Blends of Poly(ether imide) and an Aromatic Poly(ether amide): Phase Behavior and CO$_2$ Transport Properties

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ABSTRACT: Blends of poly(ether imide)(PEI, Ultem 1000) and an aromatic poly(ether amide) were studied. Although homogeneous or heterogeneous blends can be obtained depending on the blend preparation method, the inherent miscibility of the mixture was finally established. The so-called enthalpy relaxation method was used to detect one or two glass transition temperatures in the blends in spite of the similarity of the pure component transitions. Fourier transform infrared analysis provided additional evidence of the specific interactions, which could be in the origin of the miscibility. A preliminary study of the influence of the homogeneity level in the transport properties of the blend films was also undertaken. Carbon dioxide at 1 bar was used as a penetrant. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 2141–2149, 1998

Key words: poly(ether imide); aromatic poly(ether amide); polymer blends; enthalpic relaxation; transport properties

INTRODUCTION

Polyimides are one of the most investigated families of polymers for membrane separation. The structure–permeability relationships of these polymers have been investigated extensively since the pioneering work of Hoehn.[1] Members of this family exhibit a markedly higher gas solubility, as well as a higher permeability, than many other glassy polymers. The prior observations of Hoehn[2] and Coleman and Koros[3] that substituents reducing interchain packing and increasing intrachain segmental rigidity increase permeability were confirmed by Langsam and Burgoyne.[4] This is a consequence of the general influence of the chemical structure on the two processes involved in the permeation phenomenon. For instance, the introduction of bulky moieties can disrupted chain packing, increasing the penetrant diffusion coefficient. The introduction of such functional groups can also alter the penetrant solubility.

Similar studies concerning aromatic polyamides have also been carried out in last years.[5–10] Aromatic polyamides offer excellent thermal and mechanical properties and good chemical resistance. They are easily spun into hollow fibers, appropriate for high-performance gas separation modules. In spite of their high cohesive energy densities and very efficient polymer chain packing, aromatic polyamides can exhibit a wide range of permeabilities values depending on their structure.[6]

Since the properties of both families of polymers are relatively complementary, it is reason-

able to consider the possibilities of their polymer mixtures in potencial applications in gas separation membranes. A previous study is, however, necessary in order to adequately characterize the miscibility of such type of mixtures. As a preliminary system, we have selected a poly(ether imide) (PEI), Ultem 1000®, and an aromatic poly(ether amide) (PEA) synthesized in our laboratories. Both polymers contain the bisphenol A moiety.

Polyimide blends have been reviewed, including examples of mixtures, where chemical interaction occurs.[11–12] For many of the solvent-cast polyimide blends,[12–14] an apparent miscibility is observed, mainly due to kinetic constraints imposed by the solvent-casting process. For instance,[13] Ultem 1000 forms homogeneous solvent-cast blends with poly(benzimidazole) which evolve to irreversible phase separation at temperatures above the blend T_g. The same amorphous polyimide (Ultem 1000) has been used in other blending studies.[12,15–19]

Nakata et al.[20] have reported a miscible blend of a different poly(ether imide) with an aramid. From these results and some previous calculations with the so-called MG&PC software,[21] we hypothesized that Ultem 1000 and an aromatic poly(ether amide) based on bisphenol A might form a miscible blend with potential applications in gas separation processes. However, preliminary results showed us the influence of the blend preparation method in the homogeneity level finally attained in the mixture.

In this article, we will primarily try to demonstrate the intrinsic miscibility of the blend components. Different preparation methods and thermal histories will be used. Given the different possible homogeneity levels existing in our mixtures, we will measure carbon dioxide transport properties through blends with different morphologies in order to check the effect of the microstructure on the final permeabilities of the polymer blend membranes.

EXPERIMENTAL SECTION

Materials and Procedures

The aromatic polyamide (PEA) has been 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 chlorosilane as an activator. Its inherent viscosity at 25°C in

DMA and its glass transition temperature were, respectively, 1.41 dL/g and 230°C. It has the following structure:
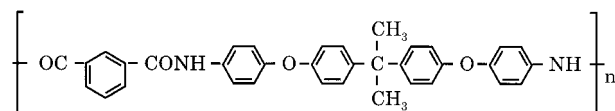
Poly(ether imide) (PEI, Ultem 1000) was used as supplied by General Electric Company Ltd, having a glass transition temperature of 218°C. It has the following structure:
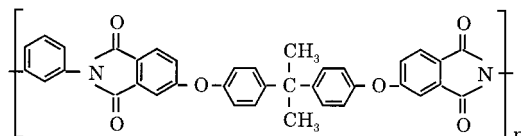
and a number-average molecular weight of 20,000.

N,N-Dimethylacetamide (DMA) was supplied by Aldrich Chem. Co., their purity being higher than 99%. The rest of the employed solvents, dimethyl sulfoxide (DMSO), pyridine (Pyr) and N,N-dimethylformamide (DMF), were supplied by Panreac. All the polymers and solvents were used without further purification.

Blend samples for DSC were obtained from clear solutions, with polymer concentration of 2% (w/v). These solutions were obtained under stirring at different temperatures depending on the solvent (110°C for DMSO, 70°C for DMF and DMA, and 30°C for Pyr). Films were prepared by casting the solutions onto hot plates at 100, 60, and 30°C, respectively. Alternatively, samples were also obtained by precipitating the same solutions in a large excess of NaCl solutions 20% (w/v) in water. The precipitated samples were washed twice with a 10% (w/v) NaCl solution and with pure water. All the samples were subsequently dried in a vacuum oven at 100°C for 10 days and, finally, at 150°C for 32 h. In all cases, blend composition is expressed in weight percentage.

In order to miscibilize heterogeneous mixtures, aging treatments were carried out in an oil bath keeping the samples under vacuum and at 245°C for 2 or 4 h. With these conditions, we tried to minimize, as much as possible, the possible incidence of interchange reactions.

Enthalpy relaxations were carried out using two different oil baths. DSC pans containing the samples under study were submerged in a first bath at 260°C for 10 min. They were quickly trans-

ferred to another bath at 210°C, where they were kept for 72 h. This annealing temperature was selected, after different tests with the pure components of our blends, as the most adequate conditions in order to get intense and well-resolved peaks. After the annealing treatment, the samples were quenched in a water–ice mixture, and DSC scans were immediately carried out at a heating rate of 20°C min^{-1} from 130 to 270°C. This procedure is similar to that described in a recent review about the different possibilities of enthalpy relaxation studies in characterizing multicomponents systems.[22] After a rapid cooling, a second scan was performed at the same rate and within the same temperature range. A Perkin–Elmer DSC-2C calorimeter was used with samples weighing between 9–12 mg. Glass transition temperatures were measured at the midpoint of the transition.

Electron microscopy (EM) measurements were carried out after gold coating of etched fracture surfaces using a Hitachi S-2700 scanning microscope operated at 12 and 15 KV. Cast films for EM were prepared from clear solutions of 5% (w/v) polymer concentration in DMSO, after a slow evaporation of the solvent in order to avoid bubles generation. The drying procedure was similar to that described above with an additional step in which the temperature was raised from 150 to 245°C at a rate of 3°C min^{-1} under vacuum. Then, the samples were frozen in liquid nitrogen and stretched up to its fracture, after which they were etched in chloroform for 1 h and finally dried.

Fourier transform infrared (FTIR) spectra were carried out in a Nicolet 5 DXC spectrometer taking 64 scans at a 4 cm^{-1} resolution. Measurements at elevated temperatures were carried out using a SPECAC high-temperature cell. The films were obtained by casting DMA solutions onto hot glass plates. The films were thin enough to be within an absorbance range where the Lambert–Beer law is obeyed.

CO$_2$ sorption measurements at 30°C and a pressure of 1 bar were carried out in a D-200 Cahn electrobalance with a sensitivity of 0.1 μg. The required films were dried with identical procedure to that above described for the EM measurements. Finally, the samples were conditioned in a vacuum oven at 100°C for 48 h. Then, they were introduced in the microbalance, where they remained 12 hs under vacuum before opening the chamber to the penetrant. The gas solubility (C_0) was calculated from the weight gain after sorption equi-

librium was reached, by means of the following relation:

$$C_0 = \frac{22414 \, M_\infty}{MW_{gas} V_{plm}} \qquad (1)$$

where M_∞ is the penetrant equilibrium mass in mg, MW_{gas} is the penetrant molecular mass, and V_{plm} is the polymer volume in cm^3; C_0 is in (cm^{3}STP/cm^3). From C_0 and assuming that the system polymer–penetrant studied obeys Henry's law, the solubility coefficient is given by $S = C_0/P$.

Under the experimental conditions used in this study, the fractional amount M_t/M_∞ of penetrant absorbed by the polymer film at time t, is given by[23] the following:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \left[\frac{8}{(2n+1)^2\pi^2} \right]$$
$$\times \exp\left[\frac{-D(2n+1)^2\pi^2 t}{4l^2} \right] \quad (2)$$

where M_t is the weight gain at time t, n is an integer, l is the film thickness, and D is the diffusion coefficient in cm^2/s. For long times, the previous equation can be approximated by

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left[\frac{-D\pi^2}{l^2} t \right] \qquad (3)$$

and D can be calculated from the linear portions of $\ln(1 - M_t/M_\infty)$ versus time representations.

If S and D are supposed to be concentration independent, the permeability (in barrers) is easily calculated as

$$P = DS(10^{10}/76) \qquad (4)$$

RESULTS AND DISCUSSION

Enthalpy Recovery Experiments

The evaluation of the phase behavior of blends of PEI and PEA is complicated by the proximity of the glass transition temperatures of both materials. Until relatively recently,[24] it has generally been believed that thermoanalytical techniques, for example, DSC, could not be used to examine the phase behavior in polymer blends whose constituents had T_gs in close proximity to each other
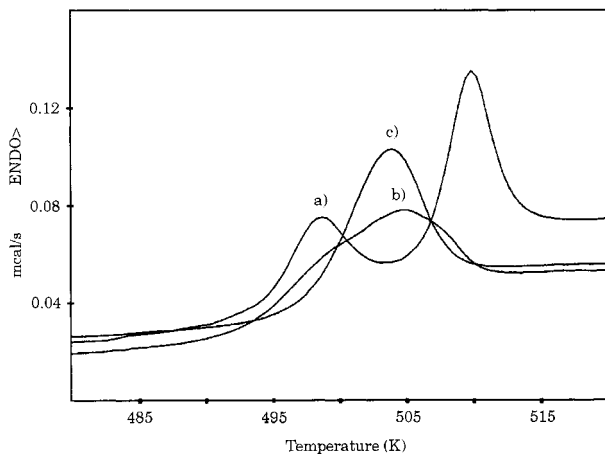
Figure 1   DSC enthalpy recovery peaks of PEA–PEI samples prepared by different methods: (a) physical mixture; (b) cast from a pyridine solution; (c) precipitated from a DMSO solution.

(10–20°C apart). But, after the consideration of the physical aging[25] and the inherent structural dependence of its kinetics[26] in the form of the enthalpy recovery, it has been shown[22,27,28] that this process is a sensitive tool for testing phase behavior in blends.

When a polymer is annealed at a temperature T_a below its T_g, there is an enthalpy loss that is recovered when the sample is heated through its glass transition temperature. The different behavior of different polymers in relaxation processes provides a valuable way to investigate the level of mixing existing in a polymer mixture. In a phase separated blend, it is possible to generate two aging peaks, with aging kinetics usually close to those of the pure polymers. A miscible blend, in contrast, will generate a single peak indicating aging kinetics intermediate between those of the pure polymers.

Figure 1 is indicative of the capacity of the experiments based on enthalpic relaxation to evidence the different level of homogeneity in blends prepared by different methods. Using a 50/50 blend as a reference, samples prepared by physical mixing of the solid powders, by casting or by solution–precipitation are compared. The figure clearly shows that, in our particular blend, the influence of the preparation method has to be considered. This is more clearly evidenced by Figure 2, which shows thermograms of different PEA–PEI compositions prepared by casting from (a) DMSO solutions and (b) by precipitation of these DMSO solutions on NaCl solutions. In both types of mixtures, evidence of heterogeneity at composi-

tions where PEI is predominant are clear. In the case of cast samples, compositions higher than 50% in PEI show a shoulder similar to that present in pure PEI. In precipitated mixtures, the shoulder is only observed at PEI concentrations equal or higher than 85%. This can be due to an incomplete DMSO elimination or to the fact that DMSO is better solvent for PEA than for PEI. In the case of precipitated mixtures, a similar behavior could occur. The heterogeneity induced by the preparation method is also evidenced by EM micrographs after chloroform etching of the PEI regions (PEA is immiscible in chloroform). Figure 3 shows the fracture surface of a PEA–PEI 30/70 blend, with the porous morphology that resulted after the PEI extraction.

We have previous experiences in such type of behavior. For instance, in mixtures of poly(methyl methacrylate) and poly(hydroxy ether of bisphenol A) the preparation method led to different levels of homogeneity in a mixture, which was
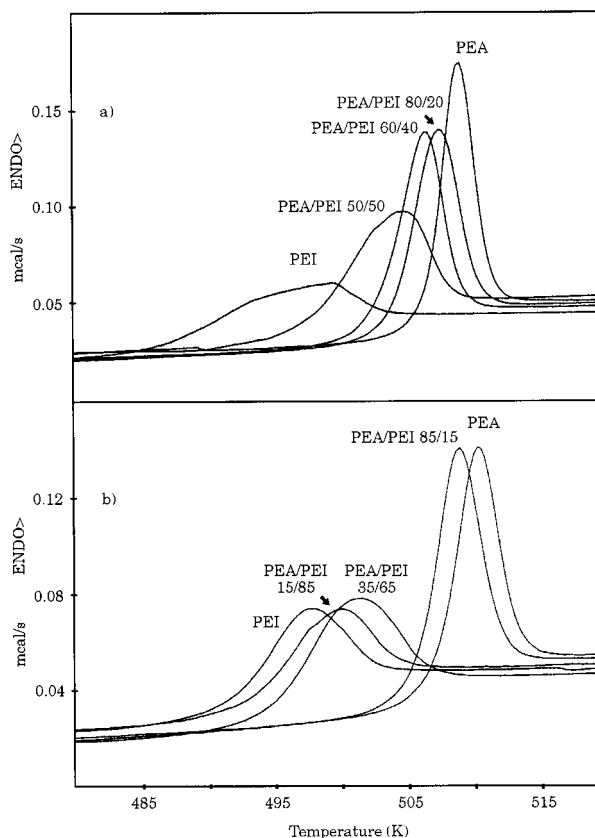

Figure 2   Enthalpy relaxation peaks of PEA–PEI blends prepared (a) by casting from DMSO solutions and (b) from DMSO solutions and precipitation on NaCl–water solutions.
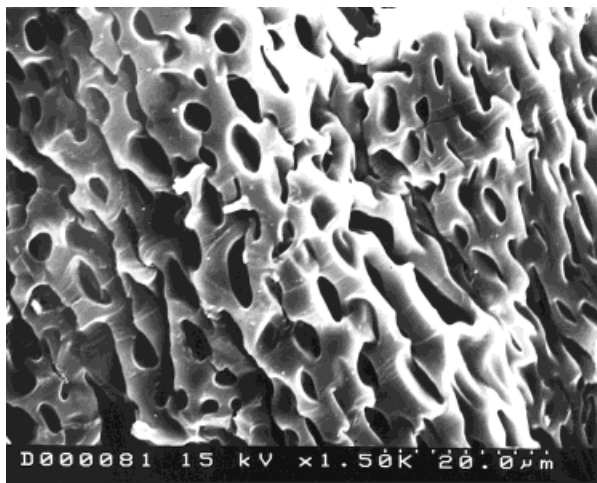
Figure 3 EM micrograph of a PEA–PEI 30 : 70 blend after etching with chloroform.

finally defined as completely miscible up to temperatures far above 200°C.[29,30] The solvent-induced heterogeneity disappeared after an adequate thermal treatment above the glass transition temperatures of the components. For this reason, we have annealed our mixtures at 245°C, in vacuo, for different periods of time, after which they were subjected to the standard procedure in order to get the relaxation peaks.

Figure 4 shows the results of the mixtures annealed at 245°C for 2 and 4 h. Both 50/50 mixtures and the pure PEI present only one well defined peak, although a shoulder is still present in compositions equal or higher than 60% PEI. When the annealing treatment was extended to 4 h [Fig. 4(b)], even the sample with 70% PEI gave only one peak after the enthalpy relaxation strategy. Figure 5 shows enthalpy recovery peaks of a mixture with 70% PEI, prepared by casting from DMSO solutions, after different annealing times at 245°C. The evolution from a wide two-peak thermogram to a narrower and single peak is evidenced.

In all these heat treatments, the remaining question is the possibility of interchange reactions between the blend functional groups. This usually leads to the formation of block or random copolymers (depending of the treatment time). These copolymers can play an active interfacial role, improving the blend compatibility. Evidence of interchange reactions in our blends were found after 6 h of annealing at 245°C. Probably due to the formation of some crosslinked structures, blends subjected to this treatment were not completely soluble in DMSO at the same conditions at which

blends without heat treatments (or heated during 2 or 4 h) were completely soluble. Additionally, new peaks arising from the formation of new chemical entities were not detected by ^{13}C nuclear magnetic resonance (^{13}C-NMR) up to a treatment time of 16 h.

When samples prepared by precipitation of DMSO solutions were subjected to the same treatment, a time of 2 h was enough to give a unique relaxation peak in all the investigated samples [see Fig. 6(a)]. This confirms the higher heterogeneity level produced by the casting method. Since the use of DMSO as a solvent was cumbersome and given that it was easier to dissolve our blends in DMF, DMA, or pyridine than in DMSO, samples were also prepared from solutions in these solvents (It is interesting to note that we had to heat at 110°C when using DMSO, whereas we only needed 70°C for DMF and DMA and 30°C for pyridine). Figure 6(b) shows the enthalpy recovery peaks of samples prepared by solution in
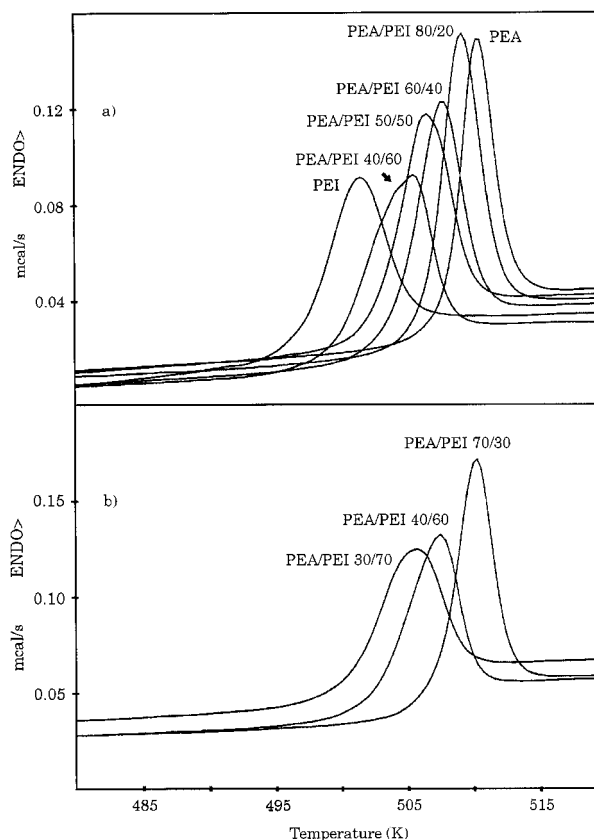

Figure 4 Enthalpy relaxation peaks for PEA–PEI blends obtained by casting from DMSO solutions after annealing at 245°C: (a) 2-h annealing time; (b) 4-h annealing time.
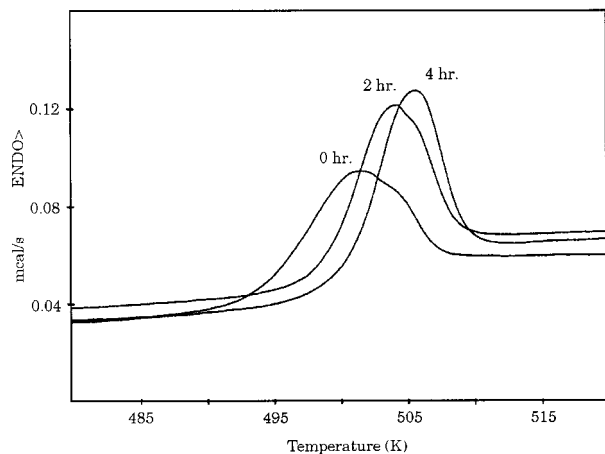
Figure 5 Influence of the annealing time on the enthalpy relaxation of a PEA–PEI 30 : 70 blend obtained by casting from a DMSO solution.

DMA and subsequent precipitation, after a homogenization at 245°C for 2 h. Similar results were obtained with samples precipitated from DMF and pyridine solutions. Without the homogenization procedure at 245°C, the behavior was similar to that found in DMSO solutions.

In summarizing the annealing treatments, we could infer that they allowed to remiscibilize heterogeneous PEA–PEI blends obtained by casting or precipitation. For high PEI concentration samples and, particularly for those obtained from casting, longer annealing times are required to assure their total remiscibilization. Results with precipitated mixtures are particularly interesting, given the usual technological preparation of membranes by coagulating polymer solutions with a precipitant.

Although the annealing process to get miscibility seems to be adequately controlled, we tried to visualize the transition from a heterogeneous to a homogeneous mixture using scanning electron microscopy (SEM). However, the required samples for such study are much thicker than those used in the enthalpy recovery experiments. Consequently, severe heating treatments (giving rise to interchange reactions) would be required to get homogeneous samples. Using conditions of temperature and time where interchange reactions can be excluded, SEM micrographs did not conclusively show a complete miscibilization process.

Additional attempts were performed to prepare homogeneous blends by melt-mixing or freezing-drying. All of them were unsuccessful. In the first case, the high viscosity of the melt required high processing temperatures, which induced a rapid

degradation of the mixtures. In the freezing-drying method, the use of DMSO as a solvent was probably not the best alternative.

As a conclusion of our experimental attempts, Figure 7 summarizes the evolution of the T_g in different PEA–PEI compositions prepared by different methods and subjected to adequate aging procedures to induce miscibility. The nearly linear T_g-composition relationship is a good proof of the miscibility between the blend components. Additionally, the good agreement between the T_g values obtained with blends prepared by different methods demonstrates that equilibrium conditions were attained in all the cases.

FTIR Spectra of PEA–PEI Blends

Blends of aromatic–aliphatic and fully aromatic polyamides have been previously studied.[21,31,32] In
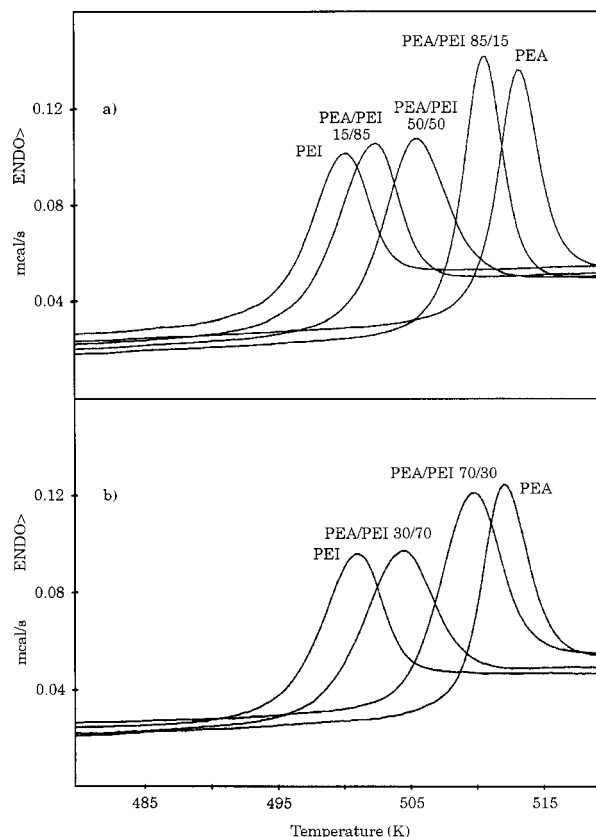

Figure 6 Enthalpy relaxation peaks for the PEA–PEI blends: (a) prepared by precipitation of DMSO solutions on NaCl–water solutions after 2 h at 245°C; (b) obtained from DMA solutions by precipitation on NaCl–water solutions and identical annealing treatments.
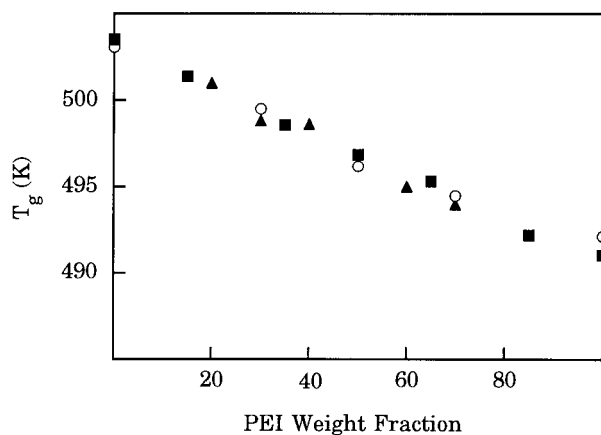
Figure 7 Glass transition temperatures (second scan) for PEA–PEI samples depending on the preparation method and annealing treatment: (▲) by casting from DMSO solutions and 4 h at 245°C; (■) by precipitation of DMSO solutions on NaCl–water solutions and 2 h at 245°C; (○) by precipitation of DMA solutions on NaCl–water solutions and 2 h at 245°C.

all these articles, FTIR spectroscopy was able to evidence the existence of specific, hydrogen bonding type interactions between the components of the mixture. However, the existence of such a type of interactions is not a conclusive proof of miscibility at a molecular level.

The FTIR 1720–1620 cm^{-1} region, corresponding to the stretching vibration of the amide carbonyl group (Amide I band) is the range in which most of the IR studies have been carried out. This broad band is the consequence of the partial superposition of vibrations arising from two very different situations of the carbonyl groups: one corresponds to the free amide carbonyls, and the other one is a consequence of carbonyl groups involved in self-associations by hydrogen bonds with NH groups. In the case of our PEA, these bands are centered, respectively, at 1680–1670 ("free" carbonyls) and 1660–1650 cm^{-1} (associated carbonyls). In comparing it with other aliphatic–aromatic polyamides,[31,32] our PEA has a minor number of self-associated amide carbonyls.

If PEA and any other polymer containing adequate basic functional groups could be able to interact via hydrogen bonds, as expected in the case of forming miscible blends, the new associations would be formed after breaking some self-associations of NH and carbonyl PEA groups. Consequently, the number of self-associated carbonyls in the blends should decrease in relation to those appearing in pure PEA. In this sense, Figure 8

collects spectra of PEA–PEI blends at different compositions and at 25°C. Although at this temperature, both polymers and their mixtures are below their glass transition temperatures, these T_gs are high enough to assume that during the cooling process the mixed liquid state of the mixture has been adequately frozen.

In this figure, the intensity of the self-associated carbonyl band decreases strongly as the blends become richer in PEI. This behavior is similar to that found in some mixtures of aliphatic–aromatic polyamides and poly(ethylene oxide).[31,32] Although PEI is considered as a poor proton-accepting polymer,[33] a significant molecular mixing should be necessary to explain the decrease in the PEA self-association level. However, this does not mean that the blends must be in a single phase. In fact, we have previously demonstrated that samples prepared by casting can show one or two enthalpy recovery peaks, depending on the composition.

In any case, FTIR spectra, as those shown in Figure 8, are qualitatively evidencing that some kind of molecular mixing had occurred in the blend, regardless of whether they were perfectly mixed or not. This is particularly true if this situation is compared with the FTIR spectra of some clearly immiscible blends between aliphatic–aromatic polyamides and PEO,[31,32] where the carbonyl band does not suffer changes similar to those observed in Figure 8. However, in our case, truly miscible blends and partially miscible or nonequilibrium heterogeneous blends show similar trends in the carbonyl region.
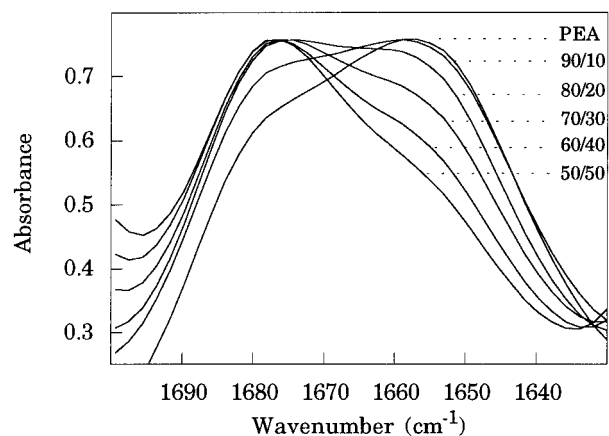
Finally, a 50/50 blend was used as a test of the

Figure 8 1700–1630 cm^{-1} FTIR region (at room temperature) of the PEA–PEI blends obtained by casting from DMSO solutions.

Table I   CO$_2$ Transport Properties of PEI, PEA, and Blends

Polymer Film	C_0 (cm^3 STP cm^{-3})	$D \times 10^{10}$ (cm^2 s^{-1})	Permeability (barrers)
PEI	6.4	13.8	1.2
PEA	5.8	62.4	4.7
50/50 one phase	6.0	27.7	2.2
50/50 two phases	6.1	23.5	1.9

FTIR possibilities to evidence the changes occurring in the blend when a thermal miscibilization process is applied. Unfortunately, no significant differences were found between the spectra of a 50/50 blend with and without thermal treatment at 245°C. This is consistent with some level of random mixing in all cases. Annealing treatments would improve the uniformity of the mixtures but without giving detectable changes in the wave number or peak intensity of the investigated bands.

Sorption Measurements

For this purpose, four films of similar thickness were prepared from DMSO solutions corresponding to pure PEA (thickness 15.9 μm), pure PEI (12.6 μm), a PEA–PEI 50 : 50 that has an unique enthalpy recovery peak (14.7 μm), and a PEA–PEI 50 : 50 that presents two enthalpy recovery peaks (13.6 μm). Table I resumes the CO$_2$ transport properties of the different investigated samples.

Both permeability and diffusion coefficients for PEI–CO$_2$ are in good agreement to those reported by Barbari et al.[34] No significant differences were found in films of the two different blends as far as the solubility is concerned, perhaps the more reliable experimental data accessible to our experimental device. The solubility coefficient seems to follow the additive rule. The diffusion coefficient, the other experimental parameter obtained from our sorption curves, is subjected to a larger uncertainty, but results from homogeneous and heterogeneous blends do not differ significantly. Both deviate negatively from the additive rule, perhaps as a consequence of the specific interactions occurring in the mixture. Similar negative deviations from the additive rule have been observed in other mixtures with[35] and without[36] specific interactions between the functional groups of the components. Finally, the permeability, indirectly measured as the product of S and D, is higher in

the homogeneous blend, but this result must be taken with caution given the D uncertainties previously mentioned. Further studies, covering direct measurements of the permeability and sorption experiments at higher pressures are being carried out.

CONCLUSIONS

In this article, blends of a poly(ether imide) and an aromatic poly(ether amide) have been studied. Our data seem to prove their intrinsic miscibility although, as in other blends, solvent-cast films were unhomogeneous and needed annealing treatments in order to get truly miscible mixtures. However, blends prepared by precipitation of the same solutions exhibited, in general, improved levels of homogeneity. Preliminary carbon dioxide sorption experiments were carried out both in homogeneous and heterogeneous blends. Diffusion and permeability coefficients deviated from the additive rule. However, the homogeneity level did not seem to affect the transport properties.

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