Fourier transform infra-red spectroscopy on the thermo-oxidative degradation of polybenzimidazole and of a polybenzimidazole/polyetherimide blend

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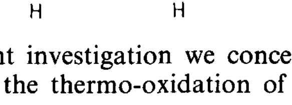
The thermo-oxidative degradation of the polybenzimidazole material, poly[(2,2′-*m*-phenylene)-5,5′-bibenzimidazole] (PBI), and of a blend of PBI with the polyetherimide, poly[2,2′-bis(3,4-dicarboxyphenoxy) phenylpropane-2-phenylene bisimide] (Ultem 1000), was investigated by Fourier transform infra-red (*FT*i.r.) spectroscopy. An experimental protocol and the necessary instrumentation were developed for real-time monitoring of the molecular changes occurring during the process. The spectroscopic data provided information about the mechanism and the kinetics of the thermo-oxidative degradation in its early stages. The *FT*i.r. spectra of the PBI/Ultem 1000 blend were analysed by subtraction spectroscopy, and the application of this technique allowed us to selectively follow the fate of the two components in the blend. No chemical interaction between PBI and Ultem 1000 was detectable by *FT*i.r. spectroscopy during the degradation process.

(Keywords: Fourier transform infra-red spectroscopy; polymer blends; polybenzimidazole; Ultem 1000; thermo-oxidative degradation)

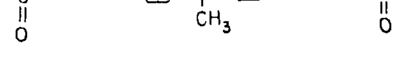
INTRODUCTION

Poly[(2,2′-*m*-phenylene)-5,5′-bibenzimidazole] (PBI) is a high-performance polymer that has received considerable attention in recent years because of its outstanding ability to withstand extreme conditions without an extensive loss of properties. It has, for example, been widely used in the aerospace industry, where thermal stability is a primary requirement. However, whereas in inert atmospheres the total weight loss of PBI is negligible up to 600°C, a much more pronounced effect has been observed for the same temperature range in oxidizing environments. In air, the thermo-oxidative stability of PBI is comparable to that of the copolymer poly(tetrafluoroethylene-*co*-hexafluoropropylene) with the rate of decomposition[1] given by $K = 10^9 \exp(-36\,000)(RT)^{-1}$. It is important to understand the mechanism governing this thermo-oxidative phenomenon in order to develop suitable methods for stabilizing PBI against the action of oxidizing agents.



In the present investigation we concentrated on the early stages of the thermo-oxidation of PBI, in which only a very limited weight loss is observed but, as will be shown in the discussion, readily detectable changes in the molecular structure take place. Few published reports have concerned the decomposition of PBI in oxidizing environments, and most of these are based on weight-loss measurements. This deficiency is partly due to the experimental difficulties encountered in the acquisition of meaningful spectroscopic data at elevated temperatures over extended periods of time (350°C, 35 h). We have found Fourier transform infra-red (*FT*i.r.) spectroscopy to be a very suitable spectroscopic technique for investigating such a system, because of the method's sensitivity, optical stability, and photometric accuracy.

Within the last decade, a novel class of quasi-miscible polymer blends based on PBI and aromatic polyimides has been discovered[2]. In particular, the blend formed by PBI and a commercial polyetherimide (Ultem 1000) has shown most promising characteristics for large-scale applications. The thermo-oxidative behaviour of a representative composition of such a blend system has also been investigated by using the same experimental approach. Information about the mechanism governing this degradative phenomenon has been derived and compared with that obtained for the pure components.



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EXPERIMENTAL

Materials

PBI was supplied by the Celanese Corporation in the form of an additive-free, finely ground powder. Ultem 1000 was a commercial-grade product of the General Electric Company, with $M_w = 30\,000 \pm 10\,000$ and $M_n = 12\,000 \pm 4000$. The two polymers were used as received. The glass transition temperatures (T_gs) of PBI and Ultem 1000 are 420 and 220°C, respectively.

Sample preparation

Thin polymeric films (5–20 μm in thickness) were prepared by casting from 1.0 wt/vol% solutions of PBI in dimethylacetamide (composition of 85/15 wt% PBI/Ultem 1000 in the case of the blend) on glass plates in a N_2 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 at 200°C, under vacuum, for at least a further 3 days.

Techniques

*FT*i.r. spectra were obtained at 4 cm^{-1} resolution with a Mattson Cygnus 100 *FT*i.r. spectrometer which was equipped with a deuterated triglycine sulfate detector (DTGS) and a germanium/KBr beam splitter. The scanned wavenumber range was 4000 to 400 cm^{-1}, and 30 spectra were signal averaged in the conventional manner to reduce the noise. The interferogram data were Fourier transformed by using a triangular apodization function. The frequency scale was internally calibrated by using a reference He–Ne laser to an accuracy of 0.02 cm^{-1}. All films used in this study were sufficiently thin to absorb in a range where the Beer–Lambert law is obeyed. To perform the high-temperature kinetic measurements, a special environmental chamber was developed. This was based on the Spectra-Tech HT 32 high-temperature cell, appropriately modified to accommodate gas inlet and outlet ports for the provision of a required atmosphere in the chamber. A third port was added to accommodate a chromel–alumel thermocouple, which was in direct contact with the polymeric film, and was used for the continuous monitoring of the sample temperature during the experiment. The environmental chamber was fitted with two NaCl windows; the unit was controlled by an Omega CN 2010 programmable heat controller to an accuracy of ±1°C. To define unambiguously the zero of the time scale, the environmental chamber was purged with an inert gas (N_2) during the warm-up period, which usually took 20–30 min. After stabilization of the temperature at 350°C, the purging gas was replaced by dry air (at a reference time = 0) and data collection was started.

RESULTS AND DISCUSSION

Band assignments of PBI

The transmission spectrum of PBI at room temperature is shown in *Figure 1a*, with the observed absorptions and the tentative band assignments given in *Table 1*. Normal coordinate analyses of imidazole and benzimidazole by Cordes and Walter[3] and band assignments from Bellamy[4] were used for the interpretation of the spectrum.

In a previous contribution in which the molecular interactions occurring in PBI/Ultem 1000 blends were investigated[5], the PBI spectral region between 3500 and 2500 cm^{-1} was analysed in detail. In particular, the relatively sharp peak centred at 3415 cm^{-1} was attributed to the stretching vibration of isolated, non-hydrogen-bonded N–H groups, and the very broad, asymmetric absorption, approximately centred at 3145 cm^{-1}, was assigned to self-associated, hydrogen-bonded N–H groups. A third low-intensity peak at 3063 cm^{-1} was attributed to the stretching modes of the aromatic C–H groups. The region near 1650–1500 cm^{-1} is very characteristic of benzimidazoles[3]. The C=C/C=N stretching vibrations (1612 cm^{-1}) are observed in this region, as well as ring modes which are characteristic of the conjugation between the benzene and the imidazole rings (1590 cm^{-1}). Strong absorptions due to in-plane ring modes are found at 1458 and 1438 cm^{-1}, whereas an imidazole ring-breathing mode gives rise to a rather broad peak at 1280 cm^{-1}. The in-plane C–H deformations that are characteristic of substituted benzimidazoles are found in the region 1230–1090 cm^{-1}, and two typical benzene ring modes are found at 1011 and 980 cm^{-1}. Finally, in the range 900–800 cm^{-1} we can observe the out-of-plane deformations of the substituted benzene rings, whose behaviour resembles that observed in low-molecular-weight benzene-like compounds.

The transmission spectrum of PBI measured at 350°C is shown in *Figure 1b*. The most noticeable difference between the spectrum collected at 350°C and that collected at room temperature is observed in the N–H-stretching region: at 350°C, the broad absorption at 3145 cm^{-1} is greatly decreased in intensity, thereby leading to better resolution of the two peaks at 3415 cm^{-1} and 3063 cm^{-1}. This effect is attributed to a decrease with temperature of the average value of the molar absorption coefficient ε_{3145} of this complex band, rather than to a decrease in concentration of the species responsible for the absorption (i.e. self-associated N–H

Table 1 Tentative band assignments of PBI

Wavenumber[a] (cm^{-1})	Tentative assignment
3415 (s)	'Free' non-hydrogen-bonded N–H stretching
3145 (b)	Self-associated N–H stretching
3063 (w)	Aromatic C–H stretching
1612 (m)	C=C/C=N stretching
1590 (m)	Ring vibration characteristics of conjugation between benzene and imidazole rings
1534 (m)	In-plane ring vibration characteristic of 2-substituted benzimidazole
1443 (vs)	In-plane ring vibration characteristic of 2,6-disubstituted benzimidazole
1410 (m, sh)	C–C stretching
1286 (m)	Imidazole ring breathing
1226 (w)	In-plane C–H deformation of 2,6-disubstituted benzimidazole
1011 (w)	Benzene-ring vibration
980 (w)	Benzene-ring vibration
902 (w)	C–H out-of-plane bending of a single hydrogen in substituted benzene rings
846 (m)	C–H out-of-plane bending of two adjacent hydrogens in substituted benzene rings
801 (s)	Heterocyclic-ring vibration or C–H out-of-plane bending of three adjacent hydrogens in substituted benzene rings
705 (m, sh)	Heterocyclic-ring vibration
692 (m)	C–H out-of-plane bending of 3,4-disubstituted biphenyl

[a] Peak positions refer to spectra collected at ambient temperatures: s, strong; m, medium; w, weak; sh, shoulder; vs, very strong

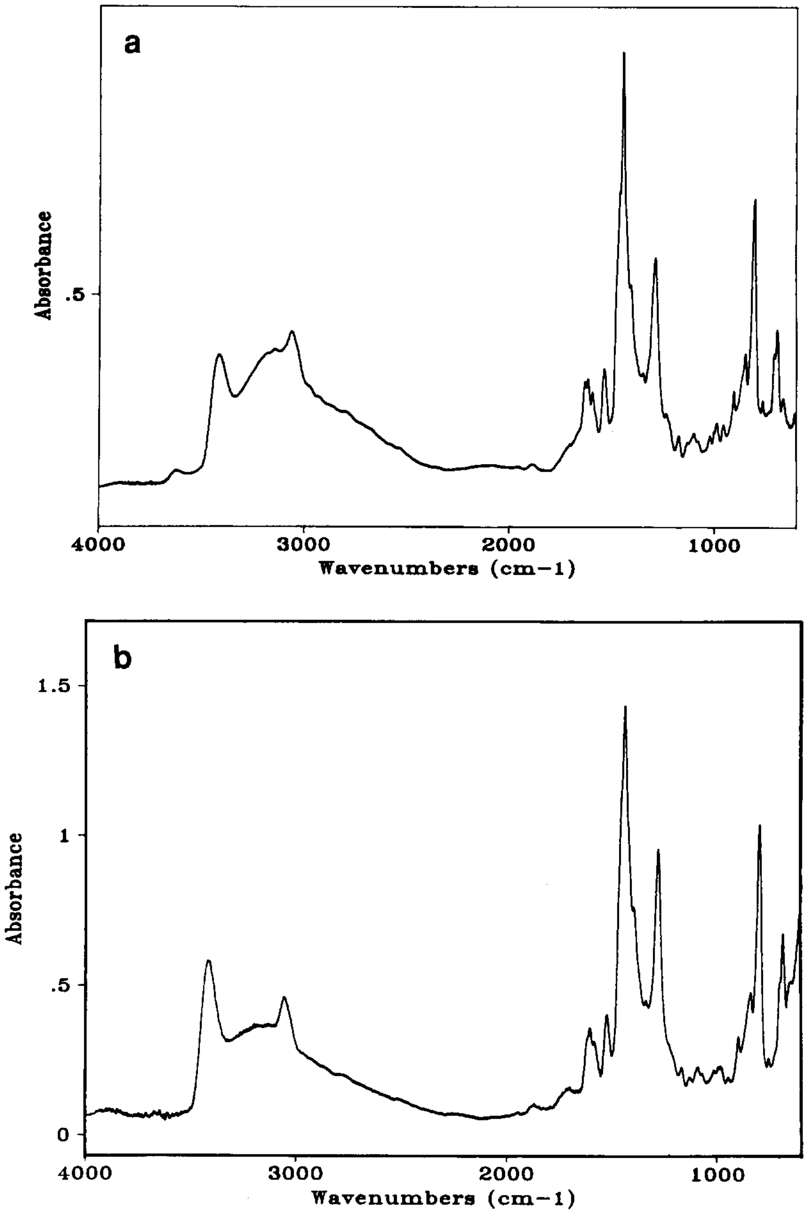

Figure 1 *FT*i.r. transmission spectra of PBI measured at: (a) 25°C; (b) 350°C

groups). Due to the fact that at 350°C PBI is still well below its glass transition temperature of 420°C, for kinetic reasons the concentration of self-associated N–H groups would not be expected to change significantly[6]. In the region from 2000 to 600 cm^{-1}, only a slight shift toward lower wavenumbers and a broadening of some of the peaks are observed, so the tentative assignments proposed for the room-temperature spectrum can be directly extended to the one collected at 350°C.

Thermo-oxidative degradation of PBI

A thin film of PBI ($\sim$20 μm in thickness) was subjected to thermal-degradation experiments in a high-temperature environmental chamber which was purged continuously with dry air at 350°C. The chamber was directly mounted in the *FT*i.r. spectrometer, and infra-red spectra were obtained at 30-min intervals for the real-time monitoring of structural changes during the experiment. Typically, these kinetic measurements lasted 35 h. At the end of the experiment, the PBI film appeared clear and homogeneous, although the colour had changed from pale yellow to amber. A very limited weight loss was also detected (from 3 to 5%).

Figure 2 shows the PBI spectra at 350°C, at the beginning of, and at several periods throughout the experiment. Several features are immediately apparent: the peaks at 3415, 3145, 1438, 1280, and 801 cm^{-1} considerably decrease in intensity; moreover, the peaks in the spectral region from 1500 to 1200 cm^{-1} become broader and less well resolved, suggesting the appearance of new absorptions that are not detectable because of their coincidence with the strong PBI peaks appearing in this frequency range. However, as shown in the inset, two new absorptions can be definitely identified: one of these occurs at 2222 cm^{-1} as a sharp, well-resolved peak and is attributed to the stretching vibration of aromatic nitrile groups[4]. The other is a broader band, approximately centred at 1715 cm^{-1}, and is indicative of the formation of carbonyl groups. A closer examination of this spectral region reveals the presence of more than one component. In particular, *Figure 3* shows the results of the deconvolution of this region for the spectrum

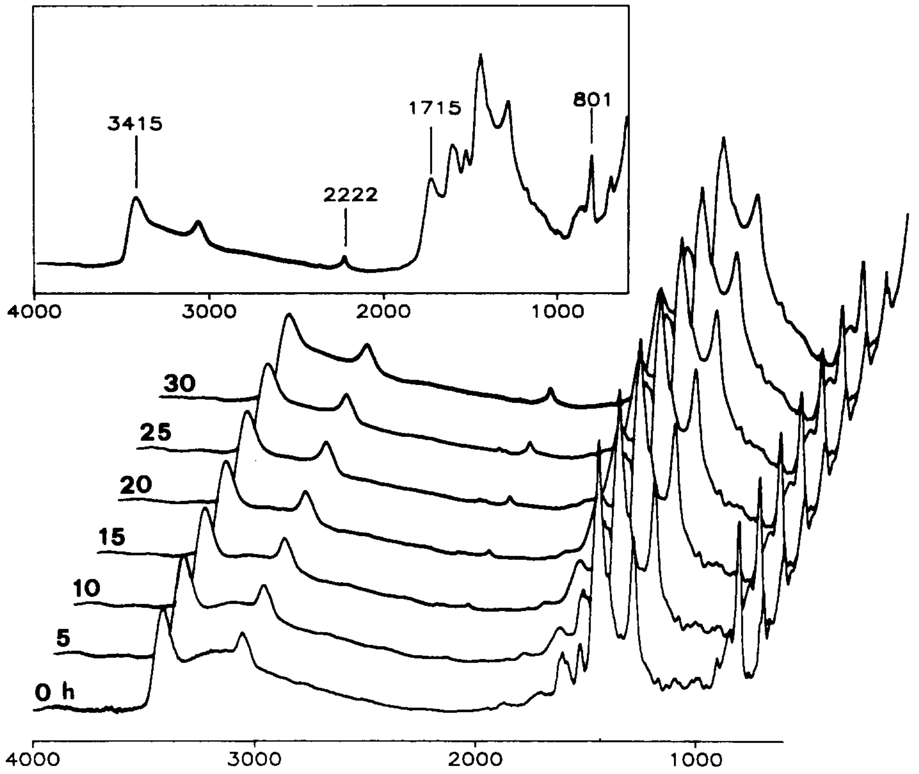

Figure 2 *FT*i.r. spectra of PBI measured at 350°C during the thermo-oxidative experiment, with degradation times as indicated. The inset refers to the final spectrum after 35 h

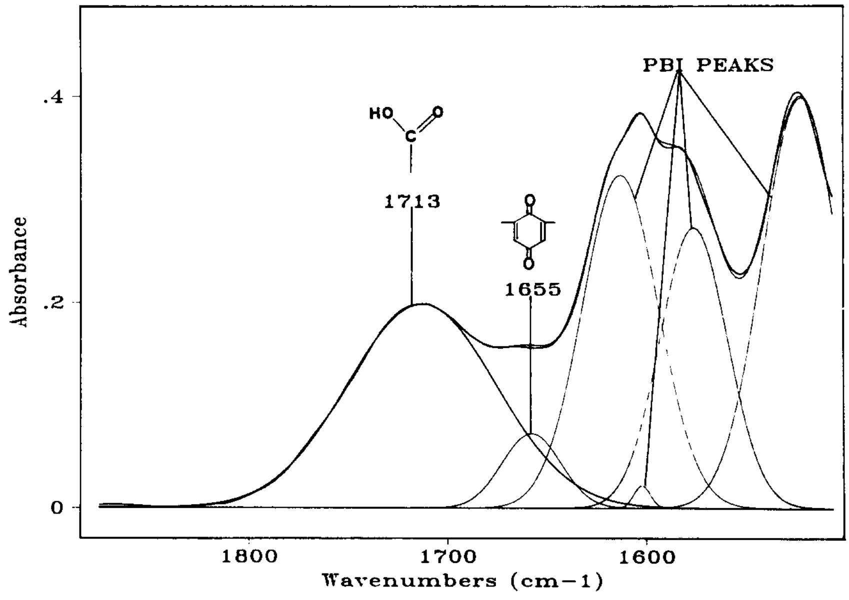

Figure 3 Curve-fitting analysis, over the range 1800 to 1500 cm^{-1}, of the *FT*i.r. spectrum of PBI obtained at 350°C after 600 min

collected at 350°C after a period of 600 min. The multicomponent spectral profile was resolved by applying the curve-fitting procedure described by Maddams[7]. To improve the uniqueness of the fit, the base line, the lineshape function (Gaussian), and the number of peaks (as determined by second-derivative analysis) were fixed during the best-fit calculations by using the peak positions and the widths of the components.

In *Figure 3* the four components at 1624, 1607, 1572, and 1522 cm^{-1} constitute the original bands of PBI, whereas the two components at 1713 and 1655 cm^{-1} are due to the oxidative degradation of the polymer. We noted that the complex carbonyl region can be satisfactorily resolved with a minimum of two Gaussian components. The band at 1655 cm^{-1} has been assigned to conjugated ketonic structures and, more specifically, to a quinone structure of type **1**. The assignment of the

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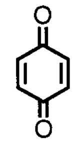


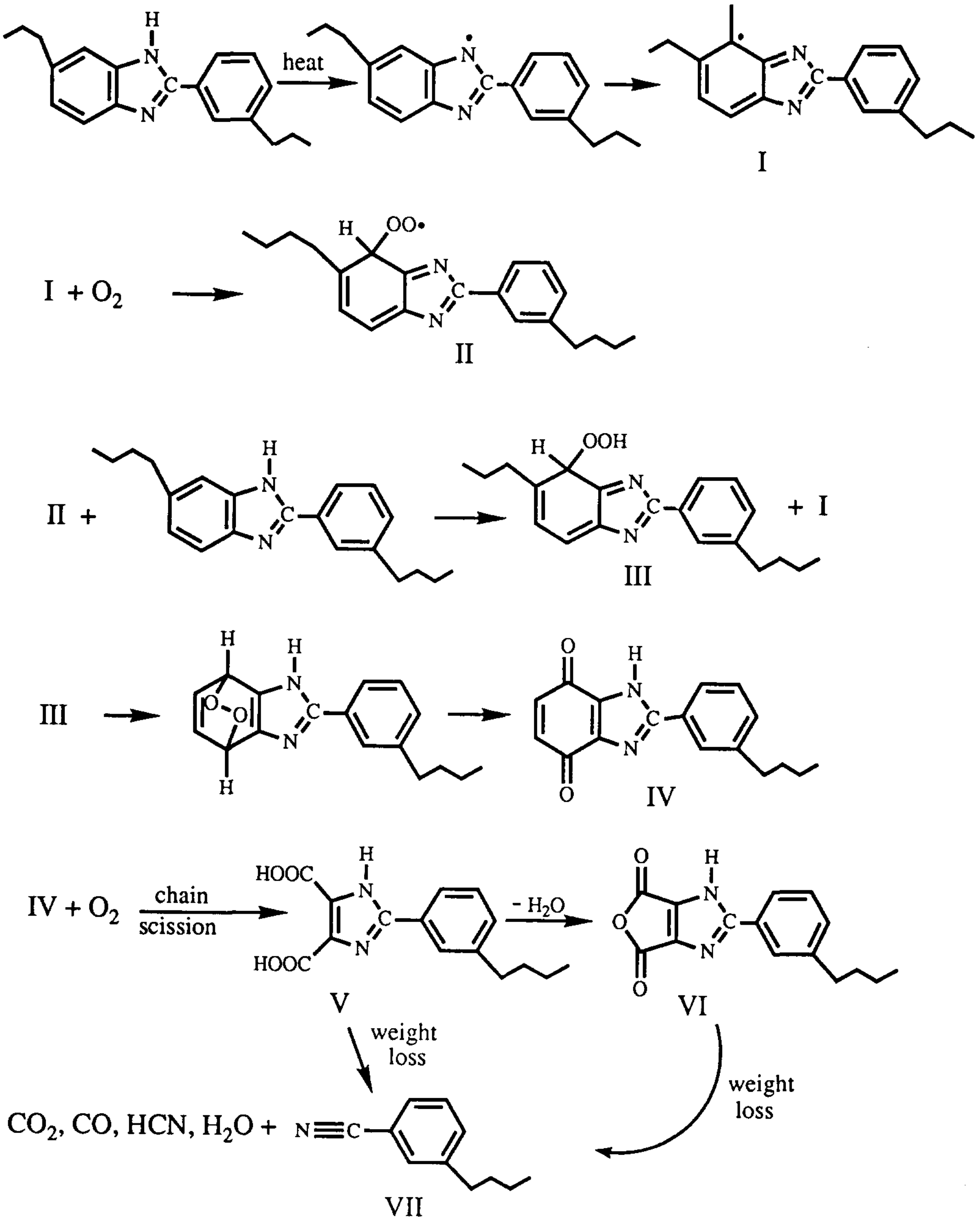
1713 cm^{-1} component is less straightforward: the peak position would be characteristic of saturated aliphatic ketones, but, considering the molecular structure of PBI, it seems very unlikely that such a product could result from an oxidative attack on the polymeric substrate.

Nevertheless, the full width (at half height) of this component (87 cm^{-1}) is considerably larger than that observed for typical isolated C=O stretching vibrations (25–30 cm^{-1}), where association effects do not occur. Thus we propose that, although the band at 1713 cm^{-1} can be satisfactorily fitted with a single Gaussian, it is in fact a more complex profile. A dicarboxylic acid structure would account for the observed peak position; moreover, a strong hydrogen-bonding interaction would cause considerable band broadening on the lower-frequency side of the peak. Although neither curve-fitting analysis nor second- or higher-derivative spectroscopy yielded any additional evidence, it is possible that a further carboxylic component is present on the higher-frequency side of the 1713 cm^{-1} band. This component could be due to the presence of anhydride groups.

A reaction scheme for the early stages of the PBI thermo-oxidative degradation must account for the following experimental observations.

- The concentration of N–H groups gradually, and continuously, decreases during the process.
- The oxidative attack results in the cleavage of imidazole rings and eventually leads to the formation of aromatic nitrile groups.
- Several carboxylic and carbonyl groups are formed, among which quinone and dicarboxylic acid structures have been tentatively identified.

A mechanism, first proposed by Conley *et al.* for the oxidation of low-molecular-weight model compounds related to PBI[8], can reasonably account for the experimental observations just discussed (see *Scheme 1*).



Scheme 1

We postulate that the thermo-oxidative degradation of PBI proceeds through a radical mechanism, initiated by hydrogen abstraction from the imididazolic N–H groups. The radical species thus formed evolve further, giving rise to the quinone, dicarboxylic acid, and benzonitrile structures (identified by *FT*i.r. analysis), and to chain-scission reactions.

We have already noted that a number of the PBI peaks show a steady decrease in intensity as a function of degradation time, and therefore the spectral data allow us to follow, quantitatively, the kinetics of the degradation process. For such treatment of the data, we have focused on the peaks at 3415 and 801 cm^{-1} because of their less severe overlapping with neighbouring bands and because of the possibility of identifying a reasonable base line. *Figure 4* shows the absorbance at these peaks as a function of reaction time; because the film thickness remains essentially unchanged throughout the experiment, these absorbance values can be considered proportional to the concentration of the species responsible for the relative absorptions. The absorbance data of *Figure 4* allow us to calculate the conversion, $\alpha(t)$, of the relative groups as a function of time in the usual way.

The concentration of free N–H groups decreases linearly over the whole time interval that was investigated (see *Figure 5*), whereas the concentration of the groups responsible for the absorption at 801 cm^{-1} decreases at a faster rate, and also to a larger extent. Specifically, the initial rate of conversion of the latter groups (3.40×10^{-4} min^{-1}) is about twice that of the former (1.83×10^{-4} min^{-1}). This behaviour can be interpreted in two ways: assuming that the assignment proposed for the 801 cm^{-1} peak (C–H bending in the *m*-phenyl substituents) is correct, then there should be an alternative and concurrent reaction pathway that proceeds faster and to a larger extent, involving hydrogen abstraction from the *m*-substituted phenyl groups in PBI. This mechanism could be responsible for the cross-linking processes observed in the early stages of the experiments: in fact, after 30 min at 350°C in air, the solubility of PBI in dimethylacetamide drops from 100 to 3 wt/vol%.

Alternatively, we could postulate that the absorption at 801 cm^{-1} has a different origin and is mostly due to a heterocyclic-ring vibration. In this case, the observed decrease in its intensity would simply indicate the disruption of the benzimidazolic ring system following the oxygen attack on the N–H groups, as postulated by the proposed reaction mechanism. The observation that the rate, as well as the extent of conversion, calculated from the absorbance of the 801 cm^{-1} peak, are both larger than those calculated from the 3415 cm^{-1} peak, would then be easily explained by assuming that the kinetic parameters relative to the N–H groups are only partially related. In fact, as already noted, the peak at 3415 cm^{-1} is due to the stretching vibration of the 'free' N–H groups, whereas the self-associated ones give rise to the complex band centred at 3145 cm^{-1}. Because of the complex shape of the absorption in the region between 3500 and 3000 cm^{-1}, it is difficult to obtain overall conversion parameters for the N–H groups, but these parameters will be substantially larger than those calculated from the 3415-cm^{-1} component alone, because we also observe that the intensity of the 3145-cm^{-1} band gradually decreases with degradation time (see *Figure 2*). To definitely address this important point, the assignment of the peak at 801 cm^{-1} has to be certain. One possible way of accomplishing this task is to use a PBI sample which has been deuterated in the positions of interest; work is in progress to synthesize such a product.

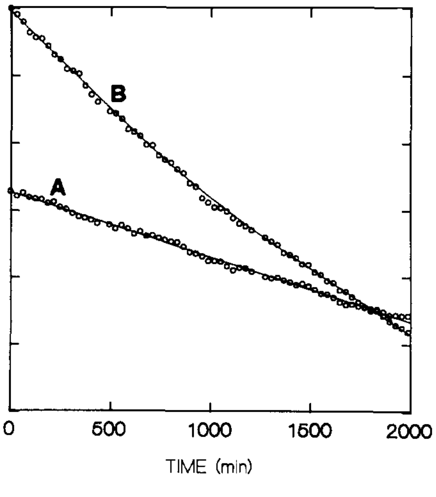


Figure 4 Variation in the absorbance of selected peaks in the *FT*i.r. spectra of PBI measured at 350°C, as a function of degradation time: (A) 3415 cm^{-1}; (B) 801 cm^{-1}

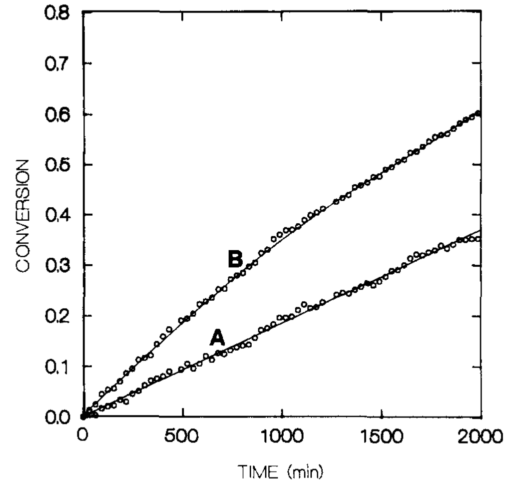


Figure 5 Conversion curves, plotted as a function of degradation time, using the absorption data of *Figure 4*, for the peaks: (A) 3415 cm^{-1}; (B) 801 cm^{-1}

Figure 6 shows the absorbances of the aromatic nitrile groups at 2222 cm^{-1} (curve A) and of the carbonyl peak centred at 1715 cm^{-1} (curve B), plotted as a function of degradation time. A finite value of absorbance is observed at zero time for the carbonyl groups (0.070 absorbance units (a.u.)). This effect is attributed to thermo-oxidative processes that occur to a very limited extent during the synthesis and prior processing of PBI. Both curves A and B display a linear increase of absorbance with degradation time; however, the slope of the curve relative to the carbonyl absorption (2.0×10^{-4} a.u. min^{-1}) is about 7 times greater than that relative to the aromatic nitrile peak at 2222 cm^{-1} (3.0×10^{-5} a.u. min^{-1}), and the final absorbance value of the carbonyl peak is 7.5 times larger than that relative to the nitrile group. If we assume that the molar absorptivities of the two groups are comparable, then the above kinetic behaviour would indicate that the carbonyl groups are formed at both a higher rate and to a greater extent, with respect to the aromatic nitriles. In other words, under our experimental

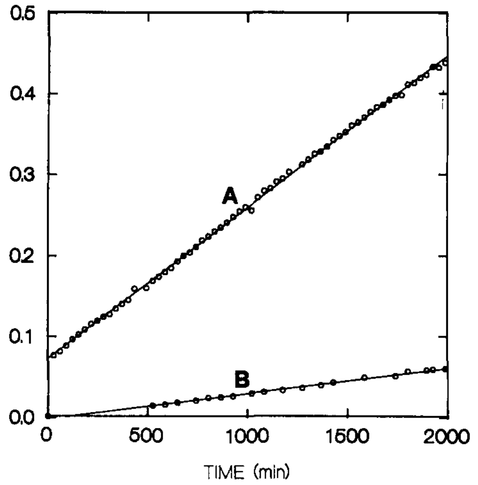


Figure 6 Variation in the absorbance of selected peaks in the *FT*i.r. spectra of PBI measured at 350°C, as a function of degradation time: (A) 1716 cm^{-1}; (B) 2222 cm^{-1}

conditions, the oxygen attack on the polymeric substrate would proceed at a relatively high rate up to the formation of unsaturated dicarboxylic acids and anhydrides; the last step, by which aromatic nitriles are formed and the low-molecular-weight compounds, H_2O, HCN, CO_2, and CO, evolve (the step mainly responsible for the weight loss of the polymeric substrate), would be much slower. This overall mechanism would account for the very limited weight loss detected at the end of the experiment.

Thermo-oxidative degradation of a PBI/Ultem 1000 blend

It has been found that PBI can form metastable, miscible blends with a number of aromatic polyimides[2,5,6]. The system that has been most investigated is the PBI/Ultem 1000 blend, which (when cast from appropriate solvent systems) forms clear films and exhibits single T_g values and single $\tan\delta$ relaxations, intermediate to those of the pure components. In addition, specific intermolecular interactions among the components are detected by both *FT*i.r. and solid-state n.m.r. spectroscopic techniques[5,6,9].

Preliminary results on the thermo-oxidative stability of this blend system obtained by thermogravimetric analysis (t.g.a.) showed that at 390°C the weight loss of an 85/15 (wt%) PBI/Ultem 1000 blend is considerably greater than that exhibited by the two pure components (see *Figure 7*). To confirm such an effect and to obtain further information about its mechanistic basis, the same experimental approach used for PBI was adopted. A typical composition (85/15 (wt%) PBI/Ultem 1000) was subjected to a thermo-oxidative process at 350°C for 35 h in the environmental chamber of the *FT*i.r. spectrometer, and the process was monitored by collecting i.r. spectra at intervals of 30 min. The results were compared with those obtained for the two pure components.

Before discussing these results, we will briefly describe the *FT*i.r. spectra of Ultem 1000 and also that of the blend, which form the basis of the interpretation of the spectroscopic data. *Figure 8* shows the spectra of PBI, Ultem 1000, and the 85/15 (wt%) blend at 350°C at the beginning of the experiment. The PBI spectrum has already been discussed in the preceding section. The spectrum of Ultem 1000 shows a $\nu_{C=O}$ overtone at 3485 cm^{-1} and, in the C–H stretching region, the typical pattern of bisphenol-A-based polymers[4]. The symmetric and asymmetric C=O stretching vibrations of the imide carbonyls give rise to the characteristic doublet at 1779 and 1725 cm^{-1} (imide I mode). The various ring-stretching modes fall in the range from 1620 to 1445 cm^{-1}, and at 1358 cm^{-1} we observe a strong, rather broad absorption attributed to a highly coupled mode of the type ν(CN)(CO)(NC) (imide II mode)[10]. Finally, in the region from 900 to 625 cm^{-1} we see the out-of-plane deformation modes of the aromatic C–H groups. The peak positions and the relative assignments are given for the Ultem 1000 spectrum recorded at room temperature; however, as in the case of PBI, the above considerations can be extended, with no modifications required, to the spectrum obtained at 350°C (see *Figure 8*, middle curve)[6].

The *FT*i.r. spectrum of the blend (see *Figure 8*, top curve) is practically coincident with that of the pure PBI in the region from 4000 to 2000 cm^{-1}, owing to the low intensity of the Ultem-1000 absorptions in this spectral range and also to its low concentration in the blend. In

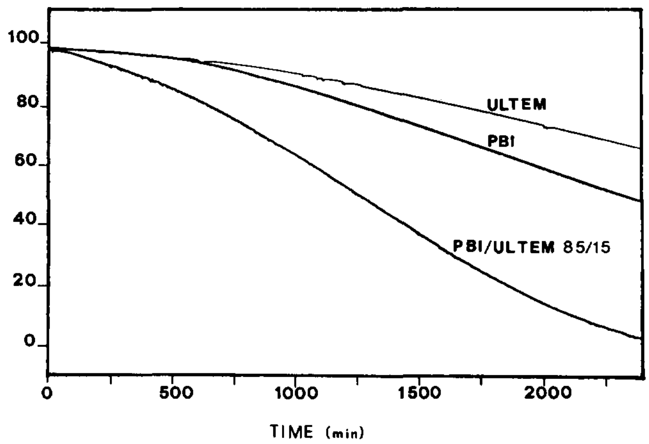


Figure 7 Isothermal thermogravimetric measurements carried out at 390°C on pure Ultem 1000, pure PBI, and the 85/15 (wt%) PBI/Ultem 1000 blend

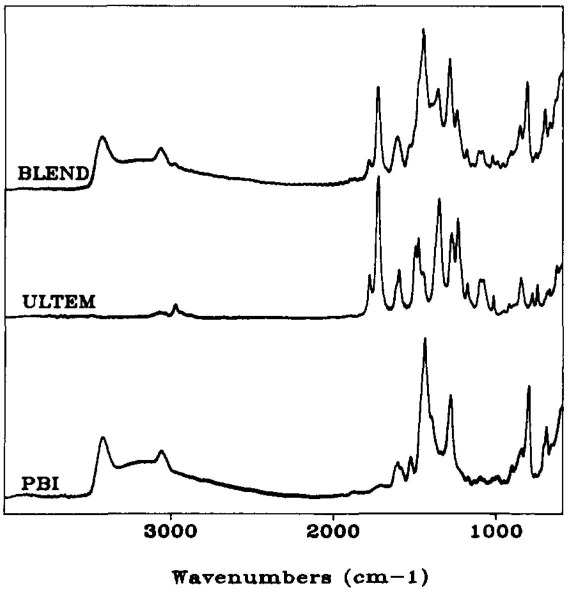


Figure 8 *FT*i.r. spectra of PBI, Ultem 1000, and the 85/15 (wt%) PBI/Ultem 1000 blend, measured at 350°C at the beginning of the thermo-oxidative experiment

the carbonyl region, the imide doublet is evident, and remains well defined and resolved. The region from 1650 to 1300 cm^{-1} appears to be rather complex because of the overlap of intense absorptions by both components. In the lower frequency range (1250–600 cm^{-1}), the spectrum again closely resembles that of PBI; in particular, the 801-cm^{-1} PBI peak, which was used previously to monitor the PBI degradation process, is still completely resolved and well suited for the purpose.

Figure 9 depicts the spectra of the blend (measured at 350°C), at the beginning of the experiment (A), after 14 h (B), and after 28 h (C). It is immediately evident that, as in the case of the pure PBI, the peaks at 3415 cm^{-1} ('free' N–H groups), 3145 cm^{-1} (self-associated N–H groups), and 801 cm^{-1}, considerably decrease in intensity, while the new peak at 2222 cm^{-1}, attributed to aromatic nitriles, appears. Analysis of the region from 1800 to 1300 cm^{-1} is not as straightforward. The imide doublet (1779 and 1725 cm^{-1}) gradually becomes less well resolved, but its overall intensity does not decrease, as one would expect, as a result of the Ultem 1000 degradation[11]. Instead, its intensity, which remains constant in the early stages of the experiment, increases slightly at longer times. This apparently surprising result can be interpreted in terms of new absorptions appearing in the carbonyl region, as a result of the oxidative attack on the blend and, more specifically, on the PBI component. Indeed, peaks such as those observed in the range from 1800 to 1600 cm^{-1} in the spectrum of oxidized PBI (see *Figure 3*) would fully explain the spectral features observed in the case of the blend, and we will discuss this point in more detail later.

As we did for PBI, we can evaluate the conversion of the groups responsible for the absorptions at 3415 and 801 cm^{-1} on the basis of the decrease in intensity of the respective peaks. The kinetic data are reported in *Figure 10* and *Figure 11*, together with the data obtained for pure PBI. We note that the concentrations of both groups decrease faster, and to a greater extent, in the blend than in pure PBI; this result confirms the findings of the t.g.a. studies, which indicate that the presence of Ultem 1000 reduces the thermo-oxidative stability of the blend. To obtain further insight into the mechanistic aspects of this phenomenon, we have applied spectral subtraction analysis: we attempted to isolate the spectrum of pure Ultem 1000 by digitally subtracting the spectrum of the pure PBI from that of the blend. The above analysis is based on the assumption that the blend spectrum is a linear combination of the spectra of the two components or, in other words, that the two components are completely independent and do not interact with each other from a vibrational point of view. This assumption is not completely correct in our case: in fact, it has been demonstrated by *FT*i.r. analysis that in the blend, PBI and Ultem 1000 have a hydrogen-bonding interaction that significantly affects the N–H stretching and the carbonyl-stretching regions[5]. However, the interaction is highly localized, selectively involving the N–H groups of PBI and the polyimide carbonyls; the other regions of the spectra of the two components in the blend remain essentially unaffected. We have already noted that for PBI the molecular interactions cause vibrational effects only in the N–H stretching region; in this contribution we concentrate our attention on the

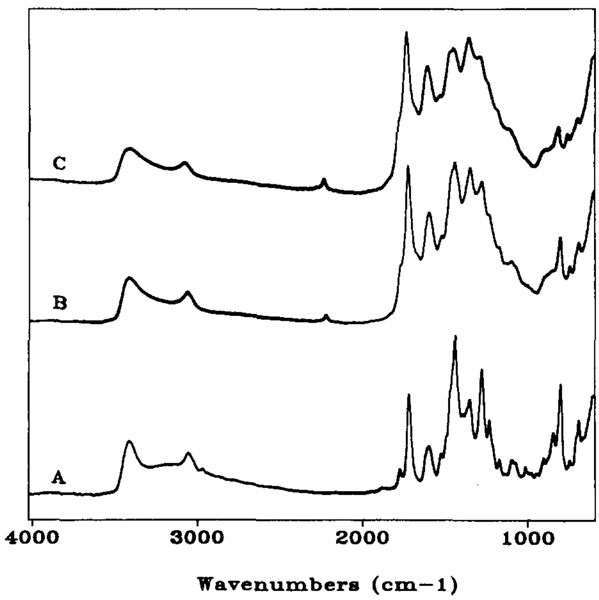


Figure 9 *FT*i.r. spectra of the 85/15 (wt%) PBI/Ultem 1000 blend measured at 350°C, with results obtained: (A) at the beginning of the experiment; (B) after 14 h; (C) after 28 h

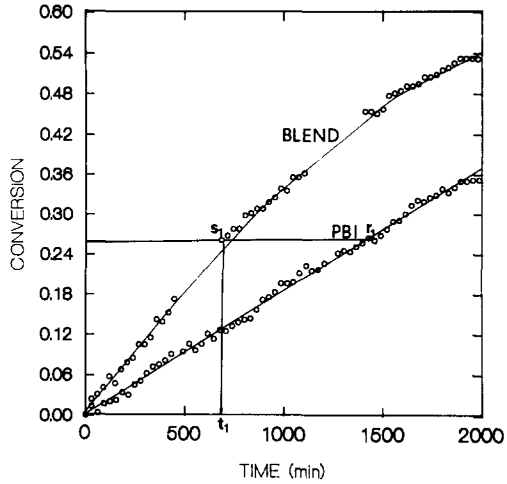


Figure 10 Conversion curves, relative to the 3415-cm^{-1} peak, plotted as a function of degradation time, for pure PBI and for the 85/15 (wt%) PBI/Ultem 1000 blend (see text for definitions of s_1 and r_1)

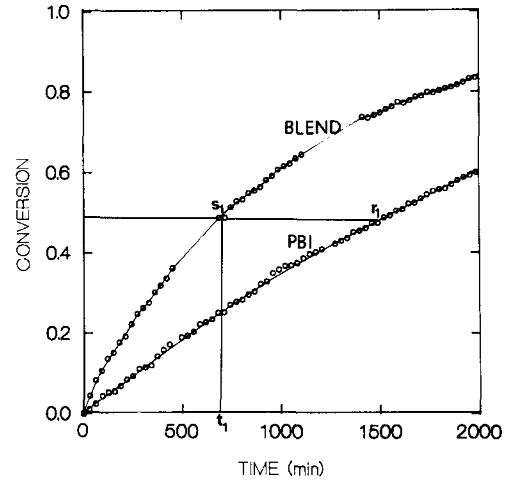


Figure 11 Conversion curves, relative to the 800-cm^{-1} peak, plotted as a function of degradation time, for pure PBI and for the 85/15 (wt%) PBI/Ultem 1000 blend (see text for definitions of s_1 and r_1)

region from 2000 to 600 cm^{-1}, where Ultem 1000 displays its most intense and characteristic absorptions (see *Figure 8*, middle curve), so interactional effects can be ignored. (Later, however, we will discuss some features that are brought out by subtraction spectroscopy and are directly related to such effects.)

The results of spectral subtraction on the blend spectrum at a time zero (i.e. at the beginning of the thermo-oxidative experiment) are remarkably 'clean'. A residual spectrum, obtained by subtracting the spectrum of PBI from that of the blend (a subtraction that reduces the 801-cm^{-1} PBI peak to the base line), is practically coincident with that of Ultem 1000 in the region from 2000 to 600 cm^{-1} (see *Figure 12*). Isolation of the spectrum of the polyimide would allow us to selectively monitor the fate of the minor component during the degradation process. However, to achieve this, a subtraction spectrum must be obtainable at any time during the process, and at this point a problem arises: because the PBI spectrum changes quite substantially with reaction time, an appropriate criterion is needed to choose the correct reference spectrum to subtract at times other than zero.

Consequently, we chose to use a PBI spectrum and a blend spectrum for which conversion was equal in terms of the 3415 cm^{-1} and/or the 800-cm^{-1} peaks. The situation is schematically represented in *Figure 10* and *Figure 11*. To obtain the difference spectrum which is representative of Ultem 1000 in the blend at time t_1, the PBI spectrum corresponding to the point r_1 was subtracted from the blend spectrum corresponding to the point s_1. Exactly the same results were obtained by using either the conversion curves relative to the 3415-cm^{-1} peak, or those relative to the 800-cm^{-1} peak. The use of such a criterion for the choice of the reference spectrum is based on the assumption that, from the mechanistic point of view, the PBI component behaves in the blend exactly as it does in the pure state, the only difference being that in the blend all the thermo-oxidative processes are accelerated.

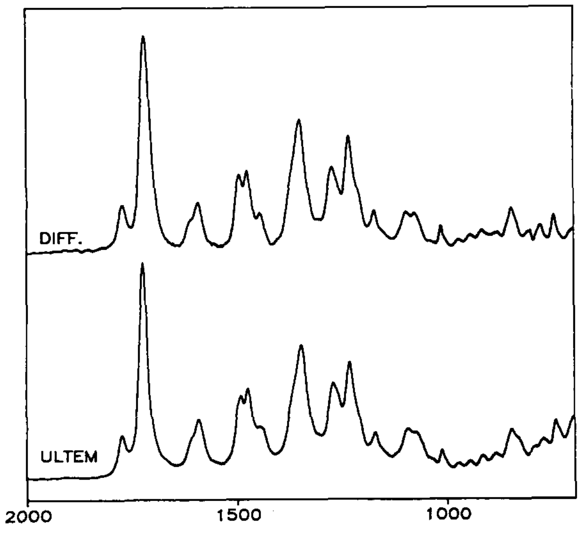


Figure 12 *FT*i.r. difference spectrum (Blend–PBI) over the range from 2000 to 600 cm^{-1} (upper curve), compared with the *FT*i.r. spectrum of ULTEM 1000 (lower curve) measured over the same region. All spectra were obtained at 350°C at zero time

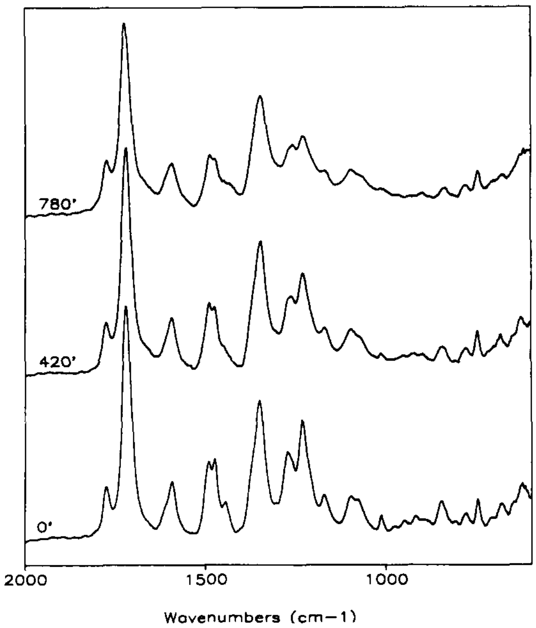


Figure 13 *FT*i.r. difference spectra (Blend–PBI) over the range from 2000 to 600 cm^{-1}, measured at 350°C, with results obtained at the beginning of the experiment, after 420 min, and after 780 min

Figure 13 shows three representative difference spectra, obtained by the above method, for reaction times of 0, 7, and 13 h. Here, and in all other cases, the result of the subtraction analysis is satisfactory, and the spectra correspond closely to those obtained with an Ultem-1000 film sample subjected to the same experimental conditions (to be discussed later). It is important to note that the appropriate choice of the reference spectrum is critical. Using a PBI spectrum, other than that selected by the method previously outlined, gives rise to a difference spectrum in which derivative-type features are clearly evident, especially in the carbonyl region. The fact that by difference spectroscopy it is possible to isolate the spectrum of the polyimide at any reaction time indicates that the PBI reference spectrum exactly matches, particularly in the carbonyl region, the spectrum of the PBI component in the blend. Even minor differences in the peak positions, and/or in the ratio of their intensities, produce clearly detectable derivative-type features in the resultant difference spectrum. This result is a strong confirmation that the mechanism of the thermo-oxidative processes of PBI in the blend is the same as that of PBI in the pure, amorphous state; the same groups are consumed (this is directly monitored by *FT*i.r. spectroscopy) and the same products are formed (this, in turn, is indirectly indicated by difference spectroscopy). Thus, during its thermo-oxidative degradation, PBI does not appear to interact chemically with Ultem 1000; the presence of the polyimide has only the effect of accelerating these processes.

Although we succeeded in isolating the spectrum of the polyimide from that of the blend, it was not possible to isolate the spectrum of PBI, although such a spectrum would be very useful in that it would directly show the presence of the carbonyl groups formed upon oxidation. We were unable to isolate this spectrum because, as already mentioned, the hydrogen-bonding interaction taking place among the N–H groups of PBI and the imide carbonyls of Ultem 1000 causes a shift of the main phthalimide absorption with respect to its position in an unperturbed state (1725 cm^{-1}). Such a shift is a function of the blend composition; in the present case (85/15 wt% composition), the shift, as measured at 350°C at time zero, is 5.5 cm^{-1} (see later). Therefore, because of this effect, a spectrum of pure Ultem 1000 in the amorphous phase cannot be used as a reliable reference for spectral subtraction; if we try to use such a spectrum, the typical features that indicate band shifts in the reference appear in the subtraction result (see *Figure 14*). These features mask the region in which we are most interested (1800–1600 cm^{-1}), thereby making the difference spectrum thus obtained, meaningless.

To compare the behaviour of Ultem 1000 in the blend with that in the pure amorphous phase, we have performed the thermo-oxidation experiment on a polyimide film cast from methylene chloride, under the same experimental conditions. The mechanism of the oxidative degradation of aromatic polyimides has been widely documented in the literature[11]. In the case of Ultem 1000 it proceeds through the homolytic cleavage of the propylidene moieties, followed by radical transfer, and, eventually, disruption of the phthalimide rings and evolution of low-molecular-weight volatiles.

In the *FT*i.r. spectra collected during the oxidation process, we clearly observed the decrease in concentration of the propylidene groups (see *Figure 15a*), as well as the decrease of the peaks associated with the carbonyl groups (1779, 1725, and 1385 cm^{-1}) and with the phthalimide rings (see *Figure 15b*). An important first observation is that the spectra of *Figure 15b* closely correspond to the spectra obtained from the PBI/Ultem 1000 blend by subtraction spectroscopy (compare *Figure 15b* and *Figure 13*). This result indicates that, as with the polyimide in pure PBI, the polyimide in the blend also undergoes oxidation through the same mechanism which is active in the pure, amorphous state. To monitor the rate of degradation, we measured, from the intensity of the main phthalimide absorption at 1725 cm^{-1}, the conversion of the phthalimide groups as a function of the degradation time. The results are reported in *Figure 16*, where curve A refers to the data obtained on pure

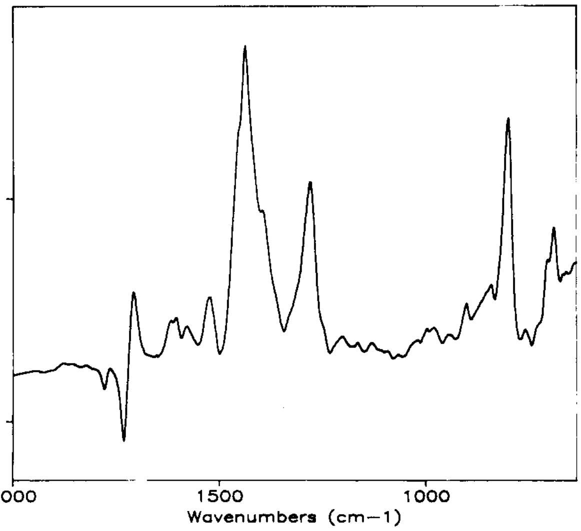


Figure 14 *FT*i.r. difference spectrum (Blend–ULTEM 1000) over the range from 2000 to 600 cm^{-1}, for measurements made at 350°C at the beginning of the experiment

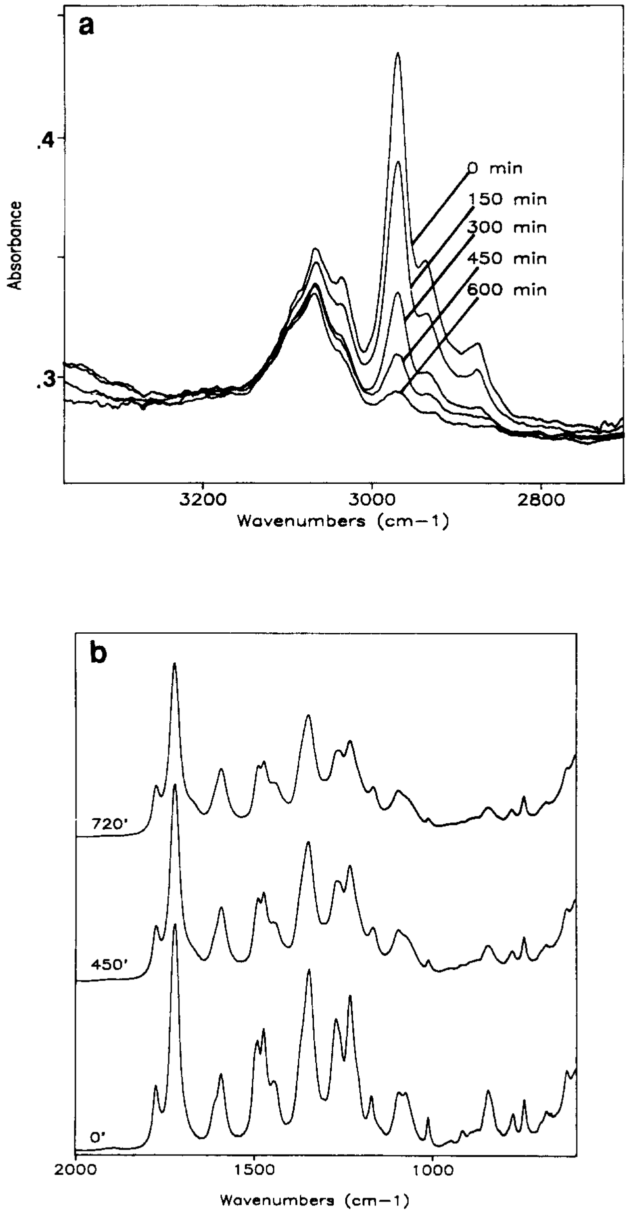


Figure 15 *FT*i.r. spectra of Ultem 1000 in the region: (a) from 3300 to 2700 cm^{-1} and; (b) from 2000 to 600 cm^{-1}. All measurements were obtained at 350°C with degradation times as indicated

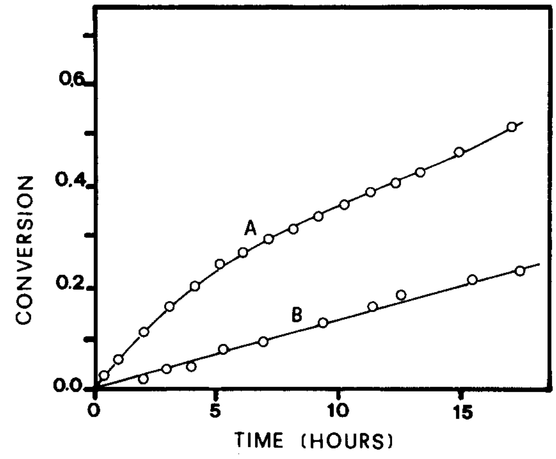


Figure 16 Conversion of the $\nu_{as,CO}$ peak of Ultem 1000, as a function of degradation time, determined for: (A) pure Ultem 1000 and; (B) the 85/15 (wt%) PBI/ULTEM 1000 blend

Ultem 1000, and curve B represents the behaviour of the polyimide in the blend (data derived from the spectra of *Figure 13*). In this case, it is found that the polyimide undergoes degradation at a faster rate, and to a larger extent, when in the pure, amorphous phase, than when it is blended with PBI.

These findings can be summarized as follows.

- In the PBI/Ultem 1000 (85/15 wt%) blend, the two components undergo thermo-oxidative degradation independently. *FT*i.r. analysis does not provide any evidence of chemical interactions between the components that might produce new reaction pathways.
- For PBI, the rate of degradation is accelerated in the blend relative to that in the pure state, whereas for Ultem 1000, the opposite is true.

It is important to stress that the above conclusions apply to the 85/15 wt% composition, which is the only one so far investigated, and it is difficult to predict whether they are generally applicable to the whole range of compositions.

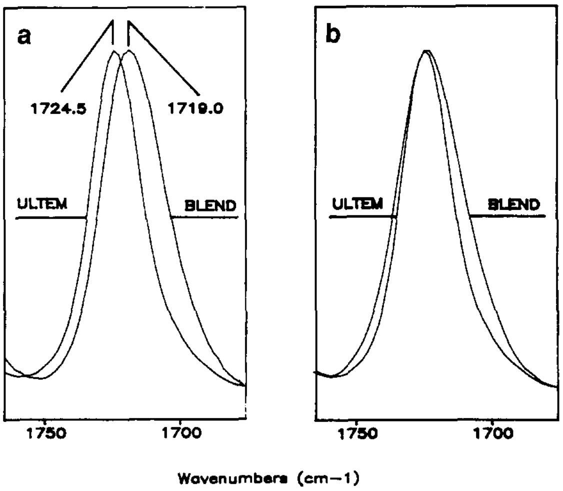


Figure 17 The $\nu_{as,CO}$ peak of Ultem 1000 in pure polyetherimide and in the 85/15 (wt%) PBI/Ultem 1000 blend, obtained from *FT*i.r. measurements carried out: (a) at 350°C. Data obtained: at the beginning of the thermo-oxidative experiment; (b) after 12 h

An explanation of the opposite effects that have been observed for the degradation rates of the two components can be presented on the basis of simple physical considerations. It is well known that in the vicinity of the glass transition temperature (T_g) of a polymeric material, all the thermo-oxidative processes are abruptly accelerated because of diffusion effects[12]. For pure PBI, the temperature at which the present thermo-oxidative experiment is carried out, T_d (350°C), lies 70°C below its T_g (420°C): under such conditions, all the degradation processes are very slow. Conversely, the initial T_g of the PBI/Ultem 1000 blend is 365°C, and has a relatively broad transition region[2,6]. Thus, for the blend, T_d is very close to the T_g of the material, with a consequent acceleration of all the degradative phenomena. For Ultem 1000, however, the T_g is 220°C, so in the pure amorphous phase the thermo-oxidative experiment was carried out at 130°C above the T_g of the polyimide. In the blend, T_d is just below the T_g of the material, and the degradation is correspondingly retarded.

All the experimental results that have been obtained indicate that the effects observed in the kinetics of the thermo-oxidative process in a PBI/Ultem 1000 blend have a physical, rather than a chemical, basis.

Finally, it is worthwhile to mention the effect, indicated by difference spectroscopy, of degradation time on the molecular interactions between the two components. We have already noted that hydrogen-bonding interactions between the N–H groups of PBI, which act as proton donors, and the imide carbonyls of Ultem 1000, which function as proton acceptors, cause a shift toward lower wavenumbers and a band broadening of the asymmetric stretching vibration of the C=O groups. At zero time, this shift amounts to 5.5 cm^{-1} (see *Figure 17a*). From the difference spectra representative of Ultem 1000 in the blend, we have found that this shift gradually and continuously decreases as a function of the degradation time (see *Figure 18*). After 12 h, the peak

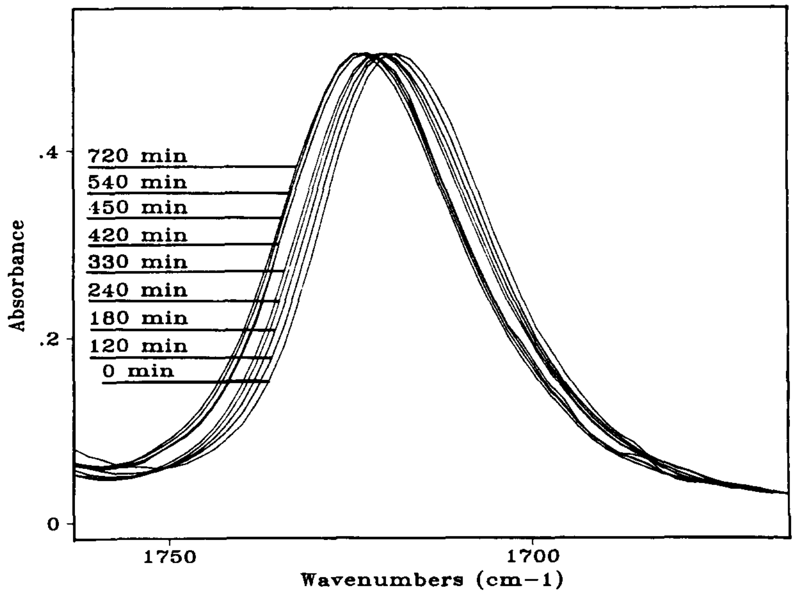


Figure 18 The $\nu_{as,CO}$ peak of Ultem 1000 in the 85/15 (wt%) PBI/Ultem 1000 blend as obtained by *FT*i.r. difference spectroscopy, for the degradation times as indicated

position reaches the value observed in pure Ultem 1000 (at 1725.5 cm^{-1}) and does not decrease any further (see *Figure 17b* and *Figure 18*). These observations can be explained by assuming that the number of molecular interactions gradually decreases during the thermo-oxidative experiment, possibly because of the consumption of the N–H groups of PBI, and also because of concurrent phase separation[6]. When the position of the main phthalimide peak reaches that observed in the pure Ultem 1000, all the hydrogen-bonding interactions are dissociated, and it is likely that a phase-separation phenomenon has occurred.

CONCLUSIONS

*FT*i.r. spectroscopy has proved to be a useful technique for investigating the early stages of the thermo-oxidative degradations of both PBI and a PBI/Ultem 1000 blend. For PBI, spectroscopic data have suggested a possible reaction scheme, and kinetic data have provided further information about the various stages of an apparently complex mechanism. For the PBI/Ultem 1000 blend, the same experimental approach used for pure PBI was adopted; the *FT*i.r. measurements indicate that, for the particular composition investigated, the two components undergo thermo-oxidative degradation without interacting chemically with each other. Furthermore, it was found that the rate of degradation of PBI in the blend is accelerated with respect to the pure state, whereas the opposite was observed for the degradation of Ultem 1000. An explanation of such an effect, based on physical considerations, has been advanced. Finally, the results of spectral subtraction analysis indicate that, operating concurrently with the thermo-oxidative processes, a phase-separation phenomenon occurs in the blend.

ACKNOWLEDGEMENT

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