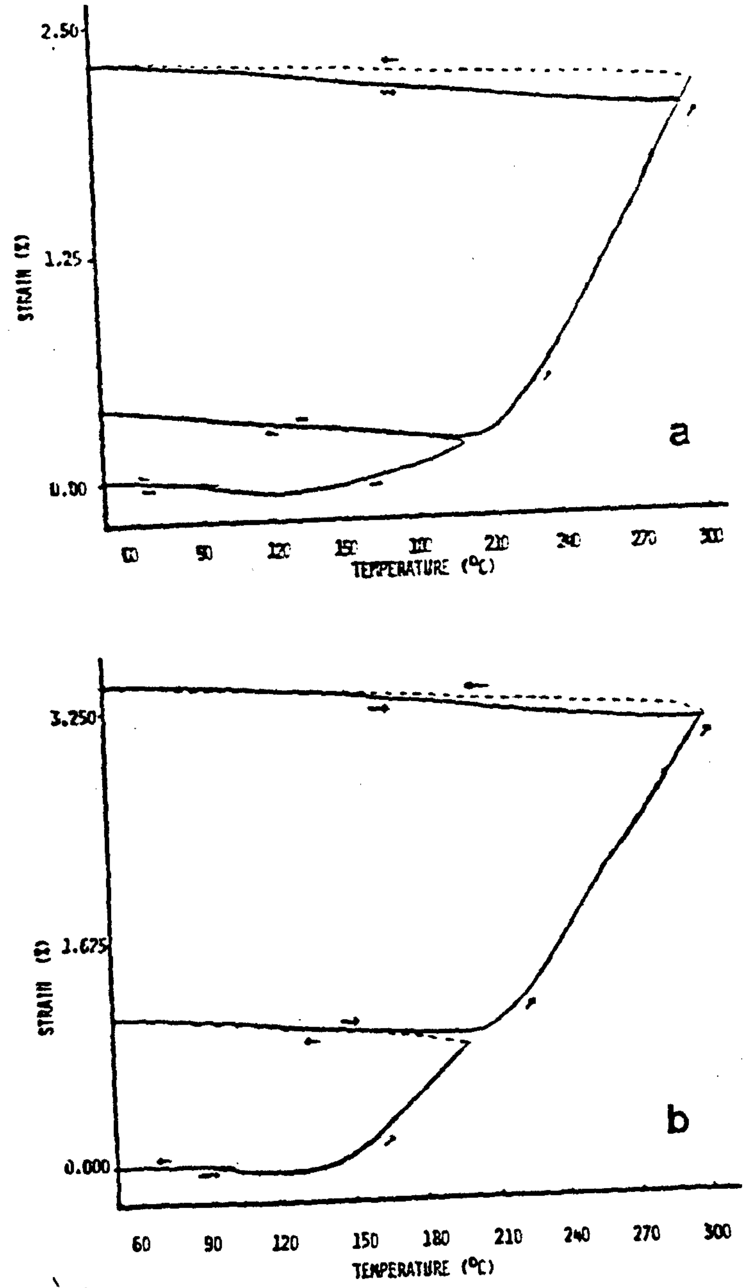

Figure 22: Strain-temperature results for an as-spun fiber of (a) PBT30 spun from 2.0% solution, (b) 75/25 PEEK/PBT spun from a 2.0% solution.

PPA solutions has been given by demonstrating that the force to break the wet fiber was equivalent to that of the dry fiber.[31] We have measured the breaking force for wet PEEK/PBT fibers, with the results shown in Figure 23. The force required to break the wet fiber is less than that for the dried fiber, but still represents a substantial load-bearing capacity in the wet composite fiber.

3.3.2 PEEK/PBO Compsites

Composite fibers with 5 to 30 weight percent of PBO were wet spun from an isotropic 4.0 wt.% MSA solution, air dried, hot-drawn and tensile-tested, with the results shown in Figure 24. The modulus and strength increase slightly with increasing PBO content, but the best properties (70/30 PEEK/PBO) are still inferior to that of melt-processed PEEK. By washing the PEEK away with H_2SO_4, the internal PBO structure could be observed. Figure 25 shows the discrete domains observed with the 90/10 PEEK/PBO fiber. The 70/30 composite fiber has a continuous, open structure of PBO, similar to those observed for the PEEK/PBT fibers spun slightly below the critical concentration. A 70/30 PEEK/PBO fiber was spun from a 3.0 wt.% MSA solution and hot-drawn at a draw ratio of 1.4. The as-spun and hot-drawn tensile moduli were 3.6 and 5.1 GPa, and the tensile strengths were 6.0 and 9.0 MPa, respectively, indicating that the PEEK/PBO/MSA system has a similar dependence of tensile properties on solution concentration as the PEEK/PBT/MSA system.

3.4 Nylon 6,6/PBT Composites

The first section of this report described the effect of heat-treatment conditions, tension and temperature for nylon/PBT fibers at a 70/30 composition. We have examined the importance of solution concentration in the nylon/PBT fibers using a matrix of nylon 6,6 with a number average molecular weight of 13,700.

Figure 26 shows the effect of concentration on the tensile properties of 75/25 N66/PBT30 fibers. In contrast to the behavior with a PEEK matrix, there is no dramatic effect of concentration in the isotropic region and, in fact, the fiber spun from a birefringent solution of 4.0% concentration has a stiffness of about half that of fibers spun from an isotropic solution. There is a similar dependence of the tensile strength on the concentration. Scanning electron micrographs of tensile-tested fibers

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[31] L.A. Pottick and R.J. Farris, *TAPPI Symposium (Nonwoven), 65,* April (1985).

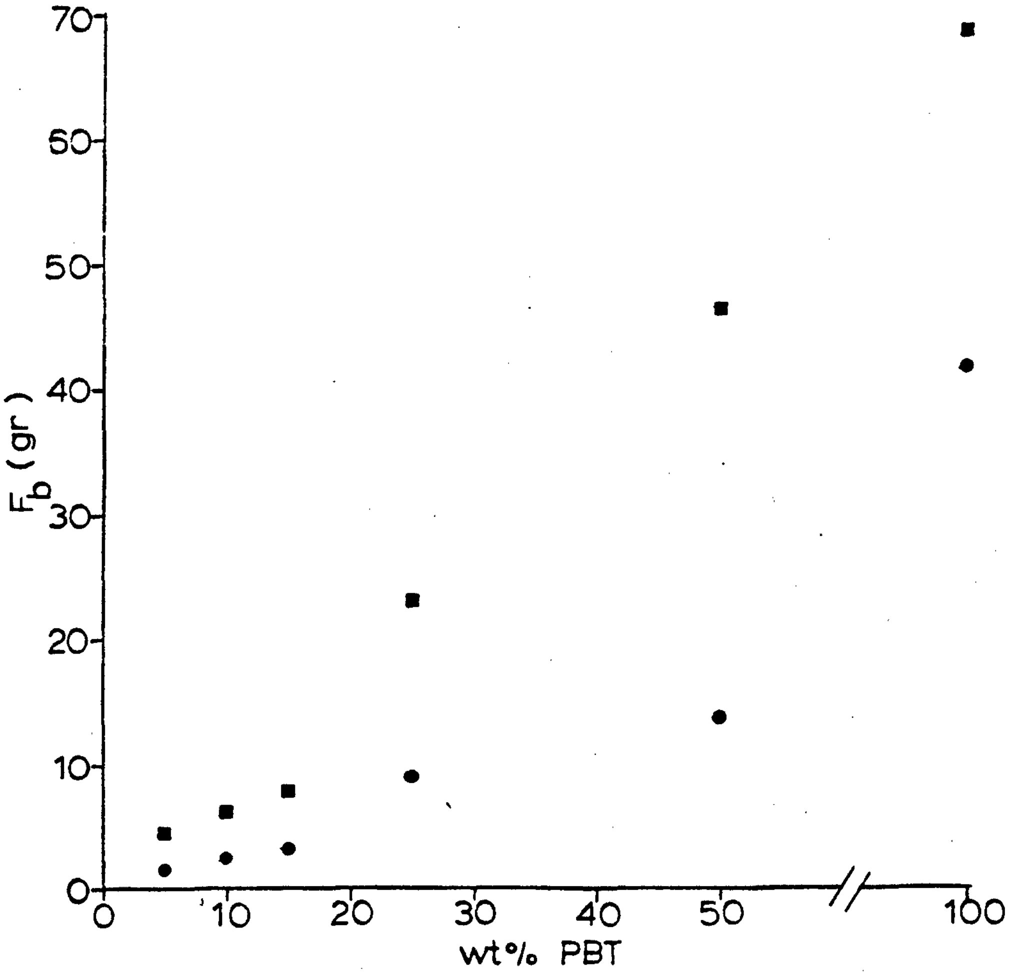

Figure 23: Breaking force for wet (•) and dry (□) PEEK/PBT30 composite fibers spun from a 2.0% solution in MSA.

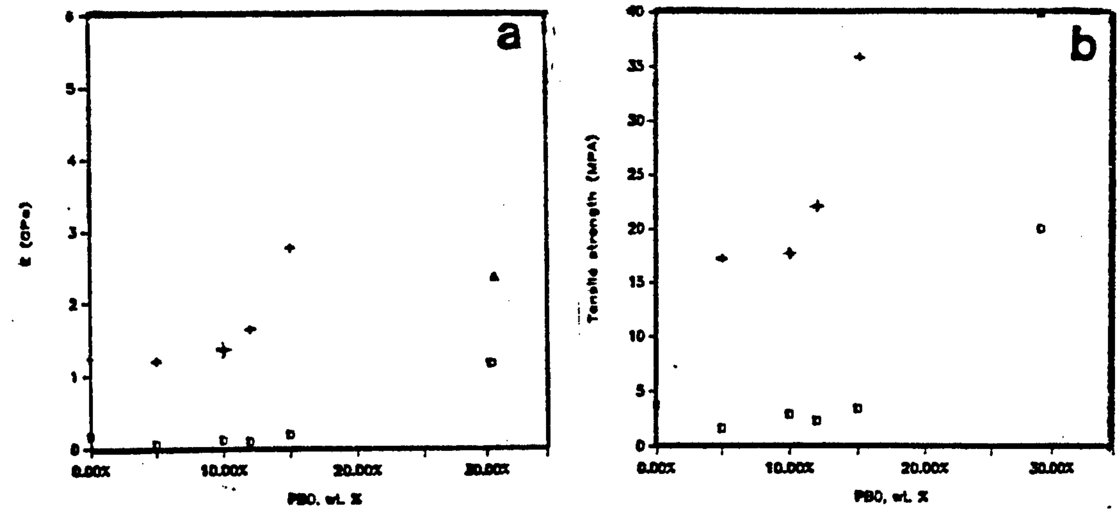

Figure 24: Tensile properties for PEEK/PBO fibers spun from 4.0% isotropic solution in MSA. As-spun (□), hot-drawn (+) and heat-treated at 400°C (△); (a) modulus, (b) strength.

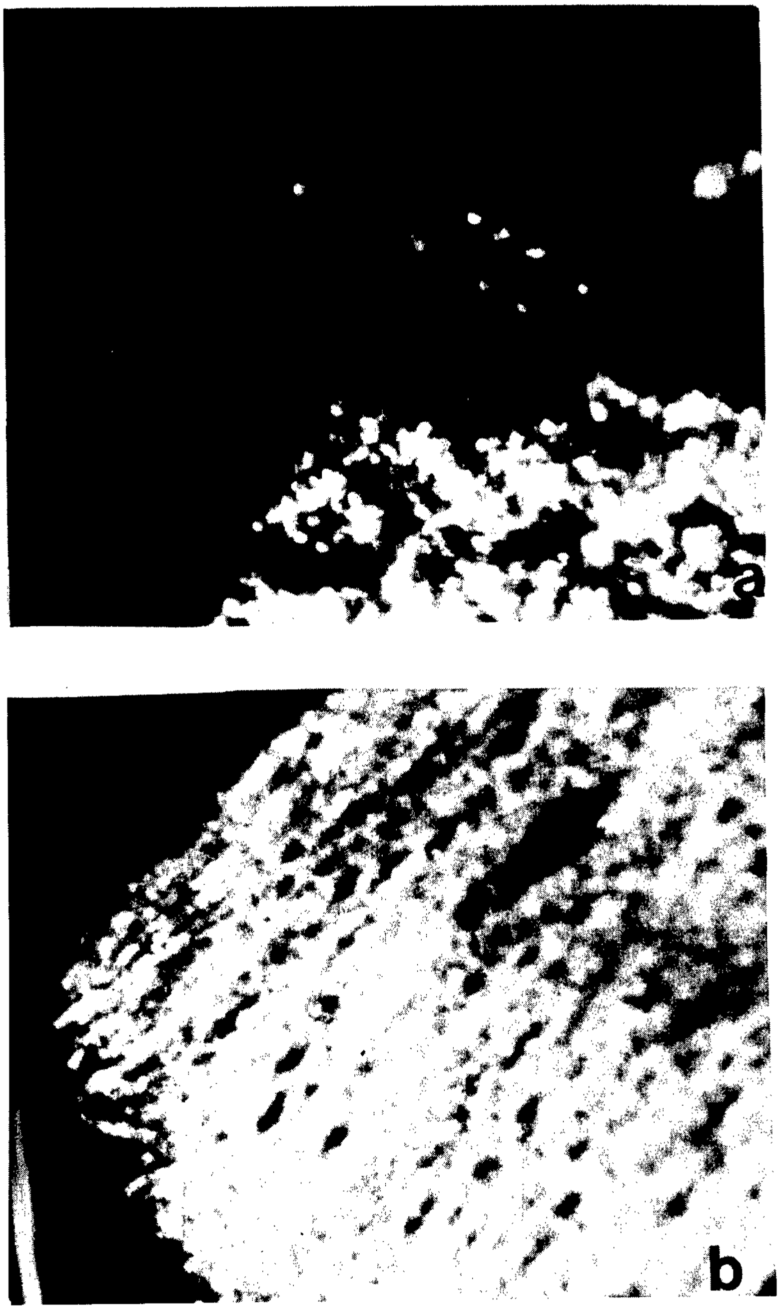

Figure 25: Optical micrograph of as-spun PEEK/PBO fiber spun from a 4.0% solution after being exposed to H_2SO_4, (a) 90/10, (b) 70/30.

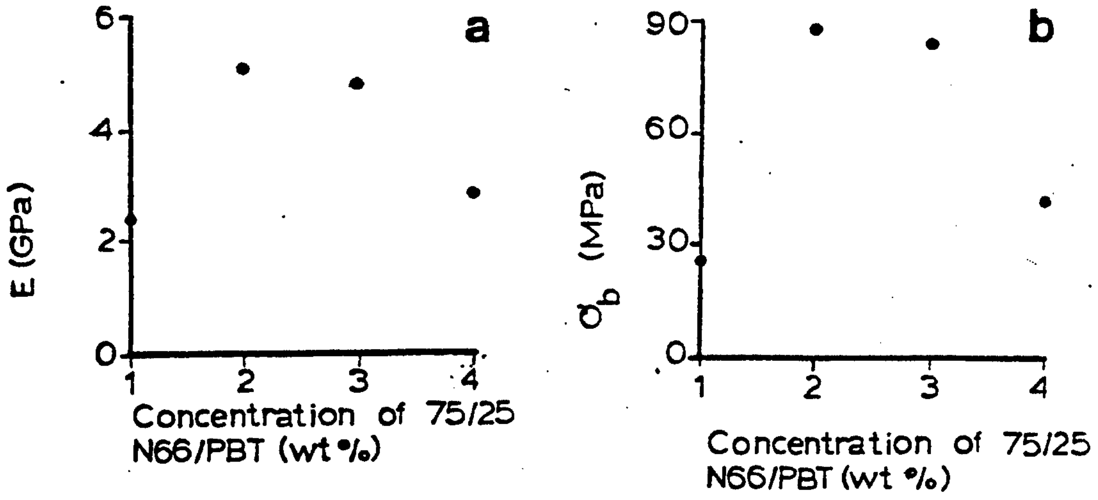

Figure 26: Tensile properties for as-spun 75/25 N66/PBT30 fiber vs. the total polymer concentration in MSA for the spinning solution, (a) modulus, (b) strength.

are shown in Figure 27. The fiber diameters increase roughly in proportion to the solution concentration.

The difference in sensitivity to the solution concentration between nylon and PEEK matrices depends on the difference in the solubilities of the two materials as well as any difference in the rate of coagulation into a crystalline or amorphous form. For example, if the matrix is significantly more soluble than the rodlike component, the rods will precipitate before the matrix and a network structure can form over relatively large length scales, without interference from the other component. On the other hand, if the rod and matrix materials have a similar solubility, the microfibrillar network may or may not form, depending on the relative amounts of the components and on the intrinsic rates of precipitation. We found that 3.8 cc of water produces a turbid solution when added, with rapid stirring, to 1.0 cc of a 2.0% solution of N66 in MSA. In contrast, 0.15 cc was required to initiate precipitation in 1.0 cc of a PEEK/MSA solution of the same concentration, while a PBT/MSA solution required the addition of 0.20 cc of water. We can interpret the coagulation process in Nylon/PBT composites as the initial formation of a PBT network, followed by the much slower formation of a semicrystalline nylon phase. In contrast, PEEK coagulates on the same time scale as PBT and can significantly disrupt the network formation, unless PBT is the predominant component.

Fibers of N66/PBT30 with various weight ratios of the polymers were also spun from a 2.0% MSA solution. Figure 28 compares the tensile properties for the as-spun fibers with wet-stretched fibers, and with those heat-treated at 300°C with no tension. The modulus and strength increase with wet-stretching, heat-treatment, and increasing PBT content. However, these numbers are not representative of the optimum processing conditions and are expected to increase with increased draw and tension during heat treatment.[32]

The thermal behavior of as-spun, 75/25 N66/PBT fibers prepared from 2.0, 3.0, and 4.0% solutions were examined with DSC. In Figure 29, scans for the composite fibers are compared to N66 spun from a 15.0% solution (because of N66 slow rate of coagulation, the high concentration was necessary to spin a fiber). The composite fibers have the same T_m, which is a few degrees higher than the T_m measured for neat N66, indicating the presence of a separate, semicrystalline N66 phase. This higher melting for the composites is consistent with the N66 solution-crystallizing onto a PBT structure. The properties of N66/PBT composite fibers, however, are relatively

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[32] See Section 1 of this report and the references described there.

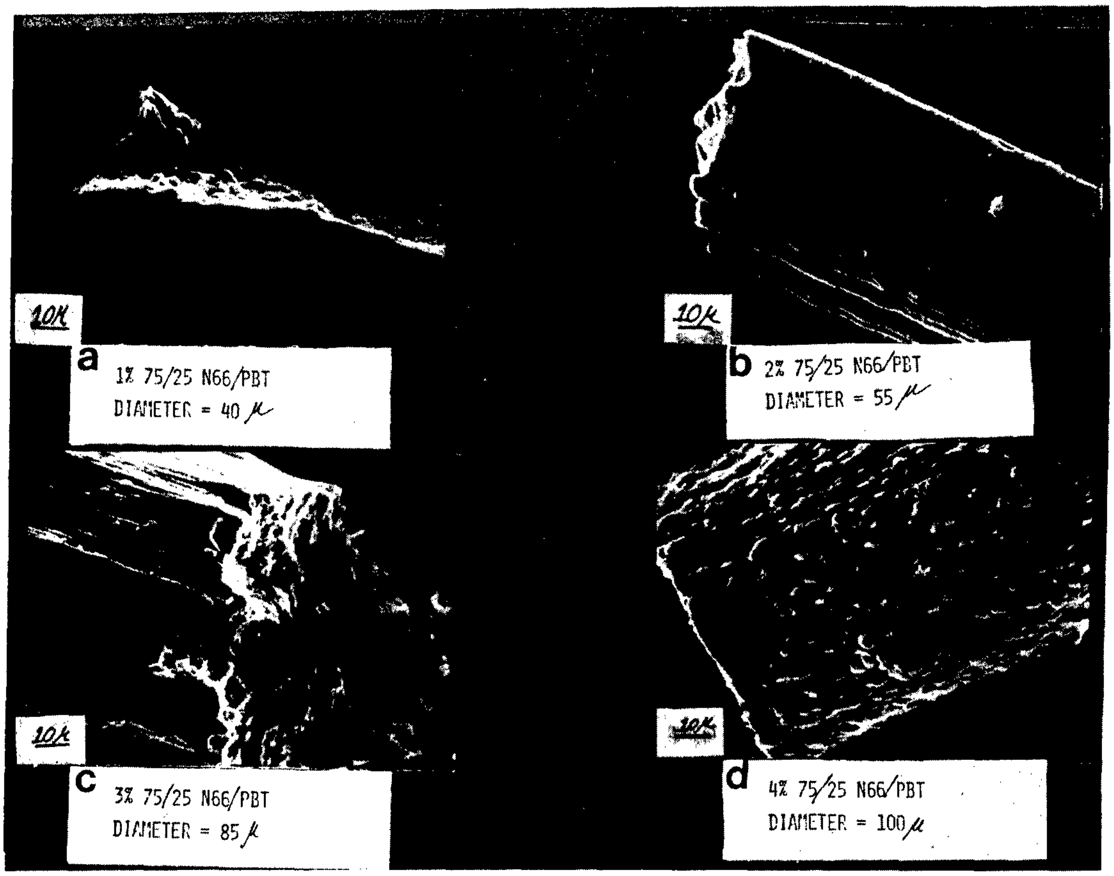

Figure 27: Scanning electron micrographs of as-spun 75/25 N66/PBT30 fibers spun from (a) 1.0% solution, (b) 2.0% solution, (c) 3.0% solution, (d) 4.0% solution.

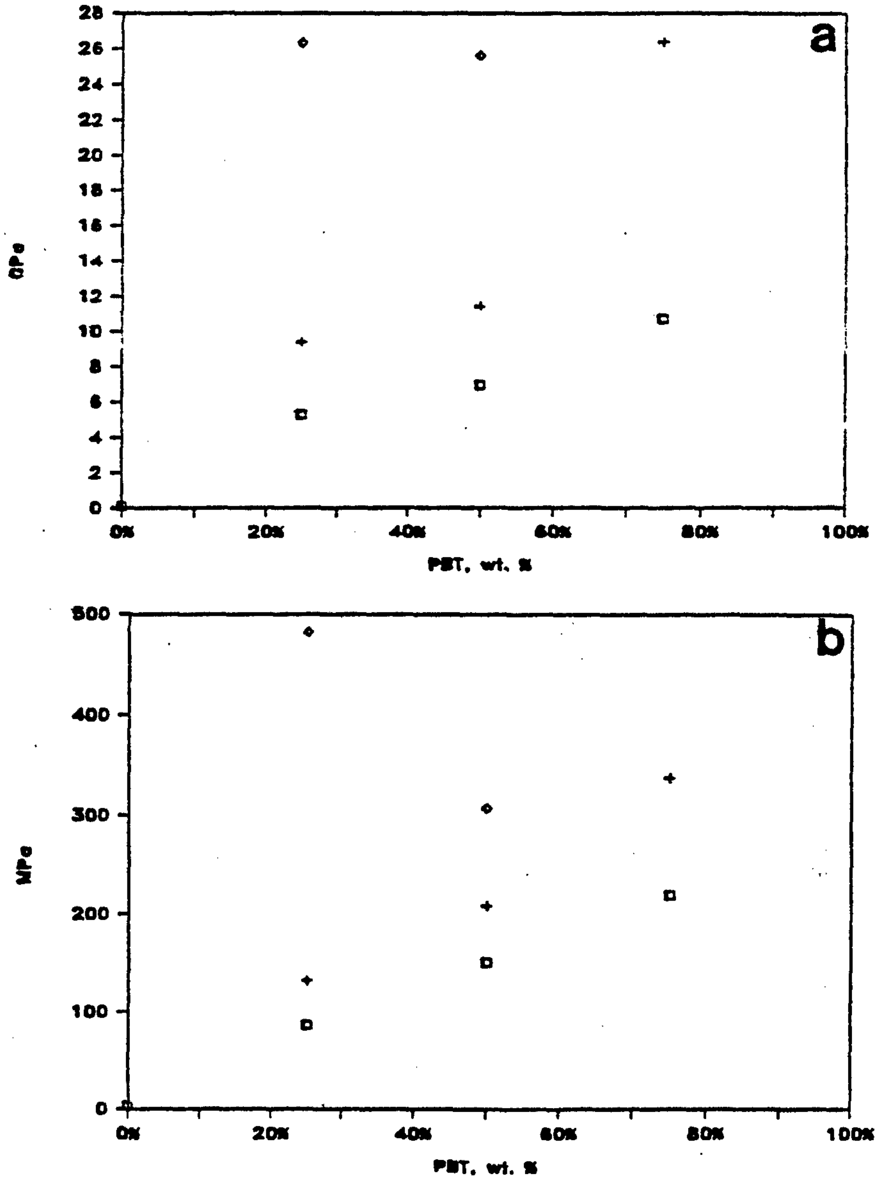

Figure 28: Tensile properties for 75/25 N66 PBT30 fibers, spun from 2.0% solution in MSA. As-spun (□), wet-stretched (+) and heat- treated at 300°C (◇); (a) modulus, (b) strength.

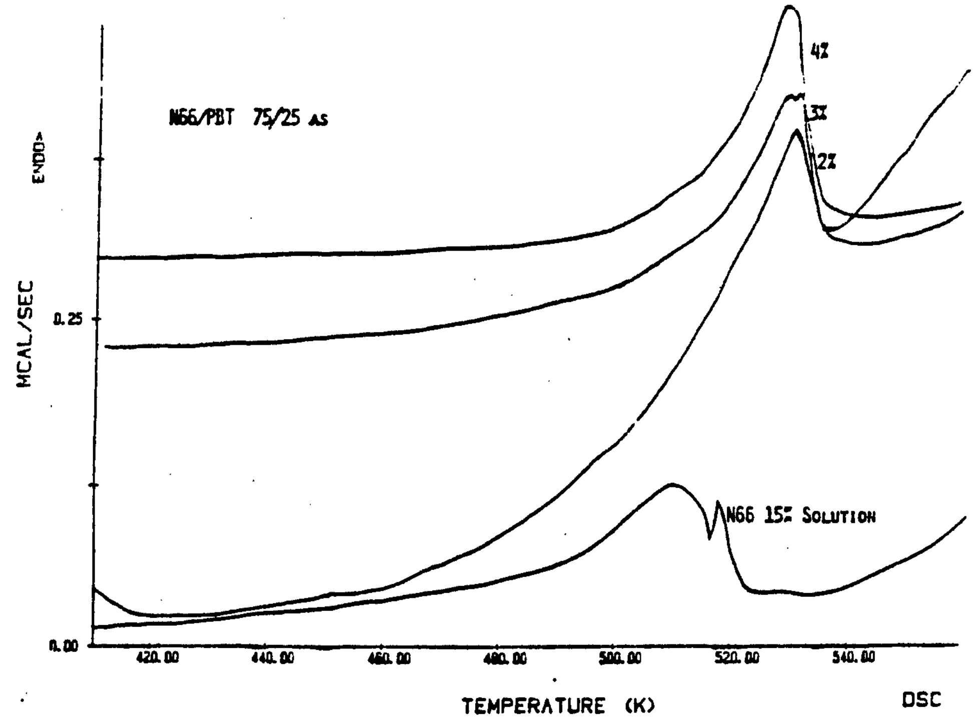

Figure 29: **Differential scanning calorimetry scans for as-spun 75/25 N66/PBT30 spun from 2.0, 3.0, and 4.0% solutions in MSA and for as-spun N66 fiber spun from a 15.0% solution.**

independent of solution concentration and this difference is attributed to the N66 having a much slower rate of coagulation than either PEEK or PBT. The coagulation behavior is a consequence of the solution conformations, since N66 is a flexible coil in MSA, while the PEEK is known to be relatively "stiff" in solution.

3.5 Conclusions

The existence of a continuous microfibrillar network has recently been demonstrated for pure PBT fibers.[33]

Some evidence for the formation of a PBT network in molecular composites is shown here. First, the tensile modulus and strength have a dramatic increase between 20 and 25 weight percent PBT; this is consistent with an abrupt or percolation threshold for the formation of the network. Also, the modulus, strength and the strain to break for PEEK/PBT fibers of 25% or less PBT increase significantly as a result of heat-treatment, suggesting that a perfection of the network occurs. A continuous structure of PBT was observed with optical microscopy for PEEK/PBT fibers when the PEEK matrix was removed with H_2SO_4. This structure is composed of domains that can vary in size and connectivity. The smallest dimension can range from approximately 1 to 50 microns and the domains may be discrete or connected in a sample-spanning fibrillar structure, depending primarily on the solution concentrations of the polymers. The domains probably contain a microfibrillar structure on a smaller scale, as dicussed in Section 6 of this report.

DSC shows that PEEK/PBT fibers have the same thermal transitions as PEEK, indicating that semicrystalline domains of PEEK are present in the composite fibers. TMA shows that the composite fibers are dimensionally stable at high temperature, even above the T_g of the matrix, only after an initial exposure to high temperature. The breaking force for wet composite fibers is a substantial fraction of that for the corresponding dry fibers. A study of N66/PBT fibers using transmission electron microscopy and X-ray scattering to provide a more quantative description of the network are discussed in Section 6. DSC scans of the N66/PBT fibers showed them to have the same T_m, slightly higher than the melting of pure N66.

The implications for further studies of molecular composites are as follows. During

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[33] The mechanical property evidence of L.A. Pottick and R.J. Farris, *TAPPI Symposium (Nonwoven), 65,* April (1985) was used to infer the existence of such a microstructure. Y. Cohen and E.L. Thomas, *Polym. Eng. Sci., 25,* 1093 (1985) showed the first direct evidence using electron microscopy.

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, this network structure will span the sample and will result in mechanical properites that are dominated by the PBT properties; this is the case for nylon 6,6. Otherwise, discontinuous domains of PBT can form, resulting in poor mechanical properties; this is observed for PEEK at certain concentrations. At a sufficiently low concentration, the PBT network cannot form a continuous fiber and poor mechanical properties can result. Thus, there can be an optimum concentration of polymer in solution if the matrix coagulates on the same time scale as the PBT; however, if the PBT composition is high enough, the effect of the matrix is secondary.

4. Properties of PBT/Nylon 6,6 Films

4.1 Introduction

As discussed in the previous sections of this report, there is evidence that PBT found to reinforce thermoplastics by forming continuous networks throughout the fibers. It is then questionable that composites of PBT/thermoplastics can be melt-processed, however, by analogy to conventional prepreg-composites, it is likely that composite films of PBT in thermoplastic matrices can be compression-molded into large planar isotropic objects for structural applications.

4.2 Experimental

The materials and solution preparation were described in Sections 2 and 3 of this report. A concentration of 2.0 wt% total polymer in MSA was used since solutions at all of the different compositions of PBT/Nylon 6,6 remain isotropic at this concentration, and since the 30/70 PBT/Nylon 6,6 composites prepared from two weight percent and the critical concentration (3.7 wt %), have comparable tensile properties. The mixing apparatus consisted of a variable speed stirring rod in a glass flask. The system is kept under a nitrogen atmosphere for the duration of the mixing process, which ranged from one to two weeks. No significant degradation of Nylon 6,6 was found to occur as long as the solution was used within two weeks.[34]

A schematic drawing of the film extrusion apparatus is shown in Figure 30. It consists of a i) solution delivery, ii) coathanger die, iii) take-up device, iv) coagulation bath. The solution was extruded at a rate of 1.38 cc/min through a Teflon barrel. The slit area of the film die was 0.19 cm^2. The solution coming out of the die goes directly onto a take-up roll mounted on a glass tube. The take-up speed is adjusted to be equal to the extrusion rate of the film. Coagulated wet films were rinsed with running water for one day and then neutralized in 50 percent NaOH aqueous solution for one day and again washed with water. The films were dried under press-platens at 1000 psi for 30 minutes before heating the press to 130°C to eliminate water.

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[34] D.G. Baird, *J. Rheol.* *25*, (6) 591 (1980).

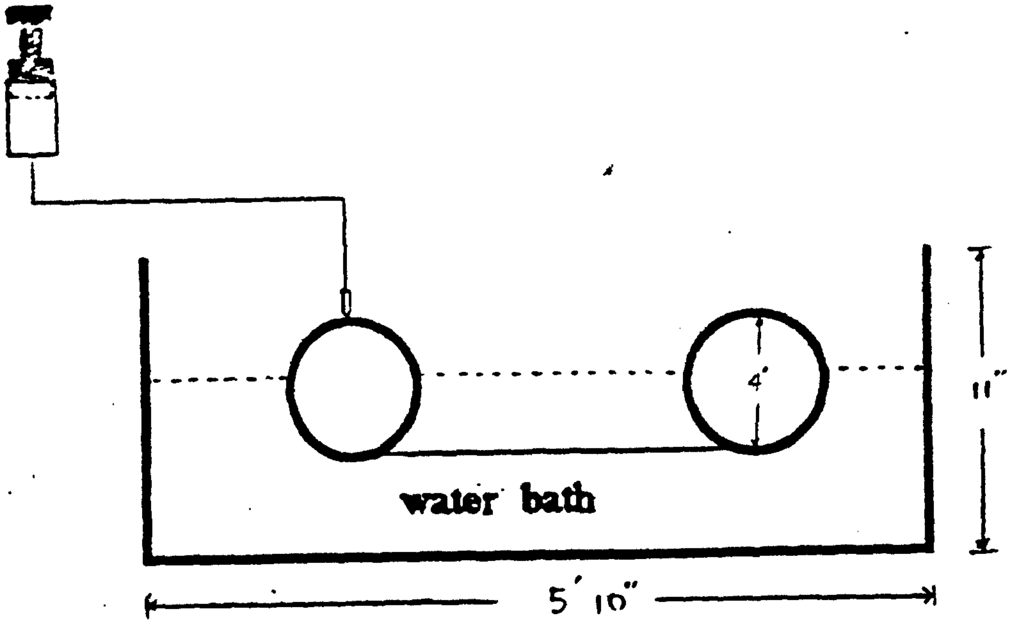

Figure 30: Schematic of the film spinning apparatus.

4.2.1 Property Measurements

For mechanical testing, films with a gauge length of 2.0 cm were tested in both the axial and transverse directions on an Instron Universal Testing Machine at a crosshead speed of 0.1 cm/min, at ambient conditions. Films were mounted on paper tabs with epoxy and cured overnight. The width and thickness of the films were measured with an optical microscope and a micrometer.

Wide-angle X-ray diffraction (WAXD) results were obtained from both flat film and diffractometric techniques with the X-ray beam perpendicular to the film surfaces. Flat film sample patterns were obtained in a Statton camera employing pin-hole collimation and a sample to film distance of 53.1 mm. Diffractometer (2θ) scans of the equatorial reflections were obtained on a Siemens D-500 diffractometer utilizing line focus collimation with a scan rate of $0.4^\circ(2\theta)$/min. CuK_α tubes operated at 40KV and 30mA were employed for both the camera and the diffractometer.

A Perkin Elmer DSC-4 Differential Scanning Calorimeter (DSC) was used to investigate the thermal transitions of the composites. The scan rate was 20°C per min, and the sample weight was about 5 mg. The dimensional changes of the composite films were measured as a function of temperature by Perkin Elmer TMA-2 Thermomechanical Analyzer (TMA). The sample was held by two clips and placed between concentric tubes as shown in Figure 31. The inner tube applied a constant stress of approximately 0.2 MPa and was connected with a linear variable differential transducer (LVDT) to monitor the change of sample dimensions (strain-temperature behavior).

One goal of processing molecular composites was to produce a useful object for structural applications. In order to accomplish this, several attempts were made at laminting composite articles. First, composite films were cut into the shape of the mold with a 40-layer pile and then compression-molded at 280°C and 2500 psi for 15 minutes. A schematic of the thermal compression molding is shown in Figure 32. Second, the composite films were ground into powders in a roller mill that produced particle sizes from 20 to 500 microns. The composite powders were then compression-molded at the same condition as the films. The three point-bending test was used to measure the modulus and strength of the molded samples.

Results and Discussion

The tensile data are shown in Figure 33. Both the modulus and the strength of the composite films increased with increasing PBT content. For the 75/25 Nylon

TMA

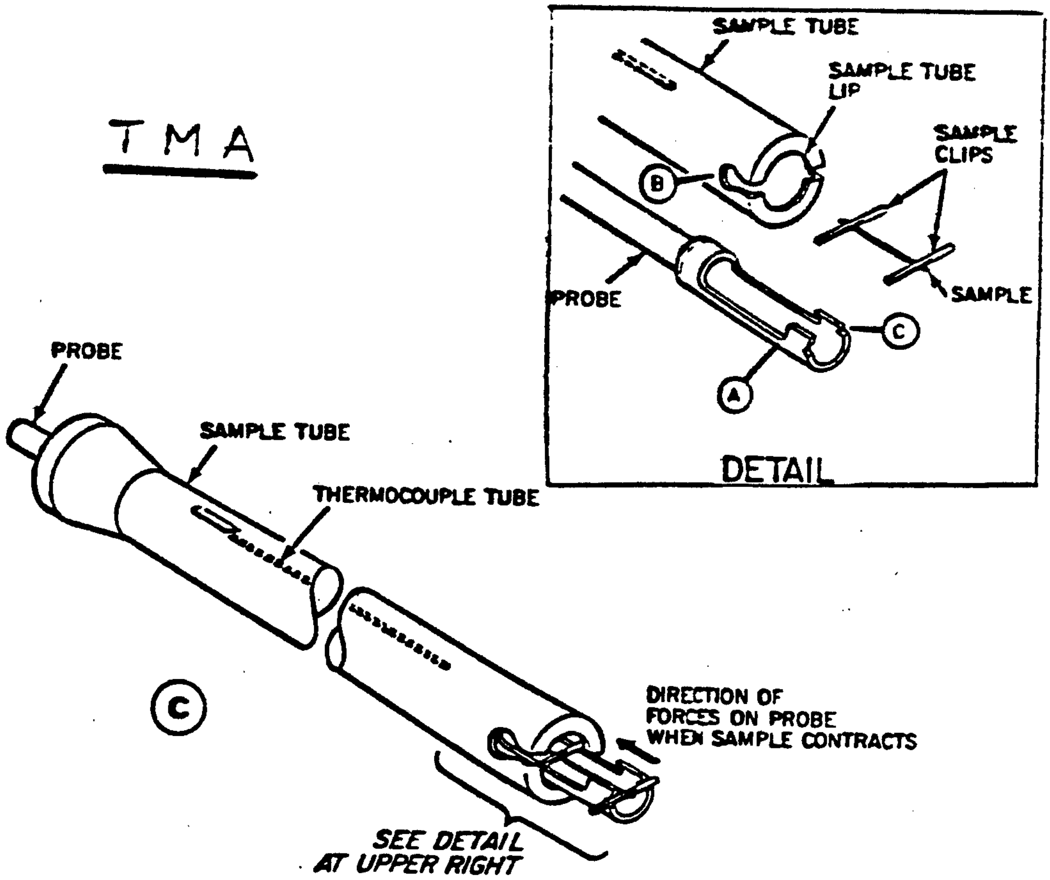

Figure 31: The sample holder for thermal mechanical analysis.

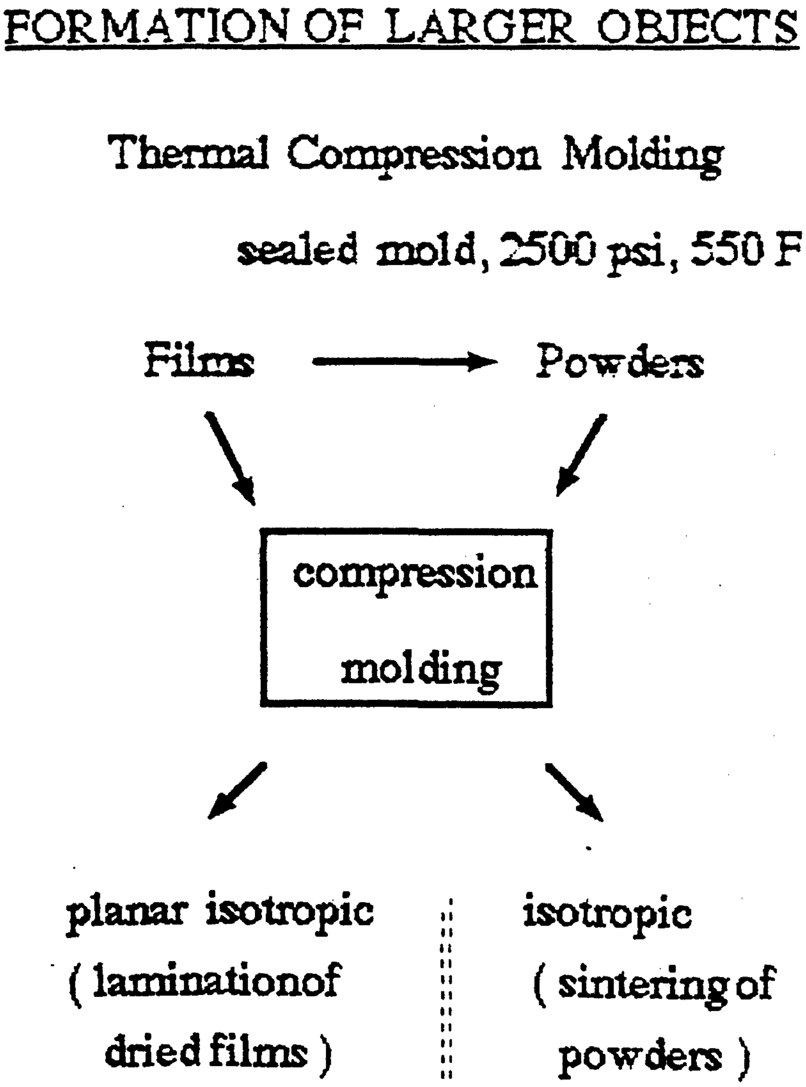

Figure 32: Schematic of the thermal compression molding of composites to form large objects.

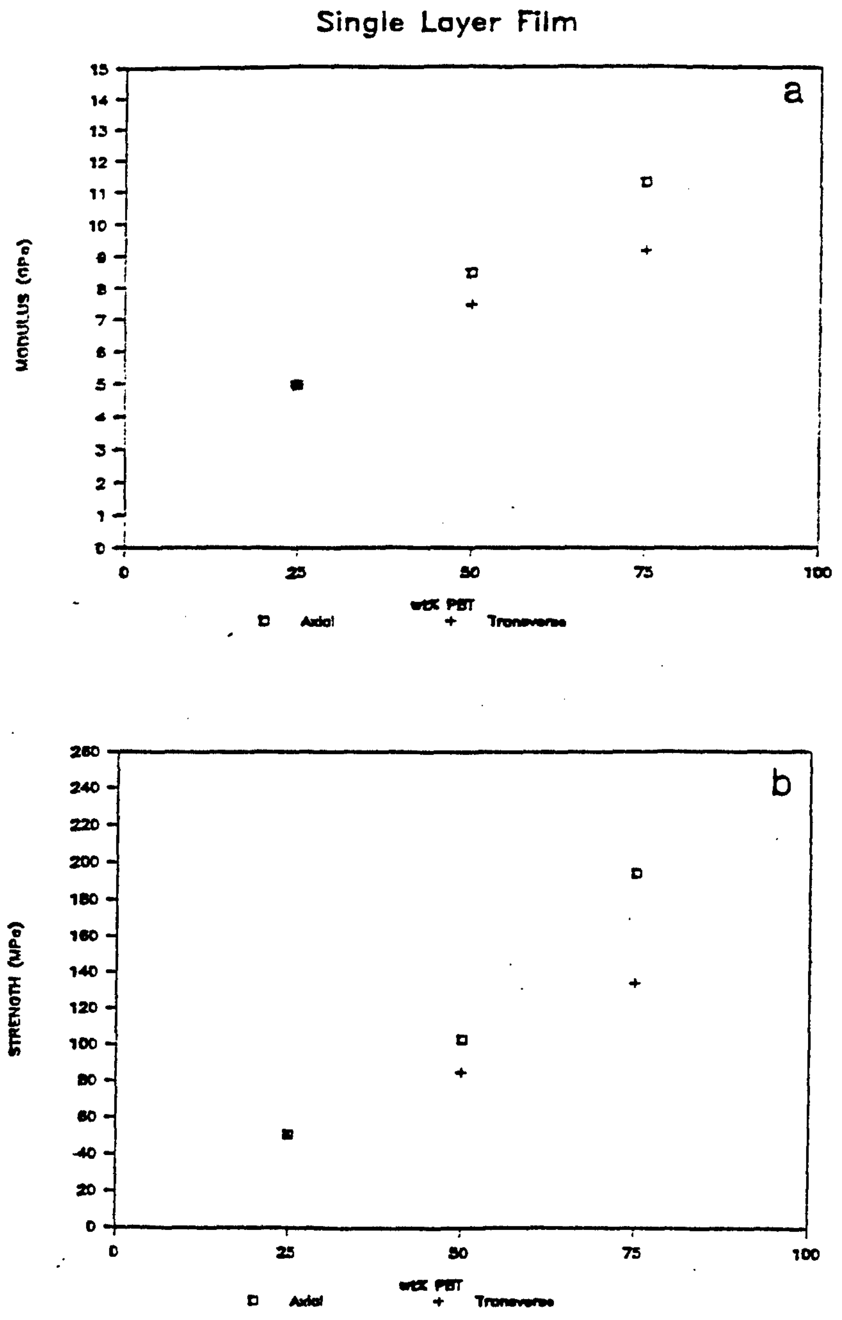

Figure 33: Tensile properties of the as-spun composite films (a) modulus and (b) strength.

6,6/PBT material, planar isotropic films are obtained. For composite films with 50 and 75% PBT, the tensile properties in the axial direction were slightly above that of transverse direction. The tensile moduli of the composite films were comparable with that of the as-spun fibers, but the strength of the films was slightly lower. This is probably due to the defects on the edges of the films.

A comparision of the microstructural characteristics of the neat polymers with the composites has been investigated through both flat film and diffractometric techniques. The WAXD patterns of the composite films and neat polymers appear in Figure 34 and show no preferential orientation. All three composite films consist of Debye rings with interplanar spacings of 12.4 and 3.5 Å that correspond to PBT[35] and 4.4 and 3.7 Å that are reflections of Nylon 6,6[36]

Wide angle X-ray diffractometer data showed no significant shift of 2θ for the composite films in comparison to neat PBT and Nylon 6,6, as shown in Figure 35. The WAXD clearly shows that phase separation is present on a scale such that there are no interactions between PBT and Nylon 6,6 crystallites during the coagulation of the isotropic ternary solution.

The DSC thermograms showed melting transitions in the composites at slightly higher temperatures than the melting point of neat Nylon 6,6 spun from MSA; typical data are shown in Figure 36. The endothermic behavior near 100°C is attributed to continued drying of the samples and disappeared upon a second scan. The melting near 260°C was attributed to the melting of a separate, semicrystalline Nylon 6,6 phase within the sample. In addition, when the composites were observed in a melting point apparatus, they did not flow at 300°C which is 40°C above the DSC observed melting temperature. At 300°C, Nylon 6,6 could be extruded from the film under 50 psi in a nitrogen atmosphere, yet the composite films remained mechanically intact.

Composites with different PBT content display distinct $\epsilon - T$ behavior. The behavior of all the composite films depends on their thermal history and subsequent reheating yields a nearly reversible $\epsilon - T$ behavior below temperatures to which the sample had been previously exposed.[37] For 75/25 PBT/N66, the axial and transverse directions have the same $\epsilon - T$ behavior as shown in Figure 37. However, for composites films with 50% and 75% PBT content, the axial and transverse directions

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[35] J.A. Odell, A. Keller, E.D.T. Atkins and M.J. Miles, *J. Mater. Sci., 16,* 3303 (1981).

[36] See, for example, the solution-spinning studies of T.A. Hancock, J.H. Spruiell and J.L. White, *J. Appl. Polym. Sci., 21,* 1227 (1977).

[37] Fabrication of parts with precise dimensional stability constraints should only be possible from materials that have been annealed at the upper temperature limit for service.

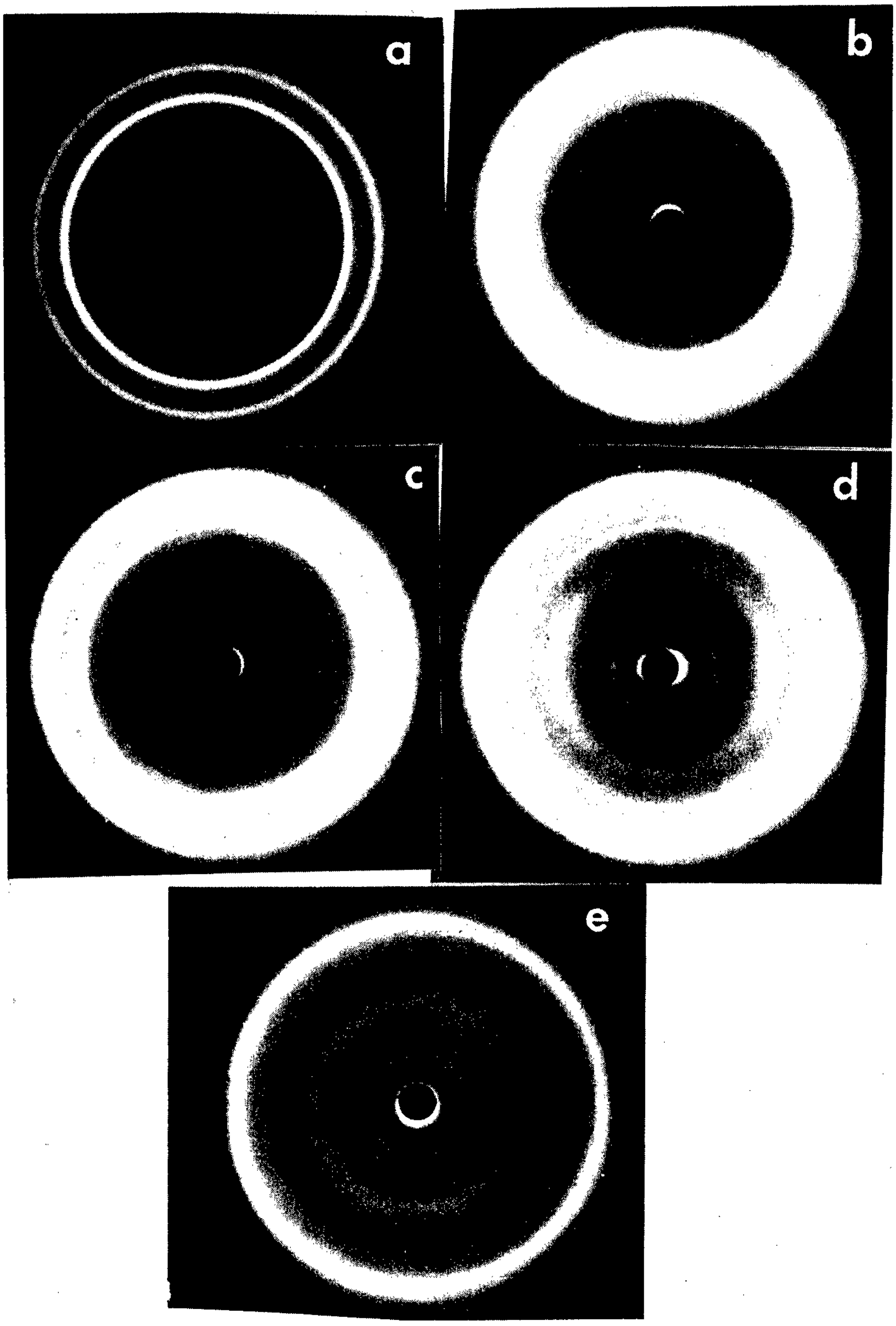

Figure 34: Wide angle X-ray diffraction patterns of Nylon 6,6 / PBT films; (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, (e) 0/100.

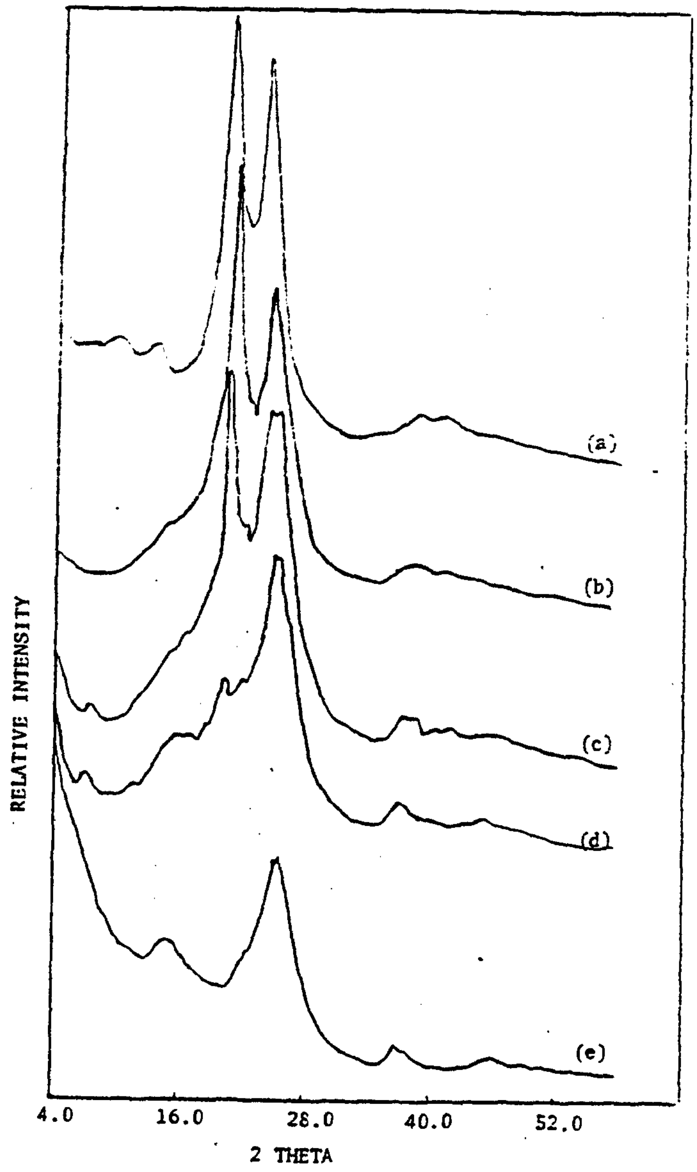

Figure 35: D-500 diffractometric scans of Nylon 6,6 / PBT films; (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, (e) 0/100.

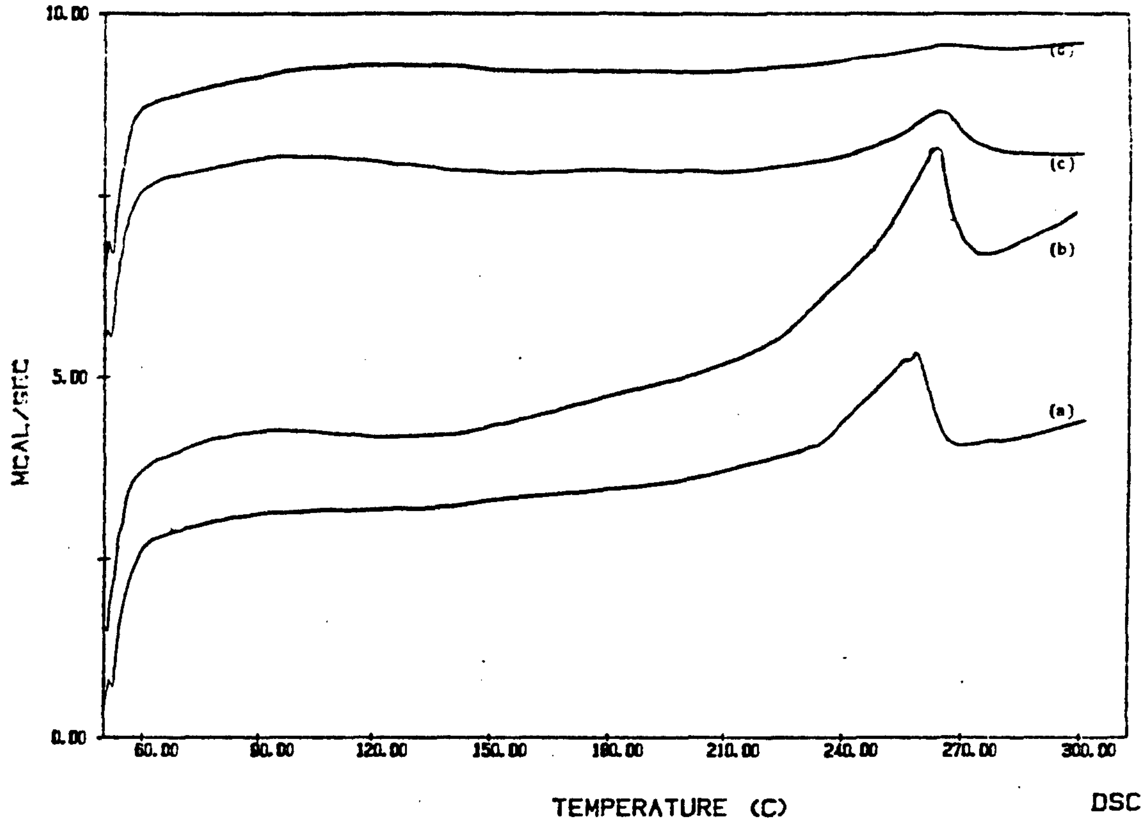

Figure 36: Differential scanning calorimeter thermograms of Nylon 6,6 / PBT composite films; (a)100/0, (b) 75/25, (c) 50/50, (d) 25/75.

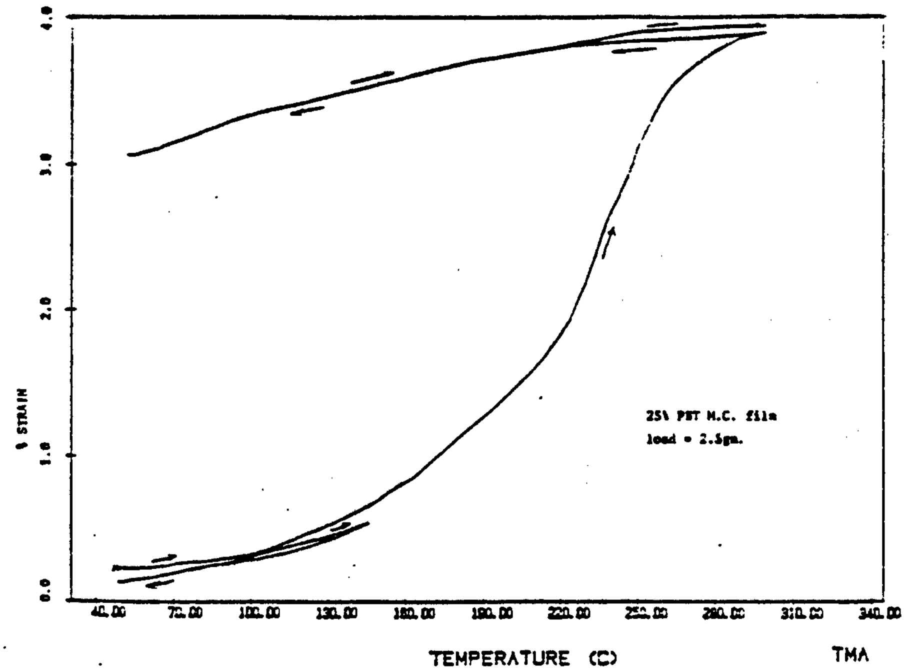

Figure 37: Strain-temperature behavior of 75/25 Nylon 6,6 / PBT composite film.

are different $\epsilon - T$ behavior, as shown in Figures 38 and 39, indicating that high rod-content films are anisotropic. It is suggested that the observed increase of strain with increasing temperature can be associated with three different mechnisms, a continued drying process, a softening of Nylon 6,6 matrix and a relaxation of internal stress built up during the coagulation and press-drying processes. In the early heating stage, below 130°C , the change of sample dimensions is due to the lost of moisture and the softening of the matrix. For the 25% PBT composite film, the softening of the matrix is more pronounced than for the composite films with higher PBT contents. In the later heating stage, the change of sample dimensions is primarily due to relaxation of the internal stresses and the melting of the matrix, where upon the sample goes to its preferrable equilibrium structure; the dimensions of the sample are thus stablized after heat-treatment. In order to support the above interpretation, the $\epsilon - T$ behavior of a 50/50 PBT/Nylon 6,6 film, annealled in a vacuum oven at 300°C for one hour. As shown in Figure 40, the dimensions of the sample stablized after annealing.

The flexural modulus and strength of the compression molded bars were shown in Figure 41. The modulus and strength of the bars that were compression-molded from films increase with increasing PBT content, and are higher than those from powders. While the modulus of the bar compression-molded from powder increases with increasing PBT contents, the strength decreases substantially. This is consistent with the hypothesis of a continuous PBT network, in the coagulated material being destroyed during the pulveriztion process. The network, which would dominate the composite strength, after being mechanically destroyed, could not be healed by heat (280°C) and pressure (2500 psi).

The lamination strength from thermal compression-molding was mainly ascribed to Nylon 6,6 and this interpretation is also supported by sulfuric acid extraction. The bars compression-molded from films were soaked in 98% sulfuric acid and delaminated into 40 layers, corresponding to the original films, within 12 hours. Furthermore, each of these 40 layers remained intact after six months soaking in sulfuric acid. The bars molded from composite powders, when soaked in sulfuric acid, simply disintegrated into individual particles within 12 hours.

Conclusions

Composite films of PBT and Nylon 6,6 spun from dilute solution in MSA show a mechanical and thermomechanical behavior similar to fibers. WAXD shows that

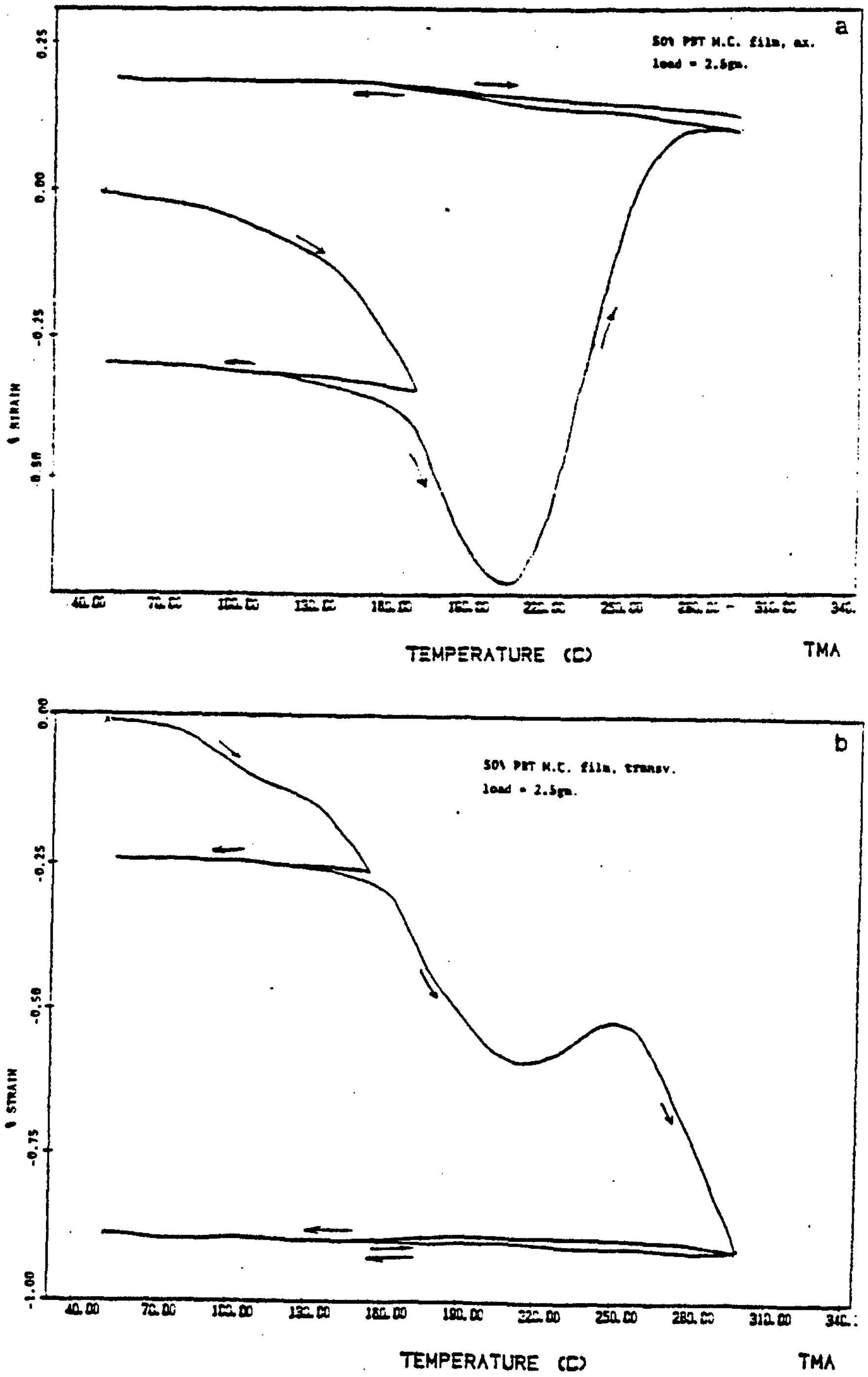

Figure 38: Strain-temperature behavior of 50/50 Nylon 6,6 / PBT film in (a) axial and (b) transverse directions.

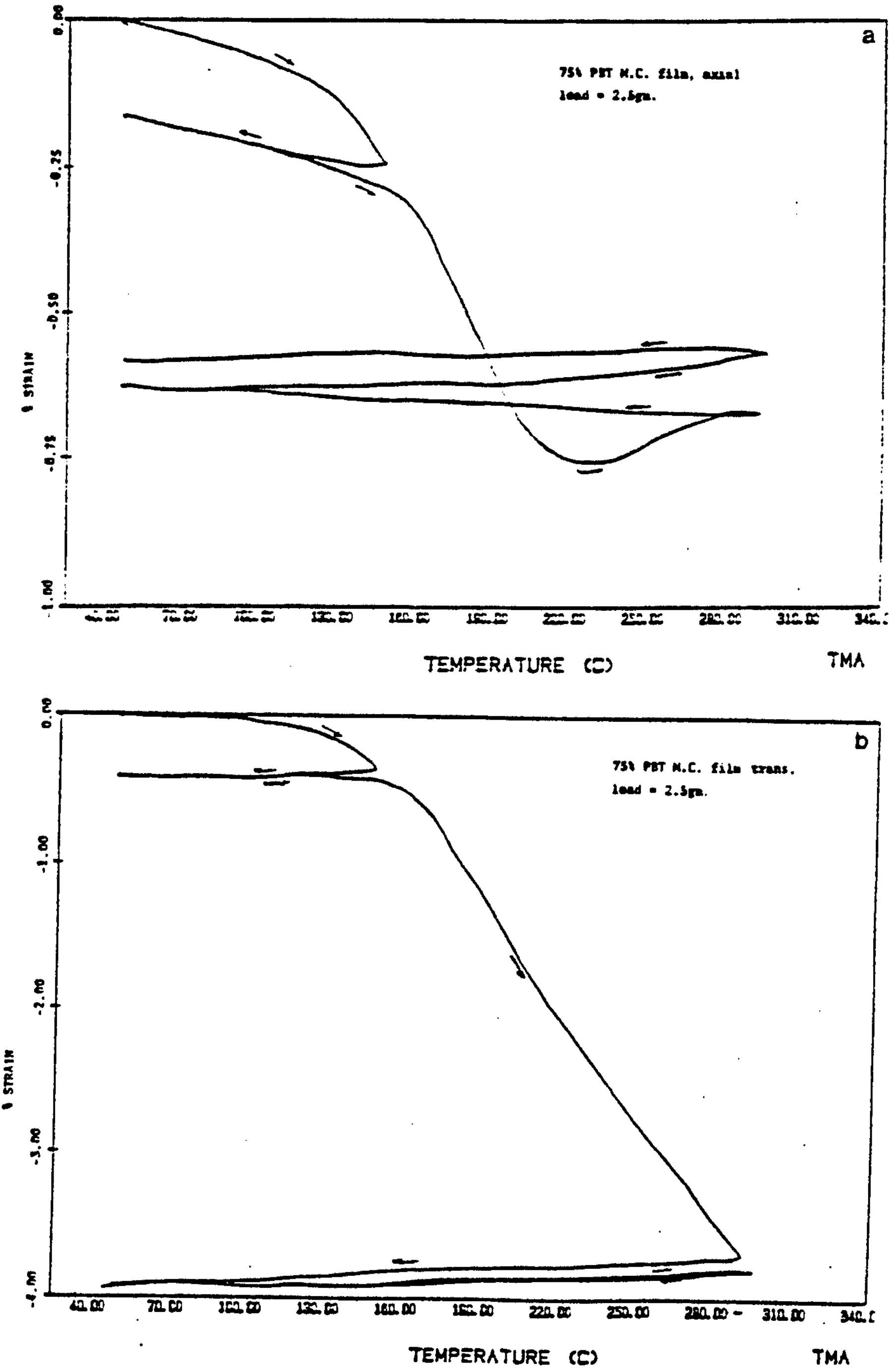

Figure 39: Strain-temperature behavior of 25/75 Nylon 6,6 / PBT film in (a) axial and (b) transverse directions.

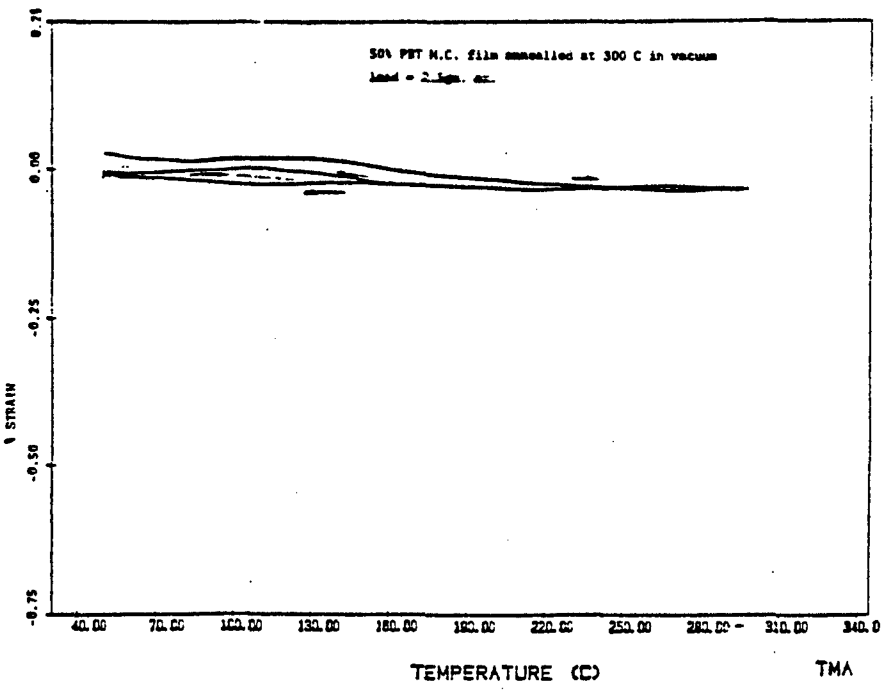

Figure 40: Strain-temperature behavior of a 50/50 Nylon 6,6 / PBT film in the axial direction after annealing at 300°C for one hour.

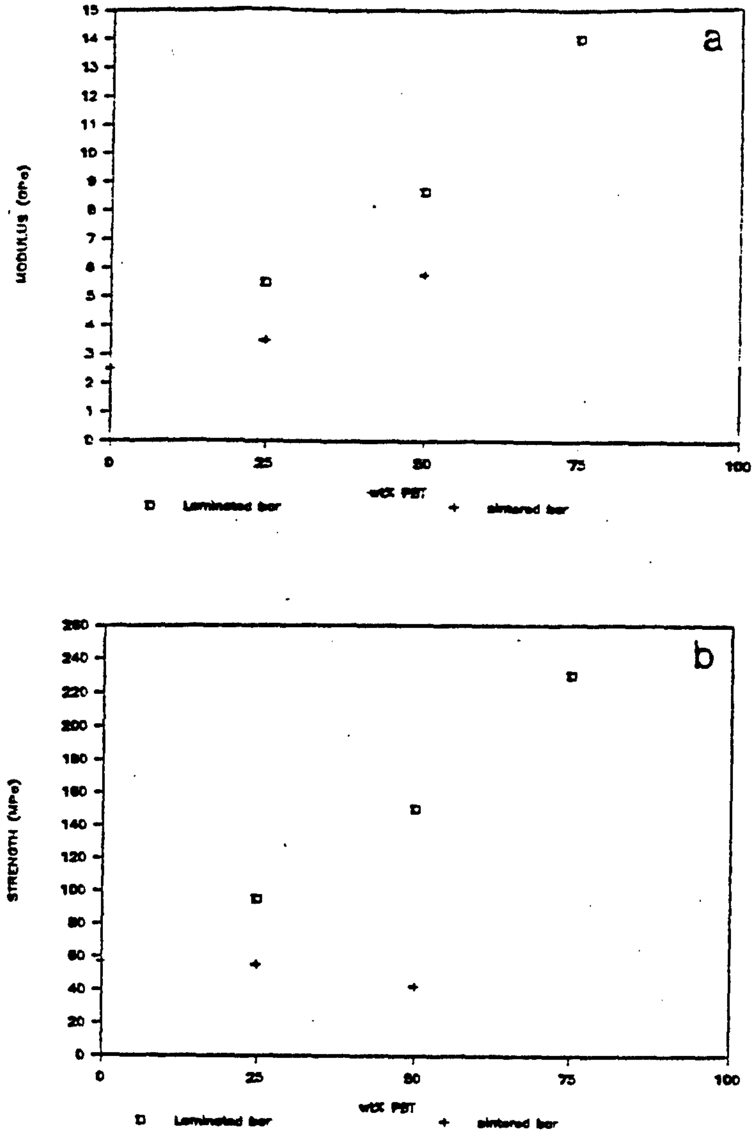

Figure 41: Flexural properties of bars that were compression-molded from composite films and powders (a) flexural modulus, (b) flexural strength.

individual PBT and Nylon 6,6 crystallites were formed during solution spinning and the absence of a shift in the d-spacings is taken as evidence for the presence of separate semicrystalline domains. All the composite films display similar thermal transitions in DSC. The temperature of the melting transition in the composites was very close to the melting temperature of Nylon 6,6 which indicates the presence of macroscopic nylon domains. TMA shows that heat-treatment relaxes the internal stresses in the composite films that are generated during the coagulation and drying processes, and stablizes the composite dimensions. Composites of PBT/Nylon 6,6 could be compression-molded into larger objects, but the lamination strength can be ascribed entirely to Nylon 6,6. No significant reinforcement of PBT in the interface of the laminated composites was obtained.

5. Alternative Processing Techniques

The solution processing of PBT/Nylon 6,6 and PBT/PEEK fibers and films is described in the previous sections of this report. This process involves several steps: 1) dissolution of polymers in MSA, 2) extrusion of the isotropic solution into a coaglation bath, 3) washing and neutralization, and 4) post-processing treatment. Two modified processing schemes were performed and evaluated. The intention of these two alternate processing techniques were to produce a larger form of composites, without using a high pressure extrusion die.

5.1 Experimental

All of the materials used are described in the previous section. The total polymer concentration was 2.0 weight % in MSA. The N66/PBT weight ratio was 70/30 for the sheet spinning process, 75/25 and 50/50 for the direct coagulation of composite solutions.

5.1.1 Sheet Spinning

A spinning cylindrical glass tube capable of producing 20 cm × 20 cm composite sheet was designed. A glass tube containing composite solution is supported in an aluminum holder and sealed by a Teflon stopper; a schematic is shown in Figure 42. The aluminum holder was attached to a lathe which spun the tube at approximately 1700 rpm. By means of centrifugal force, the composite solution was coated uniformly on the inner surface of the glass tube. Water was injected througth the stopper while the lathe was spinning and the composite solution was thereby partially coagulated inside the tube. The partially coagulated solution was removed from the tube and then washed and neutralized as described in the previous section. The composite was folded into a two-layer film, dried between press platens at 1000 psi and 130°C to remove water and laminate the films together.

The dried two-layer laminated films were tested using a modified scarf joint design. A schematic of this apparatus for tension/shear testing is shown in Figure 43(a). The identically milled steel pieces immobilized the samples as the tensile load was applied; Figure 43 shows the test configuration. Angles of 18° and 36° were investigated. The tensile data were obtained as described previously.

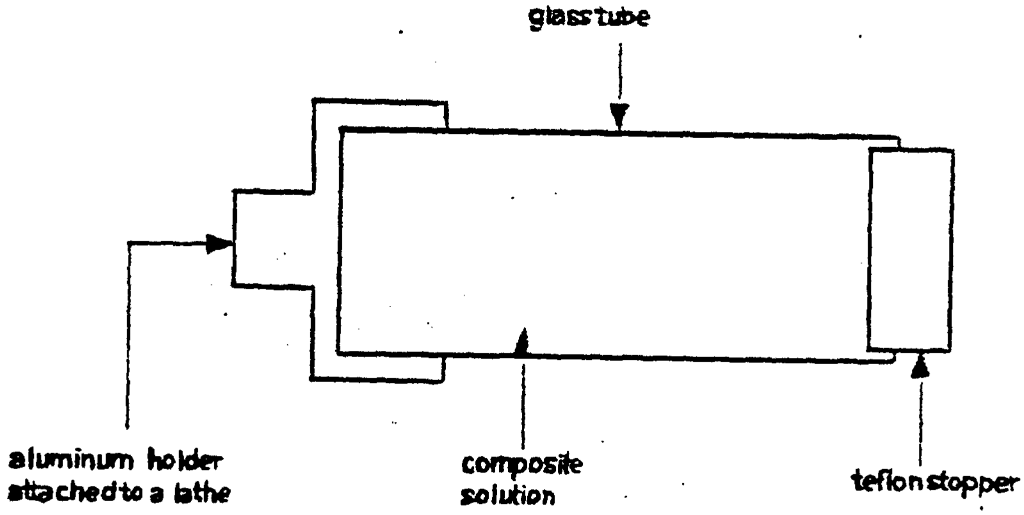

Figure 42: Composite sheet spinning apparatus.

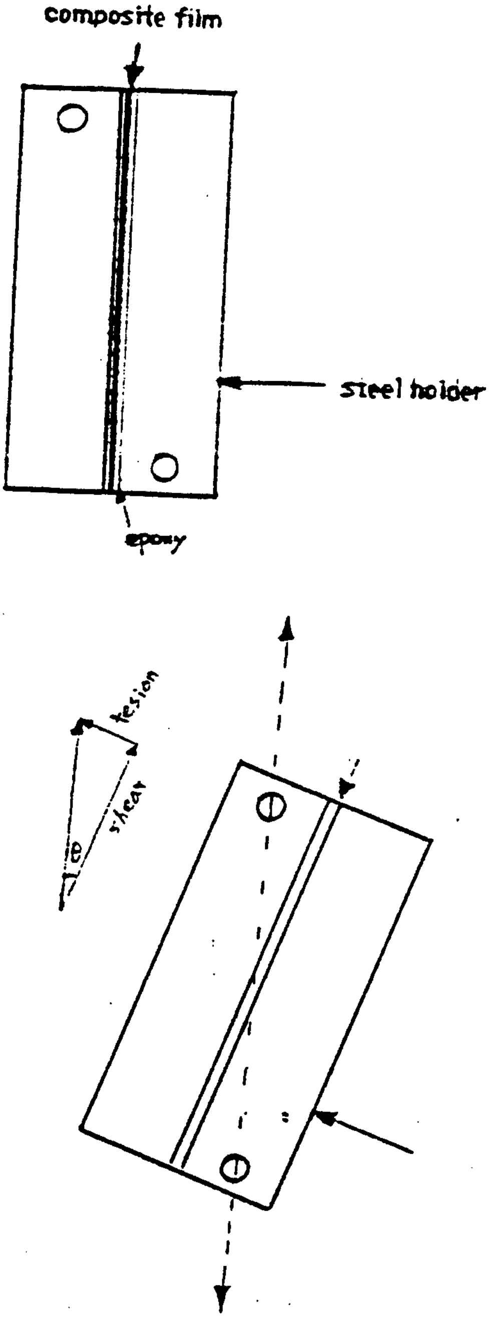

Figure 43: Schematic of the apparatus for tension/shear testing of films.

Direct Coagulation

To prepare a larger shape with a controlled geometry, composite solution was placed in a sintered stainless steel container and then coagulated by exchange of water and acid across the sintered steel membrane. After the composite block was washed and neutralized, it was dried under press platens.

Results and Discussion

The lamiation strength of the two-layer PBT/Nylon 6,6 composites exceeded the interfacial strength of the composite and epoxy. The fracture surface appeared to coincide with the epoxy-composite interface. The fracture stress was 6 MPa, independent of the test angle used. This result indicates that the composites and epoxy had poor adhesive strength. Due to the limitation of the testing apparatus the lamination strength of the two-layer composites is not known.[38]

Because of the essentially static state of the composite solution in the glass tube, no orientation was induced and a planar isotropic sheet was produced. The tensile modulus and strength of 70/30 N66/PBT composites were 3.2 GPa and 25 MPa, which are lower than those of film spinning process. A scanning electron micrograph of the fracture surface in the laminated composite is shown in Figure 44. The interface of the two laminated films could not be observed on the fractured surface.

Direct coagulation of the 50/50 PBT/Nylon 6,6 composite solution in a sintered stainless container caused minor loss of Nylon 6,6, the formation of large voids, and a decrease of the sample volume. Elemental analysis for sulfur, nitrogen, carbon, and hydrogen elements, showed that 10 weight percent of Nylon 6,6 was lost. For the direct coagulation of the 75/25 N66/PBT composite solution, extensive phase separation occurred and Nylon 6,6 was observed floating on top of the coagulated composite. This was due to the locally high concentration of the solvent. Therefore, direct coagulation of the composite solution did not seem feasible for the solution with low PBT content.

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[38] To insure that epoxy did not penetrate through the composite films, two individual layers of the dried composite films were clamped together between two steel pieces immediately after applying epoxy to the steels. The two layers of films did not have any lamination strength after epoxy was completely cured.

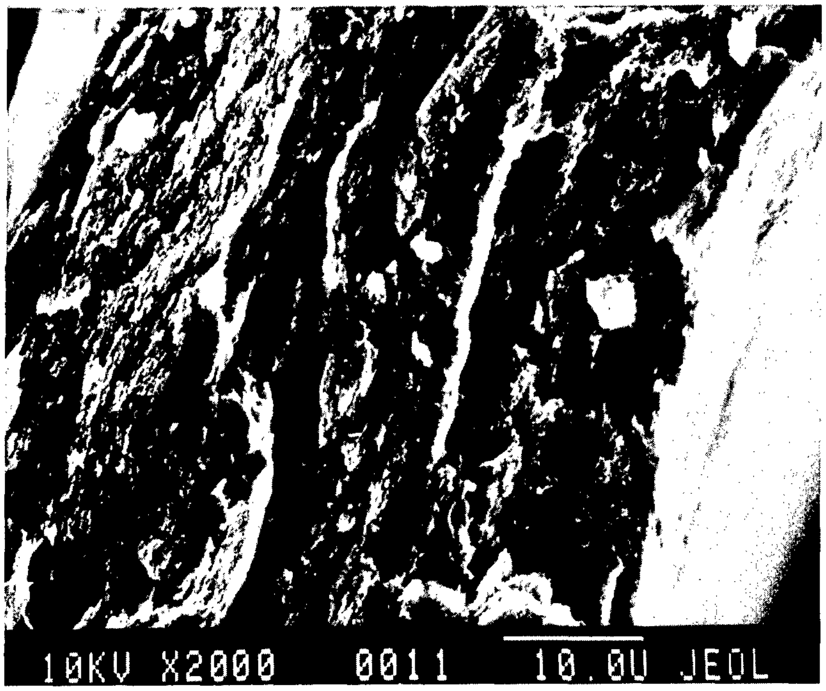

Figure 44: Fracture surface of a two-layer film, laminated in the wet state.

6. Microstructural Investigations of Nylon/PBT Composites

An important parameters in controlling the uniaxial modulus and tensile strength in fiber composites reinforced with rodlike particles is the aspect ratio, $\epsilon = 2(l/d)$, where l is the length of the rods and d is their diameter. The maximum value of ϵ and the ultimate reinforcement in a polymer-polymer composite might be envisaged as a single, rigid rod polymer molecule in a flexible macromolecular matrix, which gives rise to the term "molecular composite." However, the mechanical properties of composite fibers of poly(*p*-phenylene benzobisthia zole) (PBT) and nylon 6,6 (N66) typically do not attain the expected level of reinforcement as discussed in the previous sections of this report. In this Section, we describe an investigation of the microstructure of such materials. The processing of materials in this study was done from solutions with concentrations below the critical value.

We describe the materials, preparation and the mechanical properties of the materials in the next section, which motivate the structural investigations that follow. The structural characterization techniques used were Transmission Electron Microscopy (TEM), wide angle X-ray diffraction (WAXD), selected area electron diffraction (SAED) and small angle X-ray scattering (SAXS).

6.1 Materials

Several samples of single component as well as composite fibers and films were prepared as follows.

1. PBT with a weight average molecular weight of 41,000 was spun into a fiber from a solution containing 2% polymer in a solvent of 97.5% methane sulfonic acid (MSA) and 2.5% chlorosulfonic acid at room temperature. The fibers were coagulated in water, neutralized with NH_4OH and then heat-treated at 650°C (PBT1). The fiber modulus after heat-treatment was 265 GPa.

2. PBT with a weight average molecular weight of 36,000 was spun from 15.7% solution in polyphosphoric acid (PPA), coagulated in water, and heat-treated at 305°C for 2 minutes, (PBT2). The tensile modulus was 100 GPa. The higher concentration and viscosity of the PPA allowed the fibers to be drawn at an 8:1 ratio during the spinning and before coagulation.

3. PBT with a weight average molecular weight of 30,000 was spun from a 5% solution in MSA and coagulated in pure water at 20 °C . The fiber was dried in air and and then heat-treated at 305 °C for 2 minutes at very low tension, (PBT3).

4. Semicrystalline N66 with a weight average molecular weight of 27,400 was supplied by duPont. Fibers were spun without significant draw from a 15% solution in MSA, coagulated for 24 hrs in pure water at 20 °C and then dried in air with very little tension.

5. Two compositions of 50/50 (w/w) and 25/75 PBT/N66 fiber were spun from a 2% solution in MSA at 20 °C . The fibers were extruded through a die with a 330 micron diameter at a speed of 100 cm/min without significant drawing. The fibers were coagulated for 24 hrs in a bath of pure water at 20 °C , and then dried in air. The dried fiber was then heat-treated under very low tensions by passing it through an oven containing a dry nitrogen atmosphere. Further treatment of the fibers is described below.

6. A 60/40 PBT/N66 film, also prepared from dilute solutions in MSA, was obtained from W.W. Adams.

The first sample was prepared for comparison of the composite fibers with the properties of the highly oriented, single-component rodlike material. PBT2 was heat-treated at a lower temperature than PBT1 to correspond to the conditions used in treating the composites after processing. The spinning from rather dilute solution was chosen to simulate the concentrations typical of the spinning of the composites. The N66 could not be spun into fiber form at lower concentrations, nor could it be drawn during spinning.

6.2 Mechanical Properties and Diffraction

Tensile-testing was done on an Instron Universal Testing Machine using a cross-head speed of 0.1 cm/min. Single filaments of the fibers were mounted onto 3 cm gauge length paper tabs with epoxy. The composite fibers in the as-spun state have substantial strength as shown in Table 6 for the 50/50 N66/PBT fiber. The same fiber was also held at 425 °C for four hours to remove the nylon which degrades at 400 °C . After this treatment, the sample retained its fiber form and could be tensile tested. In fact, it was found that the fiber could carry two thirds of the load

Table 6: Mechanical Properties of 50/50 N66/PBT Fiber

	Diameter (microns)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Force at Break (g)
As-Spun	69	7.0	151	58.2
Heated at 425°C for 4 hr	49	16.2	224	38.9

that was carried prior to the treatment, as shown in Table 6. The fiber diameters were measured by optical microscopy and correspond approximately to a 50% volume change.

These data are consistent with the hypothesis that the structure of these fibers does not consist of molecularly dispersed PBT in a continuous nylon "matrix". Rather, there appears to be a continuous structure of PBT that insures the mechanical integrity of the sample when the nylon is removed. The mechanical behavior motivated a study of the microstructure, that is described in what follows.

The wide angle X-ray diffraction pattern from PBT1 in Figure 45a, shows equatorial reflections that are indicative of large crystallites that are well-oriented along the fiber axis. The pattern also shows flat, meridional reflections extending to high orders, confirming a high degree of orientation along the fiber axis. The crystal structure of PBT has been investigated by various groups[39]

Our results for the d-spacings are in agreement with the results of previous investigations for PBT that are listed in Table 7, along with the strength of the reflections.

The diffraction pattern in Figure 45b is that of PBT2. The equatorial reflections are less sharp and the third equatorial reflection is not resolved, as in the case of PBT1. However, the meridional reflections extend to high orders. PBT2 shows a lower degree of alignment along the fiber axis than PBT1 which was heat-treated at a higher temperature; this is also reflected in the lower modulus of 100 GPa *vs.* 265

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[39] E.J. Roche, T. Takahashi and E.L. Thomas, *Am. Chem. Soc. Symp. Ser., 141,* 303 (1980); J. A. Odell, A. Keller, E.D.T. Atkins, and M. J. Miles, *J. Mater. Sci., 16,* 3309 (1981).

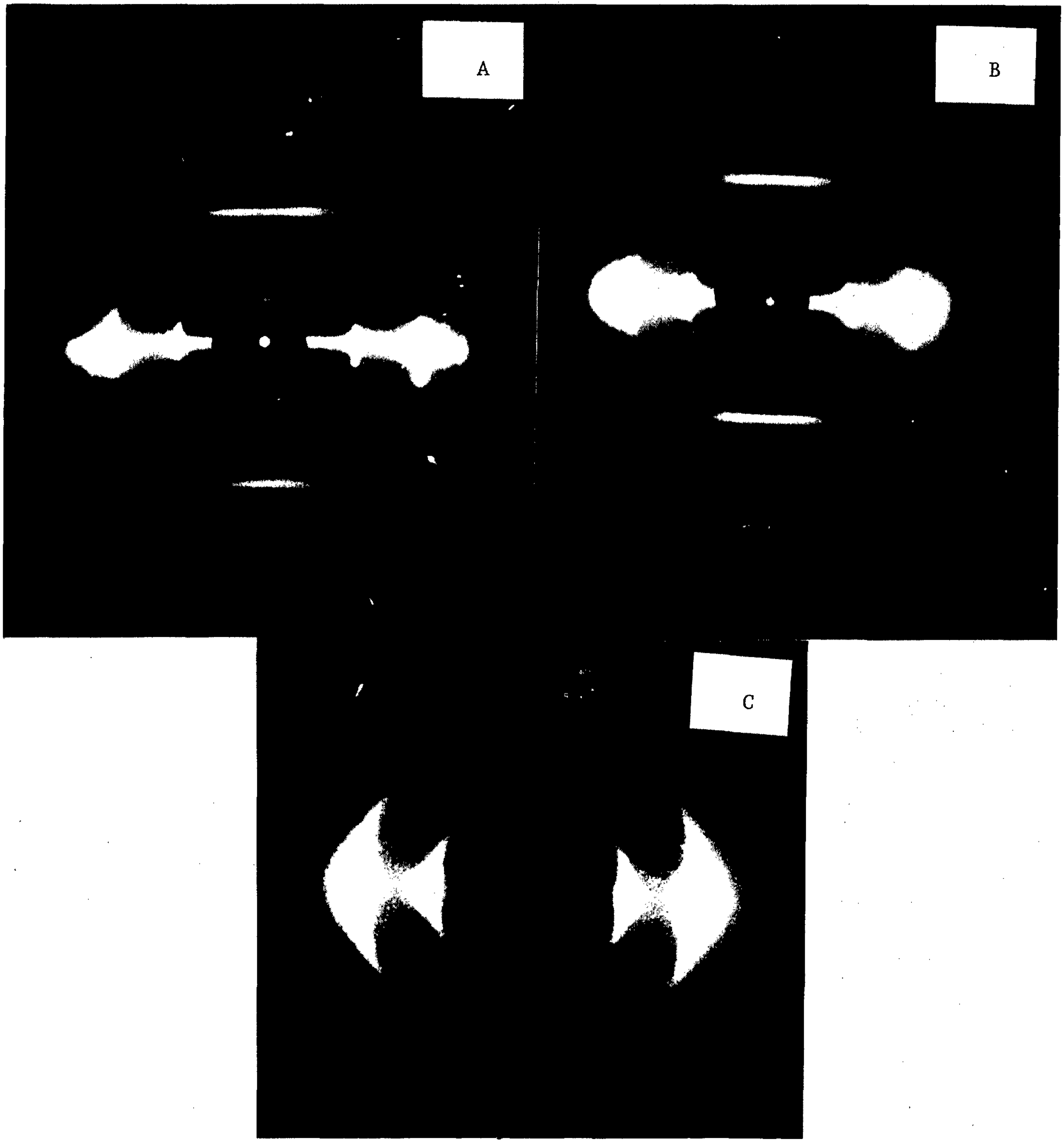

Figure 45: WAXD pattern of PBT (a) drawn and heat-treated at 650°C (b) drawn and heat-treated at 305°C (c) spun from 5% (MSA) solution, and heat-treated at 305°C .

Table 7: **The d-spacings and strengths of the reflections measured from WAXD for the composites, along with the literature values for PBT and nylon 6,6.**

d-spacing, Å	plane	comment
Nylon 6,6		
12.8	001	weak
6.4	002	medium
4.4	100	v. strong
3.7	010	v.v. strong
PBT		
12.4	001	strong (meridonal)
5.9	200	strong
3.5	110	v. strong
60/40 Composite		
11.8	001	PBT
4.5	100	N66
3.5	110 & 010	PBT & N66

GPa. The WAXD pattern of PBT3 is shown in Figure 45c. The strong arcing of the reflections indicates poor orientation along the chain axis, which should be expected because very little drawing is possible in the dilute spinning solutions.

Nylon 6,6 fibers spun from 15% solution in MSA were also examined by WAXD; the diffraction pattern is shown in Figure 46. The pattern has sharp Debye rings corresponding to interplanar spacing of 3.78, 4.47, and 6.56 Å. These correspond to the 010, 100, and 002 reflections of the triclinic structure of Bunn and Garner.[40]

The WAXD pattern of the 60/40 PBT/N66 film is shown in Figure 47. This pattern shows no specific orientation and consists of three Debye rings with interplanar spacings of 12.3 and 3.53 Å that correspond to PBT and 4.43 Å which is the (100) N66 reflection.

The replica detachment techniques reported by Minter, *et al.*[41] and Krause, *et al.*[42] were used to prepare the PBT samples, but were not successful on molecular composite samples with high nylon content, due to the cohesive nature of the nylon. For microtomy, the fibers were embedded in Spurr's low viscosity resin. Cryomicrotomy at -80°C with a glass knife was attempted, but the sections were generally too thick for useful selected area electron diffraction (SAED). Moreover, image contrast in bright field was found to be primarily due to the uneven thickness of these sections. However, cryomicrotomy at -80°C with a diamond knife was used successfully to cut thin sections for useful electron diffraction on N66 and PBT/N66 composite samples.

The 25/75 PBT/N66 fiber was examined with SAED. Diffraction patterns of both crystalline N66 and PBT were occasionally observed in the fiber, demonstrating that ordered domains of both N66 and PBT exist and therefore that the sample is phase-separated to some extent. TEM work was carried out on these samples to find the lower limit of the size of the phase-separated domains. Dark field imaging has not been successful, due to the radiation sensitivity of N66.

6.3 Transmission Electron Microscopy

The results described in the last section indicate that the samples were phase separated on some size scale and that there may be a network structure of PBT giving rise to high strengths. This motivated a study of these materials by TEM,

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[40] C. W. Bunn and E. V. Garner, *Proc. Roy. Soc., 189A,* 39 (1947).

[41] J.R. Minter, K. Shimamura and E.L. Thomas, *J. Mat. Sci., 16,* 3303 (1981).

[42] S.J. Krause, T.B. Haddock, G.E. Price, P. G. Lenhert, J.F. O'Brien, T.E. Helminiak and W.W. Adams, *J. Polymer Sci. (Phys.), 24,* 1991 (1986).

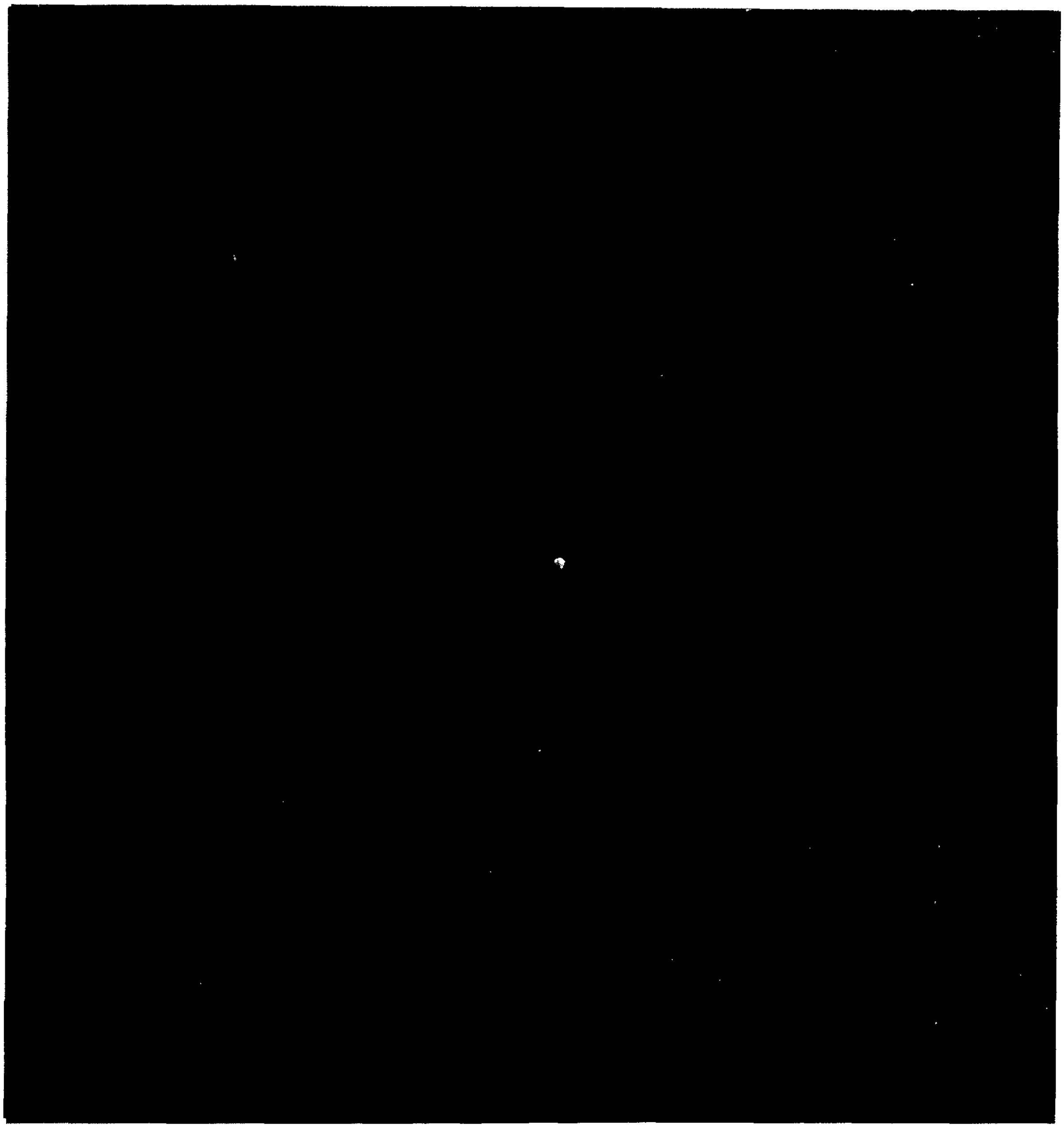

Figure 46: WAXD pattern of Nylon 6,6 fiber spun from 15% solution in MSA.

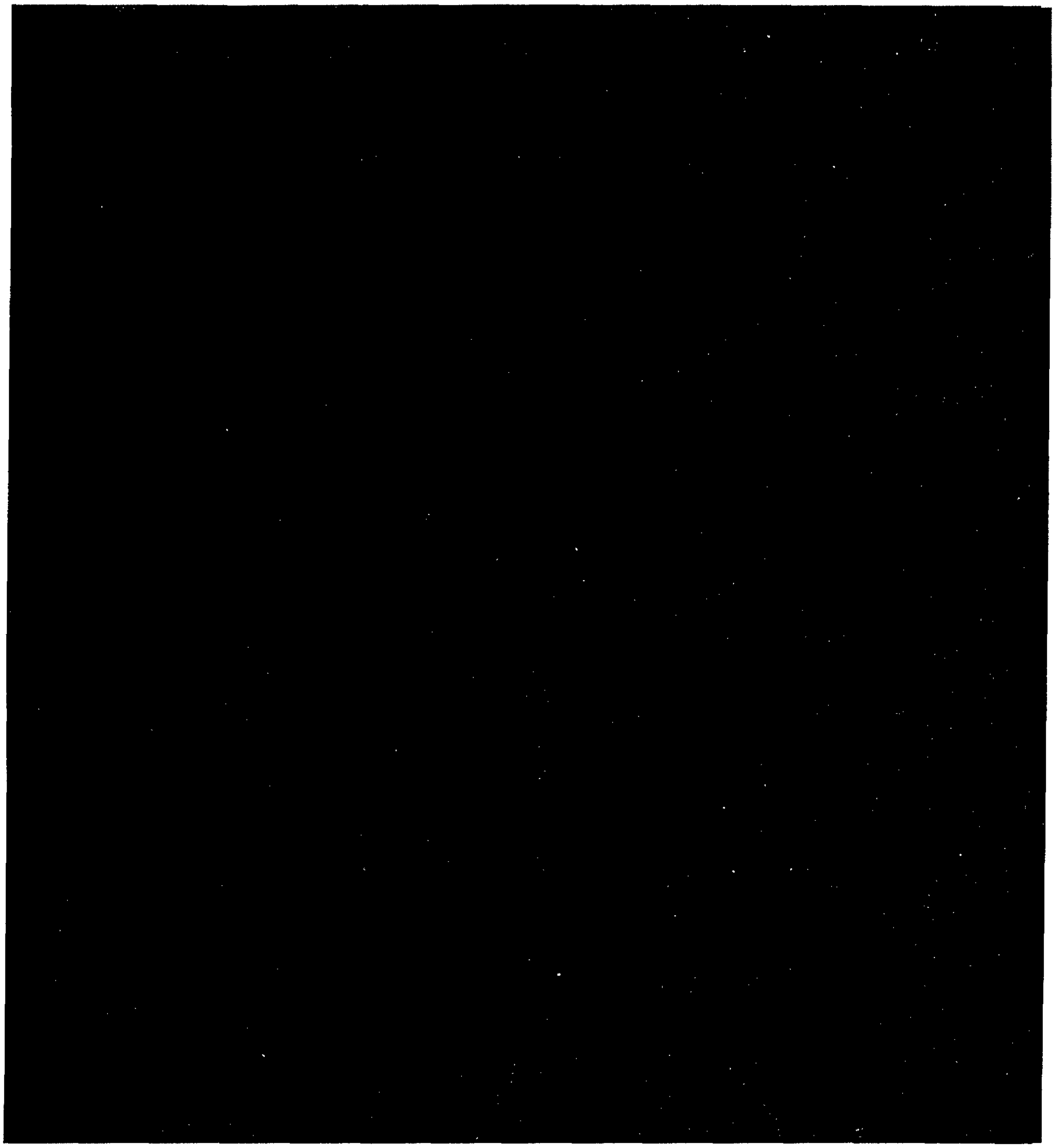

Figure 47: WAXD pattern of PBT/Nylon 6,6 composite film of 60/40 composition.

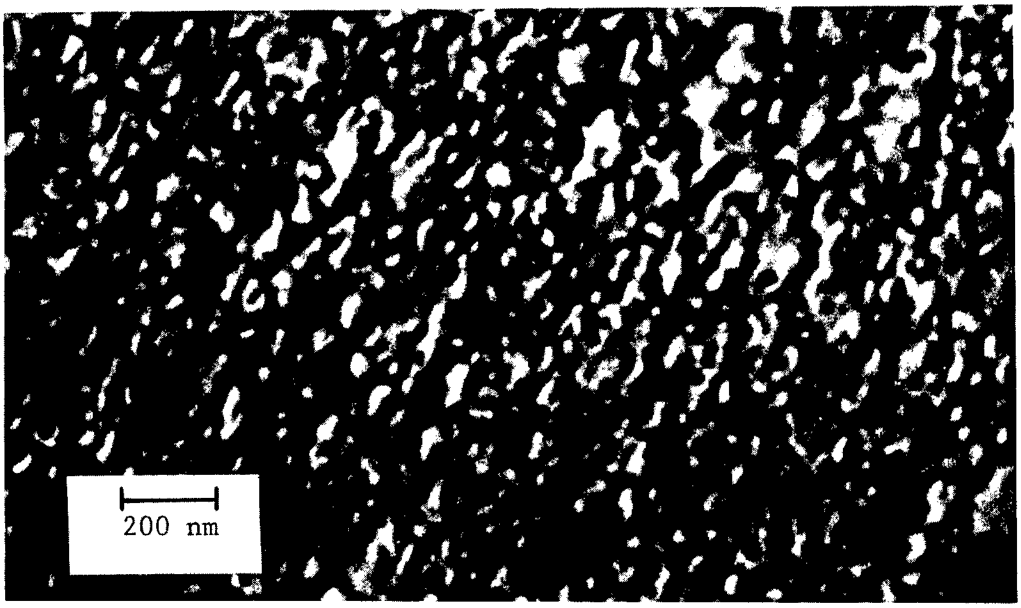

Figure 48: TEM image of 50 / 50 PBT/Nylon 6,6 Fiber.

using the sample preparation technique described by Cohen and Thomas for neat PBT materials in which a microfibrillar structure has been seen.[43] A PBT/N66 fiber, 50/50 in composition, was spun from a 2% solution in MSA and coagulated in a water bath. The water was then exchanged with ethanol and the fiber was gradually infiltrated by epoxy resin. After curing, the sample was then cryomicrotomed using a diamond knife at -80°C .

A TEM image of the fiber is shown in Figure 48. We interpret the figure as a two-dimensional image of an unoriented cross section of a *microfibrillar* network. The dark fibrils range in diameter from approximately 100 to 450 Å. These probably consist of PBT along with some nylon, although it is difficult to interpret due to the

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[43] Y. Cohen and E.L. Thomas, *Polym. Eng. Sci.*, *25*, 1093 (1985).

radiation sensitivity of nylon 6,6.

6.4 Small Angle X-Ray Scattering

The characteristic size scale for phase separation in the composites was studies using SAXS, a technique that has proven useful to study oriented single-component PBT films as described by Cohen and Thomas.[44] SAXS studies of the 60/40 PBT/N66 film were performed on a Kratky camera. A plot of the smeared intensity, $\tilde{I}(S)$, versus S, the scattering vector, is shown in Figure 49. The scattering was by a flat film with the x-ray beam perpendicular to the extrusion direction.

The interpretation of the SAXS data can be made either for the case of highly oriented samples, or for the unoriented case; Figure 47 shows that this film was essentially unoriented and the analysis proceeds as follows. We assume that PBT/N66 composite consists of two phases, ignoring the density difference of crystalline and amorphous nylon in comparison to PBT and ignoring the presence of any voids. When the interfacial boundaries in the sample are sharp, an estimate for the scale of phase separation can be made from the scattering data at high S, where a Porod analysis gives an estimate of the surface to volume ratio. The smeared scattered intensity is given as

$$\tilde{I}(S) = \tilde{K}_p\, S^{-3} + F_l \qquad (1)$$

where K_p is the Porod constant and F_l is the fluid-like scattering. The structure invariant, Q, is given by

$$Q = \int_0^\infty 2\pi S \tilde{I}_1(S)\, dS \qquad (2)$$

where $\tilde{I}_1(S) = \tilde{I}(S) - F_l$. The invariant is related to the mean squared electron density fluctuation, $< \eta^2 >$, the sample-to-detector distance, L, and the wavelength of the radiation, λ, as

$$Q = L\lambda < \eta^2 > \qquad (3)$$

In a two-component system, with sharp interfaces, we also have

$$< \eta^2 >= (\Delta\rho)^2 \phi_1 (1 - \phi_1) \qquad (4)$$

where the mass density difference between the two components is $\Delta\rho$ and ϕ_1 is the volume fraction of component 1 (PBT). The Porod constant is given by

$$\tilde{K}_p = \frac{L\lambda}{8\pi^2}\, (\Delta\rho)^2\, \frac{s}{v} \qquad (5)$$

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[44] Y. Cohen and E.L. Thomas, *J. Polym. Sci.*, in press (1987).

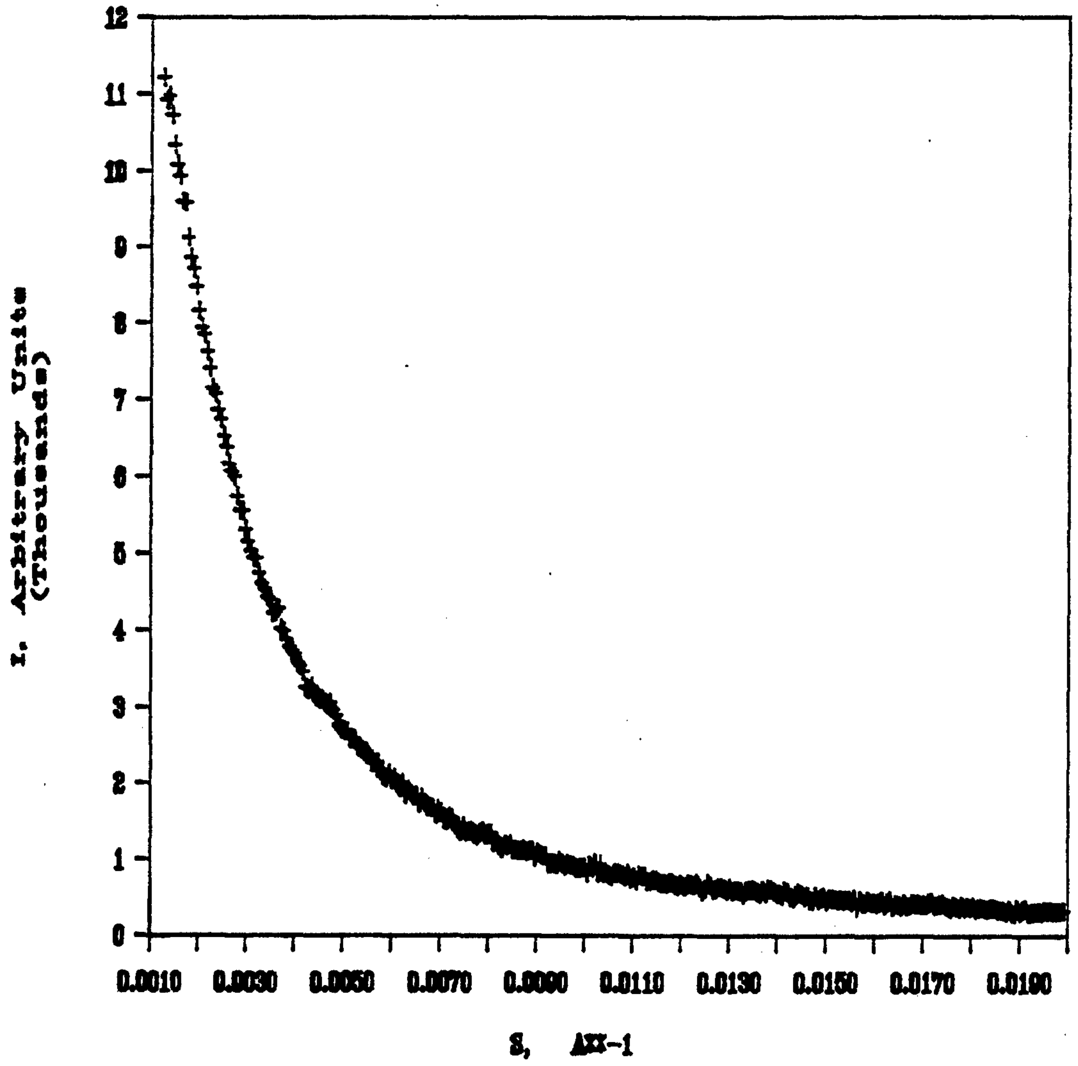

Figure 49: Plot of the smeared scattered intensity (arbitrary units) versus the scattering vector ($\text{\AA}^{-1}$).

where s is the interfacial area between the phases and v is the sample volume. Thus, the surface to volume ratio can be found from the Porod constant, the invariant and the composition as

$$\frac{s}{v} = 8\pi^2 \frac{\tilde{K}_p}{Q} \phi_1 (1 - \phi_1) \tag{6}$$

A plot of $S^3\tilde{I}(S)$ versus S^3 is given in Figure 50; $\tilde{K}_p = 8.6 \times 10^{-4}$ counts/Å^3 from the intercept and F_l = 238 counts from the slope. The invariant can be estimated from the data in Figure 49 after subtracting F_l. We find Q =1.2 counts/Å^2 and $s/v = 0.014$ Å^{-1} in the film sample.

A characteristic dimension of the microstructure can be estimated if a model for the geometry is assumed. For example, if the phases are random and unoriented, the Debye correlation function, $\gamma(r)$, is defined as[45]

$$\gamma(r) = \alpha \exp(-r/l_c) \tag{7}$$

where l_c is the correlation length for the two-phase material. We can also define a correlation length for each phase

$$l_i \equiv \frac{4\phi_i}{s/v} \tag{8}$$

Then the correlation length in the Debye correlation function, Equation 7, is given by[46]

$$\frac{1}{l_c} = \frac{1}{l_1} + \frac{1}{l_2} \tag{9}$$

If complete phase separation is assumed and the density of N66 and PBT are taken as 1.14 and 1.60 g/cc, the volume fractions are $\phi_{PBT} = 0.52$ and $\phi_{N66} = 0.48$. We find $l_{N66} = 148$ Å, $l_2 = 136$ Å and $l_c = 71$ Å.

6.5 Discussion and Conclusions

The SAXS evidence indicates that there is phase separation in the composite samples on a scale of approximately 70 Å, which is comparable to the value of 80-100 Å reported for the microstructure of, as-spun PBT[47] The tendency to form a microfibrillar structure is also consistent with the fact that PBT fibers can be spun

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[45] P. Debye and A.M. Bueche, *J. Appl. Phys.*, *20*, 518 (1949) and P. Debye, H.R. Anderson and H. Brumberger, *J. Appl. Physics*, *28*, 679 (1957).

[46] L. Kahovec, G. Porod and H. Ruck, *Kolloid Z.*, *133*, 16 (1953).

[47] Y.Cohen and E.L. Thomas, *Polym. Eng. Sci.*, *25*, 1093 (1985).

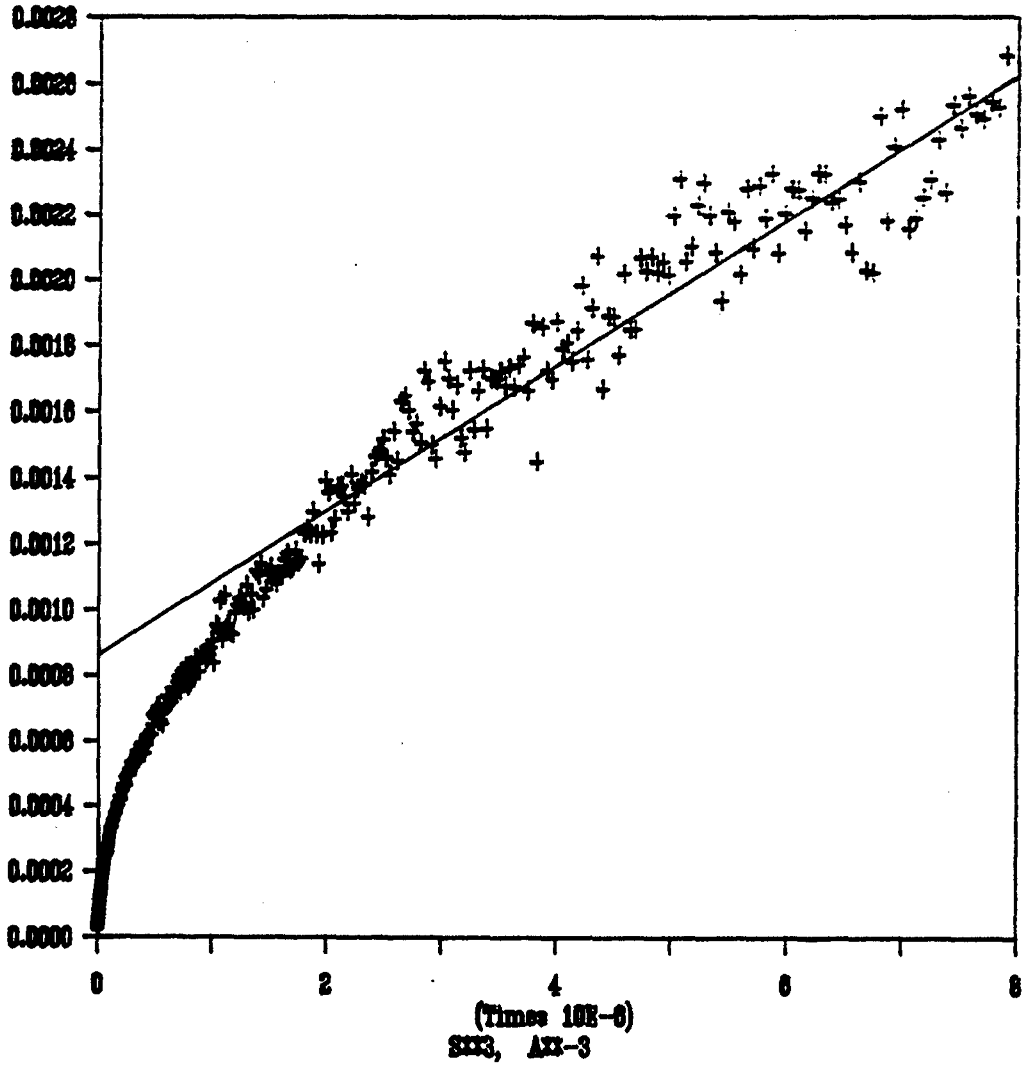

Figure 50: Kratky plot of $\tilde{I}(S)^{-2/3}$ versus S^2 for the SAXS data.

from a solution of 0.1% PBT in MSA, which is considerably lower than the concentration of PBT solutions used in the processing of these materials (2%). Moreover, the mechanical tests show that a 50/50, PBT/N66 fiber heated at 425°C (above the decomposition temperature of N66), maintained two thirds of its strength after most of the N66 was removed. We conclude that the microctructure of these composites is not the "molecular composite" but consists of a microfibrillar structure of PBT in a separate and partially crystalline N66 phase.

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