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Miscible Polybenzimidazole Blends with a Benzophenone-based Polyimide

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Synopsis

Miscible blends of the aromatic polybenzimidazole, poly(2,2(*m*-phenylene)-5,5'-benzimidazole) (PBI), and the aromatic polyimide formed from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-diaminobenzophenone (LaRC TPI) have been prepared. Blends with PBI were prepared in *N,N*-dimethylacetamide solution starting with either the polyamic acid or a 95% imidized form of LaRC TPI; the blend was then precipitated into water or cast as films. The mixture was then imidized thermally to obtain PBI/LaRC TPI blends. Evidence for miscibility was obtained in the form of single composition dependent T_g 's intermediate between those of the component polymers and single $\tan \delta$ dynamic mechanical relaxation peaks. The IR spectra displayed shifts in the N—H stretching band, thereby providing evidence for specific interactions related to the miscibility of these two polymers.

INTRODUCTION

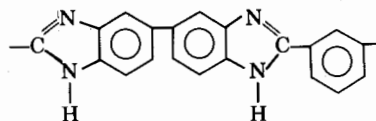
It was recently reported that blends of an aromatic polybenzimidazole (PBI) and certain aromatic polyimides (PIs) are miscible over a comparatively wide range of compositions and structural variations. This assertion was based on studies of PBI and several available PIs¹ (Table I). These polymers are all soluble in *N,N*-dimethylacetamide (DMAc), so that blends can be prepared by solution mixing, followed either by precipitating into a nonsolvent such as methanol or by casting a film. Representative examples of evidence for miscibility were presented in the form of single composition dependent T_g 's, well defined $\tan \delta$ dynamic mechanical relaxation peaks associated with these transitions, and the formation of optically clear films.

Further investigation has focused on additional thermal studies of the properties of the blend combinations described above^{2,3} and on FTIR studies to obtain evidence for the existence of specific interactions related to their mutual miscibility and to elucidate the nature of these interactions.³ For blends of PBI with the PIs, Ultem 1000, XU 218, and PI 2080, it was found that the criteria for miscibility listed above held for all three for all composition ranges although not necessarily over the entire accessible temperature regime.^{2,3} The IR studies³ revealed composition-dependent changes in the spectral properties in the benzimidazole N—H stretching band region of PBI and shifts in the phthalimide carbonyl bands of the PIs that were related to PBI/PI blend miscibility.

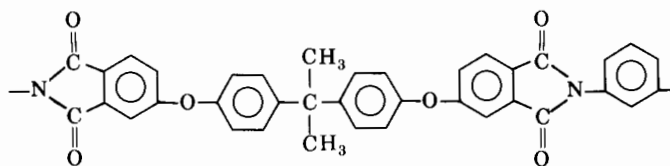
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TABLE I
Polymers Studied in PBI/PI Blend Program

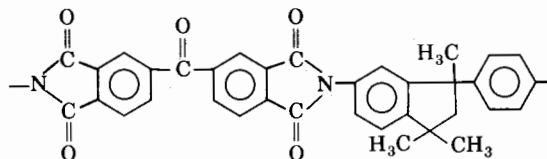
Poly(2, 2'-(*m*-phenylene)-5, 5'-bibenzimidazole)
[Celanese Corporation: PBI ($T_g = 420^\circ\text{C}$)]



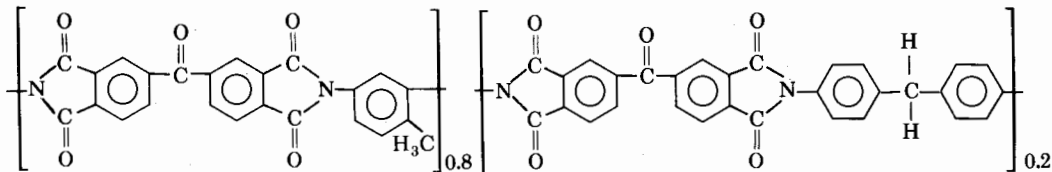
Poly[2, 2'-bis(3, 4-dicarboxyphenoxy)phenylpropane]-2-phenylene bisimide]
[General Electric Company: Ultem 1000 ($T_g = 220^\circ\text{C}$)]



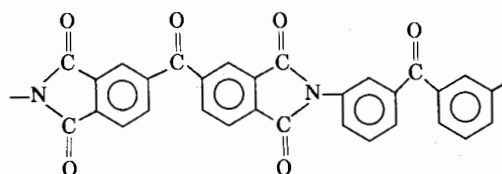
Condensation product of 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 5(6)-amino-1-(4' aminophenyl)-1,3,3-trimethylindane
[Ciba-Geigy Corporation: XU 218 ($T_g = 320^\circ\text{C}$)]



Condensation product of BTDA and a 4 : 1 molar mixture of 2, 4-toluene diisocyanate and 4, 4'-diphenylmethane diisocyanate
[Dow Chemical Co.: PI 2080 ($T_g = 310^\circ\text{C}$)]



Condensation product of BTDA and 3, 3'-diaminobenzophenone (DABP)
[Mitsui Toatsu Chemicals, Inc.: LaRC TPI ($T_g = 267^\circ\text{C}$)]



The present contribution describes blends formed from PBI^{4,5} and the PI prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 3,3'-diaminobenzophenone (DABP) with the structure and T_g shown in Table I. This material is commonly known as LaRC TPI, an acronym for Langley Research Center (NASA) Thermoplastic Polyimide.^{6,7} The present study was undertaken to determine if LaRC TPI was also miscible with PBI and, by using the polyamic acid (PAA) form of LaRC TPI (LaRC PAA), to establish whether in fact PBI/PI blends could be prepared by solution blending PBIs with PIs in their polyamic form followed by imidization. A recent review⁸ which describes the blending of polyimides with a variety of homopolymers and copolymers (but not with PBI) includes several cases⁹⁻¹¹ in which the polyimide component was blended in its PAA form and then imidized in the blend. This procedure is required in systems where the fully imidized material is not thermoplastic and/or has limited or no solubility.

EXPERIMENTAL

As-received PBI powder (Celanese) was dissolved in *N,N*-dimethylacetamide (DMAc) at 225°C for 30 min under nitrogen in a high pressure vessel, leaving an undissolved residue of about 0.25 wt% that was removed by filtration. The LaRC PAA (Mitsui Toatsu Chemicals, Inc.) was supplied as a 30% (w/v) solution in *bis*(2-methoxyethyl)ether (diglyme) with an inherent viscosity of 0.54 dL/g at 35°C. This solution was diluted with DMAc and then concentrated several times in a rotary evaporator to remove the diglyme and obtain a 2-3 wt% solution of LaRC PAA in DMAc. Imidized powder was also obtained from the same source.

Blends were prepared by mixing 2-3 wt% solutions of the PBI and LaRC PAA or a nearly fully imidized form of LaRC TPI in DMAc. Coprecipitated powders were obtained by slowly pouring the mixed solutions in DMAc with stirring into water. The powders were filtered, washed several times with water, and then dried to constant weight at 80°C to remove the residual DMAc. Intimate (but not blended) physical mixtures were prepared by consecutively precipitating the two polymers into the same vessel. The individual homopolymers were subjected to the same treatment in control experiments.

Films of these materials were prepared by casting 2-3% (w/v) solutions of the polymers in DMAc on glass under nitrogen at 80°C for 24 h. The films were washed in water at 50°C for 24 h and then dried under vacuum at 80°C.

Infrared spectra were acquired using an IBM IR/30 FTIR spectrometer at a resolution of 2 cm⁻¹ with 5-20 μm thick films. For the study of the imidization reaction the films were cast on NaCl windows and not washed with water. The powders were analyzed in the form of KBr pellets. A minimum of 30 scans for the films and 300 scans for the pellets were signal averaged.

Wide-angle x-ray diffraction patterns were obtained with a D-500 Siemens diffractometer with nickel-filtered Cu K_α radiation.

DSC scans were obtained under nitrogen with a Perkin-Elmer DSC-7 differential scanning calorimeter with sample sizes of approximately 20 mg, using a scanning rate of 20°C/min.

The dynamic mechanical analyses were carried out in a Polymer Laboratories DTMA apparatus operating at a frequency of 10 Hz and a heating rate of 3°C/min. The thickness of the analyzed films was in the range 20–70 μm . The thermal treatments described below were conducted in the DTMA oven under nitrogen with a heating rate of 5°C/min.

RESULTS AND DISCUSSION

PBI/LaRC PAA BLENDS

The miscibility of PBI/PAA blends cannot generally be ascertained using calorimetrically obtained T_g 's because the PAA component converts to PI during the scanning process. Thus PBI/LaRC PAA blends were prepared and characterized using FTIR at ambient temperature. Shifts of the carbonyl

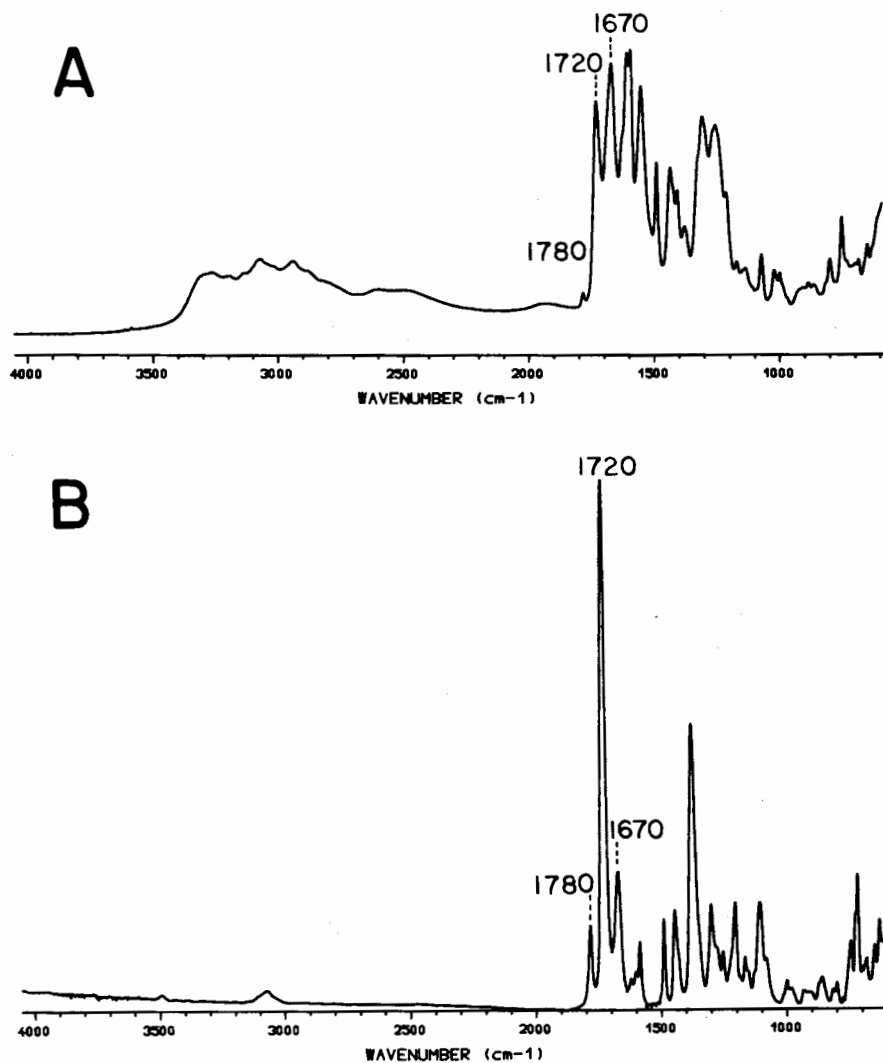


Fig. 1. FTIR spectra in the 4000–600 cm^{-1} range for LaRC PAA (A), fully imidized LaRC TPI (B), and pure PBI (C).

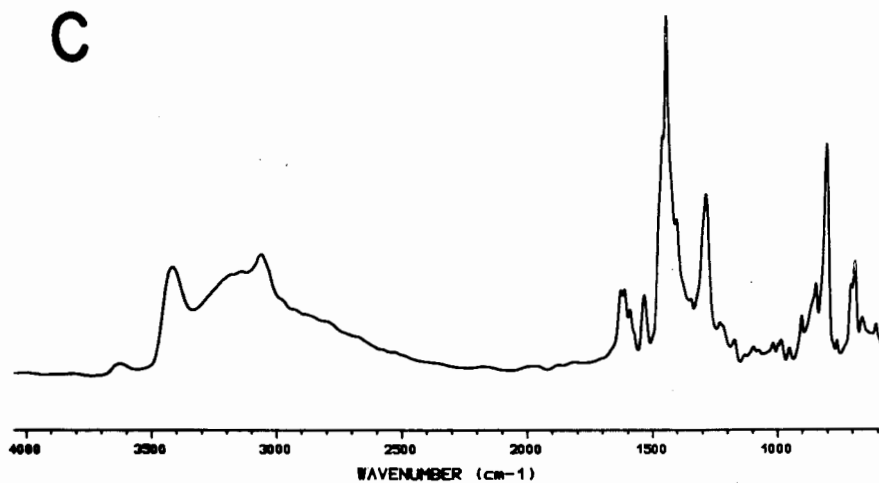


Fig. 1. (Continued from the previous page.)

bands were not observed in either the blends prepared in the form of precipitated powders or in as-cast films. The N—H stretching region cannot be used because strong absorptions attributed to the PAA are present in addition to the N—H stretching band of PBI.

Thermal Imidization of LaRC PAA

The imidization of several polyamic acids has been investigated using IR spectroscopy,¹²⁻¹⁸ including LaRC PAA.¹⁶ As in the latter study¹⁶ we used the change in intensity of the two phthalimide carbonyl stretching bands located at about 1780 and 1720 cm^{-1} ^{19,20} to follow the reaction, with the benzophenone carbonyl band at about 1670 cm^{-1} ²¹ taken as a reference peak. Figure 1A and B compare the spectra of LaRC PAA (A) and fully imidized LaRC TPI (B), obtained from LaRC PAA by annealing at 350°C for 1 h. Fortunately, as shown in Figure 1C, in this region the absorbance of PBI is fairly weak and does not interfere with the bands under consideration in the blends; hence subtraction of the spectra was not required.

Figure 2 shows the absorbances of the 1780 and 1720 cm^{-1} bands relative to that of the 1670 cm^{-1} reference band for pure LaRC PAA converting to LaRC TPI (dashed line) and a 50/50 wt% PBI/LaRC PAA blend converting to a PBI/LaRC TPI blend (solid line) as function of curing temperature, wherein the same sample was successively annealed at the temperature indicated by the individual data points. The small retardation of the imidization reaction displayed in the blend (solid line) is analogous to the result found in a different polyamic acid dispersed in an amorphous polyamide matrix with a high softening point.¹⁷ In the present study both the pure and the blended LaRC PAAs reach an equivalent level of imidization as is seen from the plateau values shown in Figure 2, and the imidization is substantially completed after the 1 h cure at 250°C. The right hand ordinate shows a normalized scale which may be used to represent mole fraction imidization. Both of the ratios shown in Figure 2, and the entire IR spectra of LaRC TPI alone or in PBI/LaRC TPI blends, remain substantially unchanged after full imidization and after successive 1 h treatments over the range 250–450°C.

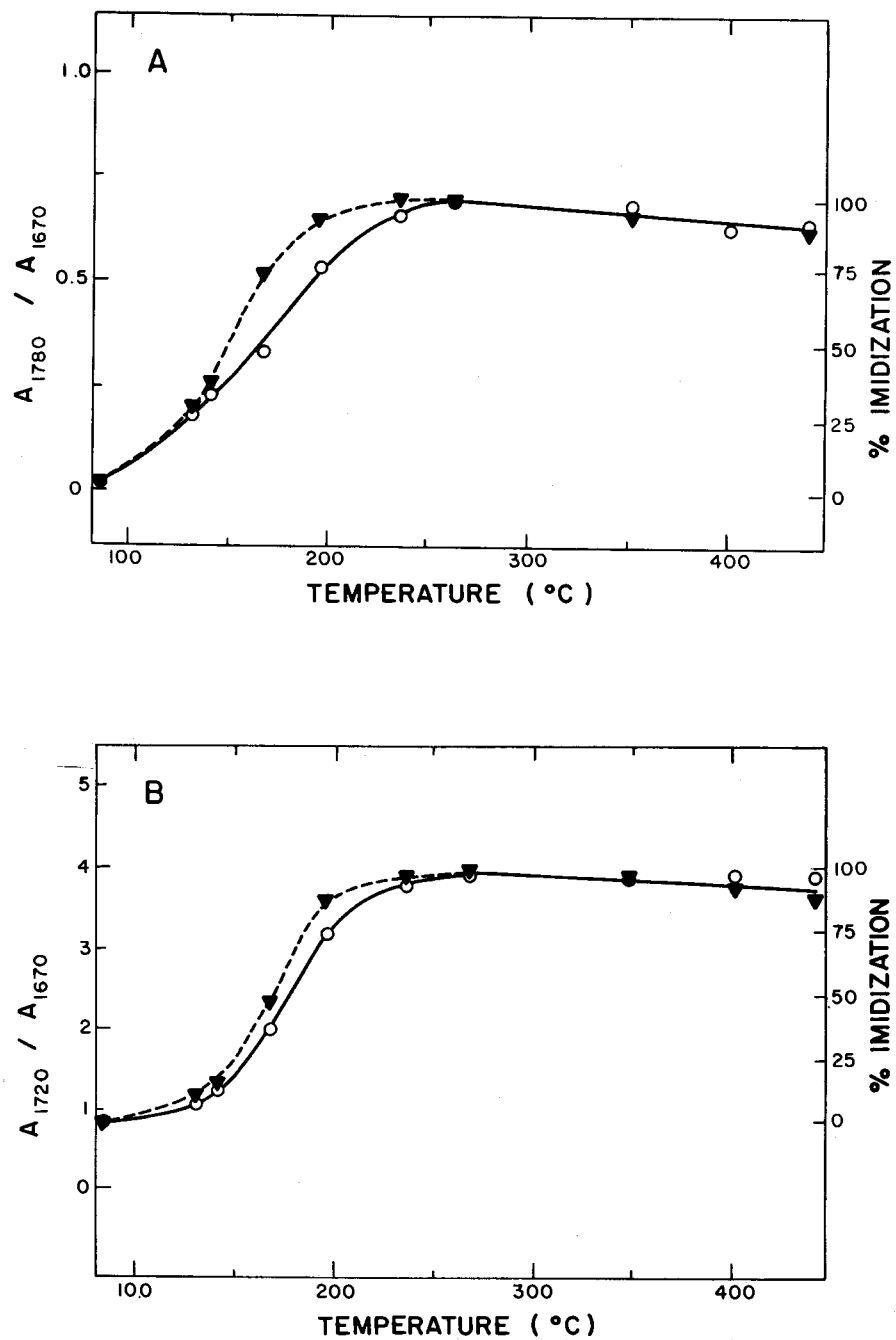


Fig. 2. Absorbances of the imide carbonyl bands at 1780 cm^{-1} (A) and at 1720 cm^{-1} (B) relative to that of the benzophenone reference band at 1670 cm^{-1} as a function of curing temperature for pure LaRC PAA converting to LaRC TPI (dashed line) and for a 50:50 wt% PBI/LaRC PAA blend converting to a PBI/LaRC TPI blend (solid line). Each sample was successively annealed for 1 h at each of the temperatures indicated by the data points.

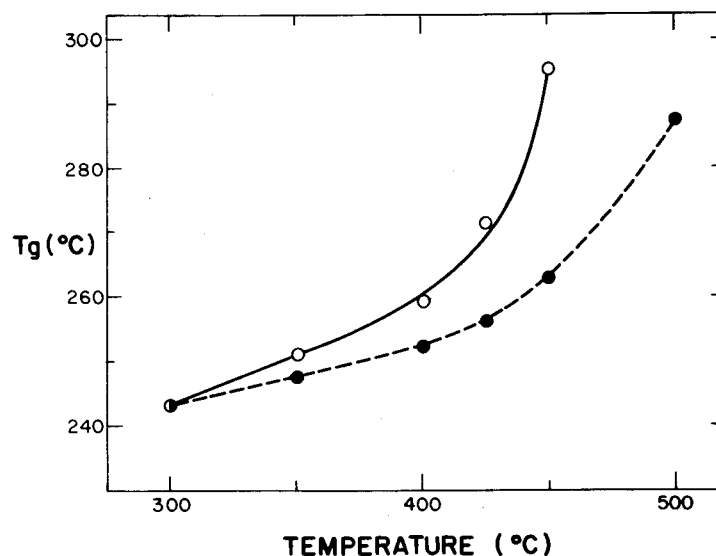


Fig. 3. T_g 's of fully imidized LaRC TPI samples which were successively annealed for 1 h (solid line) or 5 min (dashed line) at each of the temperatures indicated by the data points. After annealing the samples were quenched to 50°C.

Properties of LaRC TPI

Figure 3 shows T_g 's of pure LaRC TPI samples that had been fully imidized by successively heating for 1 h each at 100, 200, and 300°C and then subjected to additional annealing as described in the figure caption. Equivalent results were obtained for LaRC TPI powder obtained directly from the manufacturer. The observed increase in T_g is accompanied by a decrease in ΔC_p and diminished solubility in dichloroacetic acid, thereby indicating the onset of a thermally activated crosslinking reaction. Thus these samples were somewhat less thermally stable than the PBI used; the latter has been shown to exhibit structural stability as manifested by constant T_g and ΔC_p values obtained during repeated DSC scans to temperatures as high as 450°C.^{2,3}

Figure 4 shows wide-angle x-ray diffraction patterns of a cast film (curve a) and of a precipitated powder (curve b) of LaRC TPI prepared from LaRC PAA by successively curing at 100 and 200°C with a 1 h anneal at each temperature. From Figure 2 it can be determined that these materials are about 95% ($\pm 2\%$) imidized. It is clear that in the film the polymer is somewhat crystalline, whereas in the powder (which, in effect, has been quenched by precipitation) it is completely amorphous. DSC scans indicate the presence of a typical melting endotherm located at about 275°C²² in the film but not in the powder. After melting at 300°C and quenching to room temperature, both x-ray and DSC analysis showed the films to be completely amorphous. The imidized as-received powder (whose thermal/solvent history was unknown) was found to be somewhat crystalline and to behave similarly to the film sample prepared in this study. It may be noted that both the 95% imidized material described above and the LaRC TPI as-received powder were completely soluble in DMAc.

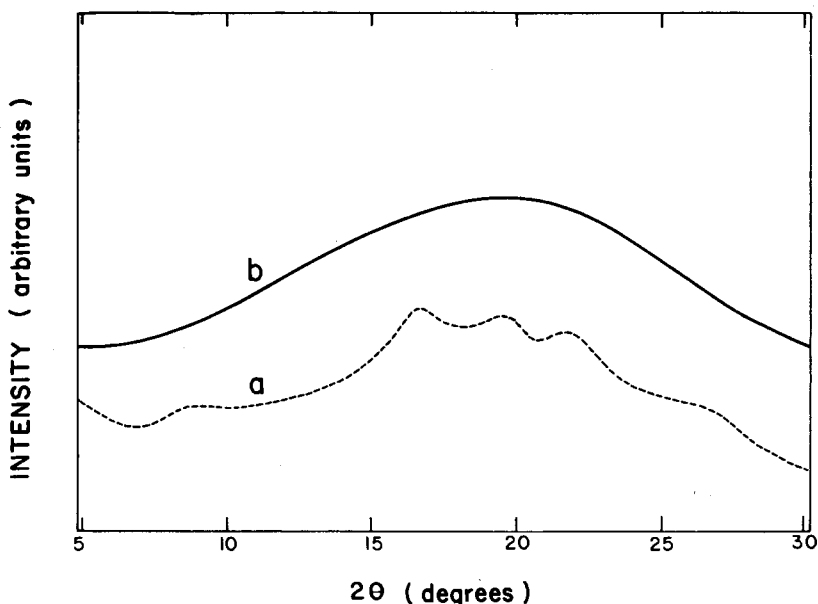


Fig. 4. Wide-angle x-ray diffraction patterns of (a) 95% imidized LaRC TPI cast film and (b) precipitated powder. Samples were prepared by successively curing for 1 h at 100 and 200°C.

PBI / LaRC TPI Blends

All the blended PBI/LaRC PAA samples were successively treated at 100, 200 and 300°C for 1 h at each temperature in accordance with a generally used imidization procedure^{6,7} to obtain fully imidized, amorphous samples. Figure 5 shows DSC scans for powder blend samples in which the well-defined glass transition of pure LaRC TPI (curve a) is broadened and shifted toward higher temperatures upon blending with PBI. Figure 6 shows the composition-dependent T_g 's of various blends. These values are subject to some error because of crosslinking reaction that occurs in LaRC TPI above 300°C, but this does not alter the fact that single composition-dependent T_g 's are observed for all blend compositions and that this system may be considered miscible.

The T_g 's of cast films of the blends were somewhat less well defined in the DSC scans, but again single composition-dependent T_g 's intermediate between those of the constituent polymers were detected. For example Figure 7 shows a single $\tan \alpha$ dynamic mechanical relaxation peak for a film of a 50/50 wt% film blend lying between the glass transitions of the two component polymers.

Figure 8A shows the normalized IR spectra in the region 3500–3000 cm^{-1} for a 50/50 wt% physical (consecutively precipitated) powder mixture (curve a) of the two polymers and for a 50/50 wt% coprecipitated blend (curve b). The N—H stretching band in the physical mixture is quite close to the position of this stretching band for the pure PBI powder (3420 cm^{-1}). The same band in the blend is displaced by nearly 40 cm^{-1} toward lower frequencies, a change similar to that observed for other miscible PBI/PI blend films of this composition.³ Although the spectra for samples formed in KBr pellets had a somewhat high noise level in this region, the shift was well defined and reproducible. Figure 8B shows the same region, for a pure PBI cast film (curve

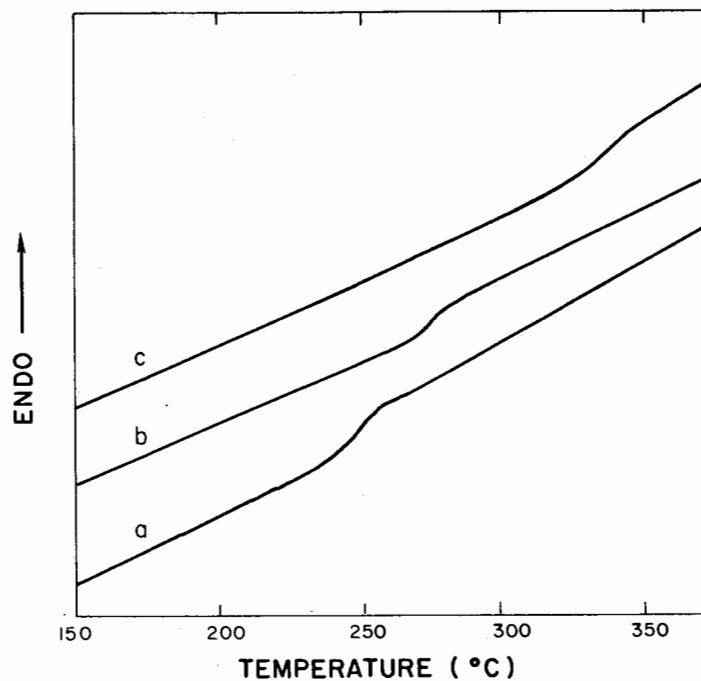


Fig. 5. DSC scans for fully imidized, amorphous powders of (a) pure LaRC TPI, (b) a 30:70 wt% PBI/LaRC TPI blend, and (c) an 80:20 wt% PBI/LaRC TPI blend.

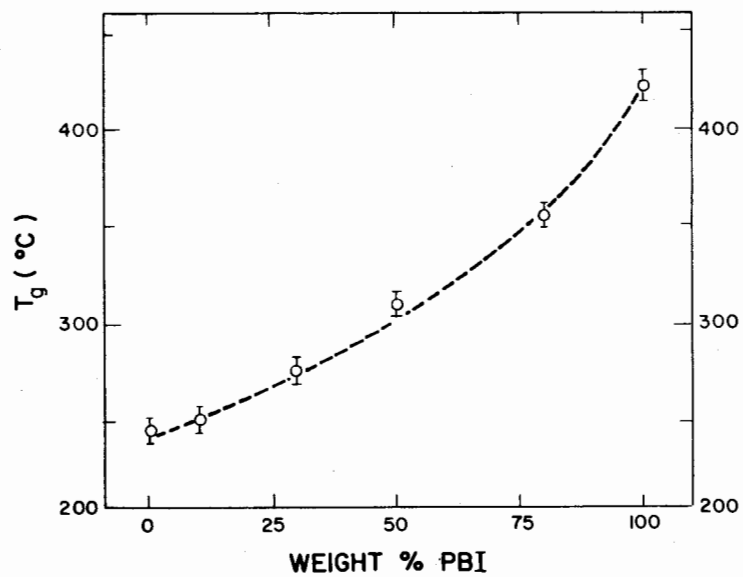


Fig. 6. Composition-dependent T_g 's for PBI/fully imidized amorphous LaRC TPI blends.

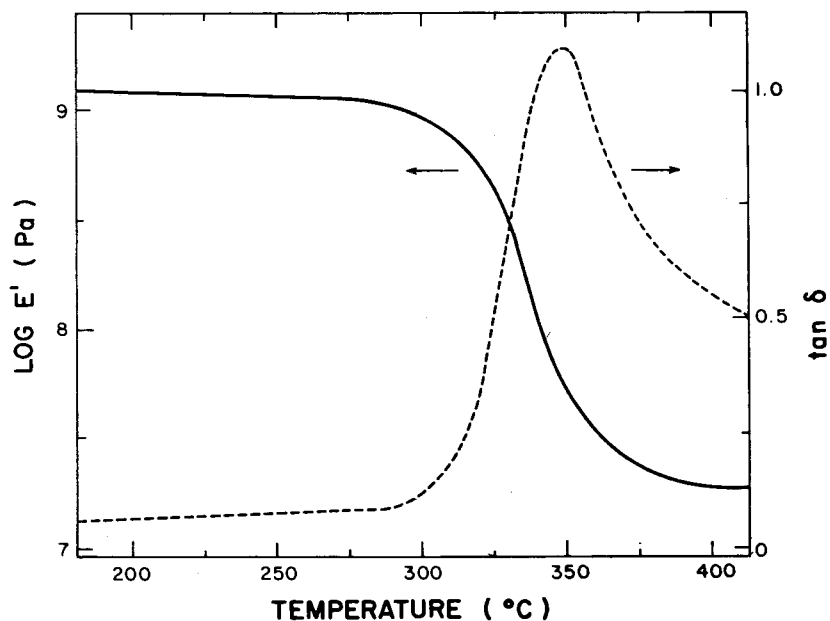


Fig. 7. Dynamic mechanical analysis for a 50:50 wt% blend of PBI with fully imidized amorphous LaRC TPI.

a) and for a 50/50 wt% film blend (curve b). For the cast film blend a shift of the N—H stretching band of about 40 cm^{-1} is again observed. The aromatic ring C—H stretching band (3065 cm^{-1}) is also shown in Figure 8B; it is noted that its position is unchanged by blending. Thus the spectral properties for the blend of PBI with fully imidized amorphous LaRC TPI in the N—H stretching region are similar to those described elsewhere for blends of PBI with XU 218 and Ultem 1000.³

Figure 9A shows the most intense (1720 cm^{-1}) phthalimide carbonyl band, for the 50/50 wt% physical mixture (curve a) and for the 50/50 wt% powder blend (curve b); Figure 9B shows the same region for a pure LaRC film (curve a) and for a PBI/LaRC 90/10 wt% film (curve b). In contrast to the observation in blends of PBI with other polyimides,³ well-defined shifts were not exhibited by either of the two phthalimide carbonyl bands or by the benzophenone carbonyl band. However, the curves in each of the cases shown in Figure 9 are somewhat skewed toward lower frequencies, thereby indicating that either the imide or phthalimide groups are participating in interactions relating to the miscibility of these blends. For blends of PBI with Ultem 1000, XU 218, and PI 2080, phthalimide carbonyl group band shifts up to 6, 6, and 3 cm^{-1} , respectively, were observed.³

Blends of PBI with LaRC TPI were also prepared following an alternative procedure. First, LaRC PAA was precipitated in water, dried, and cured by successively heating at 100 and 200°C with 1 h anneal at each temperature to obtain a powder which was about $95 \pm 2\%$ imidized (according to Fig. 2) but still soluble in DMAc. Mixed DMAc solutions of PBI and of this material were used to prepare films and powders as previously described and heated at 300°C for 1 h to complete the imidization. Single composition-dependent T_g 's

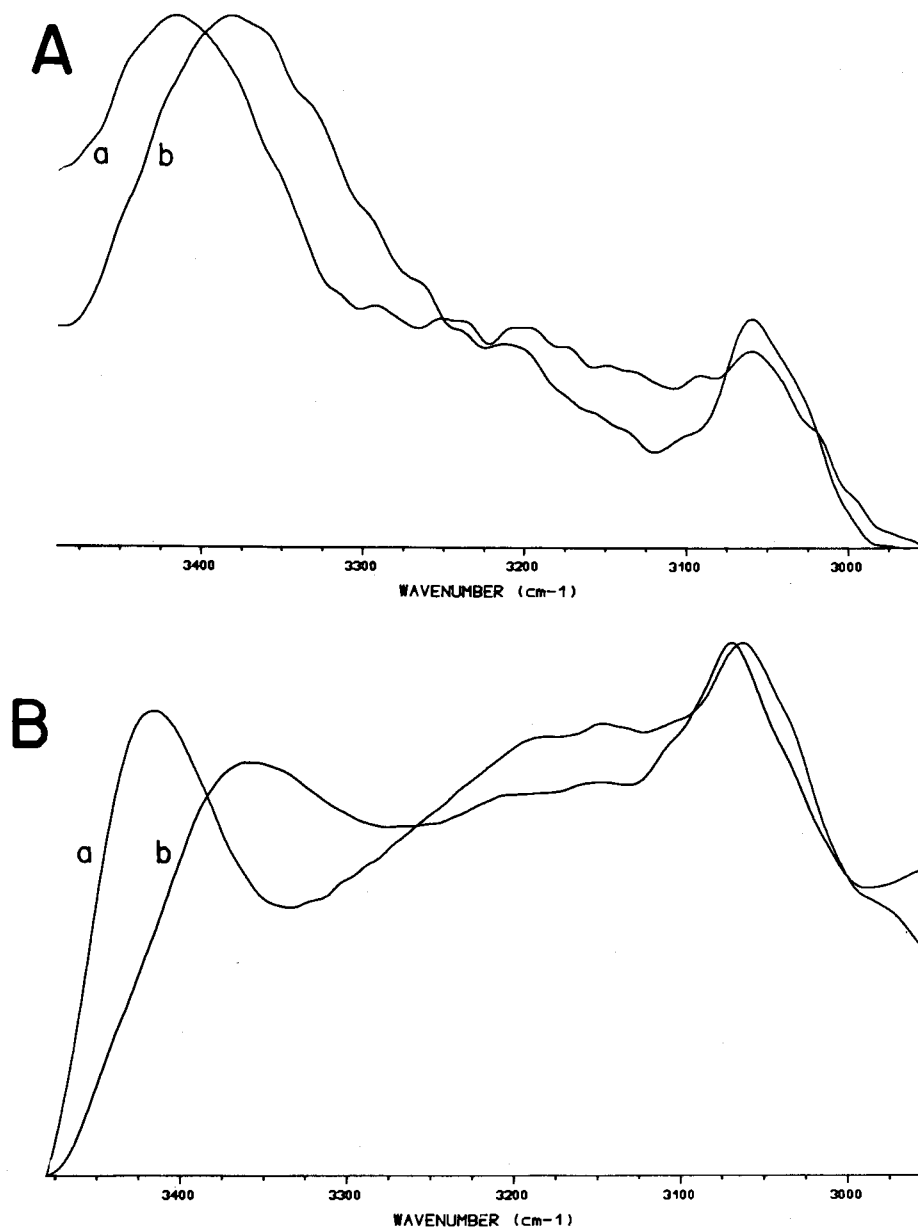


Fig. 8. FTIR spectra in the N—H ($3500\text{--}3000\text{ cm}^{-1}$) stretching band region. (A) A 50 : 50 wt% PBI LaRC TPI physically mixed powder (a) and a coprecipitated miscible powder blend (b). (B) Pure PBI film (a) and a 50 : 50 wt% PBI LaRC TPI miscible film blend (b). All LaRC TPI components were fully imidized.

lying between the component polymers were observed, and it was concluded that these blends were also miscible. Substantial shifts in the N—H stretching band (40 cm^{-1}) were observed.

In contrast to blends of PBI with other polyimides, it was not possible to observe phase separation in this system by annealing at elevated temperatures because such treatment caused the LaRC TPI to crosslink to such an extent

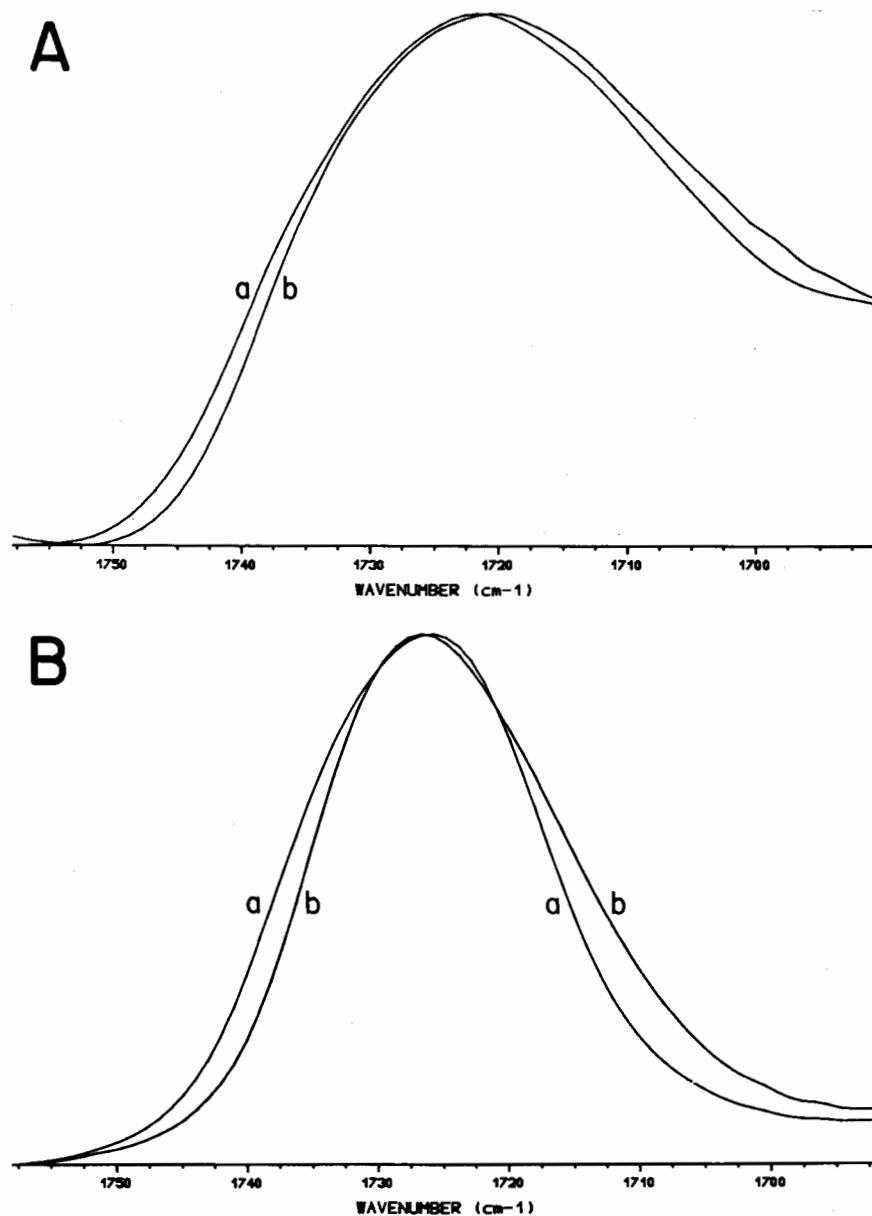


Fig. 9. FTIR spectra in the carbonyl ($1750\text{--}1700\text{ cm}^{-1}$) stretching band region. (A) A 50:50 wt% PBI/LaRC TPI physically mixed powder (a) and a coprecipitated miscible powder blend (b). (B) Pure LaRC TPI film (a) and a 90:10 wt% PBI/LaRC TPI miscible blend film (b). All LaRC TPI components were fully imidized.

that the glass transition rapidly became undetectable. Phase separation studies using FTIR spectroscopy, analogous to those reported for PBI/Ultem 1000 and PBI/PI 2080 blends,³ were carried out, but annealing of the blends at temperatures up to 450°C did not eliminate the observed shifts. However, crosslinking may have limited the mobility of the polymer chains and thereby inhibited phase separation even if the latter were thermodynamically favored.

CONCLUSION

Miscible blends of PBI with LaRC TPI can be prepared by blending either the soluble PAA form or a 95% imidized form of LaRC TPI, both of which are soluble in DMAc, with PBI in DMAc solution, recovered as a powder or film, and subsequently imidized. These blends displayed single composition-dependent T_g 's intermediate between those of the parent homopolymers and a single dynamic mechanical $\tan \delta$ relaxation peak for a 50/50 wt% blend. IR spectral shifts in the PBI N—H stretching band also were observed. High temperature phase separation could not be detected, and it is postulated that this has been prevented by crosslinking of the LaRC TPI component.

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References

1. L. Leung, D. J. Williams, F. E. Karasz, and W. J. MacKnight, *Polym. Bull.*, **16**, 457 (1986).
2. S. Choe, D. J. Williams, F. E. Karasz, and W. J. MacKnight, submitted for publication.
3. G. Guerra, S. Choe, D. J. Williams, F. E. Karasz, and W. J. MacKnight, *Macromolecules* (in press).
4. H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 551 (1961).
5. G. M. Moelter, R. F. Tetreault, and M. J. Hefferson, *Polym. News*, **9**, 134 (1983).
6. V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2275 (1976).
7. A. K. St. Clair and T. L. St. Clair, in *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984, Vol. 2, p. 977.
8. J. M. Adduci, in *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984, Vol. 2, p. 1023.
9. J. P. King, U.S. Patent 3,668,193 (1972).
10. J. C. Fang, U.S. Patent 3,592,952 (1971).
11. A. K. St. Clair, T. L. St. Clair, and L. T. Taylor, NASA Case No. LAR 72640-1, Pat. Appl. (1979).
12. J. A. Kreuz, A. L. Endrey, F. P. Gay, and C. E. Sroog, *J. Polymer Sci., A-1*, **4**, 2607 (1966).
13. L. A. Laius, M. I. Bessonov, and F. S. Florinskii, *Polym. Sci. U.S.S.R.*, **9**, 2470 (1977).
14. S. V. Lavrou, A. Ye. Kardash, and A. N. Pravednikov, *Polym. Sci. U.S.S.R.*, **19**, 2727 (1977).
15. S. Numata, K. Fujisaki, and N. Kinjo, in *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984, Vol. 1, p. 259.
16. P. D. Frayer, in *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984, Vol. 1, p. 273.
17. L. A. Laius and M. I. Tsapovetsky in *Polyimides*, K. L. Mittal, Ed., Plenum Press, New York, 1984, Vol. 1, p. 295.
18. R. J. Angelo, R. C. Golike, W. E. Tatum, and J. A. Kreuz in *Proceedings of the Second International Conference on Polyimides, October 30, 1985, Ellenville, New York*, Plenum Press, New York, p. 631.
19. T. Matsuo, *Bull. Chem. Soc. Japan.*, **37**, 1844 (1964).
20. H. K. Reimschuessel, L. G. Roldan, and J. P. Sibilis, *J. Polym. Sci. A-2*, **6**, 559 (1968).
21. D. Dalphin and A. Wick, *Tabulation of Infrared Spectral Data*, Wiley-Interscience, New York, 1977, Chap. 4.2.
22. T. L. St. Clair, private communication

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