polymer

Interaction, miscibility and phase inversion in PBI/PI blends

E. Földes[a,*], E. Fekete[a], F.E. Karasz[c], B. Pukánszky[a, b]

[a]*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary*
[b]*Technical University of Budapest, Department of Plastics and Rubber Technology, H-1521 Budapest, P.O. Box 92, Hungary*
[c]*University of Massachusetts at Amherst, Department of Polymer Science and Engineering, Amherst, MA 01003, USA*

Abstract

The miscibility of polybenzimidazole {poly[2,2′-(m-phenylene)-5,5′-bibenzimidazole], (PBI)} and a polyimide {poly[2,2′-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane-m-phenylenediimine) (PI)} was studied in the entire composition range. Films were cast from solution by a procedure developed in a preliminary work. The blends were studied by FT-IR spectroscopy, thermal and thermomechanical methods, and by measuring vapour absorption at an ambient temperature. Direct relationships were found between the strength of hydrogen-bonding of the components, the glass transition temperature of the blends, and the solvent diffusion rate (water and 1,2,4-trichlorobenzene). The results of the experiments indicate partial miscibility between the two polymers. Phase inversion occurs between 0.4 and 0.6 PI content. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Phase inversion; Blends; Polybenzimidazole

1. Introduction

Blends of polybenzimidazole {poly[2,2′-(m-phenylene)-5,5′-bibenzimidazole], (PBI)} and several polyimides (PI) have been widely investigated in the last 12 years because of the theoretical and practical importance of these high performance polymers. From the very initial studies, it was claimed that miscibility occurs over a wide composition range, as the blends displayed single intermediate glass transitions (T_g) in the first DSC heating [2]. Further studies revealed phase separation upon annealing [2–4], and the phase behaviour of the systems was found to be dependent both on the type of polyimide and thermal history. Thus blends of PBI with the condensation product of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4′-aminophenyl)-1,3,3-trimethylindane (XU 218, Ciba-Geigy) showed phase separation only above 400°C, at temperatures determined by the composition [4]. From calorimetric studies of blends of PBI with poly[2,2′-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane-m-phenylenediimine] (Ultem 1000, General Electric) it was

inferred that phase separation might occur between ambient temperature and the glass transition temperature, if it were not prohibited by the restricted mobility of the polymer chains in the glassy state [2]. Infrared studies revealed hydrogen bonding between the N–H groups of PBI and the carbonyl groups of PI [5] which relaxed during the thermal treatment resulting phase separation [6,7].

For the PBI/Ultem 1000 system the actual phase separation could not be detected below T_g either by DSC [2] or by dielectric relaxation [8]. The only direct evidence for the existence of separate phases seems to be the results of mechanical relaxation experiments. The loss tangent measured at 1 Hz shows two or three composition dependent maxima between the glass transition temperatures of the components [8].

Complex relaxation studies drew attention to the importance of the sample preparation technique—especially the amount of residual solvent and water—in the properties of binary blends of PBI and Ultem 1000 [8]. As a consequence, sample preparation conditions were studied in the first phase [1] of an intensive study on the composition/structure/property relationships in PBI/Ultem 1000 blends. The results of the study of interactions, miscibility and phase behaviour of this polymer pair prepared by the selected technique are presented in this paper.

* Corresponding author. Tel.: +36-1-325-9045; fax: +36-1-325-7554.
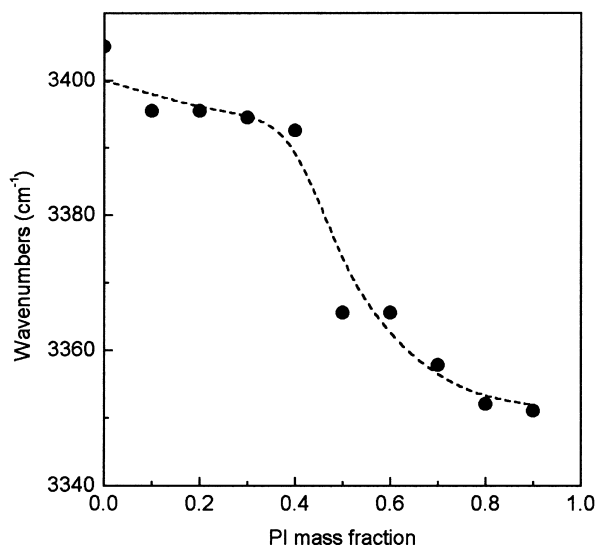*E-mail address:* efoldes@cric.chemres.hu (E. Földes)

Fig. 1. Composition dependence of the frequency of N–H stretching vibration.

2. Experimental

2.1. Materials

Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI); Hoechst Celanese Corp; $T_g = 420°C$; density: 1.269 g/cm^3.
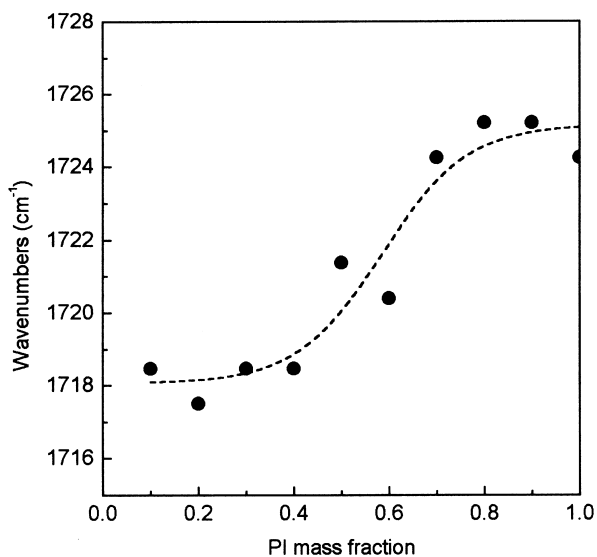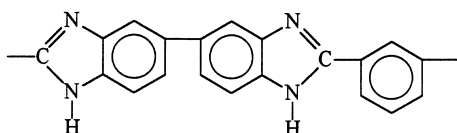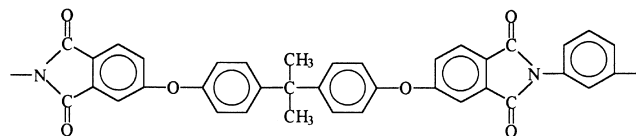

Fig. 2. Composition dependence of the frequency of C=O stretching vibration.

Poly[2,2'-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane-m-phenylenediimine] (PI); grade Ultem 1000; General Electric Co; $M_w = 30\ 000 \pm 10\ 000$, $M_n = 12\ 000 \pm 4000$ g/mol; $T_g = 220°C$; density: 1.187 g/cm^3.

2.2. Sample preparation

The sample preparation technique was developed in a preliminary study carried out to determine the effects of preparation conditions on the stability, residual solvent and water content of the polymer [1]. In this study, 2 w/w% solutions of PBI and PI were prepared using *N,N'*-dimethyl acetamide. The PI solution was prepared under ambient conditions, while PBI was dissolved in a stainless steel reactor at 260°C under 3–4 bar pressure for 2 h and then diluted to 2%. Films of about 100 μm were cast from the two polymers and their blends in the entire composition range from 0 to 1 mass fraction of PI in steps of 0.1. Most of the solvent was evaporated in a ventilated oven held at 80°C for about 60 h. The resulting films were washed at 60°C for 7 days to remove the remaining solvent, then dried at 190°C for 300 h in order to remove traces of moisture. Optically clear films were obtained for each blend composition. The dried films were stored in a desiccator at ambient temperature until the actual measurements.

2.3. Measuring techniques

Infrared spectroscopic measurements were made using a Mattson Galaxy 3020 FT-IR Spectrometer (Unicam Ltd.). Thermal analysis was performed with a Perkin–Elmer DSC-2 cell under nitrogen atmosphere between 50 and 450°C at a heating rate of 20°C/min. Thermomechanical analysis was carried out on a Du Pont TMA 943 system between 25 and 500°C at a heating rate of 5°C/min in the stretching mode using a 7–12 mg/mm^2 load.

The absorption of water and 1,2,4-trichlorobenzene (TCB) vapour was studied on film samples of 80 mm diameter at an ambient temperature (23°C). The diffusion coefficient and the equilibrium vapour uptake was determined from the time dependence of absorption.

3. Results and discussion

The FT-IR spectroscopic study of PBI/PI blends of varying composition confirmed the results of earlier experiments [5,6]. The N–H stretching vibration of PBI shifts to lower frequencies with increasing PI content (Fig. 1). The differences between the present and earlier results observed at
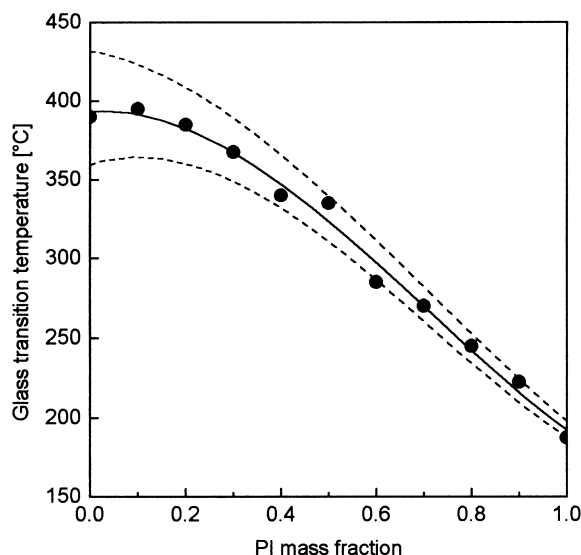
Fig. 3. Composition dependence of the glass transition temperature and its range determined by TMA at a rate of 5°C/min.

high PI contents are attributed to the different sample preparation techniques. They indicate that the strength of interaction between the two polymers is influenced by the traces of moisture remaining in the blend after washing and drying. The changes in the carbonyl stretching absorption frequencies (ν_{CO}) of PI are less pronounced than those of the N–H groups of PBI, but they are unambiguous. Fig. 2 shows the ν_{CO} values of the lower frequency absorption peak as a function of composition; the maximum at 1779 cm^{-1} shows a similar trend. The C=O maximum decreases with increasing PBI content of the blend. The function is non-linear; a sharp decrease can be observed between 0.3 and 0.6 PBI contents.
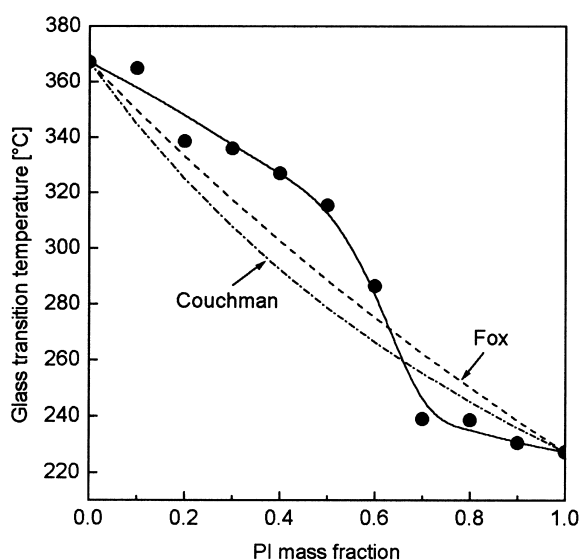

Fig. 4. Composition dependence of the glass transition temperatures determined by DSC at rate of 20°C/min. The dashed lines were calculated by the equations of Fox [13] and Couchman [15].

Attention must be directed to the relatively small, 50 and 7 cm^{-1} maximum shifts of the N–H and C=O frequencies, respectively, which imply comparatively weak hydrogen bonding between the two polymers, especially when we consider the shifts of the same absorption peaks in amides and polyamides (130–150 and 70–80 cm^{-1}, respectively) [9–11]. The relatively weak attraction can be explained by the superposition of two effects: stiffness of the chains composed of aromatic rings, as well as self-association of the components. According to Tang et al. [12] the electron-acceptor diimide groups and the electron-donor aromatic units of the PI studied here form charge-transfer complexes resulting in aggregation of the solid polymer. Self-association of PBI is indicated by its high glass transition temperature and the complex shape of the infrared absorption region between 3500 and 2500 cm^{-1} (see Refs. [5,6]). In these blends interaction competes with self-association of the components.

The effect of specific interactions (intermolecular hydrogen bonding) on the physical properties of the blends was studied by measuring the glass transitions by TMA and DSC. PBI displays a broad transition region; PI shows a much narrower transition. Both thermal techniques yielded single intermediate glass transitions for the blends, as was observed earlier [2]. Fig. 3 shows the composition dependence of the glass transition temperature determined by TMA; the filled circles correspond to the inflection point of the transition curve, while the dashed lines reflect the low and high temperature limits. T_g decreases with increasing PI content of the blends, though the measured values are higher than those calculated by the Fox equation [13], Eq. (1), or by that of Gordon and Taylor [14], Eq. (2), often used for miscible polymer systems.

$$\frac{l}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \tag{1}$$

where w_1 and w_2 are the mass fractions, T_{g1} and T_{g2}, the glass transition temperatures of polymers 1 and 2.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}, \tag{2}$$

where k equals $\Delta\beta_2/\Delta\beta_1$, the volume thermal expansion coefficient changes at T_g of polymers 2 and 1.

The T_g values determined by DSC (Fig. 4) form a sigmoid curve as a function of composition. At high concentrations of both components the glass transition temperature changes only moderately, and a drop can be observed between 0.5 and 0.7 PI mass content. At small PI concentrations the measured T_g values are higher than predicted by the equations of Fox [13], Eq. (1), and Couchman [15], Eq. (3); above 0.6 mass fraction of PI the relation is reversed.

$$\ln T_g = \frac{w_1 \, \Delta c_{p1} \ln T_{g1} + w_2 \, \Delta c_{p2} \ln T_{g2}}{w_1 \, \Delta c_{p1} + w_2 \Delta c_{p2}}, \tag{3}$$
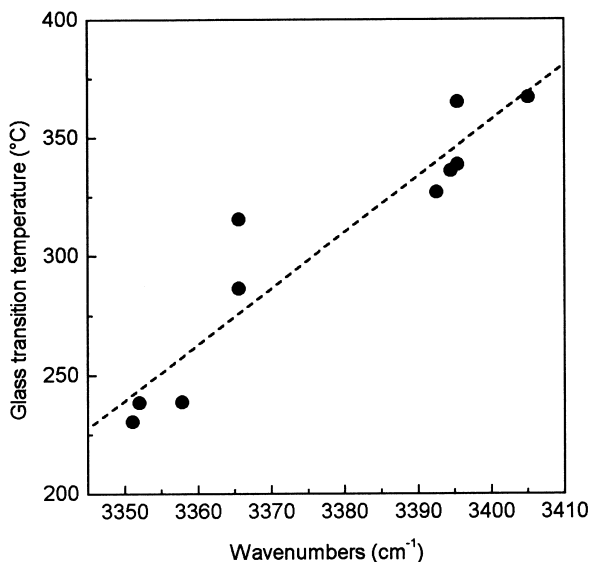
Fig. 5. Relationship between the N–H absorption frequencies and the glass transition temperatures measured by DSC.

where Δc_{p1} and Δc_{p2} are the heat capacity changes of polymers 1 and 2 at T_g.

Considering that a single T_g reflects the state of dispersion rather than the actual thermodynamical miscibility [16], the composition dependence of T_g determined by DSC suggests partial miscibility between PBI and PI with a phase inversion between 0.5 and 0.7 PI mass content. The deviation in the T_g values determined by TMA and DSC can be attributed partly to the difference in the heating rates used for the experiments, partly to the difference in nature of the functions measured by the two methods (deformation and heat capacity).

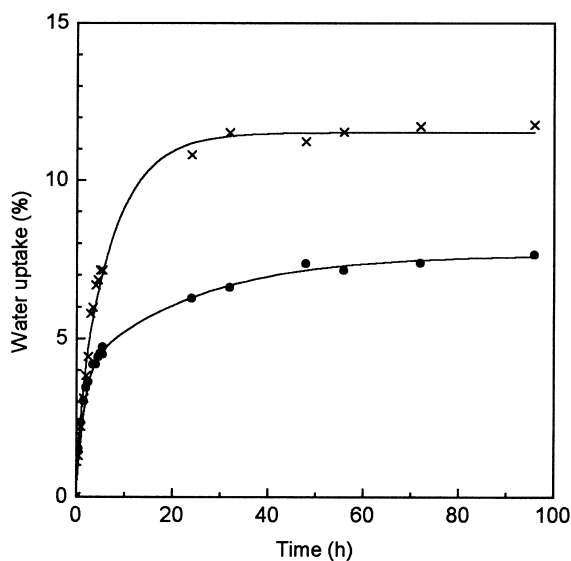The comparison of the N–H stretching vibration

Fig. 6. Time dependence of water vapour absorption of PBI/PI blends. Composition (●) 50/50, (×) 70/30; —fitted values.

frequencies with the DSC glass transition temperatures of the blends indicates a direct relationship between these quantities (Fig. 5). Similarly, good correlation is obtained when the C=O absorption peak frequencies are plotted against T_g. These results prove directly that the thermal characteristics of the blends are controlled by the strength of specific interactions between the components.

Vapour absorption is an additional probe for studying polymer/polymer miscibility [16,17]. Water and TCB vapour absorption of blend films were measured at an ambient temperature. Absorption was determined gravimetrically as a function of time.

In the case of simple Fickian diffusion, the diffusion coefficient and the equilibrium vapour uptake of a film can be determined by numerical solution of Fick's equation [18,19].

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[\frac{D(2m+1)^2 \pi^2 t}{l^2} \right], \quad (4)$$

where D is the diffusion coefficient; M_t is the amount of diffusant taken up by the film of thickness, l, at time, t; M_∞ is the equilibrium sorption attained after infinite time.

Diffusion measured in glassy polymers often deviates from the Fickian one. The anomalous effects may originate from a change in the polymer structure upon sorption (indicated by widening of the relaxation time distribution), or from the internal stress induced by swelling of the polymer [19]. In Case II or "relaxation controlled" diffusion the constant velocity of an advancing front of the boundary between swollen gel and glassy core controls the rate of vapour uptake. When the diffusion and relaxation rates are comparable, non-Fickian or anomalous diffusion occurs, and two or more parameters are required to describe the interacting diffusion and relaxation effects [19].

For the case of combined Fickian and Case II diffusion Kwei et al. [20,21] derived the following generalised equation:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} - \nu c \right], \quad (5)$$

where c is the concentration of the penetrating material at time, t, at a distance, x, from the surface contacting the source of penetrant. The second term in the square brackets describes the contribution of internal stress arising from swelling of the polymer, and ν is the velocity of Case II diffusion.

For the numerical solution of combined diffusion Berens and Hopfenberg [22] introduced a simple model which is a linear superposition of a phenomenologically independent first order term upon the ideal Fickian diffusion equation:

$$M_t = M_{t,D} + M_{t,R}, \quad (6)$$

where $M_{t,D}$ is the amount of diffusant absorbed by Fickian diffusion mechanism (corresponding to Eq. (4)), $M_{t,R}$ is the amount of diffusant absorbed by first order kinetics (Case II
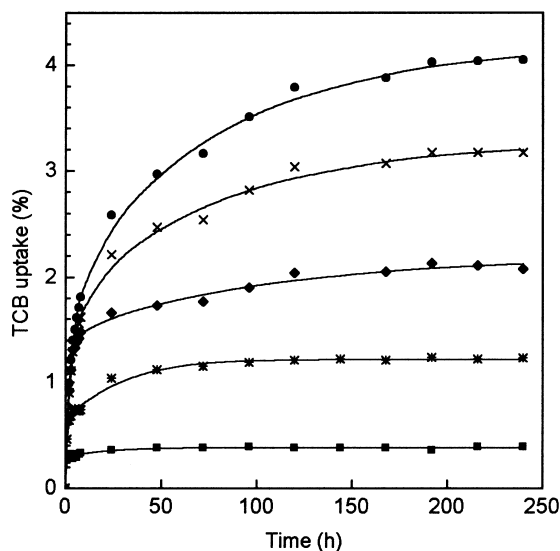
Fig. 7. Time dependence of TCB vapour absorption. Composition (●) PBI, (×) 80PBI/20PI, (◆) 60PBI/40PI, (∗) 30PBI/70PI, (■) PI;—fitted values.

mechanism):

$$\frac{M_{t,R}}{M_{\infty,R}} = 1 - \exp(-kt), \tag{7}$$

where k is the rate constant, which is independent from sample thickness.

The results of the vapour uptake experiments were evaluated by Eqs. (4) and (6) using the least-squares curve fitting method which yielded D, k and M_∞ values, as fitting parameters.

In the case of water sorption, the mechanism was found to differ for PBI and PI. Water uptake of PBI is relatively high, but slow, and can be described by simple Fickian diffusion (Eq. (4)). The equilibrium water sorption of PI is small, and the penetration proceeds with a combined mechanism starting with a relatively high diffusion rate followed by a relaxation controlled mechanism (Eq. (6)). The behaviour of the blends is composition-dependent. At high PBI contents the water uptake is diffusion controlled, at higher

PI contents, starting with a mass fraction of 0.4, the sorption mechanism changes and becomes a two-step process. For illustration the sorption curves of PBI/PI 70/30 and 50/50 are shown in Fig. 6, where the measured values are represented by symbols and the fitted ones by continuous lines.

Sorption of TCB is a combined mechanism in both the neat polymers and in the blends (Fig. 7). The equilibrium uptake of TCB is always lower than that of water, and it is higher in PBI than in PI.

The characteristic parameters computed from the measured sorption curves are summarised in Table 1 for water and in Table 2 for TCB. The diffusion coefficients of the two solvents do not differ substantially, especially in the range of 0.4–0.7 PI content. However, the diffusion coefficients of water are lower at low PI contents and higher at high PI concentrations than those of TCB. The composition dependence of the diffusion coefficients of both solvents is non-linear either on a linear or on a logarithmic scale (Fig. 8). D is low at low PI contents, increases slowly with increasing PI concentration in the case of TCB, and can be considered to be independent of the composition up to 0.3 PI mass fraction in the case of water. A major increase in the Fickian diffusion coefficients starts at PI contents between 0.3 and 0.4 for water, and between 0.4 and 0.5 for TCB.

Comparing the results yielded by the different techniques, a linear relationship is obtained between the logarithm of the diffusion coefficient and the wavenumber of the N–H absorption peak. Fig. 9 shows the correlation determined from the sorption of TCB. The diffusion rates of water yield a similar relationship. According to a number of empirical equations the logarithm of the diffusion coefficient of small molecules is a linear function of the reciprocal specific free volume of the polymer [23] or polymer blend [24]. The relationships shown in Figs. 8 and 9 indicate that the specific free volume of PBI/PI blends decreases linearly with increasing polymer/polymer interaction strength which is reflected in the shift of the N–H absorption peaks to lower frequencies, and is a non-linear function of the blend composition. This correlation proves the significant role of

Table 1
Characteristics determined from the water vapour uptake of PBI/PI blends

PI mass content	D (cm^2/s)	k (1/s)	$M_{\infty,D}$ (%)	$M_{\infty,R}$ (%)	ΣM_∞ (%)	$\chi_{PBI,PI}$	$\chi_{W,PBI}$[a]
0	1.19×10^{-9}		21.60		21.60		1.22
0.1	5.13×10^{-10}		15.33		15.33	0.84	1.34
0.2	5.04×10^{-10}		14.87		14.87	1.88	1.29
0.3	5.56×10^{-10}		11.52		11.52	1.91	1.36
0.4	1.33×10^{-9}	1.13×10^{-5}	4.40	6.16	10.56	2.48	1.32
0.5	2.48×10^{-9}	5.75×10^{-6}	3.95	3.69	7.64	2.53	1.39
0.6	2.82×10^{-9}	5.28×10^{-6}	2.91	2.52	5.43	2.64	1.46
0.7	2.71×10^{-9}	6.72×10^{-6}	4.04	0.82	4.86	3.79	1.36
0.8	5.03×10^{-9}	2.78×10^{-5}	3.04	1.16	4.20	5.80	1.23
0.9	8.06×10^{-9}	1.33×10^{-5}	1.78	0.55	2.33	7.49	1.15
1.0	1.21×10^{-8}	1.64×10^{-5}	0.68	0.21	0.89		

[a] Hypothetical value assuming interaction only with PBI.

Table 2
Characteristics determined from the TCB vapour uptake of PBI/PI blends

PI mass content	D (cm^2/s)	k (1/s)	$M_{\infty,D}$ (%)	$M_{\infty,R}$ (%)	ΣM_∞ (%)	$\chi_{PBI,PI}$	$\chi_{T,PBI}$[a]
0	6.81×10^{-10}	1.75×10^{-6}	1.93	2.26	4.19		2.57
0.1	7.84×10^{-10}	1.81×10^{-6}	1.61	2.12	3.73	1.44	2.58
0.2	9.48×10^{-10}	1.79×10^{-6}	1.74	1.53	3.27	1.54	2.59
0.3	9.94×10^{-10}	1.63×10^{-6}	1.61	0.99	2.60	1.33	2.67
0.4	1.04×10^{-9}	1.39×10^{-6}	1.47	0.72	2.19	1.48	2.68
0.5	1.89×10^{-9}	8.56×10^{-7}	1.34	0.54	1.89	1.79	2.65
0.6	2.28×10^{-9}	4.47×10^{-6}	1.05	0.73	1.78	2.59	2.52
0.7	3.64×10^{-9}	5.45×10^{-6}	0.62	0.59	1.21	2.34	2.60
0.8	2.53×10^{-9}	5.36×10^{-6}	0.62	0.28	0.90	2.66	2.51
0.9	3.88×10^{-9}	8.24×10^{-6}	0.38	0.18	0.56	1.93	2.34
1.0	5.40×10^{-9}	7.78×10^{-6}	0.28	0.10	0.38		

[a] Hypothetical value assuming interaction only with PBI.

specific interactions in the physical structure of PBI/PI blends.

The composition dependence of parameter k (a factor proportional to the velocity of the advancing boundary front between the swollen and glassy parts) differs essentially from that of D (Fig. 10). The k values for water are believed to be high in PBI and in blends with high PBI contents, but cannot be determined, as Fickian diffusion controls the absorption process. For both solvents the rate of Case II diffusion is higher in the neat components than in the blends, and reaches a minimum between 0.5 and 0.6 PI content. The composition dependence of k (especially that calculated from TCB absorption) supports the idea of phase inversion in this range.

The composition dependence of the extrapolated equilibrium vapour uptake is shown in Fig. 11 for water and in Fig. 12 for TCB. The vapour absorption of the blends is smaller at each composition than can be expected by the rule of additivity or by considering the limiting case of a simple physical combination of pure PBI and PI phases [17] (the dashed lines in the figures represent the values calculated for this latter case). The difference can be attributed to the specific interaction of the two polymers through hydrogen bonds. This also accounts for the decreased k parameters of the blends.

As the activity of a saturated vapour sorbed in a polymer equals 1 at equilibrium, the Flory–Huggins interaction parameter, χ_{sp}, can be calculated for a solvent/polymer binary system by the following equation [17]:

$$\ln \varphi_s + (1 - \varphi_s) + \chi_{sp}(1 - \varphi_s)^2 = 0, \qquad (8)$$

where φ_s is the equilibrium volume fraction of the solvent in the binary system.

The interaction parameters determined for water are $\chi_{W,PBI}(= \chi_{sp}) = 1.22$ and $\chi_{W,PI} = 3.65$, while those for TCB are $\chi_{T,PBI} = 2.57$ and $\chi_{T,PI} = 4.82$.

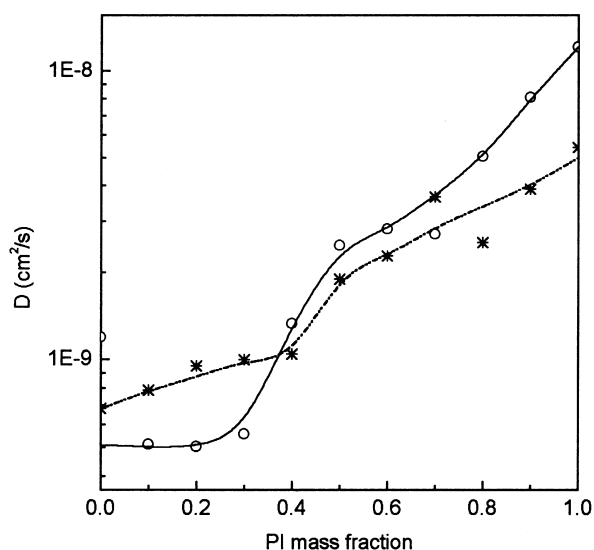The polymer/polymer interaction parameter, χ_{12}, can be

Fig. 8. Composition dependence of the Fickian diffusion coefficient of (○) water and (∗) TCB.
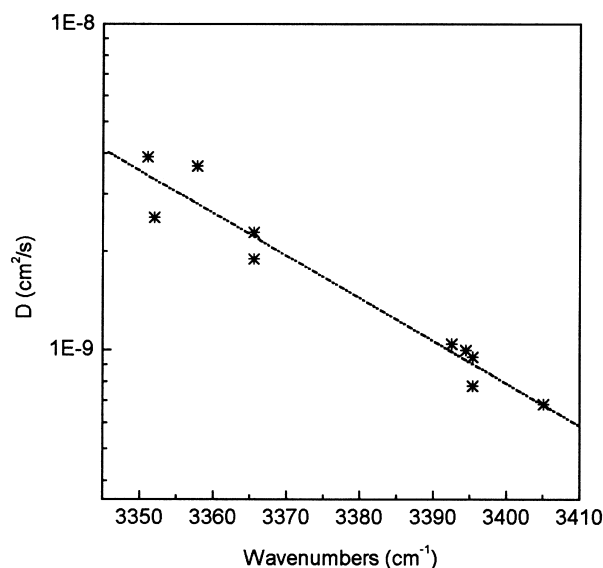

Fig. 9. Relationship between the N–H absorption frequencies of the polymer compositions and the Fickian diffusion coefficients of TCB.
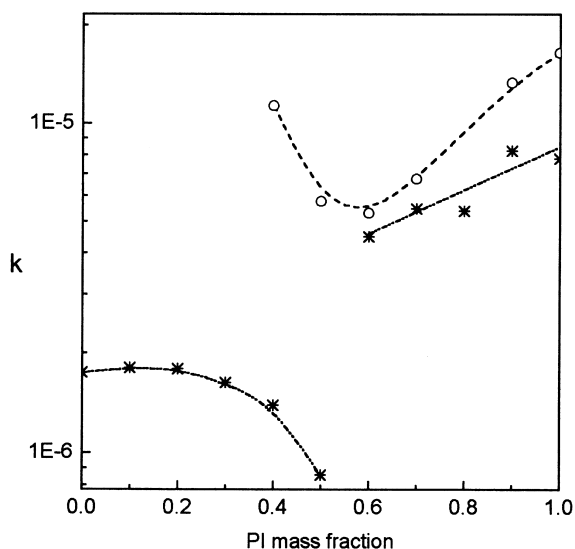
Fig. 10. Composition dependence of the parameter related to the rate of Case II diffusion of (○) water and (∗) TCB.

calculated from the equilibrium vapour absorption as follows [17]

$$\ln \phi_s + (1 - \phi_s) + (\chi_{s1}\phi_l + \chi_{s2}\phi_2)(1 - \phi_s) - \chi_{12}\phi_1\phi_2 = 0,$$
(9)

where subscript s refers to the solvent, 1 and 2 to the polymers; ϕ_i is the volume fraction of the corresponding component in the ternary system; χ_{si} is the interaction parameter for solvent with polymer i (calculated from Eq. (8)).

$\chi_{PBI,PI}(= \chi_{12})$ values calculated from the equilibrium water and TCB vapour uptake are positive numbers, and depend on the composition (Fig. 13). The results obtained from the water absorption give increasing $\chi_{PBI,PI}$ values with increasing PI content of the blend. Below 0.6 PI fraction the
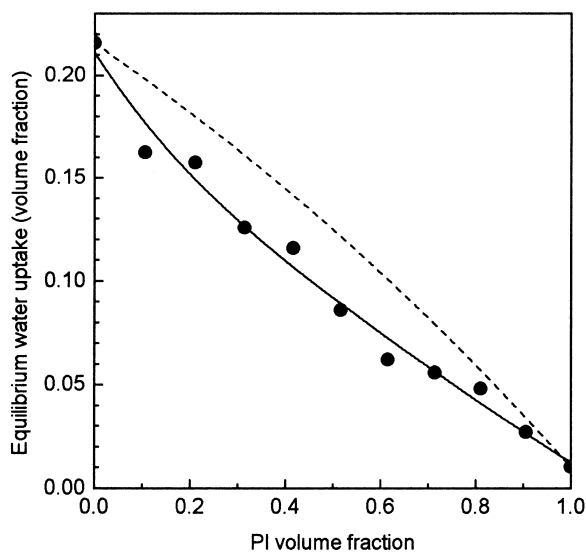

Fig. 11. Composition dependence of the equilibrium water absorption of PBI/PI blends.

change is slower than above, where the increase in the interaction parameter becomes considerable. The $\chi_{PBI,PI}$ values calculated from TCB uptake show smaller changes as a function of composition, but a sudden increase can be observed between 0.4 and 0.6 PI content. These results reveal that the solvent absorption of PBI/PI blends cannot be totally described by the factors included in Eq. (9). Considering that the equilibrium vapour sorption of PBI is much higher than that of PI for both solvents, it can be assumed that the solvent uptake of the blends is a consequence of interactions only with PBI, and PI can be considered as a neutral component. In this case Eq. (9) reduces to Eq. (8). $\chi_{W,PBI}$ and $\chi_{T,PBI}$ were calculated for each blend and found to be independent of composition (Tables 1 and 2, Fig. 14), which proves the validity of this assumption. This also implies that the strength of specific interactions is stronger for PBI/water and PBI/TCB than that between the two polymers, and that it controls the equilibrium solvent uptake of the blends.

Summarising the results we can deduce that PBI and PI do not form thermodynamically homogeneous blends in spite of intermolecular hydrogen bonding and the measured single intermediate glass transitions. The formation of a heterogeneous structure can be attributed to the stiffness and self-association of the polymer chains. A phase inversion takes place between 0.4 and 0.6 PI content.

4. Conclusions

Blends of PBI and PI were prepared over the entire composition range by film casting from N,N'-dimethyl acetamide solution using a method developed in a preliminary work. The interaction and miscibility of the components were studied as a function of composition.

FT-IR studies revealed relatively weak hydrogen bonding between the components (compared to that of polyamide chains). Thermal (DSC) and thermomechanical (TMA) experiments yielded single intermediate glass transitions for all compositions. A linear relationship was obtained between the shift of the FT-IR absorption frequencies of the hydrogen bonding groups (N–H and C=O) and the glass transition temperatures determined by DSC, which indicates that the physical structure of the blends is controlled by specific interaction of the components. The same conclusion was drawn from the composition dependence of the Fickian diffusion coefficients of water and TCB determined by absorption experiments at an ambient temperature. D is a non-linear function of composition, but its logarithm changes linearly with shift of the N–H absorption peak. The parameter determined from a combined mechanism of Fickian and Case II diffusions, and characteristic for the velocity of the advancing boundary front between swollen gel and glassy core in the polymer reveals phase inversion in the blends at around 1/1 component ratio. The Flory–Huggins interaction parameter values
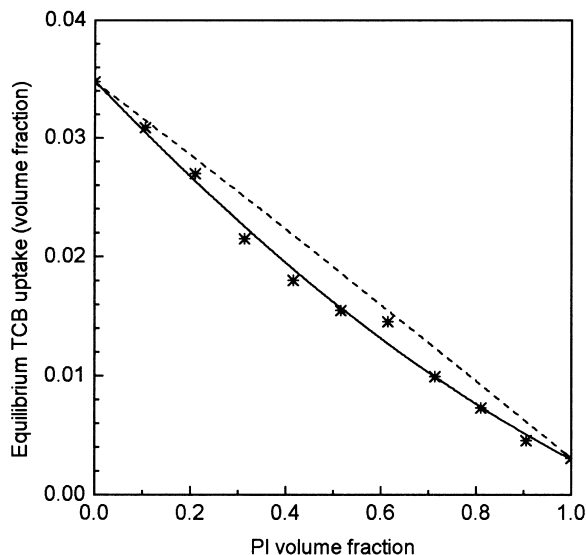
Fig. 12. Composition dependence of the equilibrium TCB absorption of PBI/PI blends.

calculated from the equilibrium vapour absorption imply that the strength of interaction between PBI and PI is lower than that for PBI/water and PBI/TCB.

Thus in spite of the observation of single glass transition we can conclude there is only partial miscibility in blends of PBI/PI. This is a consequence of the stiffness of the polymer chains and competition of intermolecular interaction with self-association of the components. Phase inversion can be observed between 0.4 and 0.6 PI content.

Acknowledgements

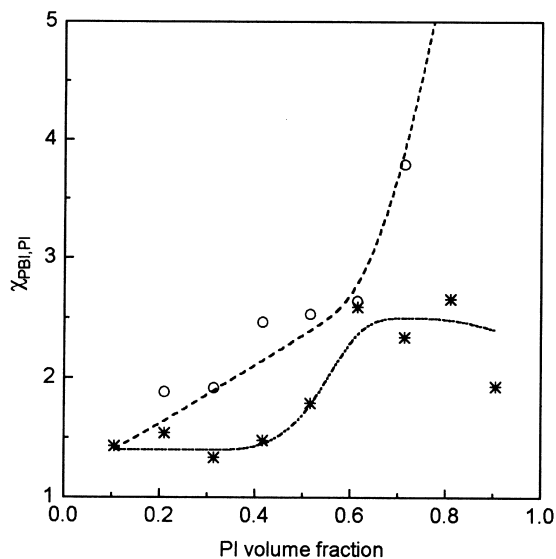One of the authors (FEK) thanks USAFOSR for support.

Fig. 13. Composition dependence of the Flory–Huggins interaction parameter derived from equilibrium absorptions of (○) water and (∗) TCB.
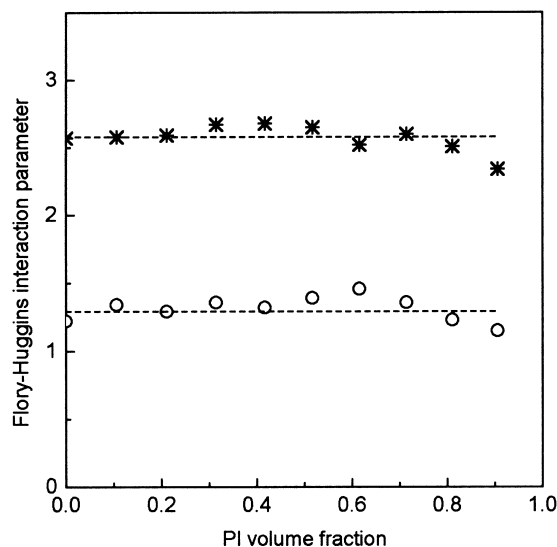

Fig. 14. Composition dependence of the Flory–Huggins interaction parameter derived from the equilibrium absorptions of (○) water and (∗) TCB by assuming interaction only with PBI.

References

[1] Fekete E, Peredy Z, Földes E, Karasz FE, Pukánszky B. Polym Bull 1997;39:93.
[2] Leung L, Williams DJ, Karasz FE, MacKnight WJ. Polym Bull 1986;16:457.
[3] Choe S, Williams DJ, MacKnight WJ, Karasz FE. Polym Mater Sci Engng 1987;36:827.
[4] Choe S, MacKnight WJ, Karasz FE. Thermal and spectroscopic behaviour in miscible polybenzimidazole/polyimide blends. In: Feger C, Khojasteh MM, McGrath JE, editors. Polyimides: materials, chemistry and characterization. Amsterdam: Elsevier, 1989. p. 25.
[5] Guerra G, Choe S, Williams DJ, Karasz FE, MacKnight WJ. Macromolecules 1988;21:231.
[6] Musto P, Karasz FE, MacKnight WJ. Macromolecules 1991;24:4762.
[7] Choe S, Karasz FE, MacKnight WJ. Phase behaviour in miscible polybenzimidazole/polyetherimide blends. In: Culbertson BM, editor. Contemporary topics in polymer science, multiphase macromolecular systems, 6. New York: Plenum Press, 1989. p. 493.
[8] Liang K, Bánhegyi G, Karasz FE, MacKnight WJ. J Polym Sci: Part B: Polym Phys 1991;29:649.
[9] Socrates G. Infrared characteristic group frequencies. New York: Wiley, 1980.
[10] Skrovanek DJ, Howe SE, Painter PC, Coleman MM. Macromolecules 1985;18:1676.
[11] Skrovanek DJ, Painter PC, Coleman MM. Macromolecules 1986;19:699.
[12] Tang H, Feng H, Luo H, Dong L, Feng Z. Eur Polym J 1997;33:519.
[13] Fox TG. Bull Am Phys Soc 1956;1:123.
[14] Gordon M, Taylor JS. J Appl Chem 1952;2:493.
[15] Couchman PR. Macromolecules 1978;11:1156.
[16] Utracki LA. Polymer alloys and blends. Thermodynamics and rheology. Munich: Hanser, 1989.

[17] Hopfenberg HB, Paul DR. Transport phenomena in polymer blends. In: Paul DR, Newman S, editors. Polymer blends, vol. 1. New York: Academic Press, 1978. p. 445 ch. 10.

[18] Crank J, Park GS. Methods of measurement. In: Crank J, Park GS, editors. Diffusion in polymers. New York: Academic Press, 1968. p. 1 ch. 1.

[19] Crank J. The mathematics of diffusion. Oxford: Clarendon Press, 1975.

[20] Kwei TK, Wang TT, Zupko HM. Macromolecules 1972;5:645.

[21] Wang TT, Kwei TK. Macromolecules 1973;6:919.

[22] Berens AR, Hopfenberg HB. Polymer 1978;19:489.

[23] Földes E. Polym Bull 1995;34:93.

[24] Gsell TC, Pearce EM, Kwei TK. Polymer 1991;32:1663.