Melt processed PLA/PCL blends: Effect of processing method on phase structure, morphology, and mechanical properties

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ABSTRACT: Poly(lactic acid) (PLA)-rich poly(lactic acid)/poly(ε-caprolactone) (PLA/PCL) blends were melt-blended at different compositions. The compositions such as 90/10 and 80/20 were obtained using three different blending methods and processed by injection molding and hot pressing. All blends were immiscible. The crystallinity of PLA increased slightly in the presence of poly(ε-caprolactone) (PCL), and the PCL exhibited fractionated crystallization in the presence of PLA. Injection molded specimens, compared with hot pressed specimens, presented much smaller PCL particles regardless of the blending method used. Some interfacial adhesion was observed in all cases. The stiffness of PLA/PCL blends decreased as the PCL content was increased and was independent of processing. Injection molded specimens showed ductile behavior and broke at elongation values close to 140%, while the elongation at break of the hot pressed specimens was clearly lower, most likely due to the larger size of the PCL particles. Although the impact strength of the blends remained low, it improved by approximately 200% with 30% PCL and by 350% with 40% PCL. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42641.

INTRODUCTION

Research and development on biopolymers and biopolymer-based materials has become one of the most important areas in macromolecular science and technology. Given the growing concern regarding diminishing oil reserves and increasing plastic waste, these renewable and/or biodegradable materials offer clear advantages. One of the most commonly studied and widely used biopolymers is poly(lactic acid) (PLA), which performs well for practical applications.[1] Poly(ε-caprolactone) (PCL), despite being derived from petroleum, is biodegradable and biocompatible and is, therefore, also considered a biopolymer. Both polymers present very different thermal and mechanical behavior. PLA offers a very good balance in low-deformation properties, but is brittle and offers poor performance against impact.[2] By contrast, PCL is a ductile polymer with high impact strength, but very low yield strength values and Young's modulus.[3] Thus, blending both polymers could lead to new biodegradable materials with well-balanced properties.

There is extensive literature on the subject of melt processed PLA/PCL blends,[4–18] in which phase structure, morphology, and mechanical properties have been analyzed. Uncompatibilized PLA and PCL are immiscible after melt blending, although

interactions between both polymers have been observed.[5] Also, in one study,[4] the system was deemed compatible. The low-strain tensile properties and the impact performance of the blends are intermediate between those of the neat components. However, although good interfacial adhesion between PLA and PCL[4] has been reported, ductility in tensile tests has only been achieved at high PCL contents.[5–7]

Different compatibilizing agents have been added to PLA/PCL blends in an attempt to improve their structure and properties. In blends prepared in solution, the addition of different synthesized poly(L-lactic acid)-poly(ε-caprolactone)-poly(L-lactic acid) (PLLA-PCL-PLLA),[8] poly(ε-caprolactone)-poly(ethylene glycol) PCL-PEG,[9] and PLLA-PCL[10] copolymers led to improved compatibility and even to enhanced miscibility of PLA and PCL.[9] Furthermore, the presence of small amounts of L-lysine tri-isocyanate (LTI) during melt blending, led to different grafting and cross-linking reactions between PLA and PCL.[11] As a result, the average particle size of the dispersed phase decreased and the interfacial adhesion improved. The compatibilizing effect of LTI strongly affected the mechanical performance of the blends. Thus, PLA/PCL blends with high PLA contents became ductile[11,12] and their impact properties also improved.[13,14] Annealing of compatibilized PLA/PCL/LTI (85/15/1) blend[15] led to

improved bending properties and as a result of the presence of LTI, additional chemical reactions between PLA and PCL were induced during annealing, and cavity formation was totally suppressed and the deformation was greater.[15] However, in the uncompatibilized PLA/PCL (85/15) blend, annealing suppressed the ductile deformation. In other studies, the addition of small amounts of dicumyl peroxide (DCP) during processing of the blends also helped to improve PLA/PCL ductility[4,16] and impact strength[4] by causing crosslinking reactions between PLA and PCL. The same observations were reported in the PLA/PCL/triphenyl phosphite (TPP) system.[17]

PLA and PCL have commonly been melt blended in internal mixers at different temperatures and shear forces.[4,5,10–14,16,18] However, from an industrial point of view, the use of a twin screw extruder is more suitable, as mixing is usually more efficient, blending times are lower, and productivity is greater. PLA and PCL have been blended previously in different types of extruders.[3,7,10,15,19]

It is well known that the morphology and the properties of a polymer blend can be modified by changing the processing parameters in the melt state.[20] In a recent study,[19] changes in the size of the PCL particles in an 80/20 PLA/PCL blend were analyzed by varying temperature and shear forces during processing. The crystallinity of PLA was also controlled by adding an effective nucleating agent and applying a post-annealing process. The impact strength of the 80/20 PLA/PCL blend was linked to the PCL particle size and the degree of crystallinity of the PLA matrix.

In this study, PLA/PCL blends were obtained by different blending and processing methods. The mechanical properties of the blends were measured and scanning electron microscopy (SEM), dynamic mechanical analysis (DMTA), differential scanning calorimetry (DSC), and melt viscosity data were all used to examine the relationship between the blends' structure and properties.

EXPERIMENTAL

The PLA used was injection molding grade, NATUREWORKS 3052D (96% L-lactide and density 1.24 g cm^{-3}), purchased from Resinex Spain S.L. The PCL was CAPA 6800 (Mw = 80,000 g mol^{-1}), purchased from Solvay. PLA was dried overnight before processing, in a dehumidifier at 80°C, to avoid possible moisture-induced degradation reactions. 90/10, 80/20, 70/30, and 60/40 compositions of PLA/PCL were blended in a Collin twin-screw extruder-kneader (type ZK25, L/D ratio 30, and screw diameter 25 mm) at a screw speed of 80 rpm and a temperature of 180°C, cooled in a water bath and pelletized. The pellets were dried overnight in a dehumidifier at 80°C before injection molding. Injection molding was carried out at 180°C in a Battenfeld reciprocating screw injection molding machine (type BA-230-E, L/D ratio 17.8, and screw diameter 18 mm). The mold temperature was 25°C. This processing route is called method 1. Additional processing methods were applied to observe the effect of processing on the structure and properties of the blends. Thus, 90/10 and 80/20 PLA/PCL compositions were blended at the same temperature and screw speed in

a Collin twin-screw extruder-kneader (Teachline, L/D ratio 18, and screw diameter 25 mm) and injection molded under the same conditions as those described above (method 2), and they were also directly injection molded without previous blending (method 3). In addition, pellets of the 80/20 PLA/PCL blend obtained using method 1 were compression molded at the same temperature (180°C) in a Collin P-200-E compression molding machine (method 4). By methods 1–4 tensile (ASTM D 638 type IV, thickness 1.84 mm) and by the method 1 impact (ASTM D256, thickness 3.2 mm) specimens were obtained.

The phase structure of the blends was studied using DMTA analysis performed in a TA INSTRUMENTS Q800 DMA viscoelastometer that provided the plot of the loss tangent (tanδ) against temperature. All scans were carried out in single cantilever mode at a constant heating rate of 4°C min^{-1}, between 0°C and 100°C for neat PLA, and between −100°C and 100°C for the binary blends.

The melting behavior of the blends was studied by DSC using a Perkin Elmer DSC-7 calorimeter calibrated with reference to an Indium standard. The samples were first heated from 30°C to 200°C at 20°C min^{-1}, then cooled at the same rate, and reheated again. The melting (Tm) and crystallization (Tc) temperatures of PLA and PCL were determined in both heating scans from the maxima of the corresponding peaks. PLA crystallinity was calculated from melting and crystallization enthalpies, determined using the areas of the corresponding peaks, and a ΔH_f^∞ value of 93 J g^{-1} for 100% crystalline PLA.[21]

The surfaces of cryogenically fractured tensile specimens were observed by SEM, after gold coating, using a Hitachi S-2700 electron microscope. Micrographs of the most representative inner regions of the specimens were obtained.

The interfacial tension between PLA and PCL was calculated using the harmonic equation of Wu [eq. (1)][22]

$$\gamma_{12} = \gamma_1 + \gamma_2 + \frac{4\gamma_1^d \gamma_2^d}{(\gamma_1^d + \gamma_2^d)} + \frac{4\gamma_1^p \gamma_2^p}{(\gamma_1^p + \gamma_2^p)} \qquad (1)$$

where subscripts 1 and 2 represent PLA and PCL, respectively. Polar (γ^p), dispersive (γ^d), and total (γ) surface energies of PLA and PCL were determined from the corresponding contact angles of both polymers with water and ethylene glycol using a CAM 100 goniometer (KSV).

Measurements of the torque for kneading of the blends were taken in a DSM MICRO 5 co-rotating twin-screw microextruder. About 4 g of the studied material were tested for each composition, at 80 rpm and 180°C.

The viscosity of PLA and PCL was determined in a Göttfert Rheo-Tester 1000 capillary rheometer with a 30/1 L/D ratio. Tests were carried out at 180°C in a strain rate range of between 10 and 20,000 s^{-1}.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in a Brucker Avance DPX 300 with a resonance frequency of 300.16 MHz using 5 mm O. D. sample tubes. All spectra were obtained at room temperature (297.6 K) from solutions in 0.7 mL of deuterated chloroform (CDCl$_3$). The
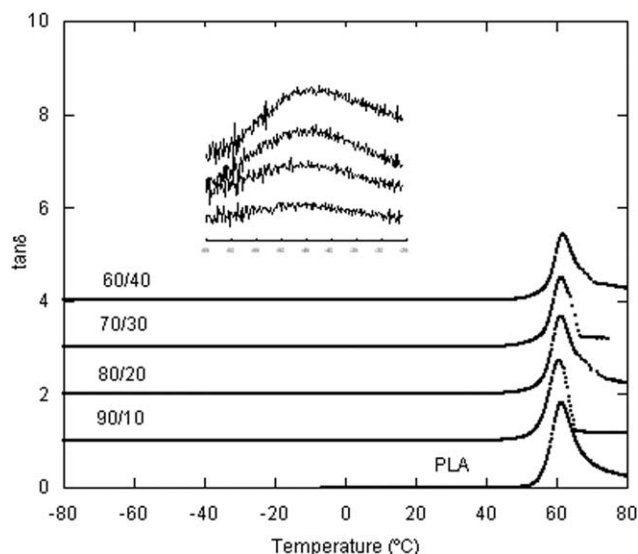
Figure 1. The tan δ vs. temperature plots of neat PLA and blends processed by method 1. The insert shows the signal amplification of the curves between $-65°C$ and $-25°C$.

experimental conditions were as follows: 10 mg of sample, 3 s acquisition time; 16 s delay time; 8.5 μs pulse; spectral width 4500 Hz, and 32 scans.

The tensile tests were carried out using an Instron 4301 tensile tester. Young's modulus was determined at a cross-head speed of 1 mm min^{-1} by means of an extensometer, and the yield stress and the elongation at break were measured at a cross-head speed of 10 mm min^{-1}. A minimum of five tensile specimens were tested for each reported value.

Izod Impact tests were carried out on notched specimens using a CEAST 6458/000 pendulum. The notches (depth 2.54 mm and radius 0.25 mm) were machined after injection molding. A minimum of eight impact specimens were tested for each reported value.

RESULTS AND DISCUSSION

Phase Structure

Figure 1 shows tan δ vs. temperature plots of the PLA/PCL compositions, which were processed using method 1. The glass transition temperature of neat PLA was 61.2°C. The PCL was not processed in this study, but the glass transition temperature of injection molded CAPA 6800 PCL has been reported to be centered at $-45°C$.[3] Regarding the blends, two tan δ peaks were observed. The high temperature peak corresponds to the PLA phase, and the low temperature peak in the amplified plot to the PCL phase. The maxima of both tan δ peaks were almost unaltered in the different blend compositions (the corresponding temperatures were $61.2 \pm 0.4°C$ and $-45.0 \pm 0.3°C$), suggesting full immiscibility of the PLA with the PCL. This has been the general behavior reported for PLA/PCL blends. Only Lopez-Rodriguez et al.[5] and Sakai et al.[23] reported partial miscibility between both polymers by applying the Fox equation;[24] and estimated that a very small amount of PCL was dissolved in PLA. Elsewhere, Takayama et al.[13] mentioned that the addition of LTI improved miscibility in the PLA/PCL 85/15 blend. How-

ever, this conclusion was based on the reduced size of PCL particles caused by the LTI; no parameters were calculated to determine the degree of miscibility.

The intensity of the PLA peaks in Figure 1 was clearly greater than the low temperature peaks even in the case of the 40% PCL containing blend. This has probably to do with the crystallinity levels of PLA and PCL in the blends. As we will see below, PCL is highly crystalline, while PLA is virtually amorphous or slightly crystalline. High crystallinity usually leads to low intensity of the glass transition due to the small fraction of the amorphous phase and the hindered mobility of the amorphous segments close to crystalline structures.

Figure 2 shows the first DSC heating scans of neat PLA and 80/20 and 60/40 PLA/PCL blends. Due to its slow crystallization kinetics,[25] PLA was unable to fully crystallize from the melt during cooling in the injection mold in any of the studied compositions, eventually crystallizing during the heating scan. The wide exotherms, centered at approximately 125°C for PLA and at 105–110°C for the blends, reflect these crystallization processes. Similarly, no PLA crystallization peak was observed on cooling at 20°C/min in the calorimeter, with crystallization again occurring in the second heating scan. Regarding to PCL, its melting endotherm (Tm = 64°C for neat PCL) appeared close to the Tg of PLA, so that its level of crystallinity could not be accurately determined.

Table I summarizes the data obtained from the first heating scans. As shown, the presence of PCL led to a clear decrease in the crystallization temperature of PLA indicating, in keeping with previous studies,[5,7,11,12,23] a nucleating effect of PCL. In any case, the crystallinity of PLA remained very low, close to 9% at most. Sarasua and coworkers[5] observed that dispersed PCL particles increased the crystallinity of PLA in a casted 80/20 PLA/PCL blend. The same authors compared the dynamic crystallization behavior of neat PLA with the 60/40 PLA/PCL blend with a heating rate of 10°C min^{-1}. The blend showed
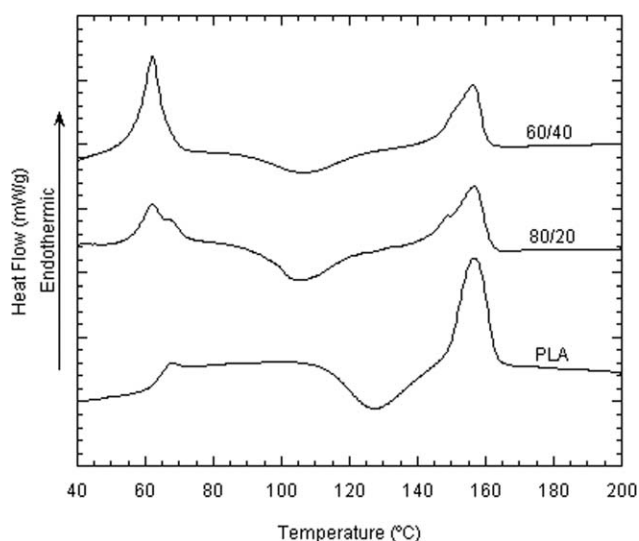

Figure 2. First DSC scans of PLA and the 80/20 and 60/40 PLA/PCL blends processed by method 1.

Table I. Calorimetric Data Obtained from the First Heating Scans of PLA and PLA/PCL Blends Processed by Method 1

Composition (PLA/PCL)	Tc PLA (°C)	Tm PLA (°C)	Xc PLA (%)	Tm PCL (°C)
100/0	125.1	155.1	0	–
90/10	110.7	158.1	9.2	61.7
80/20	104.7	156.7	4.7	62.0
70/30	104.7	155.4	3.4	61.1
60/40	107.7	156.3	3.4	62.0

two exothermic peaks, at 100°C and just before the melting endotherm. This second peak was attributed to the possible recrystallization of imperfect PLA crystals into more perfect α crystals. In a separate study, Sakai et al.,[23] having performed analyses at a heating rate of 20°C min^{-1}, observed that PCL enhanced the nucleation of PLA at low temperatures, but had an insignificant effect on crystal growth, perhaps due to the low miscibility of the blend. Consequently, the enhanced cold crystallization was due to the increase in the number of nuclei generated at lower temperatures, induced by the presence of PCL.

Table I also shows that the melting temperature of PLA remained almost constant. In the case of the melting temperature of PCL, a scarcely significant 2°C decrease was observed in all the blends with respect to that of neat PCL.

Morphology

Figure 3 shows micrographs reflecting the most representative inner (core) part of cryogenically fractured surfaces of 90/10, 80/20, 70/30, and 60/40 PLA/PCL tensile specimens prepared by method 1. As it is seen, all the blends showed biphasic morphology regardless of the composition, confirming the immiscibility of PLA with PCL. PCL particles were uniformly dispersed in the PLA matrix and the particle size was homogeneous and very small in all the compositions, with an average diameter of few hundred nanometers. The particle size seemed to increase slightly at higher PCL contents, but remained very small even in the 60/40 composition. This morphology is very different to that observed by other authors for unmodified PLA/PCL blends, where the average PCL particle size was clearly higher.[6,7,26] While some debonded particles were observed in Figure 3, the fractures showed a partially cohesive character, suggesting some interfacial adhesion between PLA and PCL in the solid state. Taking into account both observations, i.e. the small particle size and the fairly good interfacial adhesion, it seems that the blending conditions used in this study were more effective than those used in previous works on uncompatibilized PLA/PCL blends,[4,14,15] even when compared with blends prepared using extruders with higher L/D ratios.[4,15]

With regard to the PCL phase morphology, Wu et al.[26] reported that, in an uncompatibilized PLA/PCL system, it changed from spherical in the 80/20 composition to fibrillar in the 60/40 composition. In the blends in this study, the appearance of the PCL
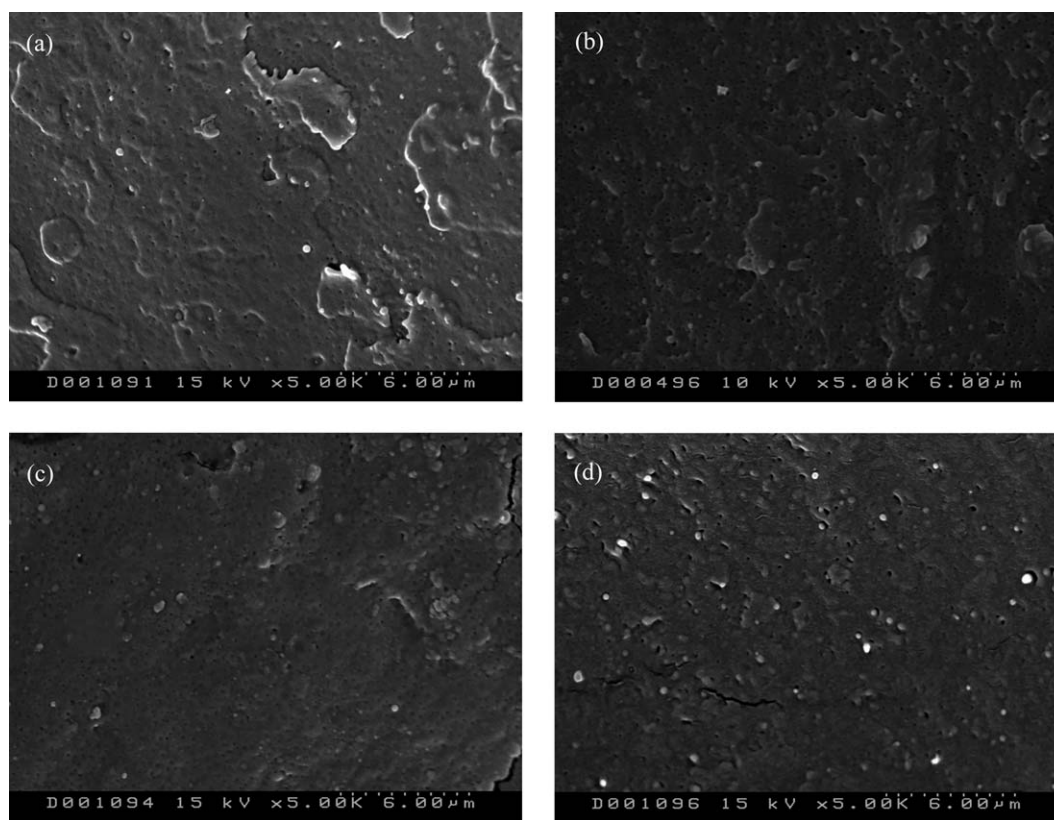

Figure 3. SEM micrographs of fracture surfaces of cryogenically fractured tensile specimens of 90/10 (a), 80/20 (b), 70/30 (c), and 60/40 (d) PLA/PCL blends.
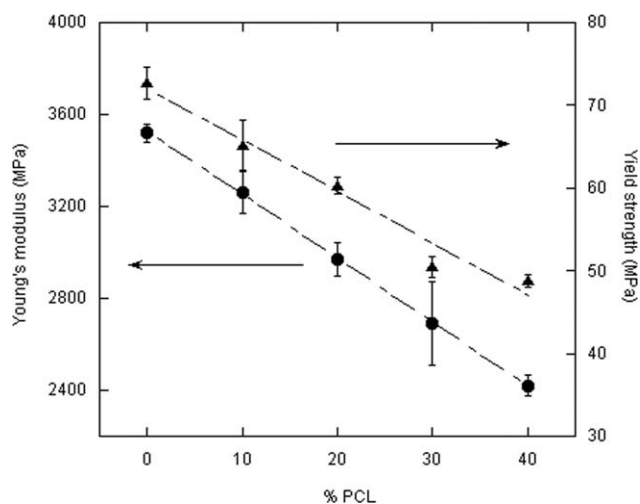
Figure 4. Young's modulus (●) and yield strength (▲) behavior of the blends.

particles remained almost the same in all the compositions and very similar to that of compatibilized blends.[10–14]

So, the morphology of the PLA/PCL blends in the present work suggests that, under the processing conditions used here, both polymers jointly form an immiscible but most likely compatible blend in the PLA-rich region. In contrast with previous works[7–13] it was not necessary to add a compatibilizing agent in order to obtain very small PCL particles and interfacial adhesion between both components.

The resulting interfacial tension for the PLA/PCL blends in this work was 1.55 mN m^{-1}. This value is comparable, although slightly higher, to those calculated respectively by Wu *et al.*[27] (0.9 mN m^{-1}) and Noroozi *et al.*[28] (1.206 mN m^{-1}). In agreement with previous works, this low interfacial tension accounts for the interfacial adhesion observed in PLA/PCL blends,[29] and is also consistent[30,31] with the small size of the particles in Figure 3.

The viscosity ratio of PLA and PCL ($\eta_{PLA}/\eta_{PCL}\sim0.95$ in all the measured strain rate range) is another factor that tends to reduce the dispersed particle size.[32,33] It could be speculated that, despite the similar interfacial tension values, this viscosity effect is probably responsible for the different particle sizes observed in other studies. Thus, their combined effect could contribute to the small PCL particle size in PLA/PCL blends obtained in the present work.

Mechanical Properties

Figure 4 shows Young's modulus and the yield stress of neat PLA and the PLA/PCL blends as a function of composition. Both properties decreased as the PCL content increased, in agreement to that observed in previous works based on immiscible polymer blends consisting of a stiff matrix and soft dispersed particles.[3,34] Phase separated PCL droplets impaired both properties as a result of its low Young's modulus (410 ± 20 MPa) and yield stress (14 ± 0.2 MPa).

In any case, thanks to the high modulus of PLA, the experimental values stayed well above 2000 MPa, even after 40% PCL was added. This is an important finding as it suggests that these blends will probably still be apt for use in most of the traditional applications of PLA. The decrease in the yield strength is considerably more significant, but it still remained close to 50 MPa at 40% PCL contents.

The elongation at break of PLA and the blends is shown against composition in Figure 5. PLA is known to be very brittle and appears so in Figure 5. By contrast, PCL is very ductile, with an elongation at break of 425 ± 20%.[3] As it can be observed in Figure 5, the addition of only 10% PCL leads to a clear change in the fracture behavior of PLA, so that the 90/10 blend has an elongation at break of 140%, and remains virtually unchanged at higher PCL concentrations. Increased ductility of PLA in blends with PCL has been reported by other authors.[7] However, in these reported cases, and, with the exception of systems in which a compatibilizer was added during the blending process, the transition to ductility took place at PCL contents of over 30%.[4,11,12,16] In other works, while the presence of some interfacial adhesion between PLA and PCL was reported,[5] ductility did not increase until the intermediate 50/50 composition was reached.

If we examine the reasons for the different elongation at break values presented in this study and in previous articles, it is known that the elongation at break of rigid polymers is affected by the testing rate, generally decreasing as the testing rate increases.[35] In several previous works on PLA/PCL blends,[4,5,7,16] the elongation rate used in tensile tests was 50 mm min^{-1}, instead of 10 mm min^{-1}, which was used in this study. Thus, the elongation at break values in Figure 5 may have been partially affected by the testing rate. In fact, tensile tests carried out on the 80/20 blends in this study at 50 mm/min led to an elongation at break of 13.6 ± 2.7%. Therefore, the differences between the data contained in Figure 5 and those in the literature are probably affected, at least partially, by the differences in the testing rate.

However, low elongation at break values have also been obtained in previous studies involving PLA/PCL blends, using
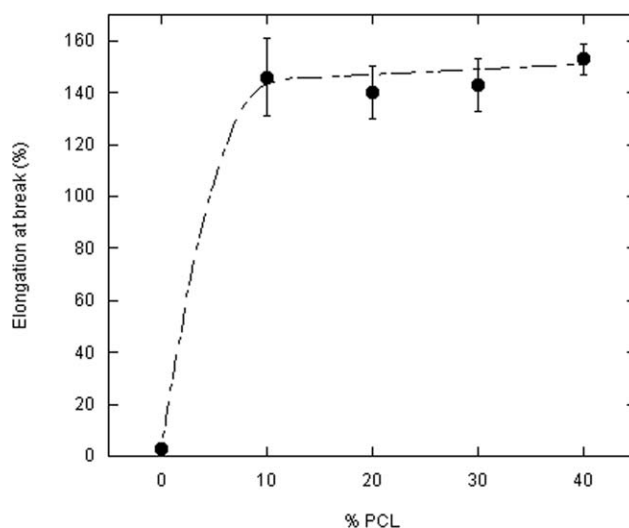

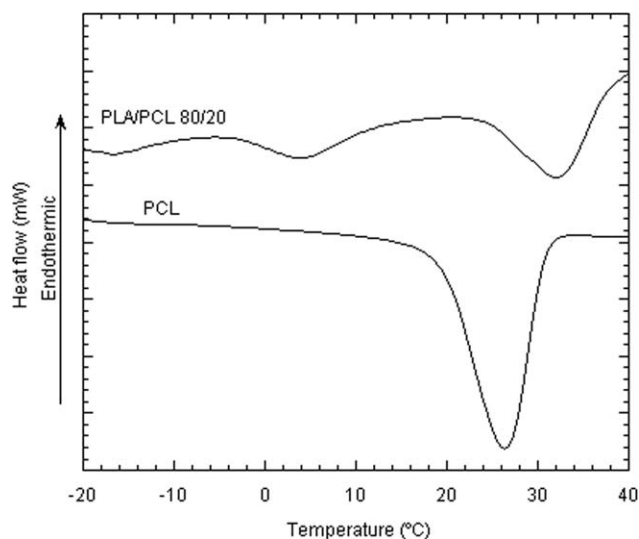**Figure 5.** Elongation at break of the blends.

Figure 6. Cooling scans of PCL and the 80/20 PLA/PCL blend between 40°C and −20°C. Cooling rate: 20°C/min

elongation rates lower than 10 mm min^{-1}.[6,8,9,11] Furthermore, when the morphology of the PLA/PCL blends in Figure 3 is compared with that of previous studies, it is clear that the blends of this study resemble the morphology of compatibilized blends[11–14] more than they resemble uncompatibilized ones.[5–7,12] So, the morphology of the blends, which is characterized by a very small particle size[4,35,36] together with the existence of some interfacial adhesion[37,38] and the high elongation at break values shown in Figure 5 would all suggest that these PLA/PCL blends are mechanically compatible.

It has been reported[36] that fractionated crystallization of PCL can occur in blends with other polymers on cooling from the melt, therefore it is possible for some fraction of PCL to crystallize even at temperatures below room temperature. If this is true for the PLA/PCL blends in this study, some fraction of usually crystallized PCL could have remained in an amorphous state in the dispersed PCL particles, making these particles more deformable than expected, thus contributing to the improved ductility of the blends. Figure 6 shows DSC cooling scans from the melt of neat PCL and the PLA/PCL 80/20 blend. As the figure shows, fractionated crystallization occurred in the blend. In order to check whether this phenomenon affected the ductility values in Figure 5, some specimens of the PLA/PCL 80/20 blend were kept at a temperature of −40°C for 24 h for the PCL to crystallize completely. They were then tensile tested. The ductility value obtained was $167 \pm 10\%$, ruling out fractionated crystallization as the cause of the high ductility of the blends.

Another possible reason for the high ductility values in Figure 5 is the occurrence of interchange reactions between PLA and PCL during processing, which may have compatibilized the blends. As mentioned previously, the addition of compatibilizers DCP and LTI to PLA/PCL blends foments interchange reactions between both polymers, giving rise to ductile materials.[4,11,12,16]

In order to check whether the interchange reactions also affected the compatibility observed in this study, ^{1}H-NMR

analysis[17] and torque measurements[4,11] were carried out for different blend compositions. The representative signals of the LA-CL dyad (at 2.37 and 4.11 ppm)[37] did not appear in the NMR spectra of the blends and, furthermore, no viscosity peaks were appreciated in the torque-time plots up to a kneading time of 20 min, clearly higher than the residence time the blends spent in the melt state during extrusion and injection molding. Consequently, interchange reactions were ruled out as a possible explanation for the morphology and ductility of the blends.

Effect of Processing Method

To gain further insight into the morphology and mechanical behavior of PLA/PCL blends, the 90/10 and 80/20 compositions were prepared using less effective processing methods than the standard procedure (Method 1). Thus, processing was carried out by methods 2 and 3 described in the experimental section. In Figure 7, the morphology of the 80/20 blend processed by method 2 (low L/D extruder and ulterior injection molding) [Figure 7(a)] and method 3 (direct injection molding) [Figure 7(b)] is shown. Although the particles obtained using methods 2 and 3 are slightly bigger than using more favorable method 1, they were still very small.

The mechanical properties were also very similar, as shown in Table II. The 90/10 blend produced similar results. So, irrespective of the procedure used, with and without previous blending, the morphology, and mechanical properties, in particular the elongation at break of the blends did not vary. This would strongly suggest that the injection molding process is the most important step for establishing them in our PLA/PCL blends. Given that the morphology and properties of these blends did not change during any of the processing methods used, and they remained stable when fractionated crystallization of PCL was avoided, it points to the small particle size and the interfacial adhesion as responsible for the high ductility of the blends.

This proposition was evaluated by processing the 80/20 blend prepared in the high L/D extruder by compression molding (method 4). This molding procedure involves a short and multidirectional flow, with a very low shear level. As the molding times are relatively long (5 min), there is a good chance of the particles coalescing. In Figure 7(c), the morphology obtained is shown. The particles are visibly larger than those obtained using methods 1–3 after injection molding, although there was still some adhesion.

The ductility was 50%, i.e. clearly lower. Taking into account the aforementioned particle size, it appears, as expected, that there is a relation between particle size and ductility: larger particles leading to less ductility. Therefore, the positive ductility values obtained for the blends processed with methods 1–3, involving injection molding, are attributed to the small size of the particles and the interfacial adhesion. This behavior is consistent with that shown by other PLA-based phase-separated blends.[38,39]

Impact Strength

As previously mentioned, PLA is a brittle polymer and consequently offers very poor impact strength.[40] By contrast, PCL offers good impact strength (400 ± 50 J/m). Therefore, PCL
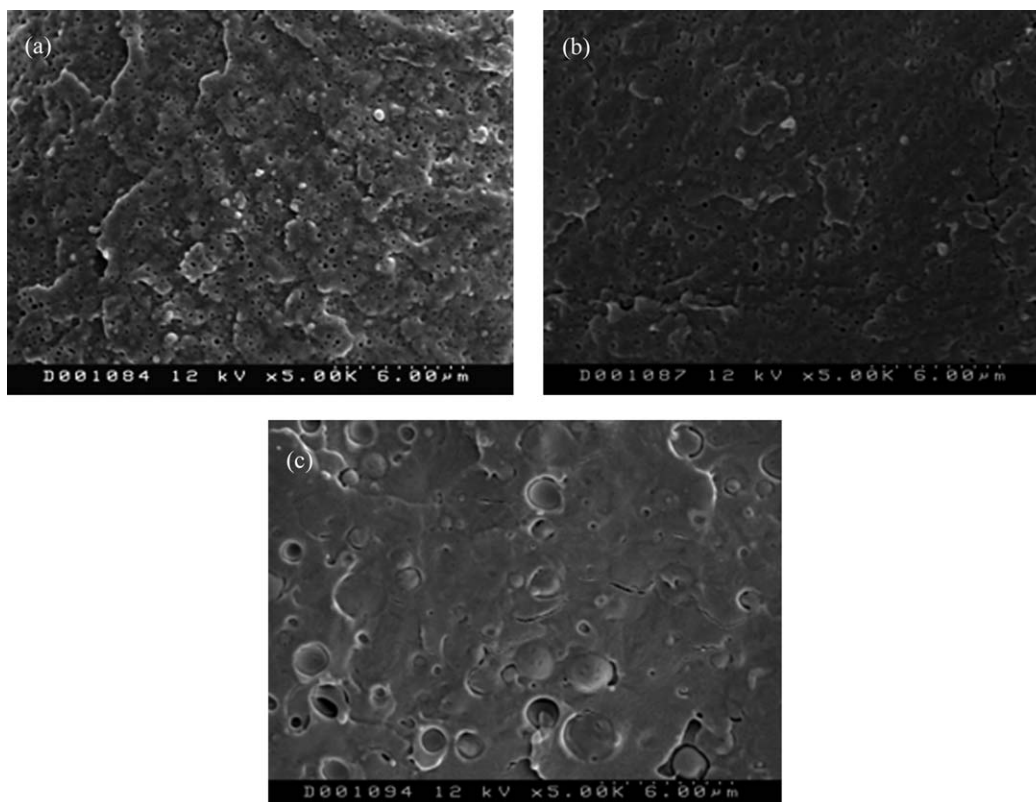
Figure 7. SEM micrographs of cryogenically fractured surfaces of PLA/PCL 80/20 tensile specimens processed by methods 2(a), 3(b), and 4(c).

could potentially improve the poor toughness of PLA. Figure 8 shows the Izod impact strength of the PLA/PCL blends as a function of composition. As the figure indicates, the addition of PCL led to a steady increase in impact strength. Although the absolute impact strength values remained relatively low, the relative increase was considerable (approximately 200% with 30% PCL and 350% with 40% PCL). The impact performance of the 40% PCL blend was comparable to that of some uncompatibilized PLA/elastomer 80/20 blends.[41] The behavior of the impact strength is clearly different to that of the ductility (Figure 5).

The intrinsic differences between tensile and impact tests (strain rate, state of stress, and notch presence-absence) probably account for this difference. In addition to this, the PCL particles in injection molded PLA/PCL blends, regardless of the blending method used (method 1 [Figure 3(b)], method 2 [Figure 7(a)] or method 3 [Figure 7(b)]), were too small to effectively

improve the impact strength of PLA, taking into account recent results reported by Bai et al.[19] They observed that, in the case of 80/20 amorphous PLA/PCL blends, the highest impact strength (corresponding to supertoughness) is obtained when the average PCL particle diameter is close to 0.9 μm. This is clearly larger than the particles in the 80/20 blends here, and could be the reason for the lower impact strength results in Figure 8.
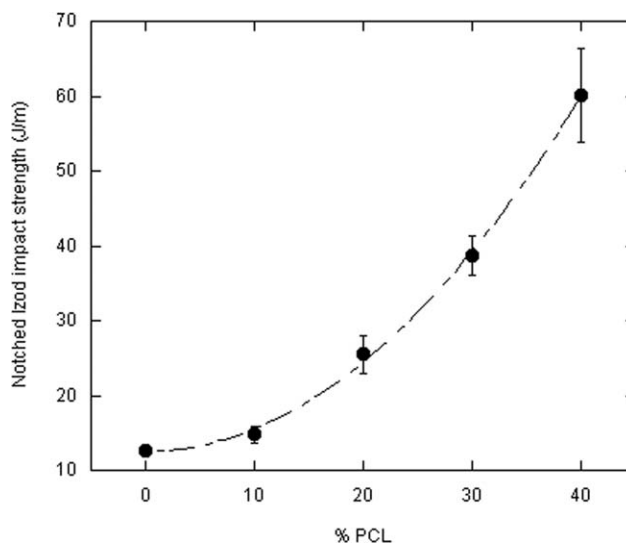
Table II. Young's Modulus, Yield Strength, and Elongation at Break Values of the PLA/PCL 80/20 Blend Processed by Methods 1–4

Method	Young's modulus (MPa)	Yield strength (MPa)	Elongation at break (%)
1	2,970±70	60.3±1.0	140±10
2	2,900±10	57.2±0.3	142±3
3	2,900±40	54.8±1.2	136±5
4	2,890±55	51.9±1.1	50.5±10.2

Figure 8. Notched Izod impact strength of PLA/PCL blends.

Table III. Vicat Softening Temperatures of PLA/PCL Blends

Composition (PLA/PCL)	Vicat temperature (°C)
PLA	63.2±0.2
90/10	62.6±0.2
80/20	61±0.2
70/30	60.4±0.1
60/40	59.8±0.2

Vicat Softening Temperature

Calorimetric analysis showed that some PLA crystallized in the PLA/PCL blends, probably due to a nucleating effect of PCL, especially in the 90/10 composition, where crystallinity increased to approximately 9%. There is a correlation between the Vicat softening temperature of PLA and its degree of crystallinity,[42] since an increase in the Vicat temperature from a Tg-dependent temperature to a Tm-related one was observed in three different PLA samples after annealing.

Table III shows the Vicat temperatures of PLA and PLA/PCL blends. As observed, the improved crystallinity of PLA did not affect the Vicat temperature of the 90/10 blend, probably because the crystallinity obtained was not enough to effectively reinforce the material. Despite this (taking into account the mechanical performance of the blends), the results of the Vicat tests were satisfactory inasmuch as the presence of PCL, a polymer whose thermal properties are similar to those of an elastomer, hardly affected the thermal stability of PLA.

CONCLUSIONS

Melt blended and injection molded PLA/PCL blends with a dominant PLA content were fully immiscible as their Tg-s did not change when compared with the values for the individual components. PCL caused imperfect PLA crystals to appear, slightly improving its crystallinity. The PCL dispersed particles were very small and there was some interfacial adhesion between PLA and PCL. No interchange reactions between both polymers were deduced from the ^{1}H NMR and torque measurements. There was a decrease in Young's modulus and the yield strength, and the impact strength increased when PCL was added to the PLA. Due to both the interfacial adhesion between PLA and PCL and the reduced size of the particles, the elongation at break for PLA was greatly improved in the blends. 90/10 and 80/20 PLA/PCL compositions were also processed with less efficient mixing procedures and by hot pressing, and the effects of PCL crystallinity and the testing rate were also analyzed. The ductility of the blends remained constant in all cases except for the compression-molded samples, where there was an evident increase in the size of the particles. The dimensional stability against temperature, estimated by the Vicat softening point, remained similar to that of PLA in the blends.

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