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Linear unsaturated polyester + poly(ε-caprolactone) blends: Calorimetric behaviour and morphology

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Abstract

Blends of a linear unsaturated polyester (LUP, commercially named Al100) with poly(ε-caprolactone) (PCL) of different molecular weights have been studied. The miscibility and crystallinity have been analyzed through FT-IR spectroscopy, differential scanning calorimetry (DSC) and environmental scanning electronic microscopy (ESEM). All the blends were subjected to the same heat treatment consisting of crystallizing during 45 min at constant temperature (10, 20, 30 or 40 °C). The glass transition temperature, T_g, and fusion temperature, T_{fus}, have been determined in the whole composition range for each blend. The T_g-composition dependence and the high degree of crystallinity detected at intermediate blend compositions denote an anomalous behaviour that could indicate the lack of homogeneity (phase separation) in the different blends studied. The ESEM measurements confirm the lack of homogeneity of the amorphous region in blends with high content of LUP. The results have been discussed as a function of the crystallization temperature and the molecular weight of PCL.

Keywords: Miscibility; Glass transition temperature; Unsaturated polyester blends; Morphology

1. Introduction

The study of the structure-properties relationships, in the field of thermosets used as composites matrices, has received attention from the scientific and technological community. Among thermosetting resins, unsaturated polyesters, UP, are commonly used as matrix for fibber reinforced composites. UP are used in a wide variety of markets (construction, marine, transportation, aircraft); in these applications, UP are used as a replacement of the traditional materials. The success of UP is due to their properties like easy fabrication, low weight, high strength, corrosion resistance and low cost [1]. Like other thermosets, UP resins are blended with several additives to enhance their properties. In this way, low-profile additives (LPAs) are used in UP formulations to improve the surface quality of moulded part, compensating for resin shrinkage [2–5]. A LPA is a thermoplastic material that is miscible or partially miscible with UP before curing and becomes incompatible at some time during curing process. In the literature there are studies about blends involving a thermoplastic polymer as poly(methylmethacrylate) or poly(vinylacetate) [3–6] but there are not many studies about blends formed with a semicrystalline polymer as poly(ε-caprolactone) (PCL) and thermosetting component as UP or epoxy resins [7,8].

As it is known, the UP thermosetting resins are obtained from a relatively low molecular weight polymer (linear UP) dissolved in styrene monomer (ST). The curing reaction between ST and linear UP is a free radical crosslinking copolymerization that leads to a heterogeneous structure through intramolecular reactions [9–11]. Taking into account that semicrystalline PCL has two phase morphology, it is not surprising that the cured UP resins blended with PCL have a complex structure. Therefore, as a previous stage in the study of cure reaction of UP resins in presence of PCL, it seems interesting to analyze the behaviour of blends formed by PCL and linear unsaturated polyester (LUP). In a previous paper, we presented some results concerning to these blends [12]. In the present work, we study blends of a phtalic polyester, LUPAl100, mixed with PCL of different molecular weights. The study consists of Fourier transformed-infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC), and environmental scanning electronic microscopy (ESEM). In particular, glass transition temperatures, T_g, and fusion temperatures, T_{fus} have been

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Table 1
Characteristics of poly(ε-caprolactone) and LUPAlLUPAl100

Polymer	M_n	T_g (°C)	T_{fus} (°C)	Crystallinity degree, X (%)	$r = M_w/M_n$
PCL50	50000	−62[a]	59.5[a]	59[a]	1.6
PCL18	18000	−62[a]	57[a]	51[a]	1.4
PCL2	2000	−64[b]	50[b]	62[b]	1.4
LUPAl100	2300	42	–	–	–

[a] Values obtained from the second scan for samples crystallised at 40 °C.
[b] Values obtained from the second scan for samples crystallised at 20 °C.

determined as a function of the blend composition, for blends of LUPAl100 + PCL. The melting behaviour of crystalline polymers depends, in a significant way, on the thermal story of the samples; therefore, in all the cases the same thermal treatment has been used. The miscibility of LUP + PCL blends has been analyzed in the whole composition range as a function of the molecular weight of PCL. The thermal behaviour of these blends will be explained as a function of their morphology, determined through ESEM measurements.

2. Experimental

2.1. Polymers

The LUP (Estratil Al100) was provided by Plastiform (Spain). LUP was dissolved in chloroform and precipitated in methanol in order to remove styrene contained in the commercial products. Nuclear magnetic resonance (^{1}H NMR) spectroscopy was used to characterize the linear polyester. Al100 consists of phtalic anhydride (PA), maleic anhydride (MA), and 1,2-propylene glycol (PG); the relative composition calculated from ^{1}H NMR measurements was PA:MA:PG = 5:2:7. The number average molecular weight, M_n, calculated from the acid value is shown in Table 1. The poly(ε-caprolactone) (PCL) was provided by Polysciences Eppelheim (Germany). The M_n and polydispersity index, M_w/M_n, of PCL obtained by gel permeation chromatography (GPC) in tetrahydrofuran (THF), are shown in Table 1.

2.2. Preparation of samples

For DSC and FT-IR measurements films of PCL ($M_w = 50 \times 10^3$, 18×10^3 and 2×10^3), LUPAl100 and blends of the two polymers with different compositions were prepared by mixing appropriate amounts of polymer solutions in chloroform and casting onto a glass surface. The solvent was evaporated slowly at room temperature and resulting films were dried under vacuum oven at 70 °C to remove completely any residual solvent. For ESEM measurements, the protocol in sample preparation was the same that after described, but in this case it was necessary to prepare samples with 1 mm of thickness.

2.3. Fourier transformed-infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained using a Galaxy model apparatus from Mattson at 2 cm^{-1} resolution in transmission mode. At least 32 scans were averaged for each spectrum. The films of the blend were cast directly onto KBr windows. Care was taken to keep the films thin enough for Lambert–Beer law to be valid.

2.4. Differential scanning calorimetry

A Mettler Toledo mod. 821e differential scanning calorimeter was used for determining the glass transition temperatures (T_g), fusion and crystallization behaviour. The instrument was calibrated with *n*-octane, indium and zinc and the measurements were conducted under nitrogen atmosphere. In all the cases, pans of aluminium of 40 μl, were used and the weight of the samples were kept in the range 7–14 mg.

2.5. ESEM

Environmental scanning electron microscopy (ESEM) has been used to study the morphology of LUPAl100 + PCL blends. Due to the non-conducting nature of the samples, the environmental mode was selected. A Phillips XL 30 instrument was used with beam energy of 20 kV, verifying that these experimental conditions did not produce severe damage on the samples. The water vapour pressure was 0.5–0.8 Torr, corresponding to a relative humidity of ≈5%. The magnification in the study varied from 100× to 2000×. The fracture surfaces were observed.

2.6. Heat treatment and differential scanning calorimetry measurements

The samples were first heated to 120 °C for 10 min to ensure complete fusion of PCL crystals, after that were cooled rapidly to the crystallization temperature (T_c). The selected crystallization temperatures were $T_c = 10$, 20, 30 and 40 °C. Following the crystallization treatment at T_c, which lasted 45 min, the samples were fast cooled to −90 °C and then were heated at 10 °C min^{-1} to 150 °C obtaining their glass transition temperature (T_g) and the fusion temperature (T_{fus}).

The midpoint of the heat capacity change has been taken as T_g. In order to identify the multiple endotherms, the maximum of the endothermic transitions is taken as T_{fus}. The heat of fusion (ΔH_{fus}) was evaluated from the areas of melting peaks.

3. Results and discussion

3.1. FT-IR results

The FT-IR spectroscopy has been extensively used to detect and identify the presence of intermolecular interactions between different polymer components in many compatible blends [13–17]. In the systems LUPAl100 + PCL, it could be possible to find favourable intermolecular interactions between C=O groups of PCL and those of LUP and also between the carbonyl group of PCL and the hydroxyl terminal groups of LUPAl100. The hydrogen bond interactions would affect to the hydroxyl stretching band of LUPAl100, located between 3200 and 3500 cm^{-1}, unfortunately this band is very weak in this region, which make impossible to obtain reliable information. Other possibility is to analyze the carbonyl stretching region

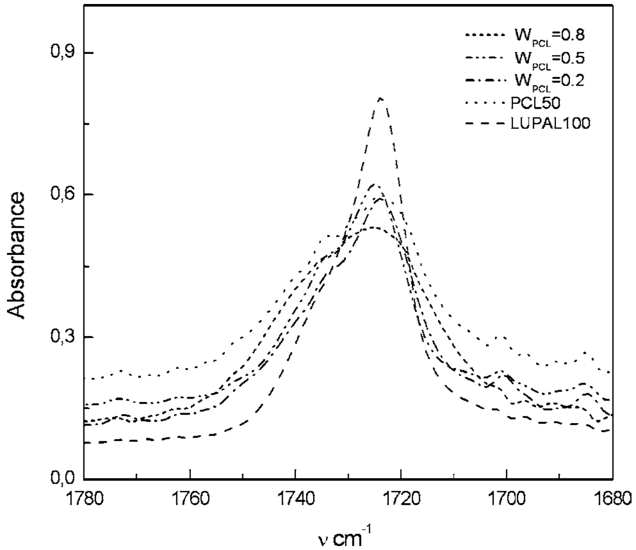


Fig. 1. FT-IR spectra in the region 1780–1680 cm^{-1} for blends of LUPAl100 + PCL50 at $T = 25\,^{\circ}\mathrm{C}$.

(1800–1650 cm^{-1}). Fig. 1 shows the corresponding spectra for blends of LUPAl100 + PCL50 with different content of PCL at room temperature. The carbonyl band of LUPAl100 is broad and shows two spectral components at 1725 and 1736 cm^{-1}. These two contributions could be related with the existence of intramolecular hydrogen bonding between carbonyl groups and terminal hydroxyl groups of the LUPAl molecular chains. However, taking into account the relative amount of carbonyl groups to terminal hydroxyls groups in LUPAl100, it is more reliable to consider that the spectral components of the carbonyl band are related with the different surroundings of the carbonyl groups in maleic and phtalic esters. The PCL spectrum has been reported and analyzed in detail by Coleman and Zarian [13]. As PCL is a semicrystalline polymer, in the solid state, the infrared spectrum consists of contributions from crystalline and amorphous phases. In this sense, the band occurring in 1800–1650 cm^{-1} region shows two spectral components at 1724 and 1734 cm^{-1} corresponding to stretching of the carbonyl groups in crystalline and amorphous conformations, respectively [13].

As it can be seen the carbonyl stretch absorption of the ester groups of PCL in the crystalline phase obscures the carbonyl stretch absorption of the ester groups of LUP and PCL located in the amorphous phase. Consequently is hard to obtain information about the existence of intermolecular interactions between PCL and LUPAl100 from the results shown in Fig. 1.

3.2. DSC results

The melting behaviour of crystalline polymers depends on the conditions under which they have been crystallized. In this study, it has been selected several crystallization temperatures ranging between 10 and 40 °C and a fixed time of crystallization of 45 min. Figs. 2–4 show the thermograms for LUPAl100 + PCL50, LUPAl100 + PCL18 and LUPAl100 + PCL2 blends of different composition expressed in weight fraction of PCL. These thermograms were obtained after the samples were crystallized for 45 min at $T_c = 30\,^{\circ}\mathrm{C}$ for PCL50 blends, $T_c = 40\,^{\circ}\mathrm{C}$ for PCL18 blends and at $T_c = 20\,^{\circ}\mathrm{C}$ for PCL2 blends. It is apparent from the thermograms that PCL crystallizes from blends having $W_{\mathrm{PCL}} \geq 0.4$ (for $W_{\mathrm{PCL}} \cong 0.3$ blends a very small fusion endotherm is observed).

Relating to T_g it can be observed:

- Whichever T_c is, for $W_{\mathrm{PCL}} \leq 0.3$ the thermograms only show a T_g which reveals the presence of an amorphous phase and for $1 > W_{\mathrm{PCL}} \geq 0.7$, the thermograms show a T_g corresponding to the amorphous phase, in addition to the endotherm of the crystalline phase.
- For $0.5 \geq W_{\mathrm{PCL}} \geq 0.4$, T_g can not be detected. The thermograms only show the endotherm corresponding to the crystalline phase of PCL. This behaviour is observed mainly as lower T_c is.

For blends compositions where T_g is detected, T_g values are located between those corresponding to neat polymers (PCL and LUPAl100), therefore the cystallizable component, PCL, would be divided between the pure crystalline phase and the mixed amorphous phase. This behaviour is representative of miscible polymers blends [15–18]. Figs. 5 and 6 summarize the T_g and T_{fus} as a function of W_{PCL} for LUPAl100 + PCL blends.

3.2.1. Glass transition temperature in LUPAl100 + PCL blends

In Figs. 5 and 6, the filled circles represent the dependence of T_g with the overall blend composition, W_{PCL}. Also, it is possible to represent T_g versus W_{PCL} of the amorphous phase in the blend. To calculate the composition of the amorphous phase, it is necessary to know the amount of PCL in the crystalline phase. The crystallinity degree, X_c, was calculated by the following equation:

$$X_{\mathrm{c}} = \frac{1}{\Delta H_f^0} \frac{\Delta H_f}{W_{\mathrm{PCL}}} \times 100 \qquad (1)$$

where ΔH_{f} is the heat of fusion of PCL in the blend, W_{PCL} is the overall blend composition and $\Delta H_f^0 = 32.4\,\mathrm{cal\,g^{-1}}$ is the heat of fusion of 100% crystalline PCL [19]. Open circles in Figs. 5 and 6 represent the dependence of T_g with W_{PCL} of the amorphous phase.

From the results in Fig. 5, it can be deduced:

(A) When T_g is represented versus W_{PCL} corresponding to the amorphous phase, it is difficult to draw a continuous curve that represents the behaviour of the blends, in the whole of the composition range for blends containing PCL50 and PCL18. Only LUPAl100 + PCL2 blends show a continuous dependence of T_g with the amorphous blend composition.

(B) As it was mentioned above, LUPAl100 + PCL blends show a gap in T_g versus W_{PCL} dependence (filled circles) at intermediate blend compositions, due to in the corresponding thermograms is not detected any glass transition.

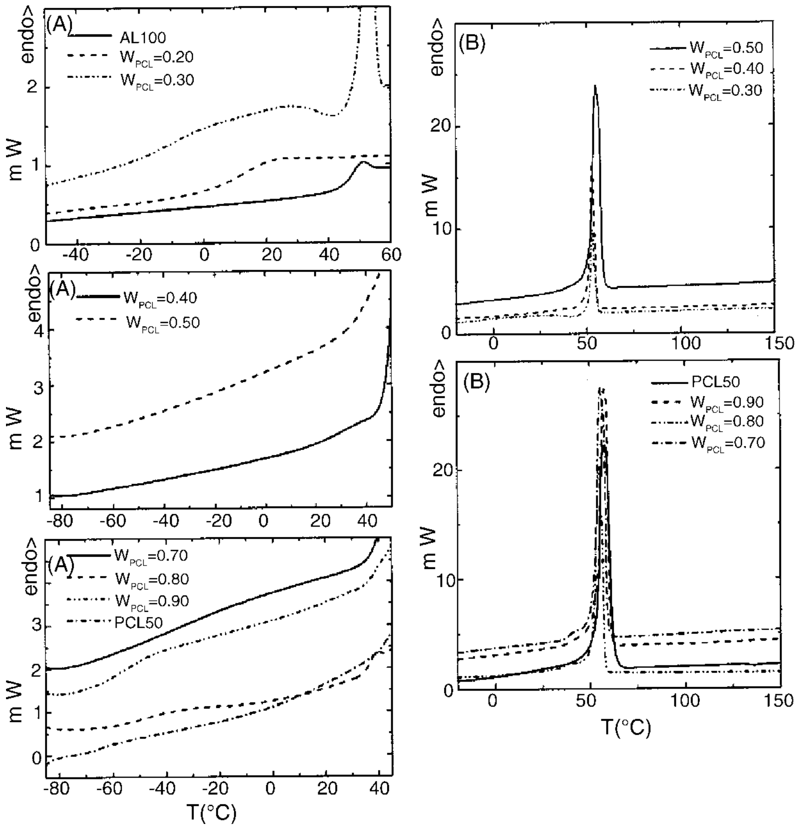


Fig. 2. Thermograms of LUPAl100 + PCL50 blends as a function of blend compositions, W_{PCL}, after isothermal crystallization at 30 °C. (A) Glass transition zone and (B) fusion temperature zone.

The anomalous behaviour is more evident for LUPAl100 + PCL blends when the blends are kept at lower temperatures before the thermal analysis is carried out. Fig. 6 shows T_g versus W_{PCL} for LUPAl100 + PCL18 at T_c = 10, 20 and 30 °C. The lower is the crystallization temperature, the wider is the gap in the composition blend in which the glass transition is not detected. Similar behaviour is obtained for LUPAl100 + PCL50 blends.

3.2.2. Crystallization of PCL in the blends

Like in other blends containing PCL [17,18], in LUPAl100 + PCL blends the fusion endotherms are broader,

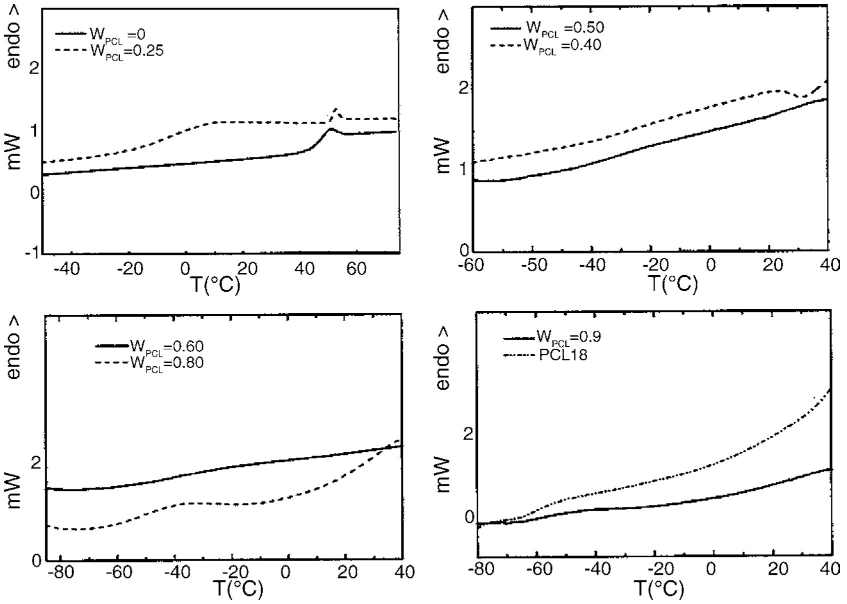


Fig. 3. Thermograms of LUPAl100 + PCL18 blends as a function of blend compositions, W_{PCL}, after isothermal crystallization at 40 °C, in the glass transition zone.

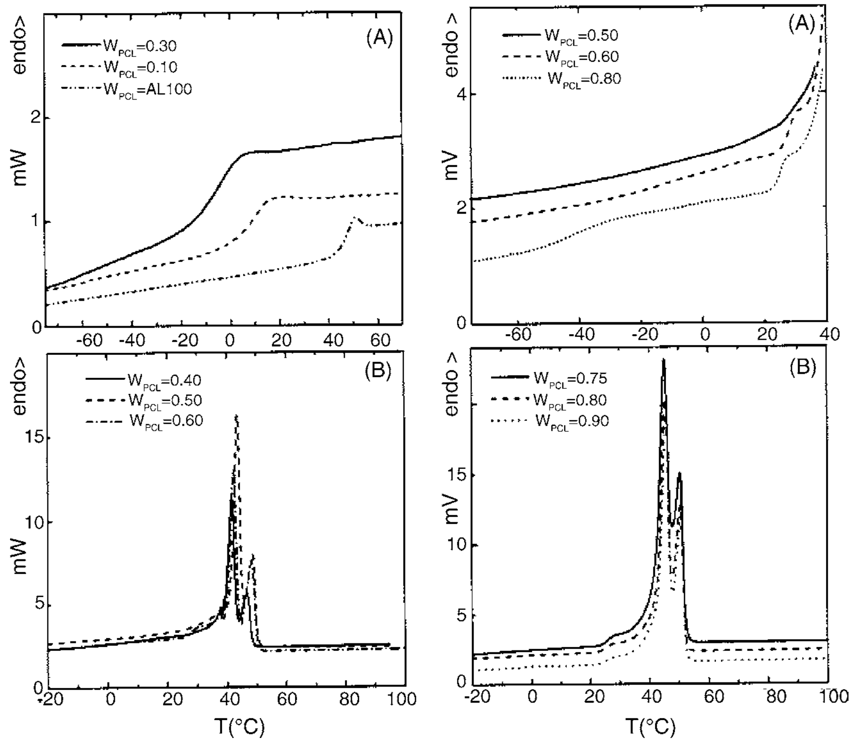


Fig. 4. Thermograms of LUPAl100 + PCL2 blends as a function blend compositions, W_{PCL}, after isothermal crystallization at 20 °C. (A) Glass transition zone and (B) fusion zone.

presenting a double melting peak, mainly, for low cystallization temperatures (10 and 20 °C). The reasons for this behaviour have been discussed extensively in the literature [20–23] and it is believed that it is the overall result of imperfect crystallization of PCL. It is well known that crystallization is a function of T_c, and more perfect crystals are obtained when the difference between T_{fus} and T_c is small. Fig. 7 shows the PCL crystallinities, X_c (%), that are developed in the course

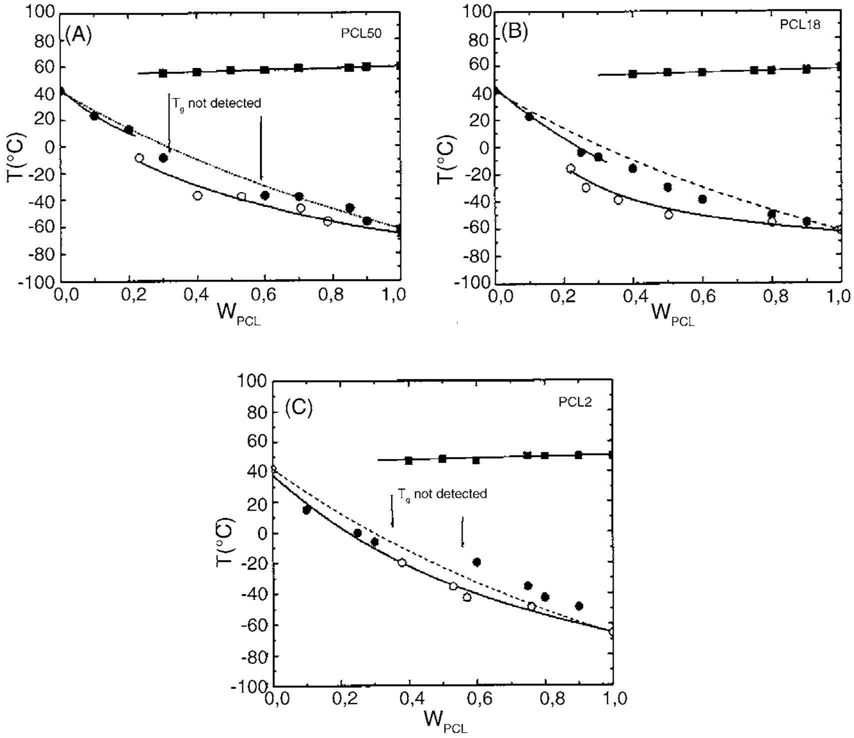


Fig. 5. Dependence of fusion temperature (■) and glass transition temperature (○, ●) on the weight fraction of PCL, W_{PCL} (●, overall blend composition; ○, amorphous blend composition). (A) LUPAl100 + PCL50 blends crystallized at 40 °C; (B) LUPAl100 + PCL18 crystallized at 40 °C and (C) LUPAl100 + PCL2 crystallized at 20 °C. (—) Polynomial fits to experimental data; (- - -) Fox equation.

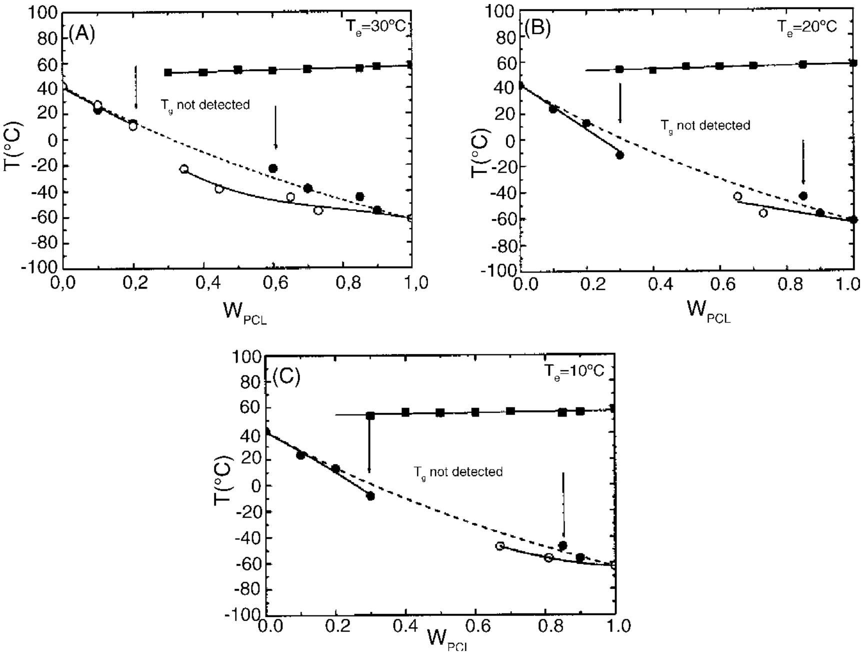


Fig. 6. Dependence of fusion temperature (■) and glass transition temperature (●, ○) on the weight fraction of PCL, W_{PCL}, for LUPAl100 + PCL18 blends (●, overall blend composition; ○, amorphous blend composition). (A) Crystallized at 30 °C; (B) crystallized at 20 C; (C) crystallized at 10 °C. (—) Polynomial fits to experimental data (- - -) Fox equation.

of different thermal conditions as a function of PCL content in the blend. There are no larges changes in X_c at different T_c's in neat PCL; an average value of $X_c = 57\%$ for PCL50 and $X_c = 54\%$ for PCL18 is obtained. For PCL2, the crystallinity degree at $T_c = 20\,°C$ reaches 62%. Fig. 7A and B illustrate that PCL18 and PCL50 crystallize in more extension in presence LUPAl100 than in pure state. However, in LUPAl100 + PCL2 blends (Fig. 7C), the degree of crystallinity remains almost constant.

It is well known that the crystallization depends on T_g of the blend. For miscible blends formed by a crystallizable polymer with low T_g and a higher T_g amorphous polymer, it could be expected that T_g of the compatible amorphous phase increases with the content of amorphous polymer in the blend. The blends studied in this paper belong to this group; PCL is a crystalline polymer with T_g (≈−60 °C) lower than T_g (≈40 °C) of the amorphous LUPAl100. For a given T_c, the T_g increases with the content of LUPAl100, as a consequence the amorphous

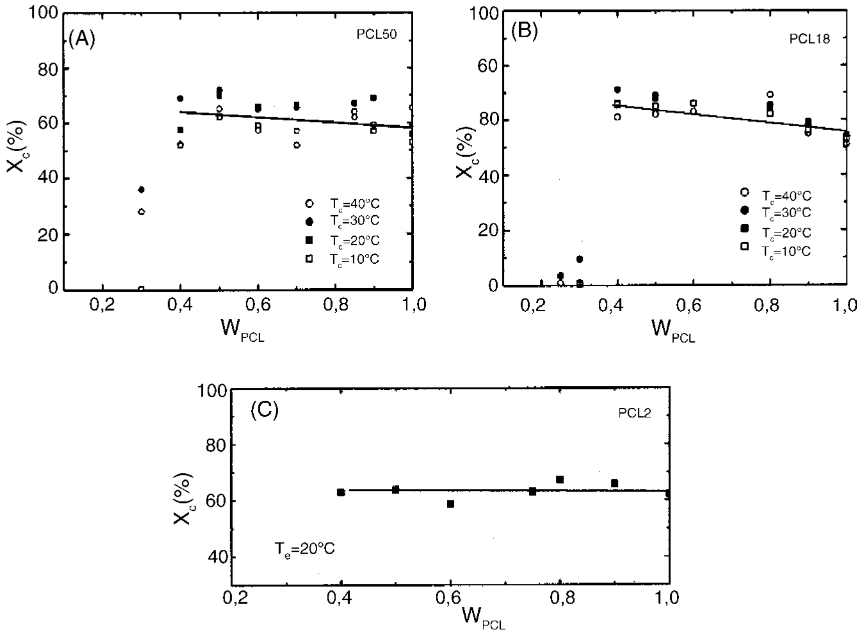


Fig. 7. Crystallinity degree, X_c (%), vs. W_{PCL} for samples of LUPAl100 + PCL, crystallized at different crystallization temperatures. (A) PCL50; (B) PCL18; (C) PCL2; (—) polynomial fits to experimental data.

Table 2
Apparent equilibrium fusion temperatures, T^0_{fus}, for PCL50 and PCL18 in PCL + LUPAl100 blends in the range 20 °C ≤ T_c ≤ 40 °C for crystallization temperatures

W_{PCL}	T^0_{fus} (°C)	
	PCL18	PCL50
1.0	58	63
0.9	55	59
0.85	54	60
0.80	54	–
0.75	52	–
0.70	–	57
0.60	52	–
0.50	54	60
0.40	53	58

phase will be stiffer and the diffusion of the segment of the crystalline polymer will be hindered. Therefore, it would be expected that X_c remains constant or decreases slightly with the content of LUPAl100. However, the behaviour observed in LUPAl100 + PCL50 and LUPAl100 + PCL18 blends is quite different, since, when the content of LUPAl100 increases in the blend, the crystallinity degree increases too (see Fig. 7). The T_g's for blends with less than 30% of PCL are close to the crystallization temperatures and consequently the crystallization of PCL cannot proceed in the crystallization time selected (45 min).

On the other hand, in all the blends studied it is observed a light decrease of the PCL fusion temperature. It is possible to estimate the equilibrium fusion temperatures (T^0_{fus}) of the blends from the T_{fus} versus T_c plots according to Hoffman–Weeks procedure [24]. In order to obtain T^0_{fus} from isothermal crystallization conditions, only the data corresponding to 20 °C ≤ T_c ≤ 40 °C have been considered. The values of T^0_{fus} obtained for PCL50 and PCL18 as function of the blends composition are given in Table 2. T^0_{fus} values obtained from the blends are lower than those for neat PCL; however, there is not a systematic variation of fusion point with blend composition as it would be expected for miscible blends.

The increase of X_c with the content of LUPAl100, the extinction of T_g at intermediate blend compositions and the small decrease of T_{fus} observed could be a sign of the lack of miscibility. Although, a unique T_g is detected at each blend composition, blends of LUPAl100 + PCL do not behave as totally miscible blends. Blends with PCL2 seem to behave lightly different that the blends with PCL50 and PCL18. In spite of the thermograms for $W_{\mathrm{PCL}} = 0.4$ and 0.5 do not show any T_g, PCL2 blends present a continuous variation of T_g with the amorphous blend composition (see Fig. 5C). Moreover, the degree of crystallinity remains constant independently of the content of LUPAl100 in the blends (Fig. 7C). From thermodynamic point of view, a decrease in the molecular weight of the polymers in a blend favours their miscibility due to the increase of the entropy of mixing. The entropic contribution to the Gibbs energy of mixing in blends with weak intermolecular interactions, like PCL2 + LUPAl100 blends, could be enough to determine higher degree of miscibility.

Guo and Zheng [7] have studied blends of PCL + ishoptalic UP. Through DSC and FT-IR measurements they conclude that the blends obtained mixing PCL and LUP are miscible in all the composition range. However, crosslinked blends, formed by a semiinterpenetrating network of linear PCL and crosslinked UP resin, show partial miscibility. The different behaviour observed in this paper respect to Guo and Zheng results could be attributed taking into account the different heat treatment of the samples. Guo and Zheng kept the samples at 140 °C for 5 min, after that the samples were quenched to −70 °C and reheating again at 20 °C min^{-1} to monitor their glass transition and fusion behaviour. In this paper, the blends remain 45 min at constant temperature; this period of time is enough to allow the diffusion of the polymer chains in the amorphous region leading to phase segregation.

3.3. Morphological analysis

Environmental scattering electron microscopy (ESEM) has been used to determine the change in blends morphology with LUPAl100 content. Fig. 8 shows the micrographs for PCL50. The fracture surface morphology of neat PCL50 corresponds to ductile fracture. The micrographs obtained are typical of semicrystalline polymers, being possible to appreciate the presence of spherulites with average diameters of 288 μm.

In Fig. 9 appears represented the micrographs obtained for the blends of LUPAl100 with different percentages of PCL50.

By comparison with Fig. 8 it can be appreciated that the blend with 50% of PCL50 is heterogeneous. It can be seen two different regions with different morphology and clearly separated. The region named 2 in Fig. 9B correspond to a phase with fractographic behaviour similar to neat PCL, therefore it could be a mixed region enriched in PCL. On the other hand, the phase named 1 in Fig. 9B shows a fracture surface morphology corresponding to fragile fracture and it would be compatible with a region with higher content of LUPAl100. The same behaviour is observed for the blend with 20% of PCL50 (Fig. 9A). It is important to note that DSC results do not detect the presence of crystalline phase for $W_{\mathrm{PCL}} < 0.3$, therefore the phase separation would correspond to amorphous region. In the blend with 80% of PCL50 is not observed phase separation being its fractographic behaviour close to the neat PCL.

ESEM micrographs seem to indicate that the increase of LUPAl100 in the blend provokes phase separation. These results allow giving an explanation of the anomalies observed in the thermal behaviour of these blends. The high values of the crystallinity degree at intermediate blend compositions (see Fig. 7) could be a consequence of the phase separation. When the content of LUPAl100 increases in the blends, ESEM results show the presence of a region with high content of LUPAl100 and therefore their glass transition temperature will be close to T_g of neat LUPAl100 (see Table 1). The proximity between T_g of this region and T_{fus} of PCL implies the overlapping of this T_g with the fusion peak of the crystalline phase. As a consequence there would be an increase in the peak area, and therefore in the calculated crystallinity degree; taking into account phase separation in the blends, the extinction of T_g at intermediate blends

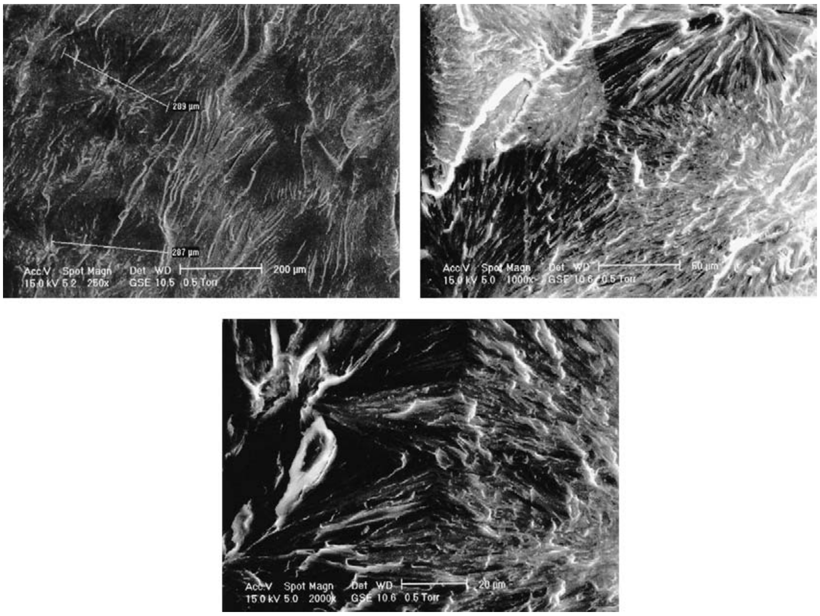
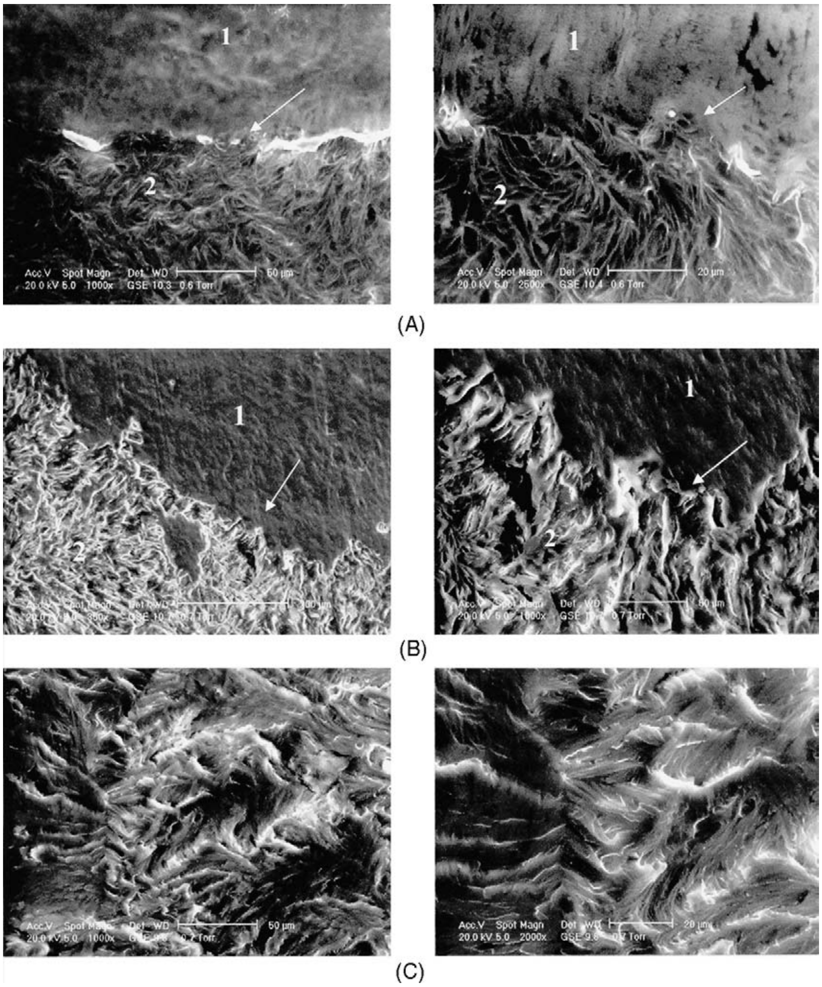


Fig. 8. ESEM micrographs of neat PCL50.



(A)

(B)

(C)

Fig. 9. ESEM micrographs of LUPAl100 with different amounts of PCL50: (A) 20%; (B) 50%; (C) 80%.

composition could be explained. PCL would be distributed among three phases (two amorphous phases + one crystalline phase) as a consequence the amorphous phase enriched in PCL would be present in so small amount that could not be detected by DSC.

4. Conclusions

- In blends containing PCL2, the degree of crystallinity of PCL remains constant as a function of the blend composition and also the dependence of T_g with W_{PCL} fits into a continuous curve, behaving as if they were miscible blends.
- The thermal behaviour of blends LUPAl100 + PCL50 and LUPAl100 + PCL18 is anomalous. It is not possible to represent the dependence of T_g versus W_{PCL} by a continuous curve. At intermediate blends compositions the T_g disappears and only is observed the PCL fusion peak. The composition range in which T_g vanishes is wider as crystallization temperature decreases. The crystallinity degree is higher as the content of LUPAl100 in the blends increases.
- The ESEM measurements confirm the lack of miscibility in LUPAl100 + PCL50. The micrographs demonstrate the existence of two phase morphology for blends of PCL50 with high content of LUPAl100.

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