

Tougher biodegradable polylactide system for bone fracture fixations: Miscibility study, phase morphology and mechanical properties.

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Abstract

Choosing materials for orthopedic implants often imposes strict requirements for the mechanical properties. Poly-L-lactide (PLLA) is widely employed for this purpose, however toughening schemes are necessary for its suitable application. Blending of PLLA and biodegradable poly(L-lactide-co- ϵ -caprolactone) copolymer (PLCL) showing a thermoplastic-elastomeric behavior has been performed in an effort to toughen the PLLA without compromising its biodegradability and biocompatibility. The miscibility state of PLLA/PLCL blend system is studied by means of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). The mechanical properties will be also discussed, as well as, phase morphology observed by Scanning Electron Microscopy (SEM).

Blends of PLLA/PLCL show different miscibility degrees depending on the blending process and the copolymer content. Blends prepared by melt-quenching show a miscibility window for compositions ≤ 30 wt. % of PLCL, while a phase separation

occurred in the rest of compositions. The toughness of PLLA was considerably improved by the addition of PLCL. The elongation at break was significantly increased.

Introduction

In the past decade new researches have further expanded the feasibility of bioresorbable polymeric fixation, eventually leading to clinical application as devices. Choosing materials for orthopedic implants usually focuses on the material and structural properties of the bone or skeletal defect to be replaced which often imposes strict requirements for the mechanical properties. Usually high mechanical strength and stiffness are extremely important in designing biodegradable devices, such as, screws, plates or pins, for bone fracture fixation (osteosynthesis procedures).

In this sense, poly(L-lactide) (PLLA) and its composites have been reported to be suitable for designing bone fracture fixations [1-10]. PLLA is a semicrystalline biodegradable thermoplastic polymer with a glass transition temperature (T_g) ~ 60 °C and melting temperature (T_m) ~ 180 °C that it is obtained by ring opening polymerization (ROP) of L-lactide. Despite the fact that PLLA shows suitable elastic modulus and mechanical strength comparable to poly(ethylene terephthalate) (PET) [11], its inherent brittleness when processed using standard processing conditions [12], limits its use in the above mentioned applications. The impact strength of PLLA has been reported to be on par with polystyrene (26 J m^{-1}) [13], another relatively brittle polymer.

From a clinical point of view, a ductile mode of deformation is desirable, since a brittle breakage of an implant before union of a fracture results in bone redisplacement and loose of material fragments, which might cause irritation or some adverse reaction [14-16]. Therefore, in order for PLLA to be suitable for applications where mechanical toughness is required, toughening schemes and improved composites or blends are needed. This strategy will improve the functionality and reliability of PLLA based implants, and in turn leading to more stable surgical processes.

Many strategies have been developed to alter the properties of a polymer. The chemical synthesis of copolymers is an interesting method in order to design new polymers with special properties. However, this method is generally more expensive, as well as, less-

industrial-practiced method than the blending operation. A proper selection and combination of polymeric components in a certain ratio might result in a blend material with optimal properties for a specific application. Numerous attempts have been made to toughen polylactides through blending with different commercial thermoplastics and rubbers [17-21]. Nonetheless, for biomedical applications biocompatible and/or biodegradable polymers have to be used. Although several works have been published regarding the use of various biodegradable polyurethanes as the dispersed phase [12,22-23], one of the most studied polymer blends of polylactide (PLA) are those containing polycaprolactone (PCL). In spite of the rubbery characteristics shown by PCL (with an elongation at break of approximately 600 %) make it an ideal counterpart for toughening polylactide, it is known that this immiscible binary blend generally leads to insignificant improvements in mechanical properties [12,24-28]. As an alternative, this work focuses on improving the toughness of PLLA by blending it with a biodegradable and bioresorbable poly(L-lactide-co- ϵ -caprolactone) copolymer (PLCL). In this work a PLCL copolymer with a molar composition of approximately 70 % L-lactide and 30 % of ϵ -caprolactone has been employed. It is an amorphous polymer with a T_g of ~ 24 °C and presents a thermoplastic-elastomeric character, i.e., elastomeric behavior, high elongation at break and high elastic recovery capacity. Moreover, in general, PLCLs offer better thermal stability during processing as well as a suitable toughness for being used as raw material in the design of implants and medical devices [29-31]. These characteristics can provide an improvement in the mechanical properties of PLLA.

In this work, a novel polymer blend system composed of PLLA and PLCL copolymer, PLLA/PLCL, is presented as an alternative biodegradable and bioresorbable material to tune the properties of PLLA. The aim of this work is to study the miscibility state, phase morphology and mechanical properties of this polymeric system.

Materials and Methods

Materials

Poly(L-lactide) (PLLA) was supplied by Biomer (Germany). The weight average molecular weight (M_w) and polydispersity index (D) were $160000 \text{ g mol}^{-1}$ and 1.70, respectively.

Poly(L-lactide-co- ϵ -caprolactone) (PLCL) of approx. 70:30 L-lactide/ ϵ -caprolactone in molar ratio was supplied by Purac Biochem (The Netherlands). The weight average molecular weight (M_w) and polydispersity index (D) measured were $176400 \text{ g mol}^{-1}$ and 1.68, respectively.

The composition of this statistical copolymer and its chain-microstructural features were well resolved with the determination of several parameters such as the randomness character ($R=0$ block character to $R=1$ random) and the number average sequence lengths of its constituent L-Lactide (LA) and ϵ -caprolactone (CL) blocks (l_{LA} and l_{CL}) by ^1H and ^{13}C Nuclear Magnetic Resonance spectroscopy (Spectra shown in Figure 1 of the supporting information). The results of the molecular characterization indicate that PLCL composition consists of 67.1 % LA and 32.9 % of CL, in molar ratio, and that presents a slight multiblock character as revealed by a randomness value of $R=0.69$. The average sequence lengths of LA and CL sequence blocks, l_{LA} and l_{CL} , were calculated to be 4.35 and 2.13.

In both cases, the molecular weight distribution was analyzed by gel permeation chromatography using a Waters 1515 chromatograph apparatus equipped with a Waters 2414 refractive index (RI) detector. Chloroform at $35 \text{ }^\circ\text{C}$ was used as the eluent and the Styragel columns were calibrated with polystyrene standards.

Blend Preparation

Blends of PLLA/PLCL system were prepared in three different ways.

- Solution/precipitation method: Chloroform solutions of polymers and their blends were prepared at concentration of 5 wv.%. Large excess of methanol was used for precipitation of polymer solutions. The precipitants were then air dried for 1 day in air and 2 days at vacuum.
- Solvent Casting method: Films of neat polymers, PLLA and PLCL, and their blends were prepared using solvent evaporation method from 5 wt.% solutions in chloroform. The resulting polymer films were first air dried for 48 h and then

dried for 7 days at vacuum at room temperature in order to assure the complete solvent evaporation.

- **Melt mixing method:** Sheets of neat polymers and their blends were prepared by melt-mixing by DSM Xplore micro-compounder (Netherlands) at 200 °C and speed of 100 rpm for 4 minutes and then conformed by compression moulding in a Collin P 200E hydraulic press (Germany) at 200 °C followed by water quenching. The resulting sheets had a thickness of 1 mm.

Determination of polymer blend miscibility

The miscibility state of the PLLA/PLCL blend system was evaluated according to the unique glass transition temperature (T_g) criterion. The most common use of T_g in determination of polymer/polymer miscibility is based on the premise that a single T_g indicates the domain size is comparable to the macromolecular radius of gyration, i.e., $2 \leq d_d \leq 15$ nm, which is necessary requisite for fulfilling the condition of the thermodynamic micibility, viz. $\Delta G_m \approx \Delta H_m \leq 0$, and $\partial^2 \Delta G_m / \partial \phi^2 > 0$. Therefore, following this criterion it is accepted, that blends displaying a single T_g are miscible [32]. The T_g behavior was analyzed by means of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

Thermal behavior was analyzed by a Q200-Differential Scanning Calorimeter (TA Instruments), calibrated with pure indium and sapphires. Two subsequent scans were performed from -60 °C to 200 °C at 20 °C min^{-1} . Thermal properties were measured in the second scan. The glass transition temperature (T_g) was determined from the inflection point of the heat flow curve, the cold crystallization temperature (T_c) and the melting temperature (T_m) from the exothermic and endothermic peak position, respectively, and the cold crystallization enthalpy (ΔH_c) and melt enthalpy (ΔH_m) were obtained calculating the area under the corresponding crystallization and melting peaks. The sample weight was between 5 and 10 mg in all cases.

Dynamic mechanical measurements were carried out using a DMA/SDTA861e (Mettler Toledo) in tensile mode. The PLLA/PLCL samples were heated from -20 °C to 90 °C at a heating rate of 3 °C min⁻¹ and a frequency of 1 Hz. The displacement and force amplitude were maintained at 30 µm and 3 N for compositions with ≥ 50 wt.% of PLCL, and 25 µm and 0.5 N for compositions < 50 wt.% of PLCL.

Mechanical properties

Tensile tests were performed at 22 °C and 50 % of relative humidity (RH) with an Instron 5565 testing machine at a crosshead speed of 5mm min⁻¹. Dumbell-shaped samples were punched out from sheets following ISO 527-2 (ISO 527-2 /5A/ 5).

Phase morphology

A JSM-6400 (JEOL) Scanning Electronic Microscope was used to observe the fracture surfaces of the broken specimens after tensile tests and analyze phase morphology of the blends. Previous to observation the polymeric specimens were coated with a thin layer of gold using a BAL-TEC SCD 004 sputter coater.

Results and Discussion

Miscibility study

The miscibility of any blend system mainly depends on the behavior of the blend components. Three different miscibility behaviors can be expected in any polymeric blend system: The components demix at all blend compositions in the pure components (fully immiscible); the components exhibit phase separation with partial solubility of the components or a miscibility gap depending on composition (partially miscible), or the components form an homogeneous phase in the whole compositional range (fully miscible). Blends of PLLA/PLCL were obtained by solution/precipitation in a chloroform/methanol pair, by solvent casting from chloroform solutions, and by melt mixing, leading to different results.

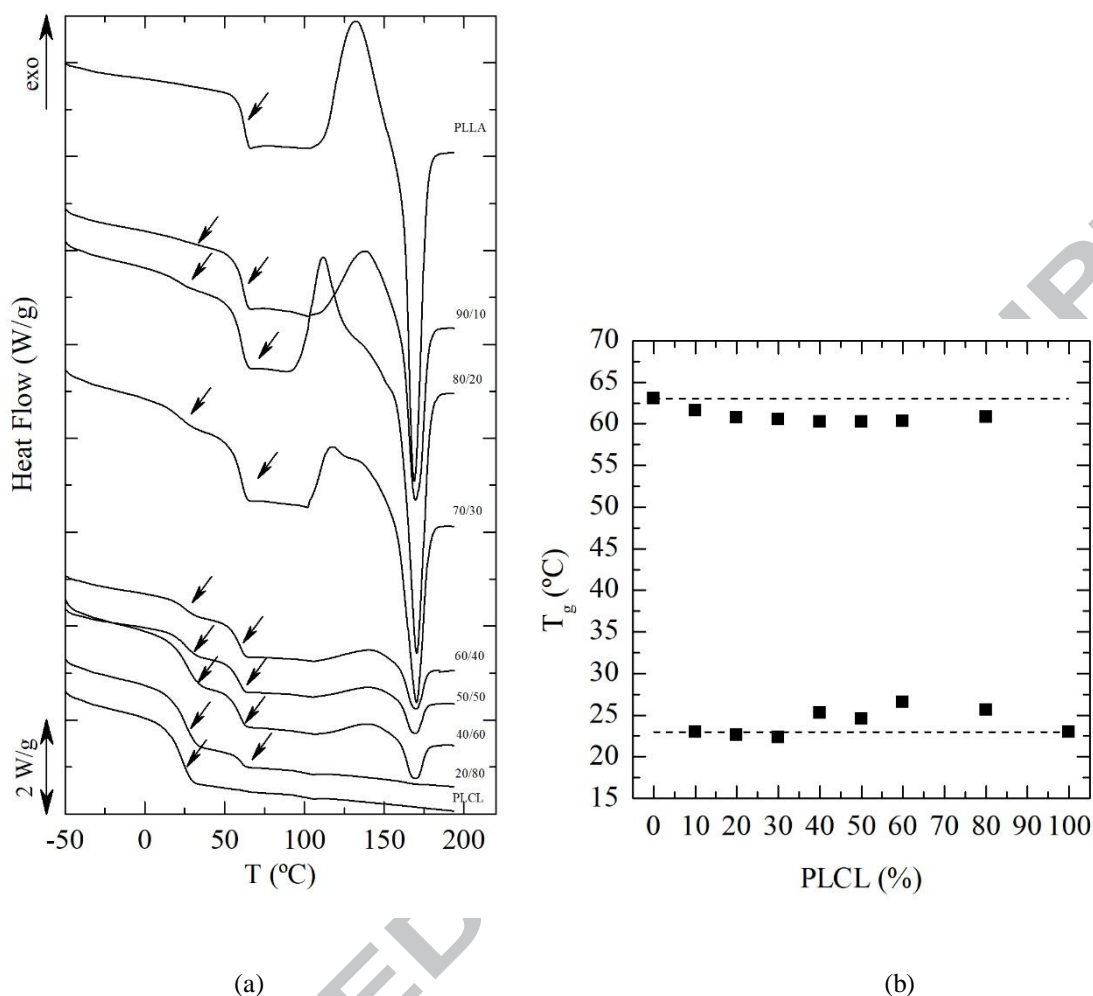


Figure 1. (a) 2nd scan DSC traces for PLLA, PLCL and PLLA/PLCL blends of different compositions obtained by solution/precipitation (b) T_g behavior depending on PLCL copolymer content for PLLA/PLCL blend system obtained by solution/precipitation. The horizontal lines represent the behavior of a fully immiscible polymer blend.

Figure 1 and Table 1 show the second DSC traces, the T_g behavior and the corresponding thermal transitions of PLLA, PLCL and PLLA/PLCL blends of different compositions obtained by solution/precipitation method. PLLA semicrystalline homopolymer shows the T_g around ~ 63 °C followed by a cold crystallization and subsequent melting peak. The T_c and T_m are located at 133 °C and 169 °C, respectively. The values for melting (ΔH_m) and cold-crystallization enthalpies (ΔH_c) are low and their net sum value is near zero, indicating that the PLLA obtained after solution/precipitation procedure was essentially amorphous. In contrast, PLCL copolymer shows only a single T_g at ~ 23 °C indicating its amorphous behavior.

Regarding PLLA/PLCL blends, all compositions show two distinctive T_g s pointed with arrows in Figure 1 (a), T_{g1} and T_{g2} , indicating a clear phase separation of the two components. No significant change is observed in their values comparing them with the T_g s of pure components, the first T_{g1} could be ascribed essentially to the PLCL copolymer and the second T_{g2} to the PLLA homopolymer. Figure 1 (b) illustrated the T_g behavior depending on PLCL content for PLLA/PLCL system obtained by solution/precipitation. In this image is clearly observed that the measured values of T_{g1} and T_{g2} are those observed for pure PLCL and PLLA which show their respective T_g s at ~ 23 °C and ~ 63 °C. This T_g behavior indicates a complete immiscibility of the components in the polymer mixtures.

Table 1. Thermal properties of PLLA, PLCL, and PLLA/PLCL blends of different compositions obtained by solution/precipitation method.

PLCL (wt.%)	T_{g1} (°C)	T_{g2} (°C)	T_c (°C)	ΔH_c (J g ⁻¹)	T_f (°C)	ΔH_f (J g ⁻¹)
0		63	133	37.1	169	38.1
10	23	62	139	18.7	170	19.5
20	23	61	112	17.9	170	21.3
30	22	61	118	13.9	170	15.3
40	25	60	141	4.3	170	4.8
50	25	60	141	2.6	170	3.4
60	27	60	140	1.9	170	2.5
80	26	61				
100	23					

Regarding the cold crystallization process, ΔH_c tends to decrease continuously with PLCL content till its complete suppression for 20/80 composition blend. Moreover, the T_c increases ~ 7 °C (from 133 °C to ~ 140 °C) with the incorporation of PLCL for most compositions, with the exception of 80/20 and 70/30 compositions which show a lower T_c than pure PLLA. Both results could be attributed to the barrier imposed by the second component, PLCL, in the chain mobility of PLLA, on the one hand retarding the formation of crystals upon heating and on the other hand even hindering the crystal

formation. No changes were observed for T_m values. It remains constant at ~ 170 °C. Moreover, both values ΔH_c and ΔH_m are quite similar, indicating that the blends obtained from solution/precipitation method were essentially amorphous.

As a comparative purposes the amorphous phase behavior of blends prepared by solvent casting method were also analyzed. The results obtained were in agreement with those of the solution/precipitation method in terms of thermal transition values and behavior (The second DSC traces and the corresponding thermal transitions of PLLA, PLCL and PLLA/PLCL blends of different compositions obtained by solvent casting are shown in Figure 5 and Table 1 of the supporting information, respectively). This results verify the immiscibility state of these polymer blends.

The above mentioned blending methods are really useful at laboratory scale in order to evaluate the miscibility behavior of any polymer blend. However, from the industrial point of view, as a previous step of any final conformation process melt-blending of components is required. Generally, melt-blending processes imply high temperatures; hence mixing at high temperature can trigger a series of chemical processes leading somewhat to different results obtained by other blending methods. Therefore, the evaluation of this PLLA/PLCL system prepared by melt-blending is considered especially important in this work.

Figure 2 and Table 2 show the second DSC traces and the corresponding thermal properties of the sheets obtained after melt-mixing and quenching in water for pure PLLA, PLCL and PLLA/PLCL blends. Interestingly, the results obtained differ from those obtained by solution/precipitation and solvent-casting methods where a clear phase separation was observed ($2 T_g$ s) for all compositions.

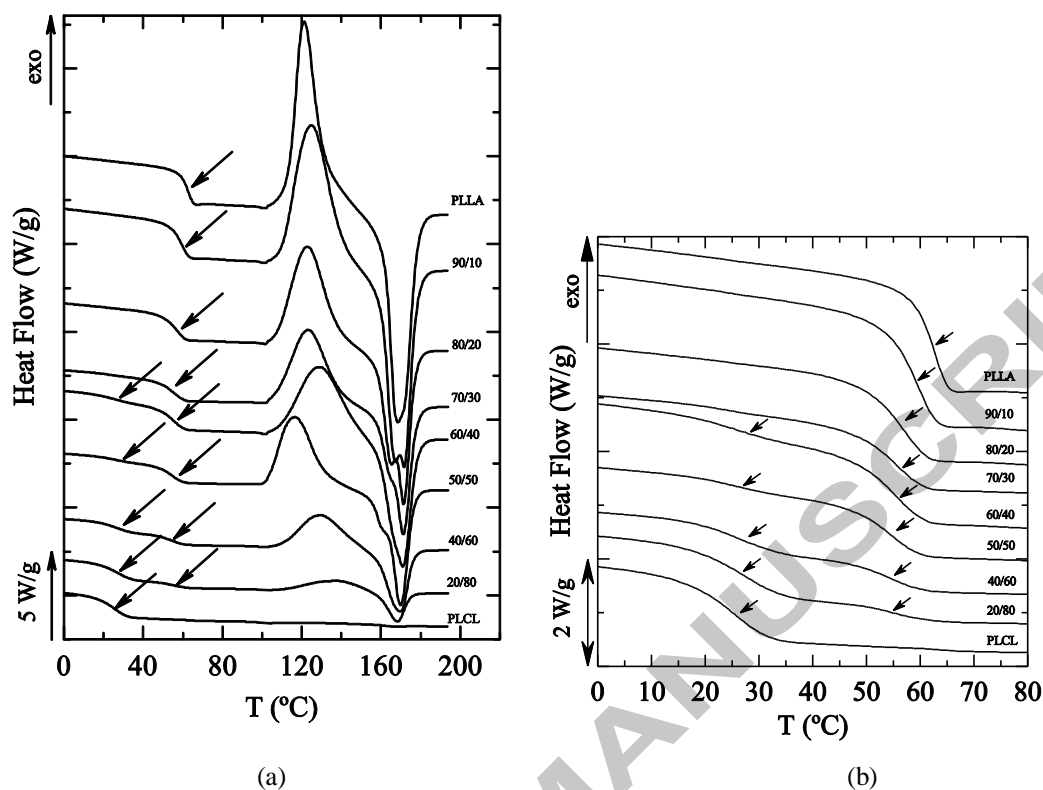


Figure 2. PLLA, PLCL and PLLA/PLCL blends of different compositions obtained by melt-blending (a) 2nd scan of DSC traces and (b) enlarged image of the T_g zone.

Table 2. Thermal properties of PLLA, PLCL, and PLLA/PLCL blends of different compositions obtained by melt-blending method.

PLCL (wt.%)	T _{g1} (°C)	T _{g2} (°C)	T _c (°C)	ΔH _c (J g ⁻¹)	T _f (°C)	ΔH _f (J g ⁻¹)
0		63	121	43.9	169	45.6
10		60	125	44.9	172	45.0
20		57	123	41.7	171	43.3
30		55	123	36.7	171	38.1
40	26	55	129	30.2	171	31.4
50	24	54	117	33.1	170	34.6
60	26	55	130	20.6	170	21.7
80	28	56	138	6.4	168	7.1
100	25					

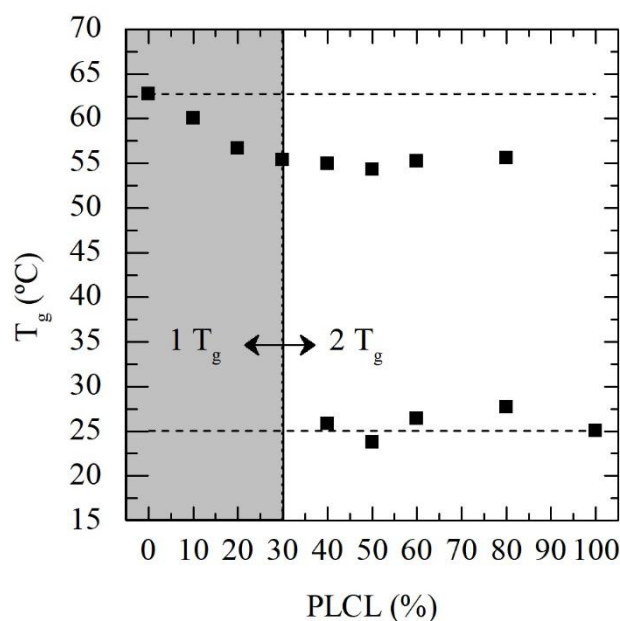


Figure 3. T_g behavior depending on PLCL copolymer content for PLLA/PLCL blend system obtained by melt blending. The horizontal lines represent the behavior of a fully immiscible polymer blend.

A single T_g is observed for blends having less than 40 wt.% of PLCL, i.e., 90/10, 80/20 and 70/30 composition, indicating a single phase in the amorphous state (see Figure 2(b)). However, in blends exceeding 40 wt.% PLCL, the system undergoes phase separation, giving one phase rich in PLLA (T_{g2}) and a second phase consisting mainly of PLCL (T_{g1}). The T_g behavior depending on PLCL content is depicted in Figure 3. As illustrated in this image, the T_g decreases with PLCL in those compositions showing a single phase behavior in the amorphous state (gray shaded area). It decreases from ~ 63 °C (pure PLLA) to ~ 55 °C (70/30 composition). Interestingly, 90/10 and 80/20 compositions show a value close to that predicted by the linear behavior of miscible polymer blends.

As mentioned before from 70/30 composition on a phase separations is observed. Whereas T_{g1} does not suffer any significant change with blend composition comparing it with the value of the pure PLCL copolymer, T_{g2} shows much lower values than that recorded for PLLA homopolymer. Furthermore, it does not suffer any alteration with PLCL content and remains constant at ~ 55 °C. Following the Fox equation (described in equation 1) for predicting the T_g of polymer blends, the amorphous phase rich in PLLA was estimated to be composed of ~ 19 wt.% of PLCL and ~ 81 wt.% of PLLA.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

To verify the results obtained by DSC, Dynamic Mechanical Analysis (DMA) tests were also performed. This technique is particularly sensitive and useful for measuring transitions, such as T_g , in polymers and polymer blends. The drop in storage modulus (E') and peak in damping factor ($\tan \delta$) indicates the glass transition (T_g) of the amorphous polymer.

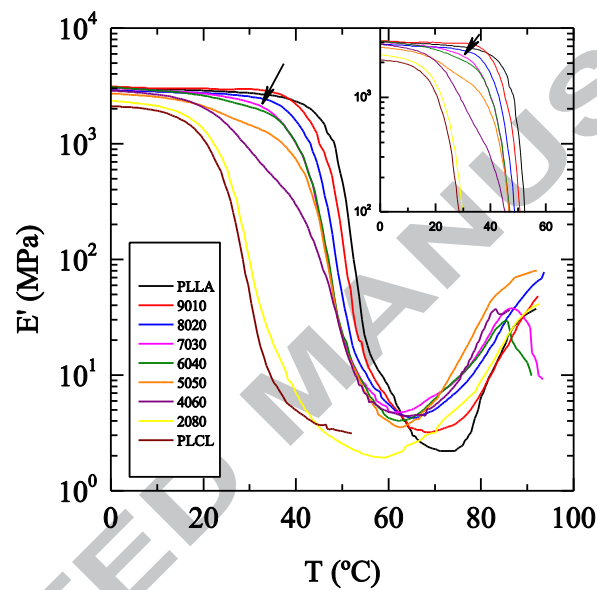
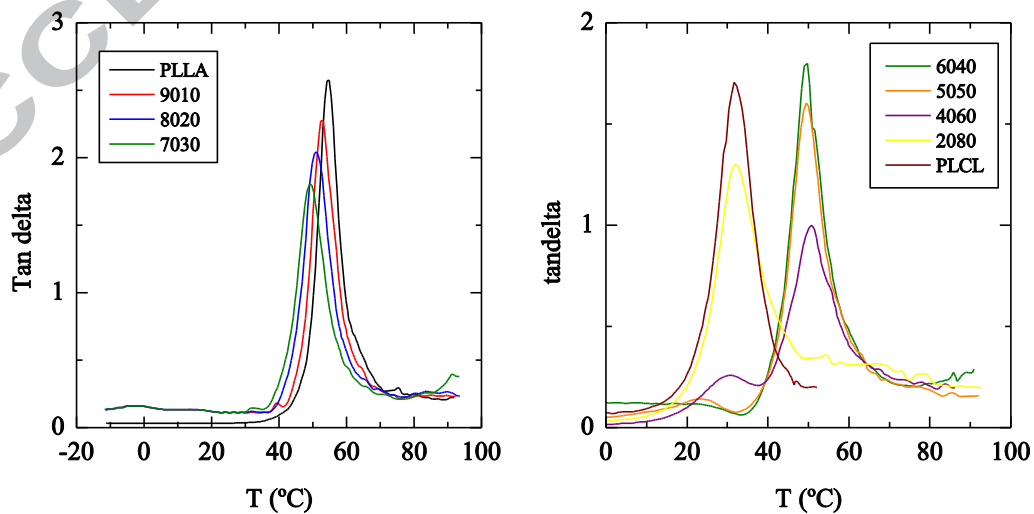


Figure 4. Temperature dependence of the dynamic mechanical spectra on storage modulus, E' , for PLLA/PLCL polymeric system.



(a)

(b)

Figure 5. Temperature dependence of the dynamic mechanical spectra on damping factor, $\tan\delta$, for PLLA/PLCL polymeric system (a) single phase compositions (b) phase separated compositions.

Figure 4 and Figure 5 show the temperature dependence of the dynamic mechanical spectra on E' and $\tan\delta$ of the PLLA/PLCL polymeric system obtained from the DMA measurements. For compositions 90/10, 80/20 and 70/30 a single drop and a single peak are found in the E' and $\tan\delta$ curves respectively. Moreover, the $\tan\delta$ peak shifts towards lower temperatures, from ~ 55 °C to ~ 49 °C, with the increase of PLCL content in the blend, indicating a decrease in T_g value as it is expected from miscible blends. On the other hand, for the rest of compositions two clear drops in E' and two $\tan\delta$ peaks are discernible in their corresponding DMA spectra. The first $\tan\delta_1$ corresponds to mainly PLCL amorphous phase (~ 30 °C), whereas the second $\tan\delta_2$ corresponds to PLLA rich amorphous phase. It is noteworthy that all phase separated compositions, i.e., 60/40, 50/50, 40/60, show their $\tan\delta_2$ at ~ 50 °C. In fact, this value corresponds to the value recorded for the miscible 80/20 blend by DMA (~ 51 °C). This result suggests that PLLA rich amorphous phase is approximately composed of ~ 20 wt.% of PLCL and ~ 80 wt.% of PLLA. All these results are consistent with the results obtained previously from DSC for this polymeric system. Therefore, from these outcomes one can infer that this specific PLLA/PLCL blend system shows a miscibility window below 40 wt.% of PLCL content, whereas for greater amounts of copolymer two different phases can be assumed.

Considering the difference in the miscibility behavior of this system when exposed to high temperature blending, the chemical mechanism responsible for such behavior has to be studied. In this work the hypothesis of the existence of transesterification reactions is supported. According to the literature, ester interchange reactions (generally called transesterification reactions) can occur in polyester blend systems at the melt state [33-38]. These include intermolecular alcoholysis (between hydroxyl end groups and ester groups), acidolysis (between carboxyl end groups and ester groups), and direct midchain ester exchange [39]. Actually, reaction of PLLA with the alcohol groups of a low-molecular weight polycaprolactone (PCL) is reported to carry out at 220 °C for 30-60 min leading to the formation of PLCL copolymer [33].

Following these hypothesis, it is believed that the fact to find a single T_g for compositions having ≤ 30 wt.% of the PLCL, and the T_{g2} decrease for the rest of compositions, is due to the formation of a new PLCL copolymer ($PLCL_t$) with a different composition and sequences of lactide (LA) and caprolactone (CL) units along the copolymer chain that can play an important rol. From our point of view, a complete reaction between both components, PLLA and PLCL, occur during the mixing and subsequent moulding conditions for compositions having ≤ 30 wt.% of PLCL leading to the formation of $PLCL_t$ and resulting in a unique T_g . The behavior of the compositions having > 30 wt.% can be explained on the basis of the reaction degree. Although reactions occur mutually between the two polymers (PLLA and PLCL), it may occur to a greater degree in one of the polymers (in ou case PLLA) and therefore more significant changes can be observed in its T_g values (T_{g2}) comparing it with the other polymer (T_{g1}).

Generally, to quantify the role of the hypothetical transesterification reactions occurring during the mixing step, experimental technique directly sensitive to chemical structure such as Nuclear Magnetic Resonance (NMR) is required. For this purpose ^{13}C NMR was performed for PLCL, melt-quenched miscible and casted immiscible PLLA/PLCL 80:20 samples, and also, for melt-quenched immiscible 40:60 composition (the corresponding NMR spectra are shown in the supporting inforation as Figure 2, Figure 3 and Figure 4). Triads of the spectra were analyzed and compared. No significant changes were observed between the relative areas of the triads resulting in a costant randomness character (R) of the copolymer. Therefore, it is not possible to assure the change of the chain microstructure of the initial PLCL copolymer durig the melt-mixing process. Moreover, it was not observed the isolated signal for lactile (171 ppm). New little signals could be observed but they can be also interpreted as signals of noise. Therefore, analyzing these data can not be demostrated the existence of transesterification reactions. Nonetheless, this technique is not particularly useful of studying the ester-interchange reaction for this specific PLLA/PLCL system. The initial PLLA, PLCL copolymer and the one formed due to the reaction, $PLCL_t$, have identical groups, and hence this fact minimizes the possibility to identify any transesterification reaction in this blend system. Moreover, if the transterification degree is low, it is hard

to detect by NMR, even a low transesterification degree can completely change the composition of the polymeric chain.

In order to prove the transesterification reaction to be the responsible of the miscibility behavior of this polymer blend the following strategy was followed. Solutions of 5 wv.% in chloroform were prepared from melt-quenched PLLA/PLCL sheets of different compositions. Films of these samples were obtained by solvent casting method and let them dry in air for 48 hours and 7 days at vacuum. DSC measurements were performed as described in the materials and methods section and then compared with the results obtained for melt-quenched samples. Figure 6 shows the second DSC traces of the cast-films obtained directly from melt-quenched sheets. Comparing Figure 2 and Figure 6, it was proved that cast-films obtained from melt-quenched sheets show the same phase behavior and thermal transition values as melt-quenched samples. A single T_g was found for compositions 90/10 (~ 59 °C), 80/20 (~ 56 °C), and 70/30 (~ 55 °C), while two different T_g s for the rest of compositions, $T_{g1} \sim 25$ °C and $T_{g2} \sim 55$ °C. These results are in total agreement with the results recorded for direct melt-quenched samples, as shown in Table 2. The unchanging values of T_g s suggest the formation of new chemical bonds between the initial components that remain stable even after the solvent-casting method; this is evidence of transesterification being responsible for the changes in phase behavior discussed in the melt-quenched PLLA/PLCL blends.

Moreover, we have observed that T_g signals of transesterificated phases are broader and the shape of the melting peak corresponding to PLLA crystals for PLLA/PLCL blends changes with respect to pure PLLA (see Figure 2a.). A double peak is observed in the blends. These two results suggest compositional heterogeneity or compositional change of polymeric chains and so they support the existence of the transesterification reaction.

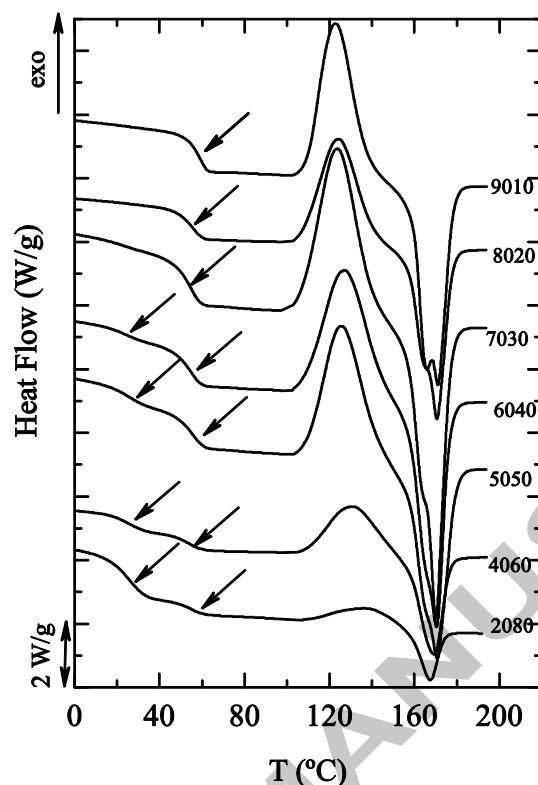


Figure 6. DSC curves of PLLA/PLCL blend system after melt-quenching and casting process.

Mechanical properties

The stiffness, the strength and the elongation at break of the melt-quenched PLLA/PLCL blends were analyzed by means of tensile tests. Figure 7 shows the representative tensile curves of pure PLLA, PLCL and its blends at different compositions and Table 3 summarizes the most relevant mechanical properties including the elastic modulus (E), the tensile strength (σ_{\max}), strain or elongation at break point (ϵ_u) and strain recovery after break (ϵ_r). It has to be pointed out that the criterion used for elastic modulus calculation was different depending on the blend composition. Young's modulus (E_{young}) was calculated for compositions showing a thermoplastic-like behavior (low amount of PLCL), whereas secant modulus at 2 % of strain for compositions showing elastomeric-like behavior (high amount of PLCL).

Neat PLLA displays a brittle fracture showing a distinct yield point with subsequent failure immediately upon the tensile load. Its tensile strength is 71 MPa, while elongation at break is only 12 %. On the contrary, PLCL behaves as an elastomeric

material exhibiting an absence of yield point and a large elongation at break of 837 %. As it is shown in Figure 7, the addition of PLCL changed clearly the mechanical behavior and improved considerably the toughness of the PLLA homopolymer increasing significantly the elongation before it breaks. For example, σ_{\max} of compositions of 20 wt.% and 40 wt.% of PLCL is 47 MPa and 28 MPa, respectively, but the elongation at break increases significantly showing values even seventeen times higher than that of neat PLLA, 204 % and 239 %, respectively.

Two different tensile behaviors are easily observed for PLLA/PLCL blends. While the stress-strain curves for 80/20, 60/40 and 50/50 compositions are typical of thermoplastic polymers showing a clear yielding behavior upon stretching, the curves for 40/60 and 20/80 compositions are typical of thermoplastic elastomeric rubbers. This result can be attributed to phase inversion phenomenon where PLCL turns into the matrix from 50/50 composition on.

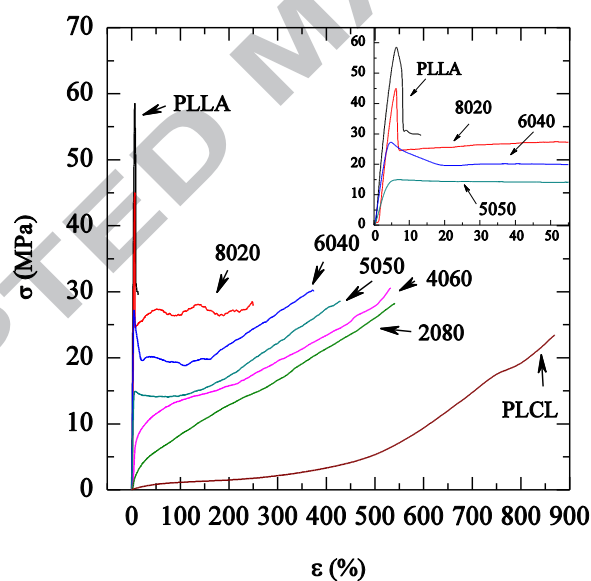


Figure 7. Representative tensile curves of PLLA/PLCL blend system after melt-quenching treatment (black) PLLA (red) 80/20 (blue) 60/40 (cyan) 50/50 (magenta) 40/60 (green) 20/80 (brown) PLCL.

Table 3. Mechanical properties of PLLA/PLCL blend system after melt-quenching treatment. E: Elastic modulus, σ_{\max} : Tensile strength, ε_u : Ultimate strain or elongation at break and ε_r : Strain recovery. ♦ Young's modulus. * Secant modulus at 2 % of deformation.

PLCL (wt.%)	E (MPa)	σ_{\max} (MPa)	ε_u (%)	ε_r (%)
0	1619±220♦	71±9	12±3	0
20	1172±69♦	47±2	204±60	7
40	837±38♦	28±2	239±80	20
50	448±37♦	29.5±2	431±11	19
60	20±4*	29±3	506±50	32
80	13±3*	28.5±2	581±64	82
100	4±3*	25.5±1	837±52	99

In general, the elongation at break increases with increasing PLCL content, while the tensile strength and the elastic modulus decrease with the addition of the copolymer. These tendencies are illustrated in Figure 8, in which the values of the elongations at break and elastic modulus are displayed for the whole blend composition. In the first case, a linear behavior is appreciated, indicating that the PLLA/PLCL blend shows an intermediate ε_u values between the two components for all the composition range. Actually, the elongation at break of PLLA increases from 12 % up to the maximum of 581 % with the incorporation of 80 wt.% of PLCL. However, the values of elastic modulus for this blend show two different behaviors. Low compositions of PLCL (< 40 wt.%) display a linear or intermediate behavior of the two pure components. When composition of PLCL increases a negative deviation to the linear behavior is noticed.

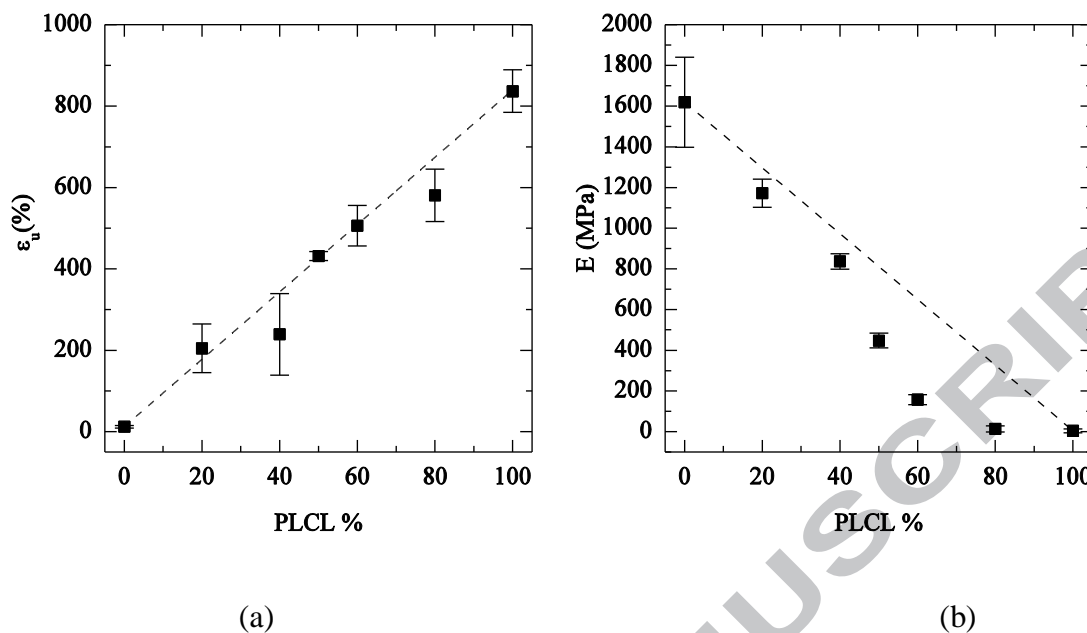


Figure 8. The change in (a) elongation at break and (b) elastic modulus depending on PLCL copolymer content for PLLA/PLCL blends. The dashed line represents the behavior of a hypothetical binary blend displaying intermediate mechanical properties between the two components.

This trend may be attributed to the phase inversion at this range of composition where PLCL acts as the matrix or simply to the fact that the elastic moduli were calculated using different criteria as explained above.

Another important fact found that should be pointed out is the strain recovery observed after the specimens were broken in the tensile tests. It was observed that PLCL copolymer specimens have the ability to recover practically its original size after being stretched. Strain recovery values (ϵ_r) of the different compositions are summarized in Table 3. As it is expected, the ϵ_r increases with PLCL content, but the most significant change in strain recovery was observed for 20/80 composition. It recovers 82 % of its ultimate deformation, while the 40/60 composition only 32 %.

As a summary, Figure 9 illustrates the comparison of the elastic modulus and tensile strength of different human tissues with the values obtained for PLLA/PLCL blends. The compositions having great amount of PLLA fall close to the shaded area corresponding to the trabecular bone, which is at first glance an optimistic outcome. Although more precise measurements are required for full understanding of the mechanical response of this

PLLA/PLCL blend system at service, these preliminary results shed light on the possibility of some of these blend compositions to be used as bone fracture fixations.

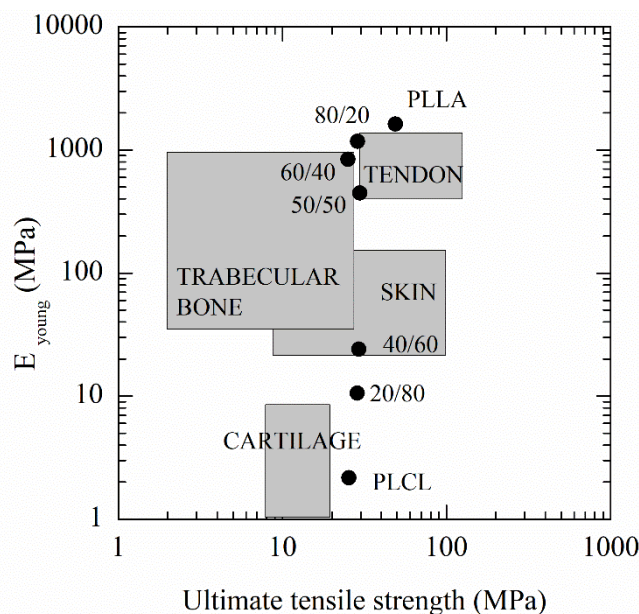


Figure 9. Comparison of the elastic modulus and tensile strength of different human tissues with the values obtained for PLLA/PLCL blends. (Data of human tissues properties are taken from [40])

Blend morphology: SEM analysis of tensile fractured surface

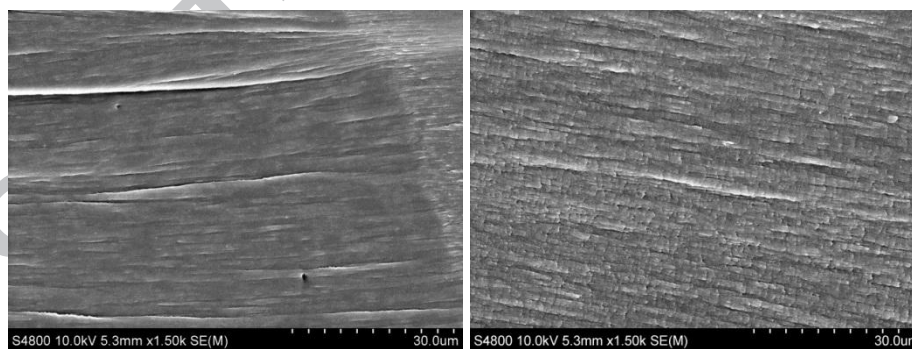
In order to get better interpretation of the blend morphology, surfaces after tensile fractures of PLLA/PLCL blends were observed by means of Scanning Electron Microscopy (SEM). The corresponding micrographs are shown in Figure 10. PLLA shows a smooth fracture surface typical of brittle polymers, indicating a lack of deformation under tensile test conditions. On the contrary, PLCL shows a smooth fracture surface typical of elastomeric polymers, where the surface deforms but it is recovered just after tensile test.

The characteristic and morphological features of fractures surfaces of PLLA/PLCL blends are dependent on the amount of each component.

SEM micrographs show one-phase behavior of 80/20 blend and rather smooth surface according to DSC and DMA results. Though not very clear for 60/40 composition, from that composition on (50/50, 40/60, 20/80) blends appear phase separated, in agreement

with the results of DSC and DMA measurements and much rougher surfaces can be observed as a result of the plastic deformation underwent during the tensile tests. The morphology observed for 60/40 and 50/50 compositions suggest a co-continuous phase structure. From these compositions on, discrete domains in a continuous matrix can be easily distinguished. These domains are homogeneously dispersed in the matrix, but the size of the dispersed phase decreases as the copolymer content increases. This is particularly evident when comparing blends with 60 and 80 wt.% of PLCL. Moreover, by comparing the micrographs it is concluded that the phase inversion occurs for the corresponding 50/50 blend.

It has to be pointed out that no clear distinct interfaces are observed in phase separated blends. This is an indicative of a good interfacial compatibility between the two phases. This is most likely attributable to the presence of the PLCL_t copolymer (the one formed due to transesterification reaction). From our point of view, the dispersed phase mainly consist of lactide unit sequences or blocks of the PLCL_t copolymer while the rest of the sequences composed of the mixture of lactide and caprolactone units (randomly distributed) act as a compatibilizer locating at the interface and improving the adhesion between the separated phases. In addition, this good compatibility is reflected in the improved mechanical properties shown by phase separated blends.



(a)

(b)

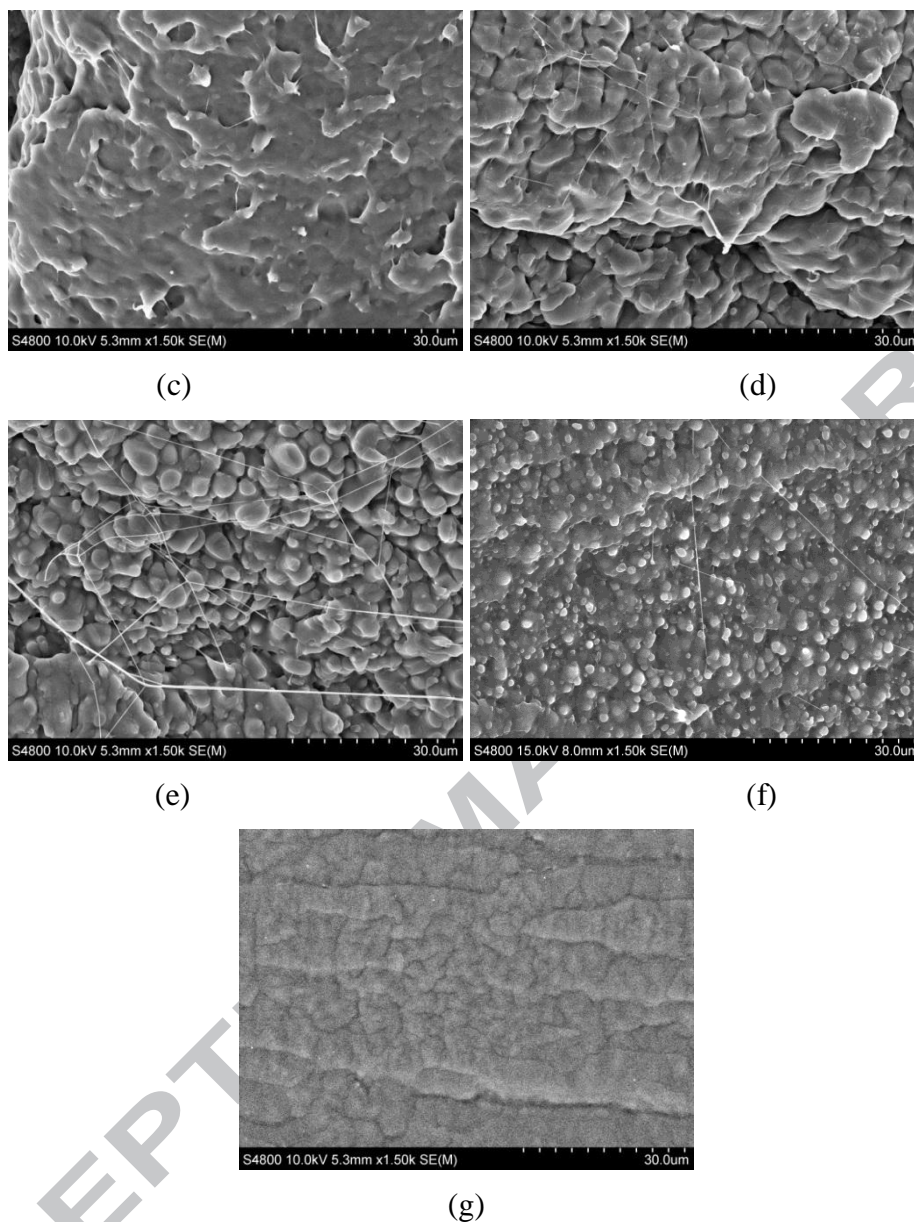


Figure 10. SEM micrographs of the tensile fractured surfaces of (a) PLLA (b) 80/20 (c) 60/40 (d) 50/50 (e) 40/60 (f) 20/80 (g) PLCL.

Conclusions

In this work the miscibility state, the mechanical properties and the phase morphology of PLLA/PLCL blends were presented and discussed.

The miscibility state was evaluated according to the unique T_g criterion by means of DSC and DMA measurements. Three different methods were accomplished in order to analyze the amorphous phase behavior of this polymeric blend. Blends prepared by

solvent casting and solution/precipitation methods showed phase separation in all the composition range indicating the immiscibility of the two components. However, a complete different phase behavior was obtained in blends prepared by melt-quenching process. A miscibility window was observed for composition ≤ 30 wt.% of PLCL, while a phase separation occurred in the rest of compositions.

We found enough evidences to suggest the transesterification reaction occurring in the blend transformation process to be the responsible of the amorphous phase behavior of melt-blended samples. If our hypothesis is correct, the new PLCL_t formed from the reaction of the initial components, PLLA and PLCL, could be the cause of finding a unique T_g for compositions with high content of PLLA and the cause of finding a PLLA rich amorphous phase with constant T_g value in the rest of composition. Moreover, by analyzing SEM images, the good interfacial adhesion encountered between the dispersed phase and the matrix in phase separated blends gave evidence of the compatibilizer role played by PLCL_t.

The toughness of PLLA was improved by the addition of PLCL copolymer. Blends with lower content than 50 wt.% of the copolymer show a typical tensile behavior of thermoplastic polymers, showing clear yielding behavior upon stretching, tensile strength (σ_{max}) values lower than the neat PLLA and significantly increased elongation at break (ϵ_u). The rest of compositions show a typical behavior of thermoplastic elastomeric rubbers with high enough tensile strength and improved elongation at break, as well as, improved strain recovery.

Although more precise measurements are required for full understanding of the mechanical response of this PLLA/PLCL blend system at service, these preliminary results shed light on the possibility of some of these blend compositions to be used as orthopaedic implants for bone fracture fixations.

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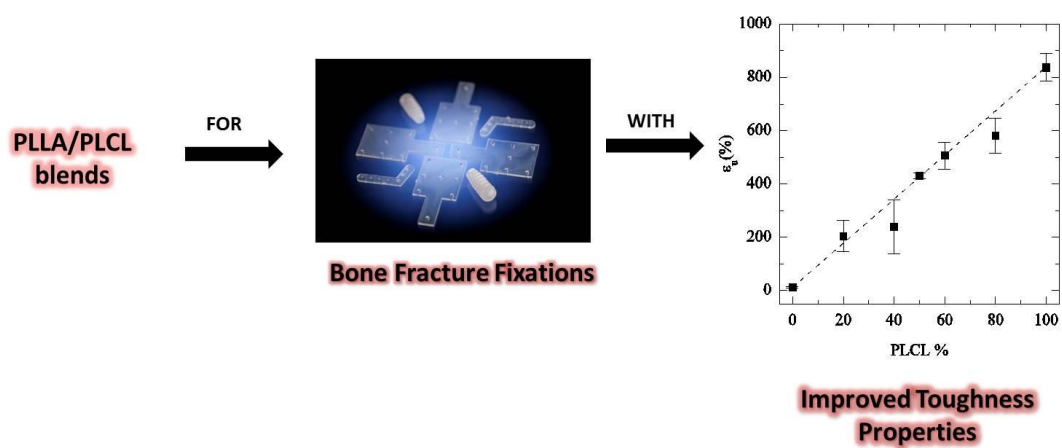
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HIGHLIGHTS

- In contrast to blends prepared by solvent casting and solution/precipitation, melt-quenched samples show a miscibility window.
- Good interfacial adhesion is observed between the dispersed phase and the matrix in phase separated blends.
- The ductility and toughness of PLLA are improved by the addition of PLCL copolymer.
- The mechanical properties of the compositions having great amount of PLLA (80-50 % wt) are close to those shown by the trabecular bone.
- Preliminary results shed light on the possibility of some of these blend compositions to be used as orthopaedic implants for bone fracture fixations.

Graphical Abstract



ACCEPTED MANUSCRIPT