

A low-environmental-impact approach for novel bio-composites based on PLLA/PCL blends and high surface area graphite

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In this work, novel graphite-based composites consisting of poly(L-lactide) (PLLA) and poly(ϵ -caprolactone) (PCL) immiscible blends are developed by means of a simple and low-environmental-impact method, which does not require the use of either solvents or graphite oxide. Indeed, the proposed approach relies on the preliminary dispersion of a high surface area graphite (HSAG) in the molten PCL by applying a sonication treatment: as a consequent of this processing, the HSAG turns out to be dispersed in the polymer matrix at a sub-micrometer level and acts as a nucleating agent for the PCL crystallization. The PCL/HSAG system (whose filler content is adjusted so as to prepare blends with final HSAG concentrations ranging from 0.1 to 0.6 wt.%) is subsequently introduced in PLLA through melt blending. SEM characterization demonstrates that the presence of HSAG modifies the morphology of the blend. In particular, at a characteristic HSAG concentration, namely 0.1 wt.%, the filler is observed to ameliorate significantly the compatibility of PLLA/PCL blends by increasing the interface adhesion between the two polymer phases.

The peculiar morphology, promoted by the presence of HSAG at the interface, is found to enhance the mechanical properties of the blend, improving the elongation at break simultaneously increasing the Young's modulus.

Keywords:

PLA
Graphite
PCL
Blends

1. Introduction

Poly(lactide) (PLA), a biodegradable and biocompatible aliphatic polyester, produced from renewable resources, has attracted increasing interest because of its low toxicity and its environmental friendliness [1–4]. Indeed, in recent years, new technologies, which allow relatively inexpensive production of high molecular weight PLA, have broadened its uses for food packing, wrap film and other consumer products [1].

However, brittleness, poor elongation at break, narrow processing window, low melt strength and lack of reactive functional groups represent important limitations for a wider application of PLA [5]. To overcome these drawbacks, different physical and chemical approaches have been attempted [6,7]. In general, one of the most practical strategy for improving

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polymer features is blending with another polymer, which method allows easily tuning the properties of the final material through a synergic combination of the (complementary) properties of the blend component(s).

Therefore, in order to reduce the brittleness of PLA, blending with a ductile (biodegradable) polymer such as poly(ϵ -caprolactone) (PCL) has been widely applied. Unfortunately, PCL/PLA blends are thermodynamically immiscible and a multiphase structure is formed, with consequent restriction for the actual performance and applicability of the material [8–10]. Several methods have been exploited to enhance the compatibility between PLA and PCL, typically the addition of polymeric compatibilizers (i.e., block copolymers) [11,12] and reactive compatibilization/mixing [13]. Another, more-recently-developed way to modify the interfacial properties of immiscible blends is the addition of inorganic fillers and nanofillers, such as carbon black [14], organoclays [15], POSS [16], carbon nanotubes and graphite [17,18], the latter being the filler employed in the present work. As far as the use of graphite is concerned, its effect on the conductive properties of polymer blends was mainly investigated, by adding relevant amount (20–30 wt.%) of the filler [19]. More recently, also graphene was used as a compatibilizing agent for immiscible blends, as it allows to modify the properties of the blend at a lower content with respect to that of graphite. Indeed, in the first work on this topic, the effect of graphene oxide (GO) on the properties of immiscible blends based on polyamide (PA) and polyphenylene oxide (PPO) was inquired [20]. The compatibilizing effect of GO was evidenced by an improvement of the blend morphology, as well as by an increment of the system ductility. It was related to the interactions of GO with both PA and PPO phases, which minimize their interfacial tension. The effect of GO on the properties of blends based on polyamide 6 (PA6) and poly(vinylidene fluoride) (PVDF) was studied by Yang et al. [21]. The above blends were prepared by preliminarily dispersing GO in a solution containing PVDF and a subsequently mixing the PVDF/GO system in PA6. In the final blends, the dimension of PVDF domains was markedly reduced and became more uniform, this revealing a well-defined compatibilizing effect of GO on these immiscible blends. Correspondingly, the ductility of the compatibilized blends was found to increase several times compared to the uncompatibilized ones. Another system which was taken into account was that based on natural rubber (NR) and high-density polyethylene (HDPE) [22]. Also in this case, the introduction of GO in the immiscible blend through a two-step procedure was found to enhance the interfacial adhesion and phase compatibility, which resulted in an increase of the mechanical properties of the material.

It is worth underlining that, in all the above mentioned works, graphene oxide, bearing hydroxy and epoxy groups on the basal planes and carboxy groups on the edges, was employed. In general, the use of GO requires a preliminary oxidation of graphite to GO and its subsequent reduction, in order to restore the sp^2 hybridization of the carbon atoms. Moreover, its dispersion in polymer matrices generally implies the use of solvents. In this light, the development of methods able to disperse graphene or exfoliated graphite in one step into a polymer matrix is a significant current research issue. In this work, for the first time, a special kind of graphite, namely a high surface area graphite (HSAG), a filler which has a high surface area, high shape anisotropy, a low number of stacked graphene layers and an extended crystalline order inside the structural layers [23], was employed as a compatibilizing agent for immiscible blends based on PLA and PCL. Indeed, the proposed approach does not require the use of solvents, as the dispersion/exfoliation of the graphite is accomplished directly in one of the components of the blend, that is PCL. The PCL/HSAG system, whose filler content was adjusted so as to prepare blends with final concentrations of HSAG ranging from 0.1 to 0.6 wt.%, was subsequently incorporated in PLA through melt blending. The influence of the filler on the morphology and properties of PLA/PCL immiscible blends was investigated.

2. Experimental section

2.1. Materials

Poly(L-lactide) (PLLA) is a commercial product from Nature Works Co. Ltd. U.S.A. (2002D, $M_n = 100.000$ g/mol) with a residual monomer content less than 0.3 wt.%. Poly(ϵ -caprolactone) was obtained from Solvay Ltd. Belgium (CAPA 6500, $M_n = 50.000$ g/mol). A high surface area graphite (HSAG), TC-307 from Asbury, is an ultra-fine powder (Fig. 1S) with a nominal BET surface area of 350 m²/g, and particle size distribution from 0.20 μ m to 20 μ m. Graphite TC-307 from Asbury was used as received.

2.2. Preparation of blends

Before accomplishing the blend preparation, both polymers were dried overnight at 40 °C. 70 wt.% of PLLA and 30 wt.% of PCL were added to 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 15 min at room temperature, followed by argon purging for 5 min. The above operations were repeated at least three times, to be sure to avoid humidity to come into contact with the reagents. Afterwards, the reactor was placed in an aluminum block oven at 180 °C and, under inert atmosphere, the polymer system was mixed for 10 min at 100 rpm. For the blends containing HSAG, an appropriate amount of the filler (see Table 1) was first dispersed in the molten PCL at 180 °C using a tip sonicator (Omni International type Sonic Ruptor 400) which was set on pulse mode, at 120 W for 30 min.

A sample was prepared by adding HSAG directly in the molten PCL and mixing for 30 min at 100 rpm (PCL-G_{1no sonic}).

Table 1
Characteristics of the prepared systems.

Sample name	HSAG (wt.%)	Sonication treatment
PCL	0	Yes
PCL-G _{0.5}	0.5	Yes
PCL-G ₁	1.0	Yes
PCL-G _{1no sonic}	1.0	No
PCL-G ₂	2.0	Yes
PLLA ₇₀ PCL ₃₀	0	-
PLLA ₇₀ PCL ₃₀ -G _{0.5}	0.15	Yes
PLLA ₇₀ PCL ₃₀ -G ₁	0.30	Yes
PLLA ₇₀ PCL ₃₀ -G ₂	0.60	Yes
PLLA ₇₀ PCL ₃₀ -G _{1no sonic}	0.30	No

Subsequently, the blends were prepared by mixing PLLA with the so-prepared PCL/HSAG systems, using the same conditions as for the neat PLLA/PCL blend. Moreover, a sample was prepared by adding HSAG directly in the PLLA/PCL system and mixing for 10 min at 100 rpm (PLLA₇₀PCL₃₀-G_{1no sonic}). Table 1 shows the characteristics of the prepared sample.

2.3. Characterization

A Zeiss Supra 40 VP field emission scanning electron microscope equipped with a backscattered electron detector was used to examine the blend morphologies. 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 calorimetric analysis was performed under a continuous nitrogen purge on a Mettler calorimetric apparatus, model DSC1 STAR^e System. 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, then cooled down to room temperature and finally heated to 200 °C again. A scanning rate of 10 °C/min was used both on heating and cooling.

The rheological properties of the PCL/HSAG nanocomposites were measured on a strain-control rheometer (Advanced Rheometric Expansion System, ARES, TA Instruments, USA) with parallel-plate geometry (diameter of 25 mm). The instrument was equipped with a convection oven in compressed gas to control the temperature. Before the measurements, the dried PCL/HSAG nanocomposites were compression-molded at 180 °C into disks with thickness of 1 mm and diameter of 25 mm. The disk-like samples were further dried at 40 °C in vacuum for 8 h before the measurements. Oscillatory frequency sweeps ranging from 0.01 to 100 rad/s with a fixed strain (chosen and selected for each sample in order to fall in the linear viscoelastic region) were performed at 180 °C in nitrogen atmosphere. After the sample loading, an approximate 5 min equilibrium time was applied prior to each frequency sweep.

The tensile properties of neat PLLA/PCL blend and PLLA/PCL/HSAG blends were determined at room temperature by an Instron Mechanical Tester (Instron 5565) at a crosshead speed of 10 mm/min using rectangular specimens with dimension of 10 × 25 × 0.5 mm. The reported property values represent an average of the results for tests run on six specimens, along with their experimental deviation.

3. Results and discussions

3.1. Preparation and characterization of PCL-G systems

This work has been preliminary focused on the preparation of composites based on HSAG and PCL, which systems were subsequently introduced in PLLA. In the frame of this approach, PCL was used as “solvent” to disperse/exfoliate HSAG.

As reported in the literature, the dispersion/exfoliation of graphite is favoured by the specific interactions occurring between the solvent – in this case the polymer – and the graphene sheets. Indeed, it was demonstrated by Hernandez et al. [24] that the exfoliation of graphite occurs for solvents whose surface energy matches that of graphene. In the case of PCL, the surface tension of the molten polymer (51 mN/m) is in the range of that of solvents, such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), characterized by a high capacity of exfoliating the graphite. Moreover, the dispersion/exfoliation of the filler was enhanced by the sonication treatment and by the exploitation of high temperatures (180 °C), at which the dispersion medium has a low viscosity. It is worth underlining that in the literature it was reported the preparation of composites based on PCL and graphite/graphene, by using either the *in-situ* polymerization with graphene oxide [25] and/or other methods, all involving the application of solvents [26,27]. The approach here reported represents an appealing, economic and environmentally friendly alternative to the above mentioned methods, as it does not require either the modification of graphite or the use of solvents.

In order to highlight the role of the preliminary dispersion of HSAG in PCL, a sample was also prepared by adding directly the filler into PCL.

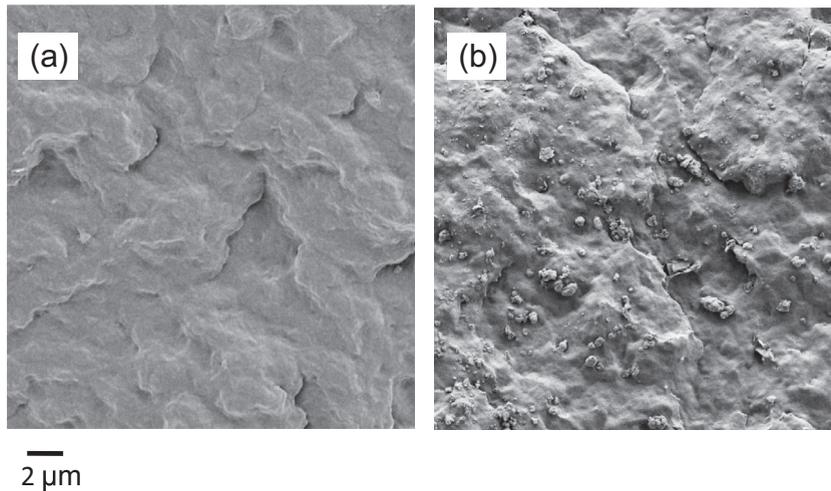


Fig. 1. SEM micrographs of: (a) PCL-G₁ and (b) PCL-G_{1no sonic}.

SEM micrograph of PCL-G₁ (Fig. 1(a)) was compared with that of the sample containing the same quantity of HSAG and which did not undergo the sonication treatment (Fig. 1(b)).

While the second sample is characterized by the presence of micrometric agglomerates of HSAG, the (fractured) surface of PCL-G₁ is completely homogenous with no visible aggregates. This finding highlights the effectiveness of the sonication treatment in the dispersion of HSAG particles of at a sub-micrometric level.

The thermal properties of the PCL-G nanocomposite systems were studied by DSC measurements.

Fig. 2(A) shows the cooling traces for neat PCL and for the composites containing different amounts of HSAG, during the non-isothermal melt crystallization at 10 °C/min. The thermal data are summarized in Table 2. While the crystallization temperature (T_{cr}) is around 25 °C for neat PCL, it shifts to 37 °C, 38 °C and 39 °C for the composites based on 0.5, 1 and 2 wt.% of graphite, respectively. The increase of T_{cr} with the addition of HSAG indicates that this filler acts as (good) nucleating agent for the crystallization of PCL. Indeed, the difference of T_{cr} between neat PCL and the nanocomposite based on 0.5 wt.% is ca. 12 °C, evidencing how the incorporation of a small amount of HSAG is capable of improving significantly the melt crystallization of PCL. Nevertheless, on further increasing the loading of the filler, the increase of T_{cr} is only of about 2 °C, showing that the nucleating action on the polymer matrix is more pronounced at low graphite content. Indeed, as reported by Zhang and Qiu [26], this behavior can be related to the saturation of the nucleating effect at high nanographite loading. Accordingly, as revealed by the increase of the crystallization enthalpy (ΔH_{cr}), the addition of graphite has a positive effect also on the

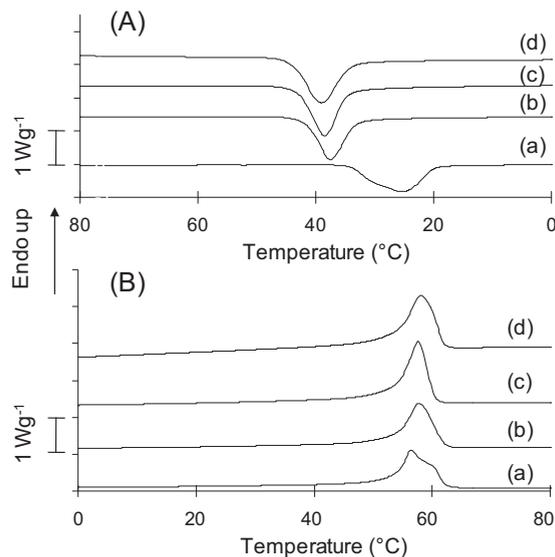


Fig. 2. (A) DSC cooling traces of: (a) PCL, (b) PCL-G_{0.5}, (c) PCL-G₁ and (d) PCL-G₂; (B) DCS heating traces of (a) PCL, (b) PCL-G_{0.5}, (c) PCL-G₁ and (d) PCL-G₂.

Table 2

Thermal properties for neat PCL and for the composites based on HSAG.

Sample name	T_{cr} (°C)	ΔH_{cr} (J/g)	T_m (°C)	ΔH_m (J/g)
PCL	25	-45	56	46
PCL-G _{0.5}	37	-51	58	52
PCL-G ₁	38	-56	57	58
PCL-G ₂	39	-57	58	64

content of crystalline phase developed during cooling, which effect tends to level off at higher graphite content (see Table 2). The enhancement of ΔH_{cr} is mirrored in the enhanced melting enthalpy (ΔH_m) of the composites samples as compared to neat PCL, whereas the melting temperature (T_m) is not significantly affected by the presence and content of HSAG.

3.2. Blends based on PLLA, PCL and HSAG (PLLA₇₀PCL₃₀-G_x)

Fig. 3 shows the SEM micrographs of the neat PLLA/PCL blend and those of the blends containing HSAG.

The first sample (Fig. 3(a)) shows a typical sea-island morphology, where the discrete PCL spherical domains, with dimensions ranging between 0.5 and 8 μm , are dispersed in the PLLA matrix. Indeed, as reported in the literature [28], the viscosity of PCL at 180 °C is far lower than that of PLA, which is indicative of a high viscosity ratio, thus favoring phase separation. In order to evidence the effect of sonication on the blend morphology, SEM analysis of a sample prepared by adding directly HSAG to the blend, without applying the sonication process, was performed (Fig. 3(b)). By comparing the micrograph reported in Fig. 3(a) and (b), it is evident that the latter sample shows a morphology similar to that of the neat blend, thus demonstrating that, in the absence of sonication, HSAG does not act as a compatibilizer for the two polymers.

Conversely, the introduction of the PCL/HSAG systems in PLLA produces a visible modification of the blend morphology. Indeed, in the blends containing 0.5 (Fig. 3(c)) and 1 wt.% (Fig. 3(d)) of HSAG the dimensions of PCL domains become more homogeneous and, especially in the case of the sample PLLA₇₀PCL₃₀-G₁, based on 1 wt.% of HSAG (see also Fig. 3(f)) with respect to PCL, their adhesion to PLLA increases significantly. It is important to underline that the addition of 2 wt.% of HSAG (Fig. 3(e)) gives only a small improvement to the blend morphology with respect to the previously described sample. This finding highlights a saturation effect of HSAG as a compatibilizing agent, likely related to a worsening of its dispersion/exfoliation at high concentration.

Generally speaking, in order to explain the effect of a filler on the morphology of immiscible blends, two possible mechanisms have been proposed. Indeed, if the filler is miscible or at least compatible with both phases, a thermodynamically driven compatibilization is likely to occur between the two polymers [29]. Conversely, when the filler is mainly dispersed in the component with stronger polarity or with lower viscosity, the selective localization changes the viscosity ratio of the two components and prevents coalescence of the domains during melt mixing, thus improving the compatibility between the two phases kinetically [29].

In this light, the influence of HSAG on the final morphology of the blend may result either from its intrinsic interfacial activity or from the increase of the PCL viscosity. Indeed, in order to support the latter hypothesis, rheological measurement on the PCL/HSAG systems were carried out. The results of the rheological tests demonstrated that the viscosity of the polymer system containing HSAG did not change with respect to that of the pristine PCL over the whole frequency range (results not shown). Combining this finding with the morphological characterization results, it is possible to draw some inferences on the two possible situations, namely that resulting from the preliminary dispersion of HSAG in PCL and the system formed when directly adding HSAG to the blend.

As illustrated in the scheme reported in Fig. 4, we hypothesize that, in the former case, HSAG, which is dispersed/exfoliated in PCL thanks to the sonication process, is able to diffuse towards the interface of the PCL domains with PLLA and, it being likely affine with both the phases, increases their interfacial adhesion. As a consequence, the filler reduces the voids between the PCL domains and the PLLA matrix (Fig. 3(f)).

It is worth underlining that the above mechanism is in agreement with that proposed to explain the effect of carbon nanotubes (CNTs) on the final morphology of immiscible blends [29,30]. Nevertheless, the exploitation of CNTs as compatibilizing agents involves their dispersion in a solvent capable of solubilizing also the polymers. Once again, HSAG, which allows to ameliorate the compatibility of immiscible blends and whose use does not require the exploitation of solvents, represents an interesting and promising alternative to the most commonly used carbon-based fillers, such as CNTs and graphene.

As for the second preparation method, as shown in the scheme of Fig. 4, when HSAG is not previously dispersed, it results to be distributed in both the phases with the formations of micrometer-sized aggregates (as indicated by the circle of Fig. 3(b)). Therefore, the filler, which does not possess a high surface area, is not able to accomplish a compatibilizing effect.

The thermal properties of the prepared blends were studied by means of DSC. Fig. 5 reports the DSC traces (as recorded during the second heating scan) for the neat PLLA₇₀PCL₃₀ and the PLLA₇₀PCL₃₀-G_x blends. Thermal data are summarized in Table 3.

The DSC trace of PLLA₇₀PCL₃₀ exhibits two independent melting peaks, the first one corresponding to PCL (at ca. 56 °C), the second one to PLLA (at ca. 150 °C). The presence of double melting peaks for PLLA, a phenomenon commonly observed for

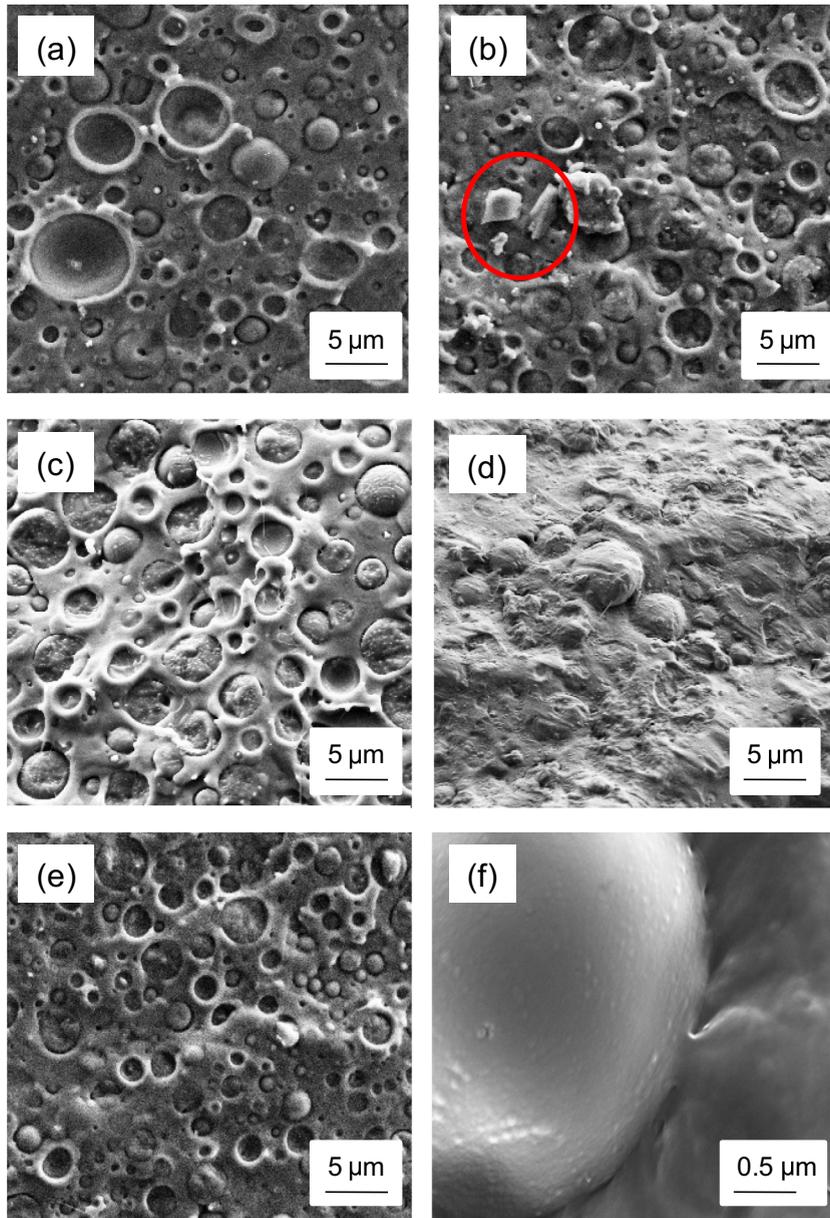


Fig. 3. FE-SEM micrographs of the blends: (a) PLLA₇₀PCL₃₀, (b) PLLA₇₀PCL₃₀-G_{no_sonic}, (c) PLLA₇₀PCL₃₀-G_{0.5}, (d) PLLA₇₀PCL₃₀-G₁, (e) PLLA₇₀PCL₃₀-G₂ and (f) detail of PLLA₇₀PCL₃₀-G₁.

semi-crystalline polyesters, is caused by the occurrence of melting and recrystallization processes. Indeed, 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) [30]. The thermal behavior of the blends prepared by adding the PCL-G systems to PLLA is similar to that of the neat PLLA/PCL blend, meaning that the presence of the compatibilizer at the interface does not affect the way the bulky polymer phases structure. Conversely, the sample PLLA₇₀PCL₃₀G_{1no_sonic}, prepared by direct addition of HSAG to the mixture, shows some differences. Indeed, both melting and crystallization enthalpies of PCL turn out to be higher than in the neat blend, while the melting enthalpy of PLLA is lower, but with a higher fraction of material crystallized on cooling, the cold crystallization peak being absent. It is worth evidencing that the observed nucleating effect of HSAG on PCL does not take place when the PCL/HSAG system is mixed into PLLA. As previously discussed, this finding might be related to the diffusion/concentration of the filler at the interface of the PCL domains. Conversely, in the case of the direct dispersion of HSAG into the blend, the micrometer-sized aggregates are capable of behaving as nucleating agents for both polymers.

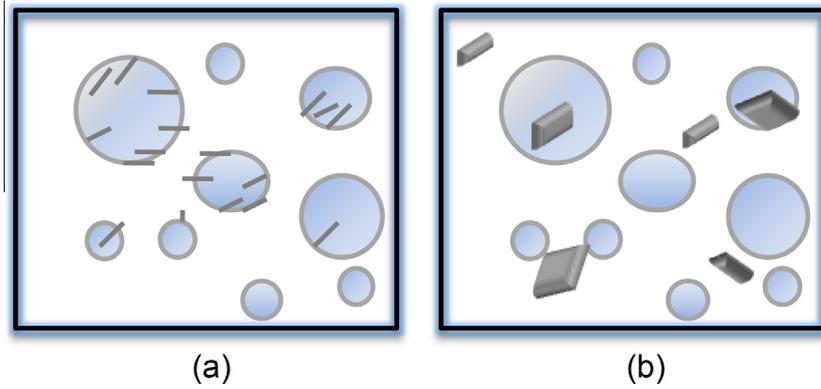


Fig. 4. Sketch of the hypothesized HSAG dispersion in the blends: (a) PLLA₇₀PCL₃₀-G_x and (b) PLLA₇₀PCL₃₀-G_{no sonic}.

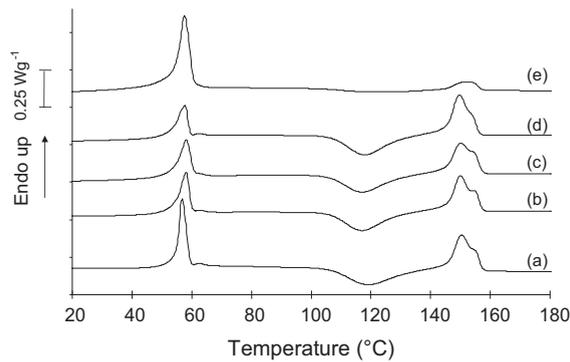


Fig. 5. DSC traces of: (a) PLLA₇₀PCL₃₀, (b) PLLA₇₀PCL₃₀-G_{0.5}, (c) PLLA₇₀PCL₃₀-G₁, (d) PLLA₇₀PCL₃₀-G₂ and (e) PLLA₇₀PCL₃₀-G_{1no sonic}.

The specific effect of HSAG on the properties of PLLA/PCL blends was highlighted by comparing the mechanical properties of the single polymers to those of the neat blend and the systems containing the filler. The stress–strain curves of the blends are shown in Fig. 6, while in Table 4 the mechanical properties of the various samples are summarized.

PLLA shows a relatively high modulus (1400 MPa) and maximum strength (65 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 (ca. 1200%). Therefore, the mechanical properties of the blend are expected to be an average between those of the two polymers, reflecting the volume ratio of the two phases, the morphology of the blend and the quality of the interfaces. Indeed, both modulus and strength for PLLA₇₀PCL₃₀ are intermediate between those of PLLA and PCL. On the contrary, the elongation at break is not significantly changed as compared with PLLA, evidencing that no toughening effect is present due to the presence of PCL and thus confirming the very low interaction at the PLA/PCL interface.

As shown in Table 4, the presence of HSAG turns out to (positively) affect both the modulus (E) and the elongation at break (ϵ_{break}). In particular, ϵ_{break} is observed to be dependent on HSAG concentration, it being maximum for the sample PLLA₇₀PCL₃₀-G₁, for which the elongation at break increases more than 300% with respect to the neat blend (Fig. 6). It must be underlined that the increase of ϵ_{break} seems to be strictly related to the final morphology of the blend, as the sample PLLA₇₀PCL₃₀-G₁, which is characterized by the highest elongation at break, is the one showing the best compatibilization. On the basis of these findings, it is possible to conclude that in our system the dramatic enhancement of the elongation at break is certainly related to a radical improvement of the compatibility of the two phases, which further demonstrates the effectiveness of HSAG as a compatibilizer between PLLA and PCL.

Table 3
Thermal properties for neat blend and for blends based on HSAG.

Sample name	T_{cr}^{PCL} (°C)	$\Delta H_{cr}^{\text{PCL}}$ (J/g)	T_m^{PCL} (°C)	ΔH_m^{PCL} (J/g)	T_{cc}^{PLLA} (°C)	$\Delta H_{cc}^{\text{PLLA}}$ (J/g)	T_m^{PLLA} (°C)	ΔH_m^{PLLA} (J/g)
PLLA ₇₀ PCL ₃₀	32	-13	57	13	119	-18	150	17
PLLA ₇₀ PCL ₃₀ -G _{0.5}	37	-10	58	10	117	-17	150	18
PLLA ₇₀ PCL ₃₀ -G ₁	37	-12	58	10	117	-18	150	17
PLLA ₇₀ PCL ₃₀ -G ₂	39	-9	58	8	118	-18	150	18
PLLA ₇₀ PCL ₃₀ -G _{1no sonic}	39	-23	58	22	-	-	152	8

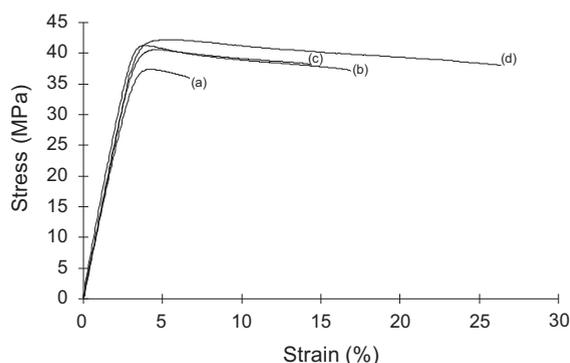


Fig. 6. Stress–strain curves of the blends: (a) PLLA₇₀PCL₃₀, (b) PLLA₇₀PCL₃₀-G_{0.5}, (c) PLLA₇₀PCL₃₀-G₂, and (d) PLLA₇₀PCL₃₀-G₁.

Table 4
Mechanical measurement results.

Sample name	E (Mpa)	σ_{\max} (Mpa)	$\varepsilon_{\text{break}}$ (%)
PLLA	1400 ± 40	65 ± 2	7 ± 1
PCL	220 ± 10	20 ± 4	1200 ± 400
PLLA ₇₀ PCL ₃₀	1077 ± 20	34 ± 2	7 ± 1
PLLA ₇₀ PCL ₃₀ -G _{0.5}	1306 ± 30	39 ± 3	12 ± 2
PLLA ₇₀ PCL ₃₀ -G ₁	1341 ± 20	40 ± 3	26 ± 3
PLLA ₇₀ PCL ₃₀ -G ₂	1357 ± 20	40 ± 1	17 ± 2

As previously underlined, also the modulus was found to be influenced by the presence of HSAG in the blend. Indeed, unlike other type of compatibilizing agents, such as block-copolymers [11,12], whose addition to blends generally causes a sharp decrease of the modulus, the use of our graphite filler even results in an increase of E for all the systems considered.

It is of utmost relevance that, conversely to the classical copolymers employed as compatibilizing agents for PLA/PCL blends, whose application requires the addition of significant amounts of filler (10–20 wt.%), in the case of the use of HSAG, the best effect of compatibilization occurs by adding only 0.3 wt.% of the filler to the blend. On the other side, comparing the behavior of HSAG with other kinds of fillers, such as multi walled carbon nanotubes (MWCNTs) [29] and talc [31], it is worth noticing that, generally, the addition of the above fillers is accompanied by a decrease of the elongation at break. Indeed, in our system the dramatic enhancement of ductility is certainly related to a radical improvement of the compatibility of the two phases.

Therefore, it is possible to conclude that the addition of HSAG simultaneously brings reinforcement and compatibilization effects into the immiscible blend system, and it allows to obtain polymer blend composites with high performances.

4. Conclusions

In this work, a facile and a low-environmental-impact approach to prepare novel composites based on the poly(L-lactide) (PLLA)/poly(ϵ -caprolactone) (PCL) blends and a high surface area graphite (HSAG) was developed. This method does not require either the use of solvents or the previous oxidation of the carbon allotrope, that are instead adopted in the classical methods reported in the literature, to achieve dispersion/exfoliation of HSAG. Indeed, such dispersion/exfoliation was accomplished by sonicating HSAG in PCL and was maintained also when the PCL/HSAG system was mixed with PLLA. The filler was shown to have a double role in tuning the final properties of the system: from one side it has a compatibilization effect for the immiscible blends, thus increasing the elongation at break, and from the other it is capable of reinforcing the material, thus increasing its toughness.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2015.06.016>.

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