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Miscibility and interactions in a mixture of poly(ethylene oxide) and an aromatic poly(ether amide)

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Results concerning a mixture of an experimental aromatic poly(ether amide) and poly(ethylene oxide) are reported. The presence of ether groups in both polymers, and the possibility of a great number of intermolecular hydrogen bonds, give rise to polymer–polymer interactions that result in partial miscibility, as it has been demonstrated by *FT*-i.r., differential scanning calorimetry and optical microscopy. These results are qualitatively consistent with theoretical phase diagrams calculated from an association model which emphasizes the role of hydrogen bond interactions in this type of blend. © 1997 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ether amide); poly(ethylene oxide); polymer blends)

INTRODUCTION

Polymers exhibit selective permeation rates to gases which can be used in separation processes. Significant advances have been achieved in order to promote structural variations in polymeric materials leading to optimize the combination of gas separation and permeability (permselectivity). As an alternative to the synthesis of entirely new homopolymer gas separation membranes, various copolymers or polymer blends have been developed from known homopolymers. The copolymers and blends are intended to optimize the gas separation properties and the mechanical properties of the homopolymers[1,2]. The blend of a highly permselective polymer, although with low permeability, as such an aromatic polyamide, with a second component with a flexible chain, such as poly(ethylene oxide), could offer an adequate combination for gas separation processes. However, this type of combined effect may be affected by the miscibility level attained between the blend components, so that a first step in developing such type of material is the systematic study of the miscibility between the blend components.

Most of the known miscible blends are composed by polymers with functional groups capable to form strong interactions. These interactions stabilize the mixture, after compensating the small contributions to the free energy of mixing arising from the combinatorial entropy and the dispersive interactions[3]. However, from a theoretical point of view, the presence of these strong specific interactions introduces a network of non-random contacts, which invalidates the use of theoretical models based on a perfectly random mixture of segments. This type of mixtures can be treated in the context of higher order mean-field approximations. For instance, in an association model developed by Painter, Coleman and coworkers[3,4], the configurations of the equilibrium distribution of hydrogen bonded chains are described by a Flory lattice model type of counting procedure. A similar assumption is used in the treatment of hydrogen bonds developed by Veytsman[5] and Panayioutou and Sanchez[6]. These approaches give identical results when the same reference state is used[7]. However, better agreement between theoretical and experimental data were obtained if the association model includes what can be thought of as an empirical 'correction term' which originally appeared in the Painter and Coleman approach as a result of an incorrect choice of reference state. In a subsequent paper, Painter *et al.*[8] analysed the origin of such discrepancies and concluded that intramolecular screening effects are important in polymer blends and solutions and could explain why the previous choice of reference states worked so well in the prediction of phase behaviour in hydrogen bonded mixtures. In this paper we will use the original Painter and Coleman free-energy equation containing the semi-empirical term mentioned above.

Models of this type are designed to be applied to blends in which one of the components is able to form strong interactions in the pure state (self-association), but can also form similar interactions with the second component of the mixture (inter-association)[3]. From *FT*-i.r. spectra it is possible to determine the constants and enthalpies which quantify the equilibria describing both type of interactions. Using these parameters, the association model can be used to calculate the free energy of mixing and other thermodynamic functions. Phase boundaries, as well as glass transition and melting temperatures, can also be derived.

Polyamide blends are adequate mixtures for such type of studies. For instance, Painter, Coleman and coworkers have studied mixtures of different aliphatic–aromatic polyamides with poly(vinyl ether)s and poly(ethylene oxide)[9,10]. In these systems, interactions between carbonyl and NH groups of the pure polyamide compete with intermolecular interactions between NH groups of the polyamide and ether groups of the second component. The situation is, in principle, more complicated in the blend under study here.

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In this case, an amorphous aromatic poly (ether amide) (PEA), based on bisphenol A, self-associates through its NH and carbonyl groups, but also through its NH and ether groups.

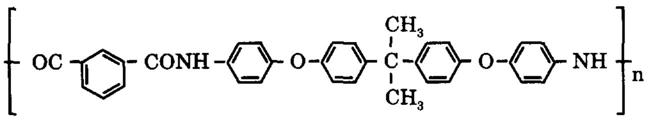
Although *FT*-i.r. can provide evidence of some kinds of interactions in a blend, it does not conclusively mean that both components are miscible at an intimate level. Accordingly, additional calorimetric and microscopy results are reported in order to clarify the certainly complex behaviour of the present amorphous-crystalline blends.

EXPERIMENTAL SECTION

Materials and procedures

N,N′-dimethylacetamide (DMA) was supplied by Aldrich Chem. Co., with a purity higher than 99%. The rest of the employed solvents were supplied by PANREAC. All other materials were used without further purification.

The aromatic polyamide (PEA) was synthesized from isophthaloyl chloride and bis-[(4′-aminophenoxy)-4-phenyl] propane by a polycondensation at low temperature in N,N-dimethyl acetamide (DMA) using trimethyl silane as an activator. After precipitation from solution and washing with water several times, it was extracted in a Sohxlet with acetone for 12 h and dried in a vacuum oven at 90°C for 20 h. Its inherent viscosity at 25°C in DMA was 1.41 dl g^{-1}. It has the following structure:



Poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) were supplied by Aldrich Chem. Co. Their molecular weights, according to the manufacturer, were 300 000 and 10 000, respectively.

Polymer solutions of 2% (w/v) in a variety of solvents (see *Table 1*) were prepared by stirring at 60°C the corresponding polymer–solvent mixtures. From these solutions, films were prepared by casting at 60°C and drying in a vacuum oven at 75°C for 48 h and at 100°C during 6 h. Alternatively, samples were obtained by precipitation of the solutions by pouring them into excess hexane–diethyl ether cooled mixture 50:50 (v/v) or pure hexane. After that, the polymer samples were washed twice with the same precipitant and dried in a vacuum oven in a similar manner to that of the cast samples. Films for *FT*-i.r. measurements were obtained by casting DMA solutions onto hot glass plates or KBr windows (for pure PEA). Drying schedules were as described above.

FT-i.r. spectra were carried out in a Nicolet 5 DXC spectrometer taking 64 scans at 4 cm^{-1} resolution. Measurements at elevated temperatures were performed using a SPECAC high-temperature cell. Films were thin enough to be within an absorbance range where the Beer–Lambert law applied.

Differential scanning calorimetry (d.s.c.) measurements were carried out in a Perkin-Elmer d.s.c.-2C calorimeter with a heating rate of 20K min^{-1} and sample weights in the 10–15 mg range. Indium and dodecane melting points were used as references.

Glass transition temperatures of pure polymers and blends were obtained in a second scan, carried out after a first one up to 520K, and a subsequent quenching to 220K at a nominal rate of 320K min^{-1}. After this treatment, T_gs were recorded at the half-height of the corresponding heat capacity jump. PEO melting points were determined at the maximum of the endothermic peaks on blend samples obtained by casting and isothermally crystallized at 6°C for 14 days after a heating treatment at 110°C for 15 min. After the crystallization, the samples were quenched in liquid nitrogen and a first scan was carried out from 220 to 380K at a 20K min^{-1} rate. The samples were then cooled to 220K, using a nominal rate of 320K min^{-1} and a second scan was performed under identical conditions to the first one. Results obtained in this way have been denoted as quenched samples.

Observations of PEO crystallization and equilibrium melting temperatures in the blends were conducted on a Leitz–Aristomet polarizing optical microscope equipped with a Mettler FP82 hot stage and a Wild–Leitz photoautomat. The cast samples were melted at 100°C for 10 min and then inserted, as quickly as possible, into a different hot stage at a prefixed T_c. Undercoolings and crystallization times were selected in order to prevent impingements. Samples were then heated at a rate of 1K min^{-1}, the melting point being measured by detecting the disappearance of the birefringent pattern using a photomultiplier inserted in the eyepiece tube of the microscope. This thermal history,

Table 1 Glass transition temperatures for PEA–PEO 50:50 w/w blend prepared by casting and precipitation, using different solvents and precipitants[a]

Solvent	Precipitant	T_{g1} (K)	T_{g2} (K)
DMA	—	300	463
DMA	HEX-DEE 50/50	306	460
DMA-toluene 90/10		304	465
DMA-toluene 90/10	HEX-DEE 50/50	304	466
DMA-DMF-toluene 45/45/10		305	466
Pyridine		303	467
Pyridine	HEX	—[b]	465
DMSO		304	466
DMSO	HEX-DEE 50/50	—[b]	468

[a] Polymer concentration 2% w/v. Solvent relations are given in volume.
[b] Glass transition temperatures overlapped the melting transition.

similar to that previously used in other PEO blend, has demonstrated[11] its capacity to give T_c–T_m trends similar to those obtained by d.s.c. at low crystallinity contents.

RESULTS AND DISCUSSION

Infrared studies of the pure PEA and its blends

Figure 1 shows the *FT*-i.r. spectra of our pure aromatic poly(ether amide) PEA in the 1720–1620 cm^{-1} range, at several temperatures above the PEA glass transition temperature. This region corresponds to the stretching vibration of the amide carbonyl group, called amide I in the literature. The broad shape of the band is a consequence of the partial superposition of vibrations arising from two different situations of the carbonyl groups: one corresponds to the free amide carbonyls and the other one to the carbonyl groups involved in associations by hydrogen bonds with NH groups. These bands are centred, respectively, at 1680 and 1660 cm^{-1}, which are slightly higher than the values reported in the case of the aromatic–aliphatic polyamides previously mentioned[9,10]. Due to the fact that hydrogen bonds are unfavoured at high temperatures, the intensity of the band corresponding to associated amide carbonyls must decrease with increasing temperature, as *Figure 1* shows. Moreover, temperature causes a slight shift in the amide carbonyl band to higher wavenumbers.

If PEA and PEO could interact via hydrogen bonds, as expected in the case of forming miscible blends, the new associations would be formed after breaking some of the associations between NH and carbonyl groups of the pure PEA. Consequently, the number of associated carbonyls in the blends must decrease in relation to those appearing in pure PEA. In this sense, *Figure 2* collects spectra of PEA–PEO blends at different compositions and 25°C. In this figure, the intensity of associated carbonyls decreases strongly as the blends become richer in PEO. This behaviour is similar to that found in some mixtures of poly(isophthalamides) (PIPA)–PEO[9,10]. In fact, at a PEA–PEO 50:50 w/w composition the associated carbonyls involved in the polyamide self-association have practically disappeared.

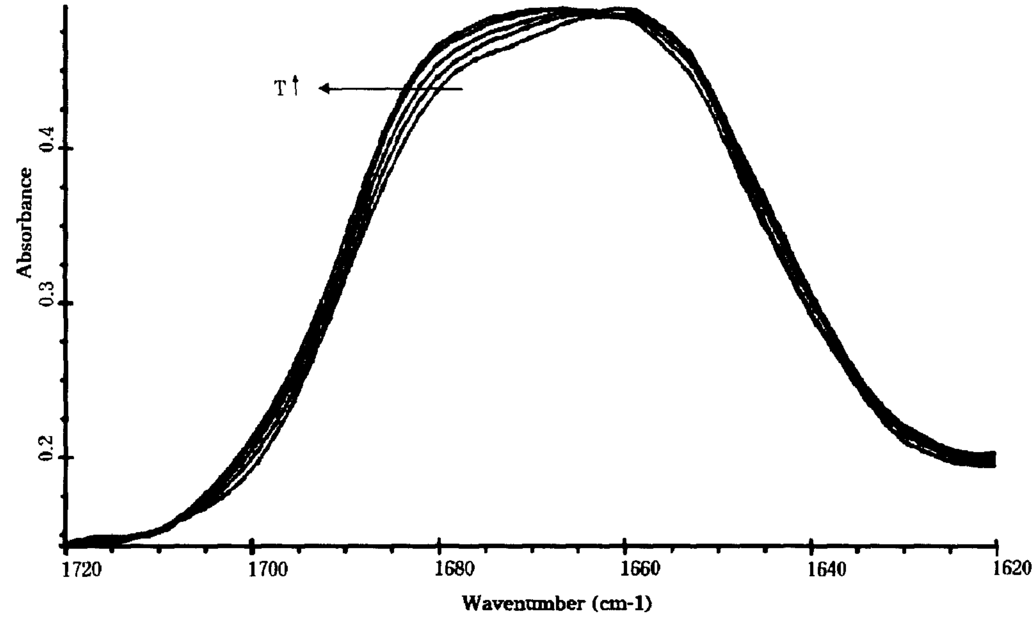


Figure 1 *FT*-i.r. spectra of PEA at 200, 235, 245, 255 and 264°C, respectively

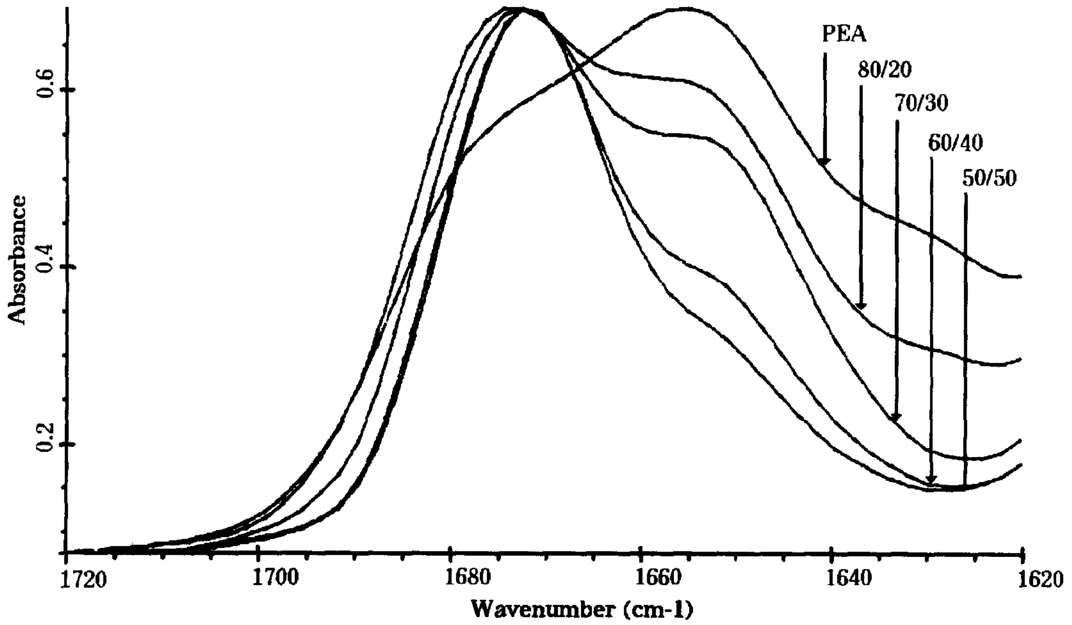


Figure 2 The 1720–1620 cm^{-1} region of various PEA–PEO blends *FT*-i.r. spectra

From this result, a significant molecular mixing between PEA and PEO can be concluded, but not necessarily a single phase.

As it occurs in the pure PEA, the relative absorbance of the carbonyls in the blends slightly decreases with increasing temperature. A more marked change has been reported, for instance, in the case of a mixture of PEO with the aliphatic–aromatic amorphous polyamide denoted as nylon MPD6[10], where a significant increase in the hydrogen-bonded carbonyl band is observed relative to that of the 'free' as the temperature is progressively raised from room temperature to 150°C. This type of behaviour has been attributed to a phase separation[10]. In our case, the temperature does not seem to affect the miscibility level attained during the blend preparation, whatever it may be.

Additional evidence of the interactions ocurring between PEA and PEO can be inferred from the NH stretching vibration region. In *Figure 3* we present the spectra of pure PEA and different PEA–PEO blend compositions in the 3100–3500 cm^{-1} region, also at 25°C. The spectra show a strong band in the 3310–3340 cm^{-1} region which corresponds to hydrogen-bonded NH groups and a smaller one ('free' NH groups), in the 3400–3450 region. In PEO–PEA blends, this last peak decreases quickly as the mixture becomes richer in PEO and finally disappears. That means that nearly all the free NH groups existing in pure PEA and some of those which were forming hydrogen bonds with its carbonyl groups are now forming hydrogen bonds with the PEO ether groups. Then, a considerably high number of associations between PEA and PEO have been formed in the mixture.

Finally, interactions between PEA and PEO could be analysed, in principle, through the stretching vibration of the C–O–C group, observed in the 1150–1085 cm^{-1} region. However, this vibration belongs to the so-called fingerprint region, where many bands correspond to vibrations of larger groups and interacting vibrational modes, making difficult the required analysis.

No significant differences were found in blends of PEA with poly(ethylene glycol) (PEG). It appeared that the lower molecular weight and the higher number of end groups did not have any influence in the level of interactions. In concluding this section, the *FT*-i.r. results of the carbonyl and NH stretching vibration regions seem to indicate that the NH groups of the poly(ether amide) prefer to interact with PEO or PEG ether groups better than with ether and carbonyl groups belonging the PEA molecules. The study ofthe thermal properties of the mixtures which are described in the next section provides more information on whether these interactions lead to the miscibility of the blends.

Glass transition temperatures

The phase behaviour of our blends was studied by determining glass transition temperatures. In *Figure 4* we illustrate some of the d.s.c. thermograms (second run) corresponding to various PEA–PEO blends obtained by precipitation. All the blends clearly showed two glass transition temperatures indicating two phases. However, the most important feature is that both T_gs were composition dependent, although the highest one remained close to the value corresponding to pure PEA, while the second one sharply decreased with increasing PEO fraction in the mixture. This indicated one phase rich in PEA and a second with a widely varying composition.

We used different blend preparation methods as a means of seeing whether the observed phase behaviour was real or an artifact due to solvent effects. For instance, if the ternary solvent–PEA–PEO system exhibited multiphase behaviour at low solvent concentrations, then the casting process could induce phase separation. Complete elimination of residual solvent did not cause remiscibilitation of the polymers, due to the high viscosity and the high T_g of one of the formed phases. Similar behaviour has been recently reported in blends of poly(methyl methacrylate)–poly(hydroxy ether of bisphenol A)[12] and poly(methyl methacrylate)–poly(vinyl acetate)[13]. For this reason, T_gs were measured in samples prepared by both disolution–precipitation and casting. Melt mixing was not used because of PEO degradation at the required temperatures.

Different solvents and solvent–precipitant pairs were used, although for the sake of simplicity only those samples prepared by casting from DMA solutions and those obtained by precipitation of DMA solutions in a cold mixture of hexane (HEX) and diethylether (DEE) 50:50 in volume are considered in *Figure 5*. In this figure the T_g–composition

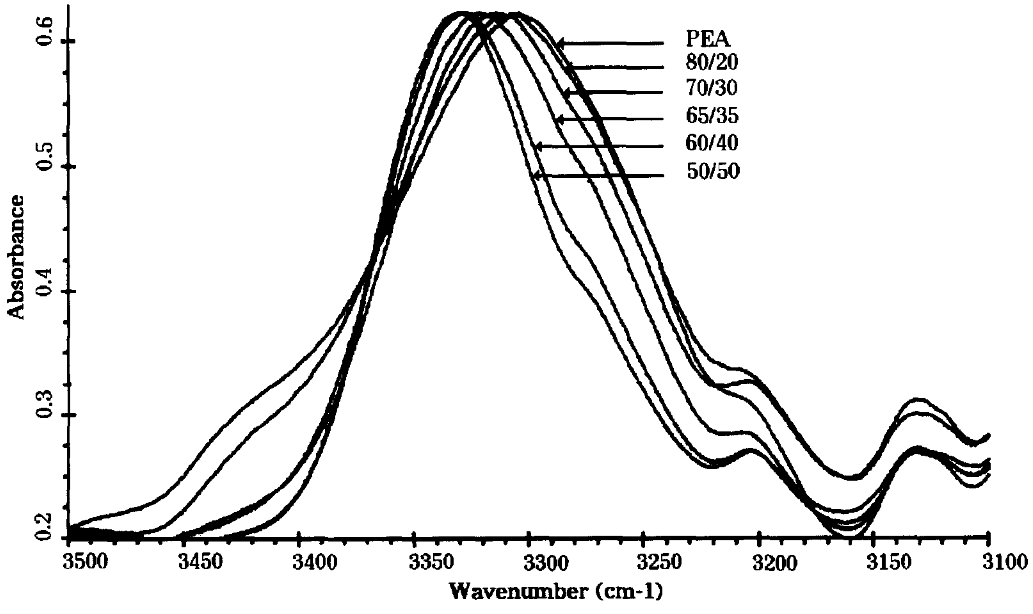


Figure 3 The 3500–3100 cm^{-1} region corresponding to the NH streching vibration in pure PEA and its mixtures with PEO

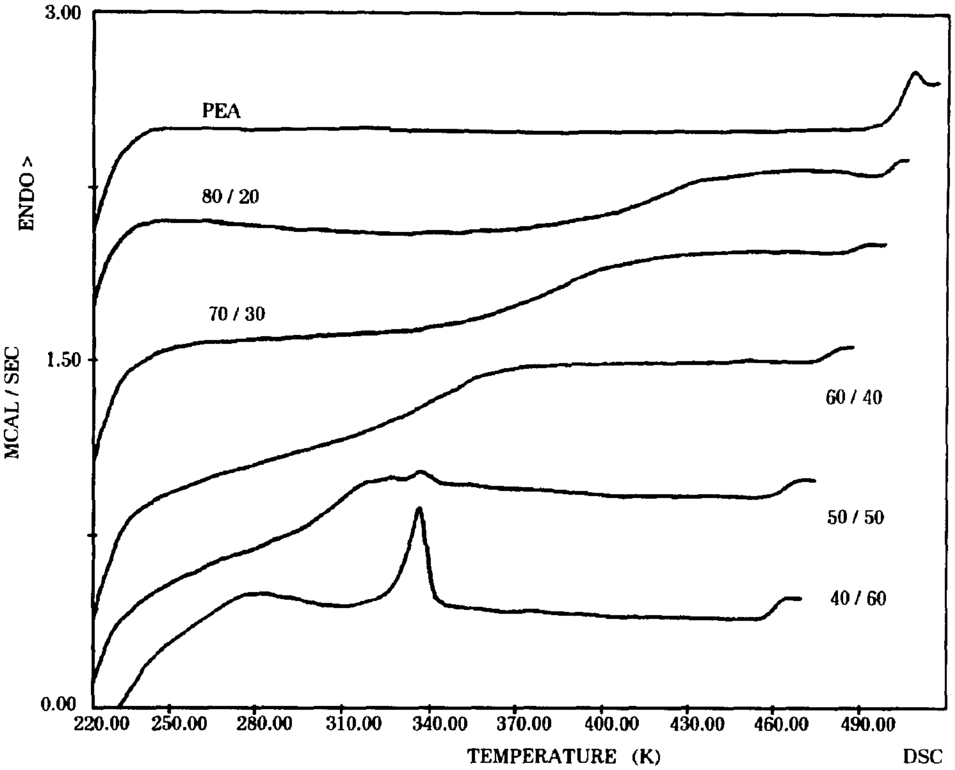


Figure 4 DSC second scans for PEA–PEO blends

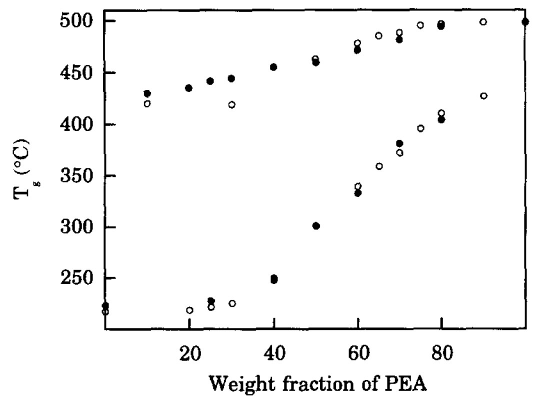


Figure 5 Glass transition temperatures determined in PEA–PEO samples prepared from DMA solutions: (●) after precipitation in hexane–diethyl ether 50:50 in volume; (○) by casting

dependence is presented covering the whole composition range. Both phases have T_g values which are composition dependent. Only in blends with compositions higher than 80% PEA in weight does the phase rich in PEA show an independent T_g value, practically equal to the pure PEA value. In PEO rich mixtures a similar effect occurs with composition of at least 70% of PEO.

A similar behaviour was found in the case of the samples prepared using other solvents and precipitants. *Table 1* summarizes the results for representative 50:50 w/w mixtures. It is clear that all these attempts in order to obtain fully miscible PEA–PEO blends were unsuccessful. In fact, the T_g values presented in *Table 1* are practically the same for all solvents used.

This situation differs from that reported in the above-mentioned case of poly(methyl methacrylate) and poly (vinyl acetate) blends[13]. It was found that, depending on the solvent used, blends prepared by casting had either one intermediate T_g, two T_gs close to the T_gs of each component or two T_gs shifted upward and downward from the T_gs of pure polymers. The shifts were attributed to a partial miscibility. In our case, the mixtures presented similar T_gs values independently of the employed solvent and the preparation method (casting or precipitation). It seems reasonable to conclude that the observed partial miscibility of the PEA–PEO mixture is not an artifact.

It is concluded that, at high PEO concentrations, one phase was practically pure PEO while in the other phase both PEO and PEA were present. At high PEA concentrations one phase was practically pure PEA while both PEO and PEA were present in the other phase. In the rest of composition range both polymers were present in phases which became substantially richer in a polymer when the amount of that polymer in the mixture increased. This behaviour was consistent with the previous evidence of mutual interaction observed by *FT*-i.r.

Melting and crystallization behaviour of PEA–PEO blends

Additional evidence of the phase behaviour could be deduced from crystallization and melting studies of the crystalline PEO phase in the range of low PEA concentrations.

In this range of composition, films of PEA–PEO blends, isothermally crystallized in the 15–56°C temperature interval, showed typical spherulitic morphology with the characteristic birefringent pattern in the form of a Maltese cross when observed by optical microscopy with crossed polarizers. As shown in *Figure 6*, the spherulite growth started to be affected when the amount of the first component reached 20% in weight. For this composition most of the observed crystallization corresponded to perfect spherulites, but some of them showed a mixed structure between a Maltese cross pattern and a semi-crystalline matrix.

Increasing amounts of PEA (the amorphous component) in the range 75–60% by weight of PEO caused the forma-

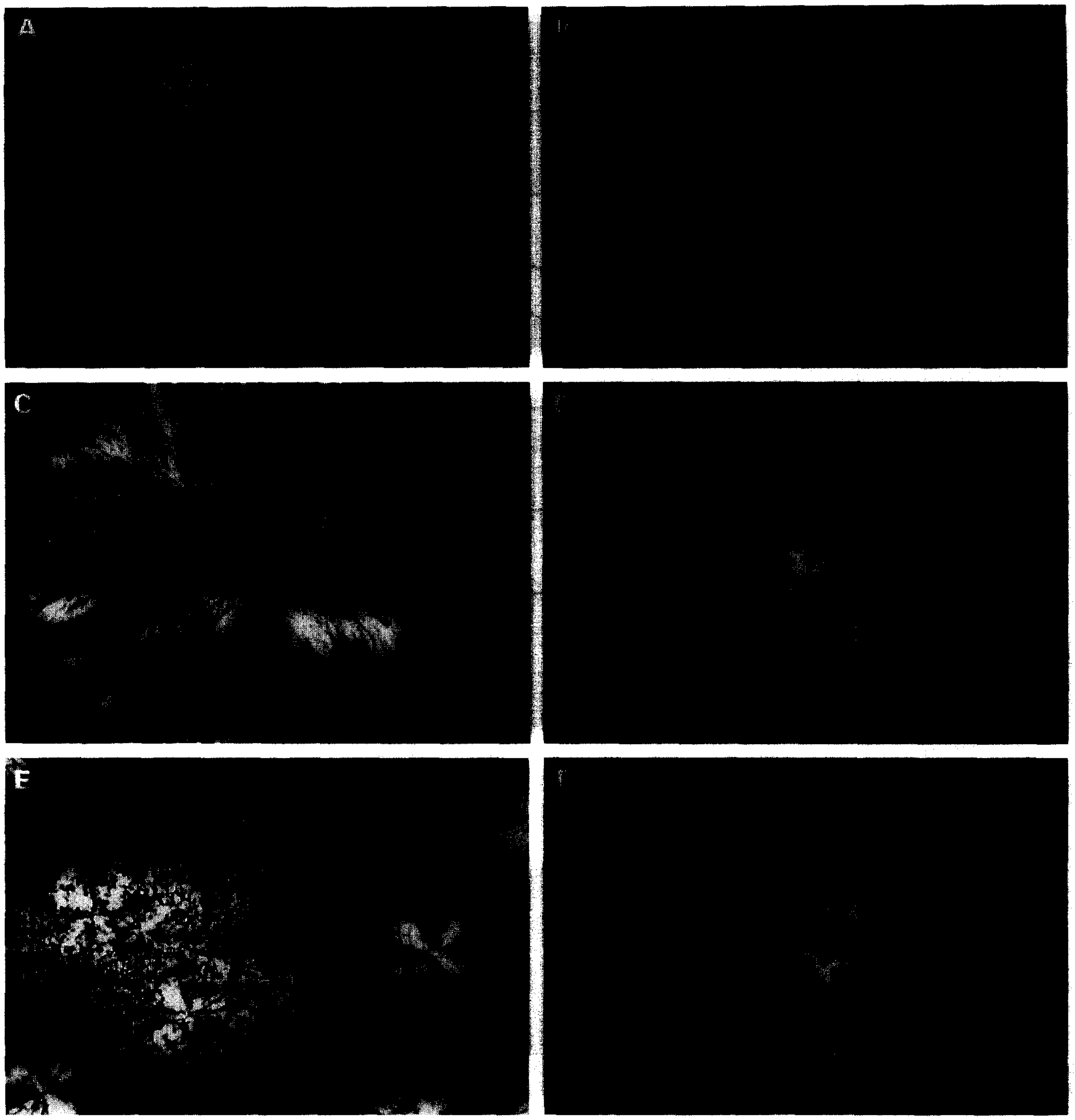


Figure 6 Optical micrographs of crystalline morphologies obtained in PEO and some of its mixtures with PEA: (A) PEO crystallized at 51°C; (B) PEA–PEO 20:80, $T_c = 47°C$; (C) PEA–PEO 20:80, $T_c = 41°C$; (D) PEA–PEO 25:75, $T_c = 40°C$; (E) PEA–PEO 30:70, $T_c = 40°C$; (F) PEA–PEO 40:60, $T_c = 30°C$

tion of PEO crystals with ill-defined borders embedded in a disordered semi-crystalline matrix. For the last composition observed, with 60% by weight of PEO, the spherical symmetry of growth of the semi-crystalline matrix, centred in the spherulitical structure was still evident.

The addition of a second component also had an influence on the melting temperature. Melting point depression of a crystalline polymer in a blend can be a result of kinetic, morphological and thermodynamic factors. To avoid the kinetic effects arising from the fact that crystals are formed at temperatures below the equilibrium melting point, the usual procedure is the determination of equilibrium melting temperatures using Hoffman–Weeks plots[14]. Plots of this type are presented in *Figure 7*. In all cases, a linear dependence between the actual melting temperature and the crystallization temperature is observed. The corresponding extrapolations should provide equilibrium melting temperatures. However, the fact that the slopes of these plots (related to the so-called morphological factor γ) were dependent on composition, would suggest[15] that morphological effects may also affect the melting point depression.

Figure 8 resumes PEA–PEO blend melting points corresponding to quenched samples, isothermally crystallized samples and equilibrium melting points from *Figure 7*. The differences in the melting point values can be due to the different scanning rate (1K min^{-1} by optical microscopy in the case of the equilibrium values and 20K min^{-1} by d.s.c. in the others), but also to the fact that microscopy values are equilibrium melting points whereas the d.s.c. ones are not. Finally, the d.s.c. measurements are taken at the maximum of the melting peak while the optical melting points are extrapolated values of the final melting data. *Figure 8* also

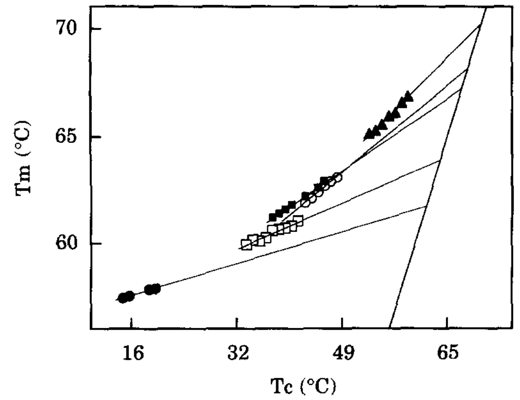


Figure 7 Hoffman–Weeks extrapolation plots for PEA–PEO blends: (▲) PEO; (○) PEA–PEO 10:90; (■) PEA–PEO 20:80; (□) PEA–PEO 30:70; (●) PEA–PEO 40:60

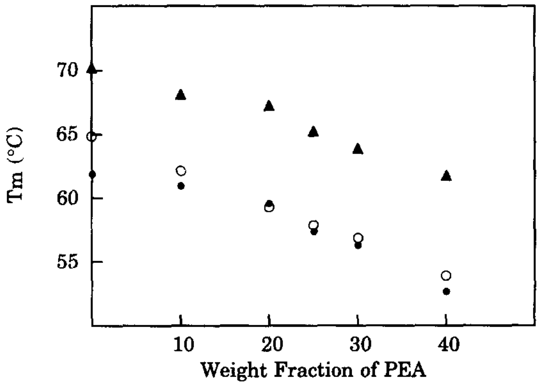


Figure 8 Melting temperatures obtained from different thermal treatments: (▲) equilibrium by Hoffman–Weeks method; (●) quenched samples; (○) samples isothermically crystallized at 6°C

shows the effect of blend composition on T_m. It seems that the amorphous component has a more significant effect on the equilibrium melting temperature when its composition is above 20%. This also occurs in quenched samples, although the melting temperature of the samples isothermally crystallized at 6°C for 14 days (measured by d.s.c.) shows a linear dependence with composition. It could be argued that, in this last case, even at low PEA concentrations PEA is also present in the PEO-rich phase.

Calculations using the association model

The association model, introduced by Coleman *et al.*[3], provides a good guide to the factors controlling the phase behaviour of the blends under study. A detailed description of the assumptions and the theoretical equations describing free-energy changes and phase behaviour has been recently published[4]. In this model, the free energy of mixing is the result of three different contributions. The first one is an almost negligible entropic contribution which tends to vanish when molecular weights increase. The second term correspond to van der Waals interactions and is described using the original Flory–Huggins interaction parameter, calculable from solubility parameters. The third one, introduced by the model, reflects the favourable contribution coming from specific interactions between the components. It can be calculated using constants and enthalpies which describe the self- and inter-association equilibria. K_B and K_A are the constants describing the formation of 'chain-like' complexes between B units and the hydrogen bonding association between A and B units, respectively. They are dimensionless magnitudes which can be calculated from *FT*-i.r. measurement on model compounds (K_B) or from polymer blends, copolymers or model compounds mixtures (K_A). A discussion about the determination of these constants has been previously published[3,4]. A brief summary has been included in a more recent paper[8], discussing the new problems encountered in applying the association model. The association enthalpies h_B and h_A quantify the temperature dependence of the corresponding equilibrium constants in terms of a Van't Hoff plot.

Molar volumes, polymerization degrees, solubility parameters and self- and inter-associations constants (K_B and K_A, respectively) and enthalpies (h_B and h_A, respectively) used in our calculations are summarized in *Table 2.* Molar volumes and solubility parameters of the pure components were calculated using a group contribution compilation elaborated by the authors of the association model[3]. PEA degree of polymerization was tentatively taken as 100. The dimensionless self-association constant and the corresponding enthalpy are those used in Ref. [10], adequately corrected after taking into account the variation of K_B with the molar volume of the polyamide. The inter-association constant K_A satisfies the relation $K_A/K_B = 0.1$, an equation which was used for blends of polyamides and polyurethanes[5]. As previously mentioned in Section 1, an additional self-association constant, which referred to the interactions between NH and ether groups, should be considered in defining PEA self-associations. These interactions compete with the similar ones betweeen NH and PEO ether groups. In comparing the two types of interactions, it seems clear that PEO ether groups are more accessible than the PEA ones protected by two phenyl rings. Consequently, in a first approximation to the problem, we did not introduce the additional self-association constant describing the interaction between NH and PEA ether groups.

Table 2 Parameters employed in phase diagram calculations[3,10]

Polymer	Molar volume (cm^3 mol^{-1})	Degree of polymerization (DP)	Solubility parameter (cal $cm^{-3})^{0.5}$	K_B at 25°C	K_A at 25°C
PEA	195.7	100	11.8	41.6	4.2
PEO	38.1	6800	9.4	—	—

Association enthalpies $h_A = h_B = -3.2$ kcal mol^{-1} [10].

Figure 9 shows the calculated phase diagram for the present system, which is an 'hour-glass' type diagram similar to that calculated for nylon MPD6–PEO blends. According to the model, two phases—each one containing predominantely one of the components—should be in equilibrium in the temperature range under consideration. In comparing this diagram with our T_gs (see *Figure 5*), the results are not completely consistent. Non-equilibrium situations related to the blend preparation and conditioning processes could be the origin of such discrepancies. It should be also remarked that the calculations must be only

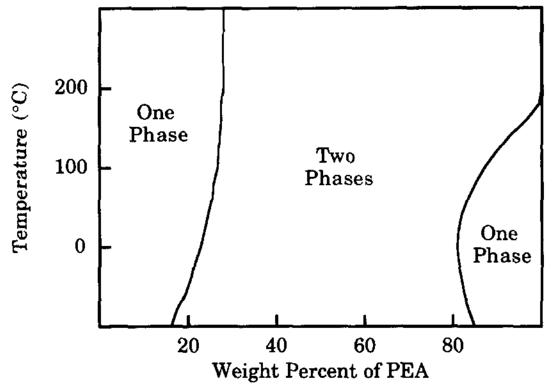


Figure 9 Phase behavior predicted by the Painter and Coleman association model for the PEA–PEO mixture

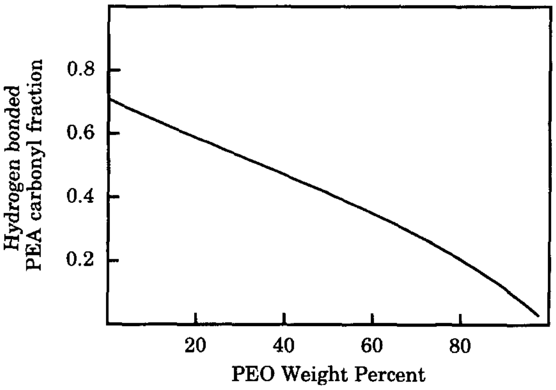


Figure 10 Plot of the simulated fraction of bonded carbonyl groups involved in association with NH groups of PEA in the PEA–PEO mixtures at 150°C

qualitatively considered, given the rough estimation of constants and enthalpies.

Figure 10 shows that this partial miscibility is still consistent with a certain level of hydrogen bonding between the blend components. This is reflected by the decreasing number of hydrogen bonds between PEA carbonyl and NH groups when the PEO composition increases. This trend is consistent with our previous discussion in the *FT*-i.r. section. Simulations of this type at different temperatures evidenced that, according to the model, the free carbonyl fraction does not change significantly with temperature, as occurs experimentally.

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