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MOLECULAR COMPOSITES-RODLIKE POLYMER REINFORCING AN AMORPHOUS POLYMER MATRIX

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

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Final Report for Period October 1978 — June 1979

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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FRED E. ARNOLD
Work Unit Scientist

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

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The concept of molecular composites utilizing rod-like aromatic heterocyclic polymers as reinforcements in coil-like heterocyclic polymer matrices has been demonstrated. A series of polymer films, prepared by vacuum casting from various solutions of rod-like polymer, amorphous polymer, and solvent, were fabricated and tested. Morphological studies of these films were conducted using x-ray diffraction and scanning electron microscopy. The results of the morphology studies showed pronounced structure and definite evidence of the ordering of the

rod-like polymer. In some cases, a second phase or conglomeration was evidenced. Analysis of the scanning electron microscopy pictures indicated that the second phase was itself a composite of rod-like and amorphous polymer. The mechanical testing showed significant increases in tensile modulus and strength with only ten percent rod-like polymer in the matrix; this was especially true after stretching of the film had been performed. Analytical equations developed for composite materials were used to calculate theoretical properties of the conglomerates and rods. All results and conclusions are presented in detail in this report.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3 Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. Co-authors were Mr. G. Husman, Dr. T. Helminiak, M. Wellman, and Mr. W. Adams, Air Force Materials Laboratory (AFWAL/MLBP); and Dr. D. Wiff and Mr. C. Benner, University of Dayton Research Institute.

This report covers research conducted from October 1978 to June 1979.

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SUMMARY

The concept of molecular composites has been demonstrated. Although the studies to date are very preliminary, the concept appears to be promising. Future work will be oriented toward characterizing the solution behavior of the polymer blends and developing processing techniques to achieve better morphology control as well as orientation control.

SECTION I

INTRODUCTION

Recent developments in the synthesis of rod-like aromatic heterocyclic polymers have generated a significant interest in the development of these polymers as structural materials. A large effort is currently being expended to characterize these polymers and to develop them into useful product forms, such as fibers, films, or sheets. The Air Force Materials Laboratory and the Air Force Office of Scientific Research are engaged in a research and development program directed toward the preparation and processing of very high strength, environmentally resistant polymers for use as structural materials in aerospace vehicles. The objective is the attainment of mechanical properties for a structural material comparable with those currently obtained with fiber reinforced composites, but with significantly higher environmental resistance and without the use of a fiber reinforcement. The materials chosen for this effort are the rigid-rod, extended-chain, aromatic-heterocyclic polymers whose physical and chemical properties show promise for achievement of the program objectives. However, these materials present special processing problems because of the extended-chain, rigid-rod structural character of the molecules. Present processing requires strong mineral or organic acid solvents and there is little opportunity to influence the polymer morphology once the material is in the solid state. One potential concept for the utilization of the rod-like polymers is molecular composites. This concept consists of blending a rod-like aromatic heterocyclic polymer with a coil-like aromatic heterocyclic polymer. The intent is to reinforce the coil-like or amorphous polymer with the rod-like polymer, thus forming a composite on the molecular level analogous to chopped fiber reinforced composites. This report discusses a study performed to demonstrate the feasibility of this concept.

SECTION II

MATERIALS AND PROCESSING

A variety of rod-like and amorphous polymers were studied in this investigation. The chemical structures of the various polymers are shown in Table 1. The polymer blends studied and their weight percents are listed in Table 2.

The polymer blends studied were processed as thin films by vacuum casting from dilute solutions. The general procedure followed was to prepare a 1-2 percent polymer solution in methane sulfonic acid and put the solution in a specially fabricated circular flat bottomed casting dish. The dish was then placed and leveled in the bottom of a sublimator. The cold finger of the sublimator was maintained at 25°C and the sublimator was continuously evacuated and heated to 60°C to facilitate the removal of the methane sulfonic acid. After the films were formed and removed from the casting dish, they were generally dried at 100°C in a vacuum oven for 24 to 48 hours. The films produced were approximately 5-cm in diameter and varied from 1.3×10^{-3} to 16.5×10^{-3} cm in thickness. Most of the films retained approximately 20 to 30 percent residual solvent.

TABLE 1

POLYMERS STUDIED

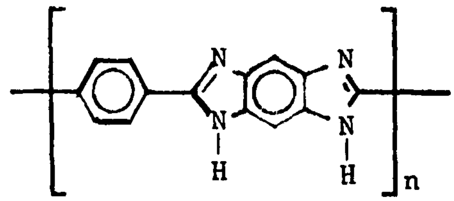
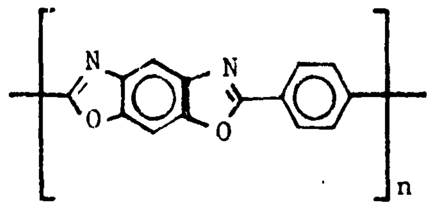
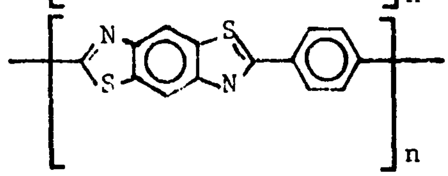
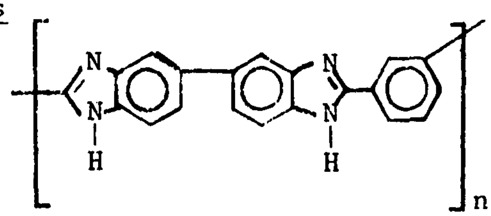
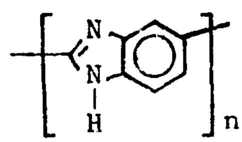
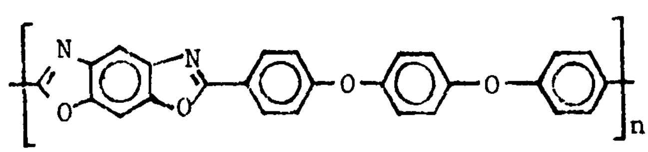
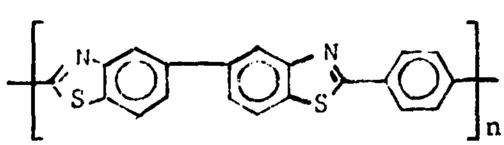
	CHEMICAL STRUCTURE	ACRONYM
Rod-Like Polymers		
1.		PDIAB
2.		PBO
3.		PBT
Coil-Like Polymers		
1.		M-PBI
2.		AB-PBI
3.		PEPBO
4.		PPBT

TABLE 2

POLYMER BLENDS STUDIED

	Matrix	Reinforcement	Weight Percents of Reinforcements
1.	M-PBI	PDIAB	0, 20, 50, 75
2.	AB-PBI	PDIAB	0, 10, 20, 30, 57, 75
3.	PPBT	PBT	0, 25, 50, 75
4.	PEPBO	PBO	0, 25, 50, 60, 75
5.	AB-PBI	PBO	0, 10, 20, 30

SECTION III

SPECIMEN PREPARATION AND TESTING

The films were cut with a razor blade into 0.635cm strips. Strips at least 2.54cm in length were used for testing, while shorter pieces were used for as-cast morphological studies. Tests were performed on an Instron universal test machine at a cross-head speed of 5.08cm (0.02 inches) per minute. After initial specimen breaks occurred, remaining pieces were retested until the length became too short to reasonable grip and test (approximately 1.5cm). This provided not only as-cast data, but also mechanically stretched data. In addition, some specimens were plasticized with methanol to permit larger amounts of stretching. After these specimens were dried of the methanol, they were mechanically tested to determine the effect of the stretching.

The results of the testing of the AB-PBI/PDIAB blends are presented in Table 3. These blends were studied in the most detail because they appeared to be the most compatible polymer blends and gave the most interesting results. Several general observations can be made about the data. In the as-cast (no stretching) polymer blends, the rod-like polymer appears to act more as a filler than a reinforcement. However, stretching (both mechanical and solvent) appears to provide some orientation and demonstrates a real reinforcing effect (strength and modulus increases). The reinforcing effect, however, does not follow a rule-of-mixtures behavior,[1] i.e., the 10 percent blend being proportionally better than the 20 percent or 30 percent blends. The

TABLE 3

MECHANICAL PROPERTIES - AB-PBI/PDIAB BLENDS

% Rod Polymer	Stretch/ % Area Reduction	Modulus (G Pa)	Strength (M Pa)	Strain (%)
0	None	1.03	79.92	98
0	Mech./20	2.00	134.36	43
0	Solvent/60	3.37	105.42	12
10	None	2.00	70.28	46
10	Mech./37	4.60	161.92	28
10	Solvent/57	6.86	315.56	14
20	None	1.58	44.10	26
20	Mech./37	2.38	82.68	15
20	Solvent/70	7.17	253.55	9
30	None	1.25	36.52	14
30	Mech./20	2.16	71.66	22
30	Solvent/60	8.96	189.48	4
57	None	1.34	28.73	5
75	None	1.51	22.32	4

57 and 75 percent blends could not be stretched because of their low strain-to-failure and no significant reinforcing was observed. Similar trends were observed with other polymer blends studied; however, the data presented in this report represents the most significant results.

SECTION IV

MORPHOLOGICAL STUDIES

The morphology of the films has been studied using scanning electron microscopy and x-ray diffraction. A careful study of scanning electron microscopy photographs explains many of the observed test results. Figures 1-4 show scanning electron microscopy photographs of the surfaces of the 0%, 10%, 20%, and 30% rod films respectively. The morphological changes are obvious. Figures 5-8 show edge views of liquid nitrogen fractures of the same four films. Several observations have been made from the study of the scanning electron microscopy photographs. A second phase or conglomerate is present in the blends. These conglomerates in the as-cast (not stretched) films appear to be symmetric and saucer shaped with an aspect ratio (length/thickness) of 2-3. The absolute size of the conglomerates increases with increasing rod content. The volume content of the conglomerates in the film is greater than the volume content of rod-like polymer, indicating that the conglomerates contain both rod-like polymer and amorphous polymer. Stretching the films changes the shape of the conglomerates, increasing the length and decreasing the width and thickness. This can be seen in Figures 9 and 10 which show edges perpendicular to and parallel to the stretch direction of a 30% rod, solvent stretched film.

A tabulation of some of the morphological phenomena is presented in Table 4. Although the measurements made were

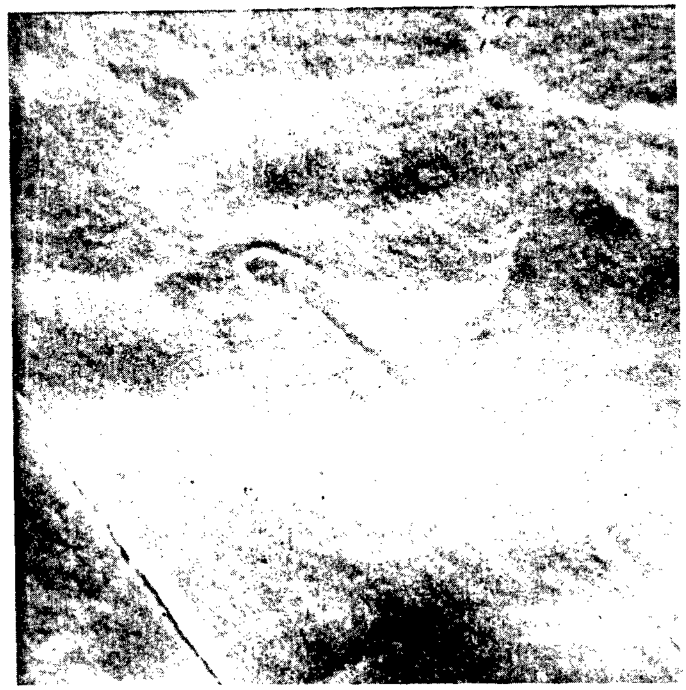


Figure 1. AB-PBI/PDIAB Polymer Blends
100% AB-PBI Surface - 3000X

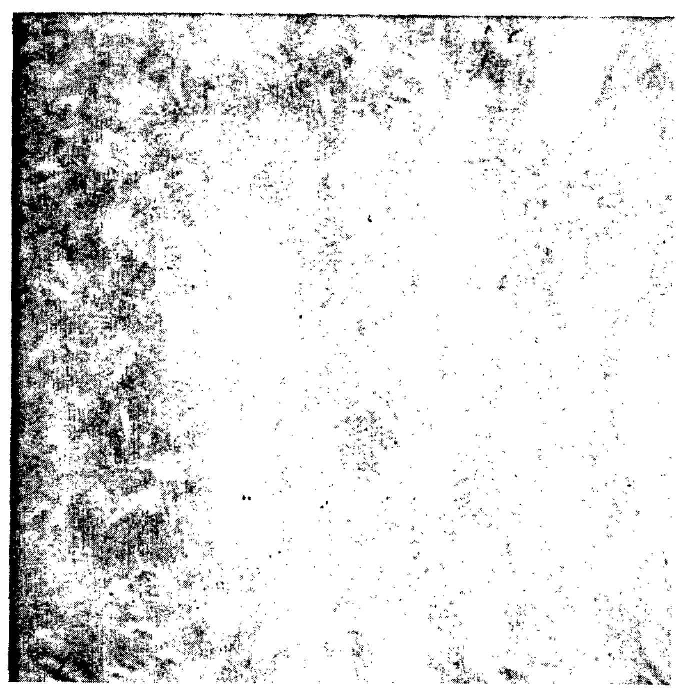


Figure 2. AB-PBI/PDIAB Polymer Blends
90% AB-PBI/10% PDIAB Surface - 3000X

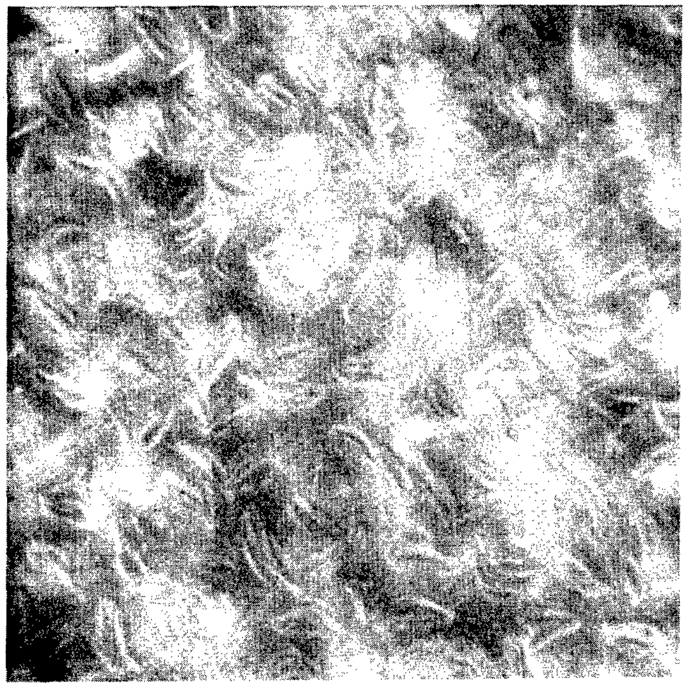


Figure 3. AB-PBI/PDIAB Polymer Blends
80% AB-PBI/20% PDIAB
Surface - 3000X

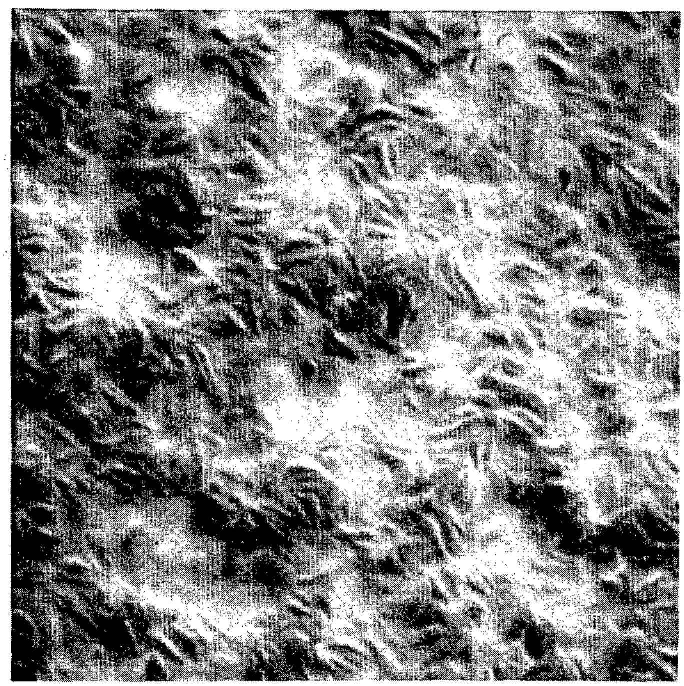


Figure 4. AB-PBI/PDIAB Polymer Blends
70% AB-PBI/30% PDIAB
Surface - 3000X

Figure 5. AB-PBI/PDIAB Polymer Blends
100% AB-PBI Edge - 3000X

Figure 6. AB-PBI/PDIAB Polymer Blends
90% AB-PBI/10% PDIAB
Edge - 3000X

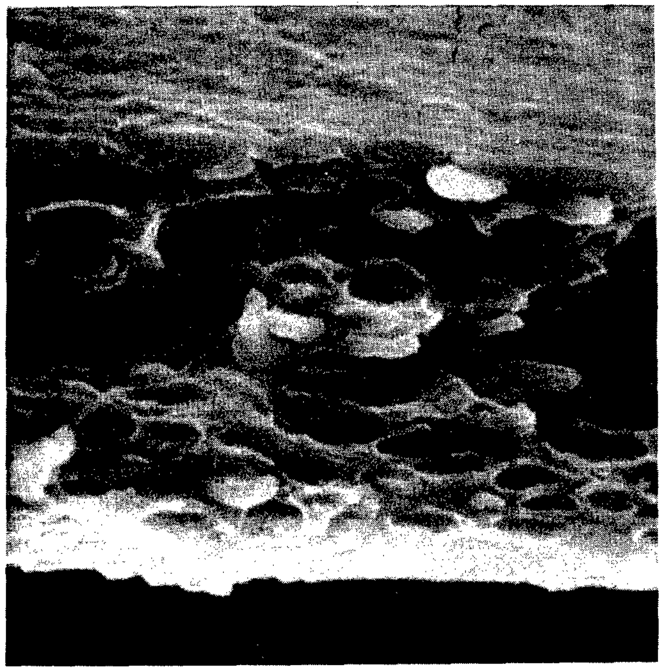


Figure 7. AB-PBI/PDIAB Polymer Blends
80% AB-PBI/20% PDIAB
Edge - 3000X

Figure 8. AB-PBI/PDIAB Polymer Blends
70% AB-PBI/30% PDIAB
Edge - 3000X

Figure 9. AB-PBI/PDIAB Polymer Blends
70% AB-PBI/30% PDIAB Solvent Stretched
Edge Perpendicular to Stretch 5000X

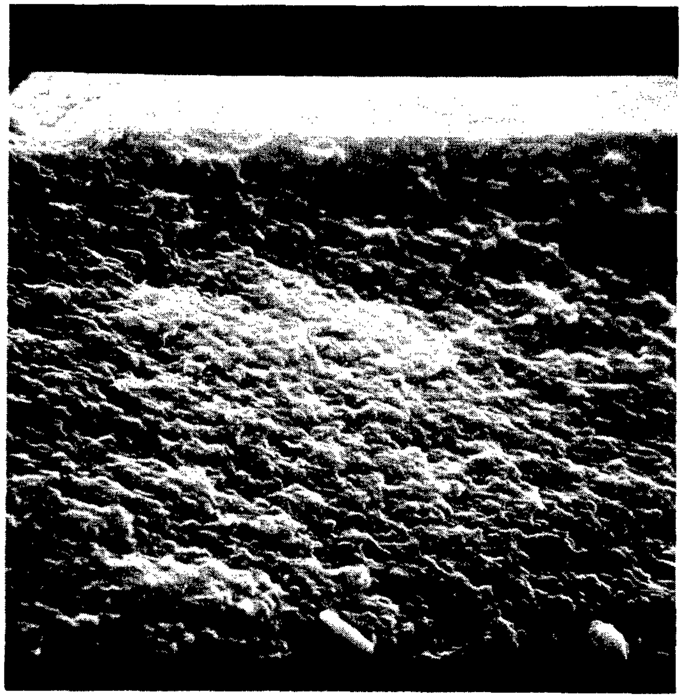
Figure 10. AB-PBI/PDIAB Polymer Blends
70% AB-PBI/30% PDIAB Solvent Stretched
Edge Parallel to Stretch 5000X

TABLE 4

MORPHOLOGY OF AB-PBI/PDIAB BLENDS

Conglomerate	90/10	80/20	70/30
Length (cm x 10^{-4})			
Initial	1.78	3.81	5.84
Mechanically Stretched	2.54	5.08	7.62
Solvent Stretched	3.81	5.08	6.35
Thickness (cm x 10^{-4})			
Initial	.635	1.27	1.91
Mechanically Stretched	.508	.889	1.27
Solvent Stretched	.254	.508	.762
Width (cm x 10^{-4})			
Initial	1.78	3.81	5.84
Mechanically Stretched	1.52	3.30	5.08
Solvent Stretched	1.02	1.14	1.27
Aspect Ratio (L/T)			
Initial	2.8	3.0	3.1
Mechanically Stretched	5.0	5.7	6.0
Solvent Stretched	15	10	8
Volume % in Film	18%	35%	53%
Volume % in Conglomerate	56%	57%	57%

relatively crude, the magnitudes of the measurements and phenomenological trends can be derived from this data. One important observation is that volume calculations indicate that the percent rod-like polymer in the conglomerates is constant, approximately 57%. This was derived by assuming all of the rod-like polymer is in the second phase. If this is true, it indicates that 57% may be an equilibrium mix condition for the two polymers. To verify this, a 57% PDIAB/ 43% AB-PBI film was prepared. As can be seen in Figure 11, no second phase was observed.



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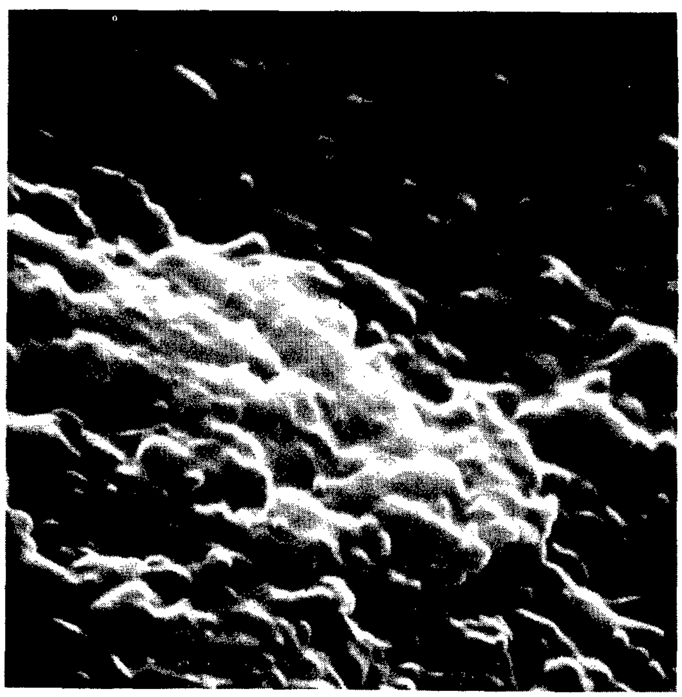

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Figure 11. 43% AB-PBI/57% PDIAB.

SECTION V

ANALYSIS

In order to develop a better understanding of the results obtained, analysis procedures developed for composite materials were utilized for determining the effective moduli of the conglomerates. The Halpin-Tsai equations[2-5] used are:

$$\frac{\bar{E}}{E_M} = \frac{(1 + \xi \eta v_f)}{(1 - \eta v_f)} \qquad (1)$$

and

$$\eta = \frac{\left(\frac{\bar{E}_f}{E_M} - 1\right)}{\left(\frac{\bar{E}_f}{E_M} + \xi\right)} \qquad (2)$$

where,

$\bar{E}$ = Composite or film modulus.

E_M = Corresponding matrix modulus.

v_f = Volume fraction of reinforcement.

$\bar{E}_f$ = Corresponding effective reinforcement modulus.

ξ = Measure of reinforcement dependent on boundary conditions (for these calculations, taken as $\xi = 2\ (a/_b)$.

The results of the analysis are shown in Table 5. Several observations can be made from these calculations. The higher effective modulus of the conglomerates in the stretched 10% rod film indicates a higher degree of orientation in these conglomerates. This increased orientation and corresponding higher aspect ratio of these conglomerates accounts for the

TABLE 5

CALCULATED CONGLOMERATE MODULUS - AB-PBI/PDIAB BLENDS

90/10	AB-PBI/PDIAB (Initial)	$\bar{E}_f$ = 16.15 G Pa
90/10	AB-PBI/PDIAB (Mech. Stretched)	$\bar{E}_f$ = 33.35 G Pa
90/10	AB-PBI/PDIAB (Solvent Stretched)	$\bar{E}_f$ = 26.23 G Pa
80/20	AB-PBI/PDIAB (Solvent Stretched)	$\bar{E}_f$ = 15.43 G Pa
70/30	AB-PBI/PDIAB (Solvent Stretched)	$\bar{E}_f$ = 14.94 G Pa

higher relative modulus observed in the 10% rod films. The magnitudes of the conglomerate moduli are high indicating relatively good translation of rod properties. Even in the most highly stretched 10% rod film, the conglomerate aspect ratio and degree of orientation are not nearly sufficient to obtain desired properties. The typical orientation achieved is shown in Figure 12, a wide angle x-ray diffraction photograph of a solvent stretched 90% ABPBI/10% PBT cast film.

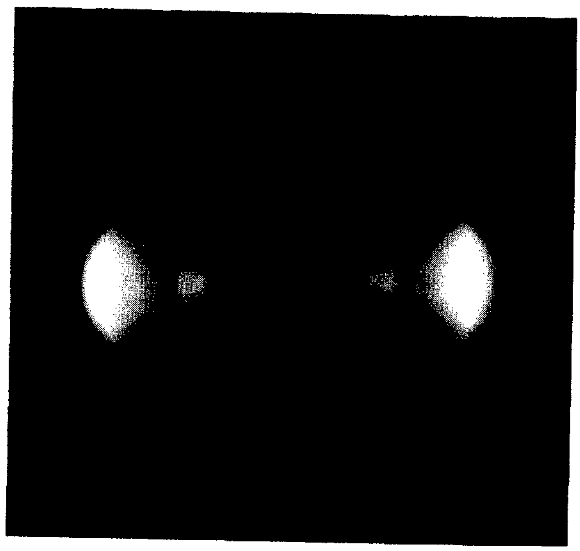


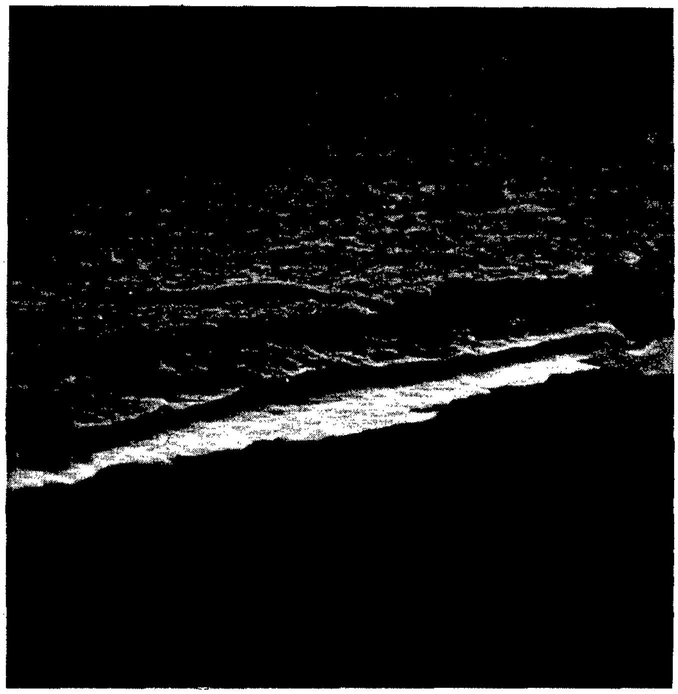
Figure 12. Flatview, WAXS Photograph of 90% ABPBI/10% PBT, Solvent Stretched.

SECTION VI

PROCESSING STUDIES

In an attempt to achieve dispersion of the rods, various processing techniques were studied. Instead of vacuum casting the films, a technique of precipitating from dilute solution in a high humidity environment was developed. A 90% ABPBI/10% PDIAB film made by this process is shown in Figure 13. As can be seen, no visible second phase is present. Mechanical properties of this film are given in Table 6. The properties are much better than those obtained from the vacuum cast films indicating excellent translation of rod properties.

A comparison of typical wide angle x-ray diffraction photographs of precipitated and stretched versus solvent cast and stretched random coil/rod-like blend is shown in Figure 14. The photographs shown are for 80% ABPBI/20% PBT, but the results are typical of the comparison between precipitated and cast films.



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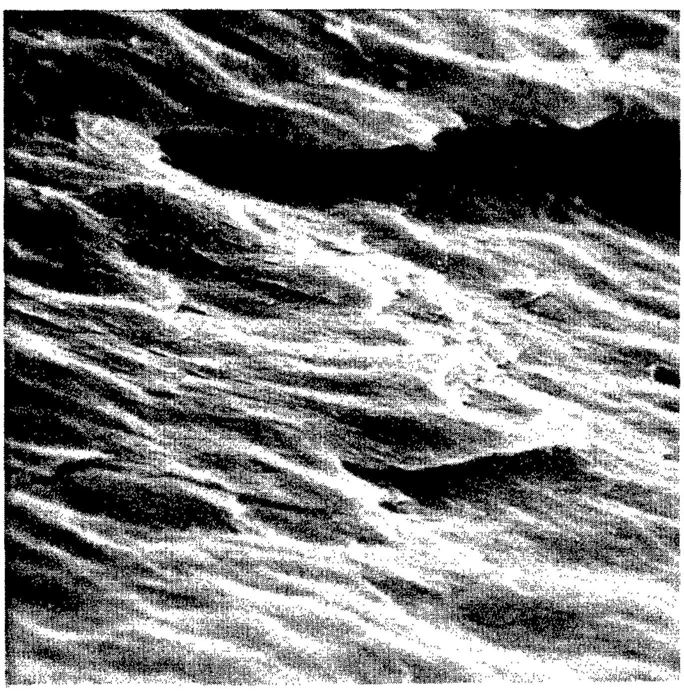


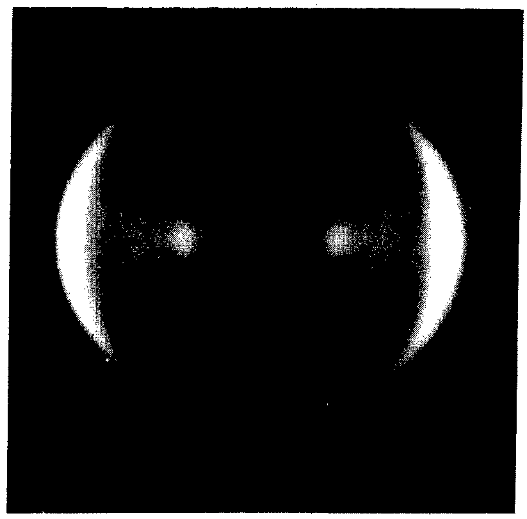
Edge - 3000X

Figure 13. 90% AB-PBI/10% PDIAB Water Precipitated.

TABLE 6

MECHANICAL PROPERTIES - 90% AB-PBI/10% PDIAB

Strength % Area Reduction	Modulus (G Pa)	(Precipitated) Strength (M Pa)	Strain (%)
None	3.08	92.39	15
Mech./5	4.00	122.09	13
Solvent/55	9.65	243.95	3



Precipitated and Stretched

Cast and Stretched

Figure 14. Flatview, WAXS Photograph of 80% ABPBI/20% PBT.

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1. The rule-of-mixture behavior commonly encountered refers to the proportioned increase in mechanical properties as the volume percentage of reinforcing material is increased, usually up to about 60%.

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