Miscibility in polybenzimidazole/polyimide sulphone blends: a comparison of blends containing fluorinated and non-fluorinated polyimide sulphone

V. Janarthanan, Frank E. Karasz* and William J. MacKnight
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

(Received 3 September 1991; accepted 12 October 1991)

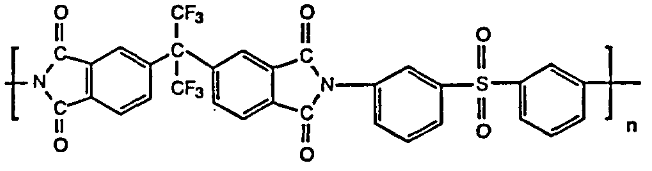
A comparison of miscibility is presented for blends containing a fluorinated and a non-fluorinated polyimide sulphone, of otherwise comparable structure, with polybenzimidazole [PBI, poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]. The miscibility behaviour was studied using Fourier transform infra-red (*FT*i.r.) spectroscopy and thermal analysis. The N–H and C=O absorbance regions in the *FT*i.r. spectra show that the fluorine-containing group in the hexafluoroisopropylidene-containing polyimide (PI1) decreases the miscibility of this polyimide with PBI, whereas the carbonyl group in the benzophenone moiety in the second polyimide (PI2) enhances miscibility. In blends with low PBI content, PI2 forms uniform hydrogen bonds with PBI, and the strength of the hydrogen bonding is maximized at a blend composition of 50/50 wt%. *FT*i.r. spectra of the blends were also obtained as a function of temperature. Above the glass transition temperature the PBI/PI2 blends contain two phases: pure PI2 (present in small amounts) and the predominant miscible phase. Analysis of the carbonyl band could be related to glass transition behaviour in the blend. Finally, an enhanced degradation of PI2 in the presence of PBI was observed and is discussed.

(**Keywords: miscibility; polybenzimidiazole; polyimide sulphone**)

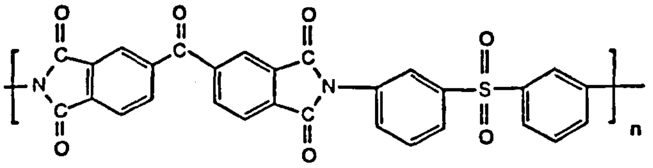
INTRODUCTION

Blends of aromatic poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (PBI) with aromatic polyimides (PIs) have been widely studied since miscibility in blends of these high performance polymers was discovered[1,2]. Spectroscopic investigations[3,4] of these systems have shown that intermolecular interactions, e.g. hydrogen bonding, are primarily responsible for miscibility in these systems. However, Fourier transform infra-red (*FT*i.r.) analysis of the pure components in the presence of low molecular weight monofunctional probes[5] indicates that PIs are relatively weak proton acceptors. This finding prompted us to explore the possibility of structural hindrance to miscibility in these systems. In the present study, two polyimide sulphones were used, one containing a hexafluoroisopropylidene group (PI1) and the second containing a benzophenone carbonyl moiety (PI2).

*FT*i.r. spectroscopy and thermal analysis were used to analyse and compare the miscibility, as a function of blend composition and temperature, of these polyimide sulphones with PBI. In addition, thermal degradation was studied in selected blends.



PI1



PI2

EXPERIMENTAL

PBI was supplied by Celanese Corporation in powder form. The polyimide sulphones PI1 and PI2 were supplied by NASA, Langley. The glass transition temperatures (T_gs) of PI1 and PI2 were 270°C and 265°C, respectively. The polyimides were used as received; PBI was dried at 200°C in vacuum for 5 days prior to use.

Thin films (20–50 μm thick) of the blends in the desired compositions were prepared by casting 3% (w/v) dimethylacetamide (DMAc) solutions of the pure components. Most of the solvent was evaporated in a dry nitrogen atmosphere at 90°C for 24 h. The films were then washed with warm water to remove residual DMAc. Finally the films were dried at 225°C under vacuum for 6 days. Thermogravimetric analysis (t.g.a.) showed less

---

*To whom correspondence should be addressed

0032-3861/92/163388-06

than 1 wt% solvent loss in the films prepared in this manner. The same films were used for both thermal analysis and *FT*i.r. spectroscopy.

*FT*i.r. spectra were obtained at a resolution of 2 cm^{-1} with a Mattson Cygnus 100 *FT*i.r. spectrometer. Fifty scans of each sample were collected and signal averaged. All films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed. The *FT*i.r. temperature measurements were performed in a Spectra-Tech HT32 high temperature cell mounted directly in the spectrometer and controlled by an Omega CN-2010 programmable temperature controller with an accuracy of $\pm1°C$. A chromel–alumel thermocouple in direct contact with the surface of the sample was used to monitor the sample temperature.

Differential scanning calorimetry (d.s.c.) experiments were conducted using a Perkin-Elmer DSC-7 calorimeter at a heating rate of 20°C min^{-1} in a nitrogen atmosphere. Samples of 10–15 mg were used for d.s.c.

RESULTS AND DISCUSSION

The N–H and C=O stretching frequency regions in the infra-red spectrum are of most interest to us. It has been reported[5] that the spectrum of pure PBI shows three absorption maxima in the N–H stretching frequency region: a narrow peak at 3410 cm^{-1} (assigned to unassociated N–H groups); a broad band centred at 3150 cm^{-1} (assigned to self-associated N–H groups); and a third peak at 3060 cm^{-1} (related to the stretching vibrations of aromatic C–H groups). The spectrum of pure PI1 displays two maxima at 1785 cm^{-1} and 1727 cm^{-1}, assigned to the symmetric and asymmetric stretching vibrations of C=O groups, respectively. An additional band at 1670 cm^{-1} in PI2 is associated with the stretching vibration of the benzophenone carbonyl group.

N–H stretching region

When PBI was blended with either PI1 or PI2, changes occurred in the N–H stretching region of PBI. The position of the band at 3410 cm^{-1} remained unchanged until the blend composition reached 70 wt% PBI in PBI/PI1 blends (*Figure 1*). The band then gradually shifted through 3400 cm^{-1} for higher PBI concentrations.

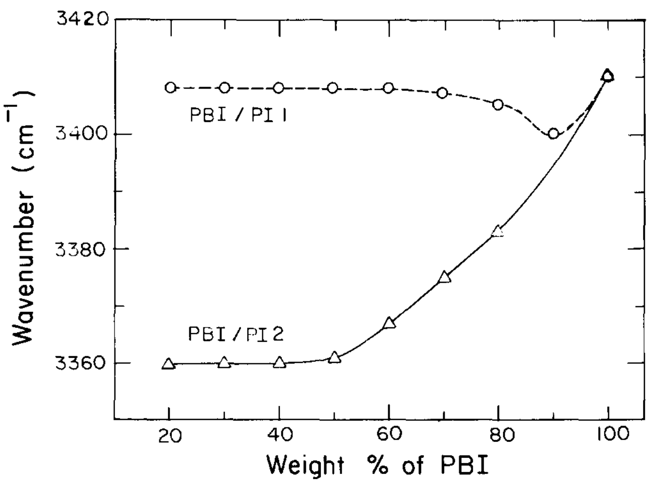


Figure 1 N–H frequency maximum *versus* wt% PBI for PBI/PI1 (○) and PBI/PI2 (△) blends

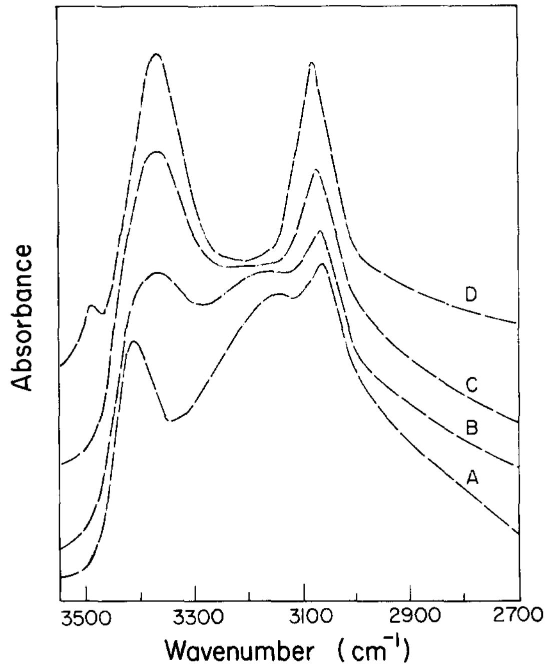


Figure 2 *FT*i.r. spectra recorded in the region 3550–2700 cm^{-1}: A, pure PBI; B, 70/30 wt% PBI/PI2 blends; C, 50/50 wt% PBI/PI2 blends; D, 20/80 wt% PBI/PI2 blends

No major changes were observed in the self-associated N–H band centred at 3150 cm^{-1} in this blend system. In contrast, the band centred at 3410 cm^{-1} shifted to lower frequencies as the concentration of PBI was decreased from 100 wt% in the PBI/PI2 blend system and reached an asymptotic value of 3360 cm^{-1} for a blend composition of 50/50 wt%. It remained at this value for lower concentrations of PBI (*Figure 1*). In addition, a substantial modification of the overall band shape occurred when the PBI content was decreased in the PBI/PI2 blends (*Figure 2*). The N–H stretching region in the PI2-containing blends (curves B, C and D) appears somewhat simpler than that of pure PBI (curve A); only a single, almost symmetric band centred at 3360 cm^{-1} was observed.

The above results can be rationalized in terms of hydrogen bonding interactions involving the N–H groups of PBI. In the PBI/PI1 blend system, the small shift to the lower frequency for high PBI contents is due to a weak interaction of the N–H groups of PBI with the imide carbonyls or the sulphone groups of PI1. No evidence of hydrogen bonding was observed at low PBI contents, and the presence of PI1 did not affect the self-associated N–H groups. In the PBI/PI2 blends, however, the band at 3410 cm^{-1} shifted to lower frequencies (to 3360 cm^{-1} for 50 wt% PI2), indicating that hydrogen bonding occurs between the N–H groups of PBI and the C=O groups of the polyimide sulphone. Further reduction of the PBI content did not affect this band, indicating that the hydrogen bonding is maximized for a blend composition of 50/50 wt% in PBI/PI2 blends. On the basis of the structure of two PIs we conclude that the CF_3 groups in PI1 prevent the interaction of PBI N–H groups with PI1 carbonyl groups for blends up to 70 wt% PBI. The observed weak interaction in PBI/PI1 blends for PBI concentrations above 70 wt% may be due to the large number of N–H groups available relative to the number of CF_3 groups in PI1; this enables a weak interaction to occur between PBI N–H groups and PI1 carbonyl groups.

A striking feature in the PBI/PI2 blend system is the overall change in the N–H absorption band shape. As the content of the PBI was reduced in the blends, the intensity of the self-associated N–H group band centred at 3150 cm^{-1} rapidly decreased while the intensity of the hydrogen bonding band at 3360 cm^{-1} increased and became more symmetric for lower PBI contents. Spectral subtraction[6] was carried out in the N–H stretching region to clarify the behaviour of the hydrogen-bonded species. *Figure 3* shows the *FT*i.r. subtracted spectra for selected compositions of PBI/PI2 blends, obtained by digitally subtracting the spectrum of pure PBI from those of the blends, with proper weighting factors. Despite the complexity of the region, the results of the subtraction are 'clean'. On eliminating the contribution due to the free and self-associated N–H groups, a single symmetric band was observed for all blend compositions.

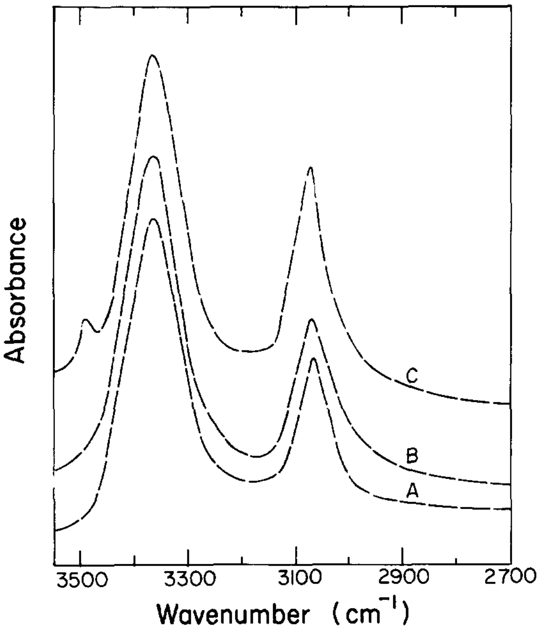


Figure 3 *FT*i.r. subtracted spectra recorded in the region 3550–2700 cm^{-1}: A, PBI subtracted from 70/30 wt% PBI/PI2 blend; B, PBI subtracted from 50/50 wt% blend; C, PBI subtracted from the 20/80 wt% PBI/PI2 blend

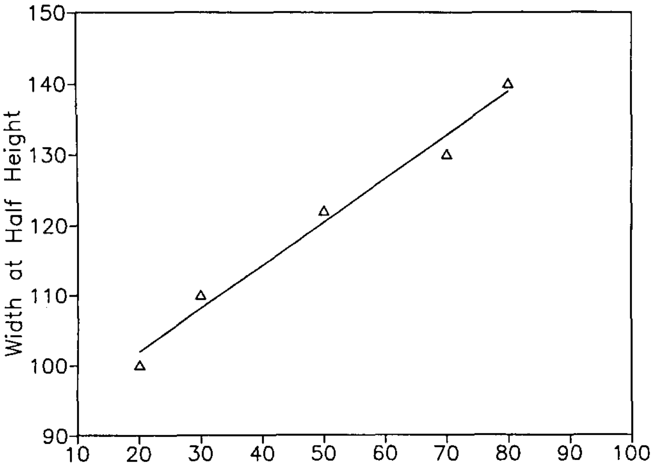


Figure 4 Width at half height of the subtracted N–H band at 3360 cm^{-1} *versus* wt% PBI in PBI/PI2 blends

The width at half height (w.h.h.) of the hydrogen bonding band at 3360 cm^{-1} was reduced considerably as the PBI content was reduced. A plot of weight percentage of PBI *versus* the w.h.h. of this band is shown in *Figure 4*. The reduction in w.h.h. indicates that the N–H groups of PBI are forming more uniform hydrogen bonds with the imide carbonyls. Uniform hydrogen bonding can be explained as follows: for high PBI contents, the hydrogen bonding distances and geometries are random because of steric effects, thus the band is broad. As the PBI content decreases in the blends, the N–H groups enter a more homogeneous hydrogen bonding distribution with uniform bond lengths between the N–H groups and the imide carbonyls. This homogeneity produces the observed narrow and symmetric hydrogen bonding band at 3360 cm^{-1}. A similar trend was observed by Farenholtz and Kwei[7] and by Moskala and Coleman[8] in their studies of blends of novalac and phenoxy resins, respectively.

Carbonyl stretching region

The reported observations of the N–H stretching frequency region might also be expected to be reflected in the imide carbonyl stretching bands at 1727 cm^{-1} and 1785 cm^{-1}. *Figures 5a* and *b* show the carbonyl stretching region of the pure polyimides and selected compositions of PBI/PI1 and PBI/PI2 blends, respectively. In *Figure 5a*, a small shift to lower frequency and a slight broadening of the band at 1727 cm^{-1} for high PBI contents (90 wt%) is seen. This behaviour is generally associated with hydrogen bonding. The band broadening is due to the appearance of a second component at lower frequency which arises because of hydrogen bonding between the N–H groups of PBI and the C=O groups of PI1. Because of the intrinsic breadth and the near overlap of the two components, it is not possible to separate them, so only qualitative information can be obtained for the PBI/PI1 system. The result is consistent with the N–H stretching vibration observation.

In contrast, in PBI/PI2 blends the behaviour of the carbonyl band can provide quantitative information about the number of C=O groups that interact with N–H groups. From *Figure 5b* it is clear that the bands at 1727 cm^{-1} and at 1785 cm^{-1} shift to lower frequency. Although this shift is small (about 4 cm^{-1}), substantial band broadening was observed and the broadening is asymmetric on the low frequency side. This asymmetry is due to the appearance of a new band at 1714 cm^{-1}, whose position was determined by using second derivative analysis[9,10].

The area of the band at 1714 cm^{-1} is a direct measure of the number of interacting C=O groups. This band can be isolated by using spectral subtraction to eliminate the absorption due to non-interacting C=O groups of PI2 in the blend; pure PI2 is used as the reference. The area of this band is plotted against the weight percentage of PI2 and is shown in *Figure 6*. It is apparent that the area of this peak increases with increasing PI2 content and remains constant above 50 wt% PI2. The details of the spectral subtraction analysis and the fraction of hydrogen-bonded carbonyl groups are shown in *Table 1*.

The preceding analysis led us to conclude that the PBI/PI1 blend system is miscible only at high PBI

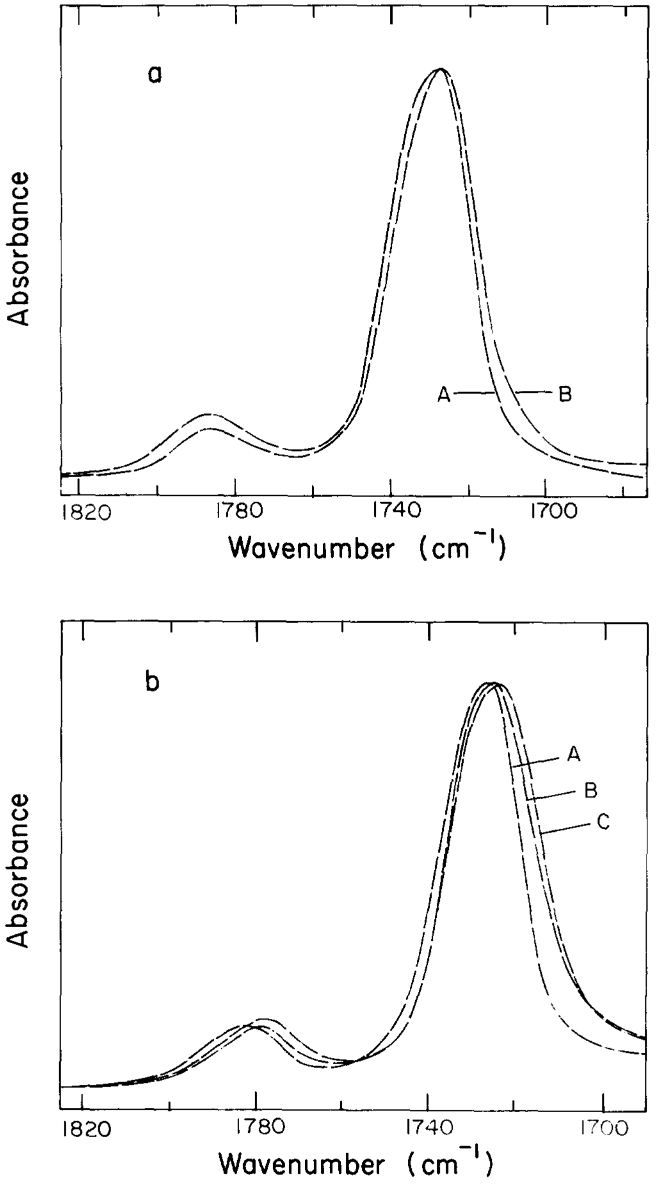


Figure 5 (a) *FT*i.r. spectra recorded in the region 1820–1680 cm^{-1}: A, pure PBI; B, 90/10 wt% PBI/PI1 blend. (b) *FT*i.r. spectra recorded in the region 1825–1690 cm^{-1}: A, pure PI2; B, 70/30 wt% PBI/PI2 blend; C, 30/70 wt% PBI/PI2 blend

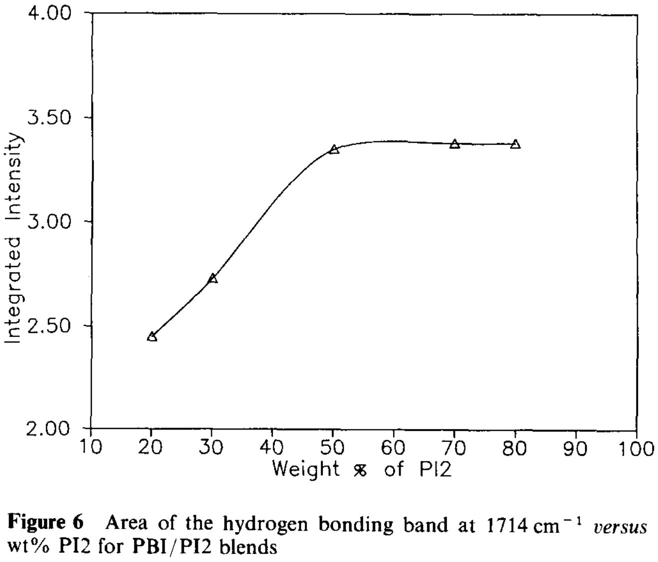


Figure 6 Area of the hydrogen bonding band at 1714 cm^{-1} *versus* wt% PI2 for PBI/PI2 blends

Table 1 Results of spectral subtraction

PBI/PI2 (wt%)	Peak position (cm^{-1})	Relative area (%)	Fraction C=O hydrogen bonded
80/20	1715	8.2	0.082
70/30	1714	10.0	0.100
50/50	1714	11.5	0.115
30/70	1714	11.4	0.114
20/80	1714	11.2	0.112

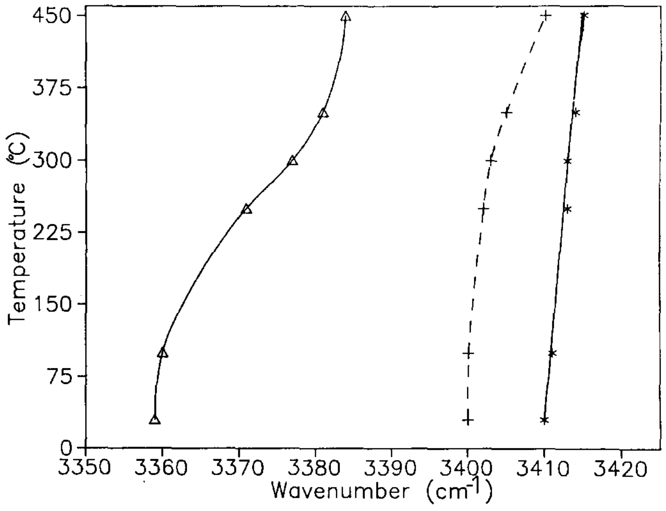


Figure 7 N–H stretching frequency *versus* temperature: ✱, pure PBI; +, 90/10 wt% PBI/PI1 blend; △, 30/70 wt% PBI/PI2 blend

contents, whereas the PBI/PI2 system is miscible over the entire composition range; the number of C=O groups involved in hydrogen bonding is maximal for 50 wt% PI2. These conclusions are consistent with the d.s.c. results discussed below.

Temperature effects

Temperature studies of miscible blend systems using *FT*i.r. spectroscopy have been reviewed extensively by Coleman and Painter[11]. By observing the frequency of the hydrogen bonded species as a function of temperature, we can obtain information on the phase separation process that may occur in an initially miscible blend system[12]. Temperature effects in the normally miscible 90/10 wt% PBI/PI1 and 30/70 wt% PBI/PI2 blends were investigated. Each sample was annealed for 10 min at selected temperatures before spectra at the respective temperatures were obtained. *Figure 7* shows a plot of the frequency maxima of the N–H stretching vibration as a function of temperature for the two systems chosen. The frequency of the unassociated N–H stretching vibrations of pure PBI is also shown for comparison. An essentially linear relationship between the unassociated N–H stretching frequency of PBI and temperature is observed for pure PBI, whereas a flat sigmoid curve is seen in the 30/70 wt% PBI/PI2 blend.

To a first approximation, the difference between the frequency observed for pure PBI and that for the blends at any given temperature is a measure of the relative strength of the hydrogen bonding interaction. From *Figure 7*, one can see that the interaction is maximized at room temperature and decreases in a non-linear fashion as the temperature is raised. The temperature at which the frequency difference between the pure component and the blends vanishes indicates that complete phase separation of the miscible blend system has occurred. For the PBI/PI1 blend, phase separation detected by this means occurs at 405°C, which corresponds to the measured T_g of the miscible blends by d.s.c. In contrast, in the PBI/PI2 system the frequency difference starts to decrease at approximately 225°C, but becomes constant for higher temperatures with a frequency difference of about 30 cm^{-1}. This finding indicates that above T_g the system phase separated to a phase corresponding to pure PI2, presumably in small domains, and a second phase corresponding to the remaining miscible phase, which is predominant (see later discussion of d.s.c. results). Even after annealing the sample at 450°C for 10 min, the frequency difference could not be eliminated. All the PBI/PI blends previously studied in this laboratory[1–4] show complete phase separation above their respective T_gs.

The potential of *FT*i.r. temperature studies in detecting the T_gs of polymers is important. A change in the slope of a plot of band intensity *versus* temperature indicates the existence of the transition[13]. This effect is more pronounced for vibrational groups that are highly polar. The areas of the $C{=}O$ bands of two blend systems, 30/70 wt% PBI/PI1 and 70/30 wt% of PBI/PI2, as a function of temperature are shown in *Figure 8*. The area of the $C{=}O$ band of PBI/PI1 is nearly constant up to 250°C, but decreases beyond that temperature (i.e. close to the T_g of the pure PI1, 270°C), a behaviour clearly indicating immiscibility. Similarly, for the miscible blend system PBI/PI2, a sudden drop in intensity occurs just before 350°C, the T_g of the blend.

D.s.c. results for PBI/PI blend system

In the d.s.c. protocols used, there are clearly two T_gs in the PBI/PI1 system for blend compositions of up to 70 wt% PBI and one T_g above 80 wt% PBI, confirming the results of *FT*i.r. spectroscopy. On the other hand, the PBI/PI2 system shows a single T_g for all the compositions investigated, indicating the miscibility of this system over the entire composition range. Both blend systems were heated above their respective T_gs, annealed for 15 min, rapidly quenched to room temperature and annealed at 225°C for 48 h. After this procedure, the PBI/PI1 system shows two T_gs for the previously one-phase compositions, a result indicating complete phase separation. In addition, the PBI/PI2 system also shows two endotherms, one corresponding to pure PI2 and the second corresponding to a partially miscible phase, in agreement with *FT*i.r. results. *Figure 9* shows the d.s.c. curves for annealed samples of 30/70 wt% PBI/PI2 and 80/20 wt% PBI/PI1 blends.

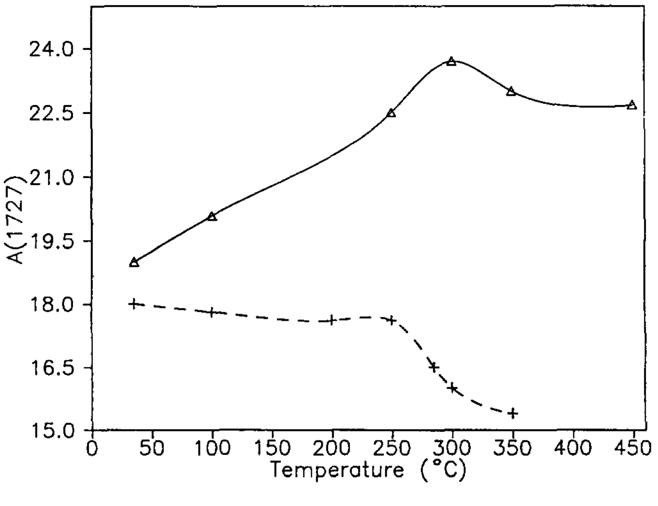


Figure 8 Area of the $C{=}O$ band at 1727 cm^{-1} *versus* temperature: +, 30/70 wt% PBI/PI1 blend; △, 70/30 wt% PBI/PI2 blend

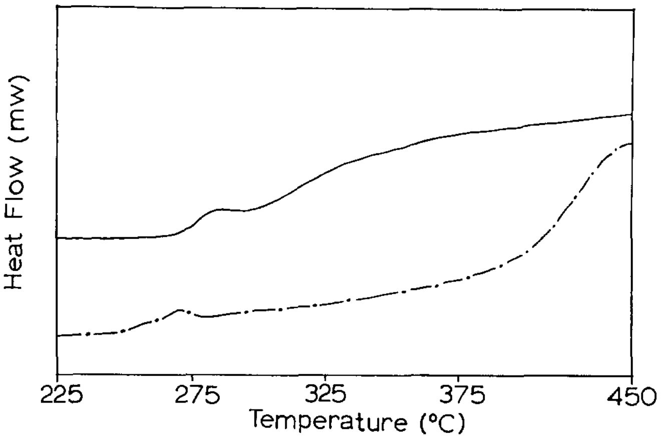


Figure 9 D.s.c. curves of annealed samples: – · –, 80/20 wt% PBI/PI1 blend; ——, 30/70 wt% PBI/PI2 blend

Degradation

Isothermal degradation measurements under N_2 were also carried out on the blends to investigate changes in the pure polyimide sulphone and in PBI/polyimide sulphone blends. Isothermal measurement of peak intensities obviously removes any effect of temperature on frequency of the bands and thickness of the film. Measurements were carried out directly in the spectrometer at 350°C over a period of 20 h.

The present analyses are mainly concerned with the carbonyl bands of PIs. The intensity of the main $C{=}O$ band at 1727 cm^{-1} and the mixed mode $N{-}C{=}O$ band at 1370 cm^{-1} decreases gradually with time. The conversion of $C{=}O$ groups as a function of time was calculated from the relative intensities of the carbonyl band at times *t* and 0, respectively, as explained by Musto *et al.*[14]. A plot of this conversion *versus* time for the 40/60 wt% PBI/PI2 miscible blend is shown in *Figure 10*. The conversion of $C{=}O$ groups for pure PI2 is also shown for comparison. It is clear from the figure that the pure PI2 shows no appreciable change. A gradual decrease in the content of $C{=}O$ groups is seen in the PBI/PI2 blend, however, and the conversion process seems to be complete after 10 h. The $N{-}C{=}O$ band at 1370 cm^{-1} decreases in the same way, a result indicating that PI2 degrades in the presence of PBI. T.g.a. also showed an increased rate of weight loss for the miscible PBI/PI2 blend system. The isothermal weight loss measured at 350°C after 20 h for the PBI/PI2 blend systems are shown in *Figure 11*. As the PBI content increased, the weight loss also increased, a result

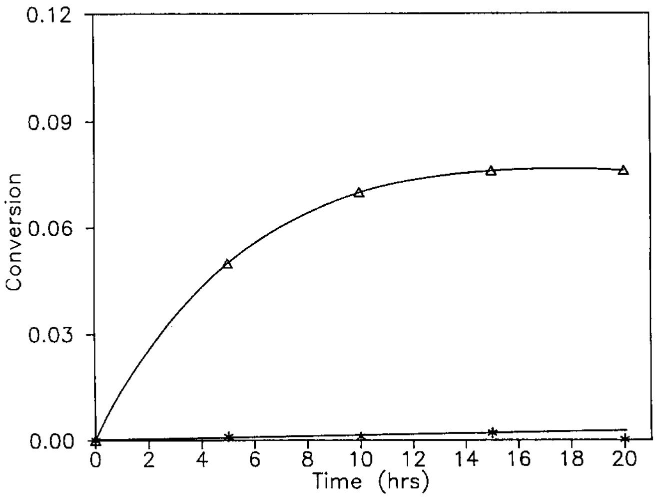


Figure 10 C=O group conversion *versus* time: ∗, pure PI2; △, 40/60 wt% PBI/PI2 blend

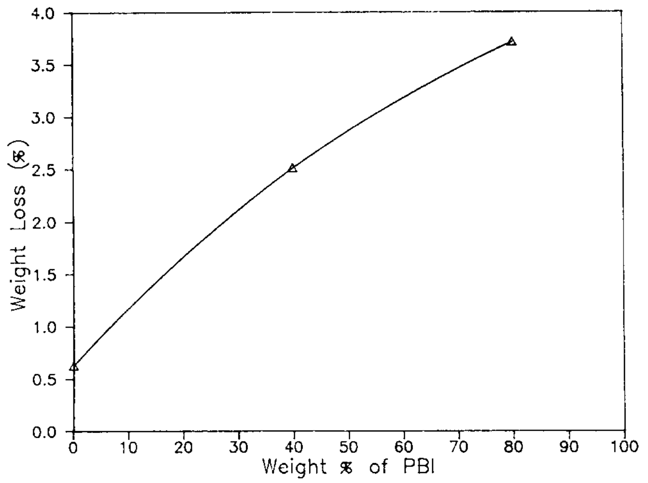


Figure 11 Isothermal weight loss *versus* PBI composition at 350°C after 20 h for PBI/PI2 blend system

indicating decreased thermal stability of the blends. In contrast, the immiscible PBI/PI1 blend did not show any spectral changes in isothermal studies. Thus, it appears that in the miscible blend system, PBI enhances the rate of thermal degradation of PI2. Work is in progress to understand the mechanism of degradation.

CONCLUSIONS

*FT*i.r. studies of two blend systems, PBI/PI1 and PBI/PI2, indicate the existence of hydrogen bonding interactions between the N–H groups of PBI and C=O groups of polyimide sulphones for all compositions of PBI/PI2 and for compositions rich in PBI for the PBI/PI1 system. Qualitatively, information about the strength of the interactions and, quantitatively, the population of C=O groups involved in hydrogen bonding is discussed. The *FT*i.r. temperature studies revealed complete phase separation of the apparently miscible PBI/PI1 blends and a partial phase separation for the PBI/PI2 system. Some details of the decomposition of the PBI/PI2 system are provided.

From the above results and the structure of the two polyimide sulphones, one can conclude that the hexafluoroisopropylidene group in PI1 strongly hinders miscibility of this polyimide with PBI, whereas the benzophenone carbonyl in PI2 interacts with the imide carbonyl and forms relatively strong hydrogen bonds with the N–H groups of PBI.

ACKNOWLEDGEMENTS

We thank Dr T. St Clair, NASA, Langley for kindly providing the polyimide sulphones. This work was supported by AFOSR grant no. 91-100.

REFERENCES

1 Leung, L., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polym. Bull.* 1986, **16**, 1457
2 Guerra, G., Choe, S., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1988, **21**, 231
3 Musto, P., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1991, **24**, 4762
4 Choe, S., MacKnight, W. J. and Karasz, F. E. in 'Polyimides: Materials, Chemistry and Characterization' (Eds C. Feger, M. M. Kholasteh and J. E. McGrath), Elsevier Science, Amsterdam, 1989
5 Musto, P., Karasz, F. E. and MacKnight, W. J. *Polymer* 1989, **30**, 1012
6 Koenig, J. L. *Appl. Spectrosc.* 1975, **29**, 293
7 Farenholtz, S. and Kwei, T. K. *Macromolecules* 1981, **14**, 1076
8 Moskala, E. J. and Coleman, M. M. *Polym. Commun.* 1983, **24**, 207
9 Singleton, F. and Collier, G. L. *J. Appl. Chem.* 1965, **6**, 495
10 Stauffer, F. R. and Sakai, H. *Appl. Opt.* 1968, **7**, 61
11 Coleman, M. M. and Painter, P. C. *Appl. Spectrosc. Rev.* 1984, **20**, 225
12 Coleman, M. M., Moskala, E. J., Painter, P. C., Walsh, D. J. and Rostami, S. *Polymer* 1983, **24**, 1410
13 Koenig, J. L. *Adv. Polym. Sci.* 1984, **54**, 87
14 Musto, P., Karasz, F. E. and MacKnight, W. J. *Polymer* 1991, **32**, 3