polymer papers

*FT*i.r. studies of polymer blends containing the poly(hydroxy ether of bisphenol A) and poly(ε-caprolactone)

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Fourier transform infra-red (*FT*i.r.) studies of the polymer blend system poly(hydroxy ether of bisphenol A) (phenoxy)–poly(ε-caprolactone) (PCL) are presented. These two polymers are miscible in the amorphous state and information concerning the presence and nature of intermolecular interactions between the two polymers has been gained. Specifically, direct evidence has been obtained for a hydrogen bonding interaction between the PCL carbonyl group and the phenoxy hydroxyl group. Significantly, the relative strength of this interaction is found to be weaker than the corresponding intermolecular hydrogen bonding interaction in pure phenoxy. In contrast, a cursory *FT*i.r. study of phenoxy–poly(ethylene oxide) blends reveals that the intermolecular interaction occuring between these two polymeric components is stronger than that occuring in pure phenoxy. In addition, PCL is a crystallizable polymer and studies performed on the PCL–phenoxy blends at room temperature have led to further information on the state of order of PCL in these blends. The ramifications of these results are discussed.

Keywords Polymer blends; compatible blends; infra-red; phenoxy polymers; polyesters; intermolecular interactions

INTRODUCTION

Fourier transform infra-red (*FT*i.r.) spectroscopy has proven to be a useful technique with which to study compatible polymer blends[1-14]. Information may be obtained concerning the presence and nature of specific intermolecular interactions and conformational changes that occur upon blending two miscible polymers. During the past five years, we have published the results of a number of binary systems where one of the components was a polyester. In fact, the polyester, poly(ε-caprolactone) (PCL) has become almost an omnipresent component in our polymer blend studies. In part, this is because PCL is an unusual polymer in that it is miscible with a wide variety of chemically distinct polymeric materials[15]. Another factor is that the carbonyl stretching frequency of PCL is sensitive to both intermolecular interactions and conformational changes associated with changes in the state of order ('crystallinity') of the polymer in these blends[3]. Excellent examples include PCL blends with poly(vinyl chloride) (PVC), poly(bisphenol A carbonate) and copolymers of vinylidene chloride[3-5,7].

In all of the examples mentioned above, it has been established that intermolecular interactions exist involving the carbonyl bond of PCL with some chemical moeity of the other component in the blend. Only in the case of the PCL–PVC blends have we been able to definitely establish the nature of a major intermolecular interaction (i.e., a hydrogen bonding type between the PCL carbonyl bond and the methine proton of PVC) with infra-red spectroscopy[9].

In this paper, we present infra-red spectral results of another compatible blend containing PCL. The second component in this study is the poly(hydroxy ether of bisphenol A) which is commonly called a phenoxy resin and which may be considered to be a model epoxy resin. Our primary interest in the PCL–phenoxy blend system stems from the possibility that relatively strong intermolecular hydrogen bonding interactions may exist between the PCL carbonyl group and the hydroxyl group of the phenoxy. Additionally, we will present results of a cursory study of the phenoxy–poly(ethylene oxide) (PEO) blend system, which are relevant to our interpretation of the spectral data obtained from the phenoxy–PCL blends.

EXPERIMENTAL

The PCL (Union Carbide Corporation—PCL 700) used in this study is the same as that used in previous studies[3] and is described by Cruz *et al.*[16] The phenoxy polymer (Aldrich Chemical Company) employed is reported to have a molecular weight (undefined) of 28 000 and a glass transition temperature (T_g) of approximately 100°C. The PEO (Polysciences, Inc.) used has a molecular weight of 300 000; a T_g of -57°C and a crystalline melting point of 67°C.

Thin films of PCL, phenoxy and the PCL–phenoxy blends, prepared for the *FT*i.r. studies, were cast from 1% tetrahydrofuran solutions (by weight) onto potassium bromide (KBr) windows at room temperature. After the majority of the solvent had evaporated the films were transferred to a vacuum dessicator to completely remove residual solvent. A similar procedure was used to prepare

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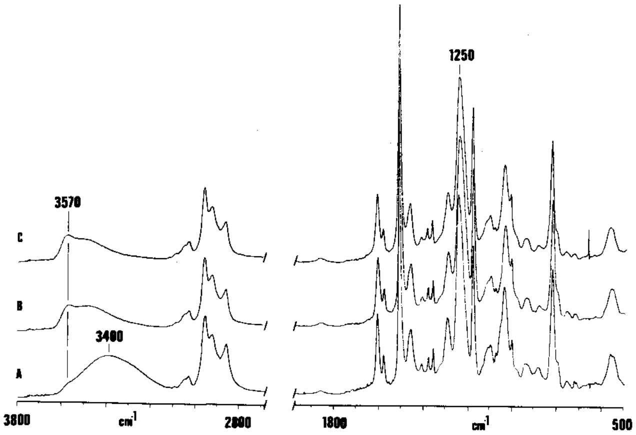


Figure 1 *FT*i.r. spectra of phenoxy recorded at (A) 35°C, (b) 120°C and (C) 150°C

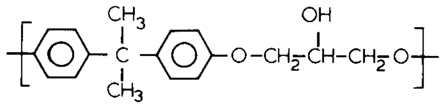
the phenoxy–PEO films except that in this case methylethylketone was used as a solvent.

Infra-red spectra were obtained on a Digilab FTS-15/B spectrometer. Two hundred scans at a resolution of 2 cm^{-1} were signal averaged and stored on a magnetic disc system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. A SPECAC high temperature cell mounted in the spectrometer was used to obtain spectra above room temperature with an accuracy of ±2°C. All the films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed[17].

RESULTS AND DISCUSSION

The infra-red spectrum of the poly(hydroxy ether of bisphenol A)

Although there are published infra-red spectra of a number of different phenoxy resins, to our knowledge there has been no detailed vibrational analysis of any of these polymers. The polymer used in this study is the poly(hydroxy ether of bisphenol A) which has the following chemical repeating unit:



The polymer in the solid state is amorphous and has a glass transition temperature of approximately 100°C. *Figure 1* shows the infra-red spectra from 500 to 3800 cm^{-1} of polymer film cast from solution and recorded at 35°, 120° and 150°C. As one might expect, the spectra are characterized by relatively narrow bands attributed to localized normal vibrations associated mainly with the rigid phenyl and methyl groups and relatively broad bands which are attributed predominantly to the remaining chemical groups which are highly coupled, conformationally sensitive modes. Of particular interest to this study, is the fact that there is a 'window' in the 1700 to 1800 cm^{-1} region of the spectrum which is essentially free of underlying absorbances. This is important as we are able to readily observe changes in the PCL carbonyl stretching mode in the phenoxy–PCL blends without serious complications. Another region of the spectrum which will be explored in depth is between 3100 and 3600 cm^{-1}. This is where the hydroxyl stretching frequencies occur and it is obvious that there are significant differences in this region as a function of temperature. We will return to this subject later in the text. More subtle changes are also noted upon heating the polymer in the 500 to 1800 cm^{-1} region of the spectrum. Significant frequency shifts and band broadening of bands in the 1200–1300 and 500–600 cm^{-1} regions are observed. Presumably, these bands contain major contributions from the C–O stretching and deformation modes. In any event, in this study we will restrict ourselves to the hydroxyl stretching region of the phenoxy spectrum.

Figure 2 shows more detailed and scale expanded spectra of the phenoxy film in the 3000 to 3800 cm^{-1} region recorded at different temperatures. The results are informative and an understanding of the spectral features observed is essential if we are to correctly interpret the subsequent infra-red results of the blends. At 35°C, (*Figure 2A*), the infra-red spectrum of the phenoxy film, which was cast from solution, exhibits a very broad band centred at 3400 cm^{-1} indicative of extensively hydrogen bonded hydroxyl groups. This is entirely consistent with self-association of the polymer chains through intermolecular hydrogen bonding of the hydroxyl groups. The minor contribution, observed as a shoulder at 3570 cm^{-1}, is attributed to unassociated (free) hydroxyl groups.

Upon heating the sample in a step-wise fashion to 150°C (*Figure 2B–D*), the relative contribution of the 3570 cm^{-1} band increases at the expense of the broad band attributed to hydrogen bonded hydroxyls. In addition, this latter band is observed to shift progressively to higher

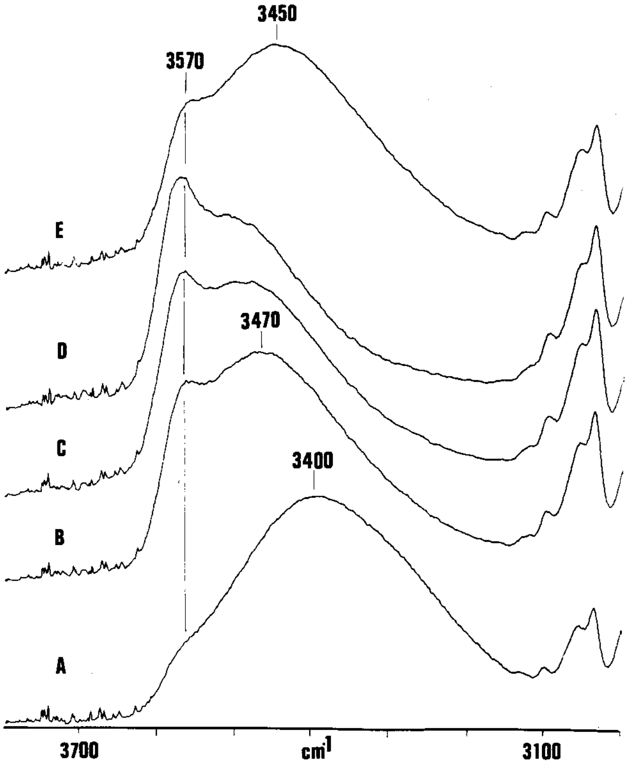


Figure 2 *FT*i.r. spectra of phenoxy from 3000 to 3800 cm^{-1} recorded at (A) 35°C, (B) 100°C, (C) 120°C, (D) 150°C and (E) 35°C after two days

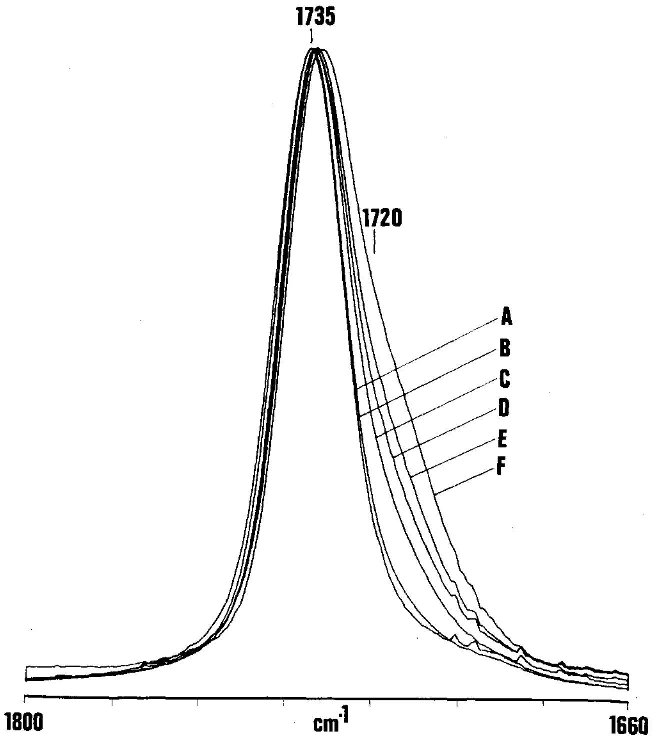


Figure 3 *FT*i.r. spectra recorded at 75°C of PCL–phenoxy blends containing: (A) 100, (B) 80, (C) 50, (D) 40, (E) 30 and (F) 20 weight percent PCL

frequencies as a function of temperature. Once again, this is relatively simple to interpret. At elevated temperatures (above the T_g of the polymer), there is sufficient energy to disrupt a significant number of the intermolecular hydrogen bonds, yielding a higher concentration of unassociated (free) hydroxyl groups. Concurrently, the average strength of the remaining intermolecular hydrogen bonded hydroxyl groups is diminished. This is reflected in the smaller difference between the frequencies of the unassociated (free) and self-associated hydroxyl groups. In other words, the shift of the hydrogen bonded hydroxyl stretching mode to higher frequency indicates a weaker hydrogen bonded system.

Upon cooling to 35°C (*Figure 2E*), it is evident that the spectrum is not identical to the original (*Figure 2A*). The relative contribution of the 3570 cm^{-1} band (free hydroxyl) is greater. This may be explained in the following manner. The original sample was cast from solution. During evaporation of the solvent, the polymer/solvent mixture becomes increasingly richer in polymer. Nevertheless, the residual solvent acts as a plasticizer and effectively reduces the T_g of the system. This allows the polymer more time to maximize the degree of intermolecular hydrogen bonding. In contrast, upon cooling from 150°C, the polymer will only have significant chain mobility above the T_g (approximately 100°C). Accordingly, as the sample cools to below 100°C the structure is frozen in place. In fact, in *Figure 2* spectrum E more closely resembles the spectrum recorded at 100°C (spectrum B) than the original recorded at 35°C (spectrum A). This is entirely consistent with the above arguments.

The infra-red spectrum of poly(ε-caprolactone)

The infra-red spectrum of PCL has been discussed in detail in a previous publication[3]. For the purposes of this paper we will only mention those features essential to this current study. The carbonyl stretching vibration of PCL in the preferred ('crystalline') and amorphous conformations are separated by 11 cm^{-1} and occur at 1724 and 1735 cm^{-1} respectively. The amorphous band is sensitive to intermolecular interactions involving the carbonyl bond and shifts of 3 to 9 cm^{-1} to lower frequencies have been observed in compatible blends depending upon the particular system[3–5,7].

PCL–phenoxy blends at 75°C

There have been previous studies performed on PCL–phenoxy blends[18,19] and it has been established that the two polymers are miscible in the amorphous state. For convenience, we will first consider the *FT*i.r. results obtained at 75°C (above the melting point of PCL) and then turn our attention to the room temperature studies.

Figure 3 shows infra-red spectra in the carbonyl stretching region (1660 to 1800 cm^{-1}) of pure PCL (denoted A) and PCL–phenoxy blends containing 80, 50, 40, 30 and 20 weight per cent PCL (denoted B–F respectively), all recorded at 75°C. The most striking feature of these spectra is the appearance and increasing intensity of a shoulder centred at approximately 1720 cm^{-1} with increasing concentration of phenoxy. This band may be reasonably assigned to a hydrogen bonded carbonyl group. In other words, this band is indicative of an intermolecular interaction involving the PCL carbonyl bond and the hydroxyl group of the phenoxy (i.e. $-C=O--H-O-$). A more subtle shift to lower frequency is also observed in the major peak at 1735 cm^{-1}. At first glance, it may be thought that this frequency shift could also be due to some form of interaction. However, as will be demonstrated below, this shift in frequency is an artifact arising from the contribution of the broad underlying band at 1720 cm^{-1}.

Figure 4 shows representative curve resolved spectra in the carbonyl region of two PCL–phenoxy blends recorded at 75°C. In all cases the spectra in this region were satisfactorily resolved into two components; one a relatively narrow band centred at 1734 cm^{-1} and another relatively broad band centred at approximately 1720 cm^{-1}.

A brief description of our curve resolving procedure is in order. Preliminary curve resolving studies of the carbonyl stretching region of the blends, using no fixed parameters except the number of bands, were used to establish a band shape. In our curve fitting program, we employ a sum function of Gaussian and Lorentzian bands which has been described in detail in a previous publication[20]. The band shape (actually, 62±2% Gaussian) was determined by a least squares optimization process of all the spectral data. Accordingly, in subsequent curve fitting analysis the band shape parameter was fixed and the computer was allowed to vary peak positions and widths. Using the least squares optimization procedure, the best fit of two curves was established. The results are summarized in *Table 1*. Considering the inherent limitations of curve fitting the results are remarkably pleasing. The peak position of the primary band (peak 1) at 1734 cm^{-1} is within one wavenumber of the band observed for pure amorphous PCL. The secondary broad peak occurs at a reasonably consistant frequency in all the blend spectra. Intuitively, the frequency and relative broadness of this band is consistent with a hydrogen bonded carbonyl group.

A major conclusion of the curve resolving studies is that only two peaks are necessary to obtain a satisfactory fit of the spectral data. Attempts were made to obtain the second derivative in this spectral region in order to substantiate this conclusion[20]. Although the results did suggest only two major components, the signal to noise ratio of the data was too poor to be definitive. Thus we cannot exclude the possibility that there are more than two components but it is generally agreed that the greatest source of error in curve resolving arises from the inclusion of too many peaks introduced to obtain a satisfactory fit. This is particularly acute when the precise band shape is unknown.

Having resolved the spectral data of the blends into the two components, we were in a position to calculate the relative areas of these two peaks. Unfortunately, the absolute absorption coefficients of the two infra-red bands are unknown. However, we postulated that the relative fraction of hydrogen bonded carbonyl groups, as measured by the area of the 1720 cm^{-1} band divided by the total area of the 1720 and 1734 cm^{-1} bands, should correlate with blend composition. A plot of the relative fraction of hydrogen carbonyl groups as a function of mole per cent phenoxy in the blends is shown in *Figure 5*. Apparently, a reasonable linear relationship exists over the composition range between 10 and 80 mole per cent phenoxy. It is important to recognize that this relationship is only approximate. Two major factors must be considered. First, the fraction of hydrogen bonded carbonyl groups has been calculated assuming identical absorption coefficients. Secondly, in any blend composition, the fraction of PCL carbonyl groups that can form hydrogen bonds with phenoxy hydroxyls will be limited by the different dimensions of the individual chemical repeating units and the physical problem of intimately mixing macromolecules. In any event, the important conclusion of the above results is that the fraction of hydrogen bonded carbonyls increases with increasing phenoxy concentration.

We now turn our attention to the hydroxyl stretching region of the PCL–phenoxy blend spectra. *Figure 6* shows infra-red spectra in the 3000 to 3800 cm^{-1} region of pure phenoxy (denoted A) and PCL–phenoxy blends containing 10, 20, 30, 40 and 50 weight per cent PCL, all recorded at 75°C. As mentioned previously, the spectrum in this region of pure phenoxy may be considered to be composed of two components; a broad band centred at 3450 cm^{-1} attributed to hydrogen bonded hydroxyl groups (self-associated) and a relatively narrow band at 3570 cm^{-1} assigned to free (non-associated) hydroxyl groups. Upon mixing with PCL, the broad hydrogen bonded hydroxyl band of the phenoxy is observed to shift to higher frequencies as a function of increasing PCL concentration. In contrast, the relative concentration of

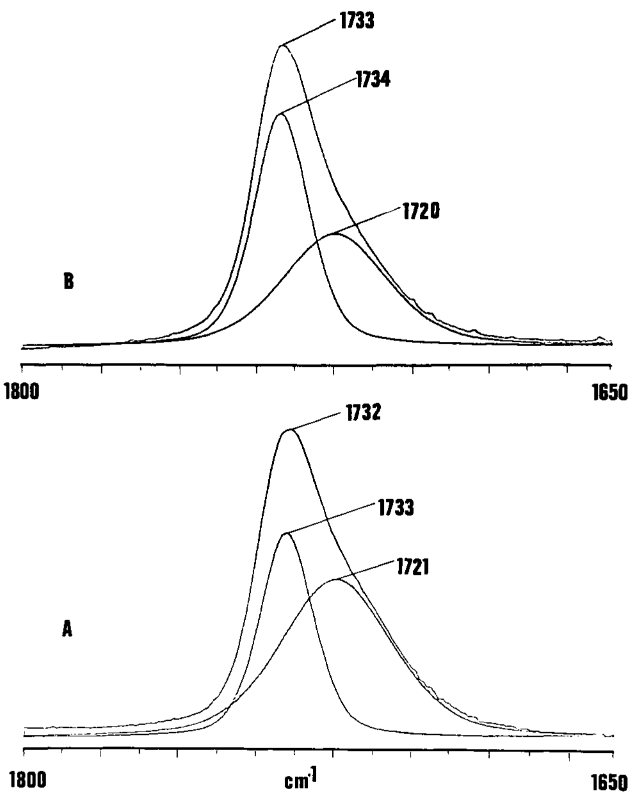


Figure 4 Curve resolved spectra of the region from 1650 to 1800 cm^{-1} at 75°C of PCL–phenoxy blends containing: (A) 20 and (B) 30 weight percent PCL

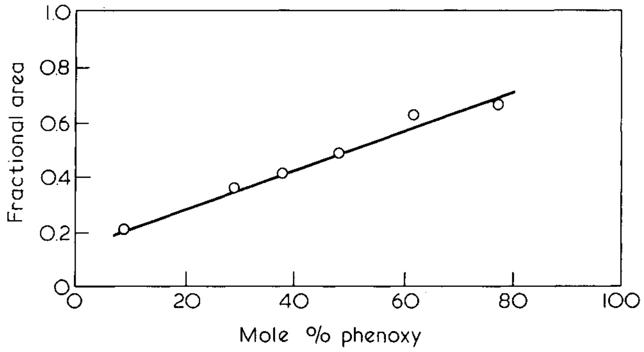


Figure 5 Plot of fractional area (peak 2/(peak 1 + peak 2)) *versus* mole percent phenoxy for PCL–phenoxy blends

Table 1 Curve resolving results of the carbonyl stretching region

Blend composition		Peak 1	Peak 2	Fractional area
PCL (wt %)	Phenoxy (wt %)	(cm^{-1})	(cm^{-1})	Peak 2/ Peak 1 + Peak 2
10 (22)*	90 (78)	1734	1722	0.66
20 (38)	80 (62)	1733	1721	0.62
30 (52)	70 (48)	1734	1720	0.48
40 (62)	60 (38)	1734	1720	0.41
50 (71)	50 (29)	1734	1720	0.35
80 (91)	20 (9)	1734	1719	0.20

* Figures in parentheses are on mole % basis

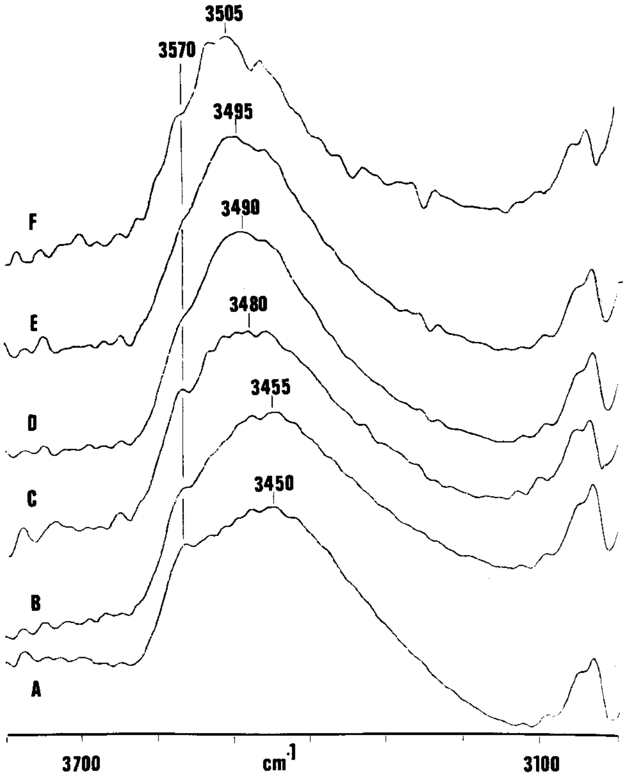


Figure 6 *FT*i.r. spectra recorded at 75°C of PCL–phenoxy blends containing: (A) 0, (B) 10, (C) 20, (D) 30, (E) 40 and (F) 50 weight percent PCL

free hydroxyls does not appear to be a strong function of PCL concentration.

The shift of an essentially uncoupled vibrational mode of a polymer to higher frequency upon mixing with another miscible polymer is not without precedence. Concurrently, we have been studying the PCL–α-deuterated PVC blend system and have observed that the C–D stretching mode increases in frequency upon blending with PCL[9]. This result was interpreted as evidence for a hydrogen bonding type of interaction involving the methine deuteron of PVC with the PCL carbonyl bond. The results of the PCL–phenoxy blends are analogous and even more convincing. It should be recalled that the free hydroxyl stretching mode of the phenoxy occurs at 3570 cm^{-1} while the self-associated hydrogen bonded hydroxyl stretching modes are centred at 3450 cm^{-1}; a difference of 120 cm^{-1}. In the blends, a significant fraction of the phenoxy hydroxyl groups are presumably associated with the PCL carbonyl groups. However, in this case the overall relative strength of the hydrogen bonds is less than that of the self-associated phenoxy hydroxyl groups. Nevertheless, there is still a shift to lower frequency relative to that of the free hydroxyl.

A question that must be addressed is, 'if the hydrogen bonding interaction is weaker in the blend compared with that of the self-associated pure phenoxy, why do these two polymers form a miscible amorphous blend?' In simple terms, for a polymer–polymer mixture of a certain composition to be miscible, the overall free energy of mixing must be zero or negative. The changes in entropy upon mixing amorphous macromolecular species is known to be relatively small but it is nonetheless generally positive and contributes a negative factor to the free energy of mixing. In the PCL–phenoxy blend system one would have to consider the enthalpic and entropic changes occurring upon forming a miscible mixture compared to both original pure amorphous polymers. Although the infra-red spectroscopic results presented above indicate that the strength of the hydrogen bonding interaction in pure phenoxy is stronger than that occurring in the blend, it is the balance between the changes in enthalpy and entropy upon mixing that is important. Given that the PCL–phenoxy blend system is miscible, this must imply that the resulting balance between the enthalpy and entropy of mixing leads to an overall decrease in the free energy of the system.

PCL–phenoxy blends at room temperature

The infra-red spectra of PCL–phenoxy blend films recorded at room temperature are further complicated by the fact that PCL can crystallize. This type of blend has been described as a crystalline/compatible blend and examples of these blends have been mentioned in the introduction.

Figure 7 shows the infra-red spectra in the carbonyl stretching region of PCL–phenoxy blends containing 50, 60, 70, 80 and 90 weight per cent phenoxy (denoted A–E respectively). The former two blend spectra exhibit three distinct components. The components at 1735 and 1725 cm^{-1} are attributed to PCL in amorphous and preferred ('crystalline') conformations respectively. A minor contribution at approximately 1718 cm^{-1} is also observed attributable to the PCL carbonyl group hydrogen bonded to the hydroxyl group of the phenoxy. At concentrations of 70 weight per cent phenoxy and

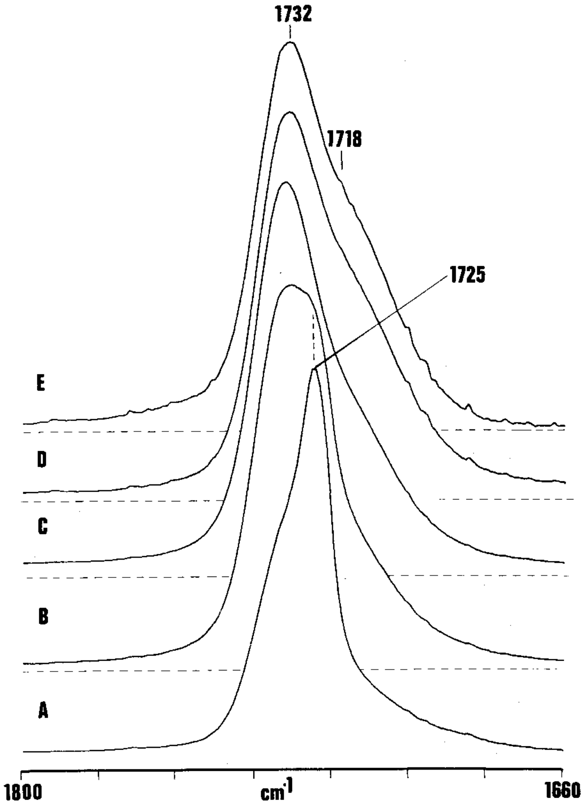


Figure 7 *FT*i.r. spectra of the region from 1800 to 1660 cm^{-1} recorded at room temperature of PCL–phenoxy blends containing: (A) 50, (B) 60, (C) 70, (D) 80 and (E) 90 weight percent phenoxy

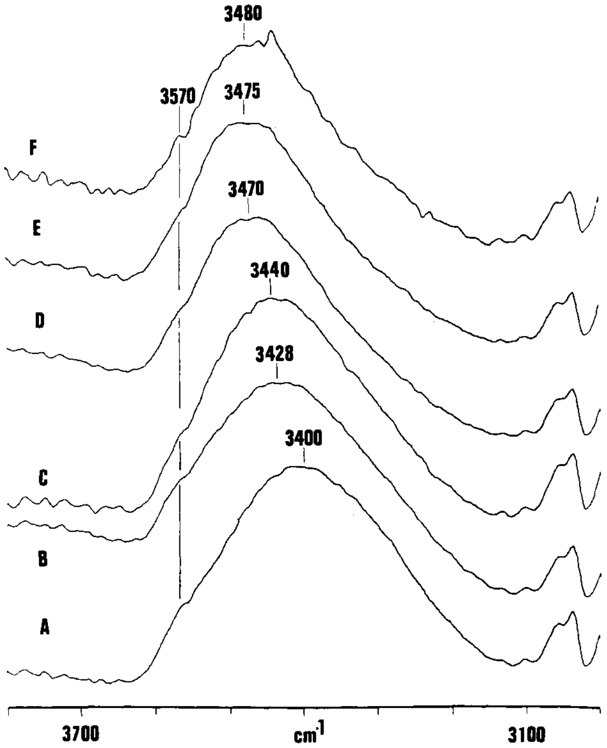


Figure 8 *FT*i.r. spectra of the region from 3800 to 3000 cm^{-1} recorded at room temperature of PCL–phenoxy blends containing: (A) 0, (B) 10, (C) 20, (D) 30, (E) 40 and (F) 50 weight percent PCL

above the PCL component of the blend appears completely amorphous. This is substantiated by curve resolving experiments similar to those described previously for the spectra recorded at 75°C. Only two peaks centred at 1733 and 1718 cm^{-1} are needed to satisfactorily fit the spectral data. The contribution of the 1718 cm^{-1} band increases as a function of phenoxy concentration in a similar manner to that discussed for the results obtained at 75°C.

Figure 8 shows the infra-red spectra in the 3000–3800 cm^{-1} region of pure phenoxy (denoted A) and PCL–phenoxy blends containing 10, 20, 30, 40 and 50 weight per cent PCL (denoted B–F respectively), all recorded at room temperature. The shift of the hydrogen bonded hydroxyl stretching mode to a higher frequency as a function of PCL concentration is similar to that observed at 75°C. However, the difference in frequency between the free hydroxyl and hydrogen bonded hydroxyl is somewhat greater at room temperature compared to 75°C. This is readily explained by temperature effects as noted for pure phenoxy (see *Figure 2*).

Phenoxy–PEO blends at room temperature

We have performed only a cursory *FT*i.r. study of the phenoxy–PEO blends but the preliminary results are relevant to the PCL–phenoxy studies reported above. Previous studies have demonstrated that phenoxy–PEO blends are compatible[21].

Figure 9 shows the infra-red spectra in the 3000–3800 cm^{-1} region of pure phenoxy (denoted A) and phenoxy–PEO blends containing 10, 20 and 50 weight per cent PEO (B–D respectively), all recorded at room temperature. The most fascinating aspect of these results is that the hydrogen bonded hydroxyl mode is observed to shift to lower frequencies as a function of PEO concentration. This is in marked contrast to the results seen in the PCL–phenoxy blends. The implication of this shift to lower frequency is that the hydrogen bonding interaction between the phenoxy hydroxyl and PEO is stronger than the corresponding self-associated hydrogen bonding in pure phenoxy.

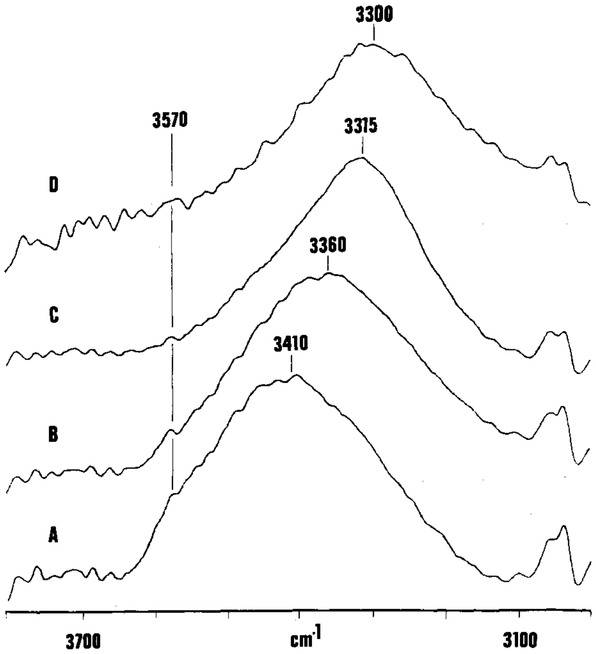


Figure 9 *FT*i.r. spectra recorded at room temperature of phenoxy–PEO blends containing: (A) 0, (B) 10, (C) 20 and (D) 50 weight percent PEO

CONCLUSIONS

FT-i.r. spectroscopy has proved to be an excellent technique with which to study the compatible PCL–phenoxy blend system. Initial temperature studies of the phenoxy polymer demonstrated that the hydroxyl stretching region of the spectrum was particularly sensitive to the degree of self-association through intermolecular hydrogen bonding. Upon blending the phenoxy with PCL, infra-red spectral changes associated with the PCL carbonyl band and the phenoxy hydroxyl band were observed. These changes were attributed to an intermolecular interaction involving the PCL carbonyl group and the phenoxy hydroxyl group in the blends. It was observed, however, that the average strength of this intermolecular interaction in the blend was weaker than the corresponding interaction in self-associated phenoxy. In contrast, the intermolecular interaction occurring in phenoxy–PEO blends was found to be stronger than that occurring in pure phenoxyl.

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