

PLA maleation: an easy and effective method to modify the properties of PLA/PCL immiscible blends

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Abstract In this study, maleic-anhydride-grafted polylactide (PLA-g-MA) was investigated as a potential compatibilizing agent for the polylactide (PLA)/poly(ϵ -caprolactone) (PCL) system, with the aim of enhancing the final properties of the two polymer blends. Indeed, PLA-g-MA was prepared via reactive blending through a free radical process and characterized by means of $^1\text{H-NMR}$ and titration measurements, which demonstrated that the employed procedure allows grafting 0.7 wt% of MA onto the polymer backbone, while avoiding a dramatic reduction of PLA molecular mass. The specific effect of the MA-grafted PLA on the features of the PLA/PCL system was highlighted by adding different amounts of PLA-g-MA to 70:30 (w/w) PLA/PCL blends, where the 70 % PLA component was progressively substituted by its maleated modification. The efficiency of PLA-g-MA as a compatibilizer for the PLA/PCL blends was assessed through SEM analysis, which showed that the dimensions of PCL domains decrease and their adhesion to PLA improves by increasing the amount of PLA-g-MA in the blends. The peculiar microstructure promoted by the presence of PLA-g-MA was found to enhance the mechanical properties of the blend, improving the elongation at break without decreasing its Young's modulus. Our study demonstrated that not only the microstructure but also the thermal properties of the blends were significantly affected by the replacement of PLA with PLA-g-MA.

Keywords Polymer blends · PLA · PCL · Compatibilization

Introduction

Poly (lactic acid) (PLA) is one of the most promising innovative plastics, it being a sustainable alternative to polyolefins [1]. Indeed, PLA, which is mostly synthesized by ring-opening polymerization of lactide [2] (a monomer produced by fermentation of glucose, in turn derived from starch harvested from corn or sugar beet), is a thermoplastic polymer with mechanical properties comparable to those of conventional polymers such as polystyrene and polyethylene [3]. Moreover, this polymer is renewable, biodegradable, and biocompatible, a set of highly attractive properties for various end-use applications [4, 5]. However, brittleness, poor elongation at break, narrow processing window, and low melt strength represent open challenges for the application of this polymer. In particular, the brittleness of PLA restricts its use in many fields. Thus, to improve the brittleness of PLA, blending with a ductile biodegradable polymer such as poly(ϵ -caprolactone) (PCL) has been widely used. However, PCL and PLA are thermodynamically incompatible with each other and can only form a multiphase structure in their blended system, with poor interfacial adhesion, which restricts its further applications. Considerable efforts have been made to enhance the compatibility between PLA and PCL by using generally established compatibilization strategies, such as the addition of polymeric compatibilizers [6–10] and reactive compatibilization methods. In particular, the latter method consists in the formation of block, graft, or cross-linked copolymers at the interface through covalent bond formation *in situ* during the reactive compatibilization step. There are two distinct processes available for copolymer formation at the interface, which are a direct process for the polymers which have reactive functionality and a mediation process by addition of a reactive compatibilizer [11].

In the case of PLA/PCL blends, different reactive compatibilizers have been used. In particular, peroxide

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compounds were added to PLA/PCL to improve the blend component compatibility by inducing a chemical interfacial cross-linking [12, 13]. More recently, Shin et al. [14] chose glycidyl methacrylate (GMA) as a compatibilizing agent, in the expectation that GMA played a role as a monomeric compatibilizer and a reactive agent at the interface between PLA and PCL phases. Indeed, the morphological study showed the reduced particle size of dispersed PCL domains and the significantly improved interfacial adhesion by the electron-beam irradiation with the addition of the GMA. Another reactive compatibilizer applied was lysine triisocyanate (LTI), which was found to decrease the immiscibility between the components, and as a result, the toughness of PLA/PCL improved [15, 16]. Haradata et al. [17], comparing the behavior of a series of compatibilizing molecules, characterized by isocyanate and epoxy groups, found that LTI was the most effective to react with both PLA and PCL and that the reactive processing improved the compatibility of PLA/PCL blends. Nevertheless, it is worth to underline that the direct reactive process is not always easy to control, and this can influence the material final properties.

A more feasible interfacial modification approach may come from the modification of the polymer matrix itself. This can be achieved by grafting a reactive moiety onto the polymer matrix, in which the moiety is capable to react in some way with the other components of the blend. Among the moieties which can be grafted to confer reactivity to otherwise nonreactive polymers, such as acrylic acid, oxazoline, and glycidyl methacrylate, maleic anhydride (MA) is generally preferred because MA is easier to handle and has low toxicity and because it does not tend to homopolymerize in normal free-radical melt-grafting conditions. The grafting of maleic anhydride onto PLA, first reported by Carlson et al. [18] and Mani et al. [19], is generally carried out in an extruder using a peroxide initiator. Since the above pioneering works, MA-grafted PLA (PLA-g-MA) was used in different blend systems, such as those based on poly(ethylene glycol) [20] and cellulose acetate [21]. Indeed, PLA-g-MA, widely applied in blends based on PLA and starch, was found to improve the compatibility and interfacial adhesion between the blend constituents [22–25]. Together with the exploitation of PLA-g-MA in polymer blends, it was also used in the development of composites and nanocomposites for improving the interfacial adhesion between the polymer and the filler/nanofiller [26–28].

In spite of the widespread application of PLA-g-MA, this work represents the first attempt to use PLA-g-MA as a compatibilizer for blends based on PLA and PCL. First, the grafting of MA onto PLA was carried out by applying a reactive-blending technique through a free radical process. Secondly, this MA-functionalized PLA was used as the reactive agent in the reactive blending of the PLA/PCL system, aimed to induce the grafting of a fraction of PCL onto the PLA-g-MA backbone so as to create more interactions

Table 1 Characteristics of PLA/PCL and PLA/PLA-g-MA/PCL blends

Sample name	PLA (wt%)	PLA-g-MA (wt%)	PCL (wt%)
PLAPCL	70	–	30
PLA(PLA-g-MA) ₁₀ PCL	63	7	30
PLA(PLA-g-MA) ₅₀ PCL	35	35	30
PLA-g-MAPCL	–	70	30

between the two polymers. The specific effect of the MA-grafted PLA was evidenced by adding different amounts of PLA-g-MA to the PLA/PCL blends and by characterizing the material final features.

Experimental

PLA is a commercial product from Nature Works Co., Ltd., USA, (2002D, Mn=100,000 g/mol) with a residual monomer content less than 0.3 wt.%, and it is characterized by the presence of only one hydroxyl terminal group. Poly(ϵ -caprolactone) was obtained from Solvay Ltd., Belgium, (CAPA 6500, Mn=50,000 g/mol), and it is characterized by having two hydroxyl end groups. 2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexane organic peroxide (Lupersol 101) and MA were purchased from Sigma-Aldrich and used as received.

The maleation of polylactide was carried out by charging PLA, MA, and Lupersol 101 into a glass reactor, namely a laboratory internal mixer provided with a mechanical stirrer (Heidolph, type RZR1), which was connected to a vacuum line and evacuated for 30 min at room temperature, followed by

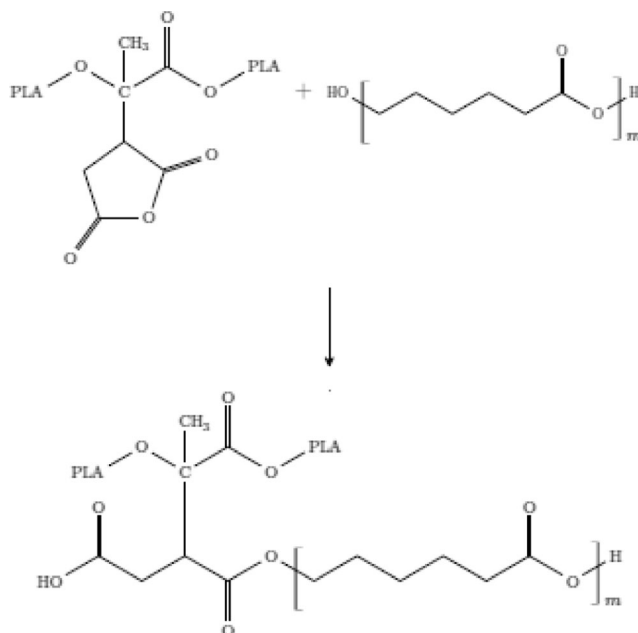


Fig. 1 Proposed reaction scheme between PLA-g-MA and PCL

purging with helium for 30 min (the above operations were repeated at least three times, to be sure to avoid humidity to come in contact with the reagents). The percentages of added Lupersol and MA were 0.5 and 6 wt%, respectively. The reactor was placed in an aluminum block oven at 180 °C, and the reaction was allowed to proceed for 10 min under stirring. The crude mixture was then dissolved in chloroform and precipitated into excess methanol in order to remove the fraction of MA not linked to the polymer.

Before blending, the polymer matrices were dried overnight at 60 °C. Blend preparation was accomplished by mixing different amounts of PLA, PLA-g-MA, and PCL

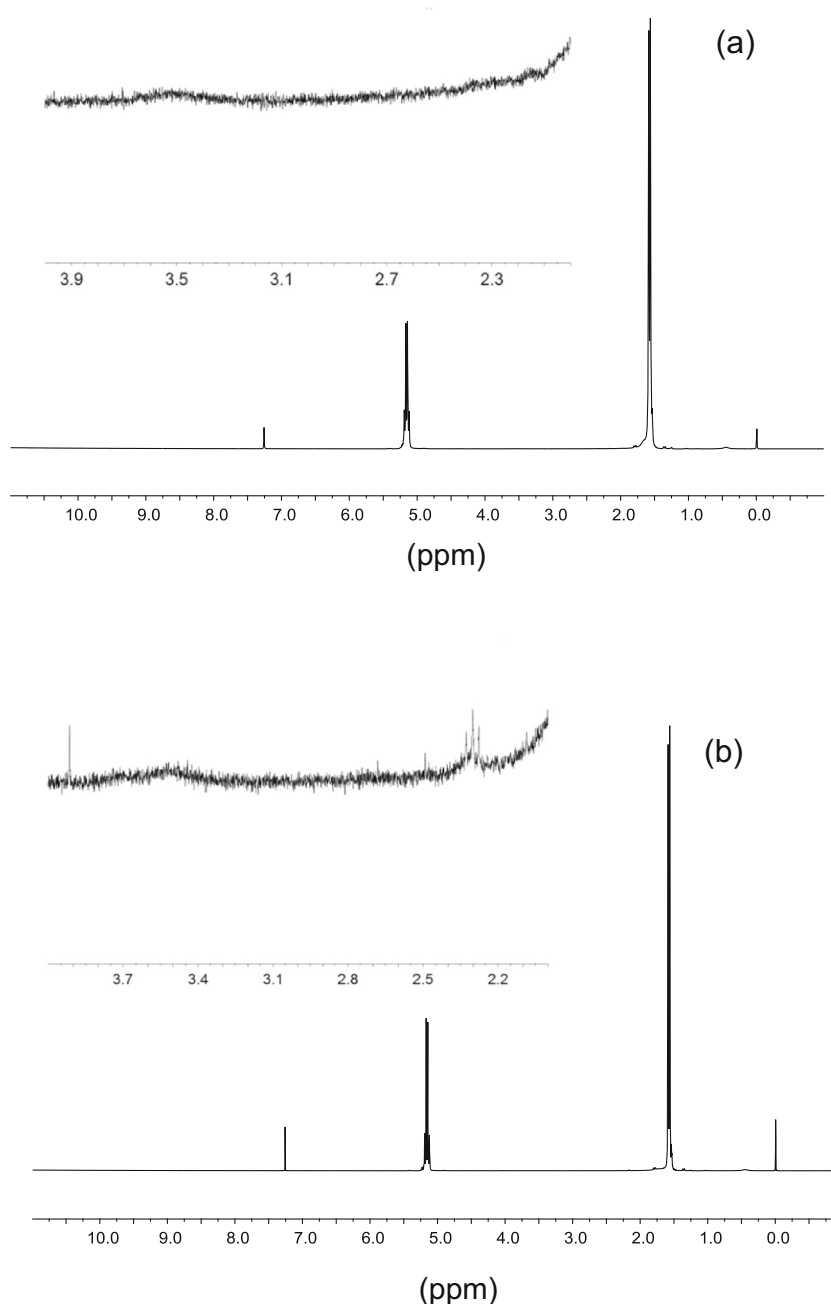
(see Table 1) and exploiting the same equipment and procedure used in the PLA maleation.

To measure the degree of grafting, 1 g of purified PLA-g-MA was dissolved in 20 mL of a chloroform–methanol (3:2) mixture, and the solution was titrated to a phenolphthalein end point using potassium hydroxide in methanol (0.01 N).

Both PLA and PLA-g-MA were characterized by means of ^1H -NMR spectroscopy: ^1H -NMR spectra were recorded with a Varian NMR Mercury Plus apparatus at a frequency of 300 MHz in CDCl_3 solutions containing TMS as internal standard.

A Zeiss Supra 40 VP field emission scanning electron microscope equipped with a backscattered electron detector

Fig. 2 ^1H -NMR spectra of **a** PLA and **b** PLA-g-MA



was used to examine the blend morphology. The specimens were submerged in liquid nitrogen for 30 min and fractured cryogenically. All samples were thinly sputter-coated with carbon using a Polaron E5100 sputter coater.

Differential scanning calorimetry analysis was performed on a Mettler calorimetric apparatus, model DSC1 STAR^c System, under a continuous nitrogen purge. Both calibrations of heat flow and temperature were based on a run in which one standard sample (indium) was heated through its melting point. The samples, having a mass between 2.5 and 6 mg, were heated from room temperature to 200 °C at a rate of 10 °C/min, then cooled down to room temperature at the predetermined rate, and finally heated to 200 °C again.

Thermogravimetric analysis (TGA) measurements were performed using a TA Instrument thermobalance, TGA 2050, under nitrogen flow, at a heating rate of 10 °C/min.

The tensile properties of PLA/PCL blends were determined by an Instron mechanical tester (Instron 5565) at a crosshead speed of 10 mm/min at room temperature using rectangular specimens with dimension of 10×25×0.5 mm. Property values reported represent an average of the results for tests run on six specimens, along with experimental deviation.

Results and discussion

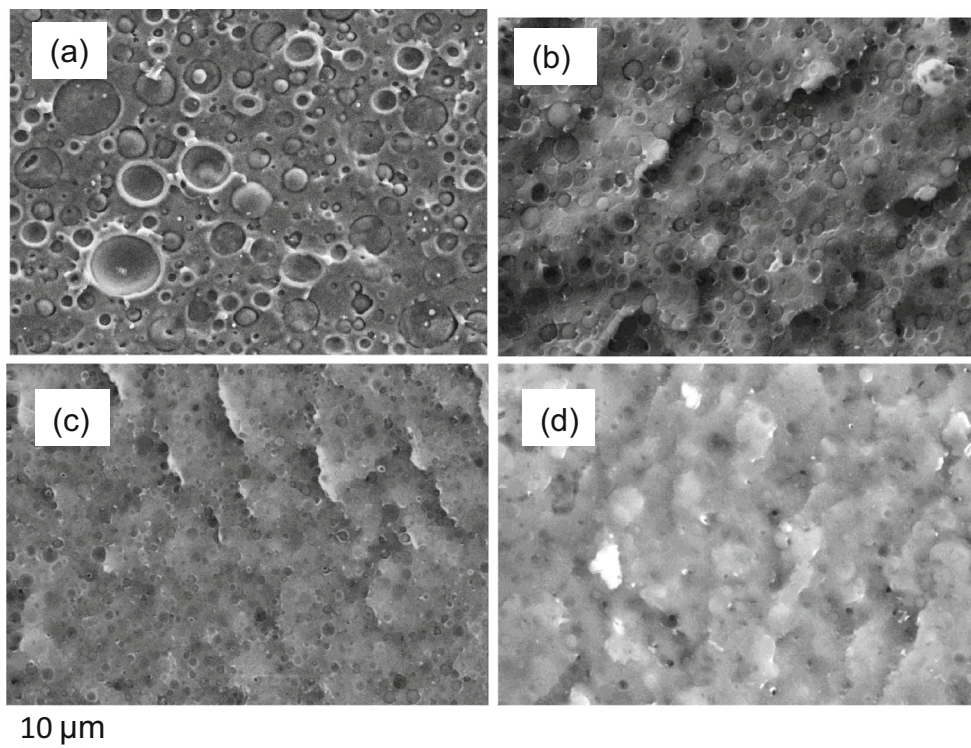
This work has been preliminary focused on the grafting of MA onto PLA. The mechanism of maleation reaction, as

already reported [18], consists in the formation of a radical and in the subsequent hydrogen abstraction, producing a PLA species which can react with MA. The resulting polymer radical can combine with another radical or further undergo a β -scission. Chain scission may also occur by either backbiting or thermohydrolysis [18]. Indeed, as schematically depicted in Fig. 1, the process of PLA maleation creates anhydride functional groups along the polymer backbone: These groups are potentially capable of reacting with the PCL hydroxyl end groups during melt blending, thus providing interfacial bonding meant to improve the compatibility between the two polymers.

It is worthwhile to underline that the above anhydride functionality might react also with the hydroxyl groups belonging to the PLA chains. Nevertheless, the reaction of MA with PCL is more likely to occur, as in the blend, the –OH groups of the PCL chains are almost double with respect to those of PLA, due to the lower molecular mass of PCL and to the fact that, conversely to PLA, both its end groups are hydroxyl type.

The grafting of MA was evaluated by ¹H-NMR and quantified by titration after elimination of the unreacted MA. Figure 2 compares the ¹H-NMR spectrum of PLA with that of PLA-g-MA. The ¹H-NMR spectrum of PLA reveals two major sets of signals with chemical shifts of about 1.5 ppm (assigned to the methyl protons) and 5.2 ppm (assigned to the methine protons of PLA). The resonance at 7.2 ppm is attributed to the deuterated chloroform solvent. In the spectrum of

Fig. 3 SEM micrographs of the blends: **a** PLAPCL, **b** PLA(PLA-g-MA)₁₀PCL, **c** PLA(PLA-g-MA)₅₀PCL, and **d** PLA-g-MAPCL



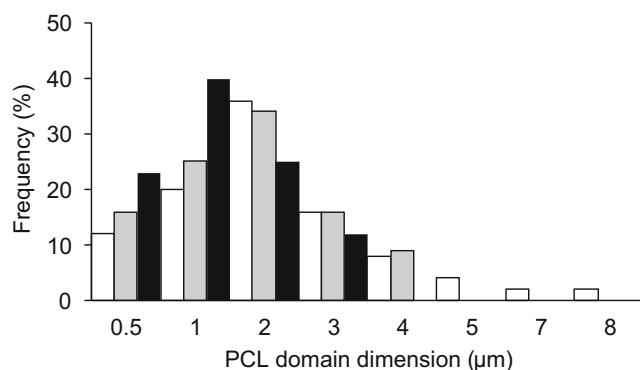


Fig. 4 PCL domain distribution in the blends: (white bar) PLAPCL, (gray bar) PLA(PLA-g-MA)₁₀PCL, and (black bar) PLA(PLA-g-MA)₅₀PCL

PLA-g-MA, the peak signals coming from MA are very weak as the grafting degree is considerably low. Only the spectra from 2.0 to 4.0 ppm were magnified (see inserts in Fig. 2), as no changes in the spectra were noted in other regions. While in the magnified spectrum of PLA, only a faint signal at about 3.5 ppm can be observed (attributable to the terminal hydroxyl protons), new resonances appear in that of PLA-g-MA. The resonances at 2.2–2.5 and 3.5–4.0 ppm can be assigned to the methine and methylene protons of the succinic anhydride ring, respectively, which suggests, as reported in the case of maleation of syndiotactic polystyrene [29], that the grafting reaction consists of single succinic anhydride rings. On the other hand, as no additional resonances were observed at 4.0–4.8 ppm (which generally arise from the side chains containing more than one succinic anhydride unit), it is possible to deduce the absence of oligomeric grafting [30].

The amount of anhydride attached to the PLA backbone was also determined by titration. Results showed that the addition of 0.5 wt% of L101 and 6 wt% of MA leads to the grafting of 0.7 wt% of MA. This finding is in line with the results reported by Hassouna et al. [20]. Moreover, viscosity measurements indicated a slight negative effect on the molecular mass of PLA, the molecular mass of PLA-g-MA decreasing by ca 10 % with respect to the starting PLA.

Blend morphological characterization

Figure 3 shows the SEM micrograph of the neat PLA/PCL blend and those of the blends containing different amounts of PLA-g-MA.

The first sample (Fig. 3a) shows a typical sea-island morphology, where the discrete PCL spherical domains, with dimensions ranging between 0.5 and 8 μm (Fig. 4), are dispersed in the PLA matrix. Indeed, as reported in the literature [31], the viscosity of PCL at 180 °C is far lower than that of PLA, which is indicative of a high viscosity ratio. It is evident that, by increasing the content of PLA-g-MA in the blend, the structure becomes finer, with the dimensions of the PCL domains decreasing significantly (Fig. 4). The evaluation of the PCL particle dimensions demonstrated that, already in the case of the PLA(PLA-g-MA)₁₀PCL blend, prepared by replacing 10 wt% of PLA with PLA-g-MA, the distribution shifts toward lower dimensions (from 4 to 0.5 μm), and it becomes even narrower when 50 wt% of PLA is replaced by PLA-g-MA. In the case of the blend based only on PLA-g-MA and PCL, the SEM morphological characterization shows an almost homogeneous microstructure. Moreover, it is possible to recognize that the decrease of the PCL domains is associated with an enhanced adhesion of the domains to the polymer matrix.

These results support the previously hypothesized formation of PCL-grafted PLA chains (Fig. 1) at the interface of the two polymers: The enhanced interactions between the two phases (with the consequent reduction of their interfacial tension) would promote their compatibility, which results in a reduction of the size of the dispersed PCL phase and enhanced adhesion.

Blend thermal properties

The thermal properties of the blends were studied by means of differential scanning calorimetry (DSC). Figure 5 reports the DSC traces (as recorded during the second heating scan) for the neat PLA/PCL and the PLA/PCL/PLA-g-MA blends. Thermal data are summarized in Table 2.

Fig. 5 DSC traces: **a** PLAPCL, **b** PLA(PLA-g-MA)₁₀PCL, **c** PLA(PLA-g-MA)₅₀PCL, and **d** PLA-g-MA/PCL

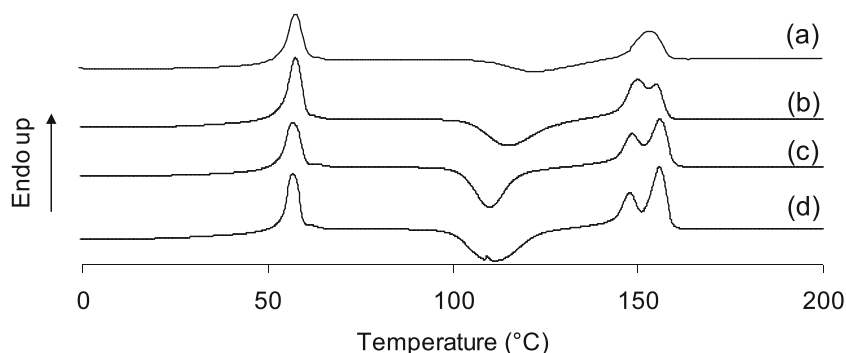


Table 2 Thermal properties for neat PLA/PCL blend and for those based on PLA-g-MA

Sample	PCL		PLA			
	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)
PLAPCL	57	29	122	−14	153	14
PLA(PLA-g-MA) ₁₀ PCL	57	35	115	−27	150	26
PLA(PLA-g-MA) ₅₀ PCL	57	33	110	−29	148	30
PLA-g-MAPCL	56	33	110	−34	148	34

All the blends show the same four thermal transitions: the glass transition (T_g) of the PLA matrix, the PCL melting peak (these two transitions being superimposed at about 56 °C), the broad exothermic peak for PLA cold crystallization, and finally the PLA melting peak(s). With comparison to the neat PLA/PCL reference, differences in the DSC traces of blend based on PLA-g-MA can be easily recognized from Fig. 5.

Indeed, while the addition of PLA-g-MA does not seem to significantly affect the melting behavior of PCL, significant variations in the crystallization and melting of PLA can be observed: with increasing the amount of PLA-g-MA in the blends, the cold crystallization peak shifts toward lower temperatures, and the crystallization enthalpy increases (see also Table 2), while the melting peak splits into two peaks (at ca 148 and 158 °C) whose resolution improves.

The first phenomenon, which is an enhancement of the crystallization of the PLA matrix when in the presence of PLA-g-MA as a compatibilizer, has already been reported for other composite systems [22, 28, 32]. In our case, we imputed the substantial observed effect to the combination of two factors, i.e., the easier crystallization of PLA-g-MA with respect to PLA (DSC results not shown)—likely due to the reduced chain size caused by the small degradation—and especially the magnified nucleating action of the PCL domains when their size is strongly reduced as the morphology is getting finer and finer. The presence of double/multiple melting peaks is a commonly observed phenomenon for semicrystalline polyesters, caused by the existence of melting and recrystallization processes. In the specific case of PLA, some authors have interpreted it as arising from a phase transition (from the less stable α' form to the more perfect α polymorph, melting at higher temperature) [33, 34]. Whatever mechanism is taking place during the heating scan of the PLA matrix (recrystallization or phase transition), it is clear that such behavior is influenced by the PLA-g-MA content in the blend, the reorganization phenomena becoming more evident together with the crystallization extent on increasing the amount of PLA-g-MA.

Conversely to the DSC data, TGA analysis (results not shown) shows that the presence of PLA-g-MA in the blends does not influence the system thermal decomposition. Clearly, the thermal stability of the blends is particularly important for applications which involve the additional treatment of the system at high temperatures.

Blend mechanical properties

The mechanical properties obtained for the different blends are summarized in Table 3. PLA is well known to be a glassy polymer at room temperature, showing a relatively high modulus (1,200 MPa) associated with a low deformation at break, namely about 7 %. On the other hand, PCL has significantly lower stiffness and resistance but exhibits a very high elongation at break (about 1,200 %). Thus, the mechanical properties of the blend are expected to be an average between the two polymers, reflecting the volume ratio of the two phases but also the morphology of the blend and the quality of the interfaces. Indeed, the modulus of the PLAPCL blend is intermediate between those of PLA and PCL, while the elongation at break is not significantly improved as compared with that of neat PLA, this evidencing no toughening due to the presence of PCL and thus confirming the very weak interfacial interaction of the simple PLA/PCL blend.

When considering the samples added with maleated PLA, an increase of the Young's modulus (E) with increasing the concentration of PLA-g-MA in the blend was found, the increment of E for the blend prepared by totally replacing PLA with PLA-g-MA (PLA-g-MAPCL) being ca 20 %, with respect to the pristine PLAPCL blend. An opposite trend was found for the elongation at break. Indeed, a relevant increase of the elongation at break was observed for PLA(PLA-g-MA)₁₀PCL, an observation which can be related to the improved compatibility between the two phases, while a further addition of PLA-g-MA causes the progressive loss of the gained ductility. In order to explain these results, it is necessary to take into account that the covalent linkages occurring between PLA-g-MA and PCL tend to increase with increasing

Table 3 Mechanical measurement results

Sample code	E (MPa)	ϵ_{break} (%)
PLA	970±100	7±1
PCL	220±10	1200±400
PLAPCL	660±20	7±2
PLA(PLA-g-MA) ₁₀ PCL	710±30	53±5
PLA(PLA-g-MA) ₅₀ PCL	770±40	21±3
PLA-g-MAPCL	790±30	12±2

concentration of maleated PLA chains in the system. Clearly, the formation of a strongly cross-linked structure at high concentration of PLA-g-MA—while promoting compatibility and interfacial adhesion—does also cause increased stiffness and embrittlement [13].

Conclusions

In this paper, the effectiveness of PLA-g-MA as a compatibilizing agent for a PLA/PCL immiscible blend was demonstrated. Indeed, the chosen strategy consists in grafting a fraction of PCL onto the PLA-g-MA backbone by reactive blending in order to create more interactions between the so-functionalized PLA and the remaining fraction of nongrafted PCL. PLA-g-MA was prepared via reactive blending through a free radical process, a method which allowed grafting 0.7 wt% of MA, without dramatically reducing the molecular mass of the polymer matrix, it decreasing by ca. 10 % with respect to the starting PLA.

By varying the concentration of PLA-g-MA, progressively replacing the PLA component in the blends, it was possible to tune the final properties of the systems. In particular, it was found that the dimensions of the PCL domain significantly decreased, and their adhesion to PLA improved by increasing the amount of PLA-g-MA in the blends. Indeed, the complete replacement of PLA with PLA-g-MA led to an almost complete compatibilization. Also, the mechanical properties resulted to be affected by the addition of PLA-g-MA in the blend. In particular, the elongation at break significantly improves in the sample characterized by the lowest concentration of maleated PLA, a phenomenon which can be ascribed to the improved compatibility of the two phases, while it decreases by increasing the amount of maleated PLA in the blend. In order to explain the above findings, the covalent linkages occurring between PLA-g-MA and PCL were taken into account, which at high concentration of maleated PLA favors the blend stiffness, simultaneously decreasing its toughness.

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