Microstructural Investigations of PBT/Nylon 6,6 Composites

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Synopsis

The microstructure of composites made from blends of poly(*p*-phenylene benzobisthiazole) [PBT] and nylon 6,6 has been investigated with wide-angle X-ray diffraction, selected area electron diffraction, and small-angle X-ray scattering techniques. The composite samples investigated were spun in both fiber and film forms from dilute solutions of methane sulfonic acid.

The structure of the composites was found to be a microfibrillar network of PBT in a matrix of partially crystalline nylon 6,6. The diameters of the PBT microfibrils were in the range of 30 to 70 Å.

INTRODUCTION

One of the 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 benzobisthiazole) (PBT) and nylon 6,6 (N66) typically do not attain the expected level of reinforcement.[1] The aim of this study is to investigate the microstructure of such materials.

PBT is intractable and cannot be processed in the melt; the PBT/N66 blends can only be processed from ternary solutions of PBT, nylon, and strong acids such as methane sulfonic acid (MSA). The solution properties and phase behavior are important in controlling the properties of blends of these two polymers. Specifically, it is necessary to avoid the isotropic-nematic phase transition in order to prevent large-scale phase separation prior to coagulation by the addition of a nonsolvent, for our present samples, water. The processing of materials in this study was done from solutions with concentrations below the critical value, which is defined as the maximum concentration of polymers in a solution at a given temperature that is still optically isotropic.[2]

We describe the processing and the mechanical properties of the materials in the next section to motivate the structural investigations that follow. The

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structural characterization techniques used were wide-angle X-ray diffraction (WAXD), selected area electron diffraction (SAED), and small-angle X-ray scattering (SAXS).

MATERIALS

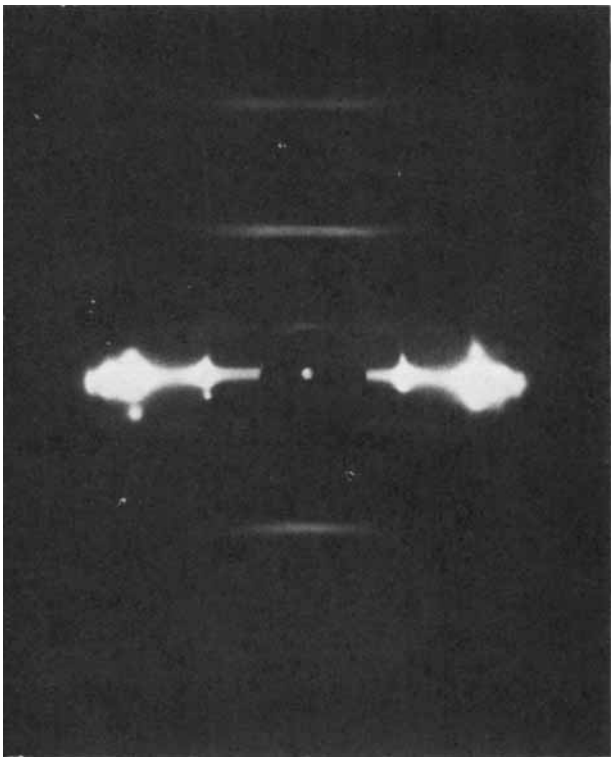
Several samples of single component as well as composite fibers and films were prepared as follows.

1. PBT was spun into a fiber from a solution containing 2% polymer in a solvent consisting 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 modulus after heat treatment was 265 GPa. The properties and processing of these fibers is discussed further in Refs. 2 and 7.
2. PBT was spun from 15.7% solution in polyphosphoric acid (PPA), coagulated in water, and heat-treated at 305°C for 2 minutes under low tensions (PBT2). 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. The tensile modulus was 100 GPa.
3. PBT was spun from a 5% solution in MSA and coagulated in pure water at 20°C. The fiber was dried in air and then heat-treated at 305°C for 2 minutes at very low tension (PBT3).
4. Semicrystalline N66 was supplied by DuPont. Fibers were spun without significant draw from a 15% solution in MSA, coagulated for 24 h 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 h in a bath of pure water at 20°C, and then dried in air. The dried fiber was then heat-treated under very low tension 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 according to the methods described in Ref. 2, 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.

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 gage length paper tabs with epoxy. The composite fibers in the as-spun state have substantial strength; the tensile modulus of the 50/50 N66/PBT fiber was 7.0 GPa and the tensile strength was 151 MPa. The same fiber was held at 425°C for 4 h to remove the nylon which degrades at 400°C. After this treatment, the sample retained its fiber form, with a modulus of 16.2 GPa and a strength of 224 MPa. In fact, the force to break the fiber after heat treatment was 38.9 g, which was approximately two thirds of the value for the as-spun material (58.2 g). The diameter of the as-spun fiber was 69 μm, compared to a value of 49 after the extended heat treatment. The diameters



(a)

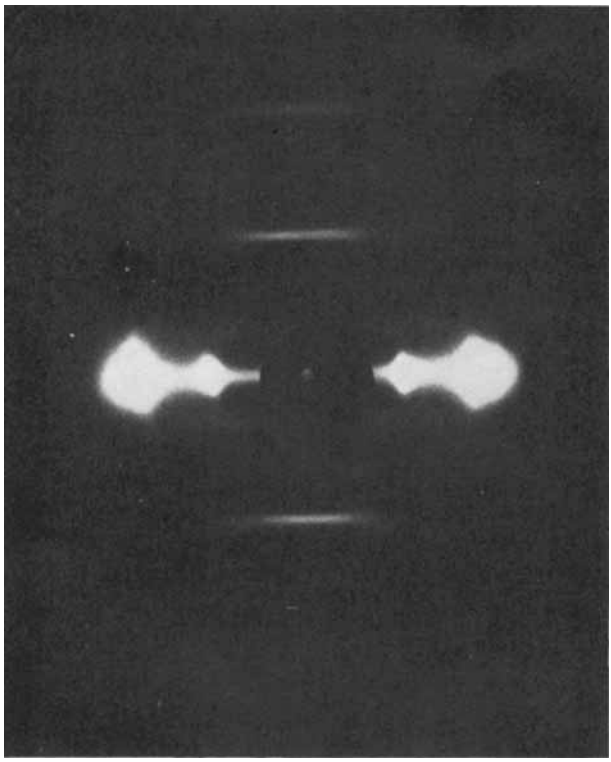
Fig. 1. WAXD pattern of PBT (a) drawn and heat-treated at 650°C (PBT1), (b) drawn and heat-treated at 305°C (PBT2), (c) spun from 5% (MSA) solution, and heat-treated at 305°C (PBT3).

were measured by optical microscopy and correspond approximately to a 50% volume change.

These data are inconsistent with the hypothesis that the structure of these fibers consists of molecularly dispersed PBT in a continuous nylon "matrix." Rather, there appears to be some sort of a continuous structure of PBT that insures the mechanical integrity of the sample when the nylon is removed. This mechanical behavior motivated a study of the detailed microstructure, that is described below.

The wide-angle X-ray diffraction pattern from PBT1 [Fig. 1(a)], shows equatorial reflections that are indicative of large crystallites that are well oriented along the fiber axis. The pattern also shows flat, meridional reflections again 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.[3,4] Our results for the *d*-spacings are in agreement with the results of previous investigations that are listed in Table I, along with the strength of the reflections.

The diffraction pattern in Figure 1(b) 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 again extend to high



(b)

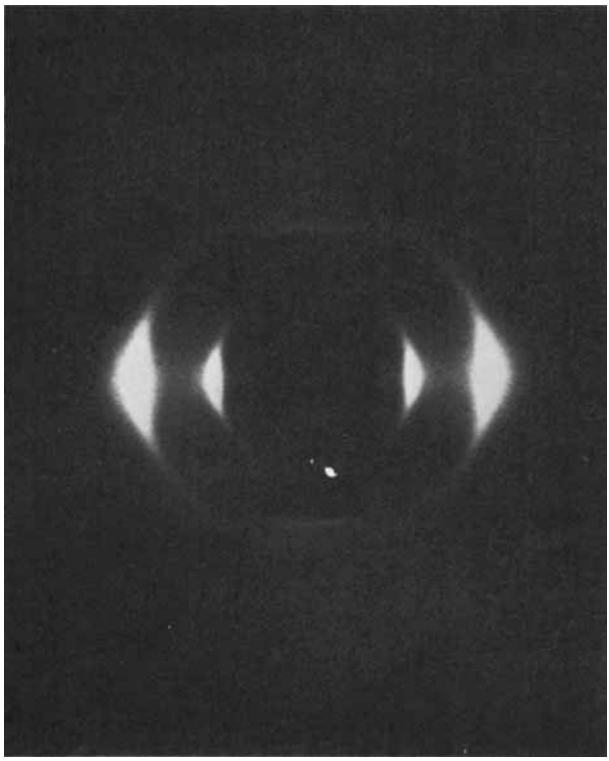
Fig. 1. (*Continued from the previous page.*)

order. 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 versus 265 GPa. The WAXD pattern of PBT3 is shown in Figure 1(c). The broad azimuthal arcing of the reflections indicates poor orientation of the chains in the draw direction, which should be expected since very little drawing is possible for these 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 2. 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.[5]

The WAXD pattern of the 60/40 PBT/N66 film is shown in Figure 3. This pattern shows no specific orientation and consists of three Debye rings, two that correspond to interplanar spacings of 12.3 and 3.53 Å in PBT and one corresponding to 4.43 Å which is the strong (100) N66 reflection.

The replica detachment techniques reported by Minter et al.[6] and Krause et al.[7] were used to prepare the PBT samples for transmission electron microscopy (TEM), 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



(c)

Fig. 1. (*Continued from the previous page.*)

TABLE I
The *d*-Spacings and Strengths of the Reflections Measured from WAXD for the Composites, Along with the Literature Values for PBT[4] and Nylon 6,6[5]

d-Spacing (Å)	Plane	Comment
Nylon 6,6		
12.8	001	Weak
6.4	002	Medium
4.4	100	Very strong
3.7	010	Very very strong
PBT		
12.4	001	Strong (meridonal)
5.9	200	Strong
3.5	110	Very strong
60/40 Composite		
11.8	001	PBT
4.5	100	N66
3.5	110 & 010	PBT & N66

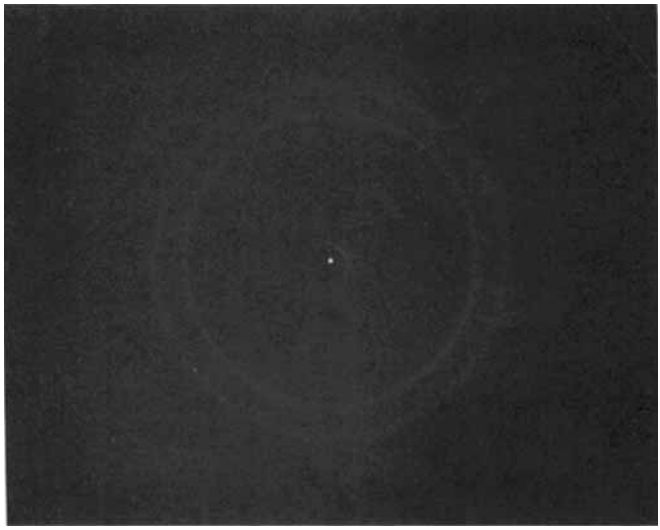


Fig. 2. WAXD pattern of nylon 6,6 fiber spun from 15% solution in MSA.

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

Fig. 3. WAXD pattern of PBT/nylon 6,6 composite film of 60/40 composition.

domains. Dark field imaging has not been successful, due to the radiation sensitivity of N66.

SMALL-ANGLE X-RAY SCATTERING

The characteristic size scale for phase separation in the composites was studied using SAXS, a technique that has proven useful to study oriented single-component PBT films as described by Cohen and Thomas.[8] 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 4. The scattering was by a flat film with the incident X-ray beam perpendicular to the extrusion direction.

Analysis of the SAXS data is possible either for the case of highly oriented samples, or for the unoriented case; Figure 3 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

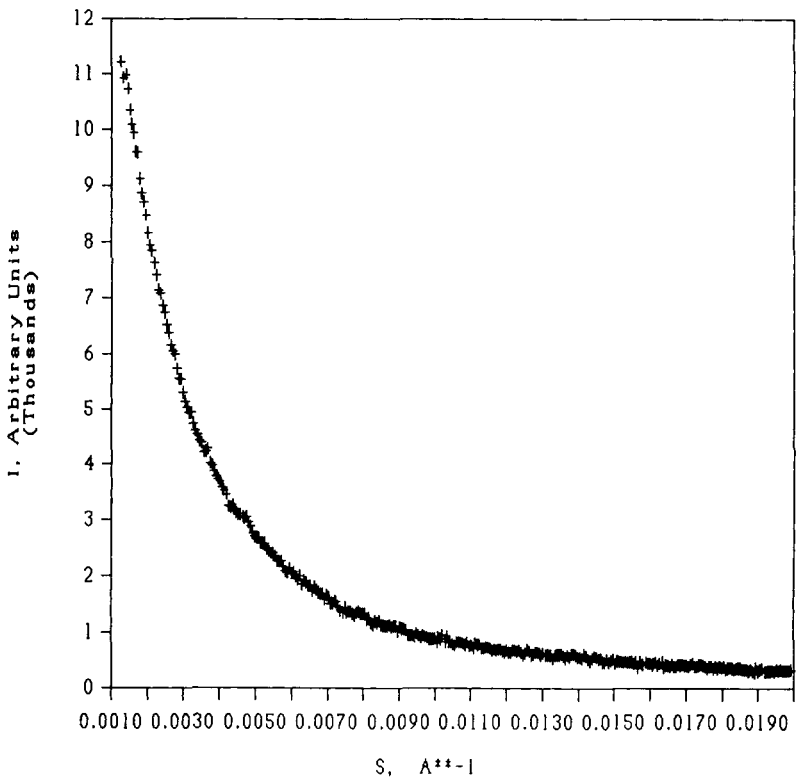


Fig. 4. Plot of the smeared scattered intensity (arbitrary units) versus the scattering vector ($Å^{-1}$).

the surface to volume ratio. The smeared scattered intensity is given as

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

where $\tilde{K}_p$ is the Porod constant and F_l is the fluild-like scattering. The structure invariant, Q, is given by

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

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

$$Q = L\lambda\langle \eta^2 \rangle \tag{3}$$

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

$$\langle \eta^2 \rangle = (\Delta\rho)^2 \phi_1(1 - \phi_1) \tag{4}$$

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

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

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 5; $\tilde{K}_p = 8.6 \times 10^{-4}$ counts/Å^3 from the intercept and $F_l = 238$ counts from the slope. The invariant can be estimated from the data in Figure 4 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, for a random, unoriented, two-phase system, the Debye correlation function, $\gamma(r)$, is defined as[9]

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

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

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

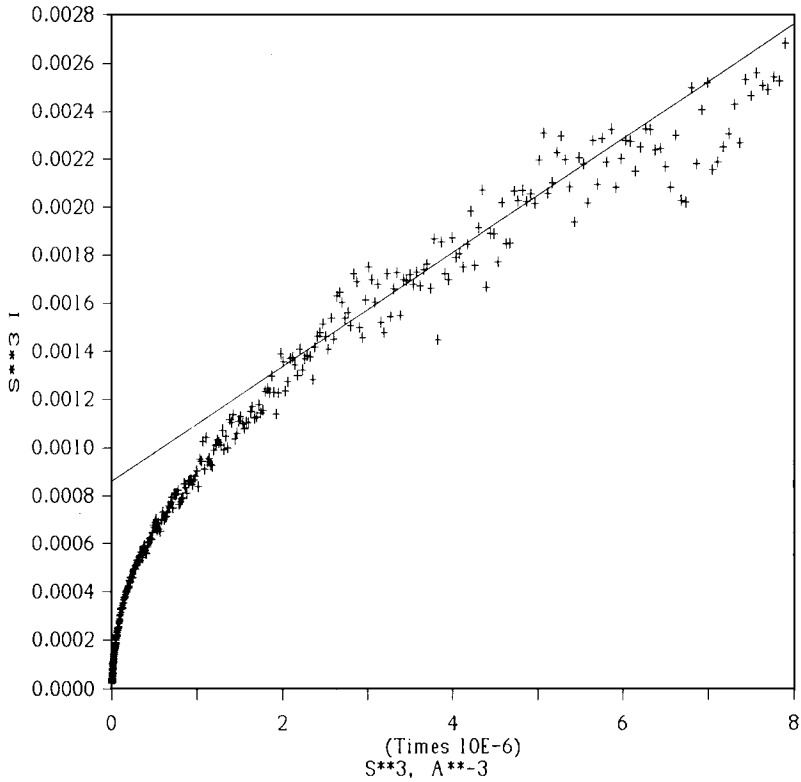


Fig. 5. Kratky plot of $S^3\tilde{I}(S)$ versus S^3 for the SAXS data shown in Figure 4.

Then the correlation length in the Debye correlation function, Eq. (7), is given by[10]

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

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 $\phi_{\mathrm{PBT}} = 0.52$ and $\phi_{\mathrm{N66}} = 0.48$. We find $l_{\mathrm{N66}} = 148$ Å, $l_2 = 136$ Å and $l_c = 71$ Å.

Another estimate of the size scale, emphasizing the data at lower S, can be made from the Debye plot of the SAXS data. The scattered intensity, $I(S)$, is the Fourier transform of $\gamma(r)$

$$I(S) = \frac{A}{\left(1 + 4\pi S^2 l_c^2\right)^2} \tag{10}$$

where A is a constant. The smeared scattered intensity, minus the correction for fluid-like scattering is found to be

$$\tilde{I}(S) - F_l = \frac{A'}{\left(1 + 4\pi^2 l_c^2 S^2\right)^{3/2}} \tag{11}$$

where $A' = A/2l_c$. Thus, the quantity $(\tilde{I}(S) - F_l)^{-2/3}$ should be a linear

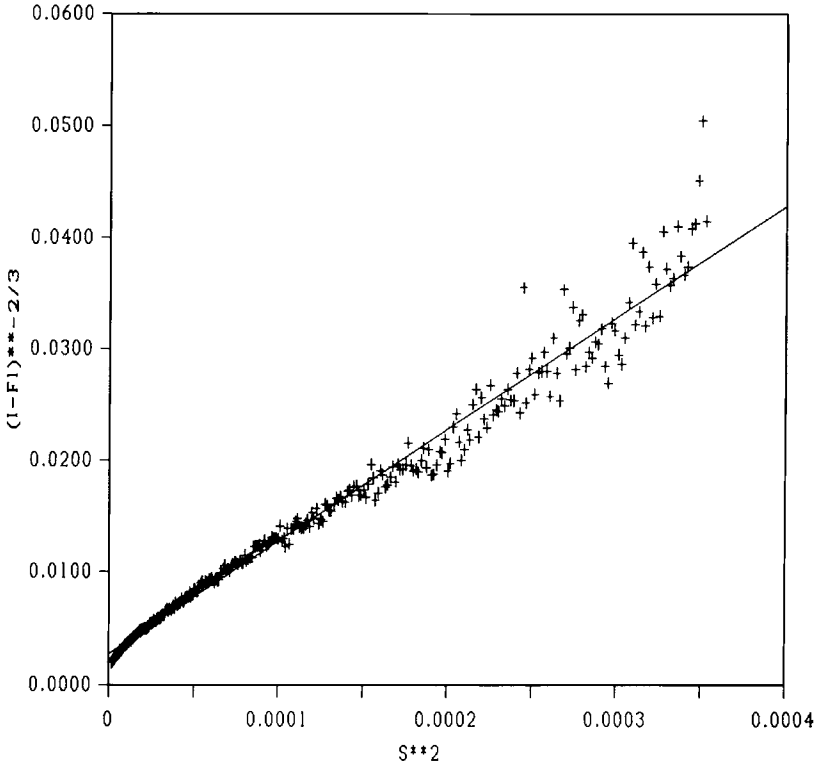


Fig. 6. Debye plot of $(\tilde{I}(S) - F_l)^{-2/3}$ versus S^2 for the SAXS data shown in Figure 4.

function of S^2. The correlation length, found from the linear fit of the data as shown in Figure 6, is $l_c = 30$ Å.

DISCUSSION AND CONCLUSIONS

The evidence from SAXS indicates that there is a phase separation in the composite samples, consistent with a microfibrillar structure of the PBT phase; the microfibril diameters are in the range of 30 to 70 Å. This size range is comparable to the value of 100 Å reported for the microstructure of pure, as-spun PBT.[8] The tendency to form a microfibrillar structure is also consistent with the fact that PBT fibers can be spun from a solution of 0.1% PBT in MSA, which is considerably lower than the concentration of PBT solutions used in the processing of the composite materials studied here (2%).

Wide-angle X-ray scattering and selected area electron diffraction studies confirmed the presence of separate crystalline or semicrystalline domains of both N66 and PBT in the composites. The mechanical tests also showed 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 microstructure 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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