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Miscible blends of aromatic polybenzimidazoles and aromatic polyimides

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Summary

A new family of high performance, miscible polymer blends based on aromatic polybenzimidazoles and aromatic polyimides has been discovered. Preliminary evidence, obtained with commercially available, soluble polymers suggests that polymers of these generic types may be miscible over a wide range of compositions and structural variations. Blend miscibility was evidenced in the form of single T_g's and well-defined single tan δ relaxations intermediate to those of the component polymers, the formation of clear films and, in one case, enhanced solvent resistance.

Introduction

The use of polymeric materials in areas of application traditionally dominated by metals and ceramics has been steadily increasing. These developments have come about through four traditional routes, and combinations thereof: (a) new polymers, (b) control of morphology, (c) reinforcement and (d) blending. In terms of the development of high performance polymer systems for use in the 300 to 400°C range, only approaches (a), (b) and (c) have received widespread attention, whereas (d) has been largely neglected. We have undertaken a program focussed on the preparation of high performance polymer blends, and the development of a fundamental understanding of the phase behavior of these blends. As a first step in this program, some blends formed from aromatic polybenzimidazoles (PBI) and aromatic polyimides (PI), which generally contain either the benzimidazole or 2,6-benzobisimidazole and the phthalimide or pyromellitimide moieties coupled with other aromatic moieties in their repeat unit structures, have been examined. It is well known that high molar mass homopolymer pairs are generally not miscible, but we believe that polymers of these generic types may be miscible over a wide range of blend compositions and structural variations. This assertion is based on exploratory work conducted with commercially available soluble materials. For the samples examined, miscibility was evidenced by single T_g's (obtained in differential scanning calorimetry) and by well-defined tan δ relaxations (obtained in dynamic mechanical analyses) lying between those of the constituent polymers, by the formation of clear films and, in one case, by enhanced solvent resistance. The interactions which give rise to this miscibility are as yet poorly understood, and the limits of miscibility in terms of structure, composition and temperature remain to be established.

The exploratory studies were conducted with polymers that are soluble in N,N-dimethylacetamide (DMAc) so that blends could be prepared

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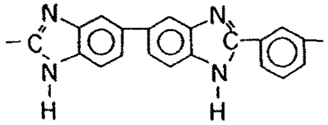
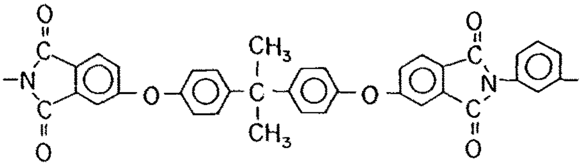
either by precipitating blended materials in solution into a non-solvent such as methanol or by casting a film. The polybenzimidazole [poly-2,2'(m-phenylene)-5,5' bibenzimidazole], (Celanese Corporation), was used as a representative PBI component(1). This PBI is an amorphous homopolymer with a T_g of 425°C and the chemical structure given below.

Celanese PBI



A representative aromatic polyetherimide (PEI), [poly(2,2'-bis(3,4-dicarboxyphenoxy) phenylpropane)-2-phenylene bisimide)] (General Electric: Ultem 1000), is an amorphous thermoplastic with a T_g of 217°C, number and weight average molecular weights of 12,000 and 30,000, respectively, and the following chemical structure(2).

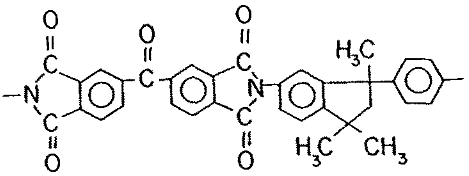
Ultem 1000



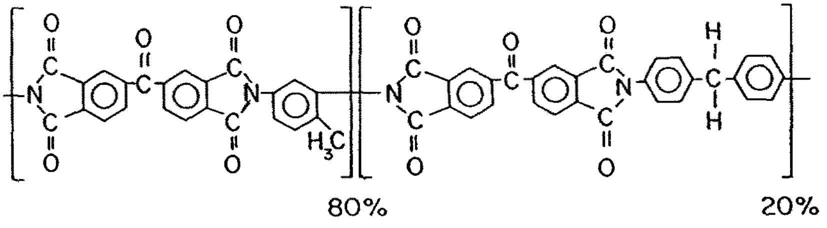
Blends containing two other polyetherimides (General Electric: Ultem D5000 and 6000) were also investigated. These PEIs are copolymers with structures related to that of Ultem 1000 in that a portion of the m-phenylene diamine of Ultem 1000 is replaced with a mixture of toluene diamines(3). Only a few exploratory experiments were conducted with these materials because their structures are not well defined.

The polyimides (PIs) were represented by products formed from benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4' aminophenyl)-1,3,3-trimethylindane with a T_g of 320°C (Ciba-Geigy: XU 218) and benzophenone tetracarboxylic dianhydride and a 4/1 molar mixture of 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate with a T_g of 310°C (Dow Chemical Co.: 2080). The chemical structures are given below(4,5):

XU 218



Dow 2080



Experimental

Blends were prepared by mixing 2% (w/v) solutions of PBI and the respective PIs in DMAc in the desired proportions. The PIs employed dissolved readily in DMAc under ambient conditions. PBI dissolved in a pressure vessel at 225°C for 30 min. under nitrogen leaving an insoluble residue of about 0.25% by weight, which was removed by filtration.

Solutions containing the two polymer components in the desired composition ratio were added to methanol to yield a precipitated blend in the form of a fine powder. Subsequently, the powder was washed with methanol or water to remove residual DMAc and then vacuum dried at 150°C for several days. Additionally, thin films were cast from 2 to 4% (w/v) solutions of the blends in the desired compositions on flat glass plates. The solvent was evaporated in a dry nitrogen atmosphere at about 125°C for 24 hours. After about 85 to 90% of the solvent was evaporated, the remaining solvent was removed by washing the film with hot water (about 50°C) for several days. Finally, the films were dried *in vacuo* overnight at 125 to 150°C. In the case of the PEI-containing blends, moisture had to be excluded until most of the solvent was removed, and the compositions could not be heated above their T_g's or phase separation would result.

DSC experiments were conducted on the precipitated polymer blends using a Perkin-Elmer DSC-7 Differential Microcalorimeter controlled by a 7500 PC. A heating rate of 25°C/min under nitrogen was used.

DMA experiments were carried out using a Polymer Laboratories DMTA equipped with a high temperature (500°C) head. Approximately 1mm thick films were studied under nitrogen in the flexural mode at constant strain. Data were collected at 1 Hz at a heating rate of 4 °C/min.

An IBM Model 38 FTIR spectrometer and pellets molded from a mixture of powdered polymer and potassium bromide (KBr) were used for the infrared (IR) spectral analysis. The samples were kept under vacuum and the scan range was from 400 to 4000 cm^{-1} with the sample under vacuum. A Zeiss optical microscope with a polarizing lens and mounted with a 35mm camera was used for microscopy studies.

Results and Discussion

The appearance of either a single glass transition measured calorimetrically, or a single narrow tan δ relaxation obtained by DMA, lying at temperatures between those of the individual constituents is a generally accepted criterion for miscibility in a binary polymer blend. As a rule, the intermediate T_g of the miscible blend will lie close to that predicted by a linear interpolation of the T_g's of the blend constituents. Physical mixtures or phase separated blends of two polymers will display two T_g's corresponding to the compositions of each phase. In addition, amorphous miscible blends should form clear films. In this report, we present results which demonstrate the general property of PBI/PI blend miscibility. Sufficient data have been collected to establish the premise that blends of these generic types may be miscible over quite a wide range of compositions and structural variations.

The most important step in film preparation was found to be the removal of residual DMAc which can act as a very efficient plasticizer.

Most of the DMAc (85 to 90%) could be easily removed during the initial stages of film casting on glass plates: the remainder was removed with difficulty. This difficulty increased with higher PBI contents. Generally, heat and vacuum cycles alone were not sufficient for removing residual small amounts of DMAc and temperatures in excess of about 350°C were avoided because such exposure might induce phase separation and/or thermal decomposition. The most satisfactory method for removing the last several percent of DMAc was prolonged washing with continuously changing hot (50°C) water. The water wash was followed by extended vacuum drying at 125 to 150°C. Clear films of blends containing all three polyimides with PBI contents ranging from 10 to 90% were prepared.

Calorimetric studies were generally performed on washed and dried precipitated powders. Table 1 lists the T_g's for the three Ultem-containing 50/50 wt % blends with PBI which had been subjected to two DSC scans. The first scan, from room temperature to about 450°C, was performed on a freshly prepared sample. As can be seen, a single intermediate T_g was observed for each blend during the first scan indicating miscibility. The samples were cooled to 50°C and scanned again. In each case two T_g's, corresponding to those of a relatively pure Ultem 1000 phase and of a PBI-rich phase, were observed indicating that phase separation had occurred when the blend was heated above its T_g.

Table 1 Glass transition temperatures of 50/50 wt % PBI/PEI miscible powder blends.

Sample		T_g, Midpoint (°C)			
Polymer A	Polymer B	Low		High	Comments
Ultem 1000	PBI		344		First scan
		207		418	Second scan
Ultem D5000	PBI		341		First scan
		214		414	Second scan
Ultem 6000	PBI		330		First scan
		225		419	Second Scan

Single DSC scans were carried out using powdered samples prepared as described above of blend compositions ranging from about 5 to 95 wt % Ultem 1000. The single T_g values obtained during this scan were used to construct Figure 1 where it can be seen that PBI and Ultem 1000 are miscible in all proportions when prepared by the described procedure. The blend T_g's are slightly higher than those predicted by linear interpolation of the T_g's of PBI and Ultem 1000. Phase separation resulted in all cases when a second DSC scan was performed after quenching from 450°C.

Films of PBI/Ultem 1000 blends with compositions of 25/75, 50/50 and 75/25 wt % were phase separated by heating at 50°C/min to 450°C and quenching in the DSC. The 50/50 wt % blend was similarly heated and annealed at 350°C--about 5°C above Tg--and quenched. All the films were examined using an optical microscope, and all displayed gross domains readily discernable at magnifications of 25 to 40X, verifying that phase decomposition had indeed occurred.

These results imply that the major portion of the equilibrium phase boundary for PBI/Ultem 1000 blends probably lies between room temperature and the glass transition. Actual phase separation did not occur above the phase boundary until T_g was reached because of the restricted mobility of the polymer chains in the glassy state.

Table 2 lists the T_g's for a 50/50 wt % PBI/XU 218 blend prepared by precipitating from DMAc solution into methanol. In the absence of thermal aging a single intermediate T_g of 380°C was observed. This transition is a few degrees above that predicted by a linear interpolation and was found to increase up to about 400°C as the annealing temperature increased to 440°C, which is ascribed to the onset of thermally induced crosslinking. At an annealing temperature of 450°C two T_g's were observed indicating that phase separation had occurred. Apparently, the phase boundary for this particular blend occurs in the vicinity of 440 to 450°C. However, phase rehomogenization could not be observed.

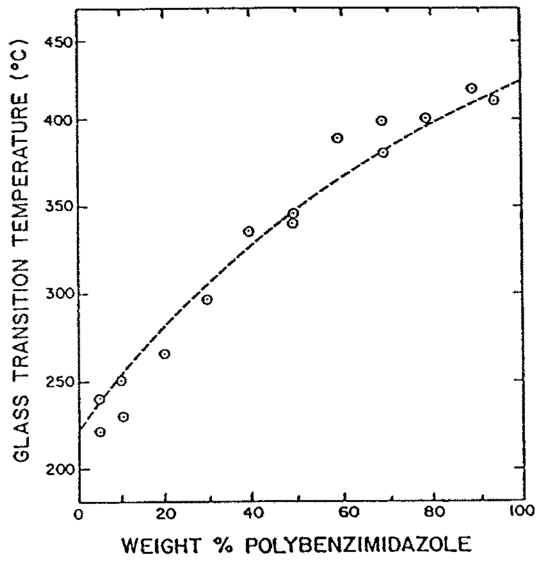


Figure 1. Glass transition temperature of PBI/Ultem 1000 blends.

Table 2 Glass transition temperatures of 50/50 wt % PBI/XU 218 blends.

Aging Conditions	Low	T_g Midpoint (°C) Intermediate	High
None	-	380	-
380°C, 5 min.	-	380	-
390°C, 10 min.	-	384	-
400°C, 5 min	-	386	-
400°C, 60 min.	-	392	-
410°C, 5 min.	-	385	-
420°C, 5 min.	-	395	-
440°C, 5 min.	-	404	-
450°C, 5 min.	336	-	403
450°C, 30 min.	310		410

Single T_g's were also obtained for 70/30, 50/50 and 30/70 wt % PBI/2080 blends for which the T_g's (392, 359 and 336°C, respectively) were also close to those predicted by a linear interpolation.

Figures 2 and 3 show representative tan δ relaxation peaks for a film of the 50/50 wt % PBI/XU 218 blend subjected to the indicated thermal histories. Figure 2 shows the temperature dependence of tan δ for pure XU 218 (T_g = 327°C), pure PBI (T_g = 434°C) and the observed single relaxation peak for a 50/50 blend thermally annealed in the DMA by heating at 4°C/min to 350°C, quenching to 50°C and rescanning at 4°C/min to 450°C. The temperature of the tan δ peak for the blend (374°C) is close to the calorimetrically determined T_g value (380°C) shown in Table 2. Figure 3 shows the tan δ temperature dependence for the 50/50 wt % blend subjected to additional thermal conditioning by heating to 380, 400 and 450°C in the DMTA. A shift in the tan δ peaks to higher temperatures (391, 399 and 416°C) and a decrease in the peak height are noted, suggesting the onset of thermally induced crosslinking as discussed above. The appearance of shoulders on the tan δ peaks at lower temperatures suggests the onset of phase separation as the samples were heated. These data clearly support the existence of a miscible blend. Similar data were obtained for PBI/Ultem 1000 and PBI/2080 blends.

PBI/Ultem 1000 films with the compositions listed in Table 3 were immersed in methylene chloride and chloroform at room temperature. Pure Ultem 1000 dissolved rapidly in either solvent, whereas pure PBI was virtually unaffected. Table 3 lists the ratio of the percent weight loss and the percent solvent absorbed by the films for the immersion times given. Each data entry represents results for a fresh film. Substantially reduced amounts of the film were extracted by methylene chloride as the PBI content increased from 20 to 30 wt %. Equilibrium weight loss was achieved after about 18 hours immersion for films containing 20 wt % PBI and in less than 3 hours for those containing 30 wt % PBI. In chloroform substantially reduced amounts of the film were extracted by the solvent as the PBI content increased from 30 to 40 wt %. In all cases the films remained intact, although distorted, even when 50 wt % of the original material was extracted. All films could be redissolved in DMAc indicating that crosslinking had not occurred during the film preparation. Thus, the addition of PBI greatly enhanced the resistance of Ultem 1000 to dissolution by the chlorinated hydrocarbon solvents tested. These results imply that a strong specific attractive interaction exists between PBI and Ultem 1000.

Miscibility in binary homopolymer blends is generally attributed to the existence of specific interactions. In the systems presently under investigation there are at least three possible sources of interaction: (a) hydrogen bonding between the carbonyl groups of the imide ring and the amine group of the imidazole ring, (b) π-orbital interactions between the imide and imidazole rings or (c) charge transfer interaction between the phthalimide and benzimidazole fused ring systems. To elucidate the nature of the interactions giving rise to miscibility, FTIR studies were performed on PBI/Ultem 1000 blends.

Infrared spectra were obtained for two 50/50 wt % PBI/Ultem 1000 blend samples using KBr pellets. One of the samples was a blend precipitated from DMF; the other was prepared by physically mixing the powdered, pure components. Two discernible differences in the blend samples were detected: the 1779 and 1724 cm^{-1} absorption maxima in the sample prepared by mixing the powdered components were shifted to 1776 and 1720 cm^{-1},

Figure 2. Dynamic mechanical analysis of PBI, XU 218 and a 50/50 wt% miscible blend thermally annealed at 350°C.

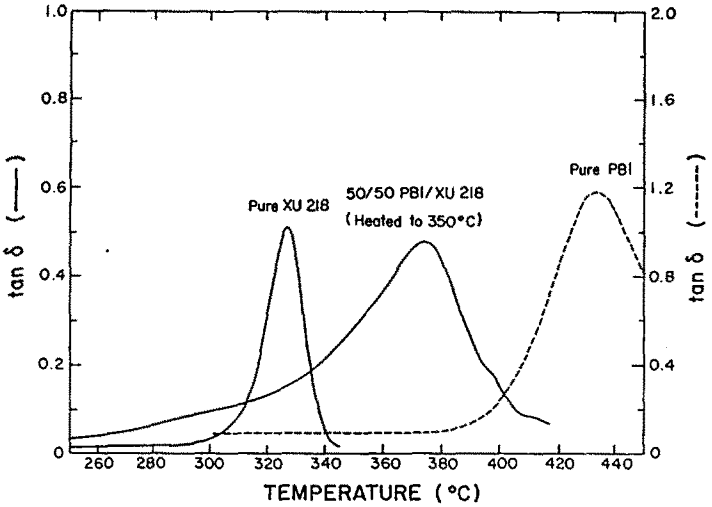


Figure 3. Dynamic mechanical analysis of a 50/50 wt % PBI/XU 218 miscible blend thermally annealed at 380, 400 and 450°C.

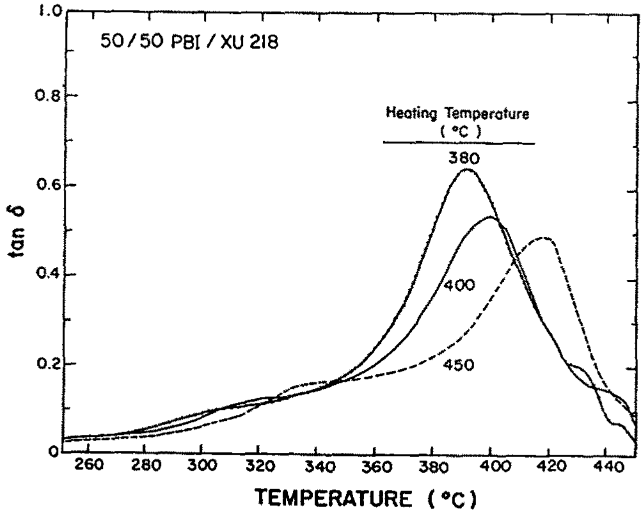


Table 3 Solubility Studies of PBI/Ultem 1000 Immersed Films

Blend Composition PBI/Ultem 1000 (wt %)			% Mass Lost/% Solvent Absorbed 25 Hrs.		4 days
			Methylene Chloride		
0/100			100/-		100/-
10/90			53/16		55/31
20/80			26/15		28/23
30/70			5/17		8/21
40/60			5/20		4/21
100/0			0/0		0/0
			Chloroform		
0/100			100/-		100/-
10/90			63/49		69/54
20/80			9/6		47/41
30/70			2/5		17/23
40/60			1/5		2/20
100/0			1/0		2/0
			% Mass Lost in Methylene Chloride		
	3 hrs.	6 hrs.	12 hrs.	18 hrs.	25 hrs.
20/80	13	19	22	25	26
30/70	4	3	4	4	5

respectively, in the sample precipitated from DMF. The shifting of the carbonyl bands to lower wavenumbers indicates an interaction which involved this group. A similar shift has been observed in polyester and poly(vinyl chloride) blends and has been ascribed to specific intermolecular interactions involving the carbonyl bond(6). The region showing the N-H stretch (2800 to 3400 cm^{-1}) was also examined, but because of the very broad absorption peaks no significant differences could be detected. These studies are continuing with model compounds.

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