RESEARCH ARTICLE

High-Impact PLA in Compatibilized PLA/PCL Blends: Optimization of Blend Composition and Type and Content of Compatibilizer

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In this work, the effectiveness of seven commercial compatibilizers is tested in polylactide (PLA)/poly(ϵ-caprolactone) (PCL) blends with different compositions to obtain a high-impact PLA. None of the compatibilizers is effective for 90/10 and 80/20 PLA/PCL compositions, as no improvement of the impact strength is observed. For the 70/30 composition, compatibilizers having glycidyl methacrylate (GMA) and acrylate groups in their structure are proved the most effective, as the morphological change towards co-continuity induced by them leads to significant impact strength improvements (of ≈345% and 90% with respect to the neat PLA and the noncompatibilized PLA/PCL 70/30 blend, respectively). The 70/30 PLA/PCL composition, as it shows the best balance of properties, and the best compatibilizer (ElvaloyPTW) are chosen to carry out the optimization of the compatibilizer content. It is found that adding 6 phr to the blend results in highly toughened and ductile blends while maintaining a high modulus and yield strength values. Larger compatibilizer contents lead to even higher impact strength values, but the low-strain mechanical properties are notably reduced. Thus, in this work, a simple and easily scalable method to produce high-impact PLA is shown, as it implies the compounding of three commercially available components without involving any toxic solvents.

1. Introduction

Due to the current issues related to the lack of fossil resources and the accumulation of plastic waste, over the past decades, many researchers have focused on the investigation of biobased and compostable polymers since their expansion could prevent the accumulation of solid waste and decrease the use of non-renewable resources. Poly(lactic acid) or polylactide (PLA) is one of the most extensively researched biobased and biodegradable polymers used for this purpose. It is currently one of the most commercially developed biopolymers.[1,2] PLA is synthesized from lactic acid, obtained through the fermentation of sugar or starch.[3] It possesses high modulus and strength, good clarity, and barrier properties. Thanks to these characteristics and its good thermal processability, PLA has been used in industrial sectors such as textile, packaging, construction, or automotive. Moreover, due to its biodegradability, non-toxicity, and bioresorbability, it has been used in biomedical applications such as drug delivery systems, sutures, and tissue engineering.[1,3,4]

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Although PLA possesses good characteristics and can be molded with standard polymer processing equipments,[5] it shows certain drawbacks, primarily related to its thermal and mechanical properties, which limit its production and use in different applications.[1] PLA has a low glass transition temperature (T_g) (55–60 °C) and crystallization rate, limiting the usage of PLA to applications with relatively low service temperatures.[1,4,6,7] On the other hand, PLA also suffers from inherent brittleness and a very low toughness at room temperature. Hence, the use of PLA may be limited in applications where high elongation or plastic deformation at high impact rates are required.[8,9]

A widespread and cost-effective method to overcome the drawback of the mechanical properties is to blend PLA with ductile polymers.[7,10] Poly(ϵ-caprolactone) (PCL) is a ductile semicrystalline aliphatic polyester, with T_g and $T_m \approx -60$ °C and 55–70 °C, respectively.[1,11] Although it is a nonbiobased polymer, PCL is biodegradable and biocompatible, as well as PLA. These characteristics make PCL a suitable candidate to be blended with PLA since biodegradability and biocompatibility will be maintained.[1,11] Due to its low T_g, PCL exhibits high elongation at break ($\approx 600\%$[8]) and toughness. Therefore, adding PCL to PLA as a secondary phase could improve the ductility and toughness of PLA.[1]

In general, elongation at break of PLA has been easily enhanced (85–400%) by melt blending it with PCL,[12–18] even if, in some cases, poor or no increment has also been reported.[19–23] However, owing to the immiscibility between both polymers, improving the impact toughness of PLA/PCL blends is more challenging, though some good attempts have been made in this field. In this sense, it has been proved that the PCL concentration, the crystallinity of the PLA matrix, the PLA/PCL viscosity ratio, and the processing conditions are key factors that need to be optimized to improve the impact strength of PLA.[24–29] Nevertheless, achieving the optimal composition, processing conditions, and morphology is not always possible. That is why, high impact strength values or supertoughness are not usually reported in the literature for PLA/PCL blends.[12–14,19]

To overcome this issue, different kinds of compatibilizers have been used to tune the morphology and compatibility of the blends and develop a PLA/PCL blend with high impact resistance. Vilay et al.[30] used a polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) triblock copolymer as a compatibilizer for PLA70/PCL30 blends. They observed a shift in the T_g and T_m of PLA and PCL towards each other, indicating an increase in compatibility, as well as a significant improvement in the toughness of PLA/PCL blends. The authors attributed this to the polar interactions between PLA, PCL, and the copolymer.

Reactive compatibilization has also proved effective when compatibilizing PLA/PCL blends. Harada et al.[31] prepared PLA/PCL blends with four different reactive processing agents. Blends with lysine triisocyanate (LTI) showed the best results, significantly improving unnotched and notched Charpy impact strength. Hou et al.[32] used different amounts of ethylene-methyl acrylate-glycidyl methacrylate (EMA-GMA) to enhance the toughness of PLA90/PCL10 blends. With 8 phr of EMA-GMA the highest impact strength was achieved, 64.31 kJ m^{-2}, ≈ 23 times higher than that of neat PLA. However, the methods proposed in the literature do not seem easily implementable at an industrial level, either because lab-synthetized compatibilizers or components that are difficult to acquire at a large scale were employed or because the blending technique used was not continuous.

In the present work, the fabrication of a high-impact PLA was sought using an easy and industrially scalable process. With this purpose, compatibilized PLA/PCL blends were prepared by melt mixing in a twin screw extruder, using seven different commercially available compatibilizers. The PLA/PCL composition, compatibilizer type, and content were optimized. To do that, the prepared compositions' morphology and the mechanical and thermal properties were determined and compared. As a reference, the corresponding noncompatibilized PLA/PCL blends and neat PLA with the different compatibilizers were prepared and characterized.

2. Experimental Section

2.1. Materials

The PLA used in this work was a commercially available extrusion grade PLA (Ingeo Biopolymer 4032D, 1.2–1.6% D-isomer lactide) supplied by NatureWorks (Minneapolis, MN, USA). PCL (CAPA 6800) was purchased from Ingevity (North Charleston, SC, USA) with a molecular weight of 80 000 g mol^{-1}. Dow Chemicals (Midland, MI, USA) donated the seven polyethylene-based copolymers employed as compatibilizers. The chemical structure of each copolymer is summarized in **Table 1**. Although the exact chemical composition of BiomaxSG120 is unknown, it consists of an ethylene-acrylate terpolymer specifically designed for PLA, bearing epoxy moieties.[33]

2.2. Sample Preparation

Before melt processing, all the materials were dried overnight to avoid moisture-induced degradation. The PLA was dried in a dehumidifier at 80 °C, and the PCL and the compatibilizers were dried in an oven at 40 °C. Compatibilized PLA/PCL blends (PLA/PCL/C) having 90/10, 80/20, and 70/30 PLA/PCL compositions were melt blended in a Collin Teach-Line ZK25 T SCD 15 twin-screw extruder (L/D ratio 18 and screw diameter 25 mm) (Ebersberg, Bavaria, Germany). In all the cases, the content of the compatibilizer was set at 10 wt.% with respect to PCL, i.e., 90/10/1, 80/20/2, and 70/30/3. A screw speed of 200 rpm and a processing temperature of 190 °C were employed, and the extrudates were cooled in a water bath and pelletized. Noncompatibilized PLA/PCL blends were also prepared as a reference. In addition, to assess if the compatibilizers have any effect on the properties of neat PLA, blends of PLA with 3 phr of each type of compatibilizer (100/0/3) were also prepared. Based on the obtained results, 60/40 and 60/40/4 compositions were also prepared using the compatibilizer ElvaloyPTW. Moreover, to study the effect of the amount of compatibilizer, 70/30 blends with 1.5, 4.5, 6, 10, and 15 phr of ElvaloyPTW and 60/40 with 8 and 16 phr of ElvaloyPTW were prepared. Table S1, Supporting Information, summarizes all the compositions prepared in this work.

Before injection molding, the pellets were dried overnight in a dehumidifier at 80 °C. Tensile (ASTM D-638 type IV) and impact (ASTM D-256) specimens were prepared by injection molding, which was carried out in a Battenfeld BA-230-E (Wittmann,

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Table 1. Polyethylene-based copolymers used as compatibilizers and their composition.

Compatibilizer	Comonomers [wt.%]				
	nButylacrylate (BA)	Vinyl acetate (VA)	Glycidyl methacrylate (GMA)	Ethyl acrylate (EA)	Methyl acrylate (MA)
Elvaloy4170	21		9		
ElvaloyPTW	28		5.3		
Elvaloy5160		20	5.3		
ElvaloyAC12024S					24
ElvaloyAC2618				18	
ElvaloyAC2615				15	
BiomaxSG120			Unknown		

Kottingbrunn, Austria) machine equipped with a reciprocating screw (L/D ratio 30 and screw diameter 18 mm) at 190 °C. The mold temperature was set at 20 °C.

2.3. Characterization and Testing Methods

2.3.1. Dynamic Mechanical Thermal Analysis (DMTA)

The phase structure of the samples was studied through dynamic mechanical thermal analysis (DMTA) performed in a TA Instruments Q800 DMA viscoelastometer (New Castle, DE, USA). Measurements were carried out in single cantilever geometry between −100 °C and 130 °C at a constant heating rate of 4 °C min^{-1}. In the case of neat PCL, the testing temperature range was from −100 °C to 25 °C. Experiments were conducted at a constant frequency of 1 Hz with an amplitude of 15 μm. Two samples were analyzed per composition.

2.3.2. Differential Scanning Calorimetry (DSC)

Thermal properties of the blends were analyzed by differential scanning calorimetry (DSC) in a Perkin Elmer D8000 calorimeter (Waltham, MA, USA) under dry nitrogen atmosphere with a flow of 20 mL min^{-1}. The equipment was calibrated with indium and tin standards. Samples for DSC scans were taken from injection molded specimens and heated from 25 °C to 200 °C at 20 °C min^{-1}. From those heating scans, melting (T_m) and cold crystallization (T_{cc}) peak temperatures were obtained. The degree of crystallinity (X_c) of PLA in the injected specimens was determined according to Equation 1[29]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{w_f \Delta H_m^0} \qquad (1)$$

where ΔH_m and ΔH_{cc} are the measured enthalpies of melting and cold crystallization, respectively, w_f represents the weight fraction of PLA in the blend, and ΔH_m^0 is the melting enthalpy of completely crystalline PLA (93.6 J g^{-1}[1,29]). Since the melting endotherm of PCL appears at the same position as the T_g of PLA, the X_c of PCL within the blends could not be determined. To calculate the X_c of neat PCL, a value of 139.5 J g^{-1} was used.[34] Two samples were measured per composition.

2.3.3. Transmission Electron Microscopy (TEM)

The morphology of the blends was determined by transmission electron microscopy (TEM) using a TEM microscope TECNAI G2-20 TWIN TEM equipped with LaB6 filament operating at an accelerating voltage of 200 kV (ThermoFisher Scientific, Waltham, MA, USA). For that purpose, samples were cut in ultra-thin sections of 90 nm with a diamond knife and at cryogenic conditions on a Leica EMFC 6 ultramicrotome device (Leica Geosystems AG, Unterentfelden, Switzerland). Those sections were mounted on 200-mesh copper grids.

2.3.4. Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) Spectroscopy

To determine whether the compatibilizers could react with the PLA and the PCL, Fourier transform infrared-Attenuated total reflectance (FTIR-ATR) spectroscopy measurements were performed on a Nicolet 6700 FTIR coupled to an ATR accessory (Golden Gate) (ThermoFisher Scientific, Waltham, MA, USA). Measurements were performed directly to injection molded specimens. Spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The final spectra were the average over 32 scans.

2.3.5. Tensile Testing

Tensile tests were performed using an Instron 5569 tensile tester (Instron, Norwood, MA, USA). A crosshead speed of 10 mm min^{-1} was used, and the elastic modulus, the yield strength, and the elongation at break were determined from the obtained stress-strain curves. At least five tensile specimens were tested for each reported value.

2.3.6. Notched Izod Impact Testing

Notched Izod impact strength was determined using a Ceast 6548/000 pendulum (Instron, Norwood, MA, USA). Notches were machined according to ASTM D-256 (depth 2.54 mm and radius 0.25 mm). Reported average values were obtained from a minimum of eight impact specimens.
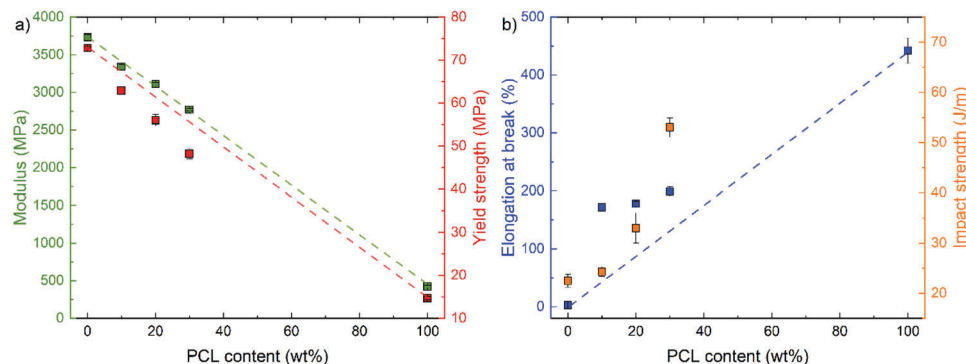
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Figure 1. a) Modulus and yield strength and b) elongation at break and impact strength, as a function of the PCL content. Dashed lines represent a simple additive law for mixtures.

3. Results and Discussion

For the sake of clarity, the results obtained in the present work have been divided into four sections. The first one summarizes the results of the reference noncompatibilized PLA/PCL blends. In the second section, as some of the copolymers used in this study have been reported to act as impact modifiers for PLA,[35,36] the effect of the compatibilizers on neat PLA is briefly analyzed. In the third section, the influence of the compatibilizer type on the properties of the compatibilized PLA/PCL/C blends is studied. Finally, in the last section, the effect of the amount of one of the best compatibilizers (ElvaloyPTW) is analyzed.

3.1. Reference Noncompatibilized PLA/PCL Blends: Influence of PCL Content

The phase structure of noncompatibilized PLA/PCL blends was studied by DMTA. Figure S1, Supporting Information, shows the tan δ versus temperature plots of PLA, PCL, and PLA/PCL blends, while the T_g values for both PLA and PCL are summarized in Table S2, Supporting Information. The T_g of neat PLA and PCL were 73.5 ± 0.2 °C and −37.6 ± 0.7 °C, respectively. All the PLA/PCL blends display two tan δ peaks at approximately the same position as the neat components, pointing to the blends being immiscible, as it has been widely reported for melt-blended PLA/PCL blends.[12,13,17,37,38]

Figure S2, Supporting Information, shows the first DSC heating scans for PLA, PCL, and PLA/PCL blends. Data extracted from them are summarized in Table S2, Supporting Information. As pointed out in the introduction, PLA shows a very slow crystallization rate. As a consequence, PLA is unable to crystallize during injection molding. On the contrary, PLA chains can rearrange and crystallize during heating in the DSC. In neat PLA, the cold crystallization appears at 101.3 °C. In the PLA/PCL blends, the cold crystallization temperature (T_{cc}) shifts towards lower temperatures as the PCL content increases. This shift is a consequence of the nucleating effect exerted by the PCL[12,19,31,38] inducing the lower cold crystallization of PLA.[24,25,39] As shown in Figure S2 and Table S2, Supporting Information, the T_m of PLA shows a decreasing trend with the PCL content, though the variations are slight. On the contrary, the addition of PCL slightly enhances the crystallinity degree of PLA due to the already discussed nucleat-

ing effect.[19] Nevertheless, the differences between the X_c of neat PLA and PLA within PLA/PCL blends are small.

Figure 1 shows the mechanical parameters obtained by tensile and impact tests for the reference noncompatibilized PLA/PCL blends as a function of the PCL content. Dashed lines represent a simple additive law for mixtures. The data of the impact strength value of neat PCL is not shown in Figure 1b since the specimens did not break during the impact test. PLA and PCL show Young's modulus of 3730 MPa and 424 MPa, respectively. In noncompatibilized PLA/PCL blends, it is observed that the modulus decreases linearly as the amount of PCL increases (Figure 1a), which is typical for PLA/PCL systems.[12,18,20,37] Similarly, the yield strength also decreases with increasing the PCL content, showing a negative deviation from the additive law for mixtures.

As pointed out in the introduction, brittleness is one of the main drawbacks of PLA. Indeed, the elongation at break of the neat PLA employed in this work is 3%. By contrast, the PCL does not break until it has reached a deformation of 442%. In Figure 1b, it can be seen that adding 10 wt.% of PCL to PLA leads to a significant improvement in the elongation at break, reaching a value of 172%. The ductility continues increasing slightly with further addition of PCL, displaying a positive deviation from the law of mixtures. Similar trends were seen in other works, though the brittle-ductile transition happens at higher PCL contents.[15,16,37]

Regarding the impact strength, PLA displays a value of 22 J m^{-1}, another demonstration of its inherent fragility, whereas PCL does not break under the testing conditions employed in this work. The impact strength of the noncompatibilized PLA/PCL blends does not significantly change until 30 wt.% of PCL is added to PLA, a composition that shows a value almost double to that of neat PLA. Thus, even if by adding 10 wt.% of PCL, the ductility of PLA is improved significantly, more than that content is needed to increase the impact strength, and considerably higher PCL contents are required in order to enhance the toughness of PLA. Nevertheless, despite the impact strength of PLA being improved in the 70/30 composition, the attained value is still low for applications where high impact strength is required.

The morphology of the noncompatibilized blends was analyzed by TEM (**Figure 2**) to determine the reason behind the change in toughness observed when the PCL content changes from 20 wt.% (33 J m^{-1}) to 30 wt.% (53 J m^{-1}). In the

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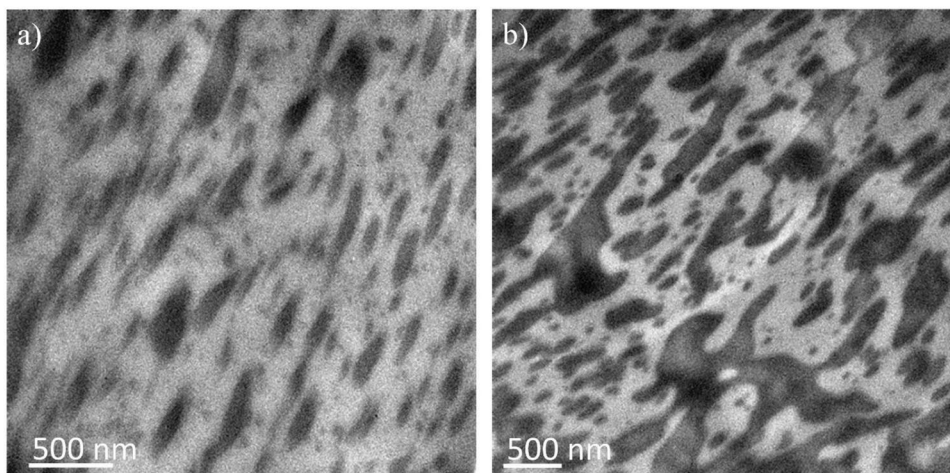Open Access

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Figure 2. TEM micrographs of a) 80/20 and b) 70/30 blends.

micrographs, the light grey areas (low contrast) correspond to the PLA phase, whereas the dark grey (high contrast) one represents the PCL. As can be seen, both blends show a biphasic morphology regardless of the amount of PCL, corroborating the immiscibility between PLA and PCL. A sea-island morphology is observed for the 80/20 blend (Figure 2a), where PCL droplets are slightly elongated due to the orientation induced during injection molding. With 30 wt.% of PCL (Figure 2b), bigger and more elongated PCL particles are observed. Botlhoko et al.[37] also noted that as the percentage of PCL in PLA matrix was increased, PCL particles became bigger and more irregular, leading to a larger particle size distribution.

Considering the aforementioned impact strength values, the formation of a morphology between sea-island and co-continuous, which features PCL particles with different sizes and irregular shapes, is deemed necessary for the PCL to cause the improvement of the impact strength of the PLA.

3.2. Reference PLA/0/C Blends: Influence of Compatibilizer Type on Neat PLA

Table S3, Supporting Information, summarizes the thermal parameters from DMTA and DSC for neat PLA and the 100/0/3 PLA/PCL/C compositions with the different compatibilizers. The addition of the compatibilizers does not influence the T_g, T_m, or X_c of PLA. By contrast, the T_{cc} of PLA is reduced from 101.3 °C to 94.4–92.0 °C, with the exception of the compatibilizers ElvaloyAC2018 and ElvaloyAC2015, for which the reduction is smaller. Thus, similar to PCL addition, low amounts of compatibilizers in PLA cause a nucleation effect on its crystallization process.

Figure 3 shows the mechanical parameters obtained by tensile and impact tests for neat PLA and 100/0/3 compositions. The data for PLA are represented with straight dashed lines. As expected, if their soft nature is considered, the addition of compatibilizers to neat PLA produces small decreases in its modulus and yield strength (Figures 3a,b, respectively), regardless of the type used. On the contrary, the effect of the compatibilizers on the elongation at break of PLA differed significantly from

one another as a function of their chemical structure. As can be observed in Figure 3c, when compatibilizers that contain epoxy moieties within their chemical structure are used (BiomaxSG120, ElvaloyPTW, Elvaloy4170, and Elvaloy5160), the elongation at break increases up to values higher than 135%. With compatibilizers that contain ethyl acrylate comonomers (Elvaloy2618 and Elvaloy2615) the resultant elongation at break values are lower than the ones mentioned before but still higher than that of neat PLA. By contrast, the blend with ElvaloyAC12024S, which contains methyl acrylate as a comonomer, shows no improvement in the ductility of the PLA. From these results, it is clear that the interactions/reactions that might occur between the copolymers and the PLA are different depending on the chemical structure of the comonomers constituting the copolymers. This effect will be discussed later on. On the other hand, it must be noted that although adding a suitable compatibilizer to PLA is enough to increase its elongation at break considerably, it does not alter the impact strength of PLA, as shown in Figure 3d.

3.3. Compatibilized PLA/PCL Blends (PLA/PCL/C): Influence of the Compatibilizer Type

Figure 4a,b show, respectively, the T_g values of PCL and PLA for all the studied PLA/PCL/C compositions. The addition of compatibilizers has no influence on the T_g of PLA, regardless of the copolymer nature. As shown in Figure 4a, the T_g of PCL displays more variations, although no significant trend can be appreciated. As also mentioned in the SI, both the low intensity and the width of the transition make it difficult to determine the T_g of the PCL accurately. Similarly, the T_{cc}, T_m, and X_c of PLA show no significant changes with the incorporation of the compatibilizers, as can be seen in **Figure 5**. In the case of X_c, there are more deviations from the value of neat PLA, but considering the error in the measurements, the differences encountered are not very significant, and the variations do not follow any specific trends.

Figure 6 shows the mechanical parameters obtained by tensile and impact tests for each PLA/PCL/C composition. As can be observed, the modulus and yield strength do not significantly
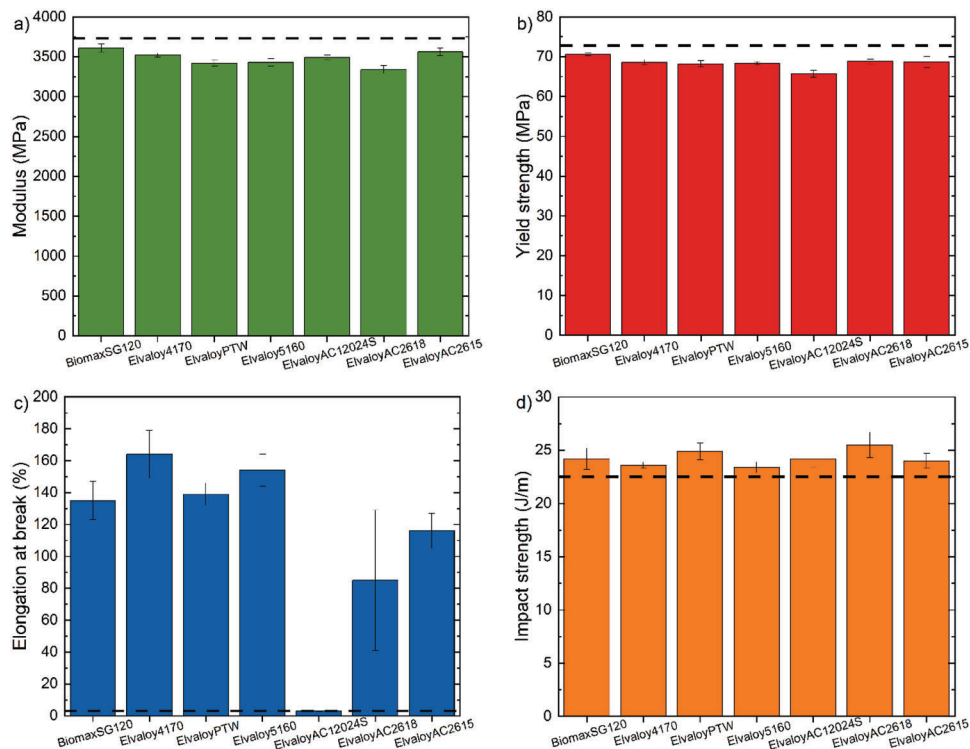
Figure 3. a) Modulus, b) yield strength, c) elongation at break, and d) impact strength of neat PLA and PLA/0/C blends. Dashed lines represent the values of neat PLA.

vary with the used compatibilizer, regardless of the PLA/PCL composition. It is noteworthy that, even in the compatibilized blends with 30 wt.% of PCL, the modulus remains relatively high ($\geq$2480 MPa) in all the cases. These results suggest that the studied blends could be used in applications where high stiffness is required. The drop in the yield strength is considerable compared with neat PLA, but the values do not differ too much from the ones of PLA/PCL blends.

As can be observed in Figure 6c, the addition of the compatibilizers barely affected the initially high elongation at break values of the blends, and the compatibilized blends showed ductility values higher than 160%, regardless of the PLA/PCL composi-

tion and the type of compatibilizer used. This is true except for 90/10 and 80/20 blends compatibilized with ElvaloyAC12024S that showed elongation at break values significantly lower than those of the reference noncompatibilized PLA/PCL blends. This was coincidentally the only compatibilizer that did not improve the ductility of neat PLA (Figure 3c). Meyva et al.[40] blended a PLA with an ethylene-methyl acrylate (EMA) copolymer with the same MA percentage (24 wt.%). Although they used an EMA copolymer amount as high as 20 wt.%, no significant improvement in the elongation at break of PLA was observed (from 1.95% of neat PLA to 3.76%), suggesting poor compatibility between PLA and EMA copolymer. Similarly, other works also reported
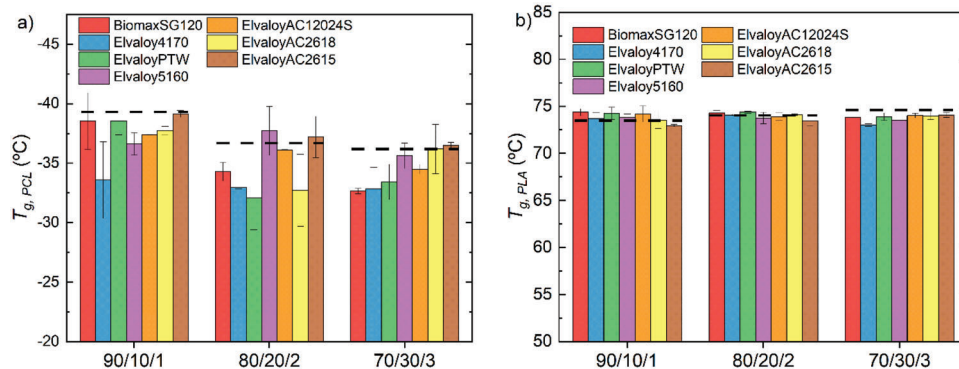

Figure 4. T_g values of a) PCL and b) PLA, obtained by DMTA, for each PLA/PCL/C composition. Dashed lines represent the values of reference noncompatibilized PLA/PCL blends.
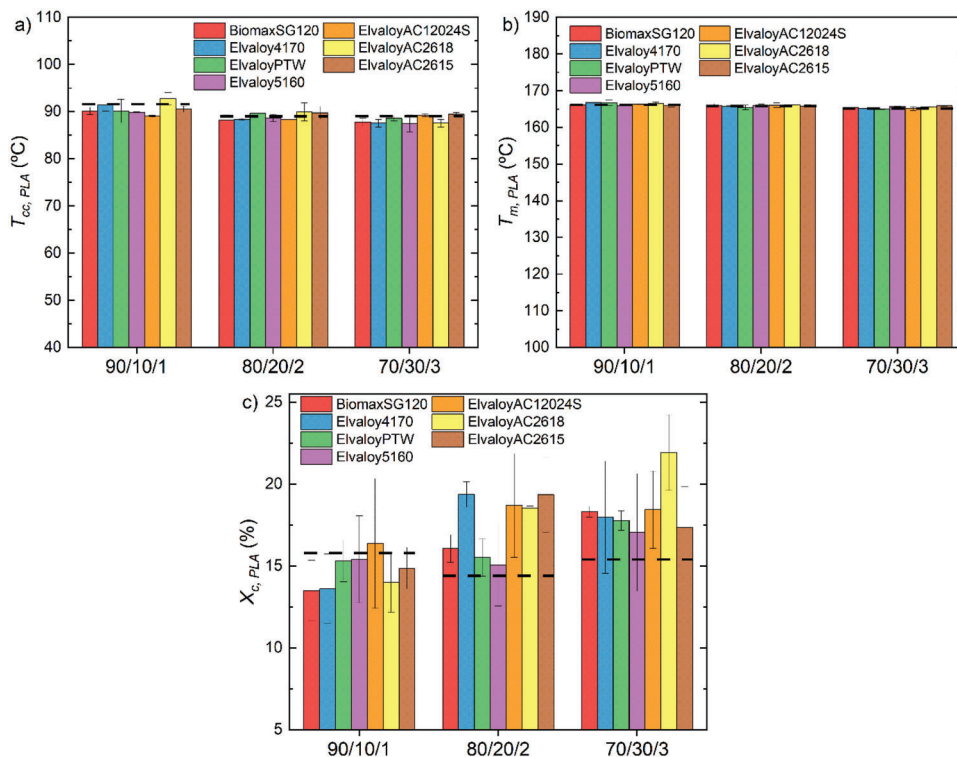
Figure 5. a) T_{cc}, b) T_m, and c) X_c of PLA for each PLA/PCL/C composition. Dashed lines represent the values of the reference noncompatibilized PLA/PCL blends.
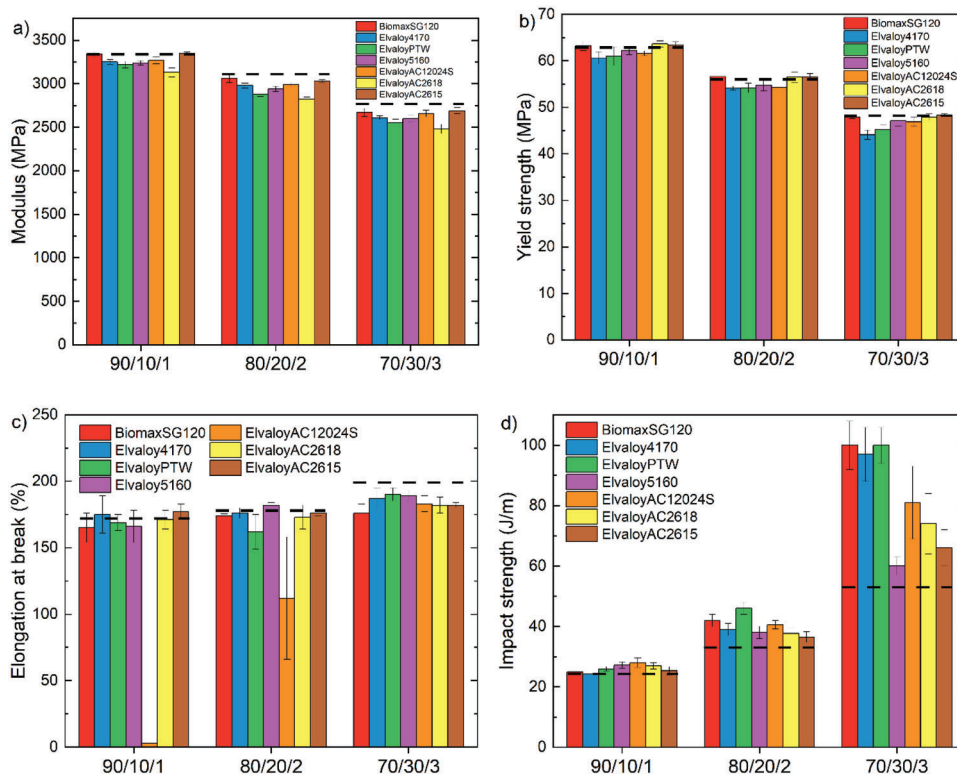

Figure 6. a) Modulus, b) yield strength, c) elongation at break, and d) impact strength for each PLA/PCL/C composition. Dashed lines represent the values of the reference noncompatibilized PLA/PCL blends.
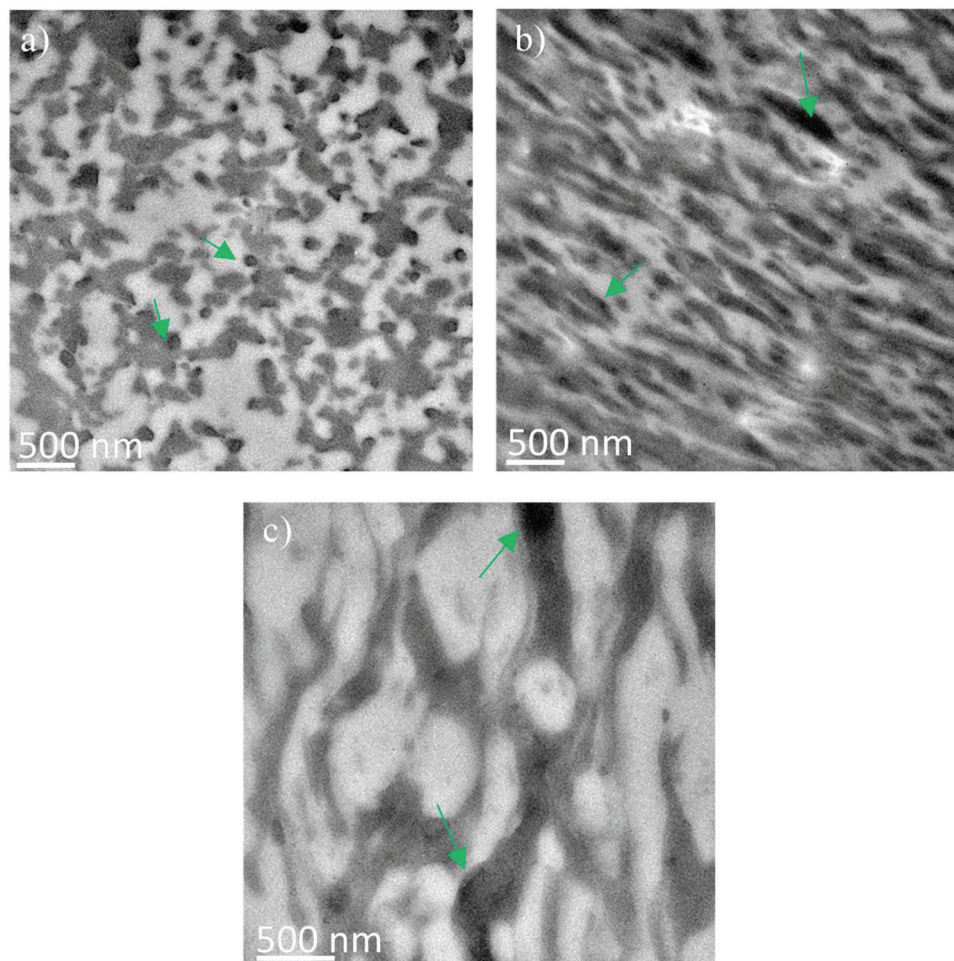
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Figure 7. TEM micrographs of a) 70/30/Elvaloy5160 3, b) 70/30/ElvaloyAC12024S 3, and c) 70/30/ElvaloyPTW 3.

small or no improvements in ductility when blending PLA or other polymeric materials with EMA copolymers.[41–43] This indicates that the presence of methyl acrylate groups in the compatibilizer leads to a premature failure of the blends, at least at low PCL contents. At high PCL contents, the effect of PCL prevails over that of ElvaloyAC12024S.

Figure 6d shows the impact strength of all the studied PLA/PCL/C blends. As can be seen, for blends containing 10 and 20 wt.% of PCL, the impact strength values of the compatibilized blends do not differ from one compatibilizer to another. Moreover, the obtained values are almost equal to those of noncompatibilized PLA/PCL blends in the case of 90/10/1 compositions and slightly higher for 80/20/2 compositions. In contrast, for the 70/30/3 blends, the effect of each compatibilizer is significantly different. While with Elvaloy5160, an impact strength value of 60 J m^{-1} is achieved, a value slightly higher than that of the noncompatibilized 70/30 blend (53 J m^{-1}), with BiomaxSG120, ElvaloyPTW, and Elvaloy4170, impact strength values between 97 and 100 J m^{-1} are obtained, which are 345% and 90% higher than that of the neat PLA and the noncompatibilized 70/30 blend, respectively. Furthermore, intermediate values between 66 and 81 J m^{-1} are obtained with ElvaloyAC12024S, ElvaloyAC2618, and ElvaloyAC2615.

To shed light on the reasons for the differences observed in the impact strength, the morphology of the blends was analyzed by TEM. **Figure 7** shows the TEM micrographs of 70/30/3 compositions with the compatibilizers that showed the lowest, intermediate, and highest impact strength values, respectively: Elvaloy5160, ElvaloyAC12024S, and ElvaloyPTW. As can be observed in the micrographs, even if the PLA/PCL composition is the same in the three blends, the final morphology varies with the used compatibilizer. With Elvaloy5160 (Figure 7a), deformed PCL droplets dispersed all over the PLA matrix are seen. On the other hand, ElvaloyAC12024 (Figure 7b) induces the elongation of PCL droplets compared to the morphology of the noncompatibilized 70/30 blend (Figure 2b). Finally, the presence of ElvaloyPTW causes the change of the morphology of the noncompatibilized 70/30 blend into a cocontinuous structure. It is worth mentioning that inside PCL droplets, darker zones are observed in all the micrographs (marked with green arrows). These zones correspond to the compatibilizer phase, which possesses higher electronic density. The presence of these black particles in the PCL phase implies that the compatibilizers, regardless of their chemical structure, have a higher affinity towards the PCL phase.

If the impact strength values of the analyzed blends are taken into account, and considering that for all the blends, the
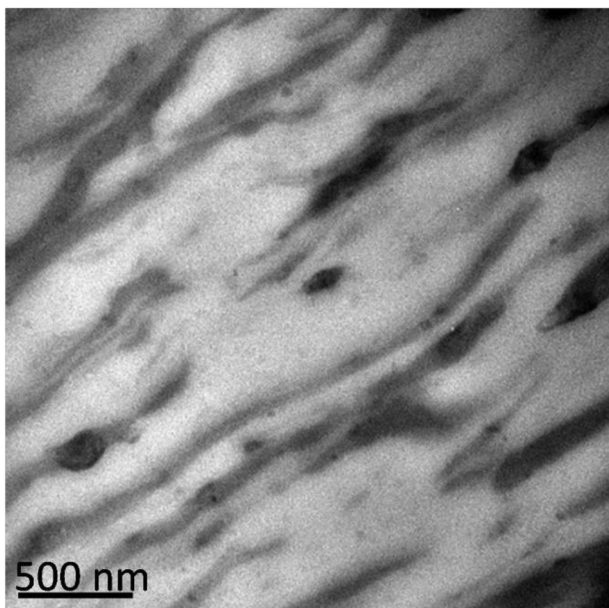
Figure 8. TEM micrograph of 80/20/ElvaloyPTW 2.

crystallinity, and the thermal transitions are quite similar, it can be concluded that the different morphologies induced by the presence of the different compatibilizers are the responsible for the variations observed. Since the rest of the parameters that may affect the morphology are kept constant, the chemical structure of the different compatibilizers must be responsible for promoting the formation of one or another type of morphological structure and, consequently, better or worse impact strength values. The results in Figure 6d indicate that achieving a cocontinuous morphology is the key to obtaining highly toughened blends, and the best comonomer combination to do so is the one composed of GMA and acrylate groups (BiomaxSG120, Elvaloy4170, and ElvaloyPTW).

Hou et al.[32] analyzed the effect of different concentrations of the EMA-GMA terpolymer on the morphology and properties of PLA/PCL blends having a composition of 90/10. They observed that some of the compatibilizers adhered to the PCL dispersed particles serving as a bridge between the PCL particles and PLA matrix through the chemical reactions between the epoxy groups of the EMA-GMA and the carboxyl and hydroxyl end groups of PLA and PCL, which led to an improvement of the interfacial adhesion. This possibility is analyzed in the following section. Moreover, the authors observed that, at high EMA-GMA contents, the compatibilizer particles also connected the PCL particles between them, resulting in a shish-like structure. A similar behavior –coalescence and elongation of the PCL phase– is observed in the present work, but only when some compatibilizers were used. Moreover, the extent of the morphological change seems to be dependent on the comonomers present in the compatibilizer, as discussed in the previous paragraphs.

On the other side, as observed in Figure 6d, the compatibilizers effectively enhance the impact strength of the noncompatibilized blends only when 30 wt.% of PCL is added to the blends. To ascertain why their presence is ineffective in the other studied compositions, **Figure 8** shows the TEM micrograph of the

80/20 blend compatibilized with ElvaloyPTW. If the morphologies of the noncompatibilized 80/20 (Figure 2a) and the 80/20/ElvaloyPTW 2 (Figure 8) blends are compared, it can be observed that the dispersed phase is further elongated in the presence of the compatibilizer, showing almost a fibril-like shape. However, a cocontinuous morphology is not reached. In conclusion, when PLA/PCL blends are compatibilized with ElvaloyPTW, the morphology of the blends changes towards a co-continuous morphology. Nonetheless, PCL contents higher than 20 wt.% are needed to achieve a completely co-continuous structure, which is necessary to improve the impact strength in the blends under study.

Based on the above results, 60/40 and 60/40/ElvaloyPTW 4 blends were prepared to confirm if the cocontinuity is responsible for the improved toughness. The noncompatibilized 60/40 blend shows an impact strength of 148 J m^{-1}, which is 6.6 times higher than that of neat PLA. Despite this, when the same blend is compatibilized with ElvaloyPTW, an impact strength of 383 J m^{-1} is achieved. It has to be highlighted that the specimens of this last composition do not entirely break during the impact tests, which means that the real impact strength of 60/40/ElvaloyPTW 4 is even higher than the reported value.

Figure 9 shows the TEM micrographs of cryogenically fractured surfaces of 60/40 and 60/40/ElvaloyPTW 4 blends. In the PLA60/PCL40 blend, a morphology near to cocontinuity is seen, indicating that the phase inversion could be close to that composition. For PLA/PCL blends, cocontinuity has been observed at PCL contents between 40 and 55 wt.%.[18,28,37,44] As can be observed in Figure 9b, the surface of 60/40/ElvaloyPTW 4 shows a cocontinuous structure, thereby confirming that ElvaloyPTW induces a change in the morphology of PLA/PCL blends towards cocontinuity, which in turn causes a significant improvement in impact strength.

3.4. PLA/PCL/ElvaloyPTW Blends: Effect of Compatibilizer Content

To see the effect of the amount of compatibilizer on the properties of the PLA/PCL/C blends, a compatibilizer was selected among those that gave the best results in the previous section. Thus, ElvaloyPTW was chosen and added in different contents to 70/30 blends since these compositions showed the best balance of mechanical properties.

Figure 10 shows the T_g values of PLA and PCL for all the 70/30/ElvaloyPTW blends. While the T_g of PLA does not vary significantly, the T_g of PCL shows an increasing trend with increasing the ElvaloyPTW content. These results are in agreement with the ones reported by Hou et al.[32] who observed a shift in the T_g of PCL as they increased the content of EMA-GMA in PLA/PCL blends, due to the interfacial interactions between the end groups of PLA and PCL with the epoxy groups of the compatibilizer. The improved interfacial adhesion provoked by the compatibilizer and its tendency to locate inside the PCL phase (as will be shown and discussed later), hindering the mobility of the PCL phase, could be the reasons behind the behavior observed for the T_g of the PCL.

As previously mentioned, the epoxy groups within the compatibilizers have been reported to be able to react with the carboxyl and hydroxyl end groups of PLA and PCL during melt
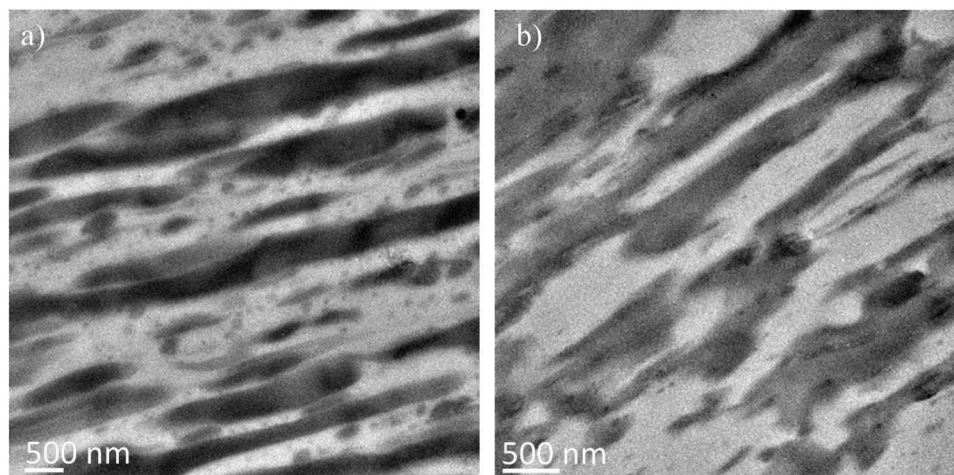
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Figure 9. TEM micrographs of a) 60/40 and b) 60/40/ElvaloyPTW 4 blends.

blending,[32] thus promoting the compatibility between both polymers. As in the present work four copolymers with epoxy moieties have been used to compatibilize the PLA and PCL phases (ElvaloyPTW among them), FT-IR analysis has been employed to prove if any reaction happens among the components during extrusion. **Figure 11** shows the experimental FT-IR spectra of neat ElvaloyPTW, and the noncompatibilized 70/30 and 70/30/ElvaloyPTW composition with the maximum compatibilizer content (70/30/15). The theoretical 70/30/ElvaloyPTW 15 spectrum, built up considering the spectra of the neat components and their concentration in the blend, is also shown in Figure 11. In the 70/30 blend, a few characteristic bands of neat PLA and PCL can be observed. Bands located at 2995 cm^{-1} and 2945 cm^{-1} were assigned to the asymmetrical and symmetrical –CH– and –CH$_3$– stretching of PLA, while the signals of –CH$_2$– stretching of PCL were observed at 2945 cm^{-1} and 2868 cm^{-1}. Absorption bands corresponding to C=O stretching of PLA and PCL were observed at 1752 cm^{-1} and 1724 cm^{-1}, respectively. Peaks at 1460 cm^{-1} and 1375 cm^{-1} corresponded to –CH$_3$– bend-

ing vibration of PLA, whereas the absorption band at 1470 cm^{-1} was attributed to –CH$_2$– bending vibration of PCL. Stretching vibration peaks of ester groups (–C–C(O)–O–) appeared between 1025 and 1300 cm^{-1}, while the peaks corresponding to the skeletal vibration of -CH$_2$- were those at 731–756 cm^{-1}. Regarding the spectra of the ElvaloyPTW, the bands at 2918 cm^{-1} and 2849 cm^{-1} corresponded to the asymmetrical and symmetrical stretching vibration of –CH–, –CH$_2$–, and –CH$_3$–, at 1733 cm^{-1} to the C=O stretching, the band at 1168 cm^{-1} to the stretching vibration of ester groups (–C–C(O)–O–), and the one at 910 cm^{-1} to the characteristic absorption band of the epoxy group bending.

The reaction between the epoxy groups of ElvaloyPTW and the hydroxyl and carboxyl end groups of PLA and PCL can be followed by the disappearance of the peak at 910 cm^{-1}, which is the characteristic absorption band of the epoxy group. A scheme of this reaction is shown in Figure S3, Supporting Information. In the experimental spectra of 70/30/ElvaloyPTW 15, that characteristic band cannot be observed (Figure 11b), suggesting that the epoxy functional groups were consumed during melt blending, as it has been reported in previous studies.[32] However, as the intensity of this band is already small in the spectra of neat ElvaloyPTW, it could also be that the disappearance of the band in the blend may be simply because of the low content of the copolymer within the mixture. For that reason, theoretically calculated spectra of 70/30/ElvaloyPTW 15 is also shown in Figure 11. The theoretical spectra shows that a small shoulder at 910 cm^{-1} corresponding to the epoxy groups should appear if there was no reaction between ElvaloyPTW and the polyesters. Thus, the reaction between the hydroxyl and carboxyl end groups of PLA and/or PCL and the epoxy groups of ElvaloyPTW during extrusion was confirmed, as also observed previously in the literature for PLA/PCL blends compatibilized with similar copolymers.[32] The reaction between PLA and ElvaloyPTW or similar ethylene-based copolymers containing GMA, i.e., epoxy moieties, has also been confirmed by FTIR spectroscopy in previous works.[45–48]

Figure 12 shows the thermal parameters obtained by DSC for 70/30/ElvaloyPTW compositions. As can be observed, increases in the amount of ElvaloyPTW do not provoke any significant
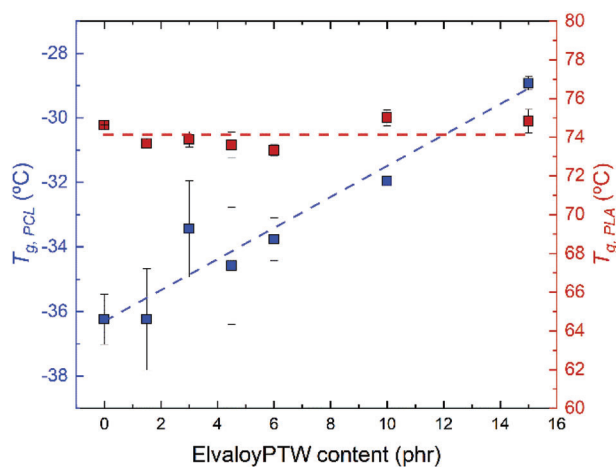

Figure 10. T_g of PCL and PLA for 70/30/ElvaloyPTW blends as a function of the ElvaloyPTW content.

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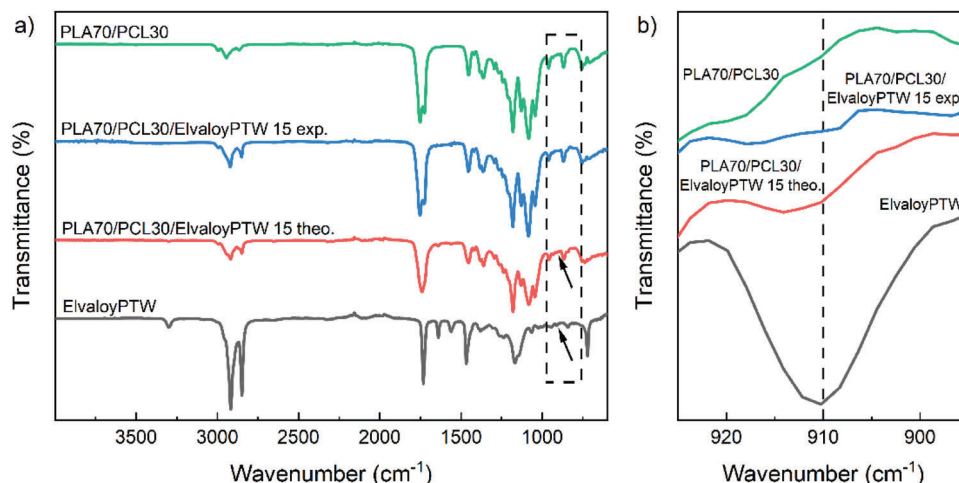*Open Access*

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Figure 11. a) FT-IR spectra of ElvaloyPTW, and the noncompatibilized 70/30 and 70/30/ElvaloyPTW 15 blends. In the case of the 70/30/ElvaloyPTW 15 blend, the theoretically calculated spectra is also shown. b) Magnification of the FT-IR spectra in the range of 880–950 cm^{-1}.

change in either of the thermal parameters of PLA, i.e., the T_{cc}, T_m, and X_c.

Figure 13 shows the mechanical properties obtained by tensile and impact tests for 70/30/ElvaloyPTW blends, as a function of the ElvaloyPTW content. Modulus and yield strength (Figure 13a) of the blends decrease with increasing the compatibilizer content, as was observed in Figure 3a-b and 6a-b when the effect of adding the compatibilizer to the neat PLA and PLA/PCL blends was analyzed, respectively. Conversely, the elongation at break remains almost constant at values ≈190–218% until an ElvaloyPTW content of 6 phr is added. With larger ElvaloyPTW contents, the elongation at break drops to 86% (Figure 13b). This behavior is directly related to the morphology, as discussed in the following paragraphs. Regarding the impact strength, it barely changes with the addition of 1.5 phr of ElvaloyPTW, while for higher compatibilizer contents, the impact strength increases linearly as the amount of compatibilizer increases. The values marked with an asterisk in Figure 13b, i.e., compatibilized PLA/PCL (70/30) blends containing 10 and 15 phr of ElvaloyPTW, indicate that the samples do not completely break during impact tests, which means that the real impact strength values for those compositions are even larger than the reported ones.

To analyze the reason why at high ElvaloyPTW contents, a dramatic drop of the elongation at break occurs, the morphology of 70/30/ElvaloyPTW 15 was observed by TEM (**Figure 14**). The PCL phase still shows a co-continuous structure, as pointed out by red arrows. The areas that appear even darker than PCL in Figure 14 correspond to the ElvaloyPTW phase, and they can be observed within the PCL phase (green arrows). As mentioned before, the presence of these black particles in the PCL phase implies that the compatibilizer has a higher affinity towards the PCL phase. Unlike in the morphology of the 70/30/ElvaloyPTW 3 (Figure 7c), relatively big ElvaloyPTW particles can be observed. Consequently, ElvaloyPTW may have a dual role in the blends containing high concentrations of it. Besides acting as a compatibilizer, it can also act as an impact modifier, which would explain the dramatic increase observed in the impact strength at high ElvaloyPTW contents.[32] Large ElvaloyPTW particles could also be responsible for the reduction observed in the elongation at break. It has been reported in the literature that an excess in the added compatibilizer amount can lead to the formation of a third phase, which may be located in one of the other two polymeric phases. The presence of the third phase provoked decreases in mechanical properties, elongation at break among them.[49–51] Moreover,
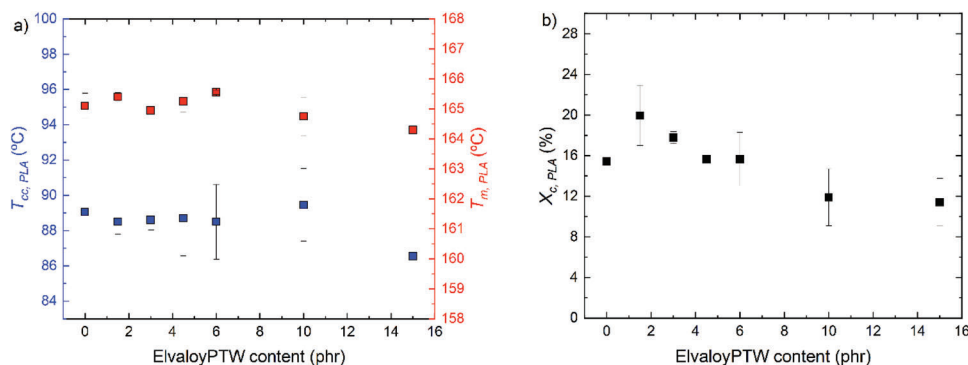

Figure 12. a) T_{cc} and T_m, and b) X_c of PLA, as a function of ElvaloyPTW content for 70/30/ElvaloyPTW blends.

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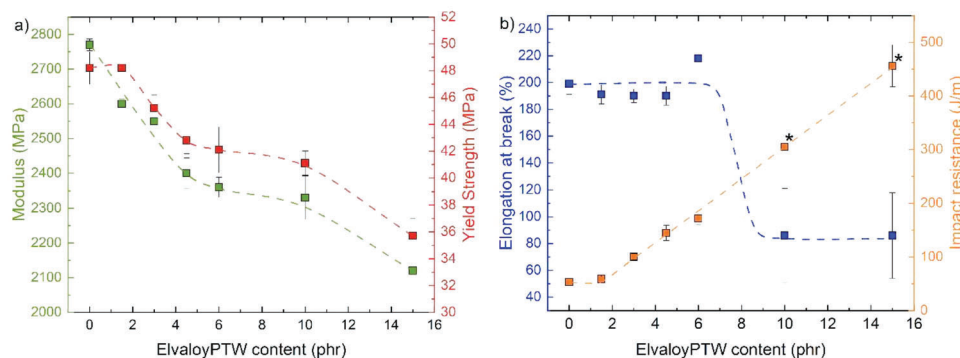Open Access
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Figure 13. a) Modulus and yield strength, and b) elongation at break and impact strength, as a function of ElvaloyPTW content, for 70/30/ElvaloyPTW compositions.

the localization of the ElvaloyPTW into the PCL phase would explain the increase in the T_g of PCL observed in Figure 10.

Based on the results shown in Figure 13, the optimum mechanical properties are attained in the 70/30/ElvaloyPTW 6 composition, as it shows the best balance of high- and low-strain properties. This is because adding 10 phr of ElvaloyPTW leads to a significant increase in the impact strength while the modulus and yield strength are almost maintained. However, a sharp decrease in elongation at break is observed for this composition, though the blend is still ductile. Greater compatibilizer contents lead to a further increase in impact strength, reaching almost supertough values. Nonetheless, the low-strain properties decline, losing the good balance between the different mechanical properties.

To confirm the above-explained results, 60/40/ElvaloyPTW 8 and 60/40/ElvaloyPTW 16 blends were prepared. The effect of the content of ElvaloyPTW on the thermal properties of 60/40 blends is explained in the SI (see Figure S4, Supporting Information). **Figure 15** shows the variation of the mechanical properties

of 60/40/ElvaloyPTW as a function of the compatibilizer content. Similarly to 70/30/ElvaloyPTW blends, the modulus and yield strength decrease with increasing the compatibilizer content. Supertough values were achieved with ElvaloyPTW contents higher than 8 phr. Note that the specimens with 8 and 16 phr of compatibilizer do not break entirely during the impact test, which means that the real impact strength values are even larger. However, the elongation at break dramatically reduces with a compatibilizer amount of 16 phr. As was the case for the 70/30/ElvaloyPTW blends, it seems that there is an optimum copolymer content for ductility.

Figure 16 shows a TEM micrograph of the 60/40/ElvaloyPTW 16 blend. The observed morphology is quite similar to the one of 70/30/ElvaloyPTW 15 (Figure 14), where the PCL phase shows a co-continuous structure (red arrows) with ElvaloyPTW droplets (green arrows) within it. As explained above, the particular localization of the ElvaloyPTW droplets might be responsible for the observed increase in the T_g of PCL (Figure S4, Supporting Information) and the dramatic reduction of the ductility (Figure 15b). Moreover, combining such ElvaloyPTW droplets with the co-continuous structure of the PCL phase led to achieving supertough blends.
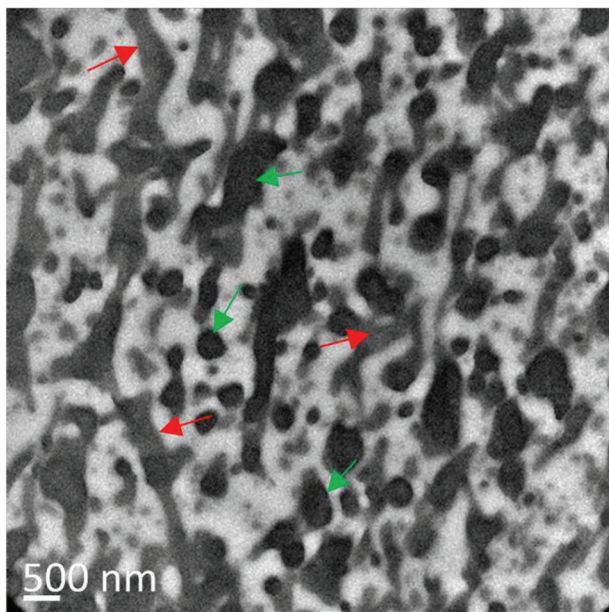
4. Conclusions

In this work, compatibilized PLA/PCL/C blends were prepared using seven polyethylene-based commercial copolymers as compatibilizers. The PCL content, the type of compatibilizer, and its amount were optimized to achieve high-impact PLA. Regarding the reference noncompatibilized PLA/PCL blends, it was observed that while small amounts of PCL (10 wt.%) are enough to improve the ductility of PLA dramatically, PCL contents higher than 30 wt.% are required to enhance its impact strength significantly. The morphological study revealed that a morphology in between sea-island and co-continuous was responsible for the observed improvement in impact strength. As a reference, the effect of the different compatibilizers on neat PLA was studied. It was observed that suitable compatibilizers contain epoxy moieties (BiomaxSG120, ElvaloyPTW, Elvaloy4170, and Elvaloy5160) that can successfully enhance the ductility of PLA, as they react with the end groups of PLA, ensuring good adhesion between the PLA matrix and the compatibilizer dispersed phase. Intermediate elongation at break values were achieved with copolymers
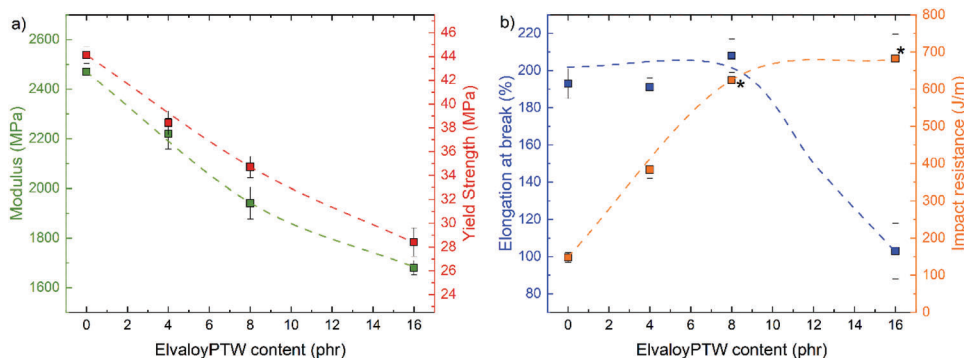

Figure 14. TEM micrograph of 70/30/ElvaloyPTW 15. Red arrows point out the PCL phase, while green arrows indicate the ElvaloyPTW.

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Figure 15. a) Modulus and yield strength, and b) elongation at break and impact strength, as a function of ElvaloyPTW content, for 60/40/ElvaloyPTW compositions.

containing ethyl acrylate comonomer (ElvaloyAC2618 and ElvaloyAC2615), while the compatibilizer containing methyl acrylate (ElvaloyAC12024S) did not produce any change in the ductility of PLA. Nevertheless, no improvement was observed in impact strength with neither of the compatibilizers on neat PLA.

Regarding the compatibilized PLA/PCL blends, all the PLA/PCL/C blends showed a highly ductile behavior, except for the blend compatibilized with ElvaloyAC12024S, which hindered the ductility of the blends at low PCL contents. Significant improvements in impact strength were only observed once PCL contents larger than 30 wt.% were used. With compatibilizers containing both GMA and acrylate groups (BiomaxSG120, ElvaloyPTW, and Elvaloy4170), impact strength values 4.4 times higher than that of the neat PLA were achieved. In contrast, no difference was observed with the copolymer containing GMA and vinyl acetate groups (Elvaloy5160) compared to the 70/30 blends. Intermediate impact strength values were obtained with the other three compatibilizers (ElvaloyAC12024S, ElvaloyAC2618,

and ElvaloyAC2615), which only contain acrylate groups. A co-continuous structure was the best morphology to achieve highly toughened blends. Finally, when analyzing the effect of the ElvaloyPTW content, it was concluded that the composition 70/30/ElvaloyPTW 6 shows the best balance of high- and low-strain properties, as higher compatibilizer contents allowed obtaining super-tough blends, but with significantly lower low-strain properties.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
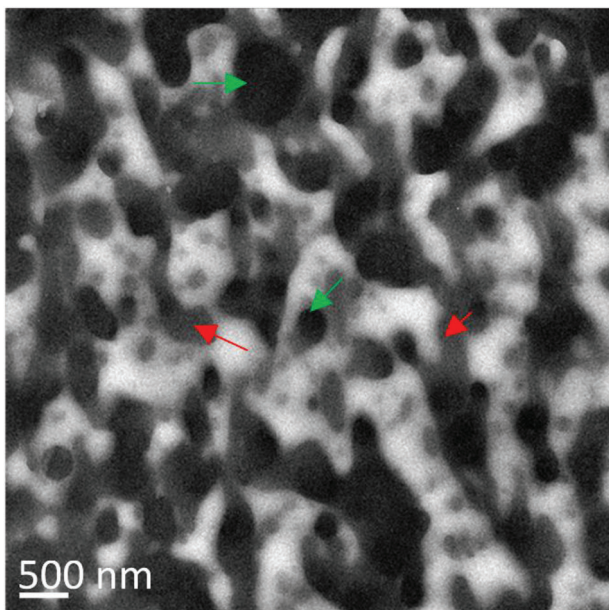
Figure 16. TEM micrograph of 60/40/ElvaloyPTW 16. Red arrows indicate the PCL phase, while green arrows indicate the ElvaloyPTW.

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