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Fourier transform infrared spectroscopy investigations of polybenzimidazole/poly(bisphenol-A carbonate) blends

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The results of a Fourier transform infrared spectroscopy (*FT*i.r.) study of the blend formed by poly(2,2′-*m*-phenylene)-5,5′-bibenzimidazole (PBI) and poly-[2,2-propane-bis(4-phenyl carbonate)] (PC) are discussed. The spectral features observed in the N–H stretching and carbonyl stretching regions of all the compositions investigated have been interpreted in terms of hydrogen bonding interactions occurring between the N–H groups of PBI and the C=O groups of PC. Qualitative as well as quantitative information about these interactions has derived. The *FT*i.r. results indicate a high degree of molecular mixing between the two components at all blend compositions. A spectroscopic study as a function of temperature of a single blend composition (50/50 wt%) is also reported. A quantitative analysis of the carbonyl region in the spectra yielded information about the onset temperature of large scale molecular mobility. A strong catalytic effect of PBI on the thermal degradation of PC was observed and is also discussed.

(Keywords: Fourier transform infrared spectroscopy; polymer blends; polybenzimidazole; poly(bisphenol-A carbonate); blend miscibility; thermal)

INTRODUCTION

Efforts have been devoted in recent years to the preparation and development of miscible blends based on an aromatic polybenzimidazole, poly(2,2-*m*-phenylene)-5,5′-(bibenzimidazole), PBI. In particular, a new class of blends based on PBI and aromatic polyimides has been discovered. Spectroscopic studies of these systems[1–4] showed that intermolecular interactions of the hydrogen bonding type occur among the components; the interactions are related to the observed miscibility in the blends. A Fourier transform infrared (*FT*i.r.) analysis of the pure components in the presence of low molecular weight monofunctional probes[3] indicated that PBI possesses a strong tendency to form hydrogen bonds, acting as proton donor while the polyimides are comparatively weak proton acceptors.

These results prompted us to explore the possibility of mixing PBI with stronger proton-accepting polymers to enhance the strength of the intermolecular interactions which promote miscibility. After careful consideration of the reactivities and thermal stabilities of the various proton accepting polymers already described in the literature, 'bisphenol-A' polycarbonate (PC) was selected. This polymer is in fact well known for its ability to form miscible blends in which strong interactions occur among the components[5–7]. In particular, a hydroxyl containing styrene copolymer, poly(styrene-co-vinyl phenyl hexafluorodimethyl carbinol) (PHFA), was found to be miscible with PC, whereas polystyrene itself is immiscible. In infrared spectroscopic studies it was observed that the *para*-hydroxyl stretching frequency of PHFA, which occurs at 3520 cm^{-1} in the pure copolymer, shifted to 3450 cm^{-1} in the blend, thus suggesting the occurrence of hydrogen bonding interactions[7].

In this paper we report a *FT*i.r. spectroscopy analysis of the PBI/PC system as a function of blend composition. *Table 1* gives a list of the various compositions investigated and their respective codes. In addition, the spectral behaviour with respect to temperature of a particular composition (50/50 wt%) has been studied. The thermal behaviour, which would normally be expected to address directly the issue of phase miscibility or non-miscibility, is complex in this system and will, therefore, be discussed elsewhere[8].

EXPERIMENTAL

Materials

PBI was supplied by Celanese Corporation in the form of an additive free, finely ground powder. The bisphenol-A polycarbonate was purchased from Polyscience Inc. It had a reported M_n of 4600 and $M_w = 21\,600$.

Sample preparation

Thin polymer films (2–10 μm) were prepared by casting 4.0% (w/v) solutions of the pure components in dimethylacetamide (DMAc) in a nitrogen atmosphere at 120°C for 2 days; further drying of the samples was performed under vacuum at 160°C for an additional 3 days. Clear films were obtained for all the compositions; differential scanning calorimetry measurements showed that under the experimental conditions used to prepare the films no PC crystallinity develops.

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Table 1 Compositions and codes of the investigated blends

Composition (wt%)		
PBI	PC	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
0	100	PC

Techniques

FTi.r. spectra were obtained at 2 cm^{-1} resolution with a Mattson Cygnus 100 *FTi.r.* spectrometer equipped with a deuterated triglycine sulphate (DTGA) detector. From 30 to 100 spectra were collected and signal averaged conventionally for each sample. All the films used in this study were sufficiently thin to absorb in a range where the Lambert–Beer law is obeyed. The *FTi.r.* temperature measurements were performed 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 monitor continuously the sample temperature. All temperature measurements were made in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Spectroscopic behaviour as a function of blend composition

Figure 1 shows the *FTi.r.* spectra of pure PBI (curve a), PC (curve b) and a 50/50 wt% PBI/PC blend (curve c). The main features of the PBI spectrum have been discussed in previous contributions[3,4]. It is worth mentioning here that the region most sensitive to hydrogen bonding interactions is the N–H stretching absorption from 3500 to 2500 cm^{-1}. In the PBI spectrum this region is characterized by a relatively sharp peak centred at 3415 cm^{-1} attributed to non-interacting N–H groups and by a broad asymmetric absorption at 3145 cm^{-1} due to self-interacting hydrogen bonded N–H groups. A third low intensity absorption at 3063 cm^{-1} is attributed to the stretching modes of the aromatic C–H groups. Also of interest is the fact that the PBI spectrum shows practically no absorption in the 2000–1650 and 1100–1000 cm^{-1} regions, thus allowing the analysis of PC peaks occurring in these frequency ranges even for blend compositions rich in PBI.

In the C–H stretching region the spectrum of PC displays the characteristic pattern of bisphenol A, namely the CH_3 asymmetric and symmetric stretching vibrations centred at 2970 and 2875 cm^{-1}, respectively, and a doublet at 3060 and 3040 cm^{-1} due to the aromatic C–H stretching modes. The carbonyl stretching vibration produces a strong, well resolved peak at 1775 cm^{-1}, while the –O–C–O– stretching modes give rise to a very intense and complex multiplet with maxima at 1227, 1193 and 1163 cm^{-1}. The out-of-plane vibration of the carbonate group is observed as a rather broad absorption centred at 769 cm^{-1}. The *para*-substituted aromatic system produces well defined peaks at 1505, 1083, 1015 and 830 cm^{-1}; finally, the isopropyl structure is associated with a weak band at 1387 cm^{-1} (References 9 and 10).

In the present analysis we will be mainly concerned with the C=O stretching region, which is expected to be the most sensitive to the occurrence of hydrogen bonding interactions. *Figure 2* shows the spectra of pure PBI and of a representative blend (B55) in the 3500–2300 cm^{-1} region. A substantial broadening and displacement to lower frequency of the PBI peak at 3415 cm^{-1} is noted in the blend spectrum. A plot of the location of the N–H stretching band maxima as a function of blend composition is reported in *Figure 3*. It is worth mentioning that for the blend with the lowest PBI content (B28, 20 wt% PBI) a broad, flat absorption encompassing a 40 cm^{-1} frequency range is observed in the region of interest, making it impossible to define a band maximum. For this reason the value corresponding to this composition has not been reported in *Figure 3*. A gradual broadening and a shift to lower frequency of the 3415 cm^{-1} peak of PBI has already been observed and discussed in detail

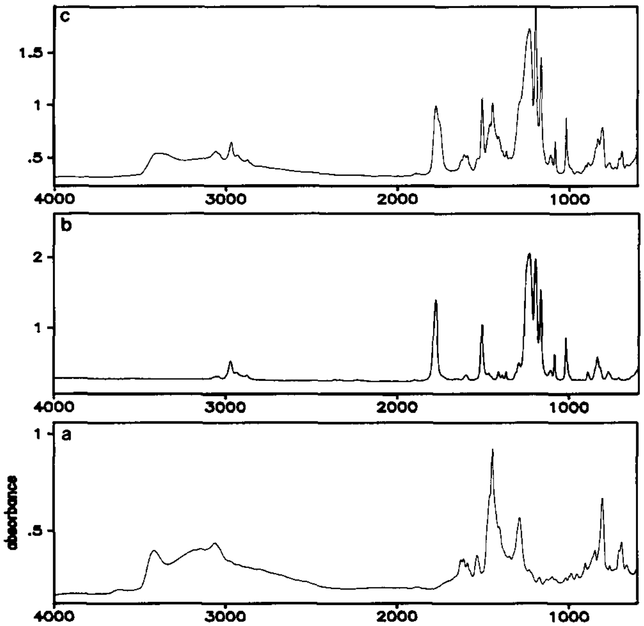

Figure 1 *FTi.r.* spectra of: (a) pure PBI; (b) pure PC; (c) B55 blend (see *Table 1*)

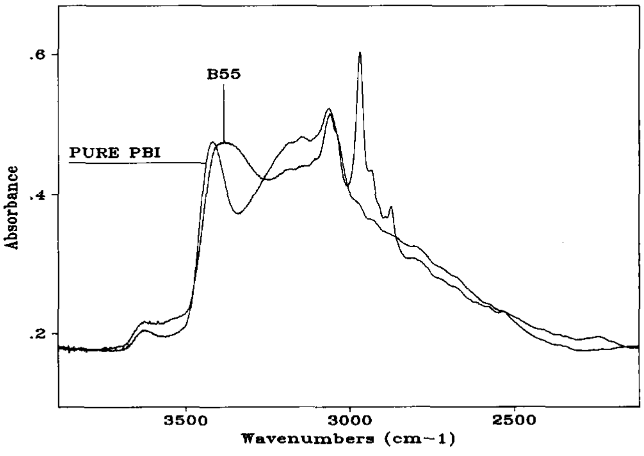

Figure 2 *FTi.r.* spectra in the 4000–2000 cm^{-1} region of pure PBI and of blend B55

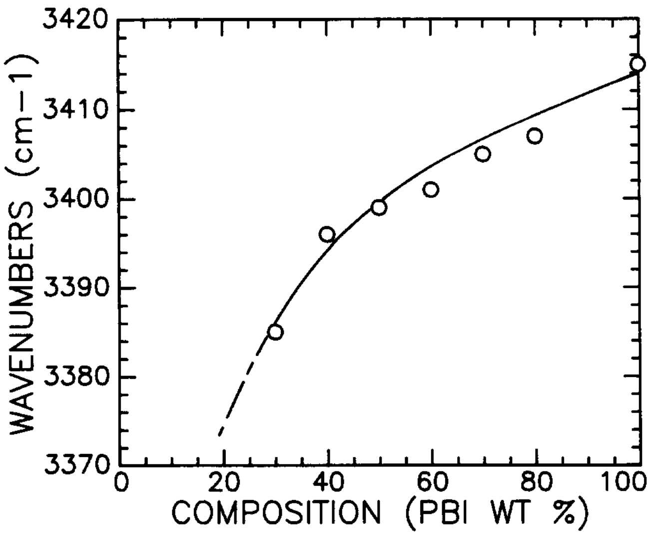

Figure 3 Location of the absorbance maxima in the N–H stretching regions as a function of blend composition

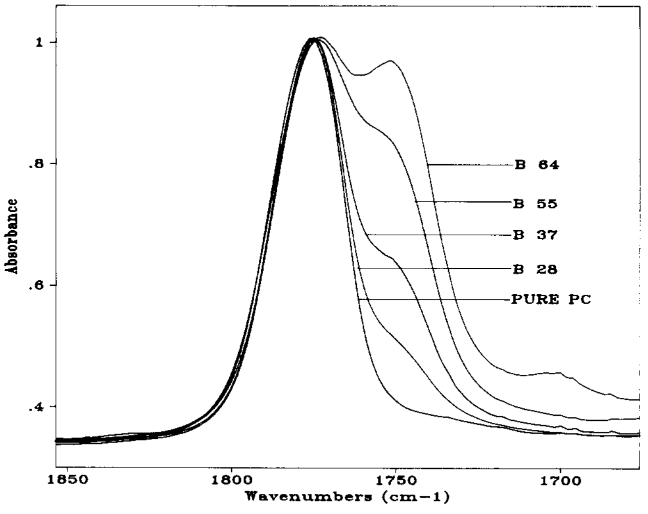

Figure 4 The carbonyl stretching vibration of PC in the pure amorphous phase and in four blends of different compositions

for some PBI/polyimide blend systems[2,4]. The effect was interpreted in terms of the occurrence of hydrogen bonding interactions involving the N–H groups of the benzimidazolic ring and the imide carbonyls; this interpretation also seems reasonable in the present case. For example, in PBI/Ultem 1000 blends, it was possible to isolate, both directly and by means of spectral subtraction analysis, the –N–H…O=C component, thus obtaining an estimation of the hydrogen bonding strength. However, for the PBI/PC system attempts to use the same approach in this spectral region were unsuccessful. This indicates a higher complexity of the ν_{N-H} absorption in the present case, which further limits its usefulness in obtaining more detailed information about the intermolecular interactions occurring in this system. This complexity could be related to the presence in the blends of trace amounts of residual solvent, which is known to be highly absorbent in this frequency range[2] and which could not be removed because of thermal instability of the blend (see below).

In *Figure 4* the carbonyl region of pure PC and of several blends is reported. It is immediately apparent that the 1775 cm^{-1} $\nu_{C=O}$ peak is split into a doublet in the presence of PBI and that the intensity of the lower frequency component increases when the PBI content in the blend is increased. This effect can be interpreted in terms of hydrogen bonding interactions between the N–H groups of the benzimidazolic moiety and the carbonyl groups of PC, in agreement with the observations made in the N–H stretching region. In fact, such an interaction weakens the force constant of the C=O double bond and thus produces a lowering in the frequency of this bond's stretching vibration. Analogous effects have been reported in the literature for blend systems in which hydrogen bonding interactions occur[11].

It was informative to perform a second derivative analysis in the carbonyl spectral region. This method[12,13] relies on the fact that the second derivative of the Gaussian or Lorentzian function, which can be used in most instances to represent the shape of infrared absorption curves, is itself a negative peak with two positive lobes (see *Figure 5a*); the sharpness of this peak, or its full width at half height (WHH) is approximately one third that of the original function and this factor can be used to separate overlapping bands by double differentiation. In *Figure 5b* the second derivative spectrum of a representative blend (B36) in the carbonyl region is shown. Two well resolved negative peaks are observed at 1775 cm^{-1} (the same frequency as for pure PC) and at 1749 cm^{-1}, indicating the presence of only two components in the carbonyl region of the blend; the exact location of their maxima is also obtained. Another method which can yield useful information in this frequency range is spectral subtraction analysis. In fact, assuming that the non-interacting carbonyl groups of PC in the blend give rise to the same unperturbed $\nu_{C=O}$ absorption observed in pure PC, it should be possible to subtract this component from the doublet at 1775 and 1750 cm^{-1} by using the $\nu_{C=O}$ peak of pure PC as reference. This hypothesis is reasonable because of the essentially isolated nature of the $\nu_{C=O}$ vibration in PC, which renders it unlikely to be perturbed by conformational effects.

In fact, it is found that in the region of interest for all the investigated compositions a remarkably 'clean' subtraction is obtained in the form of a single, highly symmetric peak centred at 1751 cm^{-1} (see *Figure 6b*). The results of these analyses are listed in detail in *Table 2*; note that both the peak position and the WHH of the 1751 cm^{-1} component remain constant for all the compositions investigated. Moreover, the peak position corresponds, within the uncertainty of the method, to that obtained by second derivative analysis. In the light

Table 2 Results of the spectral subtraction analysis of the PBI/PC blends[a]

	Hydrogen bonded C=O band			
Blend code[b]	Freq. (cm^{-1})	Width (cm^{-1})	Rel. area (%)	Fraction of interacting carbonyl groups
B28	1751	25	11.0	0.11
B37	1751	26	22.2	0.22
B46	1750	26	34.2	0.34
B55	1752	27	44.6	0.45
B64	1752	27	47.7	0.48
B73	1751	26	50.7	0.51

[a] Spectral subtraction was performed using the 1775 cm^{-1} $\nu_{C=O}$ band of pure PC as reference

[b] See *Table 1* for a list of blends used

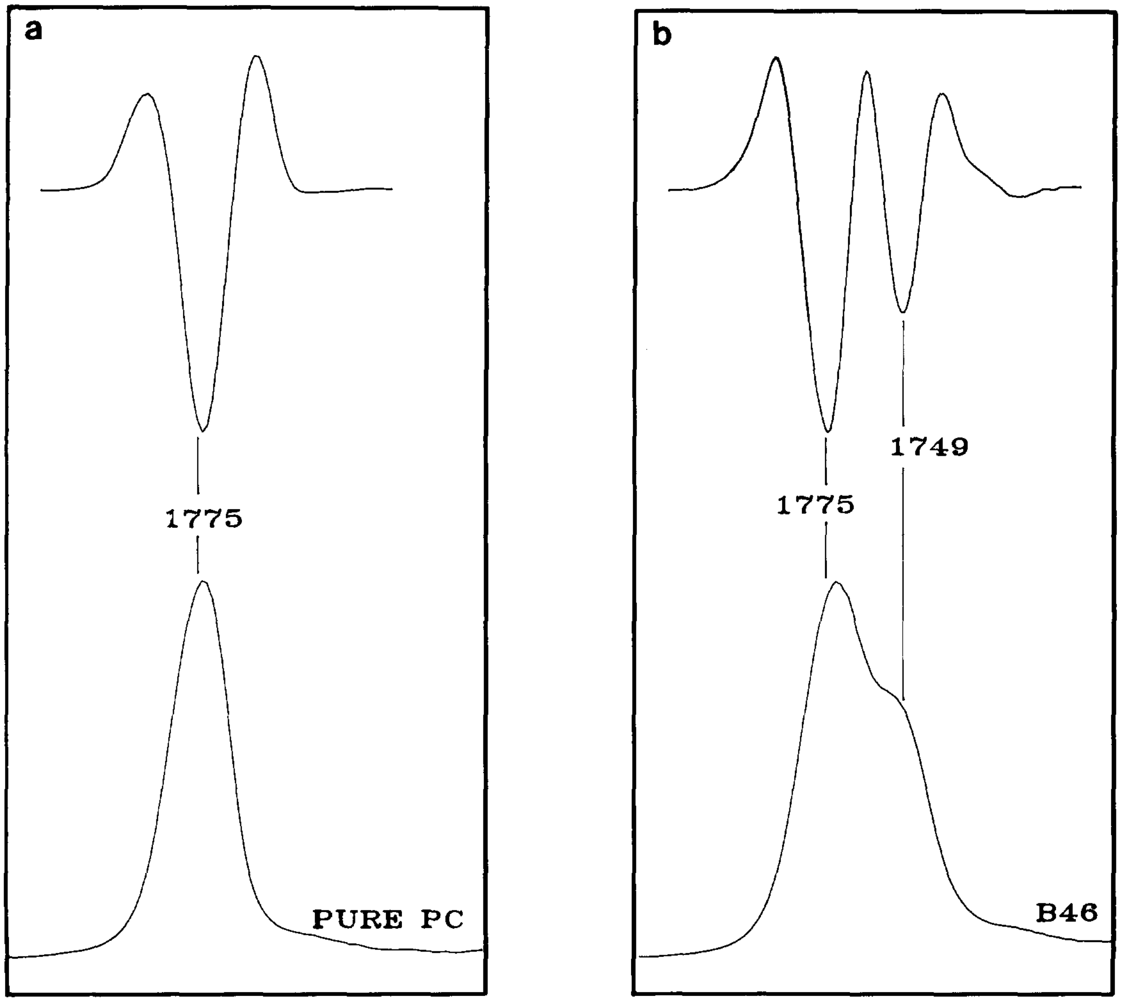

Figure 5 Second derivative spectra in the carbonyl stretching region for (a) pure PC and (b) blend B46

of the previous findings it can be concluded that in PBI/PC blends the carbonyl groups of PC exist in two different populations: those which are free from any interaction and give rise to a $\nu_{C=O}$ stretching absorption coincident with that observed in pure PC and those which are hydrogen bonded with the benzimidazolic N–H groups, whose $\nu_{C=O}$ peak occurs at a substantially lower frequency (1751 cm^{-1}). The observation that the 1751 cm^{-1} component is highly symmetrical and that its position does not change on increasing the PBI content in the blend seems to indicate the formation of adducts of well defined 1:1 stoichiometry[14–16].

It is also interesting to compare the spectroscopic behaviour of PBI/PC blends with that of the PBI/Ultem 1000 system. In the latter case the hydrogen bonding interaction produced in the main phthalimide absorption of Ultem 1000 at 1725 cm^{-1} only a shift to lower frequencies and a gradual broadening of the peak. This was due to the intrinsic breadth and closeness of the two carbonyl absorption bands (free and hydrogen bonded C=O groups), which prevented their direct spectroscopic resolution; they were resolved by applying curve fitting methods[4]. Conversely, in the PBI/PC system, while the WHH of the low frequency component remains approximately the same, the difference between the position of the free and the interacting components, $\Delta\nu$, is considerably higher (24 cm^{-1}, compared with 15 cm^{-1} in PBI/Ultem 1000), thus affording direct resolution of the doublet at 1775 and 1751 cm^{-1}. The higher value of $\Delta\nu$ implies a stronger hydrogen bonding interaction in the PBI/PC system; this result is not surprising considering that in our earlier analysis[3] the polyimides were found to be the weakest proton accepting polymers among those described in the literature.

Thus we conclude that the ν_{N-H} absorption band of PBI provides little information about hydrogen bonding interactions in PBI/PC blends. In contrast we observe that the $\nu_{C=O}$ absorption bend in PC is split into two components upon blending with PBI and that each component, corresponding to the non-interacting and interacting carbonyl groups, can be observed independently by using spectral subtraction methods.

Having isolated the $\nu_{C=O}$ absorption band of the interacting carbonyl groups by means of spectral subtraction, the knowledge of its absorptivity coefficient, ε_{1751}, would allow quantitative estimation of the population of interacting carbonyl groups, $[CO]_i$, in the blends. Unfortunately, the value of ε_{1751} in this system is not easily obtained; in fact, quantitative high temperature measurements[11] would be required, which, as will be discussed later, are complicated by the thermal instability of PC in this environment. However, it has been observed that the integrated carbonyl absorbance, normalized with respect to a PC internal standard peak (the 1015 cm^{-1} band adequately serves the purpose) remains constant even though the blend composition is

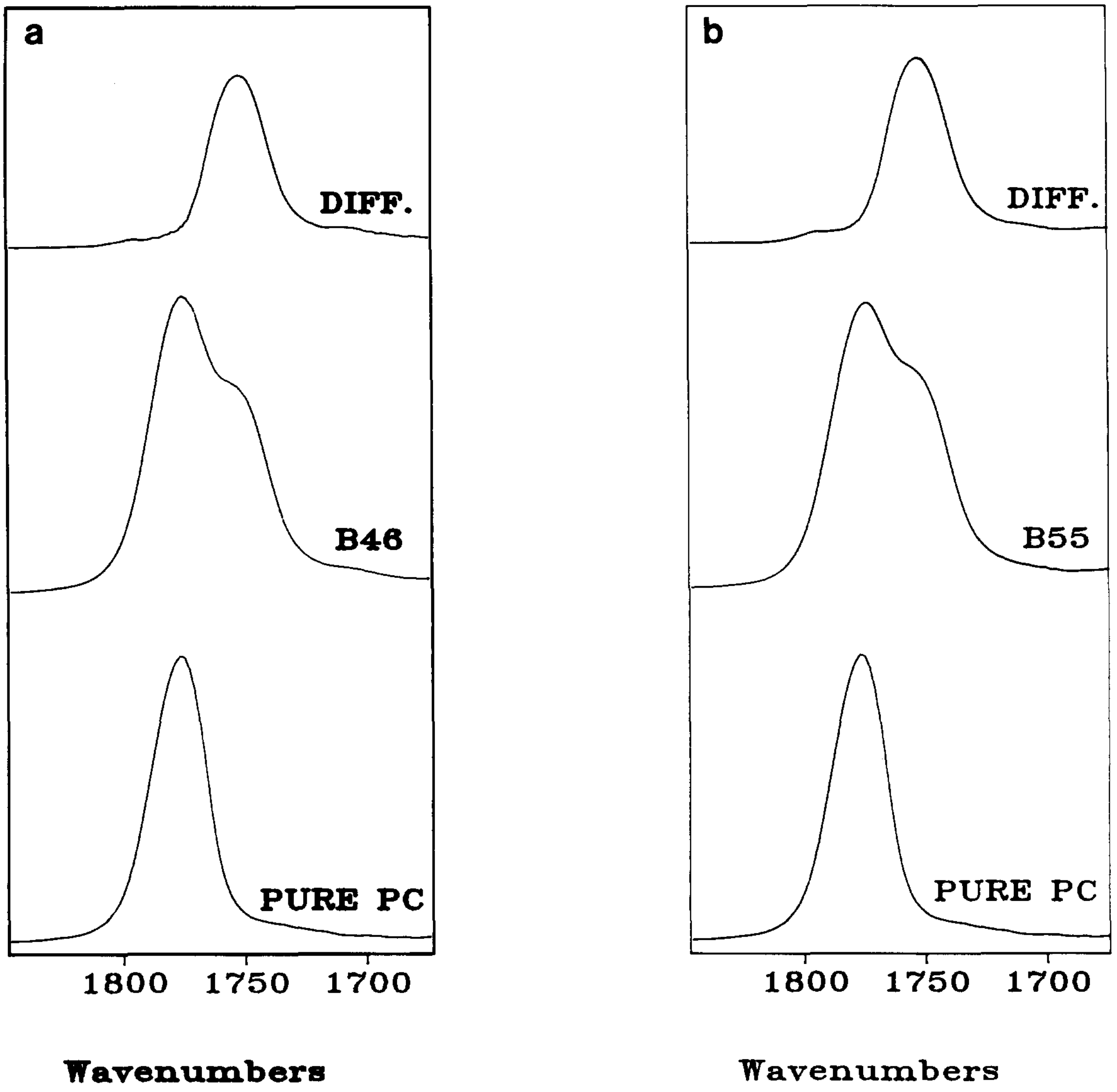

Figure 6 Spectral subtraction analysis (curves marked 'diff.') in the carbonyl region for (a) blend B46 and (b) blend B55

varied. Moreover, the value of this parameter in the blends coincides with that in pure PC (see *Figure 7*), indicating that the absorptivity coefficients of free and of interacting C=O groups are approximately equal. On this basis the fractions $[CO]_i/[CO]_{tot}$ for the various blend compositions have been calculated and are reported in the last column of *Table 2*. A plot of the percentage of hydrogen bonded carbonyls as a function of the [NH]/[CO] ratio (*Figure 8*) displays an initial linear trend in the range of ratios 0–0.7 and levels off at values close to 50% hydrogen bonding. Similar behaviour has been observed in the PBI/Ultem 1000 system[4] and in the polycaprolactone/phenoxy system[17]; steric considerations were invoked in both cases to explain the effect. In the present case the possibility must be considered that because of the rather high T_g of the resulting material[18], the number of interactions formed is controlled by the ambient casting conditions (i.e. kinetics) rather than by the thermodynamics of the system. Further investigations by systematically varying the thermal treatment to which the blends are subjected will be needed to clarify this important point. In addition it is possible that trace amounts of residual solvent still present in the material after the drying protocol could interfere with the formation of the N–H···O=C interactions by limiting their number. This effect would increase with increasing PBI content in the blend since, because of a strong interaction between the solvent, DMAc, and PBI it is more difficult

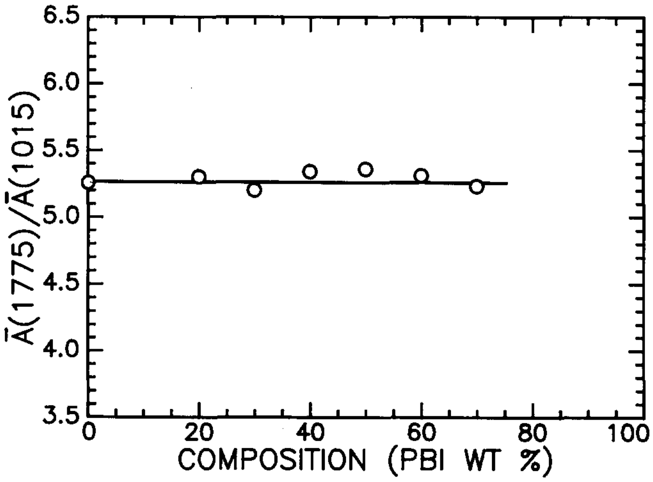

Figure 7 Normalized $\nu_{C=O}$ absorbance as a function of blend composition

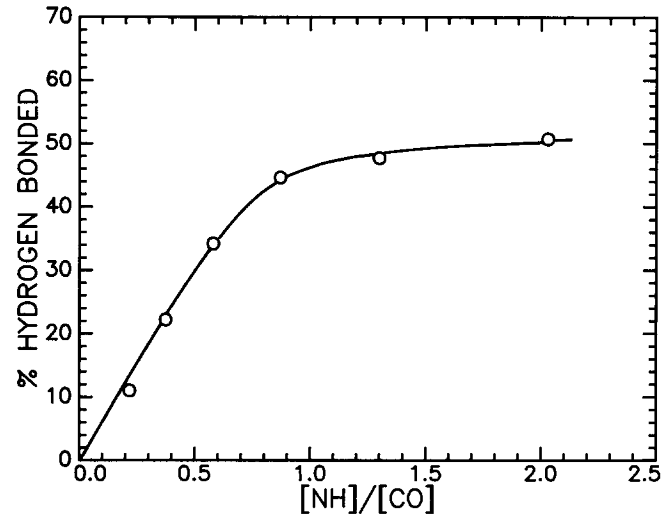

Figure 8 Percentage of hydrogen bonded carbonyl groups as a function of the [N-H]/[C=O] molar ratio

to dry the PBI completely than it is to remove the solvent from the PC.

With respect to the miscibility of the system, the *FT*i.r. results consistently indicate a high degree of mixing at the molecular level between the two components. The spectral perturbations observed in the infrared spectra and the number of interactions calculated therefrom cannot be ascribed to interactions occurring at the interfacial region between the domains of the components in a fully phase separated system. This region would represent only a very small amount of the total mass of the material and any spectral feature associated with such a region is unlikely to be detected by transmission *FT*i.r.[11]. However, considering that, for example, in the blend B28 only a small fraction (11%) of the total carbonyl groups is actually involved in interactions with N-H groups, the possibility of a two-phase system consisting of a pure PC phase and of a PBI/PC mixed phase cannot be ruled out; indeed *FT*i.r. spectroscopy cannot distinguish between such a situation and one in which only a single homogeneous phase is present. As already mentioned, the calorimetric and dynamic mechanical measurements which were performed to clarify this point were complex but were not in conflict with this conclusion[8].

Temperature behaviour of the 50/50 wt% blend

*FT*i.r. spectroscopy has proven to be an effective tool for studying the behaviour with respect to temperature in miscible blends[4,11]. In particular, by monitoring the frequency and the WHH of the asymmetric stretching vibration of the imide carbonyls as a function of temperature, information has been recently derived on the phase separation process occurring in the PBI/Ultem 1000 blend system[4]. For the PBI/PC blends, because of the better resolution of the carbonyl region, the situation appeared even more promising and an investigation of the temperature behaviour of a particular blend composition (50/50 wt%) was undertaken. It is well known that PC displays good thermal stability[18]; in fact, the integrated absorbance of the $\nu_{C=O}$ peak at 1775 cm^{-1}, $\bar{A}_{C=O}$, remains almost constant up to 350°C (only a slight linear increase is actually observed, due to a gradual broadening of the peak with temperature). At 375°C a sudden drop in $\bar{A}_{C=O}$, is observed due to the initiation of thermal degradation processes in the material under nitrogen in this temperature range (see *Figure 9a*). This result is essentially in agreement with thermogravimetric data (TGA), showing a complete weight loss process starting at temperatures slightly above 400°C. Minor differences between the onset temperatures of degradation as detected by *FT*i.r. and by TGA can be ascribed to the different heating rates used in the two experiments as well as to differences in the sample thickness. The integrated absorbance of the carbonyl region as a function of temperature for the B55 blend is reported in *Figure 9b*. The decrease in $\bar{A}_{C=O}$ starts at a lower temperature than for pure PC, thus indicating a decrease in the thermal stability of PC in the presence of PBI. Further experimental results concerning this effect will be presented below. It is also observed that the decrease of $\bar{A}_{C=O}$ with temperature is more gradual in the blend and, although the degradation processes have already begun, most of the PC is still unreacted at 300°C. Thus a detailed analysis of the spectroscopic behaviour of the blend in the 25–300°C temperature range is still feasible. In *Figure 10* the 1850–1680 cm^{-1} spectral region of the B55 sample at various temperatures is reported. In this figure the main peak around 1775 cm^{-1} has been normalized to full scale for all the spectra to illustrate the differences.

While at temperatures below 200°C the doublet shows

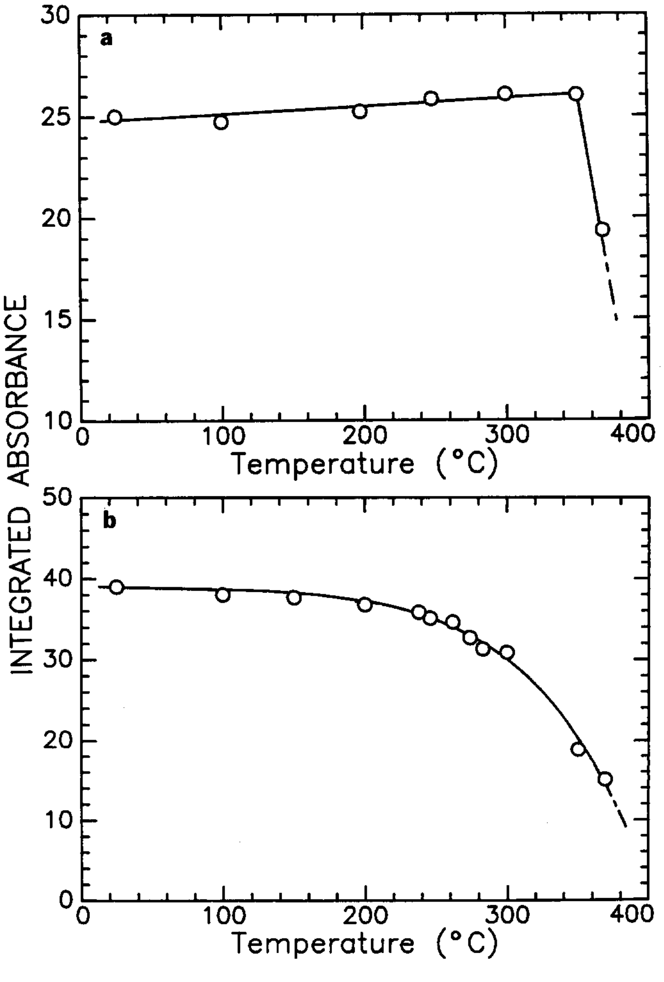

Figure 9 Integrated $\nu_{C=O}$ absorbance as a function of temperature for (a) pure PC and (b) blend B55

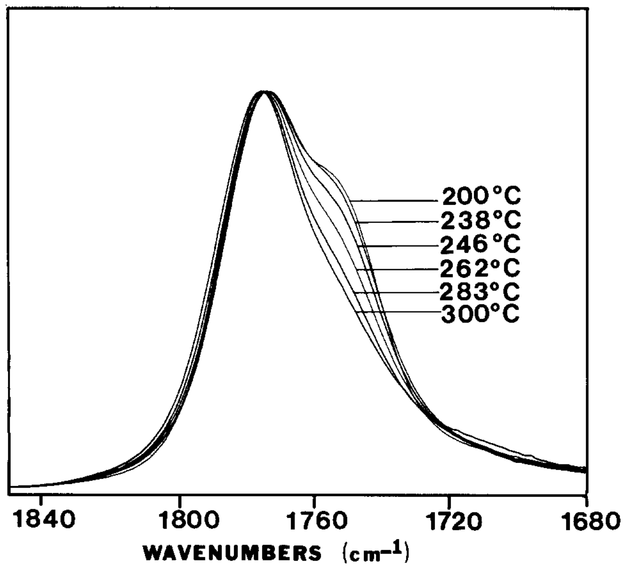

Figure 10 The carbonyl stretching region of blend B55 in the 200–300°C temperature range

no appreciable variation (these traces are not shown in *Figure 10*), starting from 238°C the low frequency component gradually and monotonically decreases in intensity with increasing temperature. This indicates a decrease in concentration of the species (hydrogen bonded carbonyls) responsible for this absorption. In principle it should be possible to obtain a quantitative estimation of the fraction $[CO]_i/[CO]_{tot}$ as a function of temperature by deconvoluting the two-component profile. However, the application of deconvolution methods to spectra collected at high temperatures is more difficult than for spectra at 25°C. For instance, the subtraction method successfully applied at room temperature does not provide reliable results above 200°C, where derivative-type features start to appear in the subtraction spectrum. This occurs because of the gradual broadening of the $\nu_{C=O}$ peak of PC at temperatures above T_g, which makes it impossible to choose a reliable reference to subtract from the blend spectra. Moreover, the resolution of the carbonyl region rapidly deteriorates with increasing temperature (see *Figure 10*), possibly because of a gradual weakening of the hydrogen bonding interaction with temperature, which causes a shift of the 1751 cm^{-1} component toward higher frequencies. To circumvent these difficulties an alternative approach was adopted; the apparent spectral resolution was first enhanced by using the Fourier self-deconvolution method (FSD) and the profiles were then fully deconvoluted by using a curve fitting procedure (see *Figure 11*).

The FSD method consists of separating an assumed lineshape function (Lorentzian) from the experimental spectrum; the process reduces the bandwidth of the absorption, thereby improving the 'apparent' resolution. One important feature which distinguishes FSD from derivative methods is that the integrated band areas are not altered by the process. Therefore, more information on the relative intensity of overlapping components is obtained at the expense of lineshape information. The FSD method is described in detail in References 19–22, while the curve fitting procedure is described in Reference 23 and in Reference 4 as applied to PBI-based blends.

Whenever possible (i.e. for the spectra collected at temperatures below 200°C), both the spectral subtraction method and the FSD method followed by curve fitting were used to evaluate quantitatively the areas of the two carbonyl components; in all cases the difference between the two estimates did not exceed 5%.

In *Figure 12* the percentage of the total integrated absorbance in the carbonyl region due to the 1751 cm^{-1} component is reported as a function of temperature. Assuming that the absorptivity ratio, $\varepsilon_{1751}/\varepsilon_{1775}$, does not change substantially with temperature, this parameter corresponds to the percentage of hydrogen bonded carbonyls in the B55 blend. It is found that the concentration of this species, constant up to 240°C, drops sharply above this temperature. This behaviour has already been observed in other hydrogen bonded polymer systems and has been interpreted in terms of their molecular mobility[4,24]. In fact, when the measuring temperature lies below the T_g of the material, the hydrogen bonding interactions are stable due to the rigidity of the polymer structure. However, as soon as the glass transition temperature is attained, the enhanced molecular mobility allows the interactions to be easily disrupted. In particular, for a miscible blend in which most of the hydrogen bonds have been dissociated no enthalpic contribution to the free energy of mixing is available and phase separation occurs.

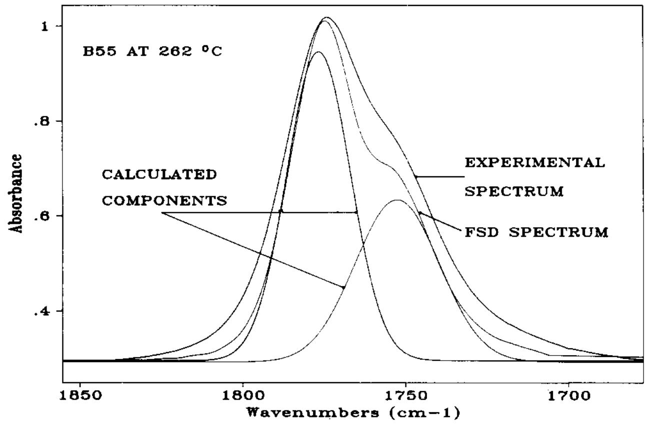

Figure 11 Experimental spectrum, FSD spectrum and the components calculated by curve fitting for blend B55 at 262°C, in the 1800–1660 cm^{-1} region. The experimental and the FSD spectra have been expanded to full scale to facilitate the comparison; see text

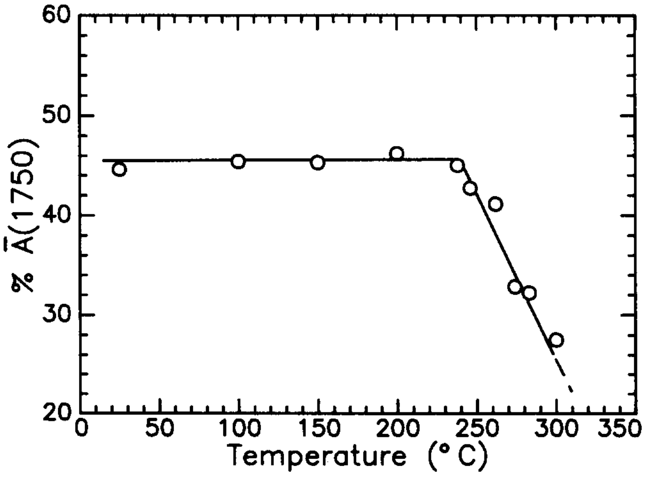

Figure 12 Percentage of the total carbonyl absorbance due to the component at 1751 cm^{-1} as a function of temperature for blend B55

Thus the drop in concentration of associated carbonyl groups with increasing temperature can be correlated both with the T_g of the B55 blend and to a phase separation process. The occurrence of a lower critical solution temperature has been observed independently by d.s.c. measurements[18]. Unfortunately, because of the reduced thermal stability of PC in the blend, extensive degradation occurs before phase separation is complete, making it difficult to study this phenomenon in detail by *FT*i.r. or possibly by any other technique. However, the plot in *Figure 12* clearly indicates that the T_g of the blend should occur at 240 ± 5°C; a value of 220°C is calculated for this composition using the Fox relation. The T_g obtained experimentally is thus higher than expected, but in many cases a positive deviation of the T_g *versus* temperature curve with respect to the theoretically calculated T_g has been observed in blend systems in which strong interactions among the components occur. Thus the result appears to be consistent with the picture of a miscible blend at this composition.

It seems worthwhile to stress, at this point, the potential of the *FT*i.r. temperature analysis in detecting phenomena such as the glass transition. For this particular system, in fact, since the thermal degradation of PC generates a strong exothermic peak, no definitive results were obtained by d.s.c.; the dynamic mechanical measurements were also difficult to interpret. Thus, although *FT*i.r. spectroscopy detects only an indirect effect of the onset of large scale molecular mobility, i.e. the dissociation of hydrogen bonding interactions, it was the only technique which afforded an unambiguous estimation of the T_g in this blend system.

*FT*i.r. spectroscopy was also used to obtain additional details about the thermal degradation of PC in the presence of PBI. To confirm the observation previously made, and to make a more quantitative comparison between the behaviour of pure PC and of PC in the presence of PBI, isothermal kinetic measurements were made. Isothermal measurements of the peak intensities remove any effect of temperature on both the frequency and intensity of the two carbonyl components. The measurement was performed at 250°C directly in the *FT*i.r. spectrometer over a 1200 min time interval; a spectrum was collected every 30 min. In *Figure 13* the 1850–1700 cm^{-1} spectral region at different reaction times is reported for the 50/50 wt% PBI/PC blend (*Figure 13a*) and for pure PC (*Figure 13b*). From the spectral data shown in *Figure 13* it is readily possible to calculate the conversion, $\alpha(t)$, of the carbonyl groups:

$$\alpha(t)=\frac{[\mathrm{CO}]_0-[\mathrm{CO}]_t}{[\mathrm{CO}]_0}$$

$$\alpha(t)=1-\frac{[\mathrm{CO}]_t}{[\mathrm{CO}]_0}$$

and, for the Beer–Lambert law:

$$A=\varepsilon l[\mathrm{CO}]$$

$$\alpha(t)=1-\frac{A_t}{A_0}$$

where the subscripts 0 and t refer to times 0 and t respectively. For the blend, [CO] represents the total concentration of carbonyl groups (i.e. free plus hydrogen bonded). The results of such an analysis are shown in *Figure 14*.

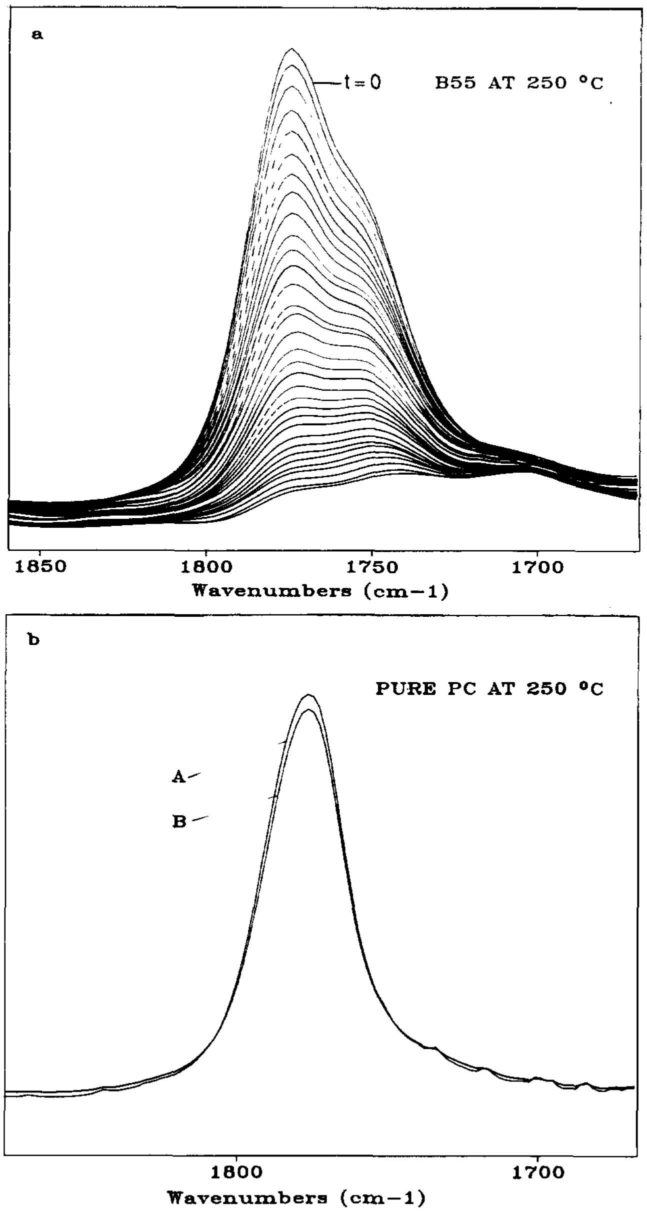

Figure 13 Isothermal kinetic measurements at 250°C for (a) blend B55 and (b) pure PC. In (a) the various traces correspond to spectra collected at intervals of 30 min from each other. In (b) traces A and B correspond to spectra collected at times 0 and 1023 minutes, respectively

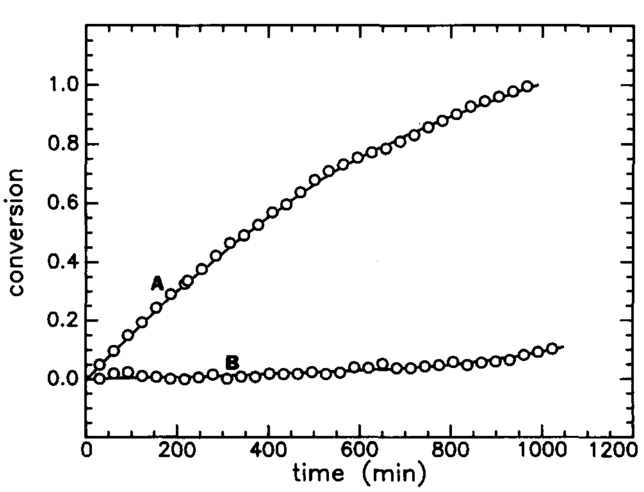

Figure 14 Conversion of the carbonyl groups as a function of time for the isothermal measurement at 250°C: curve A, blend B55; curve B, pure PC

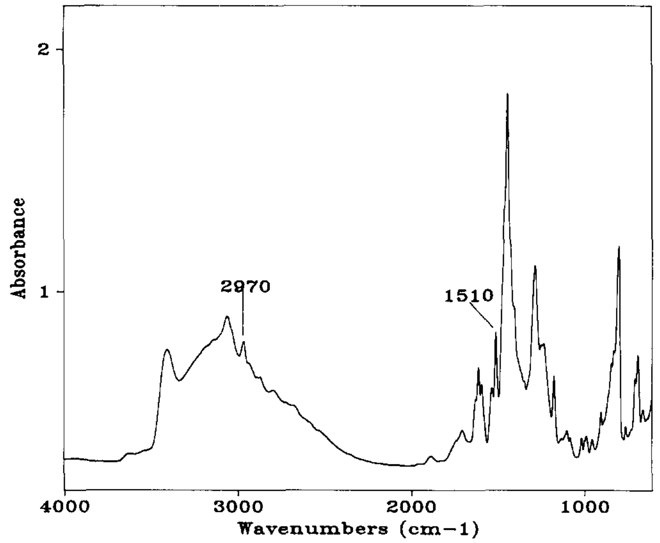

Figure 15 The *FTi.r.* spectrum of blend B55 after 1000 min of the isothermal kinetic measurement at 250°C. Spectrum collected at room temperature

It is immediately apparent that, under the experimental conditions used, pure PC shows no appreciable modification ($\alpha(t)$ is practically zero over the whole time interval), while the presence of PBI has a profound effect on the PC stability; a gradual and continuous decrease of the content of carbonyl groups is observed in the blend and the process appears to be complete after ≈ 1000 min. Also, the ν_{O-C-O} multiplet in the $1300-1100\,cm^{-1}$ region decreases analogously, indicating that PC degradation in the presence of PBI occurs mainly by dissociation of the carbonate groups.

Also of interest is the final spectrum obtained at room temperature of the B55 blend after the thermal treatment described above (*Figure 15*). It corresponds to the spectrum of pure PBI with additional, well defined peaks at 2970 and at $1510\,cm^{-1}$; broad residual features are also observed in the carbonyl and in the ν_{O-C-O} regions. The peaks at 2970 and $1510\,cm^{-1}$ could be attributed to bisphenol A monomer which, because of its low volatility at 250°C, remains partially trapped in the polymer matrix. The spectrum in *Figure 15* clearly indicates that PBI does not directly participate in the low temperature degradation processes occurring in the blend, but strongly catalyses the thermal decomposition of PC.

In the light of the findings described above it is reasonable to assume that a catalysed hydrolysis of the carbonate groups is the mechanism responsible for the decomposition of PC in the presence of PBI; further spectroscopic investigations are needed to substantiate this hypothesis.

Finally, note that, after the isothermal treatment at 250°C, a clear, homogeneous film is recovered which is not visually distinguishable from the starting material. An analysis of the morphology is currently in progress to determine structures developed in the blend as a consequence of the complete decomposition of the PC component.

CONCLUSIONS

In infrared spectroscopic studies of the N–H and the C=O stretching regions of PBI/PC blends it has been possible to establish that hydrogen bonding interactions among the N–H groups of PBI and the carbonyl groups of PC occur in the system. Qualitative information about the strength of such interactions and a quantitative estimation of the population of carbonyl groups involved in the interaction for the various investigated compositions have been derived by means of spectral subtraction analysis. The results have been compared with those obtained for the PBI/Ultem 1000 system. Extensive mixing at the molecular level has been observed for all the investigated compositions. The temperature behaviour of a 50/50 wt% composition has also been investigated by means of *FTi.r.* spectroscopy. A quantitative analysis of the carbonyl region of this blend as a function of temperature allowed an estimation of its glass transition temperature, which was found to be close to the value predicted by the Fox equation for a miscible blend.

Finally, direct spectroscopic evidence of a strong catalytic effect of PBI on the thermal decomposition of PC has been reported and discussed.

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