EFFECT OF MULTIBLOCK COPOLYMERS OF ε-CAPROLACTONE AND ETHYLENE GLYCOL ON THE COMPATIBILITY OF POLY(LACTIC ACID) AND POLY(ε-CAPROLACTONE) BLENDS USING THE PALIERNE MODEL

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Abstract - Poly(ε–caprolactone) (PCL) and poly(lactic acid) (PLA) blends are well studied because of their biodegrability and biocompatibility, but they show a remarkable phase separation. In this context, a compatibilization is necessary and the use of multiblock copolymers based on ε–caprolactone and ethylene glycol is an interesting strategy to improve the mechanical properties of the blend while retaining the biodegradable appearance. The purpose of this study is to investigate the compatibilizing effect of 1%wt of the copolymer using SEM imaging and to estimate the resulting interfacial tension using Palierne model. By means of SEM it was verified that as the copolymers are added, the droplets are more integrated in the matrix, which thus show evidence of increased adhesion between the phases. This fact was corroborated with the results of the Palierne model, in which a significant decreasing of 42% in the interfacial tension compared to the uncompatibilized blend was verified.
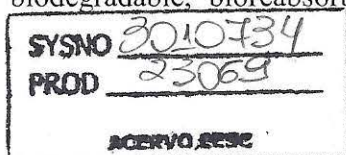**Keywords**: *biodegradable blends, PLA/PCL, compatibilization, Palierne.*

Introduction

Poly(lactic acid) (PLA) has attracted growing scientific and technological interest due to its low impact when discarded in the environment since it shows a excellent biodegradability in biological activity and/or hydrolysis. PLA has a glass transition temperature (T_g) of approximately 60°C and can be used as packaging material because of its ability to be blown and as temporary biomedical devices such as stents and scaffolds for tissue engineering. However, its optimal use is limited due to the relatively low toughness and intrinsically fragile behavior, with an elongation at break of around 5% [1]. Among several methods to improve the mechanical properties of PLA, mechanical blending with flexible polymers is the most convenient, practical and economical route to synergistically combine the advantages of the polymers [2].

Poly(ε-caprolactone), with a T_g around -60°C, is also a biocompatible and biodegradable aliphatic polyester and highly flexible at room temperature. Therefore, it is a good candidate to be blended with PLA resulting in increased toughness. Despite the fact that both are aliphatic polyesters, their blends show a remarkable separation of phases in any composition and a relatively low interfacial adhesion, which compromises the mechanical behavior of the blend [3].

Hereupon, a strategy for improving the adhesion between the phases, decreasing the interfacial tension and hence stabilizing a finer morphology, is the addition of compatibilizers, usually block copolymers which consist of one block with greater affinity for one phase of the blend while the other block exhibits greater affinity for the other phase of the blend [2].

Multiblock copolymers consisting of ε-caprolactone and ethylene glycol blocks (PCL-*b*-PEG) are biodegradable, bioreabsorbable and biocompatible and have already been used in biomedical

applications [4] and as compatibilizers in biodegradable blends [5]. They thus show as excellent candidates for the compatibilization of PLA/PCL blends.

Several techniques to determine the interfacial tension are available, and among these, the rheological methods based on small amplitude oscillatory shear (SAOS) have an advantage of being practically applicable for viscoelastic melt mixtures [6]. Important interfacial properties can be predicted *via* rheological methods based on the non-linear regression of theoretical emulsion models, such as the Palierne model [8,9] which fits the viscoelastic response with fitting parameters linked to the blend's interface, including the interfacial tension.

In this context, the purpose of this study is to synthesize random multiblock copolymers based on ethylene glycol and ε-caprolactone blocks from low molar weight polymers using diisocyanates and to use them as compatibilizers in biodegradable PLA/PCL blends. The improved adhesion between the polymer phases is inferred from interfacial tension estimation by applying the Palierne emulsion model and verified by SEM images.

Experimental

Materials

The used PLA was a Natureworks^{TM} Ingeo Biopolymer 3251 D, with 55000 Da molar weight and D-lactic acid isomer content between 1.2 and 1.6 wt %, a melting temperature (T_m) of approximately 170°C and an elongation at break of 3.5%. The used PCL was a Perstorp^{TM} CAPA6500, with a molar weight of approximately 50000 Da, a T_m around 60°C and an elongation at break of 800%. For the synthesis of the multiblock copolymer, a Perstorp^{TM} CAPA2054, a opened-chain ε-caprolactone polymer with terminal groups of –OH and molar weight around 550 Da and a Oxiteno ULTRAPEG1500 poly(ethylene glycol) with molar weight around 1500 Da were used. The diisocyanate was a hexamethylene diisocyanate (HDI) and the catalyst was the Tin (II) 2-ethyl hexanoate.

Copolymer synthesis

The random multiblock copolymer was synthesized by means of a one-step mass polycondensation, conducted in an inert nitrogen environment, with a [NCO]/[OH] ratio of approximately 0.98, thereby implying that the copolymer is terminated with –OH groups [9]. The copolymer with –OH terminal group is a way to allow reaction continuity and avoid –NCO side reactions that can crosslink the copolymer due to the formation of trifunctional intermediates such as biurets and allophanates [10]. The copolymer's total molar weight is approximately 45000 Da. Based on the molar weight of the blocks, the multiblock copolymer in this study was named as CL550PEG1550.

Blend development

PLA/PCL blends (80/20 wt %) of viscosity ratio 1.7 containing 0 and 1 wt % of multiblock copolymer CL550PEG1500 were prepared in a Thermo Scientific™ Process 11 Parallel co-rotational Twin-Screw Extruder, barrel diameter of 11 mm, L/D=40, 120 rpm and the following temperature program: 115°C / 170°C / 180°C / 180°C /190°C /190°C / 200°C / 200° C. The 80/20 ratio was chosen to meet the criteria for a droplet-matrix morphology required for the correct application of the Palierne model and due to the fact our research group determined the best results of toughness with this ratio [4,12,13].

Blend characterization

The blend morphology was verified using a scanning electron microscope (SEM) model FEI XL 50, Philips Scanning Electron Microscope, with secondary electrons mode. The samples were analyzed based on their cross section after extrusion, covered with a gold layer. The droplet size measurement was performed using Fiji ImageJ measuring 400 droplets.

The viscoelastic response was determined using a TA Instruments rheometer AR2000ex with parallel plate geometry of 25 mm in diameter. The test specimens in the form of disks with a diameter of 25 mm, were prepared by compression moulding using a Collin Presse 200 E plate press at 180°C, 50 bar pressure and 5 minutes total time. The dynamic tests were performed in a frequency range of 0.01-500 rad/s at 180°C and with a gap of 500 μm. The linear viscoelasticity regime was guaranteed by using a strain of 5%. The non-linear regression of the experimental data based on the Palierne model under the hypothesis $\beta'(\omega)=0$ and $\beta''(\omega)=0$ [8,9], was performed using the software SigmaPlot ® 12.0, establishing the blend storage modulus ($G'_b(\omega)$) as the dependent variable, ω as the oscillatory frequency, Φ as the volume fraction of the dispersed phase, G'_m as the matrix storage modulus and $p=4\alpha/R_v$ as the fitting parameter, in which α is the interfacial tension between the phases and R_v is the volume-average droplet radius.

Results and Discussion
The morphology resulting from the uncompatibilized and compatibilized samples are shown in Fig.1. As expected, the morphology demonstrated evident phase separation. In the uncompatibilized blend (Fig. 1 (a)), a discontinuous interface is observed, with pull-out droplets, which provide evidence of low adhesion between the phases. As 1 wt % of CL550PEG1550 is added (Fig.1 (b)), it is observed that some droplets still have clear interfaces, but some of them appear to be better integrated in the matrix with a more continuous interface. Some droplets appear to be smaller, but not statistically different, and harder to be verified, as an evidence of improved adhesion.
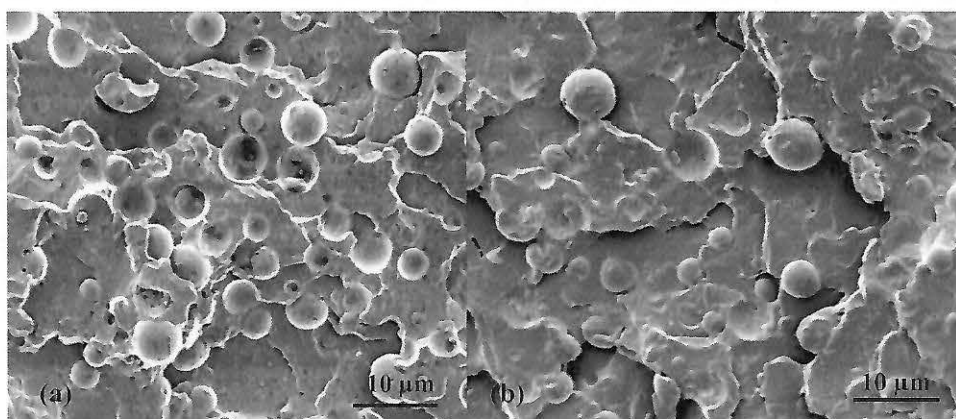

Figure 1: SEM images of uncompatibilized PLA/PCL (a) and compatibilized (b).

The results of number-average droplet radius (R_n), volume-average droplet radius (R_v) and polydispersity index (R_v/R_n) of the dispersed phase are shown in Table 1.

Table 1: Number-average droplet radius, volume-average droplet radius, and polydispersity index of the dispersed phase.

Blends	Rn (μm)	Rv(μm)	Rv/Rn
Uncompatibilized PLA/PCL	1.74 ± 0.54	2.13	1.23
PLA/PCL – CL550PEG1500 – 1%	1.60 ± 0.74	2.67	1.66

The important rheological properties, *i.e*, storage modulus (G') and loss modulus (G''), of the initial materials and blends are shown in Fig.2 (a) and (b), respectively.

In relation to the neat material's viscoelastic response (Fig.2 (a)), the low-frequency region is affected by instabilities in the measurements due to the torque reaching the experimental torque limit, which can be detected by the device. Hereupon, the curves were extrapolated in *loglog* scale according to the terminal behavior predicted by the Maxwell model, *i.e.,* $G' \propto \omega^2$ e $G'' \propto \omega^1$.
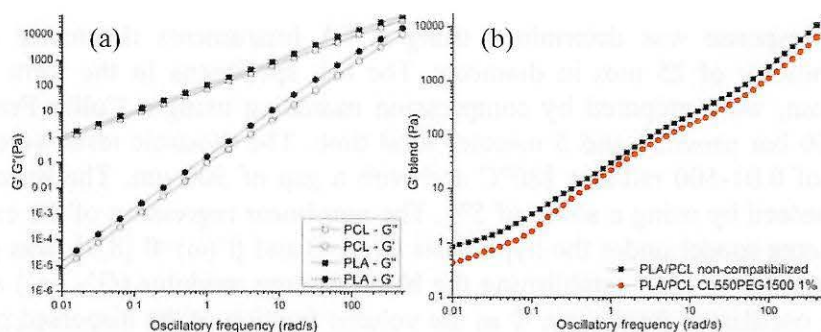
Figure 2: (a) Neat materials G' and G'' and (b) blends G' *versus* oscillatory frequency.

Analyzing the G' *versus* oscillatory frequency curves of the blends, the presence of a shoulder at intermediate frequencies is observed for both blends, which is indicative of the relaxation of the dispersed droplets in a droplet-matrix morphology. Comparing the compatibilized and uncompatibilized blends, it is noted that, as the copolymers are added, a decrease in the elasticity of the blend occurs over the whole frequency range. According to Wu *et al.* [14], in the intermediate frequencies region ($\omega > 1$), the interfacial contribution to G' of the blend is directly proportional to the ratio of the interfacial tension and the volume-average radius (G'$_{interface}$ (ω) $\propto \alpha/R_v$). Hence, according to the observed decrease in G' of the compatibilized blend compared to the uncompatibilized blend, and the fact that the volume-average radius only change slightly (as can be seen in Table 1), it is assumed that upon compatibilization the interfacial tension indeed decreases. However, in the low frequencies regions ($\omega \ll 1$), the relation between G'$_{interface}$ and the ratio of interfacial tension *versus* radius is inversely proportional (G'$_{interface}$ (ω) $\propto \eta_m^2\omega^2/(\alpha/R_v)$). It was thus expected that G' of the compatibilized blend should be higher than that of the uncompatiblized blend in the low frequencies region, but this did not happen. The reason may be related to low reliability in this region due to the fact the related torque is very close to the lower torque limit of the device. The best fits of the storage modulus of the uncompatibilized and compatibilized blends *versus* frequency by using the Palierne model are shown in Fig. 3 and the results are listed in Table 2.
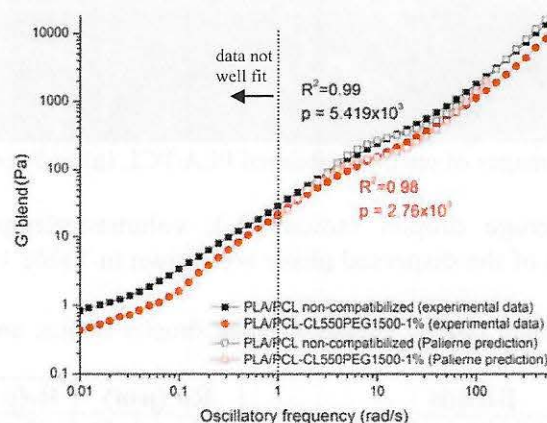

Figure 3: G'$_{blend}$ *versus* oscillatory frequency (rad/s) for the uncompatiblized and compatibilized blends together with the best Palierne fit of the data.

By analyzing the blends, it was found that a reasonable fit was obtained at intermediate and high frequencies. The model did not fit well at low frequencies ($\omega < 1$). This behavior is recurrent in literature for PLA/PCL blends [1]. The interfacial tension results obtained from the non-linear regression of the experimental data are presented in Table 2. Even though the fitting did not cover the entire frequency range, it is possible to verify that by the addition of 1 wt % of the copolymer in the uncompatibilized blend, the interfacial tension decreased by 42%, which is a clear evidence of better adhesion between phases, despite the fact that there was no statistical decrease in the droplet

sizes of the dispersed phase in the compatibilized blend as compared to the uncompatibilized blend. As seen in other study [15], additions of small amounts of a copolymer are already sufficient for a sharp decrease in interfacial tension.

Table 2: Fitting parameters from Palierne model.

Blends	R^2	$p = 4\alpha/R_v$	α (mN/m)
PLA/PCL	0.99	5.96×10^3	3.1
PLA/PCL − CL550PEG1500 − 1%	0.98	2.76×10^3	1.8

Conclusions

By means of this study, it was verified by SEM imaging that upon addition of 1 wt% of a multiblock copolymer based on ε-caprolactone and ethylene glycol in a PLA/PCL 80/20 blend, the PCL droplets appear to be more integrated in the PLA matrix, thereby hinting at increased adhesion between the phases, even though a statistical decrease in the droplet size was not observed. Moreover, this conclusion was corroborated with small amplitude oscillatory rheometry data fitted by the Palierne emulsion model. The resulting interfacial tension, as a fitting parameter for the fit at intermediate and high frequencies, was found to decrease by 42% upon compatibilization, thereby providing further evidence of an improved adhesion between the phases.

Acknowledgements

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