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Hydrogen Bonding in Polybenzimidazole/Poly(ether imide) Blends: A Spectroscopic Study

P. Musto,[†] **F. E. Karasz,*** **and W. J. MacKnight**

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: A systematic investigation by FTIR spectroscopy of the blend system consisting of the polybenzimidazole poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI) and the poly(ether imide) poly[2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane–*m*-phenylenediimine] (Ultem 1000) has been undertaken. Direct evidence of hydrogen bonding involving the N–H groups of PBI and the imide carbonyls of Ultem 1000 is presented. Qualitative as well as quantitative information concerning this molecular interaction has been obtained and is discussed. Finally an FTIR–temperature study of this quasi-miscible system is reported: by monitoring the frequency of the asymmetric stretching vibration of the imide carbonyls as a function of temperature, information has been derived on the phase separation process for various blend compositions.

Introduction

During the past several years efforts in these laboratories have been devoted to the preparation and development of high-performance polymer blends. One of the most promising systems developed is the blend formed from the polybenzimidazole poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (PBI) and a commercial poly(ether imide), poly[2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane–*m*-phenylenediimine] (commercially available as Ultem 1000).

PBI has exceptional thermal and oxidative stability[1] and is widely used as a nonflammable fiber for high-temperature applications. The aromatic polyimides are also of use in high temperature applications because of their resistance to irradiation, mechanical deformation, and solvent attack.[2] The first study carried out on this blend system[3] indicated that miscibility occurs over the whole range of blend compositions. In fact single T_g's and well-defined single tan δ relaxations intermediate between those of the pure components were detected for all the blend samples. In addition clear films were obtained by casting from a common solvent (*N,N*-dimethylacetamide, DMAc). Preliminary FTIR analyses also showed that frequency shifts of up to 55 cm^{-1} in the N–H stretching region of PBI and of up to 6 cm^{-1} in the carbonyl stretching absorptions of the Ultem 1000 occurred.[4] However, it was noted that on heating above the blend T_g phase separation readily takes place.

In the present investigation a more systematic analysis of the vibrational spectroscopic behavior of the PBI/Ultem 1000 blend over the whole composition range is reported. In particular the infrared spectral features associated with specific molecular interactions have been studied in detail to obtain a more quantitative description of the system. FTIR spectroscopy has also been used to study blend behavior as a function of temperature. The application of this relatively new approach to the determination of the phase boundary in this miscible system is discussed.

Experimental Section

Materials. PBI was supplied by Celanese Co. in the form of an additive-free, finely ground powder. The Ultem 1000 was a commercial grade product of General Electric with a molecular weight M_w = 30 000 ± 10 000 and M_n of 12 000 ± 4000. The two polymers were used as received.

Sample Preparation. Thin polymer films (2–5 μm) were prepared by csting 1.0% (w/v) DMAc solutions of the respective polymer mixtures on glass plates in a nitrogen atmosphere at 80 °C for 24 h. To remove the last traces of solvent the films were washed in water at 70 °C for 7 days and finally dried under vacuum at 200 °C for at least 3 days. The efficacy of this solvent removal protocol was confirmed by thermogravimetric measurements: less than 1% of residual solvent was detected in the films studied.

Techniques. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 2 cm^{-1} with a Mattson Cygnus 100 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The wavenumber range scanned was 4000–400 cm^{-1} and 7470 data points were collected in this region for each scan. Typically 200 spectra were signal averaged to reduce noise. The interferogram data were Fourier transformed by using a triangular apodization function. The frequency scale was internally calibrated with a reference helium–neon laser to an accuracy of 0.02 cm^{-1}. The reproducibility of the peak position in the carbonyl region was 0.2 cm^{-1} over the whole range of temperatures investigated. All the films used in this study were sufficiently thin to be within an absorbance range where Beer–Lambert law is obeyed. The FTIR–temperature measurements were carried out in a Spectra-Tech HT 32 high-temperature cell directly mounted in the spectrometer. This unit was controlled by an Omega CN-2010 programmable heat controller with an accuracy of ±1 °C. A Chromel–Alumel thermocouple in direct contact with the surface of the film was used to continuously monitor the sample temperature.

Results and Discussion

The mean features of the PBI and Ultem 1000 infrared spectra (Figure 1) have been discussed previously.[4,5] In the present investigation we will be mainly concerned with two regions of the IR spectrum, namely, the N–H stretching and the carbonyl stretching regions.

It has been shown in a previous contribution[5] that PBI shows a complex N–H absorption, which can be separated into at least three distinguishable contributions: a relatively sharp peak at 3415 cm^{-1} attributed to isolated, non-hydrogen bonded N–H groups; a very broad asymmetric absorption centered approximately at 3145 cm^{-1} attributed to self-associated, hydrogen-bonded N–H groups; and a third low-intensity peak at 3063 cm^{-1} due to the stretching modes of the aromatic C–H groups. The PBI spectrum also displays a "window" in the 2000–1650-cm^{-1} region, facilitating the detection and analysis of the Ultem 1000 carbonyl bands in the blend spectra. The FTIR spectrum

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[†] Permanent address: Istituto di Tecnologia dei Polimeri e Reologia del C. N. R., Via Toiano, 6-80072 Arco Felice, Naples, Italy.

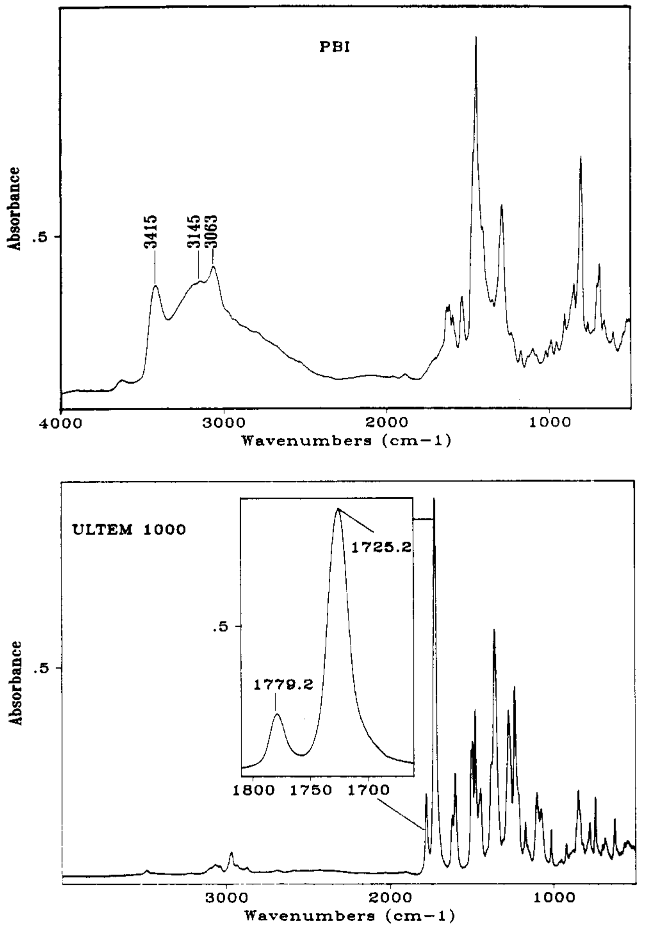

Figure 1. (a, Top) FTIR spectrum of PBI. (b, Bottom) FTIR spectrum of Ultem 1000.

Table I
Compositions and Codes of the Investigated Samples

comp, wt %		
PBI	Ultem 1000	code
100	0	PBI
80	20	B82
70	30	B73
60	40	B64
50	50	B55
40	60	B46
30	70	B37
20	80	B28
10	90	B19
0	100	Ultem 1000

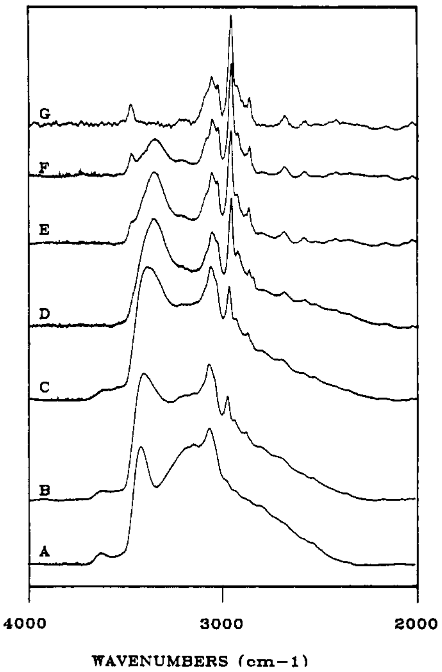

Figure 2. FTIR spectra in the 4000–2000-cm^{-1} region of (A) PBI, (B) blend B73, (C) blend B64, (D) blend B46, (E) blend B28, (F) blend B19, and (G) Ultem 1000.

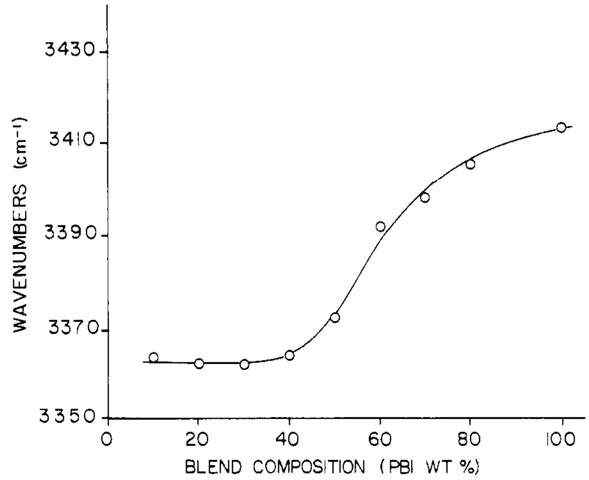

Figure 3. Location of the absorbance maxima in the N–H stretching region as a function of blend composition.

of pure Ultem 1000 shows two distinct, well-resolved absorptions at 1779.1 and 1725.2 cm^{-1} attributed respectively to the symmetric and asymmetric stretching vibrations of the imide carbonyls. It was shown in ref 5 that both PBI and Ultem 1000 are able to form hydrogen bonds and that the above-mentioned spectral regions are very sensitive to the occurrence of such interactions. In the discussion below we analyze these two regions of the IR spectrum as a function of blend composition and temperature. The various blend compositions investigated, with their respective codes, are listed in Table I.

N–H Stretching Region (3500–2500 cm^{-1}). It is immediately apparent, and has been already reported,[4] that a shift of the absorption centered at 3415 cm^{-1} in pure PBI is brought about by blending with Ultem 1000 (see Figure 2); the shift is also a rather complex function of the blend composition (see Figure 3). A more careful analysis of Figure 2 reveals that not only is the peak position shifted toward lower wavenumbers but also a substantial modification of the overall band shape occurs when the Ultem 1000 content is increased in the blend. In fact the 3415-cm^{-1} peak broadens considerably, while the complex absorption centered originally at 3145 cm^{-1} gradually decreases in intensity. For the highest Ultem 1000 contents in the blend (B28 and B19, Table I) the N–H stretching region of PBI appears much simpler than that observed in the pure polymer. (Compare Figure 2, curve A, with Figure 2, curves E and F.) For these two compositions, in fact, only a single, almost symmetric peak is detected at 3365 cm^{-1}, superimposed on a unperturbed absorptions of Ultem 1000 in this region.

Further details on the modifications occurring in this spectral region at intermediate compositions were obtained by applying spectral subtraction methods.[6] Figure 4 shows the FTIR spectrum of a representative blend (B73) in the 4000–2000-cm^{-1} range and the spectrum obtained by digitally subtracting the pure PBI spectrum from that of the B73 blend. In the same figure the spectrum of the B28 blend is shown for comparison. Despite the complexity of the region the results of the spectral subtraction analysis are remarkably "clean". By elimination of the

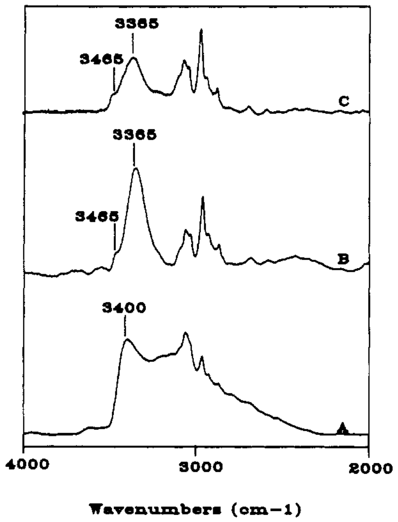

Figure 4. 4000–2000-cm^{-1} spectra of (A) blend B73, (B) subtraction spectrum B73 − PBI, and (C) blend B28.

contribution due to free and self-associated N–H groups a single, symmetrical component is obtained; its position (3365 cm^{-1}), shape, and width at half-height (70 cm^{-1}) coincide with the parameters of the band experimentally observed in the B28 spectrum (compare Figure 4, curves B and C). It is noted explicitly that the small shoulder detected at 3465 cm^{-1} in both spectra B and C of Figure 4 is an absorption belonging to Ultem 1000 (a $\nu_{C=O}$ overtone), as can be readily seen by comparing these spectra with Figure 2, curve G. Analogous results were obtained for the remaining blend compositions.

The above spectral features can be rationalized in terms of hydrogen bonding interactions involving the benzimidazolic N–H groups. Thus a new contribution centered approximately at 3365 cm^{-1} appears in the blend spectra, due to the stretching vibration of the N–H groups hydrogen bonded with the imide carbonyls. With an increase in the Ultem 1000 content the number of interacting N–H groups increases at the expense of both the free and the self-associated N–H groups; this is reflected in the FTIR spectrum by the enhanced intensity of the component at 3365 cm^{-1} and the concurrent diminution of the other two components at 3415 and 3145 cm^{-1}, respectively.

It is noted that due to the closeness of the two absorptions at 3415 and 3365 cm^{-1} and to the breadth of the latter, they are not resolved in the FTIR spectrum but appear as a single, asymmetric peak whose position and shape depends on the intensity ratio of the two components. Their natural band width and their exact position can be determined when only one is present respectively in pure PBI for the component at 3415 cm^{-1} and in the B28 and B19 blends where most of the N–H groups are interacting with the imide carbonyls and only the 3365-cm^{-1} absorption is detected. It is well-known that the shift toward lower wavenumbers observed in the stretching modes of an O–H or N–H (i.e., donor–H) group upon hydrogen bond formation is due to the weakening of the force constant of the donor–H bond. Therefore the difference among the positions of free and associated groups is a sensitive measure of the interaction strength.[7,8] In the present case a quantitative evaluation of the enthalpic content of the interaction is not possible at this point because of the lack of reliable correlations between peak shifts and thermodynamic parameters for this specific donor–acceptor pair. However the absolute value of the shift (50 cm^{-1}), when compared with the corresponding shifts observed in other N–H containing systems,[9–11] qualitatively indicates that the hydrogen bond is rather weak. This finding is in agreement with previously reported results[5] that demonstrated that, while the N–H groups of PBI can act as strong proton donors, the tendency of the imide carbonyls to accept a proton is rather poor. The net result of the interaction between these two groups is the formation of a weak hydrogen bond.

It has already been mentioned that the apparent N–H peak position in the blend spectra is determined by the intensity ratio of two unresolved components at 3415 and 3365 cm^{-1}. In this light it is also possible to analyze the complex dependence of the position of the absorbance maximum in the N–H stretching region on the blend composition (Figure 3). This parameter exhibits an initial sharp decrease and reaches a plateau value of 3365 cm^{-1} at a blend composition of approximately 50/50 wt %. Evidently starting from a 50/50 composition, the absorption at 3365 cm^{-1} largely predominates over that at 3415 cm^{-1}, thus determining the overall peak shape and position. This is not only the result of chemical effects (i.e., the increasing number of N–H groups hydrogen bonded with the carbonyls) but also, and probably to a greater extent, the result of physical effects. It is in fact well-known[7,8] that a considerable enhancement of intensity is generally observed in the fundamental N–H stretching mode when hydrogen bonding occurs: an increase of up to 10-fold has been reported for the molar absorptivity values of this band. Thus, in the present case, even at intermediate compositions, where the concentration of free and associated N–H groups could still be comparable, the intensity of the 3365-cm^{-1} component becomes largely predominant because of the higher value of its absorptivity.

From the above discussion it follows that the N–H stretching region can give valuable qualitative information about the nature and strength of the molecular interactions occurring in this blend system. However, several factors strongly limit the usefulness of this spectral region for quantitative purposes. First, at intermediate compositions the overall band shape is highly complex and the strong asymmetry of the component at 3128 cm^{-1} inhibits any attempt at deconvolution. In addition, the values of the absorptivity coefficients for the various N–H species neither are known from literature data nor are easily measurable. Thus to obtain a more quantitative understanding of this system we turned out attention to the more readily resolved carbonyl stretching region.

Carbonyl Stretching Region (1800–1650 cm^{-1}). The occurrence of a hydrogen bonding interaction involving carbonyl groups is expected to produce a spectroscopically detectable effect on the carbonyl stretching modes. In particular the lowering of the force constant determined by the interaction with the proton donor lowers the absorption frequency and broadens the carbonyl band shape considerably; generally no large intensity effects are observed.[5,11] Indeed the spectral features observed in the carbonyl region of all the investigated compositions are consistent with the occurrence of hydrogen bonding interactions.

The principal phthalimide carbonyl absorption centered at 1725.2 cm^{-1} in pure Ultem 1000 is gradually and continuously shifted toward lower frequencies by increasing the PBI concentration in the blend (Figure 5a); a maximum shift of 6 cm^{-1} is observed. The higher frequency carbonyl absorption originally centered at 1779.1 cm^{-1} displays an analogous trend, but with lower shift values (Figure 5b). These findings are in qualitative agreement with the results recently reported for a similar PBI/polyimide blend[4] and are consistent with the observations made

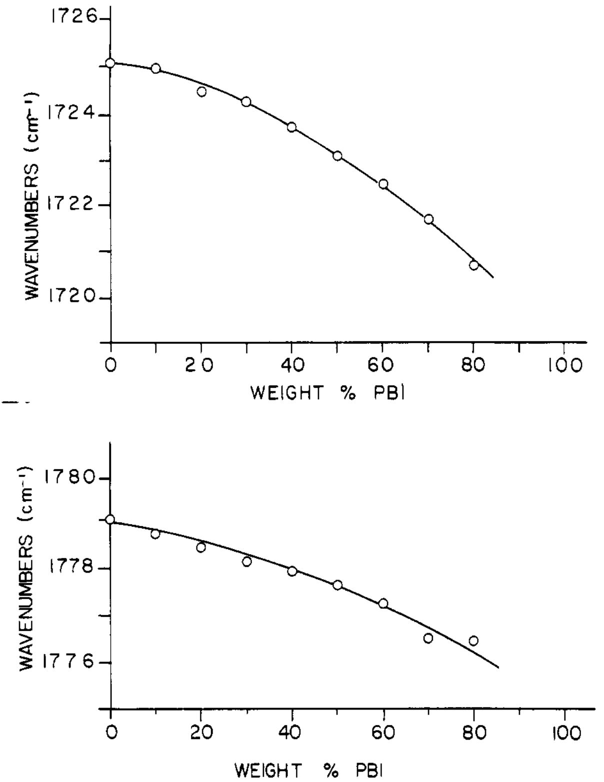

Figure 5. Location of the absorption maxima for the asymmetric (a, top) and the symmetric (b, bottom) carbonyl stretching vibrations of Ultem 1000 as a function of blend composition.

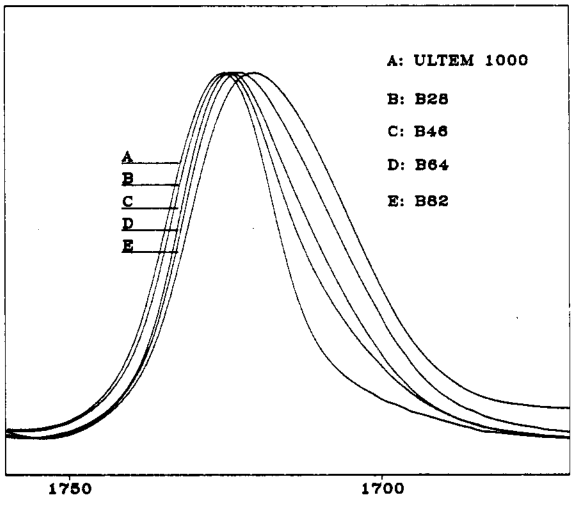

Figure 6. Asymmetric carbonyl stretching vibration of Ultem 1000 in the pure polymer and in four blends; compositions as indicated.

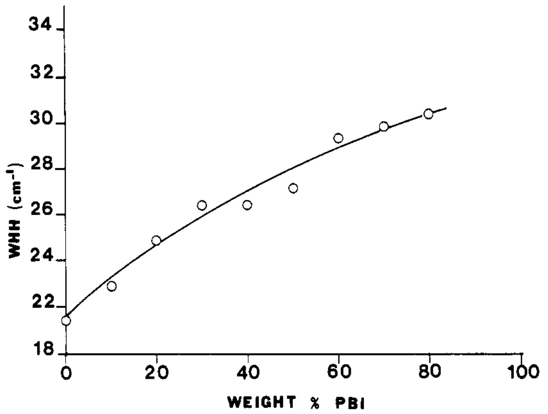

Figure 7. Width at half-height (WHH) of the $\nu_{a,C=O}$ band of Ultem 1000 as a function of blend composition.

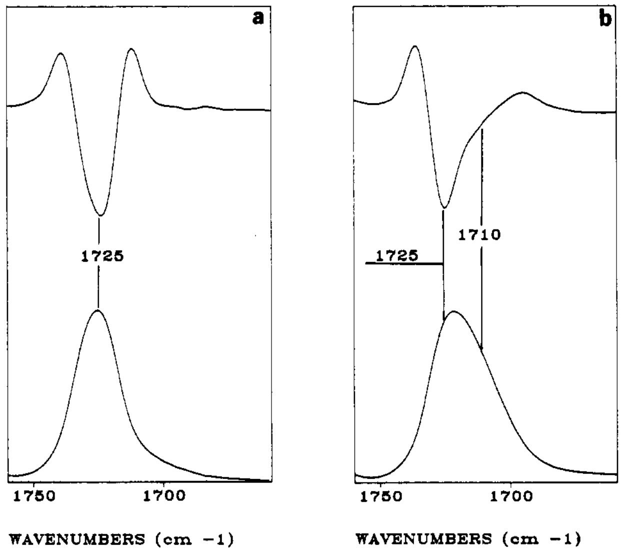

Figure 8. Second-derivative spectra in the 1770–1660-cm^{-1} region of Ultem 1000 (a) and of blend B73 (b).

on a number of different blend systems where a hydrogen bonding interaction is believed to occur.[6,12-14] The $\nu_{a,C=O}$ peak of Ultem 1000 displays a symmetrical band shape, is reasonably well resolved, and has a high absorptivity coefficient; therefore, it can be readily detected and analyzed even for blend compositions rich in PBI. For these reasons we have chosen to focus our attention on this particular absorption in an attempt to derive more quantitative information about the number of groups involved in hydrogen bonding. In Figure 6 the FTIR spectra in the 1760–1670-cm^{-1} region of pure Ultem 1000 and of a series of representative blend compositions are reported. It is immediately apparent that in all cases the shift toward lower wavenumbers is accompanied by considerable band broadening. In particular it is found that the width at half-height (WHH) of the band increases regularly with increasing PBI content in the blend (see Figure 7). Moreover the spectra displayed in Figure 6 reveal that the peak broadening is not symmetric but rather is due to the development of an increasing asymmetry in the lower frequency side of the peak. This behavior is generally associated with the presence of an unresolved two-component structure.[15] The intrinsic breadth and the closeness of the components prevent their direct spectroscopic resolution. It was possible to obtain further evidence for the presence of a multiple peak and an indication of the positions of the unresolved components by performing a second-derivative analysis[16,17] in this region. In Figure 8 it is observed that, while pure Ultem 1000 produces a single negative peak in the second-derivative spectrum, a representative blend spectrum (B73) displays a negative peak at 1725 cm^{-1} (the same position as in Ultem 1000) and a well-defined shoulder centered approximately at 1710 cm^{-1}. To resolve the overlapping components, a curve-fitting deconvolution program was used. As already stressed[9-13,18] this approach is not free from intrinsic limitations and the results obtained are often a matter of debate; a comment on the method we have used in this specific case therefore seems in order. In applying the curve-fitting analysis described in ref 18 to our experimental data, it was decided to minimize the number of parameters to be determined by the least-squares optimization procedure to improve the uniqueness of the fit. In particular the baseline, the peak

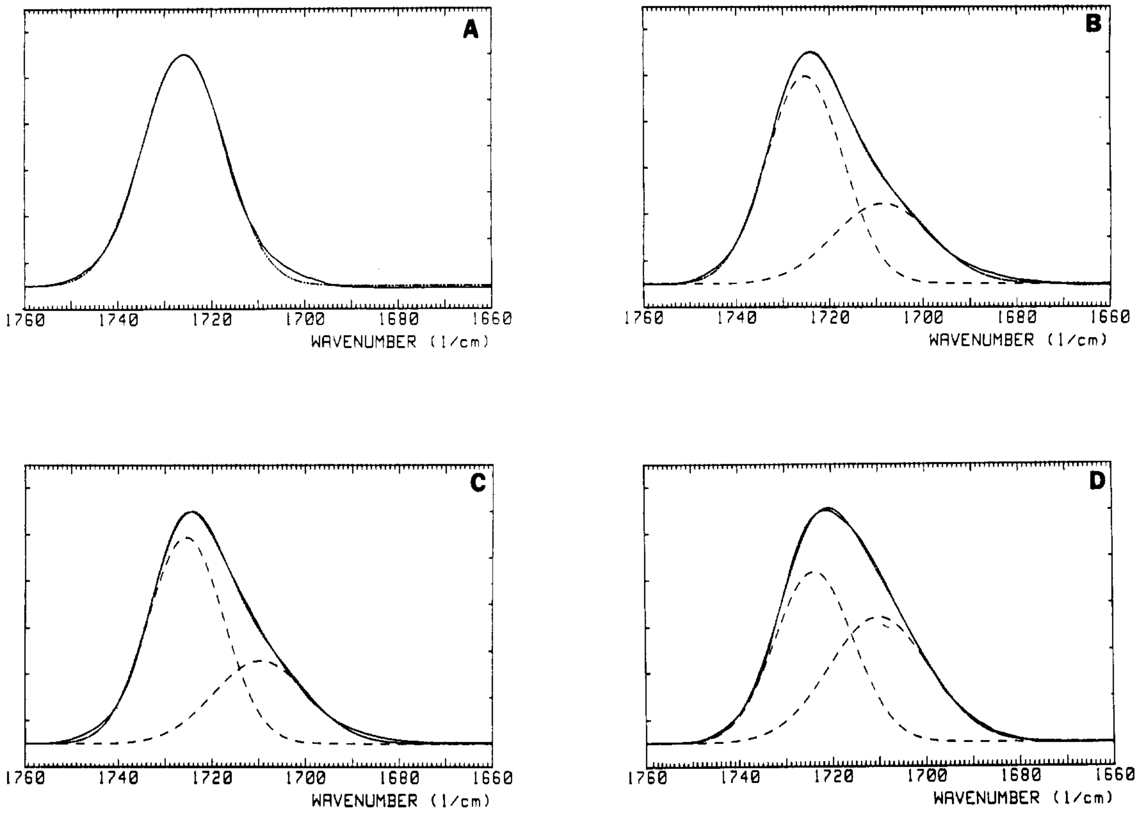

Figure 9. Curve-resolved spectra in the 1760–1660-cm^{-1} region of (A) Ultem 1000, (B) blend B37, (C) blend B46, and (D) blend B82.

Table II
Curve-Fitting Results of PBI/Ultem 1000 Blends

	"free" C═O band			hydrogen-bonded C═O band			
blend	freq, cm^{-1}	width, cm^{-1}	rel area, %	freq, cm^{-1}	width, cm^{-1}	rel area %	fractn of interacting imide groups
Ultem 1000	1725.2	20.2	100				0.00
B19	1725	19	81.4	1710	29	18.6	0.19
B28	1725	19	74.9	1709	24	25.1	0.25
B37	1725	19	68.4	1709	24	31.6	0.31
B46	1725	19	68.7	1709	23	31.3	0.33
B55	1725	19	64.9	1710	23	35.1	0.35
B64	1724	20	62.5	1709	25	37.5	0.37
B73	1724	20	61.2	1709	24	38.8	0.39
B82	1724	20	51.7	1710	25	48.3	0.48

shapes, and the number of peaks were selected as discussed below, while the program was allowed to calculate, by best fitting the experimental data, the peak positions and the widths of the components.

(i) A flat baseline was set between 1779 and 1660 cm^{-1}, which was straightforward in this spectral region for most of the blend compositions. For the compositions with the highest PBI content (B73 and B82) the subtraction of residual PBI absorptions in the lower side of this frequency range was performed to increase the baseline linearity.

(ii) The number of components was defined as two on the basis of a simple association model whereby the interacting proton acceptor groups give rise to a single separate absorption at lower frequency.

(iii) Finally, the peak shape was selected as that which best fit the experimental band shape of pure Ultem 1000. As in the case of other carbonyl-containing polymers,[9–11] it was found that a purely Gaussian profile closely fits the symmetric shape of the Ultem 1000 carbonyl absorption at 1725 cm^{-1} (see Figure 9A).

The results of the curve-fitting analysis were eventually used to validate the previous assumptions, particularly assumption (ii), which is the most physically relevant. In Figure 9 the curve-resolved spectra in the 1770–1660-cm^{-1} region for a series of representative blend compositions are reported with that for pure Ultem 1000 for comparison. It is apparent that for all blends the experimental band profile is closely fitted by the sum of two distinct components. The analytical results of the curve-fitting procedure are summarized in Table II. First it is noted that the peak position and the WHH of the high-frequency component (peak 1) remain substantially constant for all investigated compositions and are coincident, within the uncertainty of the method (±1 cm^{-1}), with the band parameters observed in pure Ultem 1000. The secondary low-frequency component (peak 2) also occurs at a reasonably constant frequency and with a constant WHH. Only in the B19 spectrum the WHH of peak 2 is considerable but in this case the extremely low intensity of this band makes the determination of its parameters more uncertain. Another relevant observation is that both the position and the broadness of peak 2 as determined by the curve-fitting analysis are consistent with the presence of hydrogen-bonded carbonyl groups. In summary the imide carbonyl absorption in the blend spectra can be regarded as being formed by two separate components: the first at 1725 cm^{-1} due to noninteracting, free imide groups and the second at 1710 cm^{-1} generated by

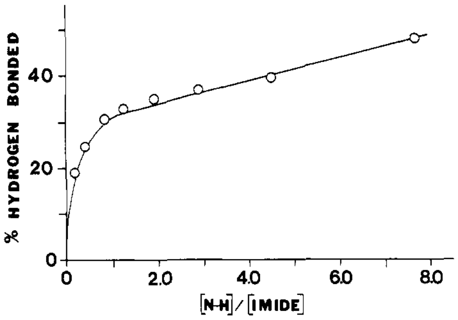

Figure 10. Percent of hydrogen-bonded imide groups as a function of the N–H/imide molar ratio.

those groups that interact with the N–H of PBI. The experimental peak position and shape are determined by the intensity ratio of these two components.

Having obtained the deconvolution of the carbonyl absorption, a knowledge of the absorptivity coefficients of the two components (or of their ratio) would allow us to directly convert the area ratios this concentration ratios. As already observed for the N–H stretching absorptions, no literature data are available for these parameters, nor is the method described by Coleman et al.[6] applicable in this particular case. However, generally no large intensity effects on the carbonyl stretching absorptions occur upon hydrogen bond formation[7,8] and it can be postulated that the two absorptivity coefficients are approximately equal. This assumption has been thoroughly discussed in the literature[7,8,13] and successfully applied to a number of analogous blend systems.[12,13] On this basis the fraction of interacting imide groups as a function of blend composition has been calculated and the results are presented in the last column of Table II. A plot of the percentage of hydrogen-bonded imide groups as a function of the [N–H]/[imide] ratio is shown in Figure 10. The most interesting feature of this figure is that even with a large excess (7-fold) of N–H groups, the number of interacting imide groups is still lower than 50%.

It is worth noting at this point the possibility that the blends under investigation were prepared in a nonequilibrium state. In fact, due to the very high T_g of the material, the number of interactions could be controlled by the casting conditions (i.e., kinetics) rather than by the thermodynamics of the system. However, it has been observed that the data obtained for this blend system compare well with analogous data obtained by Garton for a polycaprolactone (PCL)/phenoxy blend prepared under equilibrium conditions.[13] Also in the latter system an estimation was obtained of the number of interacting PCL carbonyls as a function of blend composition and a plot similar to that reported in Figure 10 was obtained. For the PCL/phenoxy blend the observation that the maximum number of interacting carbonyls was lower than 50% was tentatively explained in terms of steric limitations caused by a mismatch in the polymer repeat distances on the two components. The fact that we have observed similar behavior in a system whose components are so different in chemical structure suggests that this phenomenon has a more general physical basis.

Temperature Effects. In a previous contribution[4] it was reported that by annealing a 75/25 w/w PBI/Ultem blend at 400 °C the shift observed in the main phthalimide carbonyl absorption was eliminated. This effect was considered to be evidence of phase separation occurring at temperatures close to the T_g of the blend, and this was later confirmed by DSC studies.[19] The above preliminary experiment demonstrated that there are spectral features that in principle can be used to determine the LCST boundary of the system. Thus a more systematic investigation of a series of four different blend compositions was undertaken over a temperature range from 25 to 400 °C.

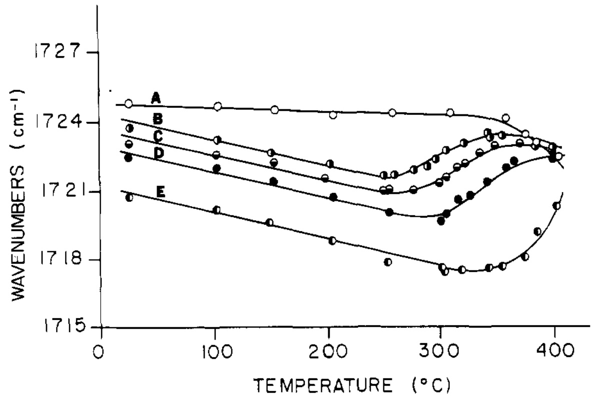

Figure 11. Peak position of the asymmetric stretching vibration of the imide carbonyl as a function of temperature for (A) Ultem 1000, (B) blend B46, (C) blend B55, (D) blend B64, and (E) blend B82.

The experiment was, however, designed in a rather different way: instead of annealing a film sample at a selected temperature and subsequently recording the FTIR spectrum at room temperature, the heat treatment was carried out directly in the spectrometer. Thus in the present study the spectra were recorded at different temperatures after allowing the sample to equilibrate for 60 min. In light of the results obtained in the previous sections we again focused our attention on the main carbonyl stretching absorption.

A preliminary analysis of the vibrational behavior of Ultem 1000 as a function of temperature showed that, in an inert atmosphere, the FTIR spectrum of the polyimide is very stable. In the temperature range between 25 and 350 °C this is observed and the spectrum recovers its original form completely when the sample is cooled to room temperature. In particular the peak position of the carbonyl absorption at 1725.2 cm^{-1} remains practically constant in this temperature range; from 350 to 400 °C a gradual decrease in the maximum frequency is observed (Figure 11, curve A). These spectral changes are only partially reversible: when the sample is cooled to ambient temperature the peak position reverts to its original value but the WHH remains higher than the initial one. This can be considered as an indication that chemical processes start to take place slowly at temperatures above 350 °C. As will become apparent, these effects must be taken into account when interpreting the temperature data relative to the various investigated blends.

Figure 11 shows the frequencies of the $\nu_{a,C=O}$ peak as a function of temperature for four different compositions (B46, B55, B64, B82) and for pure Ultem 1000. Analogous features are observed in the curves relative to all the blends: an initial linear decrease is followed by a transition region where the peak position gradually shifts to higher frequencies. The temperature at which the transition region starts depends on the blend composition; it increases as the PBI content in the blend is increased.

We have already noted above that, in the blend spectra, the $\nu_{a,C=O}$ peak is the sum of two unresolved components at 1725 and 1710 cm^{-1}. The actual position of the peak is determined by the intensity ratio of these two unresolved components. The shift toward higher wavenumbers, which is found to occur in a specific temperature range for each investigated composition, is due to the gradual disap-

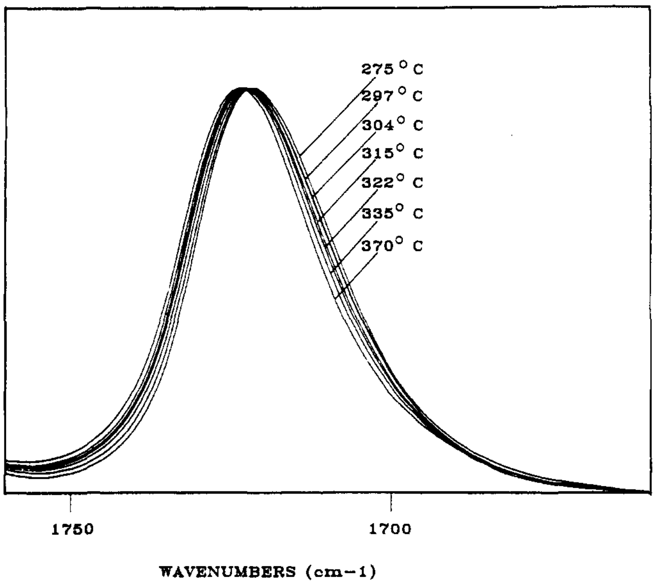

Figure 12. $\nu_{a,C=O}$ absorption of blend B55 in the temperature range 275–370 °C (the transition region).

Table III

blend	T_{onset},[a] °C	T_g,[b] °C
B46	266	269
B55	282	286
B64	300	306
B82	348	354

[a] Calculated from the frequency versus temperature curves as the intersection point of the two linear portion of the curves in the transition region. [b] Calculated from the Fox relationship $1/T_g = (W_1/G_{g,1}) + (W_2/T_{g,2})$.

pearance of the component at lower frequency, i.e., the hydrogen-bonded imide carbonyls. In other words, starting at a certain temperature, which depends on the blend composition, hydrogen bonding between imide and N–H groups starts to break down and, since the fine structure of the carbonyl absorption is unresolved, the process is reflected only in a gradual shift of the band toward higher frequencies, Figure 12. A direct relationship should exist between the temperature at which the hydrogen bonds start to dissociate and the temperature at which the onset of large-scale molecular mobility occurs.[20] In fact it is found that the temperatures at which the peak position versus temperature curves start to increase (calculated as the intersection point of the two linear portions of the curves) coincide within experimental error with the glass transition temperatures as calculated from usual Fox relation, see Table III. Moreover, it is observed that for the B46, B55, and B64 blends the final values of the peak position are very close to that observed in pure Ultem 1000 in the corresponding temperature range. This is an indication that the molecular interactions occurring in the blend are no longer present and that phase separation has occurred. If the blend samples are slowly cooled to ambient temperature (10 °C/min), the peak position of the $\nu_{a,C=O}$ absorption is coincident, within experimental uncertainty, with the position of the same band in pure Ultem 1000 at room temperature. This in turn implies that, at least in the cooling protocols used in these experiments, phase separation is not reversible (see Figure 13), and this has been observed by direct thermal analysis. For the blend composition B82 it is apparent that, in the explored temperature range, phase separation is not complete. The temperature region where phase separation is believed to occur is thus the final portion of the "transition" region where the carbonyl frequency values in the blends approach the value observed in pure Ultem 1000.

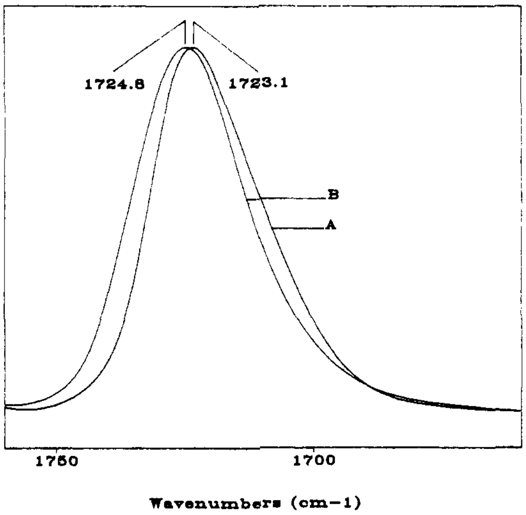

Figure 13. $\nu_{a,C=O}$ absorption of blend B55 (A) and of the same blend after thermal treatment at 400 °C, (B) spectra obtained at room temperature.

In summary, at temperatures below T_g the hydrogen bonding interactions are stable due to the rigidity of the polymer structure. When the glass transition temperature is approached, the enhanced molecular mobility allows the intrinsically weak interactions to be easily broken. Ultimately, when most of the bonds are dissociated (at the end of the transition region in the frequency–temperature curve) phase separation occurs.

No explanation is yet available for the observed negative slope of the frequency versus temperature curves below the transition region. Investigations of analogous systems for which the carbonyl region is well resolved are currently under way to obtain further insight into the temperature behavior of PBI-containing blends.

Another spectral feature that in principle can be used to monitor the decrease of hydrogen bonding as a function of temperature and hence the onset of phase separation is the width at half-height (WHH) of the $\nu_{a,C=O}$ absorption. We have already seen that the broadening of this band on the lower frequency side is determined by the presence of an unresolved component at 1710 cm^{-1}; when the number of interacting groups decreases, this component should diminish accordingly and a gradual narrowing of the carbonyl absorption should be detected. Ultimately, when all the hydrogen bonds are dissociated and phase separation occurs, a symmetrical, purely Gaussian band profile should be detected. In Figure 14 the WHH values of two-blend compositions (B46 and B55) as a function of temperature are reported together with the same curve relative to pure Ultem 1000 for comparison. It has been already mentioned that for Ultem 1000 the WHH of the 1725.2-cm^{-1} peak, which is very stable up to 350 °C, displays a sharply increasingly broadening trend in the 350–400 °C range, possibly because of chemical processes slowly starting to occur in this temperature region. The curve for the composition B46 clearly shows the expected decrease in a temperature range that closely corresponds to that where the frequency versus temperature curve displays its "transition" region (compare Figure 11, curve B, and Figure 14, curve B); as the WHH decreases the carbonyl absorption also becomes more symmetrical. However, the WHH never reaches the values observed in pure Ultem 1000, apparently because starting from 350 °C the same phenomena occurring in the pure polyimide

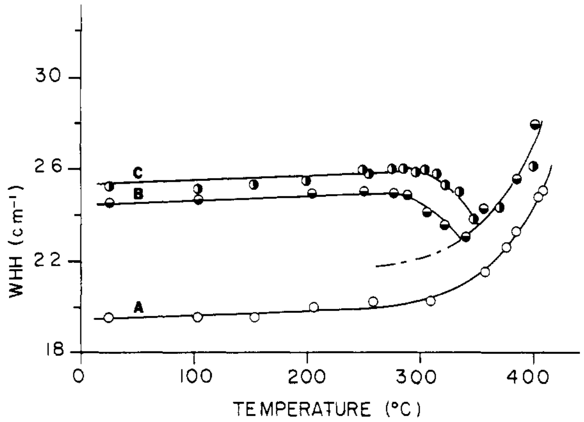

Figure 14. Width at half-height (WHH) of the $\nu_{a,C=O}$ band as a function of temperature for (A) Ultem 1000, (B) blend B46, and (C) blend B55.

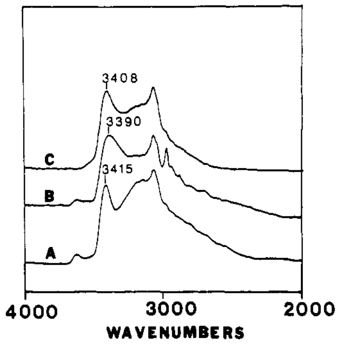

Figure 15. N–H stretching region of PBI (A), blend B64 (B), and B64 after thermal treatment at 400 °C (C). Spectra collected at room temperature.

start to take place, thus determining a WHH increase that exactly parallels that observed in Ultem 1000. The curve relative to the B55 composition is very close to the one discussed above, the only detectable difference being that the temperature at which the WHH values start to decrease is now higher. This observation is again consistent with the results of the analysis of the peak positions versus temperature. For the remaining two compositions (B64 and B82) the transition temperature is so high that the WHH decrease is no longer detectable.

To summarize the results of this section it can be stated that the occurrence of spurious phenomena in the pure polyimide somewhat obscures the effect of hydrogen bond dissociation and phase separation in the blends. However, from the above analysis it appears that both the peak position and the carbonyl band width can be successfully used to determine the onset of phase separation in blend systems where hydrogen bonding interactions occur. In particular, systems showing high thermal stability in the temperature range where phase transition occurs, and hydrogen bonds of high enthalpic content, would be ideal candidates for this analysis.

Finally it is worth mentioning that from the results of the first section one could also expect that the N–H stretching region could be used for the above analysis. In fact the broad peak centered at 3365 cm^{-1} should gradually recover the position observed in pure PBI (3415 cm^{-1}) when phase separation occurs. This effect has been observed (see Figure 15) in FTIR spectra taken at ambient temperature after the occurrence of phase separation and quenching of the sample. However, the complexity of the N–H stretching region severely limits its usefulness in a more detailed temperature analysis. In particular, observations suggest that the absorptivity coefficients of the hydrogen-bonded N–H stretching modes are highly temperature dependent; this effect has already been observed in other self-associated polymers.[9,10] Such a strong temperature dependence does not allow the separation of chemical and physical effects.

Conclusions

FTIR spectroscopy has proven to be an effective tool for studying the molecular interactions occurring in polybenzimidazole/Ultem 1000 blends. Information concerning the nature of the interactions (hydrogen bonding) and their strengths has been obtained by analyzing the N–H stretching region of PBI and the carbonyl stretching region of Ultem 1000. By applying curve-fitting techniques, an estimation of the ratio between free and hydrogen-bonded proton acceptor groups was obtained for the various investigated blend compositions. The results are in close agreement with spectroscopic data recently reported in the literature for other miscible blend systems.

FTIR spectroscopy has also been used to investigate the temperature behavior of the PBI/Ultem 1000 blend. By using the peak position and the width at half-height of the principal phthalimide absorption, it was possible to monitor the onset of hydrogen bonding dissociation and to correlate this phenomenon with the onset of large-scale molecular mobility and with the occurrence of phase separation for the various investigated compositions.

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