Does magnesium compromise the high temperature processability of novel biodegradable and bioresorbables PLLA/Mg composites?

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ABSTRACT: This paper addresses the influence of magnesium on melting behaviour and thermal stability of novel bioresorbable PLLA/Mg composites as a way to investigate their processability by conventional techniques, which likely will require a melt process at high temperature to mould the material by using a compression, extrusion or injection stage. For this purpose, and to avoid any high temperature step before analysis, films of PLLA loaded with magnesium particles of different sizes and volume fraction were prepared by solvent casting. DSC, modulated DSC and thermogravimetry analysis demonstrate that although thermal stability of PLLA is reduced, the temperature window for processing the PLLA/Mg composites by conventional thermoplastic routes is wide enough. Moreover, magnesium particles do not alter the crystallization behaviour of the polymer from the melt, which allows further annealing treatments to optimize the crystallinity in terms of the required combination of mechanical properties and degradation rate.

KEYWORDS: Biodegradable materials; Magnesium; Particle reinforced composites; Poly-L-lactic acid

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RESUMEN: *¿Compromete el magnesio la procesabilidad a elevada temperatura de nuevos materiales compuestos biodegradables y biorreabsorbibles de PLLA/Mg?.* Este trabajo aborda la influencia de magnesio en el comportamiento a fusión y en la estabilidad térmica de nuevos compuestos de PLLA / Mg biorreabsorbibles como una forma de investigar su procesabilidad mediante técnicas convencionales, lo que probablemente requerirá una etapa en estado fundido a alta temperatura para moldear el material mediante el uso de una etapa de compresión, extrusión o inyección. Para este fin, los materiales de PLLA cargados con partículas de magnesio, de diferentes tamaños y fracción de volumen, se prepararon por la técnica de disolución y colada, evitando así el procesado a alta temperatura antes del análisis. El análisis mediante DSC, DSC modulada y termogravimetría demuestra que, aunque la estabilidad térmica de PLLA se reduce, el intervalo de temperatura para su procesado por rutas convencionales es suficientemente amplio. Además, las partículas de magnesio no alteran la cristalización del polímero a partir del fundido, lo que permitirá optimizar el grado de cristalinidad mediante tratamientos posteriores de recocido y conseguir así una adecuada combinación de propiedades mecánicas y velocidad de degradación.

PALABRAS CLAVE: Ácido poli-L-láctico; Magnesio; Materiales biodegradables; Materiales compuestos reforzados con partículas

1. INTRODUCTION

Overcoming the drawbacks of conventional metallic materials for osteosynthesis implants (stainless steel 316L, titanium Ti 6Al4V) has been the driven force to develop bioresorbable biomaterials suitable to be replaced by mature bone without transient loss of mechanical support (Busam *et al.*, 2006). Among the metallic materials, Mg and its alloys have emerged as possible candidates for the development of bioresorbable implants (Witte *et al.*, 2008). Magnesium is an essential mineral for bone formation, plays a major role regulating calcium homeostasis and has a good combination of strength and fracture toughness (Staiger *et al.*, 2006). Despite the advantages that this metal offers, its use as a resorbable orthopaedic implant has not been expanded due to the fact that the reaction of Mg in a physiological medium releases hydrogen at a rate that the tissue is not able to assimilate. The result is the accumulation of hydrogen around the implant and with this, the loss of its stability (Wang *et al.*, 2009). Therefore, it is necessary to slow down the corrosion rate of Mg *in vivo* without impairing the mechanical properties. Current trends have focused on the use of alloy elements (Müller *et al.*, 2007; Castellani *et al.*, 2011), the grain size refinement (Álvarez López *et al.*, 2010), surface treatments (Carboneras *et al.*, 2010; Carboneras *et al.*, 2011) and coatings (Wong *et al.*, 2010). Unfortunately, there is currently no resorbable metallic material fulfilling the requirements for biodegradable biomaterials.

Within the polymeric materials, significant advances have been made during the last two decades and permitted, in some cases, replacement of metallic prosthetic devices by biodegradable ones. Nowadays most of the available bioresorbable osteosynthesis materials are polymeric implants made from poly (alfa-hydroxy) acids, among which are worthy to highlight Poly-L-Lactic Acid (PLLA). However, they do not meet the mechanical properties of cortical bone and they have, therefore, replaced metallic prosthetic devices only in low load bearing applications (Suuronen, 1991; Maurus *et al.*, 2004). Efforts to improve their mechanical properties and broaden their applicability in high-load bearing situations have been addressed by loading the polymer with particles of hydroxyapatite, tri-calcium phosphates, bioactive glasses or biopolymer fibres (Shikinami and Okuno, 1999; Ramakrishna *et al.*, 2001; Pinho *et al.*, 2009; Boccaccini *et al.*, 2010; Zhou *et al.*, 2012). More recently members of this group have demonstrated the feasibility of introducing Mg particles within a PLLA matrix as a new strategy to modulate its degradation rate and simultaneously, improve the bioactivity and mechanical properties of PLLA. Although previous results of the group provided a proof of concept (Cifuentes *et al.*, 2012), success of the material for a specific application will obviously depend on the appropriate design of the composite and on the corresponding processing route.

Commercially available biodegradable polymers for osteosynthesis devices are processed by conventional methods used in thermoplastic engineering. Compression, extrusion and injection moulding are used to melt the material and give it form of pins, screws, rods, plates or tacks (Middleton and Tipton, 2000; Ambrose and Clanton, 2004; Eglin and Alini, 2008). The main complication of these techniques is related to the tendency of PLLA to undergo thermal degradation during processing above 180 °C (Gogolewski *et al.*, 1993; Tsuji and Fukui, 2003; Wang and Mano, 2005). The poor thermal stability of PLLA during high processing temperatures can lead to depolymerisation and water traces can cause hydrolysis, reducing the molecular weight and affecting final product properties, including physical and mechanical properties, biodegradation kinetics and biological response (Ikarashi *et al.*, 2000; Ghosh *et al.*, 2007). For this reason PLLA must be sufficiently dried before its melting processing and processed at the minimum suitable temperature, to avoid excessive thermal degradation and reduce the lost of physical properties. PLLA is usually extruded at 200–210 °C (Middleton and Tipton, 2000; Lim *et al.*, 2008).

Thermal stability of the PLLA during processing could also be altered by the presence of Mg particles, as observed for other metallic compounds of interest to control its depolymerization into L,L-lactide for feedstock recycling (Cam and Marucci, 1997; Nishida *et al.*, 2005; Motoyama *et al.*, 2007; Chiang *et al.*, 2011). It has been demonstrated that residual metal catalysts (Sn, Fe, Zn, Al) and especially metal oxides/hydroxides (CaO, MgO, Mg(OH)$_2$) reduce the thermal stability of PLLA (Cam and Marucci, 1997; Fan *et al.*, 2004; Nishida *et al.*, 2005; Chiang *et al.*, 2011). Relevant for this investigation is that chemical reactivity of pure Mg is much higher than MgO reactivity -Mg particles are highly flammable, can spontaneously ignite and react violently with oxidising agents-, which could additionally impose a serious technical limitation during processing.

Thermal behaviour is an important aspect characterizing the physical properties of semi-crystalline polymers, and publications concerning the crystallization behaviour of PLLA have been well documented (Hoffman, 1983; Iannace and Nicolais, 1997; Miyata and Masuko, 1998; Di Lorenzo, 2001; Iannace *et al.*, 2001; Mijovic and Sy, 2002). To the authors knowledge there are not published reports that discuss neither about the effect of Mg particles on thermal degradation of PLLA nor the effect on its thermal behaviour. Therefore, the objective of this paper is to answer the following relevant questions: Does magnesium compromise the high temperature processability of PLLA/Mg composites?

How does the size and content of Mg influence the thermal stability of the material? Which would be the suitable temperature window for melt processing? Which is the effect of Mg particles in the composite melting and crystallization behaviour? Answering these questions would contribute to an overall understanding of the thermal behaviour of the composite and its relation with its properties, and hence moving forward the development of PLLA/ Mg composites with properties suitable to meet the requirement for their application in medicine.

To address the raised questions and to obtain a meaningful understanding of the Mg induced effects on poly-L-lactic acid, composites were processed by a solvent casting route, which precludes any previous thermal induced effect. For a meaningful understanding of the role of Mg, two different sizes of particles with two volume fractions were used.

2. MATERIALS AND METHODS

2.1. Materials

PLLA-biopolymer density 1.25 g cm^{-3}, melting temperature 170 °C, glass transition temperature (68 °C) was supplied by Goodfellow in form of pellets of 5 mm nominal size. Magnesium (CP: 99.8%) was purchased in powder form from the same supplier. Two particle sizes were used: big (≤250 μm) and small (≤50 μm), hereafter named Mg-B and Mg-S particles, respectively. The specific surface areas of Mg particles were measured by a standard BET method. The porous characteristics of the Mg particles were determined using a Beckman Coulter SA1100 automatic adsorption analyzer. Total surface area was determined using the BET equation in the p/p$_o$ range 0.015–0.15, (r^2>0.9999), obtaining for Mg-B particles a surface area of 0.1 m^2 g^{-1} and for Mg-S of 1.6 m^2 g^{-1}.

2.2. Composite preparation

Films were prepared by solvent casting. PLLA pellets were dissolved in chloroform at a concentration of 5 wt.%/volume. Mg particles were then added in appropriate proportions achieving nominal values of 5% and 30 wt.%, which are equivalent to 3.6% and 23.5 vol.%, respectively. The mixture was homogenized in orbital shakers at 80 rpm and then cast in Petri dishes. To avoid any previous thermal induced effect the solvent was evaporated at room temperature during 5 days. Homogeneous films of 200 and 400 μm thick were obtained. Films of polymer (PLLA) and PLLA with 5 wt.% and 30 wt.% of particles of both different sizes (PLLA5MgB, PLLA5MgS, PLLA30MgB and PLLA30MgS) were prepared. Figure 1 shows the optical micrographs of the composite films after slight polishing under dry conditions. As can be seen, Mg particles

(bright contrast) exhibit a corn-flake like morphology, irrespectively the nominal size. The 5 wt.% composition was selected for purposes of comparison with previous publications on the effect of metal compounds in the thermal degradation of the material, and the 30 wt.% composition to continue with the research conducted by this group specifically on this composite.

Additionally, to see the stability of the material under drastic conditions, the films were dried at 110 °C for 12 hours under air atmosphere and the effects of this heat treatment on the thermal stability of the material were studied. Two limit situations were compared: materials without any previous thermal effect and materials with a severe previous thermal treatment.

2.3. Thermal degradation

The study of the composite thermal decomposition was performed by thermogravimetry tests using the thermogravimetric analyzer Q50 from TA Instruments. All experiments were carried out under nitrogen atmosphere (20 ml min^{-1}) to avoid unwanted reactions. The samples were heated from 40 °C to 600 °C at a rate of 10 °C min^{-1}. The extrapolated onset temperature (T_o), that denotes the temperature at which weight loss begins, the temperature of greatest rate of change on the weight loss curve (T_p) and the final temperature (T_{end}) of thermal decomposition were determined for each material. T_o and T_{end} were calculated by finding the intersection of the baseline and the extrapolated tangent at the inflection point of the weight loss curve, and T_p, also known as the inflection point, was calculated from the first derivative of the weight loss curve.

2.4. Differential Scanning Calorimetry

The crystallization and melting behaviour of the composites was measured with Differential Scanning Calorimetry (DSC) on a TA Q100 DSC, under nitrogen atmosphere. The experimental design was based on a first heating (F10) from 25 °C to 220 °C, followed by a cooling to 25 °C (CR10), and finally a second heating to 220 °C (CR10F10), all three of them at a rate of 10 °C min^{-1}. The crystallinity was calculated by measuring the enthalpy of melting ΔH_m and cold crystallization ΔH_{cf} from the heating curves using equation (1), where ΔH_{m0} corresponds to 93.1 J g^{-1} and refers to the enthalpy of 100% crystalline PLLA (Lim *et al.*, 2008). The result is normalized taking into account the real amount of polymer in the composite (Eq. 1):

$$\% \, X_c = (\Delta H_m - \Delta H_{cf}) * 100 / \Delta H_{m0} \qquad (1)$$

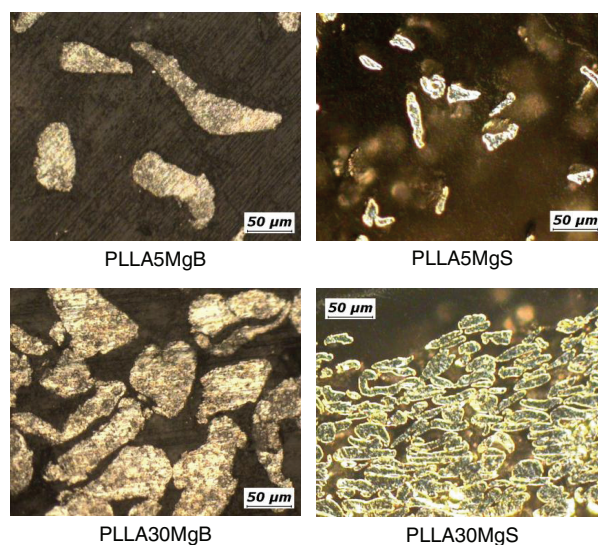The glass transition temperature was calculated as the midpoint temperature of the transformation

FIGURE 1.   Optical micrographs of PLLA/Mg particles.

1/2 ΔCp. The melting T_m and cold crystallization T_{cf} temperatures were determined as the minimum or maximum value of the corresponding transformation peak.

2.5. Modulated Differential Scanning Calorimetry

In Modulated Differential Scanning Calorimetry (MDSC), a sinusoidal temperature oscillation is overlaid on the traditional linear ramp. The net effect is that heat flow can be measured simultaneously with changes in heat capacity. The DSC heat flow is called the Total Heat Flow, and is composed by the heat flow due to heat capacity – reversing heat flow (e.g. glass transition and melting)- and the heat flow due to kinetic events – non-reversing heat flow (e.g. melting, crystallization, evaporation, enthalpic relaxation). The Total Heat Flow signal contains the sum of all thermal transitions, just in standard DSC. Experiments were carried out with the same calorimeter used on DSC studies. The aim was to analyze the effect of the thermal treatment by the separation and study of the different transitions that occur during melting on untreated and heat treated PLLA. For this study scans were performed at a heating rate of 2 °C min^{-1}, period of 60 seconds, and amplitude of 0.32 °C to separate the glass transition from the aging and to isolate the solvent effect.

3. RESULTS AND DISCUSSION

The composites were prepared by solvent casting in order to study the stability and viability of the composites with different content and size of Mg as filler due to the high reactivity of Mg, with the final objective, as commented in the introduction, of preparing these materials by extrusion, injection or compression processes. The solvent used was chloroform and removed at room temperature for 5 days to avoid the effect of any heat treatment and thus study the interaction polymer + filler. Once the thermal stability is studied by TGA, solvent removal proceeds by a drastic heat treatment to evaluate the stability margin processing of composites prepared.

3.1. Effects of Mg on the high temperature processability and thermal stability of composites

Figure 2a shows the weight loss curves for PLLA in the as-received condition (PLLA pellet) and as a solvent cast film (PLLA), and PLLA/Mg composite films with the two different contents and sizes of Mg particles. As can be seen, thermal degradation for the PLLA and PLLA/Mg films exhibit two stages of weight loss. From the comparative analysis between the films curves with that of the pellet, the first stage of weight loss can be attributed to the loss of the residual solvent (~10%), and the second stage to the thermal degradation of the polymeric matrix. The solvent that remains occluded in the films is eliminated between 80 °C and 160 °C. Interestingly, the presence of solvent does not affect the thermal stability of the PLLA since the onset (T_o) and end (T_{end}) degradation temperatures are similar to those observed for the PLLA pellet. This result is in accordance to other studies that determined that low molecular weight compounds such as residual solvents and moisture, can be removed without affecting the thermal stability of the material (Cam and Marucci, 1997; Lim *et al.*, 2008).

Relevant for this investigation is that Mg acts as a depolymerisation catalyst shifting downward the initial decomposition temperature of PLLA irrespectively the volume fraction and size (Fig. 2a). Table 1
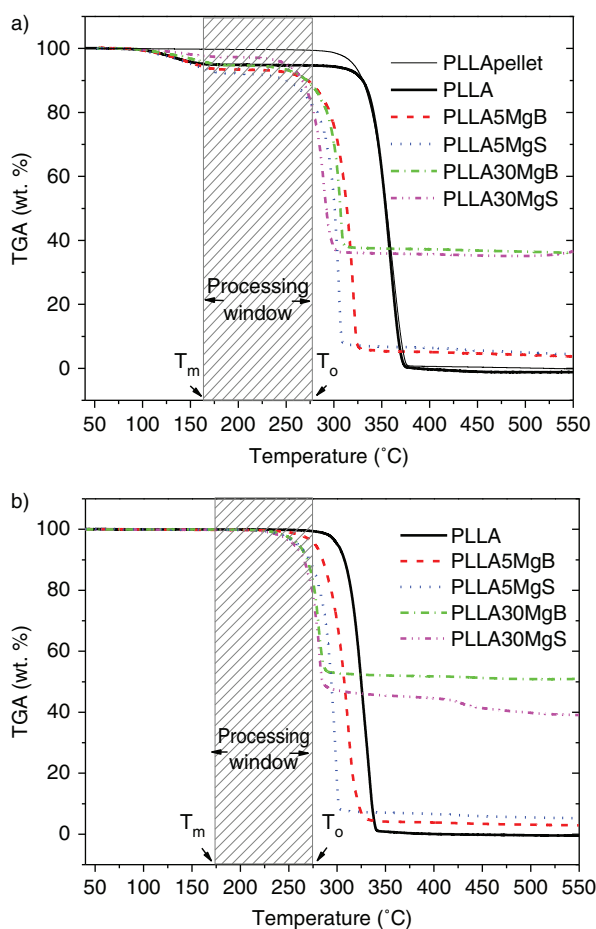
FIGURE 2. Thermogravimetric curves of PLLA/Mg films: a) Weight loss curves- Materials without thermal treatment; b)Weight loss curves - Materials treated at 110 °C during 12 hours under air atmosphere. T_m denotes the melting temperature and T_o the onset temperature of thermal decomposition.

summarizes the onset temperature of decomposition (T_o), the temperature of maximum weight loss rate (T_p), and the temperature where decomposition ends (T_{end}) for the investigated films. The processability of PLLA/Mg composites is measured here by determining the processing window obtained by thermogravimetric analysis. The beginning of this

window is defined by the minimum temperature at which the material can be melted and moulded, and the upper end is defined by the temperature at which the material begins to degrade (T_o). If the difference between these two temperatures is larger, then the material can be processed by melt techniques.

From the analysis of Figure 2 it follows that the materials filled with nominal values of 30% in weight, actually show a higher Mg content measured by TGA. Material with big particles shows a content of 37% in Figure 2a and a content near 50% in Figure 2b. Material filled with small particles show a content of 35% in Figure 2a and 40% in Figure 2b. These differences are due to the heterogeneity of the samples. In Figure 2a, the material filled with small particles and a higher amount of Mg (PLLA30MgS) is the one that presents the maximum T_o shift to lower temperatures (67 °C) when comparing with PLLA T_o and so the narrowest processing window, between melting temperature and 273 °C. The material filled with big particles and a less amount of Mg (PLLA5MgB) is the one that presents the minimum T_o shift (42 °C) and the largest processing window, between melting temperature and 298 °C. These results indicate that the processing window for the composite is smaller than for the PLLA, being narrower for the composite with the smaller Mg particles due to the higher interfacial area of the PLLA/Mg composite. For a given particle size, it also follows that the higher the content of Mg, the earlier and faster decomposition of PLLA, which is correlated to the higher catalytic active sites. Given that PLLA medical devices usually are manufactured at 200–210 °C (Middleton and Tipton, 2000; Lim *et al.*, 2008;) and taking into account that the narrowest processing window of the PLLA/Mg composites here studied ends at 273 °C, there is a difference of 60 °C between the common processing temperature and the temperature where degradation begins. Therefore, the PLLA/Mg composites are suitable for processing at high temperature, within a range of temperatures that depends on both, metal content and Mg particle size.

The effect of pure Mg compared with the effect of Mg oxides or hydroxides on PLLA thermal

TABLE 1. Onset temperature of thermal decomposition (T_o), temperature of greatest rate of weight change (T_p), and final temperature of thermal decomposition (T_{end}) of PLLA/Mg films with and without thermal treatment (110 °C/12 h)

Materials	Without thermal treatment			Treated at 110 °C/12 h in air atmosphere		
	T_o (°C)	T_p (°C)	T_{end} (°C)	T_o (°C)	T_p (°C)	T_{end} (°C)
PLLA	340	358	378	312	331	348
PLLA5MgB	298	319	332	288	311	337
PLLA5MgS	289	304	317	279	297	312
PLLA30MgB	291	305	320	271	280	300
PLLA30MgS	273	290	308	263	280	303

degradation is somewhat puzzling (Fan *et al.*, 2004; Motoyama *et al.*, 2007; Chiang *et al.*, 2011), since is more favourable despite its higher chemical reactivity. Table 2 summarizes the temperature of greatest rate of weight change (T_p) during thermal degradation of different composites of PLLA with MgO or layered double hydroxides compounds. Essentially these compounds shift T_p to a lower temperature than pure Mg does, especially when considering the effect of the double layered hydroxides compounds (Chiang *et al.*, 2011). These findings imply that Mg compounds have a stronger effect as depolymerization catalysts of PLLA than pure Mg. The moderate effect of the Mg particles on the high temperature processability of PLLA/Mg composites opens a window of opportunity for designing their fabrication through conventional methods used in thermoplastic engineering. For seek of clarity, however, it should be considered that the presence of remnant solvent in the as-processed film would preclude their use for the intended medical applications as bioresorbable material. Therefore, if starting from a solving casting approach the processing design should consider the reduction of the solvent content to a minimum, likely using an intermediate temperature stage.

To study the stability of the material under drastic conditions, the films were dried before the thermogravimetric analysis using a severe heat treatment (110 °C/12 h) under air atmosphere. Figure 2b shows representative curves of weight loss *vs.* temperature and Table 1 summarizes the relevant thermogravimetric parameters. For comparative purposes Figure 3 illustrates the first derivative curves of weight loss for the un-treated and thermally treated films. As can be seen, the thermally treated PLLA/Mg composites exhibit similar thermal stability behaviour of materials without previous treatment. The smaller the particle of Mg and the higher its content, the sooner PLLA degrades, but T_o is slightly shifted to lower temperatures when comparing with the untreated materials. Nevertheless, in spite of the aggressive thermal treatment, materials stability remains acceptable; especially in the case of samples with Mg (Fig. 3, Table 1). PLLA is the most sensitive to the treatment conditions, and experiences the biggest T_o shift towards lower temperatures (28 °C). All PLLA/Mg composites show a shift of 10 °C, except for PLLA30MgB, which undergoes a T_o change of 20 °C due to its higher Mg content. This finding implies that if the processing route considers a solvent casting step, the required thermal treatment at moderated temperatures to eliminate the solvent would narrow the processing temperature window. From the analysis of Figures 2b and 3, however, we can conclude that the thermal stability of PLLA/Mg composites would be enough to stand a drying process, even under drastic condition as those used in the present study, and still have a wide processing window where materials could be moulded without carrying excessive degradation. PLLA processability is not affected even with magnesium contents higher than 30%.

3.2. Effects of pre-heat treatments on the melting behaviour of PLLA

Heat treatments at moderate temperatures are usually applied during conventional processing of PLLA to minimize the detrimental effects induced by the water traces (Ghosh *et al.*, 2007) or, as in the present case, to eliminate remnant of the solvent. To separate and study the phenomena occurring during the melting of the PLLA in the un-treated and heat treated materials, studies of modulated differential scanning calorimetry where carried out.

TABLE 2. Effect of Mg compounds on the temperature of greatest rate of weight change (T_p) during thermal degradation of PLLA

| Material	Characteristics of Mg compounds	T_p (°C)	Experimental conditions	Reference
PLLA		360		
PLLA/MgO	<100 mm, 5%	300	9 °C min^{-1}	Chiang *et al.*, 2011
	0.2 mm, 5%	290		
	0.05 mm, 5%	280		
	0.01 mm, 5%	270		
PLLA		355	10 °C min^{-1}	Fan *et al.*, 2004
PLLA/MgO	0.01 mm, 5%	280		
PLLA	–	351		
PLLA /layered double hydroxides	1% P-LDH (Mg 200 ppm, Al 270 ppm)	327	10 °C min^{-1}	Miyata and Masuko,1998
	3% P-LDH (Mg 1370 ppm, Al 1000 ppm)	312		
	5% P-LDH (Mg 5790 ppm, Al 3200 ppm)	284		
	10% P-LDH (Mg 11100 ppm, Al 5740 ppm)	280		
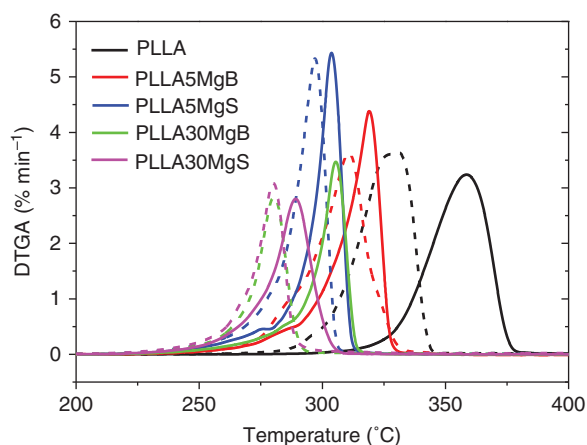
FIGURE 3. DTG curves for the decomposition of PLLA and PLLA/Mg composites. Solid lines: Materials without thermal treatment. Dashed lines: Materials treated at 110 °C during 12 hours in air atmosphere.

MDSC separates the reversing heat flow that includes the phenomena due to heat capacity and the non reversing heat flow composed by the phenomena due to kinetic events.

Figure 4a shows the MDSC curves of PLLA without thermal treatment. The conventional heat flow is composed by the reversing heat flow and the non-reversing heat flow. Three phenomena appear in the conventional heat flow: glass transition, aging and melting. The glass transition occurs at a lower temperature (50 °C) than the usual PLLA T_g (68 °C) [Material provider data], due to the presence of the remnant solvent. When a polymer is below the glass transition temperature, T_g, the subsequent recovering of physical properties towards equilibrium is termed as physical aging. The endothermic peak (enthalpy relaxation) related to aging appears during glass transition, affecting the measurement of T_g. Melting occurs at 170 °C. The conventional heat flow curve is characteristic of a material with a high crystallinity fraction.

One of the advantages of MDSC method is its ability to separate the reversible heat flow and non-reversible heat flow in the total heat flow during a phase transition. The reversing heat flow shows the glass transition without the aging effect and the melt recrystallization behaviour. T_g can be measured at 54 °C and the melt-recrystallization behaviour can be seen as two peaks within a broad melting peak. The non-reversing heat flow shows the enthalpic relaxation due to the aging, the evaporation of the solvent between 80–160 °C, and the melt-recrystallization behaviour appears, in accordance with other studies (Gracia-Fernández et al., 2012), as two exothermic peaks with an endothermic in the middle.

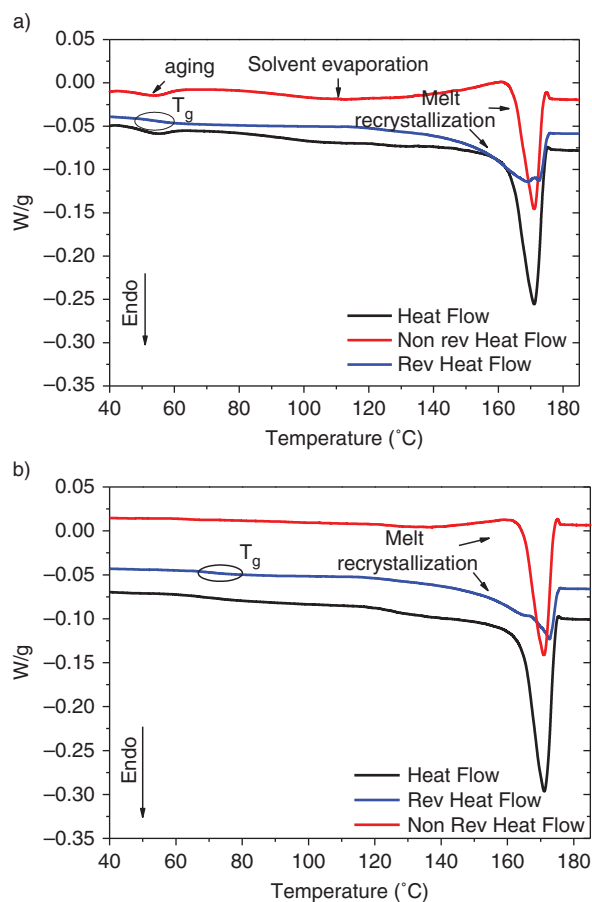Figure 4b illustrates the changes induced on the melting behaviour of PLLA after the thermal

FIGURE 4. MDSC: Conventional, reversing and non-reversing heat flow obtained with heating rate of 2 °C/min, period of 60 s, and amplitude of 0.32 °C on PLLA films a) Without thermal treatment; b) Treated at 110 °C during 12 hours in air atmosphere. T_g denotes the glass transition temperature.

treatment at 110 °C. The conventional heat flow shows T_g and the melting peak. The thermal treatment induces two relevant changes; in the distribution and size of crystals, which yields higher and narrower melting peaks, and the elimination of chloroform and aging, which shifts the glass transition at higher temperatures without the enthalpic relaxation. When the difference between the room temperature and T_g increases, more time is necessary to observe the relaxation process with the same intensity. The melting endotherm of thermal treated PLLA peaks at the same temperature of PLLA without any thermal treatment. The reversing heat flow shows the T_g and the melt-recrystallization behaviour as a peak with a shoulder. The non-reversing heat flow shows mainly the melt recrystallization phenomena in the same way as in Figure 4a, with two exothermic peaks with an endothermic in the middle (Gracia-Fernández et al., 2012).

From the MDSC study it can be stated that the melting behaviour of the PLLA and its stability, within the processing temperature window, is not

affected by the previous heat treatment despite the severe experimental conditions.

3.3. Effects of Mg in the melting and crystallization behaviour of un-treated and thermally treated PLLA/Mg composites

The effect of the particle size and content of Mg on the melting behaviour of PLLA was performed by conventional DSC on films with and without a previous thermal treatment. The study considers the analysis of three different curves corresponding to the first heating, Figure 5, the cooling from the melt, Figure 6, and the second heating, Figure 7. The relevant parameters (T_g, T_m, T_c, and f_c) obtained from the first and second heating are summarised in Table 3. It worth's to notice that whereas analysis of Figure 5 and Table 3 (F10 scans) provides information on the material, including effects induced by their processing (thermal history), Figure 7 and Table 3 (CR10F10 scans) exclusively inform about properties of the material under the thermal treatment (10 °C min^{-1}).

From the analysis of the first melting (Fig. 5a), in the samples prepared by casting without any thermal treatment, it follows that loading of PLLA with Mg particles barely affect the glass transition temperature, T_g, nor the melting temperature, T_m, irrespectively their size or volume fraction. The later is particular important since a significant decrease in the melting temperature would indicate a degradation of the PLLA.

Crystallization behaviour is critical for design purposes since it would play a critical role in determining the mechanical properties and the degradability pattern *in vivo*. It is shown that the solvent casting technique leads to materials with high crystallinity (see f_c in Table 3). The crystalline fraction of PLLA slightly increases with the reinforcement of 5% of Mg particles, but it decreases when the amount of Mg is 30 wt.%. During the crystallization of the polymer upon the evaporation of the solvent, polymer chains are aligned and fold together to form ordered regions (Mandelkern, 2002). Results show that during this process, when
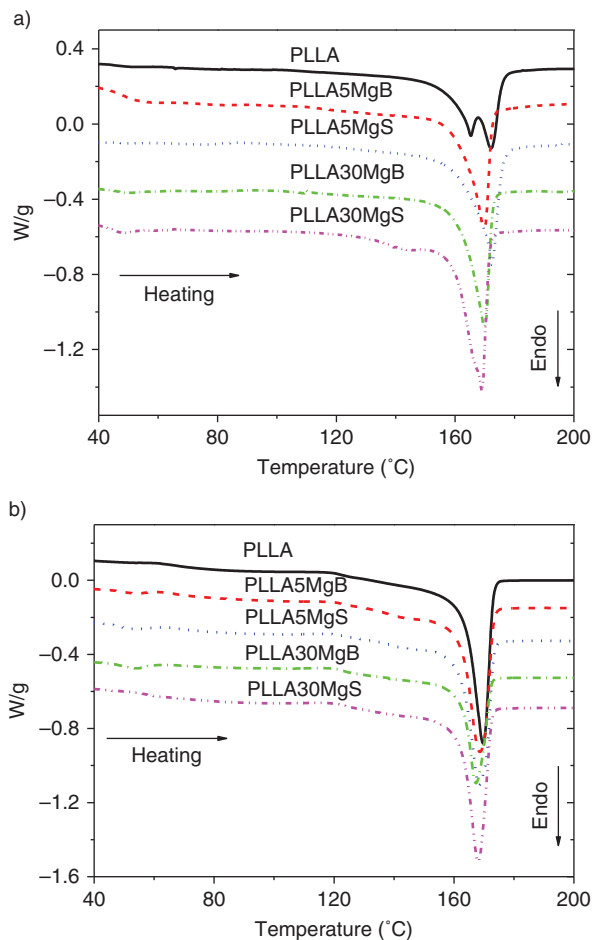
FIGURE 5. DSC curves of PLLA and PLLA/Mg films first heating (F10): a) Materials without thermal treatment; b) Materials treated at 110 °C during 12 hours in air atmosphere.
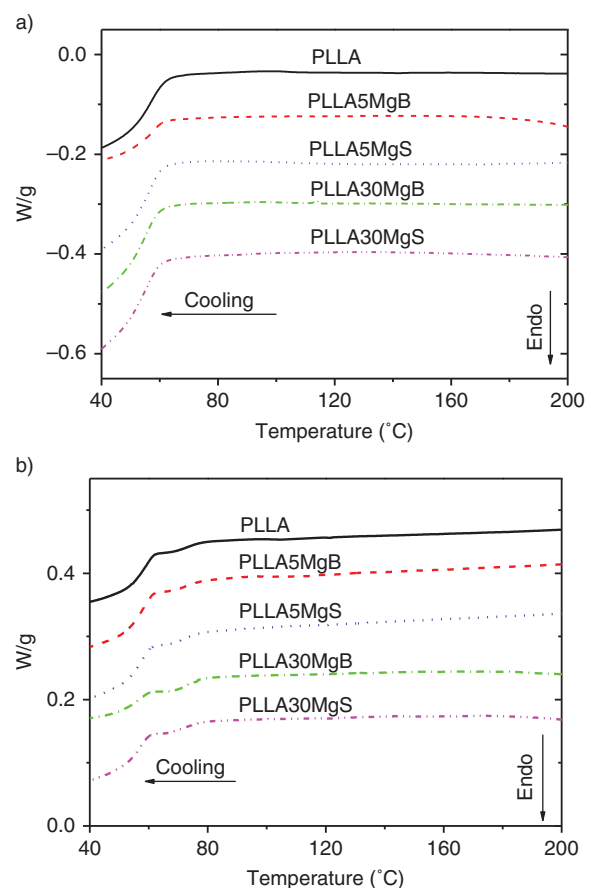
FIGURE 6. DSC curves of PLLA and PLLA/Mg films cooling from the melt (CR10): a) Materials without thermal treatment; b) Materials treated at 110 °C during 12 hours in air atmosphere.
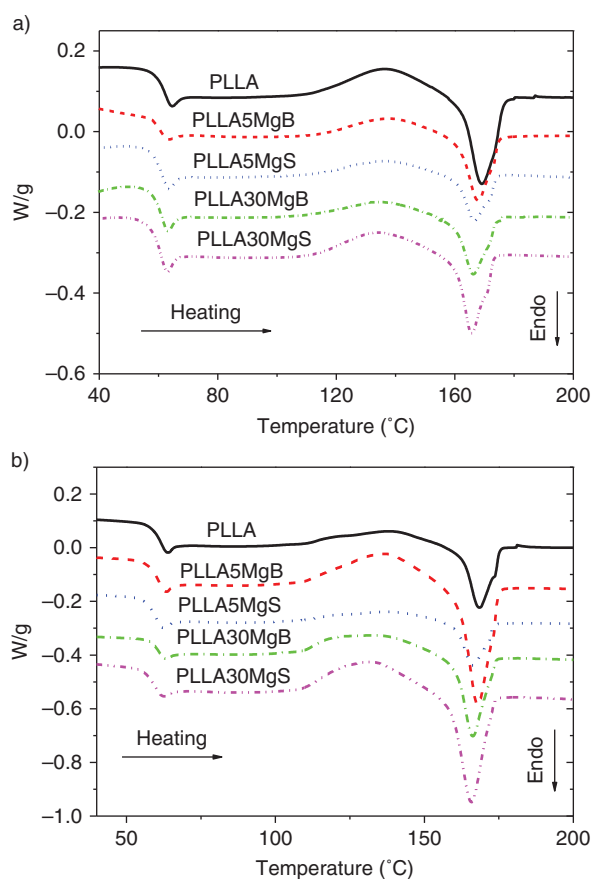
FIGURE 7. DSC curves of PLLA and PLLA/Mg films second heating (CR10F10): a) Materials without thermal treatment; b) Materials treated at 110 °C during 12 hours in air atmosphere.

the content of Mg is 5%, particles act as a nucleating agent increasing PLLA degree of crystallinity, but when the weight fraction is 30%, Mg particles act as an obstacle and impede the alignment of the molecular chains, that is the reason why the degree of crystallinity decreases.

Evidence of the composites behaviour when processing by melting is provided by analysing the PLLA capacity to crystallize during cooling from the melt (Fig. 6). Figure 6 illustrates the behaviour of PLLA and PLLA/Mg films without thermal treatment cooled from the melt (CR10), Figure 6a, and the behaviour of materials treated at 110 °C during 12 hours in air atmosphere, Figure 6b. As can be seen no significant differences between them are observed, which highlights that the drying process did not impair the matrix properties. The absence of crystallization peeks when the material is solidified at a cooling rate of 10 °C min^{-1}, indicates that Mg particles do not affect the crystallization behaviour of the polymer from the melt, yielding fully amorphous materials with crystallinity values of zero, contrary to what was observed for the solvent cast material during the first heating (Fig. 5, Table 3).

This behaviour contrasts with the important nucleation effect of different fillers in the crystallization of PLLA (Pinho *et al.*, 2009; Papageorgiou *et al.*, 2010; Dobreva *et al.*, 2010a; Dobreva *et al.*, 2010b). Heating from the amorphous condition (CR10F10 - Fig. 7) evidences a cold crystallization peak between 120 °C and 150 °C. This temperature window can be used to modulate the properties of the composite by annealing processes.

A final consideration concerns the effect of thermal treatment aimed to eliminate the remnant solvent. The associated increase of the glass transition temperature, T_g, irrespectively the Mg content, highlights the elimination of the well known plasticizing effect of the solvent. On the other hand, the crystallinity degree increases, the distribution of crystals changes and melting peaks become narrower and higher (Fig. 5b). Melting peak is characterized by the presence of fusion shoulders, due to the melting-recrystallization phenomena. The stability of PLLA during melting is not affected by the presence of Mg and degradation peaks are not detected during the first and second heating. The absence of significant changes in the other parameters highlights that PLLA/Mg composites are stable when heated within the processing temperature window, even when using severe experimental conditions.

This first approach to the preparation of composite materials with high Mg content is satisfactory by dissolution and subsequent removal of the solvent even in drastic conditions. It is confirmed that the material is stable and it is possible to process the material without degrading and without exothermic reactions involving a risk processing.

4. CONCLUSIONS

The study of the thermal stability of the composites by TGA indicates that although thermal decomposition processes of the polymer are accelerated by the presence of Mg particles, the processability of the composites is not compromised and suitable processing conditions could be acquired from this study.

The processing window depends on both, metal content and Mg particle size. The smaller the particle of Mg and the higher its content, the sooner PLLA degrades and the narrower is the processing window. PLLA/Mg composites can be processed between 165 °C and T_o °C.

The thermal stability of PLLA/Mg composites is enough to stand a severe drying process, and still have a wide processing window where materials could be moulded without carrying excessive degradation.

According to differential scanning calorimetric results, the composites are stable during heating, the presence of the metal does not alter the crystallization behaviour of the polymer from the melt, and no

TABLE 3.   Crystalline fractions (f_c) and temperatures of glass transition (T_g), melting (T_m), and cold crystallization (T_c) of PLLA/Mg films during the first heating (F10) and the second heating (CR10F10); a) Materials without thermal treatment; b) Materials treated at 110 °C during 12 hours

	a) Materials without thermal treatment				
	PLLA	**PLLAMg5B**	**PLLAMg5S**	**PLLAMg30B**	**PLLAMg30S**
F10					
T_g (°C)	46±2	47±2	36±2	40±2	41±2
T_m (°C)	172±0.5	170±0.5	172±0.5	170±0.5	169±0.5
f_c	0.48±0.04	0.56±0.04	0.52±0.04	0.47±0.04	0.46±0.04
CR10F10					
T_g (°C)	61±2	60±2	59±2	59±2	58±2
T_m (°C)	169±0.5	168±0.5	166±0.5	166±0.5	165±0.5
T_c (°C)	136±2	138±2	137±2	135±2	134±2
f_c	0±0.04	0±0.04	0±0.04	0±0.04	0±0.04
	b) Materials treated at 110 °C during 12 hours				
	PLLA	**PLLAMg5B**	**PLLAMg5S**	**PLLAMg30B**	**PLLAMg30S**
F10					
T_g (°C)	69±2	71±2	70±2	70±2	69±2
T_m (°C)	170±0.5	169±0.5	168±0.5	167±0.5	168±0.5
f_c	0.56±0.04	0.58±0.04	0.53±0.04	0.5±0.04	0.52±0.04
CR10F10					
T_g (°C)	60±2	59±2	59±2	60±2	59±2
T_m (°C)	169±0.5	168±0.5	166±0.5	166±0.5	166±0.5
T_c (°C)	138±2	137±2	137±2	133±2	132±2
f_c	0±0.04	0±0.04	0±0.04	0±0.04	0±0.04

degradation processes where detected when heating from 25 °C to 220 °C. The material is able to crystallize in the heating process; this feature means that properties optimization of the composite for the intended application would be possible by annealing treatments below the melting temperature, likely between 120 °C and 150 °C.

This work opens the possibility to process PLLA/Mg composites by thermoplastic conventional techniques such as extrusion, compression, and injection moulding.

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