

Structure and Mechanical Properties of Blends of Poly(ϵ -caprolactone) with a Poly(amino ether)

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ABSTRACT: Poly(ϵ -caprolactone) (PCL)/poly(amino ether) (PAE) blends were obtained by injection molding without any previous extrusion step in an attempt to (i) contribute to the knowledge of the relation between structure and mechanical properties in these type of blends composed of a rubbery and a glassy polymer and (ii) to find out to which extent are the PCL/PAE blends compatible, and therefore whether the biodegradability of PCL can be added as a characteristic of PAE-based applications. PCL/PAE blends are composed of a crystalline PCL phase, a pure amorphous PCL phase, and a PAE-rich phase where some PCL is present. The presence of some dissolved and probably unreacted PCL in the PAE-rich phase led to a

low interfacial tension as observed by the small size of the dispersed particles and the large interfacial area. The dependence on composition of both the modulus of elasticity and the yield stress of the blends was parallel to that of the orientation level. The elongation at break showed values similar to those of PAE in PAE-rich blends, and was slightly synergistic in very rich PCL compositions; this behavior reflects a change in the nature of the matrix, from glassy to rubbery. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3892–3899, 2008

Key words: poly(ϵ -caprolactone); poly(amino ether); blends; structure; mechanical properties

INTRODUCTION

Polymer blending continues to be one of the most attractive and studied research and development fields in Polymer Science and Technology. This is mainly due to the ability of blending to create new materials whose performance can be tailored for a given application. The efficiency of blending in the development of new polymeric materials is demonstrated by the large amount of (i) commercial blends introduced in the market¹ and (ii) patents which are registered annually.²

One of the most important problems associated with the use of plastics is the waste they give rise to. This problem is particularly relevant for packaging applications, which constitute a high proportion (37%) of the consumption of plastics in Europe³ and lead to at least 61 million tons of waste per year.⁴ Recycling is increasingly being used to reduce waste; hence, biodegradable materials have appeared as an alternative when recycling is difficult or unfavorable from an economic point of view.

A promising class of synthetic biodegradable polymers are the aliphatic polyesters, such as poly(ϵ -caprolactone) (PCL), poly(hydroxy butyrate) (PHB), poly(lactic acid), poly(glycolic acid), and poly(butylene succinate).⁵ Among them, PCL is particularly interesting due to properties such as excellent water resistance⁶ and very high flexibility.⁵ Moreover, PCL shows a remarkable ability to blend successfully with chemically different polymers.^{7–9} Thus, PCL is fully miscible^{8,9} with poly(vinyl chloride), nitrocellulose, polyepichlorohydrin, as well as with poly(hydroxy ether of bisphenol A) phenoxy,^{7–9} polycarbonate (PC),^{10–12} and styrene-acrylonitrile copolymers (SAN).¹³ Its blends with poly(vinyl acetate), polystyrene, and poly(methyl methacrylate) show mechanical compatibility, i.e., a favorable mechanical behavior,^{8,9} and those with polyethylene and polypropylene present crystalline interaction.^{8,9} Moreover, it interacts with epoxy resins^{14,15} and poly(vinyl alcohol),¹⁶ and reacts with poly(ethylene terephthalate) (PET).¹⁷ Finally, it has been used as a compatibilizer in polyurethane (PU)/SAN¹⁸ and PC/SAN¹⁹ blends, and also in SAN nanocomposites.²⁰ Nanocomposites based on PCL^{21,22} or PC/PCL blends²³ have also been studied.

Poly(amino ether) resins are a new family of thermoplastics characterized by very good barrier properties, excellent adhesion to different substrates, high optical clarity, low color, and good toughness.²⁴ Their potential applications are mainly in the pack-

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aging industry. Blends of a poly(amino ether) based on diglycidyl ether of bisphenol A (PAE) with polyamide 6,^{25–27} poly(butylene terephthalate) (PBT),²⁸ an amorphous polyamide,²⁹ and glycol-modified PET (PCTG 5445)³⁰ have been studied in our laboratory. PET/PAE blends could be obtained by mixing PET with PBT.³¹ Moreover, another poly(amino ether) has been used as a compatibilizer for polyamide 6/PBT blends.³²

Blends of PAE with biodegradable polymers may be a way to develop new packaging materials. Moreover, PAE could lead to miscible or at least mechanically compatible blends with PCL; this is due to the possibility of having specific interactions or even reactions between its lateral hydroxyl groups and the ester groups of PCL. Moreover, because these are blends of a rubbery with a glassy polymer, they will also provide insight into the relationship between structure and properties in this kind of blends.

In this work, the structure and properties of PCL/PAE blends obtained by direct injection molding are studied throughout the full composition range. The phase structure and the miscibility level of the blends were characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The possible changes of the chemical structure and the interactions between the blend components were studied by Fourier Transform infrared spectroscopy (FTIR). The orientation in the solid state and the change of free volume of mixing were also evaluated. The morphology was analyzed by scanning electron microscopy (SEM) and the mechanical properties were determined by means of both tensile and impact tests.

EXPERIMENTAL

The polymers used in this work were poly(ϵ -caprolactone) (PCL) CAPA 6800 ($M_w = 80,000$) obtained from Solvay (Warrington, UK), and a poly(amino ether) resin (PAE) supplied by Dow Chemical (Michigan, USA) under the trade name Blox. The melt flow index (MFI) of PCL was 7.3 g/10 min at 190°C and with 2.16 kg load and that of PAE, 8.5 g/10 min, determined at 200°C and with 2.16 kg load (ASTM D-1238).

Prior to blending, PAE was dried at 65°C for 6 h. No drying treatment was applied to PCL. The PCL/PAE blends were prepared by direct injection molding with 100, 80, 60, 50, 40, 30, 20, 10, and 0 PCL contents. Injection molding was carried out in a Battenfeld BA230E reciprocating screw injection molding machine to obtain tensile (ASTM D-638, type IV) and impact (ASTM D-256) specimens. The screw had a diameter of 18 mm, L/D ratio of 17.8, compression ratio of 4, and helix angle of 17.8°. All compositions

were processed at a melt temperature of 200°C, with the exception of the neat PCL that was processed at 160°C to prevent melt drooling through the nozzle of the plasticization unit of the injection molding machine, which did not occur in the rest of the compositions. The mold temperature was 20°C and the injection speed and pressure were 7.4 cm³/s (10 cm³/s for the neat PCL) and 2300 bar, respectively.

The phase behavior of the blends was analyzed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The DSC scans were carried out in a Perkin–Elmer DSC-7 calorimeter under a nitrogen atmosphere. The samples were first heated from 25 to 125°C at 20°C/min to erase any previous thermal history, and then cooled to 25°C at the maximum speed provided by the calorimeter, and subsequently reheated as in the first scan. The melting temperatures (T_m) were determined from the second heating scans. The crystalline contents of the injection molded samples were calculated from the melting enthalpies of the first heating scans, using $\Delta H_m^0 = 139.5$ J/g for 100% crystalline PCL.¹⁰ The glass transition temperatures were measured by dynamic mechanical tests carried out in a TA Instruments DMA Q800 in the flexural mode, at a frequency of 1 Hz and at a heating rate of 4°C/min from –120 to 110°C.

The possible occurrence of either interactions or reactions during processing was analyzed by FTIR spectroscopy (Nicolet Magna IR 560 spectrophotometer). The FTIR spectra were obtained from the surfaces of tensile specimens using an attenuated total reflectance (ATR) objective. Density measurements were carried out in a Mirage SD-120L electronic densitometer with *n*-butyl alcohol as the immersion liquid. To minimize the experimental error, the measurements were carried out on impact specimens (approximate weight: 2.6 g). The temperature (25°C) was controlled with a precision of $\pm 0.1^\circ\text{C}$. The specific volume of the amorphous phase of the blends was obtained from the experimental density values (ρ_b) using the equation:

$$\frac{1}{\rho_b} = \frac{1 - X_{\text{PCL}}}{\rho_a} + \frac{X_{\text{PCL}}}{\rho_{\text{PCLc}}}$$

where X_{PCL} is the crystalline content of the blend calculated by DSC as indicated previously, ρ_a is the density of the amorphous phase of the blend, and ρ_{PCLc} is the density of crystalline PCL (1.194 g/cm³).³³

The tensile tests were carried out on the injection molded specimens with an Instron 4301 tester at (23 ± 2)°C and at a crosshead speed of 10 mm/min. The Young's modulus, yield stress, break stress, and elongation at break, measured as the break strain, were obtained from the load-elongation curves. Notched Izod impact tests were carried out on a Ceast 6548/000 pendulum. The notches (depth =

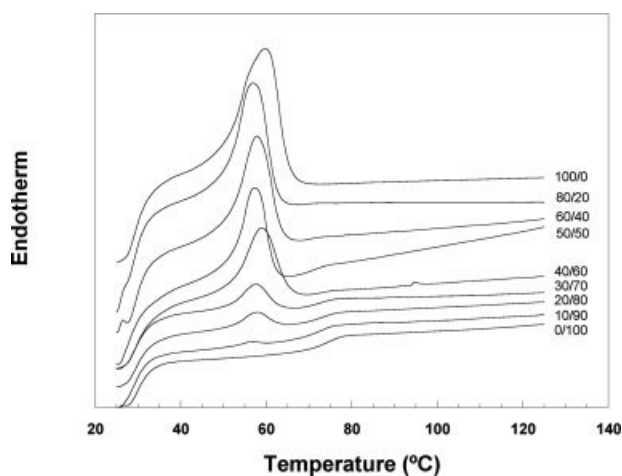


Figure 1 Second heating DSC scans of PCL/PAE blends. To aid clarity, the curves are shifted on the vertical axis.

2.54 mm and radius = 0.25 mm) were machined after injection molding. A minimum of eight specimens were tested for each reported value in both the tensile and impact tests.

The surfaces of cryogenically fractured specimens were observed by SEM after gold coating. A Hitachi S-2700 electron microscope was used at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Phase behavior

Crystalline phase

The crystalline phase of the blends was studied by DSC (Fig. 1). As can be seen, a broad melting peak centered at 60°C was obtained for pure PCL, in agreement with previous works.^{11,14} The melting peak was difficult to observe in the 10/90 composition. A second melting peak for PCL, not observed in the blends of this study, was observed in its blends with epoxy resins,^{14,34} indicating a reorganization during heating of the originally ill-crystallized polymer. As it is also observed in Figure 1, the T_m of PCL was slightly lower in the blends (3°C in the 80/20 blend) than in the neat state. Although not observed in miscible PC/PCL blends,¹¹ a T_m depression of PCL has been observed in other miscible blends as a consequence of smaller lamellar thickness.³⁵

The crystalline content of PCL is shown in Figure 2. The dependence of the crystalline content on composition was approximately linear, except at low PCL contents, where there is a negative deviation. Thus, the crystalline content of the neat PCL (42%) remained almost constant in its blends. This lack of decrease in the crystallization ability of PCL in the

presence of PAE suggests that interactions between the blend components are not strong.^{2,25}

Amorphous phase

When the amorphous phase behavior of the blends was analyzed by DSC, the T_g of PAE lied within the melting range of PCL. Moreover, the high crystallinity of PCL and its low T_g value (near -60°C)^{8,35} also made difficult the determination of this transition by DSC. For this reason, the T_g s were examined by DMA.

Two $\tan \delta$ peaks were observed in the DMA scans, revealing the presence of two amorphous phases. The intensity of the $\tan \delta$ peak of PAE was much higher than that of PCL. For this reason, the temperature ranges where the T_g s of PAE and PCL lie are shown separately in Figure 3(a,b). As can be seen in Figure 3(a), the T_g of PAE decreased slightly and continuously as the PCL content increased. At PCL contents higher than 50% the T_g was not clearly observed due to the melting of PCL. The slight decrease in the T_g of PAE indicates the presence of small amounts of PCL in the PAE-rich phase of the blends.

In Figure 3(b), the T_g of PCL is centered at -43°C . This agrees with previous results by DMTA.³⁶ A DSC measurement,³⁶ gave a value of -74°C because the technique used is known to influence the position of T_g .³⁷ Heuschen et al.³⁸ reported that the T_g of PCL varies from -60 to -71°C when the crystallinity changes from 50 to 0%. This is due to the restriction in mobility that the crystalline phase imposes on the amorphous chains.² In Figure 3(b), the T_g of PCL and the β -relaxation of PAE overlapped. In any case, no increase in the T_g of PCL with the PAE content was observed indicating the presence of a practically pure PCL phase. Thus, the PCL/PAE blends are partially miscible and are composed of a practically pure PCL phase and a PAE-rich phase that contains slight amounts of PCL, in addition to the crystalline PCL phase. This indicates that some inter-

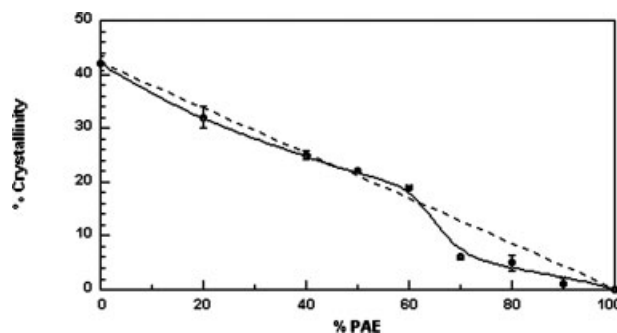


Figure 2 Crystalline content of the blends in the first DSC scan as a function of composition.

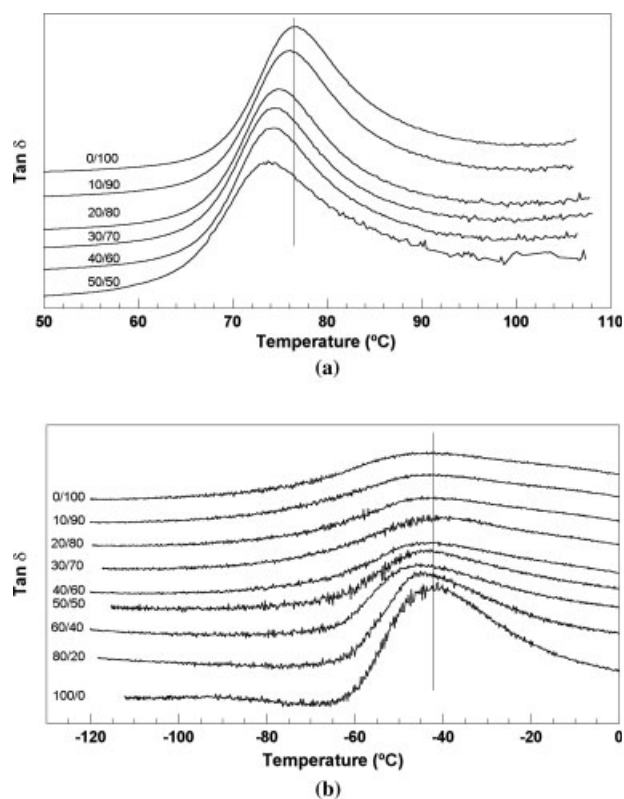


Figure 3 DMA ($\tan \delta$) plots of the PCL/PAE blends versus temperature; (a) range of $\tan \delta$ peak of PAE, (b) range of $\tan \delta$ peak of PCL. To aid clarity, the curves are shifted on the vertical axis.

action exists between the components of the blend, despite the lack of change in crystalline content.

The presence of small amounts of PCL in the PAE-rich phase could be due to intermolecular hydrogen-bonding interactions between the lateral hydroxyl groups of PAE and the carbonyl groups of PCL. This is because hydrogen-bonding has been shown to exist between PCL and polymers with lateral hydroxyl groups like phenoxy,⁷ epoxy resins,³⁴ and poly(styrene-*co*-vinyl phenol) (PSOH).³⁹ Moreover, the possibility of having interchange reactions between the ester and hydroxyl groups during processing also exists in these blends. To gain insight into which of these two scenarios is true, the blends were studied by FTIR, comparing the experimental spectra of some compositions with those calculated by weighted addition of the spectra of the neat components. Although almost no difference was observed between the experimental and the calculated spectra in the 20/80 and 40/60 PCL/PAE blends (Fig. 4), the carbonyl band of PAE-rich blends shifted slightly. These shifts can be due to either reactions or interactions between the blend components. However, taking into account their low intensity, we mainly attribute the slight partial miscibility observed to interactions between PCL and PAE,

although a very low reaction level could not be ruled out.

Morphology

Figure 5 shows representative SEM micrographs of the surfaces of cryofractured tensile specimens of blends with 80, 60, 40, and 20% PCL. Figure 5(a) shows the presence of nearly spherical particles, homogeneously distributed and with a fairly small particle size (typically 0.3 μm). This fine morphology was attributed to the presence of some PCL in the two phases of the blends, as previously observed in PCL-based¹⁵ and PAE-based^{25,28,30} blends. The particle size increased with increasing concentration of the dispersed phase because, together with the small particles, some larger (0.5–0.7 μm) particles appeared in the 60/40 blend [Fig. 5(b)]. Although some debonding was observed in some large particles, the

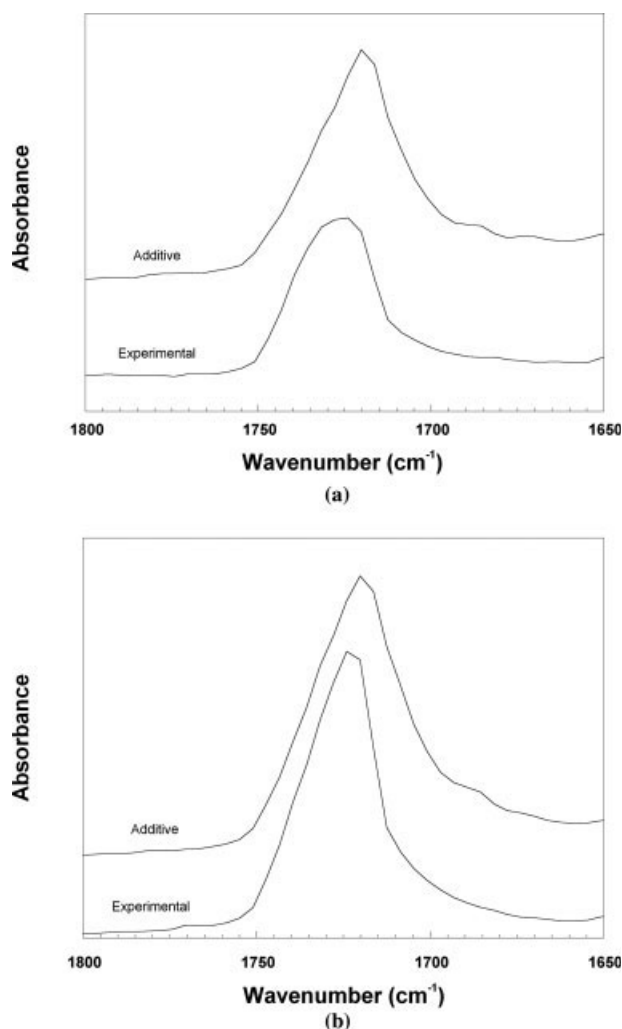


Figure 4 Comparison between experimental and calculated FTIR spectra for 20/80 (a) and 40/60 (b) blends. To aid clarity, the curves are shifted on the vertical axis.

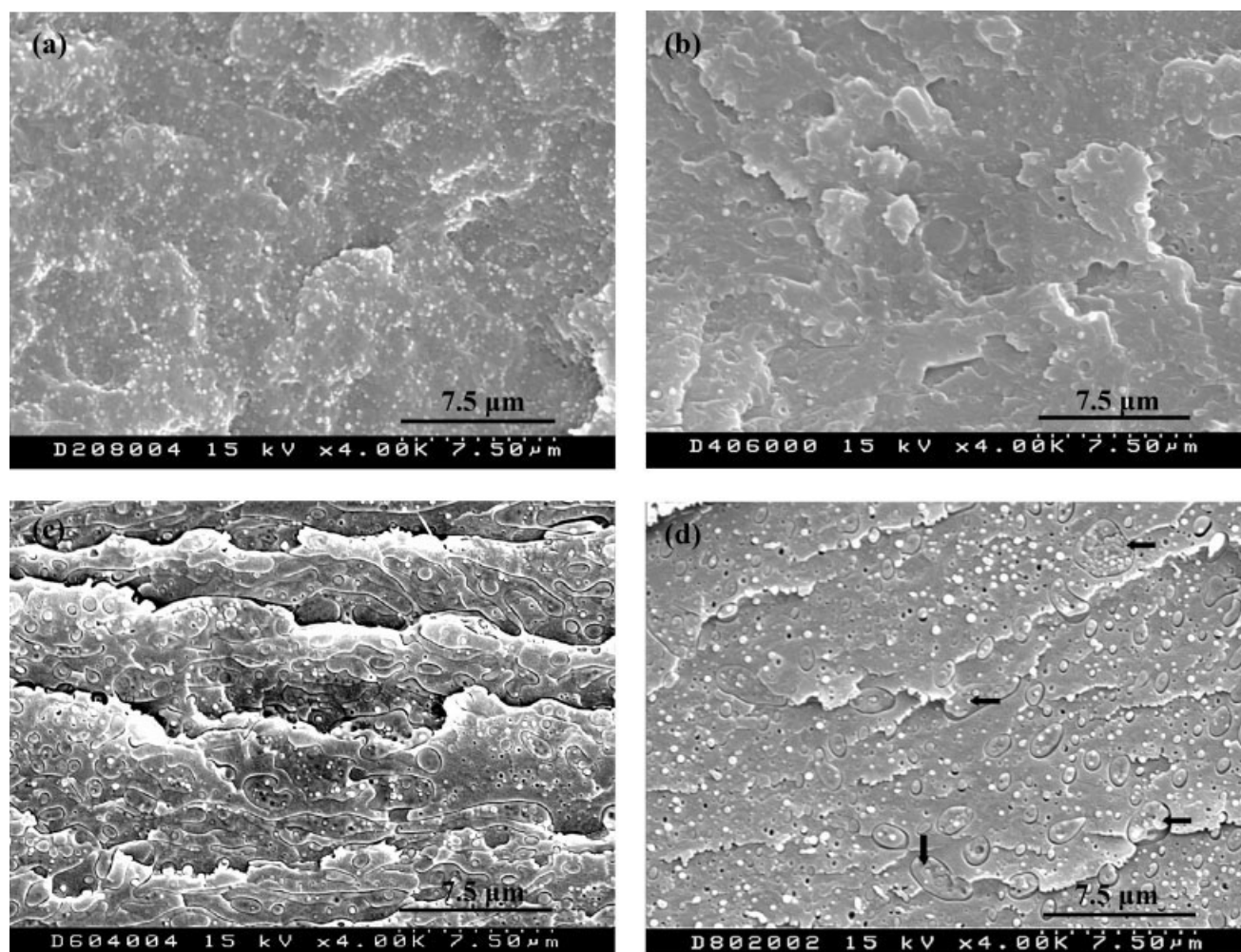


Figure 5 SEM micrographs of the PCL/PAE blends at PAE contents of 20% (a), 40% (b), 60% (c) and 80% (d). All micrographs 4000x.

dispersed particles were clearly integrated into the matrix.

The nearly cocontinuous morphology of the 40/60 composition [Fig. 5(c)] indicates that it is close to phase inversion. The particle size of the 20/80 blend [Fig. 5(d)] was larger than that of Figure 5(a). This particle size increase is attributed to the lower viscosity of PAE (kneading torque: 3 Nm) with respect to that of PCL (kneading torque: 4.6 Nm) and to the higher elasticity of the minor component. However, the most striking characteristic of Figure 5(d) is the presence of larger (1–3 μm) PCL particles with occluded subparticles. Some of these PCL particles are indicated by arrows. The nature of the occlusions must be that of the matrix. These subparticles are similar to those observed in other PAE-based blends^{29,30} and lead to a large interfacial area/particle volume ratio, indicative of a low interfacial tension. The small particle size in most of the fracture surfaces also indicates that the interfacial tension in the melt state was low, and consequently the adhe-

sion level in the solid state was high. The lack of holes in Figure 5 also testifies to a high adhesion level. Finally, both the small particle size and the complex morphology (presence of subparticles) suggest that, as observed in previous works,^{25,40} mixing by direct injection molding was very effective in the conditions of this study.

Mechanical properties

The Young's modulus and the yield stress of PCL/PAE blends as a function of composition are shown in Figures 6 and 7, respectively. As can be seen, the behavior of both properties was qualitatively similar. This is a common result in neat polymers⁴¹ and polymer blends³⁷ and is due to the fact that both properties are measured at small strains and therefore they are affected by similar structural parameters. Most experimental values were below the arithmetic average of the properties of the two pure components, mainly in the PCL-rich blends. The

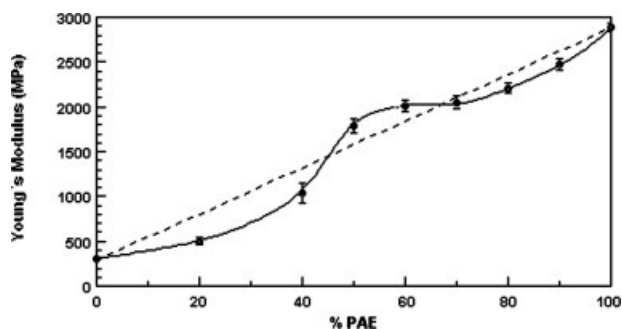


Figure 6 Young's modulus of the PCL/PAE blends as a function of composition. The dotted line is the linear extrapolation between the values of the neat components and the curve is a fitting of the experimental data.

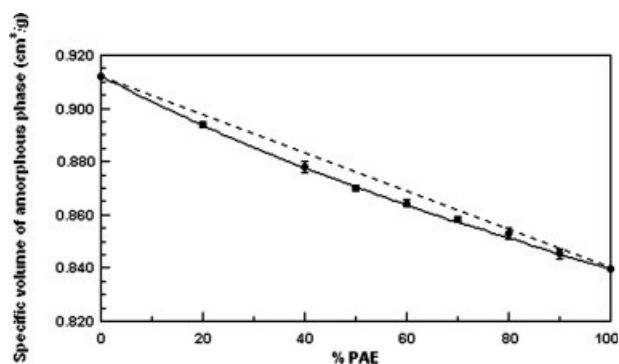


Figure 8 Specific volume of the amorphous phase of the PCL/PAE blends as a function of composition. Dotted line and curve as in Figure 6.

behavior of the 50/50 and 40/60 compositions can be attributed^{42,43} to a change in the thermal expansion coefficient and in the mobility of the phases⁴⁴ when the matrix is below T_g (PAE-rich blends) and above T_g (PCL-rich blends). This is supported by the fact that the phase inversion of the blends was located near the 40/60 composition (Fig. 5).

Three main parameters have to be considered to explain the behavior of the properties at small strains: (a) the free volume,⁴⁵ (b) the level of crystallinity of the crystallisable polymer,⁴⁶ and (c) the molecular orientation.⁴⁷ A possible effect of the interchange reactions can be discarded, because if it indeed occurred, the extent of reaction must have been very small. The free volume change on blending was studied by means of the specific volume of the amorphous phase^{28,48} shown in Figure 8 against blend composition. A slight negative deviation from linearity was observed throughout the composition range. It indicated a slight densification of the blends which stiffens the blends and consequently leads to a positive deviation with respect to linearity in the modulus and the yield stress. However, the change was close to the experimental error and, moreover, the overall behavior of the specific volume was clearly different to that of the modulus and the yield

stress. Consequently, this parameter does not explain the observed behavior of these properties against composition. The crystallinity of the blends (Fig. 2) changed in a way that was qualitatively similar to that of the small strain properties, but its change was too small to lead to the changes observed in the mechanical properties.

The orientation of the neat components and the blends was analyzed⁴⁹ by birefringence measurements at the central part of the tensile specimens and the results are shown in Figure 9 as a function of composition. As it is seen, the birefringence, and consequently the molecular orientation of the blends, is lower than the linear extrapolation between the values of the neat components with the exception of the compositions with 50 and 60% PAE contents. Reasons for different orientations in the blends compared to those in the neat state are related⁵⁰ with different free volume, entanglement density, and possible specific interactions between the components of the blends. Moreover, the viscosity of the blends and the effect of shear also change with composition, thus, changing the molecular orientation. As can be seen, the dependence of Figure 9 was parallel to that of the small strain properties. This allows us to propose that the orientation in the blends and in the

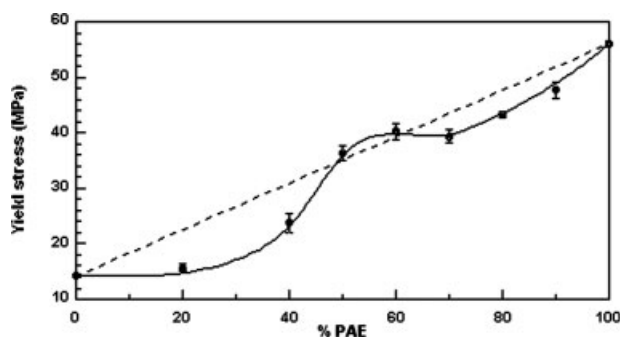


Figure 7 Yield stress of the PCL/PAE blends as a function of composition. Dotted line and curve as in Figure 6.

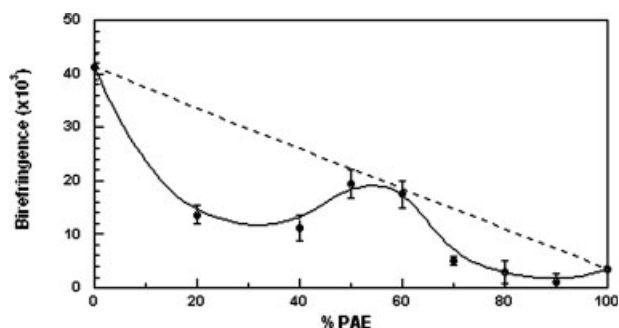


Figure 9 Birefringence of the PCL/PAE blends as a function of composition. Dotted line and curve as in Figure 6.

neat state is the main parameter that influences the small strain mechanical properties of the blends of this study.

The elongation at break of the blends is shown against composition in Figure 10. The break stress behavior was similar to that of elongation at break. As can be seen, the blends rich in PCL showed high and even slightly synergistic elongation at break values, while the intermediate and PAE-rich compositions values were close to that of pure PAE (30%). The differences in elongation at break observed are very large and cannot be related with those of the structural parameters studied in Figures 2, 8, and 9. They are most likely due to a change in the nature of the matrix of the blends, from rubbery to glassy. In other blends of glassy and rubbery polymers as Phenoxy/Hytrel⁴² and polycarbonate (PC)/Hytrel,⁴³ drastic elongation at break decreases were also observed when the nature of the matrix component changed from rubbery to glassy.

Finally, the notched impact strength of PCL/PAE blends is presented in Table I. As expected, the rubbery PCL and PCL-rich blends did not break. The impact strength of the blends increased progressively with PCL content. This behavior and that of the elongation at break agree with the small size of the dispersed phase particles discussed in the morphology section.

CONCLUSIONS

The PCL/PAE blends obtained by direct injection molding, were composed of a crystalline PCL phase, a pure amorphous PCL phase, and a PAE-rich phase with small amounts of PCL. The presence of PCL in the PAE-rich phase was attributed to intermolecular interactions, although the occurrence of a minor extent of reactions during processing cannot be fully discarded.

Despite the absence of a previous mixing stage, the morphology of the blends demonstrated effective mixing that rendered an overall fine (0.3–0.7 μm)

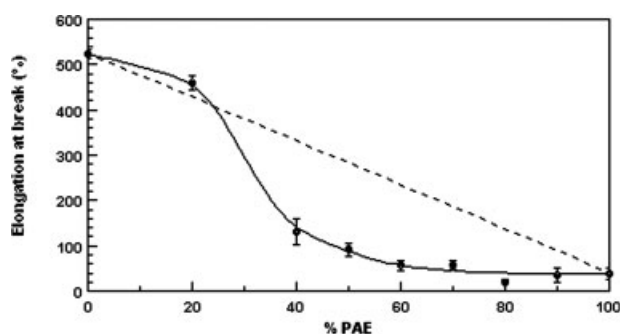


Figure 10 Elongation at break of the PCL/PAE blends as a function of composition. Dotted line and curve as in Figure 6.

TABLE I
Notched Izod Impact Strength Values of the Blends

% PAE	Impact strength (J/m)
0	NB
20	NB
40	NB
60	126 \pm 12.3
70	132.3 \pm 17.3
80	104.1 \pm 18.1
90	68.5 \pm 17.3
100	9.9 \pm 0.9

dispersed particle size. In PAE-rich blends larger particles with occluded subparticles that assured a large interphase area were present.

The dependence of Young's modulus and the yield stress on composition showed a slight negative deviation from linearity with the exception of the 50/50 and 40/60 compositions. This behavior was mainly attributed to a different orientation in the blends with respect to the pure components, based on the similarity between the plot of the birefringence and those of the Young's modulus and the yield stress. The overall behavior of the elongation at break, with values similar to or slightly higher than those of pure PAE in PAE-rich blends, and slightly synergistic in the PCL-rich compositions, was attributed to a change in the nature (glassy/rubbery) of the matrix. The high break properties values observed in the PCL-rich blends are a consequence of the homogeneous and fine morphology, and of the high adhesion between phases in the solid state, observed by SEM and attributed to the presence of some PCL in the PAE-rich phase.

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