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The Preparation and Characterization of Poly(lactic Acid)/Poly(ϵ -caprolactone) Polymer Blends: The Effect of Bisphenol A Diglycidyl Ether Addition as a Compatibilizer

Aitor Arbelaiz *, Beñat Landa and Cristina Peña-Rodríguez 

Materials + Technologies' Group (GMT), Chemical & Environmental Engineering Department, Faculty of Engineering, Gipuzkoa, University of the Basque Country UPV/EHU, 20018 Donostia-San Sebastian, Spain; blanda005@ikasle.ehu.eus (B.L.); cristina.pr@ehu.eus (C.P.-R.)

* Correspondence: aitor.arbelaiz@ehu.eus

Abstract: The problems created by conventional polymers after their end use have driven research into new biodegradable polymeric materials. PLA is a compostable polymer obtained from renewable sources, but its main drawbacks are its fragility and slow crystallization kinetics. These drawbacks limit its use in different applications. In order to overcome fragility, in the current study, different compositions of PLA/PCL blends, rich in PLA content and without and with DGEBA, were prepared and characterized by means of different techniques, such as FTIR, DSC, DMA, and the mechanical properties. Some compositions show a certain improvement in the deformation capacity compared to the neat PLA at a low test speed. However, when the test speed increases, no improvement is observed in terms of deformation capacity. By SEM, the morphology of injection-molded specimens was observed. All blends showed a biphasic morphology where the PCL droplets are dispersed within the continuous PLA matrix. In the current study, an attempt has been made to improve the compatibility and adhesion between the phases by incorporating a diglycidyl bisphenol A compound. The results obtained indicate that the epoxy groups seem to react with the end groups of the PLA chain; however, the interactions that it creates with the PCL phase are weak, which is in agreement with the FTIR and DSC results obtained.



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Keywords: poly(lactic acid); poly(ϵ -caprolactone); bisphenol A diglycidyl ether; blends; mechanical properties; thermal properties; morphology; dynamic mechanical analysis

1. Introduction

The environmental pollution associated with conventional polymers after their end use is pushing the search for compostable and biodegradable polymers. Poly(lactic acid), PLA, is a compostable polyester that is synthesized from renewable sources, such as corn starch or sugar cane. PLA presents high strength and stiffness at room temperature, which makes it a promising material as a substitute for conventional non-biodegradable petroleum-based polymers. However, PLA shows serious limitations, such as brittleness and a low heat distortion temperature. The low crystallinity degree presented by the polymer, due to a low rate of crystallization and the T_g of 55–65 °C, makes the polymer not very adequate for some applications. Blending PLA with other polymers could be an effective way to overcome these limitations. For example, poly(ϵ -caprolactone) (PCL) is also a polyester and has been extensively investigated in the past. Even though PCL is a petroleum-based polymer, its biodegradability and capacity to be elongated make it an interesting polymer. The blending of PLA with PCL is one of the most frequently used methods to modify its

toughness [1–7]. However, PLA and PCL are thermodynamically immiscible [2–4], and this causes phase separation and tends to lower the fracture properties, especially when the PCL content is increased [5]. In the literature, it was reported that PLA/PCL blends with a crystalline PLA matrix achieved a higher impact strength than blends with an amorphous PLA matrix [8]. However, this improvement is limited by the low compatibility of the PLA/PCL blends and the poor adhesion between the phases [6,9]. Usually, it is necessary to compatibilize an immiscible polymer blend to enhance the adhesion between its immiscible phases [1–9]. For example, Jeong et al. [10] prepared PLA/PCL films by using tributyl citrate (TBC) to improve their mechanical properties. The strength of the PLA/PCL films was enhanced by the co-addition of PCL and TBC. Ye et al. [11] prepared PLA/PCL blends, and as a compatibilizer, glycidyl methacrylate-grafted PLA was used. The addition of a compatibilizer improved the toughness of PLA/PCL blends. Jeon et al. [12] compatibilized blends of PCL and PLA by exposing them to electron beam irradiation in the presence of glycidyl methacrylate (GMA). They concluded that electron beam compatibilization in the presence of GMA enhanced the storage modulus, melt viscosity, and thermal stability with respect to neat PLA. Malinowski [2] combined electron radiation and triallyl isocyanurate in PLA/PCL blends. He observed that there was adhesion improvement between the phases, and furthermore, the phase separation gradually disappeared as the radiation dose rose. Carvalho et al. [13] concluded that PLA/PCL blends, compatibilized with poly(ϵ -caprolactone-*b*-tetrahydrofuran), have the potential for use in equine medicine because they are biocompatible and biodegradable, stimulate a minimal inflammatory response, and support cellular infiltration. On the other hand, Patrício and Bártolo [14] indicated that PCL/PLA blends have impact strength properties that are suitable for temporary implants. In a previous work [15], PLA/PMMA blends that were compatibilized with the addition of a poly(styrene-*co*-glycidyl methacrylate) copolymer were prepared. It was observed that the addition of the copolymer improved the interfacial adhesion between both phases, improving the elongation capability and impact resistance of the blends. The epoxy ring of a copolymer can react with the carboxyl groups and hydroxyl groups of PLA and promote the chain extension and branched architecture.

In the current study, PLA/PCL polymer blends with a high content of PLA were prepared and characterized by means of different techniques. Furthermore, the addition of bisphenol A diglycidyl ether (DGEBA) as a compatibilizer was evaluated because each molecule of DGEBA has two epoxy rings that could react with the carboxyl groups and hydroxyl groups of PLA and PCL. The main aim of the current study was to improve the compatibility and adhesion between the PLA and PCL phases. For this purpose, the incorporation of a diglycidyl bisphenol A compound in PLA/PCL blends was evaluated.

2. Materials and Methods

PLA was purchased from NatureWorks LLC Ingeo™ 3051D with a molecular weight of 106 kg mol^{-1} . Poly(ϵ -caprolactone) CAPA 6800 produced by Solvay with a molecular weight of 80 kg mol^{-1} was used. As a compatibilizer, a diglycidylether of bisphenol A (DGEBA), kindly supplied by Sigma-Aldrich (Massachusetts, United States), was used. The chemical formulas of the PLA, PCL, and diglycidylether of bisphenol A are shown in Figure 1. Regarding the amount of compatibilizer, in a previous study [15], the rheological results of PLA/PMMA blends indicated that, when the P(S-*co*-GMA) copolymer loading of 5 pph was added, the polymer flow was restricted and the viscosity value was excessive for the extrusion process. Based on these results, the amount of epoxy groups added to the PLA/PMMA blend when 5 pph copolymer was added was theoretically estimated. The value estimated for 5 g of copolymer was 0.000465 epoxy group mol; the same epoxy group mol was found in 0.79 g of DGEBA. In each 100 g of the polymer blend, 0.8 g of DGEBA

was added. A similar concentration was used by Gao et al. [16] when they modified PCL/PLA (7:3) blends with 0.6 wt% of peroxide. They observed that the blend with 0.6 wt% of peroxide showed the best mechanical improvements. Matumba et al. [17] modified the PLA/PCL blend with different contents of a styrene-acrylic multi-functional-epoxide oligomeric agent. After the addition of 0.5 wt.% of the epoxidic agent, they observed that the deformation of the break value increased.

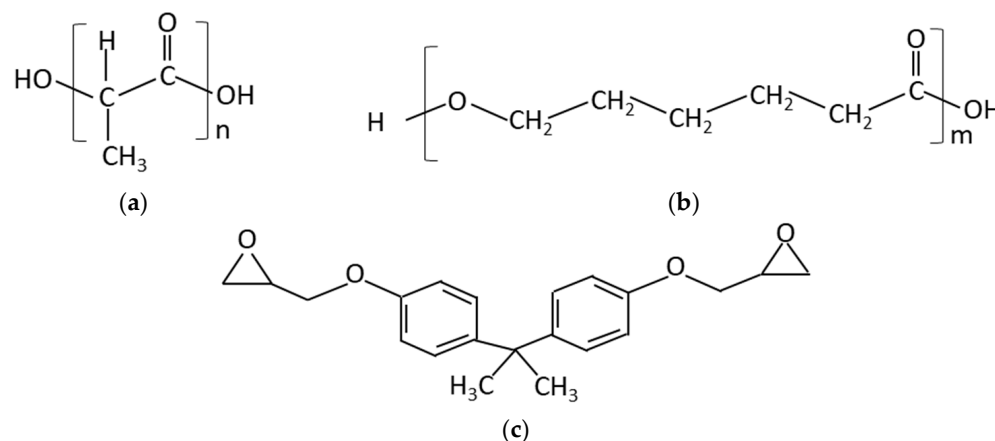


Figure 1. The chemical formulas of (a) PLA, (b) PCL, and (c) diglycidylether of bisphenol A.

2.1. Compounding and Processing of Materials

The polarity of PLA and PCL is due to their ester bonds [18]. PLA and PCL were dried for 4 h at 80 °C and 4 h at 50 °C, respectively, in an oven before blending. Different PLA/PCL compositions were prepared: 95/5, 90/10, 85/15, and 80/20. PCL was dried at a lower temperature than PLA because, at 80 °C, it would be molten. In the literature, it was suggested that the optimal composition for PLA/PCL blends was around 80/20 (w/w); this composition helps maintain the high stiffness of the PLA matrix, and the concentration of PCL particles is sufficient to achieve high toughness [19].

PLA and PCL pellets were melt-blended in a HAAKE Rheomix 600 internal mixer (Thermo Scientific, Karlsruhe, Germany) with two Banbury rotors at 185 °C with a rotor speed of 50 rpm for 5 min. The obtained blends were cooled down until room temperature and pelletized by the cutting mill SM200 (RETSCH, Hann, Germany). All pelletized samples were kept in an oven at 80 °C for 4 h prior to obtaining the tensile test specimens (ASTM-D638-10, type V) by means of a HAAKE Minijet II injection machine (Thermo Scientific). The selected injection and mold temperature values were 195 and 75 °C, respectively, while the molding pressure was set to 850 bar for 8 s.

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were obtained in a Nexus 670 spectrometer (Nicolet, Markham, ON, Canada) equipped with an MKII Golden Gate accessory (Specac, Orpington, UK). The measurements were taken in the range between 4000 and 650 cm^{-1} with a resolution of 4 cm^{-1} , and injection-molded specimens were used. The spectra were measured in reflection mode, and the force applied by the golden gate was adjusted, ensuring the firmest contact to the diamond of the solid sample.

The thermal properties were investigated by differential scanning calorimetry (DSC) using DSC 822e equipment (Mettler Toledo, L'Hospitalet de Llobregat, Spain). Samples with a weight between 5 and 10 mg were subjected to heating–cooling cycles from -60 °C to 180 °C under a nitrogen atmosphere. In order to remove the thermal history, the first heating and cooling scans were carried out at 10 °C/min, whereas the second heating

scan was taken at 3 °C/min. The degree of crystallinity (X_c) was determined according to equation (1) [20].

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{w_c \Delta H_{100\%}} 100 \quad (1)$$

where ΔH_m and ΔH_{cc} are the enthalpy of the melting process and the enthalpy of the cold-crystallization process, respectively. $\Delta H_{100\%}$ is the melt enthalpy for theoretical 100% crystalline PLA, and w_c is the weight fraction of PLA in the blend. In the current work, a value of 93 J/g was taken as the melt enthalpy of 100% crystalline PLA [21].

Dynamic mechanical analysis (DMA) measurements were carried out on an Explexor 100N (Gabo, Ahlden, Germany) using the tensile geometry. A temperature scan was carried out from −100 °C to 180 °C at a heating rate of 2 °C/min. The static deformation set was 0.005%, and the dynamic deformation was 0.01% with a frequency of 1 Hz. The values of the storage modulus (E'), the loss modulus (E''), and $\tan \delta$ were determined. The DSC, TGA, and DMA tests were carried out in duplicate.

Scanning electron microscopy (SEM) micrographs were performed by JSM-6400 equipment (JEOL, Tokyo, Japan) with a wolfram filament operating at an accelerated voltage of 20 kV. Fractured surfaces of the polymer blends were coated with gold using a Q150 TES metallizer (Quorum Technologies Ltd., Laughton, England).

Tensile tests were performed according to the ASTM D638 standard using the Insight 10 testing system (MTS Company, Eden Prairie, MN, USA) equipped with a load cell of 10 kN and pneumatic grips. The tests were performed at different deformation rates, 1, 10, and 50 mm/min, and a video extensometer was used for modulus determination. The tensile properties were averaged from at least five test specimen data.

3. Results

3.1. PLA/PCL Blends

Figure 2 shows the transparency of the prepared systems. PLA and PCL are both semi-crystalline polymers, but neat PLA specimen is transparent, indicating that it hardly crystallized during the processing and a low degree of crystallinity was achieved. On the other hand, neat PCL specimen is opaque, suggesting that the crystallization degree is considerably higher than in neat PLA one. Regarding PLA/PCL blend specimens, as the amount of PCL was increased, the transparency was found to decrease. The reduction in transparency could be ascribed to PLA and PCL polymers' immiscibility. When polymers are not miscible at the molecular level, different polymer phases are found in the blend, and due to the different refractive indices of the components, the system is opaque because light is scattered at the limits of the different phases [22]. Ross et al. [23] calculated a solubility parameter difference ($\Delta\delta$) of 1.8 (cal cm^{−3})^{1/2} for the PLLA/PCL blend using the Coleman–Painter approach [24]. The solubility parameter difference calculated by them suggested that PLLA and PCL are immiscible, which is in agreement with the transparency results obtained for the PLA/PCL blends in the current study.

Figure 3 shows the FTIR spectra of neat polymers and PLA/PCL blends. Both polymers are polyesters and, in general, showed the same bands; however, there are some differences. PLA shows CH₃ stretching at 2999 and 2944 cm^{−1}, whereas PCL shows CH₂ asymmetric stretch bands at around 2944–2866 cm^{−1}. Similarly, Jeon et al. [12] observed CH₂ stretching bands at 2942 and 2864 cm^{−1}. On the other hand, the band related to the C–C (crystal phase) of PCL can be observed at 1293 cm^{−1} [12]. As the amount of PCL was increased in the blend, the intensity of the bands related to the –CH₂– group increased. On the other hand, the band related to C=O stretching vibration was observed at 1749 and 1720 cm^{−1} for neat PLA and neat PCL, respectively. Similarly, Jeon et al. [12] observed C=O stretching vibration at 1745 cm^{−1} and 1723 cm^{−1} for PLA and PCL, respectively.

Gao et al. [16] observed these bands at 1748 and 1729 cm^{-1} for PLA and PCL, respectively. As both polymers are polyesters, in the FTIR spectra of the blends, around 1740 cm^{-1} , an intense band can be observed. It must be highlighted that only when the composition was 80/20 were the bands related to C=O clearly observed for both types of polymers, and they are located at different wavenumbers. The bands are located at 1753 and 1724 cm^{-1} for PLA and PCL, respectively. These band displacements, with respect to neat polymer spectra, suggest that some interactions formed between the PLA and PCL polymers. The intensity of these bands is proportional to the concentration of each component in the blend. However, new bands were not noticed in the blend, indicating that new chemical bonds are not created between both polymers.



Figure 2. Transparency of the prepared systems.

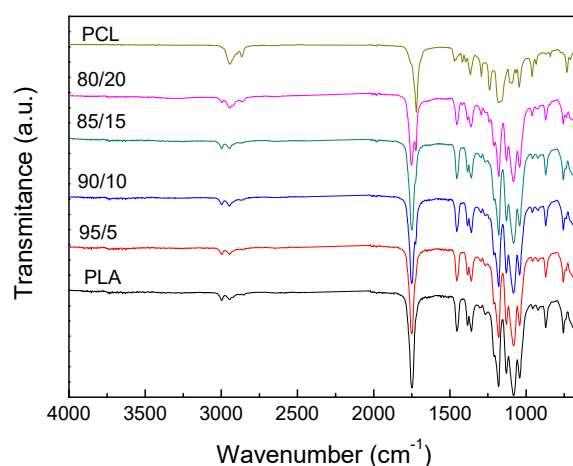


Figure 3. The FTIR spectra of the neat polymers and PLA/PCL blends.

Shuai et al. [25] suggested that when quite strong interpolymer hydrogen bonding exists in PLA blends, the carbonyl band around 1759 cm^{-1} of PLA should shift to a lower frequency, i.e., to a higher wavelength, which is in agreement with the band position change observed in the current study. Ross et al. [23] suggested that the interactions between PLLA and PCL were weak to moderate.

The thermal history of the samples was removed by melting the samples, and after this, the samples were cooled, and subsequently, the second heating run was carried out. The second heating run thermograms are shown in Figure 4, and the data are reported in Table 1.

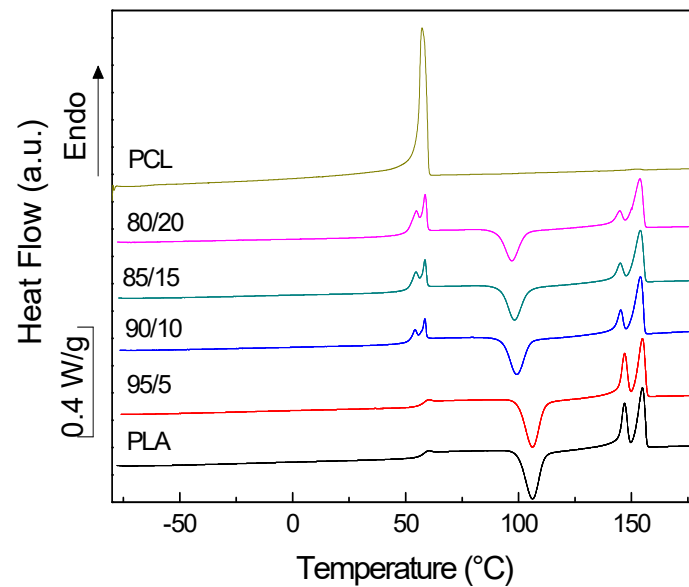


Figure 4. Second heating run thermograms of the neat polymers and prepared systems.

Table 1. The thermal properties of the prepared systems: subindexes A and B indicate PCL and PLA, respectively.

System	T _{gA} (°C)	T _{gB} (°C)	T _{mA} (°C)	ΔH _{mA} (W/g)	T _{cB} (°C)	ΔH _{cB} (W/g)	T _{mB1} (°C)	T _{mB2} (°C)	ΔH _{mB} (W/g)	X _{cA} (%)
Neat PLA	-	55.0	-	-	106.2	−1.24	147.0	155.0	1.35	0.1
95/5	n.a.	55.3	n.a.	n.a.	106.2	−1.28	147.0	155.0	1.33	0.1
90/10	n.a.	51.1	58.6	overlapped	99.2	−1.13	145.3	154.0	1.21	0.1
85/15	n.a.	50.5	58.6	overlapped	98.2	−1.01	145.1	154.1	1.12	0.1
80/20	n.a.	50.1	58.7	overlapped	97.0	−0.91	144.8	153.9	1.11	0.3
Neat PCL	−59.6	-	57.4	2.63	-	-	-	-	-	-

The neat PCL showed an endothermic peak around 57.4 °C related to the melting process of crystals. The high crystallinity of neat PCL makes the observation of the glass transition difficult since the amorphous phase is a small fraction of the sample. Furthermore, the mobility of the amorphous segments close to crystalline structures is limited [26], and consequently, the step change in specific heat capacity is difficult to observe. In the same temperature region, neat PLA showed the glass transition temperature, 56.9 °C, that can be observed as the inflection of the curve. In the PLA/PCL blends, both processes happen simultaneously, and the inflection point and the endothermic peak are overlapped, making the determination of both difficult. However, the onset temperature of glass transition related to the PLA amorphous phase can be determined accurately, and the melting temperature at the maximum of the peak of PCL can be determined for prepared blends. The glass transition temperature of a polymer blend is a criterion for the miscibility of components. In PLA/PCL blends, the glass transition temperature of the PLA phase hardly changes when varying the PCL content, indicating the immiscibility of the two polymers [27].

The peak related to PCL crystal melting increased as the content of PCL was increased in the blend. The neat PLA showed the cold crystallization process during the heating run; in the PLA/PCL blend, the cold crystallization process was also observed, but the crystallization temperature decreased as the PCL content was increased in the blend. A similar trend was observed by Navarro-Baena et al. [4] in PLA/PCL blends. Luyt and Gasmi suggested that during heating, the molten PCL influenced PLA crystal formation; the

presence of PCL stimulates cold crystallization and also influences the cold crystallization mechanism [28]. It seemed that the presence of molten PCL acted as nucleation sites for PLA. Dell'Erba et al. [6] suggested that the presence of PCL increases in the nucleation rate and consequently enhances the PLLA crystallization rate. The cold crystallization temperature decreased until 99 °C when 10 wt% PCL was added; however, beyond this PCL amount, further decreases in temperature were hardly observed. Similarly, Dell'Erba et al. [6] observed that the cold crystallization exotherm of PLA shifted to 100 °C upon blending with 10 wt% of PCL, but a further increase in PCL composition has no effect on the position of this exotherm. All PLA-based systems showed multiple melting peaks, and the height of the first peak decreased as the PCL amount increased. The presence of double melting peaks is a commonly observed phenomenon for PLA, attributing the lowest melting temperature to the melting of original crystals and the highest melting temperature to the melting of the crystals formed through the melt-recrystallization process during the heating scan [3,29,30]. All PLA-based systems hardly crystallized since the crystallinity degree related to the PLA phase was close to zero (Table 1). PLA has a very low crystallization rate [29], and even though the addition of PCL reduces the cold crystallization temperature, there is not a crystallinity degree increase. Similarly, Matta et al. [31] concluded that even though the addition of PCL accelerates the crystallization rate of PLA, its final degree of crystallinity did not change. It is observed that beyond 10% of PCL content, a slight decrease in the melting temperature of the PLA phase was observed; however, beyond this PCL content, it does not further decrease the melting temperature.

The crystallization process can be divided mainly into the nucleation and growth steps. Even though the addition of PCL induced nucleation sites, as observed by the cold crystallization temperature decrease, the final low crystallinity degree obtained for PLA suggested that those sites cannot grow in the selected processing conditions. It must be mentioned that even though the PCL phase can crystallize in the prepared blends, as the amount of PCL is considerably lower than that of PLA, the overall crystallized fraction in the blends is very low. It can be concluded that all systems are almost amorphous.

In Figure 5, the DMTA data obtained for the studied systems are shown. For clarity, in addition to the neat polymers, only the blends with the highest PCL content are shown, 15 and 20 wt%. The Neat PCL showed a decrease in storage modulus at around −50 °C, related to the glass transition temperature. After this, around 60 °C, the storage modulus decreases drastically due to the melting of the crystalline phase. Regarding the neat PLA, the storage modulus decreased drastically around 60 °C, since at this temperature, the amorphous phase gains mobility. As observed by the DSC technique, PLA was almost amorphous, and consequently, around 60 °C, the rigidity of the material was lost completely. The PLA/PCL blends showed similar spectromechanical curves to the neat PLA, which is in agreement with the literature results [31]. The low amount of PCL in the blend makes the observation of its T_g difficult. It must be mentioned that, around 60 °C, two phenomena happen simultaneously: the relaxation of PLA due to the T_g , as well as the melting of PCL [4]. The crystallinity degree of the studied systems was low, and it was not enough to retain the specimen geometry after 60 °C was achieved. The specimen deformed significantly plastically, and the test was stopped. Consequently, the cold crystallization and the subsequent melting process were not possible to observe by DMTA using the tensile mode.

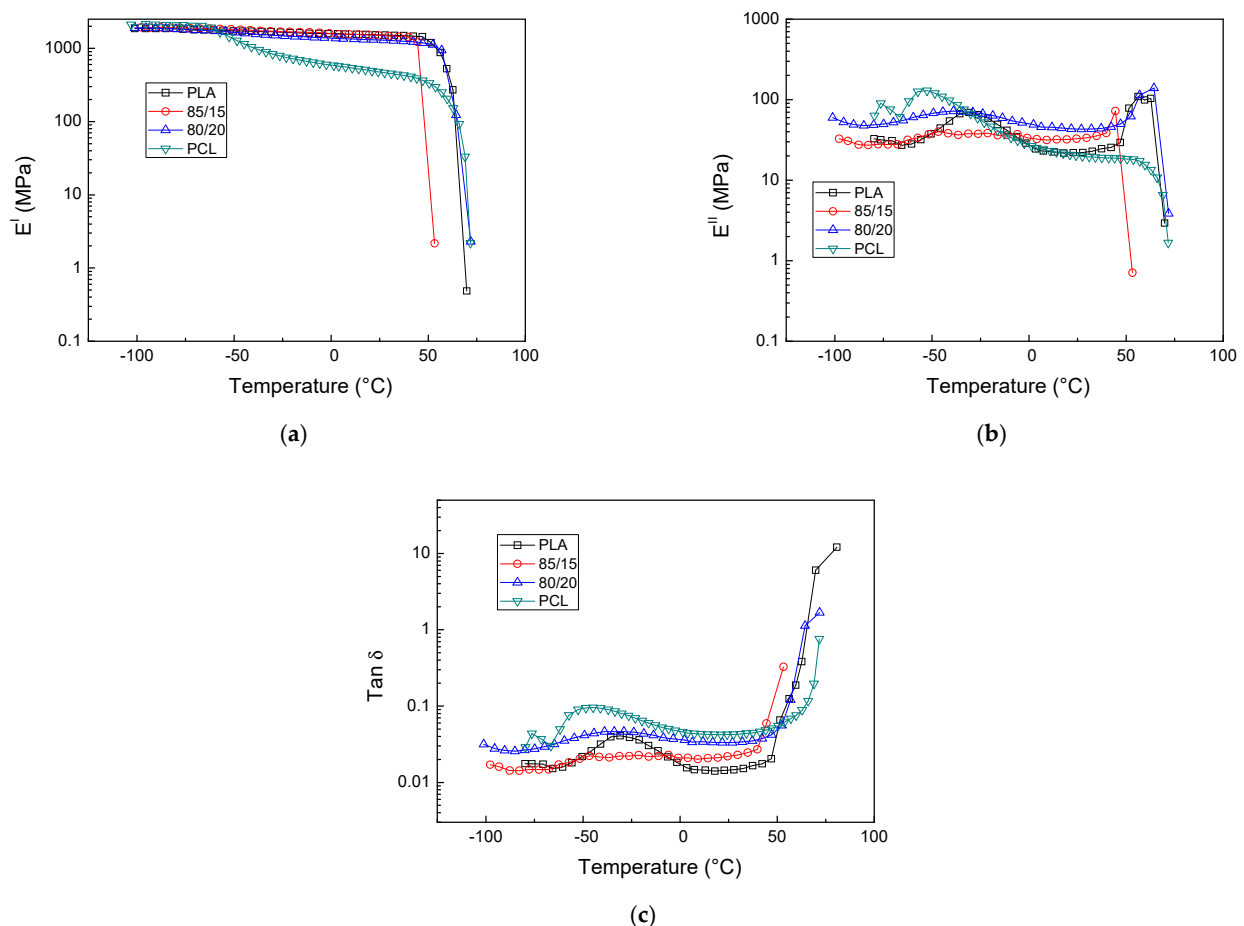


Figure 5. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ variations with the temperature.

Urquijo et al. [26] were able to observe the maxima of the $\tan \delta$ peak of the PLA phase, and they observed that the maxima were almost unaltered irrespective of blend compositions, suggesting that PLA and PCL are immiscible. Similarly, Dell'Erba et al. [6] observed in the DMTA results two glass transition temperatures in the PLA/PCL blends. The values observed in the blends were similar to those found for pure PLA and PCL, indicating that the two polymers are immiscible.

When the storage moduli at 22 °C were compared, it was noticeable that the value decreased as the PCL content increased in the blend. A similar trend was observed by Mofokeng et al. [27] for PLA/PCL blends. They suggested that some properties of the immiscible and incompatible polymer blends are averaged, taking into account the properties of individual polymers. As PCL shows the lowest modulus value at 22 °C, the blend with the highest PCL content, 80/20, showed the lowest storage modulus value with respect to blend systems. On the other hand, a peak is observed in the glassy region related to the secondary relaxation. Similarly, Starkweather et al. indicated a secondary relaxation around −50 °C for a polylactide [32]. In the PLA/PCL 80/20 and 85/15 blends, this peak appears at similar temperatures, but the height of the peak was slightly reduced.

Figure 6 shows the fractured surfaces of PLA-based systems with different magnifications. The surface features of fractured specimens are similar, and there were no appreciable differences between them at low magnification, x50. However, at a magnification of x2500, some differences can be observed when the neat PLA and PLA/PCL systems are compared. The fractured surface of the neat PLA is smoother than that of the PLA/PCL blend systems, indicating a rapid propagation of the crack with no appreciable plastic deformation, with this fracture being typical of a brittle material [33]. After the addition of PCL, the

morphology changed to a rougher surface. Furthermore, it can be observed that a biphasic morphology indicates that PLA and PCL are not miscible, which is in agreement with the DCS results and the direct visual observations reported previously. In PLA/PCL blends, Fortelný et al. [1] observed that until 30 wt% of PCL content, PCL droplets were distributed within the matrix. Similarly, in the current study, PCL particles with small sizes were uniformly dispersed within the PLA matrix; the number of these particles increased as the content of PCL increased in the studied systems. Similarly, Sunanta et al. [34] observed by SEM that spherical droplets of PCL were distributed within the PLA matrix, indicating that PLA/PCL blends were immiscible. Ostafinska et al. [35] observed that the melt viscosity of PLA is an important factor that affects the size of the PCL drops. Wachirahuttapong et al. [34] observed that the size of the droplets increases with PCL content; however, in the current study, this increase was not noticeable. Similarly, other authors observed a biphasic morphology in PLA/PCL blends [36–38]. Some of the dispersed particles are clearly visible from the matrix, suggesting that weak interfacial interactions were created between the PLA and PCL phases, which is in agreement with the observations by Correa-Pacheco et al. [39].

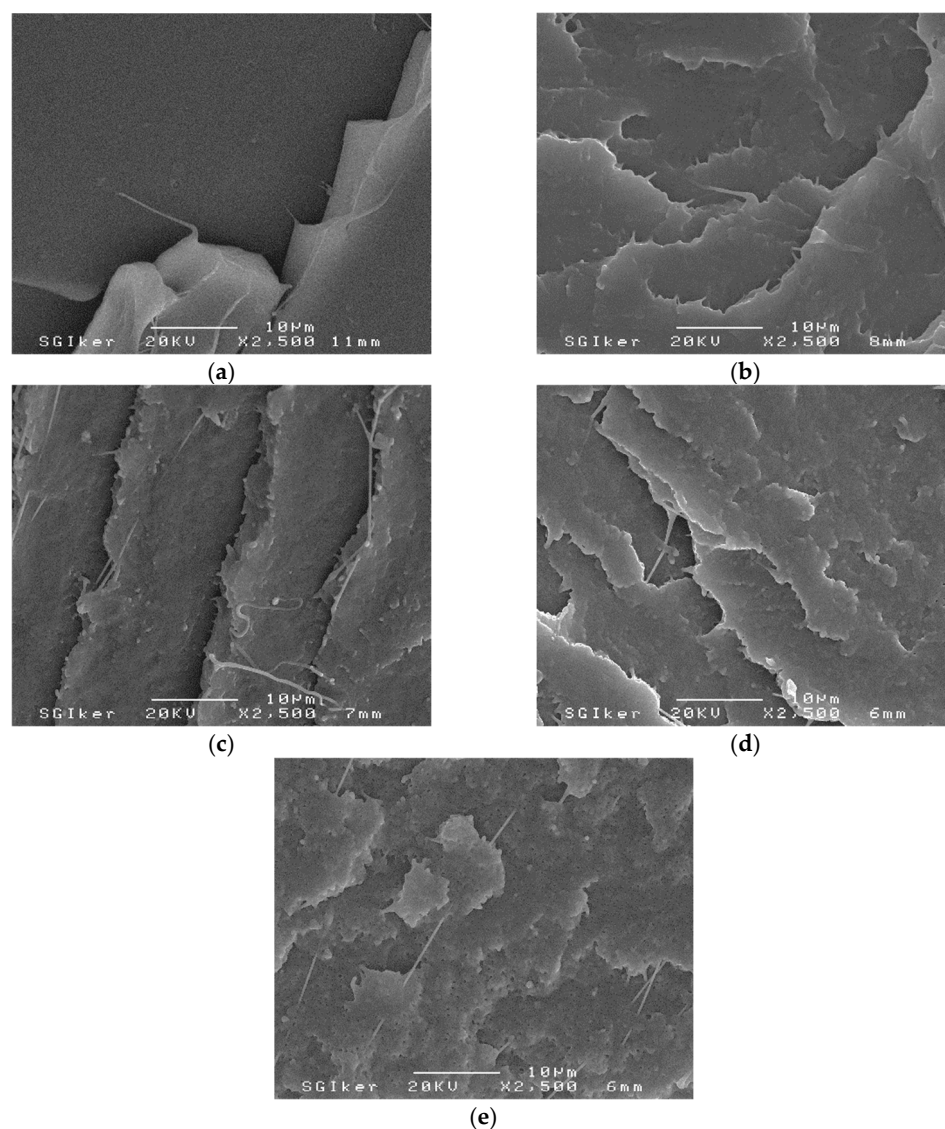


Figure 6. SEM micrographs of fractured surfaces of prepared systems with a magnification of x2500: (a) neat PLA, (b) 95/5, (c) 90/10, (d) 85/15, and (e) 80/20.

In Figure 7, the tensile properties are shown for the neat polymers and their blends determined at different test rates. The neat PCL showed a high deformation capacity, >300%, whereas the neat PLA performed as a brittle material irrespective of the test rate used. For the PLA/PCL blends, the deformation at break changed considerably when the test rate was increased. At a 1 mm/min deformation rate, the addition of PCL increased the capacity of deformation of the blends with respect to the neat PLA. At 10 wt% PCL or superior content, a significant improvement can be observed. This improvement seemed to be related to the morphology change observed in the SEM micrographs. However, the maximum deformation value reached, around 20%, is far from the neat PCL deformation capacity. Similarly, Wachirahuttapong et al. [34] observed that the addition of PCL resulted in an increase in strain at break up to 15% of PCL content; afterwards, the strain at break tends to decrease. Aliotta et al. [36] observed that after the addition of 20 wt% of PCL to PLA, the deformation at break value increased from 3.7% of the neat PLA to 24.9% of the PLA/PCL blend.

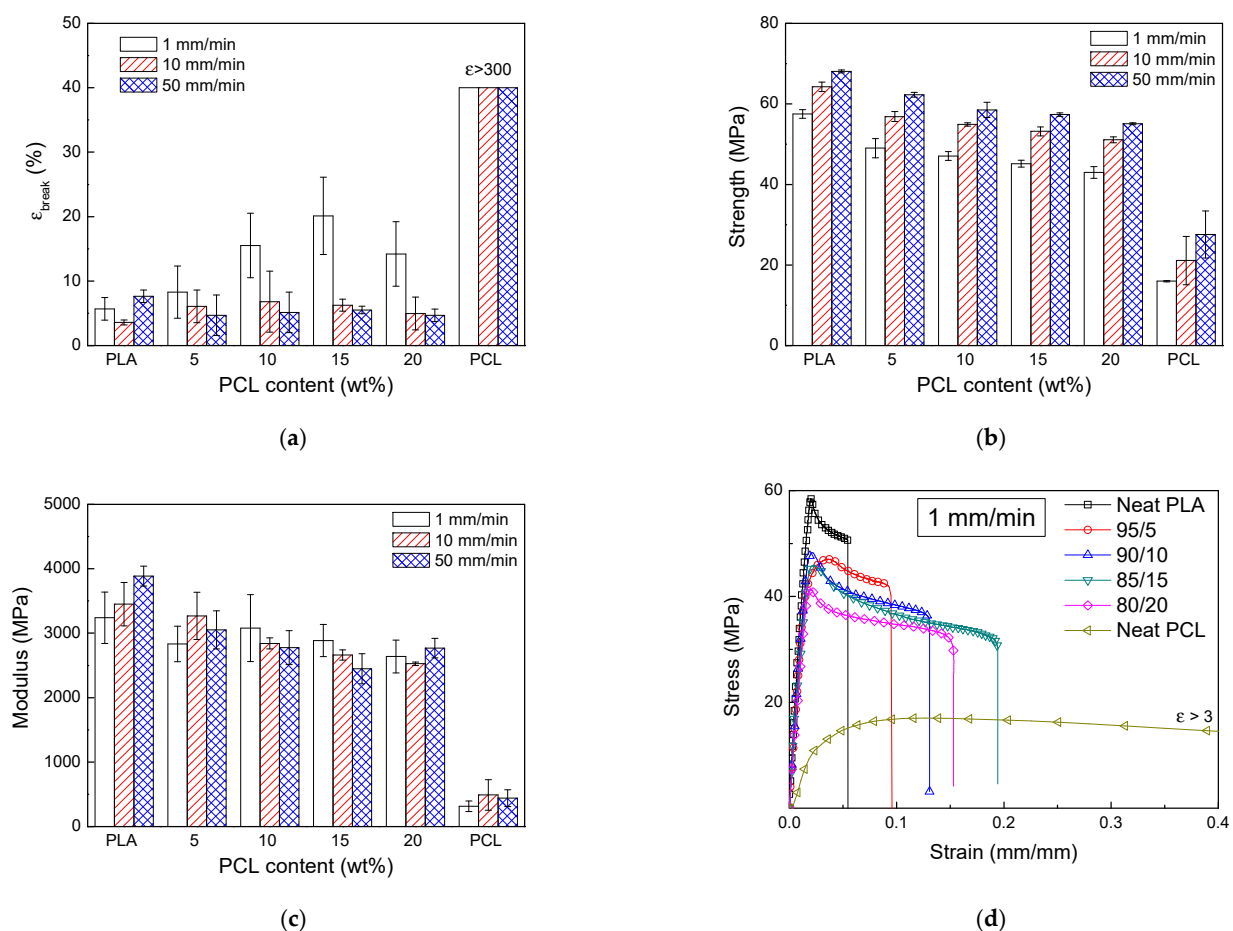


Figure 7. Tensile properties of prepared systems tested at different test rates: (a) deformation at break, (b) modulus, (c) strength, and (d) comparison of stress–strain curves.

Finotti et al. [37] observed that the deformation at break of the PLA/PCL blend with 20 wt% of PCL was around 20%, with this value being similar to the maximum deformation value reported in the current study. Similarly, Zhou et al. [40] observed that the deformation at break of the PLA/PCL blend with 20–30 wt% of PCL was around 20%. The T_g of PCL, -60°C , is below room temperature, and consequently, the amorphous phase of PCL has mobility. At some compositions of the PLA/PCL blends, the presence of PCL prevents instantaneous crack propagation [8].

It must be highlighted that when the test rate was increased, the deformation at break reduced for the PLA/PCL blend. Furthermore, in the PLA/PCL blends, no improvement was observed with respect to the neat PLA. Similarly, Urquijo et al. [26] observed that when an 80/20 composition of the PLA/PCL blend was tested at 10 and 50 mm/min, the elongation at break decreased from 140% to 13.6%. Polymers are viscoelastic materials, i.e., when polymers are strained, they exhibit both viscous and elastic characteristics. The elastic strain is instantaneous, whereas the viscous strain is time-dependent. When the strain rate was increased, the time for the materials to respond was reduced; consequently, the viscous response was limited because the molecular mobility of the polymer chains decreased [39]. In the current study, it was observed by SEM that there was a biphasic morphology, where the continuous main phase is the PLA-rich phase. The proposed adhesion mechanism between both phases showed some entanglements; however, as both polymers are not miscible, it is supposed that the diffusion of polymer chains is limited. At low deformation rates, these entanglements could transfer the stress from the continuous phase to the dispersed PCL droplets, and consequently, some deformation ability is given by the addition of PCL. However, as the test rate increased, the weak adhesion created between the two phases did not have enough time to deform, and consequently, the deformation at break values decreased considerably.

Regarding the strength and modulus values, the neat PCL showed considerably lower strength and modulus values than the neat PLA counterpart. When PCL was added to the PLA, as the amount of PCL was increased in the blend, both the strength and modulus values decreased. Matta et al. suggested that PCL spherulites formed in the continuous PLA matrix act as stress concentrators and thereby result in a decrease in tensile strength and tensile modulus [31].

The multiphase structure observed in the PLA/PCL systems, in addition to the poor interfacial adhesion, restricts its further applications [3]. Shin and Han [41] observed that compatibilized PLA/PCL blends have finer morphologies than their non-compatibilized counterparts. The morphology and interfacial strength between the dispersed and continuous phases affect the final mechanical performance of the polymer blends. In the literature, it was observed that, after the addition of chemical compounds to PLA/PCL blends that contained epoxy groups, the deformation at break increased [42]. The insufficient interfacial adhesion could cause debonding at low stress levels [38]. With the aim to improve the adhesion between the spherical shaped PCL and continuous PLA phases, bisphenol A diglycidyl ether, DGEBA, was used in the following section.

3.2. PLA/PCL Blends Modified with DGEBA

Figure 8 shows the FTIR spectra of PLA and PLA/PCL blends modified with DGEBA. When DGEBA was added, new bands were not noticed compared with systems without DGEBA. Furthermore, the band position of the carbonyl group of PCL, 1724 cm^{-1} , is practically the same as its unmodified blend counterparts, 1723 cm^{-1} . However, in contrast to the blends without DGEBA, the band located at 1749 cm^{-1} shifted in some blends until 1753 cm^{-1} , indicating that the presence of DGEBA induced new molecular interactions between the carbonyl group of PLA and DGEBA. Epoxy groups of DGEBA could react with carboxyl and hydroxyl end groups of the PLA chains, creating new ester groups. Kiattipornpithak et al. [43] confirmed by NMR the reaction between the end -COOH groups of PLA and the epoxy groups of DGEBA. Figure 9 shows the possible reactions between PLA and DGEBA. Unfortunately, the presence of those new ester groups was not easily detectable by FTIR because the bands of the ester linkages of PLA and PCL are located in the same region. On the other hand, Barros et al. [44] suggested that PCL interacts with epoxy mainly by hydrogen bonding interactions; these weak interactions are

responsible for the same band position of the carbonyl group of PCL after DGEBA addition to the blends.

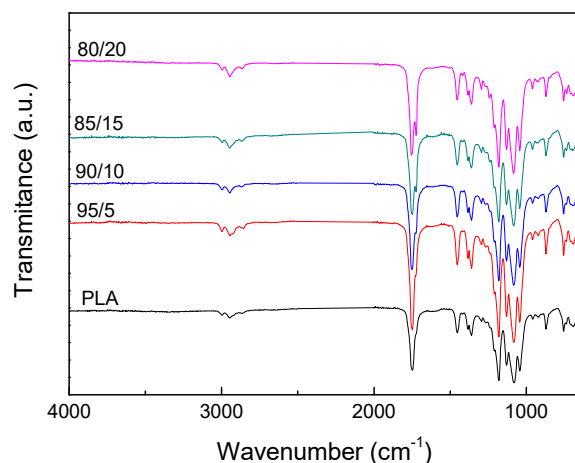


Figure 8. FTIR spectra of PLA and PLA/PCL blends modified with DGEBA.

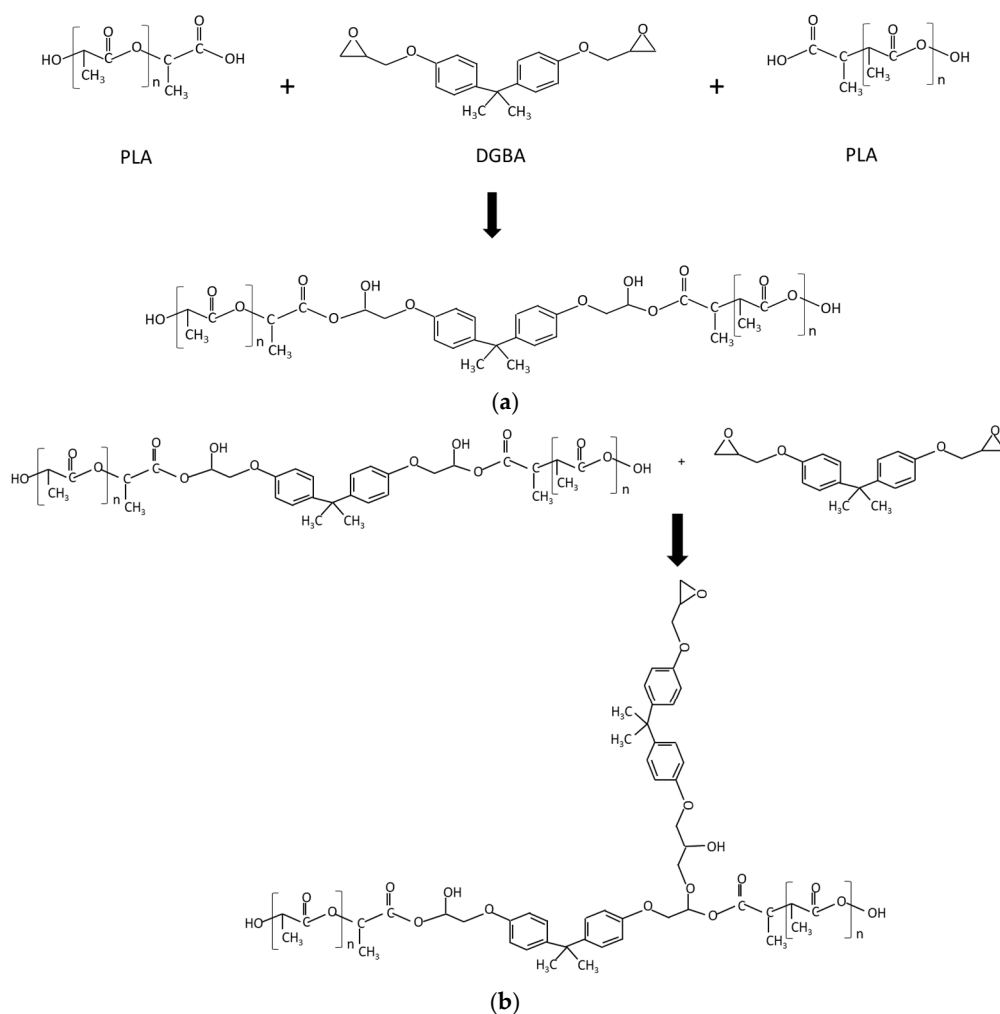


Figure 9. (a) Possible reactions between PLA chains and DGEBA, and (b) possible reaction of branching of PLA.

Figure 10 shows the second heating run thermograms of systems modified with DGEBA, and the data are reported in Table 2. After the addition of DGEBA, in general, the T_g value decreased slightly with respect to systems without a compatibilizer (Table 1). A

possible explanation could be that the branching of PLA could increase the free volume in the systems, and consequently, the mobility of the amorphous phase was favored, decreasing the glass transition temperature. The crystallization temperature, after the addition of DGEBA to the neat PLA, increased from 106.2 to 110.1 °C, indicating that the crystallization process of PLA was hindered. Contrarily, in the PLA/PCL blends, after the addition of DGEBA, it did not increase the crystallization temperature. In the PLA/PCL systems, there are probably two counteracting effects; (i) the branching of PLA makes the crystallization difficult, whereas (ii) PCL acts as a crystallization agent. The amount of added DGEBA is noticeably lower than the added PCL, and consequently, in the crystallization process, the effect of PCL addition is more important than the DGEBA addition ones. Regarding the crystallization degree, DGEBA-modified systems are almost amorphous and presented similar melting temperatures to their unmodified counterparts. Even though PCL acts as a nucleating agent, under the cooling process conditions, the PLA chains are not able to crystallize, which is in agreement with systems without DGEBA.

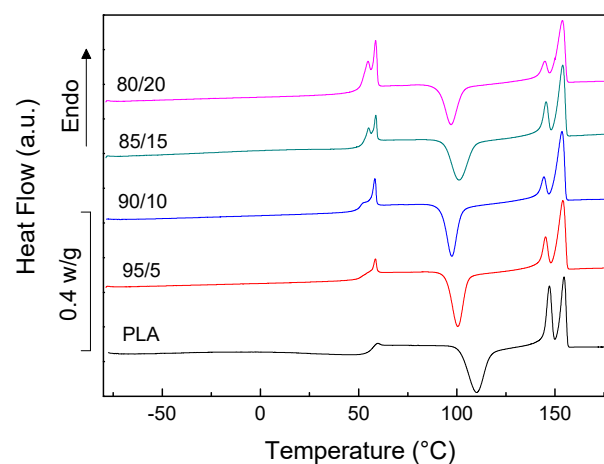


Figure 10. The second heating run thermograms of PLA and blend modified with DGEBA.

Table 2. Thermal properties of prepared systems: subindexes A and B indicate PCL and PLA, respectively.

System	T _{gA} (°C)	T _{gB} (°C)	T _{mA} (°C)	ΔH _{mA} (W/g)	T _{cB} (°C)	ΔH _{cB} (W/g)	T _{mB1} (°C)	T _{mB2} (°C)	ΔH _{mB} (W/g)	X _{cA} (%)
PLA + DGEBA	-	53.2	--	--	110.1	−1.22	149.2	154.6	1.39	0.2
95/5	n.a.	48.7	58.5	overlapped	100.5	−1.22	145.2	154.0	1.39	0.2
90/10	n.a.	48.5	58.3	overlapped	97.5	−1.03	144.4	153.6	1.30	0.3
85/15	n.a.	51.2	58.7	overlapped	101.1	−1.03	145.5	154.0	1.24	0.3
80/20	n.a.	49.1	58.6	overlapped	97.1	−0.98	144.8	153.8	1.16	0.2

Figure 11 compares the viscoelastic response of the PLA/PCL blends with 15 and 20 wt% PCL content, without and with DGEBA. As indicated previously, without DGEBA, after achieving the glass transition of PLA, the rigidity of the material was lost, the geometry of the specimen changed considerably, and the test was stopped. However, when DGEBA was added, the possible reactions between PLA and DGEBA led to chain extension and branching that led to a higher number of chain entanglements that maintained the specimen geometry after 60 °C was achieved. Consequently, the test was not stopped, and an increase in storage modulus due to the cold crystallization process was observed, as well as a decrease in modulus due to the melting process. Liu et al. prepared long-chain branching of PLA using successive reactions. They indicated that many branching points on backbones largely increase the elasticity and melt strength [45]. Similarly, the addition

of DGEBA increased the storage modulus, i.e., the elasticity character; the incorporation of DGEBA probably led to the branching of PLA.

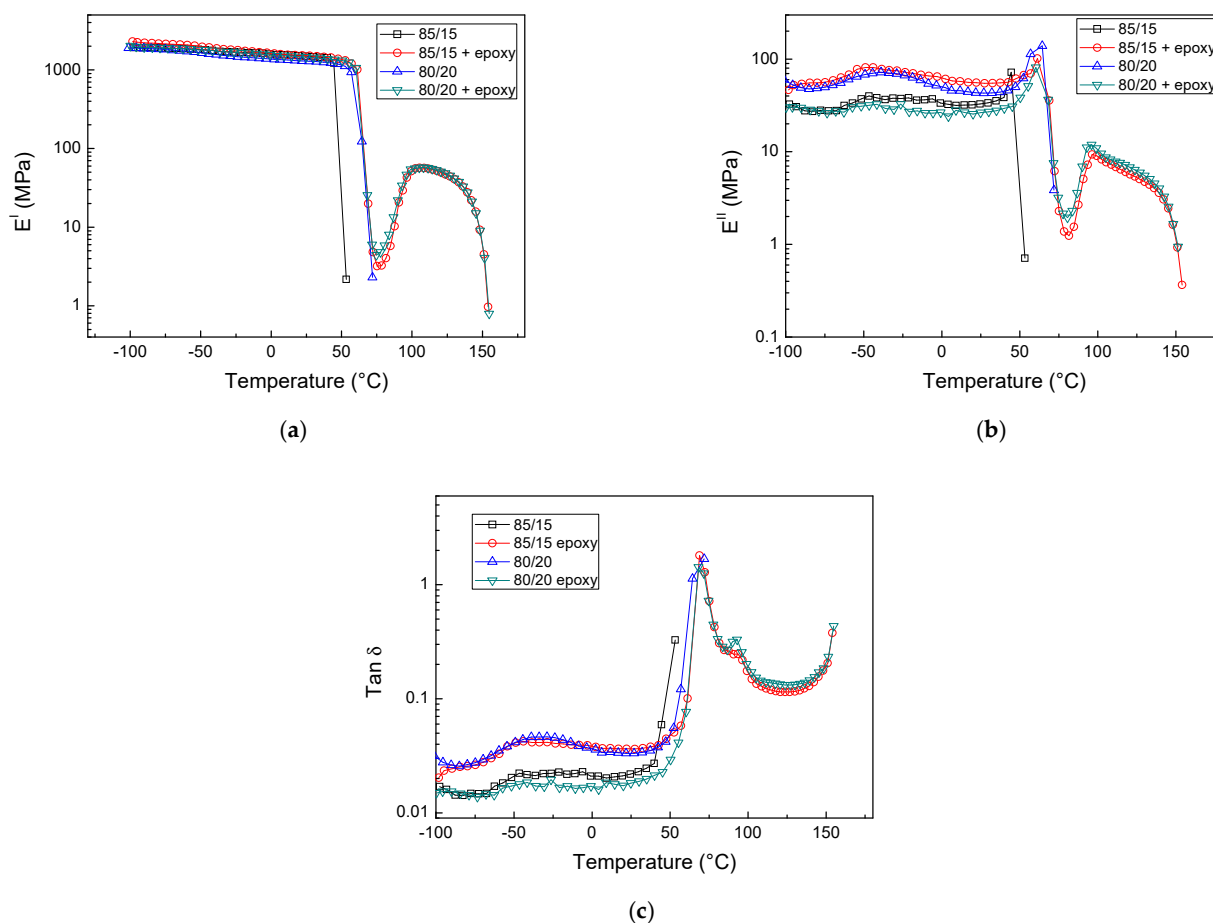


Figure 11. (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ variations with temperature.

Figure 12 shows the tensile properties of systems modified with DGEBA at different testing rates. As observed in the PLA/PCL systems without DGEBA, in general, as the amount of PCL increased, the strength and modulus values decreased. Regarding the deformation at break, at a 1 mm/min testing rate, as the content of PCL increased, the deformation value increased up to 10 wt% and, afterwards, the value decreased. However, at higher testing rates, improvements were not observed with respect to PLA, suggesting that the phase adhesion was not improved. Figure 13 shows the stress–strain curves of the prepared systems. Unmodified PLA showed very low plastic deformation, with this plastic deformation being reduced after the addition of DGEBA. In the unmodified PLA/PCL blend, the highest deformation at break value, around 20%, was obtained after the addition of 15 wt% of PCL. On the other hand, when DGEBA was added, the highest deformation at break value was achieved with 10 wt% of PCL. Matumba et al. [17] modified the PLA/PCL blend, 70/30 wt.%, with different contents of a styrene-acrylic multi-functional-epoxide oligomeric agent. After the addition of 0.5 wt.% of the epoxidic agent, they observed that the deformation of break value increased from 4.8% for the neat PLA to around 19% for the modified PLA/PCL blend. A similar deformation at break value was observed in the current study.

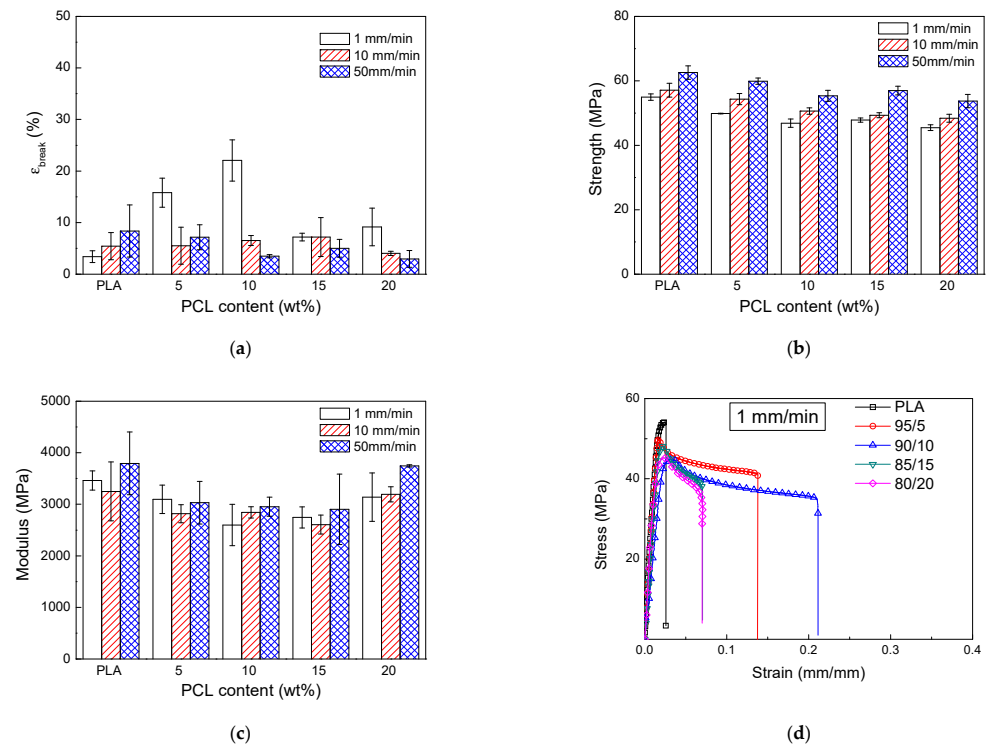


Figure 12. Tensile properties of prepared systems tested at different test rates: (a) deformation at break, (b) strength, (c) modulus, and (d) strength and stress–strain curves of systems with DGEBA.

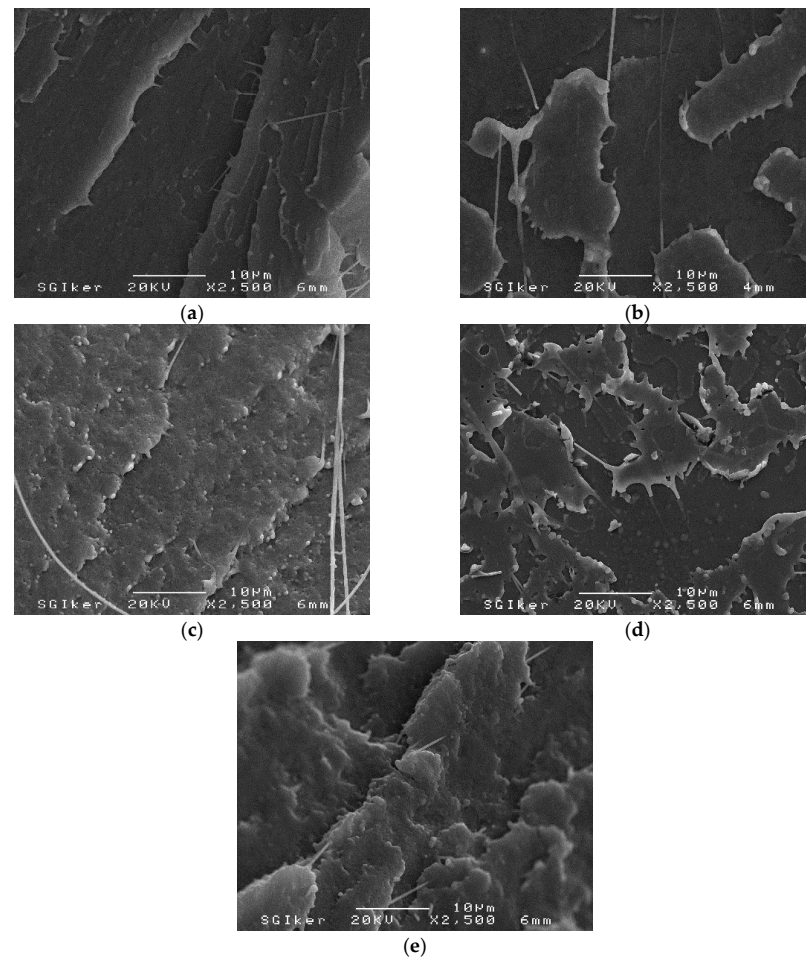


Figure 13. SEM micrographs of fractured surfaces of systems modified with DGEBA, with a magnification of $\times 2500$: (a) PLA, (b) 95/5, (c) 90/10, (d) 85/15, and (e) 80/20.

Figure 13 shows the fracture surfaces of systems modified with DGEBA. In the PLA/PCL blends, the biphasic morphology observed was similar to that of their unmodified counterparts. The addition of DGEBA did not significantly alter the morphology of the PLA/PCL blends, and consequently, the mechanical and thermal properties were similar to those of the unmodified PLA/PCL blends.

4. Conclusions

In the current study, PLA polymer, which is a brittle material at temperatures below 50 °C, was modified by adding a ductile PCL polymer. Different PLA/PCL compositions were prepared, and they were characterized by means of different characterization techniques. The visual as well as fractured surface morphology observations, in addition to the DSC results, indicated that these polymers are not miscible. The biphasic morphology based on small PCL particles uniformly dispersed within the continuous PLA matrix was observed by SEM. Regarding the mechanical properties, at a low deformation rate test, 1 mm/min, the deformation at break value increased until 20%, but it was far from the neat PCL maximum deformation capacity, higher than 300%. Furthermore, when the deformation rate increased, there was no improvement in the deformation at break value with respect to the neat PLA. FTIR data suggested that weak interactions were created between PLA and PCL. The thermomechanical stability of the PLA/PCL systems was very poor since the systems were almost amorphous, and at temperatures above 60 °C, the specimens lost totally their rigidity.

When the PLA/PCL systems were modified by adding DGEBA, even though DGEBA created some interactions with the PCL chains and reacted with the PLA chains, creating new covalent bonds, the deformation at break values did not improve with respect to systems without DGEBA. Furthermore, the same trend, as observed in systems without DGEBA, was observed, i.e., at a deformation rate of 1 mm/min, the deformation at break value increased until 20%, but at higher rates, no improvement was observed with respect to the neat PLA. It should be mentioned that the thermomechanical stability seemed to improve after the addition of DGEBA, since above 60 °C, the specimen retained some rigidity that allowed for the observation of the cold crystallization process and the melting process in the DMTA results. The possible reactions between PLA and DGEBA led to chain extension and branching that led to a higher number of chain entanglements that maintained the specimen geometry after 60 °C was achieved. Even though DGEBA was added, a biphasic structure was observed in the PLA/PCL systems, and the adhesion between both phases did not improve. The PLA/PCL blends prepared in the current study could be used as packaging material.

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