

Effect of Poly(ϵ -caprolactone-*b*-tetrahydrofuran) Triblock Copolymer Concentration on Morphological, Thermal and Mechanical Properties of Immiscible PLA/PCL Blends

Paula do Patrocínio Dias and Marcelo Aparecido Chinelatto*

Department of Materials Engineering-Campus II, São Carlos School of Engineering-EESC, University of São Paulo-USP, Av. João Dagnone, 1100-Jd. Sta Angelina, São Carlos-SP-Brazil.

*Corresponding Author: Marcelo Aparecido Chinelatto. Email: mchinelatto@sc.usp.br.

Abstract: In this study a low molecular weight triblock copolymer derived from ϵ -caprolactone and tetrahydrofuran was used as a non-reactive compatibilizer of immiscible PLA/PCL blends. Ternary blends with 0, 1.5 wt%, 3 wt% and 5 wt% copolymer and about 75 wt% PLA were prepared by single screw extrusion and characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile and Izod impact testing. SEM micrographs showed that the size of the dispersed PCL domains was practically constant regardless of copolymer concentration. This result can be explained by the low shear rate employed during processing step and a decrease of PCL viscosity by presence of the triblock copolymer. However, when the copolymer concentration increased, strain at break of PLA/PCL blends also increased. PLA/PCL blend with 0 wt% copolymer presented 2% strain at break, whereas PLA/PCL blend with 5 wt% copolymer exhibited 90%.

Keywords: Blends; non-reactive compatibilization; poly(lactic acid); poly(ϵ -caprolactone); triblock copolymer

1 Introduction

Polymer production in the world increased continually from 230 million tons in 2005-322 million tons in 2015, however few countries manage to properly dispose more than 65% of post-consumer polymers [1,2]. This means that the inappropriate disposal of polymer products is also growing continually every year, causing global problems of disposed plastics accumulation [3]. Therefore, there is a need to produce new polymeric materials susceptible to biological degradation, in order to reduce the time that current polymeric products take to fully decompose [4]. Due to the presence of hydrolysable chemical bonds, poly(lactic acid) (PLA) is a biodegradable polyester that is appealing for the industrial field, since it has good processability and is eco-friendly [5]. It is also attractive as a biomaterial through its biocompatibility and bioabsorbability [6]. However, PLA present strain at break between 2-4% at room temperature. Its brittleness and poor toughness at room temperature are characteristics which limit its usage in all areas [7].

Blending PLA with other polymers that exhibit good ductility, such as poly(ϵ -caprolactone) (PCL), is an effective method to overcome the brittle mechanical behavior of PLA [8]. Poly(ϵ -caprolactone) (PCL) is also a biodegradable, bioabsorbable and biocompatible polymer. Its elastic modulus is approximately 0.4 GPa and strain at break at room temperature above 500%. Then, due to its ductile behavior, PCL has been used as a blend component in order to develop new, tougher and more ductile materials [9-11]. Notwithstanding the foregoing, in this study it was opted to overcome PLA brittle behavior by blending it with PCL.

However, PLA and PCL are immiscible, which means PLA/PCL blends have poor interaction between both phases and consequently poor mechanical properties. According to literature, binary PLA/PCL blends

are immiscible in all proportions and usually present brittle mechanical behavior, similar to neat PLA. As a solution, many researchers seek a substance that can be used as a compatibilizer and improve the interaction between the PLA and PCL phases [12-16].

Chee et al. (2013) studied the effect of different glycidyl methacrylate (GMA) contents on PLA/PCL blends. It was noticed that increased GMA amounts resulted in better dispersion and smoother morphology. Also, an optimum strain at break of approximately 327% was obtained when GMA content was up to 3 wt%. It was concluded that the use of GMA as a compatibilizing agent enhanced the ductility and impact toughness of PLA/PCL blends [17].

Finotti et al. (2017) analyzed the effect of a low molecular weight triblock copolymer composed of ϵ -caprolactone and tetrahydrofuran on the compatibility and cytotoxicity of PLA/PCL blends. In the study, the PLA concentration on blends ranged from 95 wt% to 75 wt% and the content of triblock copolymer was kept constant at 5 wt%. The results showed that PLA/PCL containing the triblock copolymer had increased ductility, improved toughness and no toxic effect on cells [18].

This paper investigated the effect of different concentrations of a commercially available low molecular weight ϵ -caprolactone-tetrahydrofuran- ϵ -caprolactone triblock copolymer on morphological, thermal and mechanical properties of immiscible PLA/PCL blends. The main goal is to promote better interaction between PLA and PCL phases by adding the copolymer content and, therefore, to switch the mechanical behavior of PLA/PCL blends from brittle to ductile. This copolymer was chosen to be used as compatibilizer due to its non-toxic effect reported by Finotti et al. (2017). Here, PLA/PCL blends with 0, 1.5 wt%, 3 wt% and 5 wt% copolymer were prepared by melt mixing in a single screw extruder and characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and tensile and Izod impact testing.

2 Experimental

2.1 Materials

Poly(acid lactic) (PLA grade: Ingeo 3251D), manufactured by NatureWorks Co., Ltd., has 1.4% of D-PLA content, 48 MPa tensile strength, 2.5% strain at break and 16 J m⁻¹ Izod impact resistance. This PLA was developed specifically for injection and it is often used as packaging material or household goods such as plastic bowls and cups [19].

Poly(ϵ -caprolactone) (PCL grade: CAPA 6500), produced by Perstorp®, is a nontoxic and biodegradable polymer with a molecular weight of 50000 g mol⁻¹, 800% strain at break and 17.5 MPa tensile strength. Due to its low viscosity and melting temperature of around 60°C, this PCL has been used in the manufacture of orthopedic casts, adhesives and injection molded parts [20].

An ABA triblock copolymer, wherein the A portion indicates the block of ϵ -caprolactone and the B portion represents the block of tetrahydrofuran was used a compatibilizer. The average molecular weight is 2000 g mol⁻¹, polydispersity of 1.3 and low melting temperature (30-35°C), purchased from Perstorp®, with the trade name of Capa™ 7201A [21].

2.2 Blends Preparation

Before processing, the PLA was dried on an oven with air circulation at 80°C for eight hours, while the PCL was dried on a vacuum oven at 40°C for 16 hours. After the drying step, the copolymer was manually mixed for two minutes with PLA and PCL in the correct proportions for each formulation to be processed. Shortly thereafter, the processing occurred in an AX-16 single screw extruder from AXPlasticos with a 16 mm diameter screw, length to diameter ratio (L/D) of 25 and a “pineapple” distributive element type. A crescent temperature profile ranging from 175°C to 190°C was adopted; 60 rpm as the screw speed and torque of 30 N.m. Tab. 1 shows the composition of the PLA/PCL blends prepared under these conditions. The blends were dried in a vacuum oven at 40°C for 12 hours and then injected to obtain test

specimens in an Arbug AllRounder 270 equipment. The temperature profile was ranged from 160°C to 190°C and the mold temperature was 25°C.

Table 1: Composition of PLA/PCL blends

Sample	PLA (wt%)	PCL (wt%)	Copolymer (wt%)
PLA	100.0	-	-
PLAC7	93.0	-	7.0
PLAPCL	75.0	25.0	0.0
PLAPCLC1.5	73.9	24.6	1.5
PLAPCLC3	72.8	24.2	3.0
PLAPCLC5	71.3	23.7	5.0
PCL	-	100.0	-
PCLC7	-	93.0	7.0

2.3 Scanning Electron Microscopy (SEM)

Morphological characterization was carried out on liquid nitrogen-cryogenically fractured surfaces of the PLA/PCL blends. The neat polymers and PLA/PCL blends were kept in a vacuum until the analysis of samples on a Mark Phillips FEI XL50 Scanning Electron Microscope. Images were examined with Fiji image ImageJ 1.50i software and the average of particle size was determined from 300 particles manually. For elongated droplets were only considered the largest diameter.

2.4 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was performed on a DMA 8000 from Perkin Elmer. Test bars were cut off from tensile specimens with dimensions of 50 × 8 × 3.2 mm and tested in a dual cantilever bending at a frequency of 1 Hz, temperature range from -100°C to 120°C accomplished under nitrogen flow in a heating rate of 3 °C min⁻¹ and displacement of 10 μm. Storage modulus (E') and tan δ were recorded as a function of temperature.

2.5 Differential Scanning Calorimetry (DSC)

Samples of 7 mg ± 0.3 mg were analyzed using covered aluminum pans on a Perkin Elmer 8000 DSC equipped with an Intracooler II system for cooling. The temperature was set from -70°C to 190°C at 10 °C min⁻¹ with a dynamic nitrogen atmosphere flowing at 20 mL min⁻¹. The DSC was calibrated against indium as a temperature and enthalpy standard, according to manufacturer's manual. The cooling and second heating scans are reported in this paper. All enthalpy values were normalized by the weight fraction of each polymer in the blends. The values of cold crystallization enthalpy (ΔH_{cc}) of PLA were deducted from ΔH_m.

2.6 Mechanical Testing

The tensile testing was performed at 23°C as ASTM D638 standard with five type I specimens for each composition on an Instron Universal Testing Machine model 5969. The load cell used in the assay was 5 kN and a speed of 5 mm min⁻¹. The results reported are an average of the results obtained in the assay of the five tested specimens.

Izod impact testing was conducted according to ASTM D256 in the XJ Series Impact Testing Machine model X-50Z. The samples were obtained from the injection specimens for flexural testing and molded according to the dimensions described in the standard and notched in a manual carver with a notch of 2 mm. It used the hammer of 1 J with impact speed of 3.5 m s⁻¹. The results reported are an average of the results obtained in the assay of ten tested specimens.

3 Results and Discussion

The triblock copolymer is immiscible in PLA, since the PLAC7 micrograph shows a clear separation of phases with the copolymer droplets dispersed in a PLA matrix (Figs. 1(a) and 1(b)). This phase separation can be explained by the copolymer chemical structure being mostly constituted of ϵ -caprolactone, which is immiscible in PLA.

The copolymer changes the PCL surface (Figs. 1(c) and 1(d)) without presenting a phase separation, suggesting that there is a strong interaction between both components.

SEM micrographs of fracture surfaces for PLA/PCL blends and their respective particle size distribution histograms are shown in Figs. 1(e)-1(h) and average particle size are shown in Tab. 2. SEM micrographs for PLA/PCL blends show PCL droplets dispersed in a PLA matrix, classic phase separation characteristics of immiscible blends.

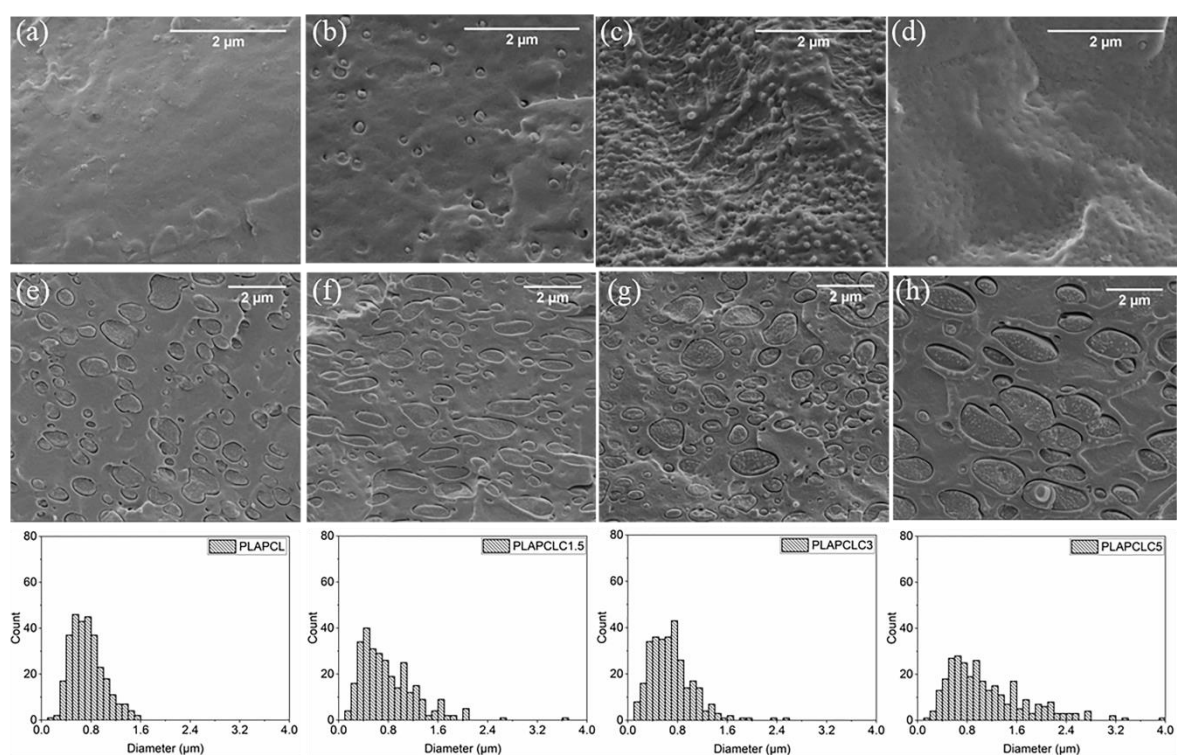


Figure 1: SEM micrographs and particle size distribution histograms of (a) PLA; (b) PLAC7; (c) PCL; (d) PCLC7; (e) PLAPCL; (f) PLAPCLC1.5; (g) PLAPCLC3; (h) PLAPCLC5

According to theory, the role of a compatibilizer in an immiscible blend is to decrease interfacial tension between the components. The interface becomes larger improving the adhesion between PLA and PCL phases [22,23]. Therefore, with the increasing concentration of compatibilizer, interfacial tension, coalescence probability of the dispersed phase and final average droplet size all should have decreased [24,25]. However, the blends containing 71 wt% PLA and 5 wt% copolymer had larger average particle sizes for the dispersed phase. Possibly, the blend with 5 wt% of copolymer reached a micelle limit and the excess of copolymer chains migrated from interface to one or both phases.

A possible explanation for the larger average size of PCL particles observed in the PLAPCLC5 blend is that the increase in the concentration of copolymer changes viscosity ratio between the dispersed phase and the matrix, hindering the droplet breaking process. Proximity between viscosity ratios of PLA and PCL

cause blend morphology to have a uniform distribution. Typically, finer morphology with lower dispersed phase size is obtained when the viscosity ratio between dispersed phase and matrix is close to 1 [26]. In this case, due to copolymer composition being mostly ϵ -caprolactone, the higher copolymer affinity by the PCL phase may have influenced viscosity ratio between phases, reducing PCL viscosity more pronouncedly than with PLA. Therefore, the addition of copolymer to the mix contributes to a lower viscosity ratio and, consequently, larger droplets.

According to literature, droplet radius depends on interfacial tension. However, processing shear rate also plays a big role on droplet shape [27]. Single screw extruders do not achieve as high shear rates as double screw extruders, therefore processing conditions are limited. Low shear rate could be another contributing factor for the slight increase in compatibilized blends average particle size.

PLA and PCL have very different mechanical behaviors at room temperature. PLA is brittle and exhibits low toughness at room temperature, drawbacks that limit its usage as eco-friendly packaging or biomaterial. As PCL is a very ductile polymer reaching over 500% strain at break.

Fig. 2 shows the mechanical properties of neat PLA and PLA/PCL blends under tensile load. The stress-strain curves shown in this figure represent the average mechanical behavior of each sample. Neat PLA showed a strain at break of less than 2% and tensile yield strength of 47.4 MPa. The stress-strain curve of neat PCL is not shown in Fig. 2 due to its high strain at break, higher than the scale used.

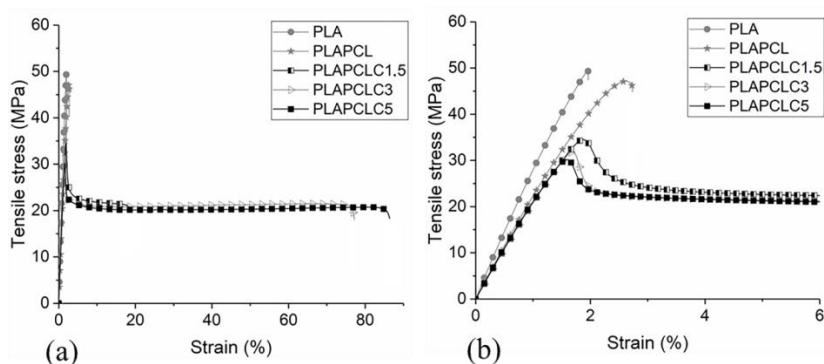


Figure 2: (a) Full range tensile stress-strain curves and (b) tensile stress-strain curves the 0-6% strain range for neat PLA and PLA/PCL blends

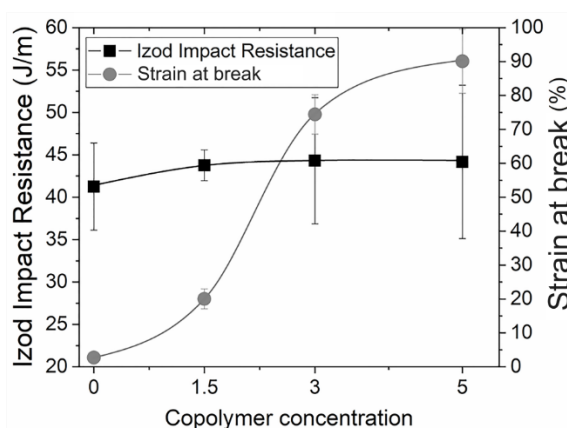
The PLAPCL blend has tensile properties similar to neat PLA, as seen in Fig. 2(b). As the copolymer content increases, strain at break of PLA/PCL blends also increases and tensile yield strength decreases. Therefore, the fracture mechanism of PLA/PCL blends at room temperature changed from brittle to ductile as the copolymer concentration enhanced. Tab. 2 exhibits the tensile properties of neat PLA, PLA/PCL blends and pure PCL.

Young's modulus and impact energy remains constant in PLAPCL blends, independent of copolymer concentration. Since strain at break and tensile yield strength are contrasting properties, tensile yield strength decreases from 47 MPa on PLAPCL to 30 MPa on compatibilized blends, due to the compatibilization promoted by the use of the copolymer, which changes the mechanical behavior of the blends from brittle to ductile [28,29].

Fig. 3 shows how the copolymer concentration influences both toughness and ductility of PLA/PCL blends. Here, toughness was evaluated considering Izod impact resistance (Tab. 2). PLA/PCL blends presented approximately 10 J m^{-1} more on Izod impact resistance than neat PLA. However, as seen in Fig. 3, copolymer concentration has no influence on toughness, something which seems to occur due to the large size of PCL droplets promoted by low shear rate at processing and low viscosity ratio between PLA and PCL induced by the copolymer [30].

Table 2: Particle average size of dispersed phase; Izod impact and tensile properties of neat PLA, PLAPCL blends and pure PCL

Blend	Particle average size of PC (μm)	Young's modulus (GPa)	Tensile yield strength (MPa)	Strain at break (%)	Izod impact resistance (Jm^{-1})
PLA	-	3.0 ± 0.1	49.7 ± 4.2	1.9 ± 0.2	28.7 ± 3.3
PLAPCL	0.70 ± 0.26	2.4 ± 0.1	47.1 ± 2.0	2.7 ± 0.1	39.8 ± 5.2
PLAPCLC1.5	0.79 ± 0.46	2.2 ± 0.1	34.5 ± 1.5	20.0 ± 2.9	43.8 ± 1.8
PLAPCLC3	0.69 ± 0.34	2.0 ± 0.1	30.7 ± 2.6	74.4 ± 5.8	43.3 ± 7.4
PLAPCLC5	1.13 ± 0.66	2.3 ± 0.1	30.2 ± 1.0	90.1 ± 9.5	42.2 ± 9.0
PCL	-	0.4 ± 0.1	16.0 ± 0.3	514.9 ± 42.9	79.1 ± 5.2

**Figure 3:** Correlation between copolymer concentrations and mechanical properties in PLA/PCL blends

PLA brittleness is characterized by low strain at break at room temperature. There was a significant change in the ductility of PLA/PCL compatibilized blends at room temperature (Figs. 2 and 3). Neat PLA and PLAPCL present 2% of strain at break, as PLAPCLC1.5, PLAPCLC3 and PLAPCLC5 have 20%, 74% and 90%, respectively (Tab. 2). Therefore, it is concluded that copolymer concentration does not play any role in the toughness mechanisms of PLA/PCL blends. At the same time, despite the poor mixing process, copolymer concentration directly influences the increase of strain at break. These results also suggest that the commercially available triblock copolymer constituted of ϵ -caprolactone and tetrahydrofuran acts as a compatibilizer of PLA and PCL, promoting better interface interaction between both phases and consequently, higher strain at break values as the copolymer content rises. The blend PLAPCLC5 presented the greatest strain at break.

Fig. 4 shows the storage modulus (E') and $\tan \delta$ as function of temperature curves of all compositions studied. DMA curves were divided in two regions in order to allow observing possible changes in the thermal behavior of PLA/PCL blends, since T_g of PCL occurs at around -60°C and T_m at around 60°C , which is when T_g of PLA occurs as well.

According to Fig. 4, the E' values of PCLC7 below -65°C remained practically constant at 4.5×10^4 MPa as neat PCL present E' values of 3.3×10^4 . This is an unexpected behavior since the triblock copolymer has a low molecular weight and it is soluble in PCL at room temperature. Thus, E' values of neat PCL should have been higher than PCLC7 at low temperature. According to the DSC curves of the first heating, the degree of crystallinity of both samples is the same and a possible explanation for this behavior can be

related to an increase in PCL chain orientation during the processing step induced by the triblock copolymer presence or by a change in lamellae size [31].

E' value of both PCL and PCLC7 start to drop at -65°C , corresponding to a loss of rigidity caused by the greater mobility that PCL chains have when they reach the T_g range. $\tan \delta$ peaks at -56°C for PCLC7 and -52°C for PCL marks their respective T_g (Fig. 4(c)). These results show that the ϵ -caprolactone and tetrahydrofuran triblock copolymer does not significantly change T_g of PCL. The storage modulus curve of PLAC7 shows a significant drop at 47°C , which is related to the range of glass temperature of PLA. In Fig. 4(d) $\tan \delta$ peak for PLAC7 and neat PLA occurs at 63°C and 67°C , respectively. These results according to SEM micrographs suggest that the ϵ -caprolactone and tetrahydrofuran triblock copolymer is immiscible in PLA and has no effect on glass transition temperature of PLA. As it occurs with neat PLA and PCL, the copolymer content has an influence on the stiffness of the blends at low temperatures. The higher the copolymer content, the higher the E' value of the blend at low temperatures.

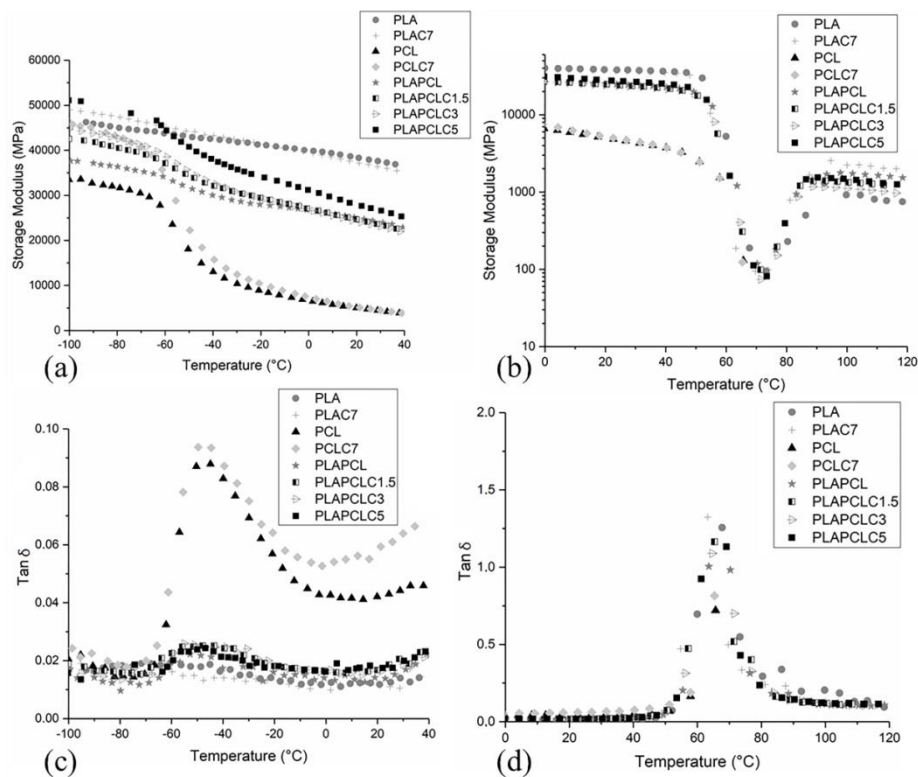


Figure 4: Storage modulus (a and b) and $\tan \delta$ (c and d) curves of neat PLA, PLA with 7 wt% copolymer, neat PCL, PCL with 7 wt% copolymer and PLA/PCL blends plotted against temperature: (a) and (c) from -100°C to 40°C ; (b) and (d) from 0°C to 120°C

Ternary PLA/PCL blends had similar storage modulus and $\tan \delta$ curves. Storage modulus curves show that the higher the content of copolymer, the higher the E' value. This increase in the storage modulus with an increasing amount of copolymer volume may occur due to the lower bulk amount of PCL, i.e., blend fraction that imparts lower stiffness to the blend, since the addition of a copolymer requires a decrease in PCL mass; or it may be due to better interaction between blend phases caused by the presence of the copolymer. $\tan \delta$ curves of PLA/PCL blends show no significant changes in the T_g of PCL, in which the T_g of PCL is about -51°C on the blends. In this case, it is not possible to analyze PLA T_g with DMTA due to same range temperature of PCL T_g and PLA T_m .

Fig. 5 shows DSC curves of the controlled cooling and second heating scans and Tab. 3 the thermal properties of all compositions studied.

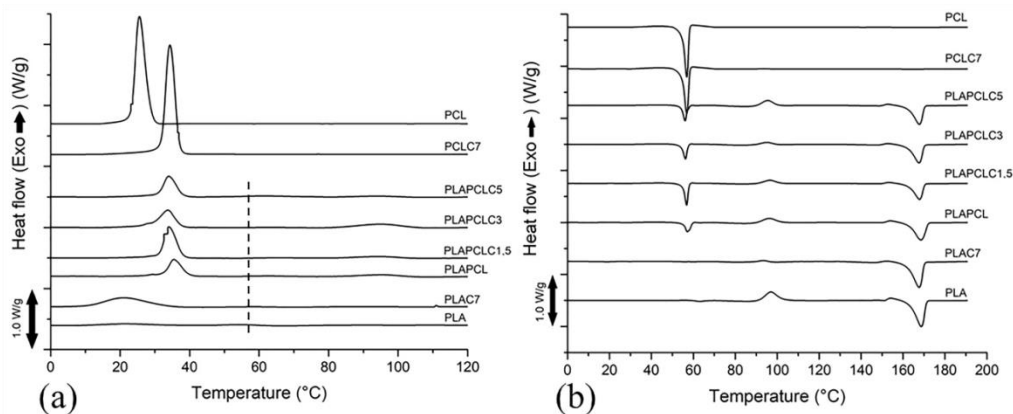


Figure 5: DSC curves of neat PLA, PLA with 7 wt% copolymer, neat PCL, PCL with 7 wt% copolymer and PLA/PCL blends: (a) cooling and (b) second heating runs

There is a clear overlap between T_m of PCL and T_g of PLA in DSC second heating curves (Fig. 5(b)) of the blends, since both occur at around 60°C . Therefore, it is impossible to further analyze the effects of the copolymer on each blend phase. On the other hand, in the DSC cooling curves (Fig. 5(a)), there is a clear separation between PLA and PCL thermal transitions.

Table 3: DSC data of PLA/PCL blends

Samples	Cooling curves			Second heating curves					
	PCL		PLA	PCL		PLA			
	T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	T_{cc} ($^\circ\text{C}$)	ΔH_{cc} (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)
PLA	-	-	64	-	-	96	37	168	6
PLAC7	-	-	56	-	-	93	33	167	10
PLAPCL	35	10	62	57	9	96	29	168	7
PLAPCLC1.5	34	17	60	56	15	96	18	167	8
PLAPCLC3	33	12	59	56	11	94	22	167	9
PLAPCLC5	34	12	59	56	11	95	21	167	8
PCLC7	34	35	-	56	41	-	-	-	-
PCL	31	39	-	56	43	-	-	-	-

The exothermic peak around 35°C (Fig. 5(b)) is related to PCL crystallization and T_g of PLA is characterized by baseline change and remains at around 60°C . Comparing DSC curves of neat PCL with PCLC7 and PLA/PCL blends, it is possible to observe a slight dislocation of PCL crystallization peak to higher temperatures, which indicates that the presence of the copolymer promotes a faster PCL crystallization. PLA T_g values remain practically constant regardless of copolymer content (Tab. 3). This result shows that the copolymer chains do not diffuse through the PLA amorphous phase, a fact that would result in a decrease of PLA T_g [32-34].

Fig. 5(b) shows DSC second heating curves of all compositions studied. DSC curves of the blends present an endothermic peak at 60°C related to the T_m of PCL. At about 100°C, there is an exothermic peak related to PLA cold crystallization. A small exothermic peak preceding an endothermic peak at 170°C occurs due to PLA crystallization and the endothermic peak is associated with the T_m of PLA. As seen in Tab. 3, there is no significant change on T_g and T_m of PLA and PCL.

4 Conclusions

In order to promote better adhesion between PLA and PCL phases and, consequentially, change the mechanical behavior from brittle to ductile of PLA/PCL blends, this study used different contents of a non-toxic, low molecular weight triblock copolymer as a compatibilizer of PLA/PCL blends. The addition of 1.5 wt%, 3 wt% and 5 wt% of triblock copolymer increased the strain at break of PLA/PCL blends. Since the blends with 5 wt% copolymer presented the best result of strain at break, reaching 90%, it is the formulation that is more promising to be further analyzed. The copolymer presence had no effect on the mean particle size of the dispersed phase and on toughness. This result may be related to the low shear rate employed mainly during extrusion, insufficient to promote an effective breakup of the PCL phase. In the interest of producing a biodegradable and biocompatible material that is attractive for both industrial and biomedical fields the further steps of this work should seek to improve toughness of PLA/PCL blends and enhance processing conditions.

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