Polybenzimidazole (PBI) and Polyarylate Blends

TAI SHUNG CHUNG and PAUL N. CHEN, SR., *Hoechst Celanese Research Division, 86 Morris Avenue, Summit, New Jersey 07901*

INTRODUCTION

The discovery of new polymeric alloys by blending commercially available polymers is an exciting trend in materials development. The ability to tailor existing materials to a new/unique set of property/performance/price specifications through combinations of materials is the key reason for this growth.

Recently, various miscible blends based on Hoechst Celanese's polybenzimidazole (PBI) and commercially available polyimides (PI) were discovered.[1–3] Blend miscibility was evidenced in the form of changes in IR spectra, single T_g's, and well-defined single tan δ relaxations. The intermolecular interaction involving the $=NH$ and carbonyl groups was the major driving force for the miscibility. We therefore conducted a program focused on the fabrication of high-performance blend fibers based on PBI. After a thorough investigation, we found that PBI not only has superior thermal/chemical properties, but also exhibits unique reactivity that enables it to interact with other functionalized polar molecules and to possibly form compatible binary systems.[4,5] As a result of PBIs reactivity, the molecular interactions between PBI and polyarylate (PA) polymers have recently been discovered at Hoechst Celanese Research Division.[6]

In this paper we present information regarding the assessment of PBI/PA compatibility, the preparation/characterizations of solution and blend film, as well as the development of PBI/PA fibers.

EXPERIMENTAL

Raw Materials

A poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI) polymer with an intrinsic viscosity of 0.7 dL/g was synthesized by Hoechst Celanese Corporation. This material is a thermoplastic polymer with a glass transition temperature around 435°C and has excellent nonflammable characteristics. Its chemistry and early development were given in the literature.[7,8]

Two types of polyarylate (PA) were used: One was Ardel D-100 made by Amoco, and the other was Durel from the Hoechst Celanese Corporation. They both are wholly aromatic polyesters derived from aromatic dicarboxylic acids and diphenols or their derivatives. Because of its chemistry, polyarylate has good heat stability and mechanical properties. As a result, it is considered a

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thermoplastic engineering resin. Figure 1 shows the chemical structures of both PBI and polyarylate. In this report, experiments were carried out using Ardel D-100 unless otherwise specified.

1-Methyl-2-pyrrolidinone (NMP) and *N,N*-dimethyl acetamide (DMAc), which were used as solvents for preparing solution blends, were purchased from either EM Science or Aldrich.

Dope Preparation

Preparation of PBI/PA/NMP Solutions for Films

Dissolution experiments were usually carried out by using 15 g samples having the following compositions: PBI/PA (100/0), (80/20), (60/40), (40/60), (20/80), and (0/100). First, the PA powders were dissolved in a 100 mL NMP solvent kept at 60°C. After dissolving the PA powders, as-spun PBI fibers were added to the clear PA solutions according to the blend compositions. The resulting solution-fiber mixtures were then heated to 120°C for 15 min to dissolve the solid materials completely.

Preparation of PBI/PA/DMAc Solution for Spinning

Two types of dopes were prepared: One had no LiCl, and the other contained LiCl. The first was prepared from blending PBI dope (27% solid in DMAc) with a PA dope (27% solid in DMAc) with weight ratios of 80/20 at 80–100°C, whereas the second was from a mixture of commercial PBI dope (25.6% solid plus 1.5% LiCl) with a PA dope (25.6% solid). Both mixed well, and the dopes were clear and transparent at that temperature.

Film Casting

Film samples with controlled thickness (2 mil) were obtained by casting the above dope solutions on a clean and dried glass plate using a Gardener knife. A laboratory vacuum oven set at 140°C and purged with dry air was used to remove most NMP solvent from the cast film. Each newly cast film was dried in the oven for 20 min, cooled to room temperature for 20 min, and finally soaked in a water bath at ambient temperature. After soaking for 30 min, the
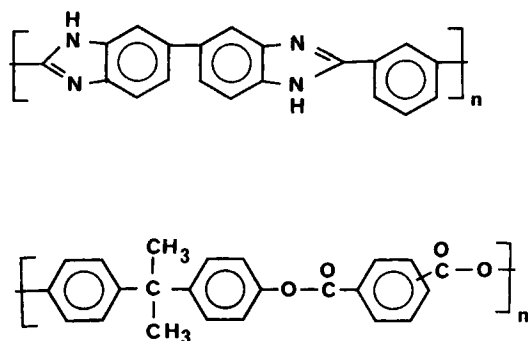

Fig. 1.   Chemical structures of both PBI and polyarylate.

films could be easily peeled off from the glass plate with the use of a razor blade. These films were immediately analyzed, and it was found that NMP contents dropped from 13% for PBI/PA (100/0) to 4% for PBI/PA (0/100) following a linear relationship with the PA content.

Fiber Spinning

Fibers were fabricated using dry spinning technology. The spinneret had 75 holes and the take-up speed was about 200 m/min. The blend dope was filtered and metered by a gear pump before extrusion from the spinneret. Fiber formed when most of the DMAc was vaporized. Generally, this was carried out during spinning by the circulated N_2 in a dry, approximately 20-ft-long column, using temperatures of about 200°C. Residual DMAc in an as-spun fiber was further removed by washing in water.

To improve physical properties, the as-spun fiber was hot-drawn by passing dried filaments through a heat-muffle furnace at approximately 400°C. Skewed rolls before and after the muffle furnace were used to accurately maintain the filaments at different speeds. The spin line tension caused the filaments to elongate, and the polymeric structure within fibers was therefore better organized.

The hot-drawn fibers were further post-treated with 2% sulfuric acid at 50°C for 0.5 h. The acid-treated fibers were heat set, or stabilized, at 380°C with a draw ratio of 0.993 to minimize their shrinkage when subsequently subjected to flame and also to increase solvent resistance.

CHARACTERIZATION

Solution Viscosity Determination

The inherent viscosity (IV) of PBI/PA solution blends was determined at 25°C with the use of the Cannon-Ubbelohode viscometer. The measurements were usually taken at three different concentrations (e.g., 1.0, 0.5, and 0.25% wt/vol) by comparing the relative viscosity of the solvent and the solution.

FT-IR

FT-IR was used to look for interactions between PBI and PA. All the samples were ground into powders. Two milligrams were mixed with 400 mg of KBr, and the mixture was pressed into a pellet for infrared analysis. Typically, interactions were found between the carbonyls and the imidazole in these systems. This was evidenced by the shift of the carbonyl band (in this case $\sim$ 1737 cm^{-1}) to lower frequency.

Transmission Electron Microscopy (TEM)

For TEM work, the samples were first embedded in epoxy; then ultrathin cross sections approximately 70 nm thick were prepared at ambient temperatures using an LKB ultramicrotome with a diamond knife. For contrast enhancement, the thin sections were stained with OsO_4 vapor at 50°C or with RuO_4 at room temperature. The stained samples were carbon coated and ex-

amined under a JEOL 100CX TEM. (This TEM technology was developed by Dr. R. T. Chen at Hoechst Celanese.)

TGA

A DuPont 1090 thermal analyzer was used to characterize the thermal properties of these blends. The temperature increase rate in the nonisothermal run was 10°C/min in a nitrogen-circulated chamber.

RESULTS AND DISCUSSION

PBI/PA Films

The compatibility between PBI and PA polymers was first noticed from the solution blends. All PBI/PA/NMP solutions were visually homogeneous and contained no insolubles. After being kept at room temperature for a period of time (e.g., several days), PBI-rich dopes started to form precipitates; however, these phased-out solids could be easily redissolved with a mild heating (e.g., 100°C for 20 min). Based on the haze level, the stability of the PBI/PA/NMP solutions, as shown in Table I, appeared to increase with the increase of the relative PA concentrations. This statement is true for both Ardel and Durel.

Figure 2 illustrates the relationship between the IV and the concentration of PBI/PA/NMP solution. It is interesting to notice that the inherent viscosity (IV) of all solution blends exhibited normal polymer solution characteristics since the IV and concentration correlations of all solutions were close to linear with small negative slopes.

At a fixed concentration (e.g., 0.5%), we noticed the IV of the solution blends exceeded the rule of mixtures (see Fig. 3). This result suggested that PBI and PA exhibited interactions in a dilute solution, so the resulting hydrodynamic sizes of the blends were greater than that of the calculated averages based on each component.

In addition, the PBI-PA interaction was further demonstrated by the FT-IR technique. Based on the carbonyl stretching of a pure PA film and an 80/20 PBI/PA film blend, we found the signal of the blend showed a dramatic downfield shift (e.g., from 1741 to 1730 cm^{-1}). This shift (see Fig. 4) indicated the existence of intermolecular H-bonding between PBI and PA in the film blend. Similar results were observed if Durel was used.

With respect to PA, an almost compatible PBI/PA blend is expected to have improved properties since PBI is known to have an excellent thermal

TABLE I
PBI/PA Dope (15% Solids) Homogeneity and Stability

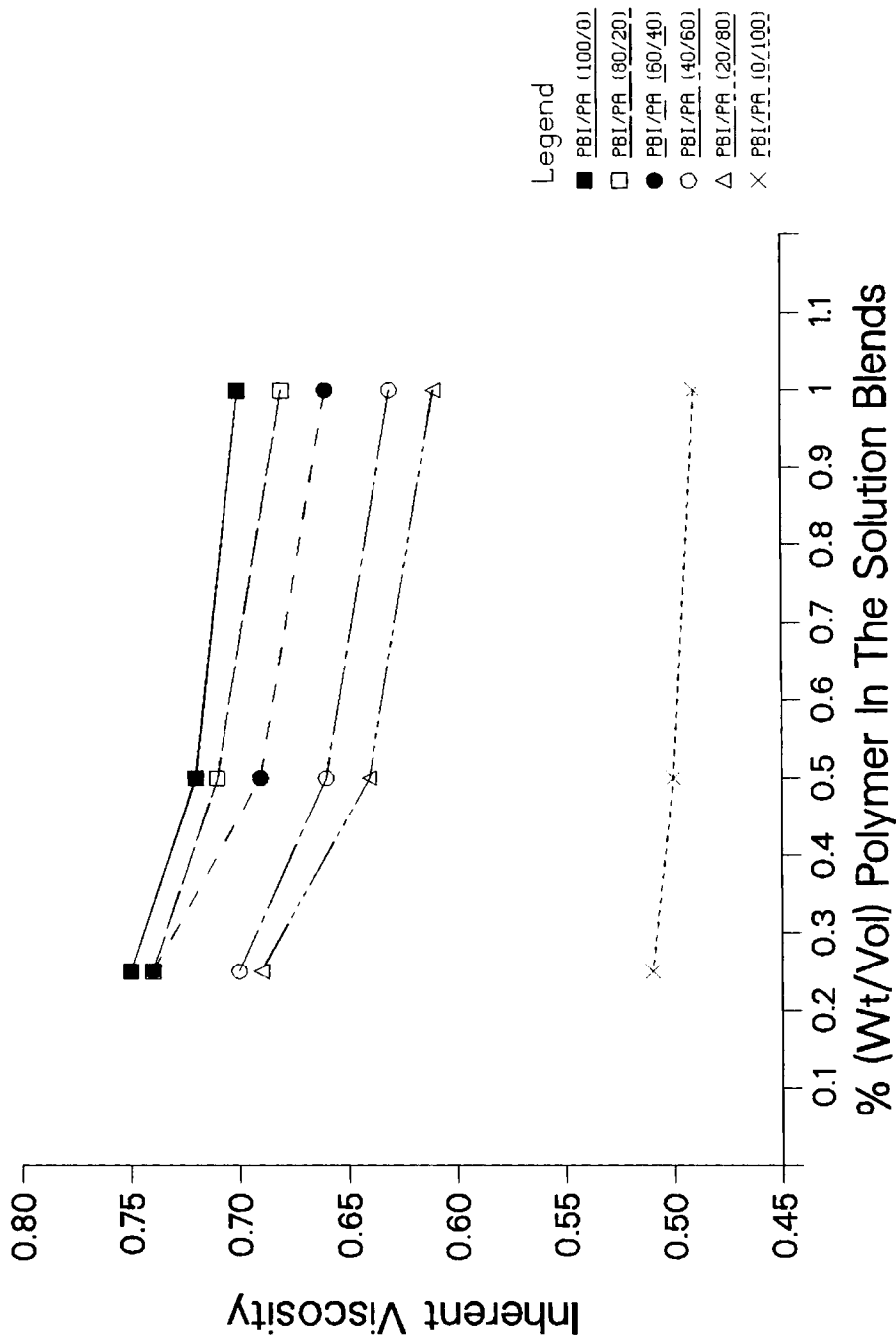|	PBI/PA wt. ratio					
	100/0	80/20	60/40	40/60	20/80	0/100
Dope homogeneity	Yes	Yes	Yes	Yes	Yes	Yes
Dope stability (days)	1	1	3	5	20	60

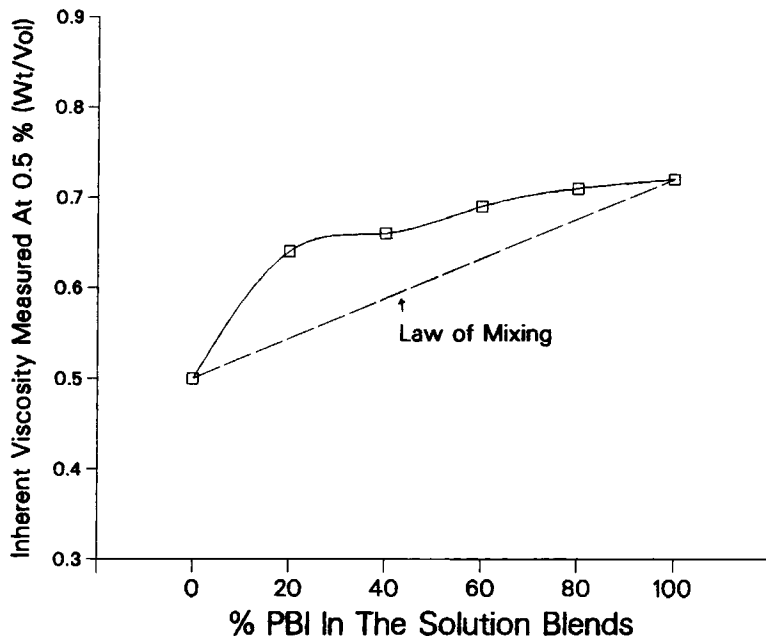Fig. 2.   Correlations between the IV and the concentration of PBI/PA/NMP solution.

Fig. 3. Relationship between the blend IV and compositions.

stability. Hence, both thermogravimetric analysis (TGA) and isothermal TGA techniques were used to determine the thermal stability of the PBI/PA film blends. The preliminary TGA results obtained in nitrogen confirmed our expectation. The thermal stability of PA in the film blends was dramatically improved with the presence of PBI, and the degree of improvement increased with the increase of the PBI concentration (see Fig. 5). Using the weight loss at 550°C as the reference, the thermal stability of the blends was almost linearly proportional to the relative concentration of PBI (see Fig. 6). This result implies that the compatibility of PBI and PA is at the molecular level and the thermal properties of PA could be dramatically improved by blending it with a thermal resistant PBI.

It is known that PA is soluble in common organic solvents, such as methylene chloride and tetrahydrofuran, whereas PBI is inert to these solvents. After blending PA with PBI, we found the solvent resistance of PA could be significantly improved. For example, a PA/PBI film blend having PBI as the minor component (20%) kept its physical integrity after soaking in a methylene chloride solvent for 30 min, whereas a pure PA film would completely dissolve within 10 s. These experiments reconfirm that intermolecular interaction between PBI and PA changes the nature of PA to some degree, thereby improving its chemical resistance. Similar results were observed if Durel was used.

Fibers

The as-spun fiber tensile properties can be summarized as shown in Table II. Since fibers made both with and without LiCl have very similar properties, the effect of LiCl on as-spun fiber structure and properties cannot be clearly concluded from these data.

FT-IR CONFIRMATION OF THE EXISTENCE OF INTER-MOLECULAR
HYDROGEN BONDING BETWEEN PBI AND PA

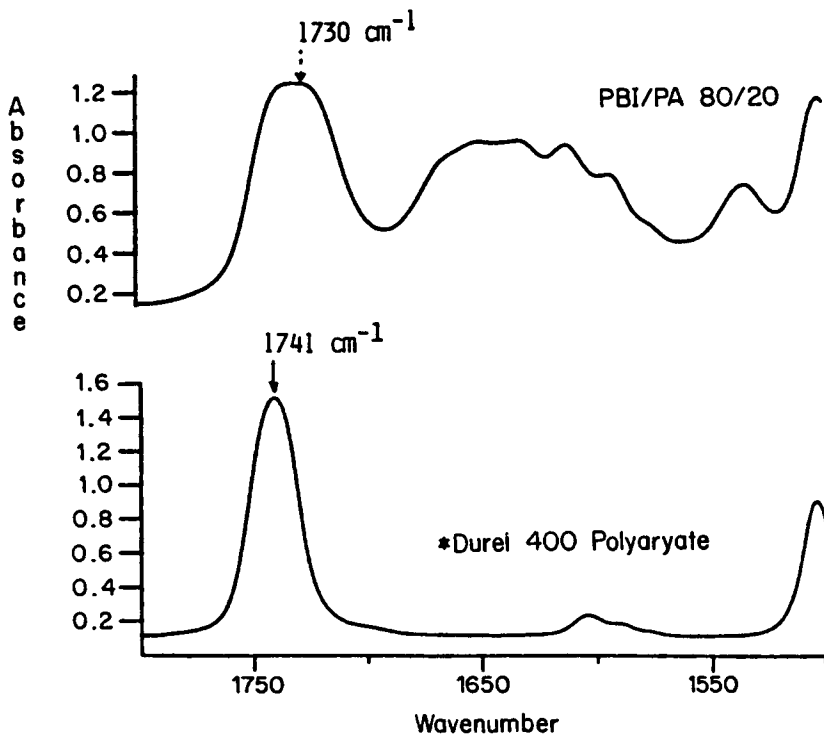CARBONYL BAND SHIFTING DUE TO H-BONDING

Fig. 4.   FT-IR confirmation of the existing of intermolecular hydrogen-bonding between PBI and PA.

These fibers were further drawn at elevated temperatures at various draw ratios. These fibers were stronger than were the as-spun fibers. Table III illustrates the effects of temperature and draw-ratio on the fiber properties. Drawing at 400°C at a ratio of 3.0 : 1 gave the best tensile modulus and strength. In carrying out these experiments, we set the drawing temperature constant and then gradually increased draw ratio until filaments started to break. This showed that the fibers could not be further drawn. We then increased the drawing temperature and repeated the previous procedure.

Table IV provides a comparison among PBI/PA and that of PBI/Ultem and PBI fibers. This comparison is based on the highest modulus and tenacity of PBI/PA and PBI/Ultem obtained from Table IV and from the literature.[9] Dry-spun PBI/PA (without LiCl) has very impressive tensile modulus and
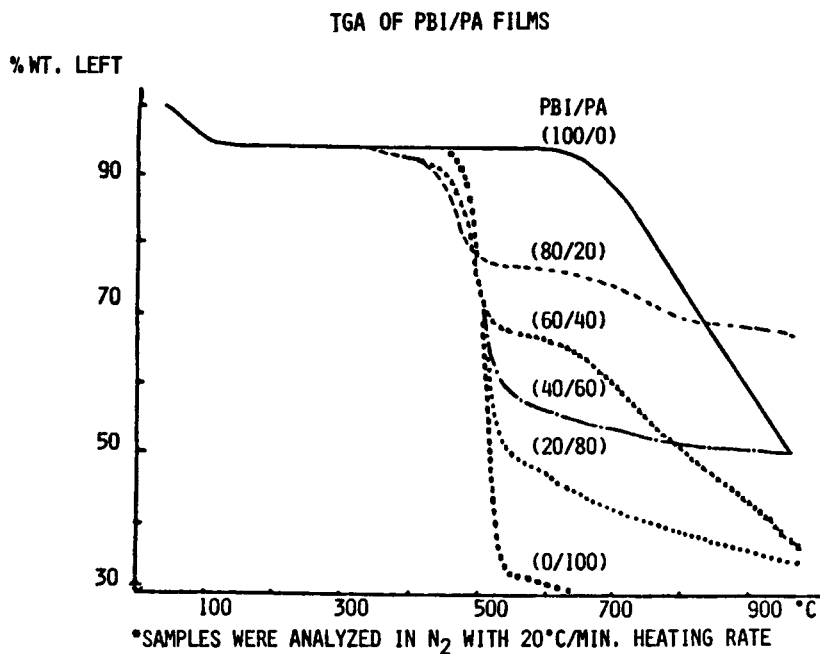
TGA OF PBI/PA FILMS

%WT. LEFT

Fig. 5. TGA study of PBI/PA film blends.

CORRELATION BETWEEN % WEIGHT LOSS
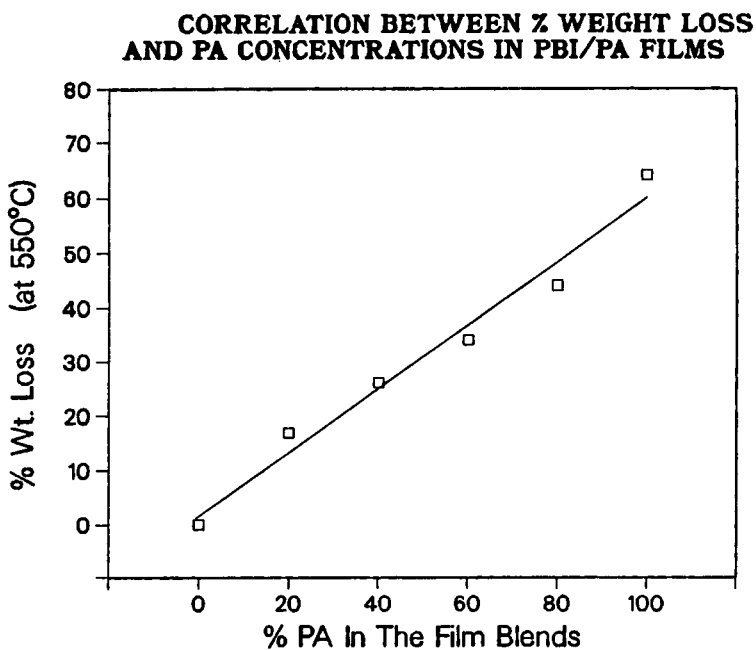AND PA CONCENTRATIONS IN PBI/PA FILMS

Fig. 6. Isothermal TGA of PBI/PA film blends.

TABLE II
Tensile Properties of As-spun 80/20 PBI/PA Fibers

Sample	Denier (DPF)	Initial modulus (G/D)	Tenacity (G/D)	Elongation (%)
PBI/PA with LiCl	3.69	48.4	1.38	73.9
PBI/PA without LiCl	5.271	42.6	1.53	87.3

TABLE III
Properties of the (80/20) PBI/PA Fibers (without LiCl)

Denier (DPF)	Draw ratio	Temperature (°C)	Modulus (G/D)	Tenacity (G/D)	Elongation (%)
1.919	2.0	400	77.69	3.118	29.50
1.915	2.5	400	91.86	3.313	17.92
1.501	3.0	400	141.15	4.611	6.75
1.668	2.0	420	66.50	2.922	33.75
1.453	3.0	420	80.74	3.378	19.75
0.951	4.0	420	113.86	4.014	11.61

TABLE IV
Tensile Properties of Hot-drawn 80/20 PBI/PA (without LiCl),
75/25 PBI/Ultem, and PBI Fibers

Material	Denier (DPF)	Draw ratio	Temperature (°C)	Modulus (G/D)	Tenacity (G/D)	Elongation (%)
80/20 PBI/PA	1.501	3.0	400	141.2	4.611	6.75
75/25 PBI/Ultem	0.96	3.0	420	112.0	4.32	9.9
PBI control	1.700	2.0	440	91.0	4.07	31.9

strength. The properties are at least comparable, or superior, to those of PBI/ Ultem fibers. Compared to standard unsulfonated PBI fibers, the PBI/PA blend fiber has higher tensile moduli and strengths than those of PBI fibers, whereas the elongations at break of the former are inferior to those of the latter. These properties indicate that the PBI/PA fibers are very suitable for engineering and aerospace applications.

The mechanical properties of hot-drawn and then acid-treated/stabilized fibers are shown in Table V. Both initial modulus and tenacity dropped because of the post-treatment, whereas their elongation increased. The weight gains for these fibers after sulfonation are interesting, and more data are given in Table VI. The sulfur content was measured by an analytic method, and the SO_3H content was calculated by assuming that every sulfur formed a SO_3H group after sulfonation. The analytic result is in agreement with the average weight gain measured by the denier change of a yarn before and after sulfonation, as well as 80% of the SO_3H value of PBI fibers.

TABLE V
Tensile Properties of Hot-drawn and Stabilized PBI/PA (without LiCl) and PBI Fibers

Sample	LiCl	Denier (DPF)	Modulus (G/D)	Tenacity (G/D)	Elongation (%)
80/20 PBI/PA (hot-drawn)	No	1.096	84.8	3.5	12.7
80/20 PBI/PA (stabilized)	No	1.274	80.1	3.1	13.4
Standard PBI (stabilized)	Yes	1.5	45	2.7	30.0

The spectra of an as-cast (80/20) PBI/PA film (as control) and its sulfonated one are displayed in Figure 7. It is dominated by the sulfur-oxygen bands near 1200, 1050, and 600 cm^{-1}. There is a distinct sharp carbonyl band near 1737 with a weak, broad low-frequency shoulder, and this indicates that the amount of polymer interaction is reduced due to the effect of sulfonation and then stabilization. However, no TEM studies were used on these samples to determine if the sulfonation affected phase separation.

If the as-spun fiber was drawn 1–2 weeks after it was spun, washed, and dried, the resultant fiber properties dropped significantly (Table VII). This phenomenon was probably caused by the evaporation of the residual DMAc solvent that reduced the phase stability of the compatible blend. In other words, DMAc played an important role in stabilizing PBI/PA (without LiCl) blends. Once DMAc was removed, a slight phase separation occurred, and therefore fiber properties were reduced. In addition, comparing these data with Table VIII indicates that fibers without LiCl generally have a higher tenacity than those with LiCl. Therefore, hot-drawing *immediately after* dry-spinning, and without LiCl, yielded fibers with much more impressive tensile modulus and tenacity that were better than those of PBI fibers. However, the elongation of the *former* was poorer than that of the *latter*.

Phase separation was evident in the TEM micrographs of OsO$_4$ stained samples of as-spun fibers (without LiCl), as shown in Figure 8. This phenomenon was in agreement with our experience when handling this fiber a few days after it was spun because it became brittle and its strength seemed to deteriorate. There are two types of PA domains present in the fibers: large, irregularly

TABLE VI
Sulfur and SO$_3$H Contents in Hot-drawn and Sulfonated Fibers

Sample	Sulfonated	S content (%)	SO$_3$H content (%)	Denier change (%)
80/20 PBI/PA (no LiCl)	No	0.01		
80/20 PBI/PA (no LiCl)	Yes	5.85	14.81	16.24
PBI	Yes		18–20	

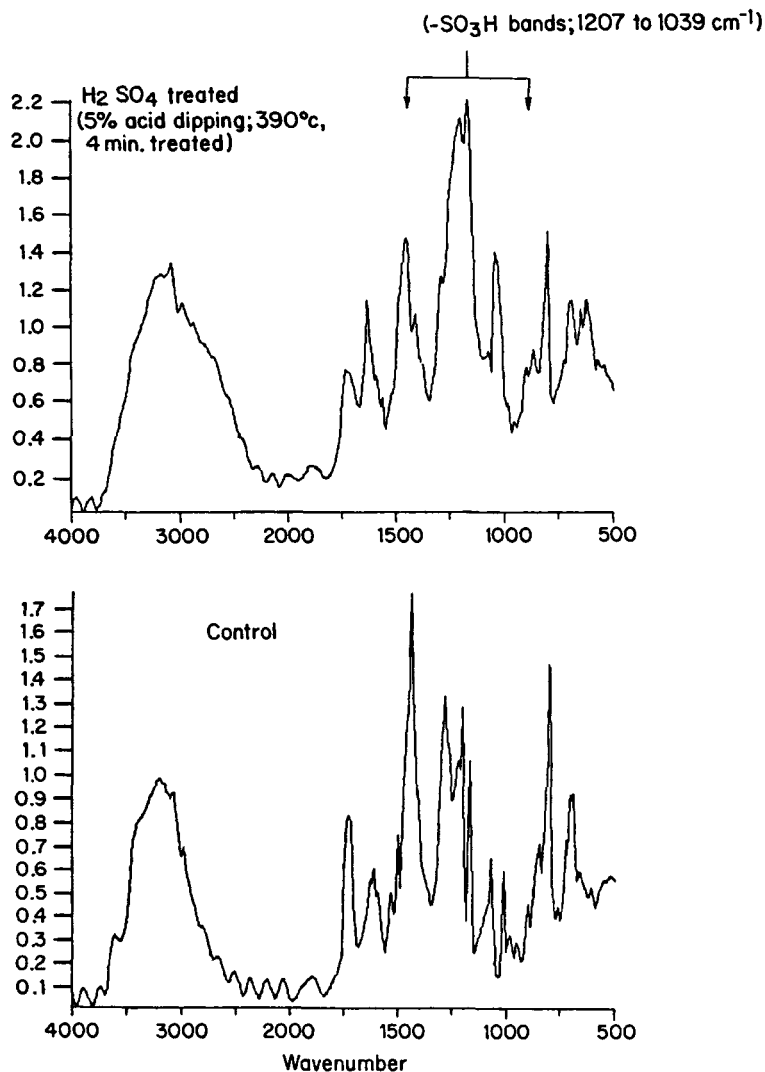FT-IR Studies Of Sulfuric Acid Treated PBI/PA (80/20) Film

Fig. 7.   FT-IR spectra for an (80/20) PBI/PA sulfonated film and for a control.

TABLE VII
Aging Effect on Tensile Properties of Hot-drawn Fibers

Sample	Denier (DPF)	Initial modulus (G/D)	Tenacity (G/D)	Elongation (%)
80/20 PBI/PA (DIAS) (no LiCl)	1.501	141.1	4.6	6.75
80/20 PBI/PA (DL) (no LiCl)	1.600	101.2	3.7	7.01

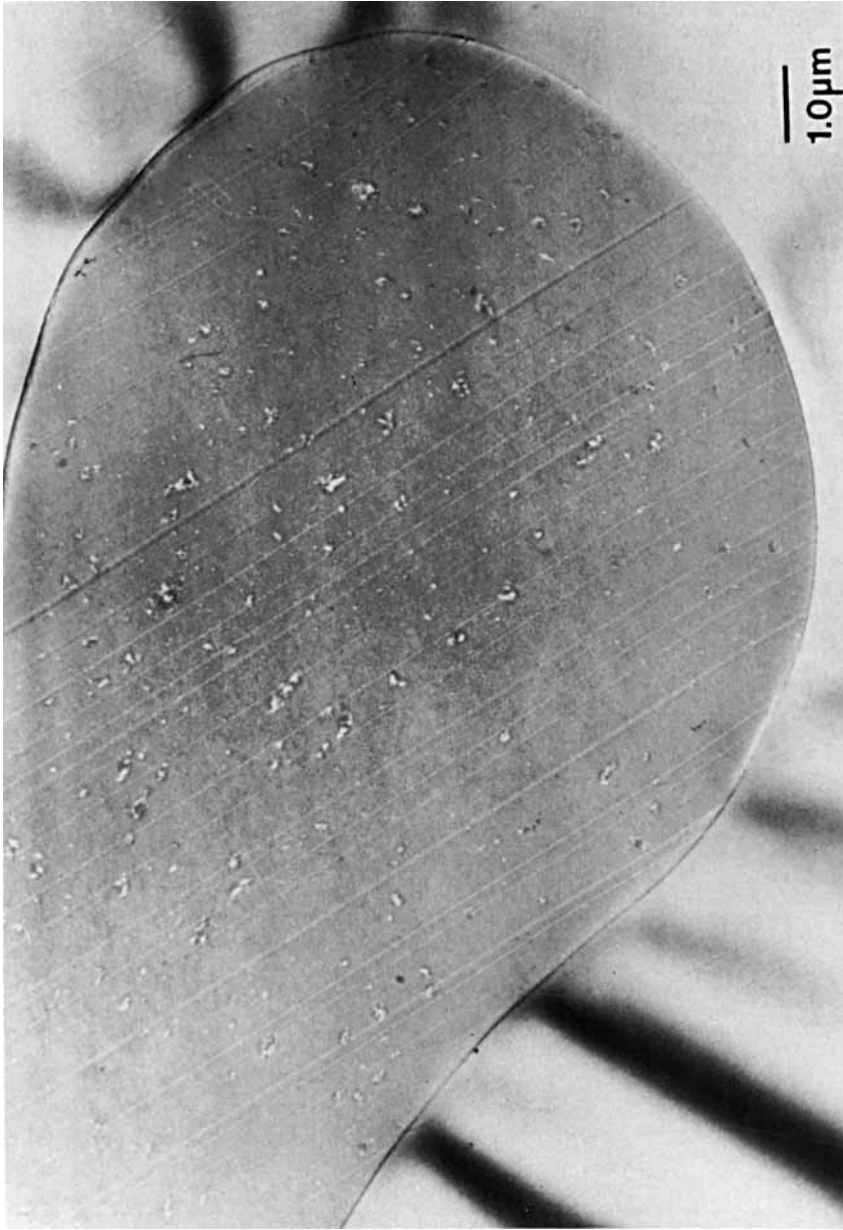DIAS = drawn immediately after spin; DL = drawn later.

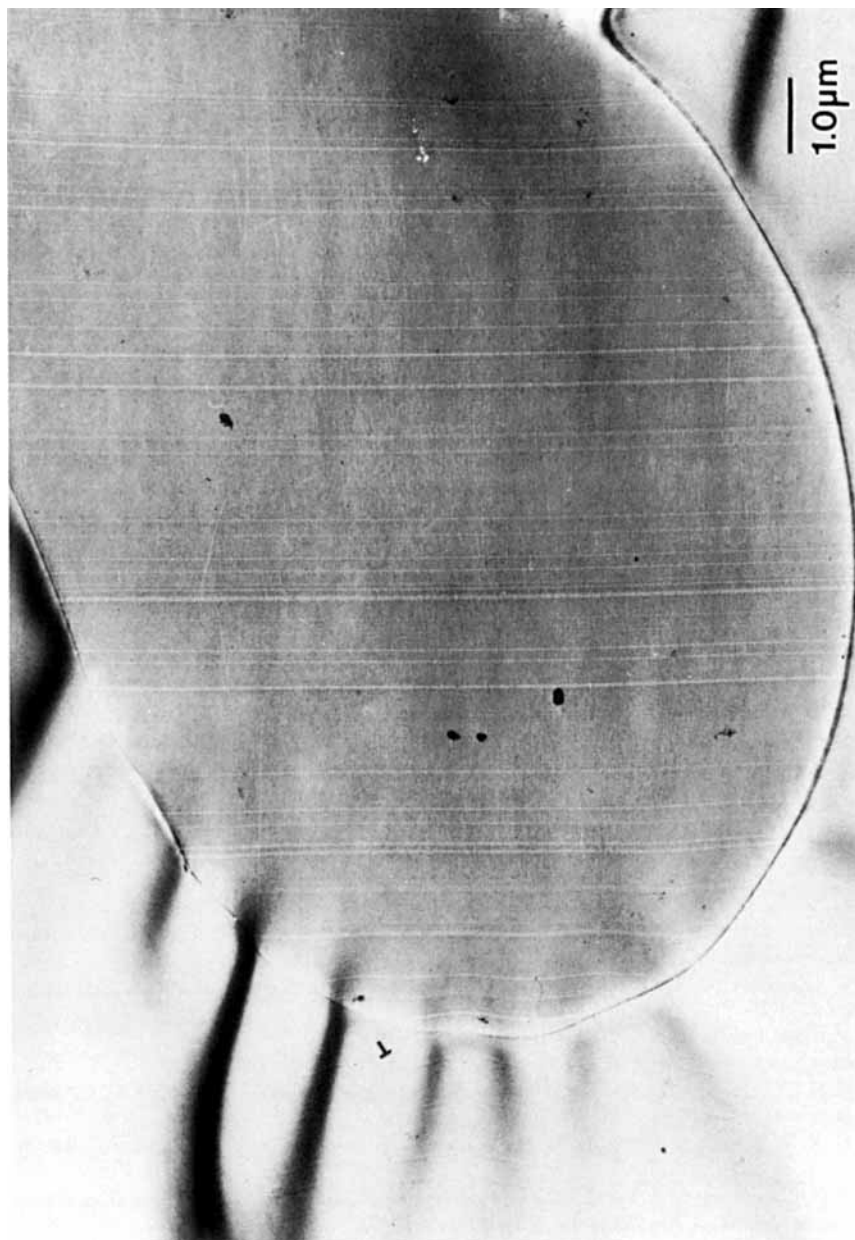Fig. 8. TEM micrographs of OsO$_4$ stained PBI/PA (without LiCl) blend fibers.

Fig. 9.   TEM micrographs of OsO$_4$ stained PBI/PA (with LiCl) blend fibers.

1.0μm

TABLE VIII
Effect of LiCl on Fiber Properties

Sample	Denier (DPF)	Initial modulus (G/D)	Tenacity (G/D)	Elongation (%)
80/20 PBI/PA (DL) (no LiCl)	1.600	101.2	3.7	7.01
80/20 PBI/PA (DL) (with LiCl)	1.141	68.3	2.17	14.23

DIAS = drawn immediately after spin; DL = drawn later.

shaped and round domains. Additional TEM examinations of the unstained samples confirmed that the features observed in the stained samples are not artifacts. In contrast, the as-spun fibers with LiCl have a uniform texture with no evident phase separation, as illustrated in Figure 9, and this structure is quite similar to the textures observed in control PBI fibers.

CONCLUSION

A new family of high-performance and processible blends based on PBI and PA was discovered. The blend systems exhibited synergistic effects on properties and offered new opportunities in the development of PBI/PA polymeric alloys.

The molecular interaction and compatibility of PBI/PA have been investigated by IR, TEM, and TGA. The results showed that the degree of interaction, as well as compatibility, depended on process conditions and addition of LiCl.

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