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Polylactide (PLA)–$CaSO_4$ composites toughened with low molecular weight and polymeric ester-like plasticizers and related performances

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ABSTRACT

Large amounts of stable β-anhydrite II (AII), a specific type of dehydrated gypsum and a by-product of lactic acid production process, can be melt-blended with bio-sourced and biodegradable polylactide (PLA) to produce economically interesting novel composites with high tensile strength and thermal stability.

To enhance their toughness, while preserving an optimal stiffness, selected low molecular weight plasticizers (bis(2-ethylhexyl) adipate and glyceryl triacetate) and polymeric adipates with different molecular weights have been mixed with a specific PLA (L/D isomer ratio of 96/4) and 40 wt% of AII using an internal kneader. Addition of up to 10 wt% plasticizer into these highly filled compositions can trigger a fourfold increase of the impact strength with respect to the compositions without any modifier, cold crystallization properties and a significant decrease of their glass transition temperature. Moreover, these ternary compositions (PLA–AII–plasticizer) are clearly characterized by easier processing, notable thermo-mechanical performances and good filler dispersion. This study represents a new approach in formulating novel melt-processable polyester grades with improved characteristic features using PLA as biodegradable polymer matrix.

1. Introduction

Biodegradable materials and more particularly biodegradable polymers issued from renewable resources currently deserve considerable attention since, for an increasing amount of applications, biodegradability offers clear advantages for both customers and environment. In this context, polylactide (PLA) is undoubtedly one of the most promising candidates for further developments [1–4]. With a tremendous increase in production capacity over these last years, PLA finds now applications in various markets (packaging and textile industries, automotive and engineering applications, etc.), requiring the tailoring of its properties to reach end-users demands. Like for other polymers, the reinforcing of this biodegradable polyester with mineral (nano)fillers [5–9], where the dispersed phase has dimensions from nanometers to several microns or more, can be an interesting solution to reduce its global cost and to improve some specific properties such as rigidity, heat deflection temperature, processability, barrier performances, etc.

In response to the demand for extending PLA applications range while reducing its production cost, it has been recently demonstrated by some of us [8,9] that commercially available PLA can be effectively melt-blended with previously thermally treated gypsum (at 500 °C, so called anhydrite II form – AII), a by-product directly issued from the lactic acid (LA) fabrication process [10,11]. These two products from the same source as origin can lead by melt-mixing to PLA composites characterized by remarkable tensile strength performances without any filler surface treatment.

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Unfortunately, at filler amount higher than 20% (by weight), the filled composites are characterized by low impact strength/toughness properties that become even poorer with increasing $CaSO_4$ (AII form) content. Accordingly, for some potential applications such as the extrusion of films or fabrication of rigid containers – blown, thermoformed and injection molded, these composites do not have the toughness/impact resistance or the ductility required by processing (e.g., to avoid the susceptibility to breaking down during extrusion) and they need to be modified in order to fulfill the industry requirements. Like for other filled polymers (PA, PET, PBT, etc.), addition of a third component into PLA–AII composites, i.e., an impact modifier, a plasticizer, etc., can represent an alternative that can be developed to obtain the required toughness/impact strength [12,13].

Plasticizers are frequently used not only to increase the flexibility and ductility of glassy polymers, but also to improve the processability or dispersion in filled systems. In this context, the ideal plasticizer for PLA can be any biodegradable product sufficiently non-volatile that has a relatively low molecular weight to produce a substantial reduction of glass transition temperature (T_g) and adequate mechanical properties, i.e., a decrease of Young's modulus values, an increase in ductility and impact strength [14,15]. It is well-known that for instance the monomer, lactide itself, is considered as one of the best plasticizers for PLA [16,17], but its drawback is that it migrates very rapidly to the polymer materials surface, which is observed when PLA with high content of lactide is processed. To find out other alternatives, different commercial or synthesized plasticizer systems have been studied: partial fatty acid esters, glycerol esters, citrates, citrate oligoesters, dicarboxylic esters [17–24], higher molecular weight plasticizers like poly(ethylene glycol) [18,25–27], poly(propylene glycol) [28] and more recently polymeric adipates [29]. With large utilization in flexible PVC applications, polyester plasticizers such as polymeric adipates have been also considered for PLA plasticization [29] due to their resistance to volatility, diffusion, extraction, and/or weathering. Their featured values can thus compete with the low molecular weight plasticizers.

In relation to the processing properties, it is worth noting that addition of plasticizer into highly filled PLA can perform other functions, such as, assisting in viscosity control and lubrication of the compound or improving filler dispersion. More particularly, plasticizers can reduce the melt viscosity of filled PLA composites, which aides in processing and extruding the polymer at lower temperatures, and can improve flexibility and reduce cracking tendencies of the finished products.

The aim of this paper is to present new strategic pathways to prepare PLA composites highly filled with calcium sulfate issued from LA production process to permit their utilization in packaging/technical applications. Addition of a third component in PLA–AII compositions, i.e., a plasticizer, has been considered as a potential method that can be developed in the main goal of preparation of highly filled composites characterized by adequate filler dispersion, improved impact strength and toughness. Among the different commercially available products shown to work well to improve PLA toughness/impact properties, low molecular weight esters, i.e., bis(2-ethylhexyl) adipate, glyceryl triacetate, as well as polymeric adipates (Glyplast), have been added as third component into highly filled PLA–AII compositions *via* melt-compounding technology and the elaborated composites were fully characterized to evidence the key-properties obtained by plasticizer addition.

2. Experimental

2.1. Materials

Poly(L,L-lactide), commercial name "Galastic", was kindly supplied by Galactic S.A. This grade is typically designed for extrusion and thermoforming applications due to a high molecular weight and a reduced fluidity in the molten state. Characteristics of PLA are as follows: number average molecular weight, $M_{n(PLA)} = 74{,}500$, index of polydispersity, $M_w/M_n = 2.0$, L/D isomer ratio of 96/4, MFI (190 °C, 2.16 kg)=6.6 g/10 min. Calcium sulfate hemihydrate ($CaSO_4.0.5H_2O$), a by-product issued from LA fabrication process with mean particle diameter of 9 μm was provided by Galactic S.A.

As low molecular weight ester-like plasticizers, glyceryl triacetate – GTA, known as "Triacetin" (Acros Organics) and bis(2-ethylhexyl) adipate, known as "dioctyl adipate" – DOA (Acros Organics) were used.

As polymeric plasticizers, two polymeric adipates were kindly supplied by Condensia Quimica S.A. (Spain): Glyplast 206/3NL – it will be noted Glyp3 and Glyplast 206/7 – Glyp7.

Table 1 shows comparative characteristics of the low molecular weight and polymeric plasticizers used in this study, together with PLA characteristics.

2.2. Melt-blending procedure and preparation of samples for characterization

Starting from β-calcium sulfate hemihydrate, β-anhydrite II (AII) was obtained by dehydration in a Nabertherm 3 L furnace at 500 °C for 1 h. AII (density = 2.72 g/cm^3) was chosen for this study because of its low sensitivity to atmospheric water absorption with respect to other calcium sulfate anhydrite forms [8,9].

Before processing by melt-blending, PLA was dried at 80 °C for 48 h under vacuum. Various plasticizers (10 wt%), previously dried at 80 °C for 1 h under vacuum, were mixed together with PLA pellets and AII at 190 °C

Table 1
Selected characteristics of PLA and plasticizers [15,29]

Product	Molecular weight (g mol^{-1})	Density (g/cm^3)	Viscosity, cP (at 25 °C)	Solubility parameter, δ (MPa$^{0.5}$)
PLA	74,500	1.25	–	20.1
DOA	370.6	0.93	13	17.6
GTA	218.2	1.16	18	20.1
Glyp3	2000	1.07	900	20.6
Glyp7	3400	1.10	4000	23.0

(moderate mixing with cam blades) by using a Brabender bench scale kneader (3 min premixing at 30 rpm – speed that allows preventing an excessive increase in torque and the protection of the device during melting of PLA, followed by 3 min mixing at 60 rpm). PLA and binary (PLA–AII) compositions have been performed in similar conditions and used as reference. Plates (3 mm thickness) were then shaped by compression molding at 190 °C by using an Agila PE20 hydraulic press. The material was first pressed at low pressure for 240 s (three degassing cycles), followed by a high-pressure cycle at 150 bars for 150 s. The samples were then cooled under pressure (50 bars). Specimens for tensile and Izod impact testing were made from plates by using a milling-machine in accordance with ASTM D 638-02a norm (specimens type V) and ASTM D 256-A norm (specimens 60 × 10 × 3 mm), respectively.

2.3. Characterization

2.3.1. Size exclusion chromatography (SEC)

Isolation of PLA from the prepared compositions for molecular weight parameters determination was carried out by first dissolving the samples in chloroform and filtering off AII particles. Then, the catalyst residues were removed by liquid–liquid extraction with a 0.1 N HCl aqueous solution and PLA was recovered by precipitation in an excess of heptane. After filtration and drying, PLA solutions were prepared in THF (10 mg polymer/5 ml solvent). Molecular weight parameters (number average molar mass, M_n and polydispersity index, M_w/M_n) of neat PLA and PLA extracted from the processed compositions were determined by size exclusion chromatography (SEC) using the procedure described elsewhere [8].

2.3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed by using a DSC Q200 from TA Instruments under nitrogen flow. The samples obtained by compression molding were investigated. The following procedure has been used: first heating scan at 10 °C/min from room temperature up to 220 °C, then scan at 10 °C/min down to -10 °C and finally, second heating scan from -10 to 220 °C at 10 °C/min. The first scan was meant to erase the thermal history of the samples. The difference between the maximum temperature of heating (220 °C) and the melting temperature of mostly amorphous PLA was chosen enough high, i.e., above 70 °C, to get rid any anterior thermal history after the first heating scan. In order to limit PLA thermal degradation upon measurement, no extra plateau was maintained at 220 °C. The events of interest, i.e., the glass transition temperature (T_g), cold crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from both DSC heating scans. The degree of crystallinity was calculated by considering a melting enthalpy of 93 J g^{-1} for 100% crystalline PLA [30].

2.3.3. Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) were performed by using a TGA Q50 (TA Instruments) with a heating ramp of 20 °C/min under air flow, from room temperature up to 600 °C (platinum pans, 60 cm^3/min air flow rate).

2.3.4. Mechanical testing measurements

Tensile testing measurements were performed by using a Lloyd LR 10K tensile bench in accordance to the ASTM D 638-02a norm at a speed rate of 10 mm/min. Notched impact strength (Izod) measurements were performed by using a Ray-Ran 2500 pendulum impact tester and a Ray-Ran 1900 notching apparatus, in accordance to the ASTM D 256 norm (Method A, 3.46 m/s impact speed, 0.668 kg hammer). All mechanical tests were carried out by using specimens previously conditioned for at least 48 h at 20 ± 1 °C under a relative humidity of 45 ± 5% and the values were averaged over five measurements.

2.3.5. Scanning electron microscopy (SEM)

A Jeol 5500 LV scanning electron microscope (SEM) was used to observe the cryo-fractured surfaces of the composites. Additional SEM analyses of the fractured surfaces were performed using a scanning electronic microscope Philips XL equipped for backscattered electron (BSE) imaging, at an accelerated voltage up to 20 kV and various magnifications.

3. Results and discussion

3.1. Preliminary considerations

The selection of a plasticizer to be used in a specific PLA composition requires the consideration of many criteria [15]: compatibility, low volatility, resistance to migration and extraction during service life, lack of toxicity, etc. Another important key criterion is the plasticizer efficiency that is determined by finding how much plasticizer must be added in the polyester matrix to give a required level of mechanical or physical response. One can assume that this efficiency is mostly related to the chemical structure of the plasticizer molecule and to its compatibility with the polymer matrix. From a molecular perspective, the plasticizer must be miscible with the polymer and characterized by similar intermolecular forces. It has been generally accepted that the most effective plasticizer closely resembles to the polymer and it is characterized by solubility parameters close to those of the polymer [31]. In this context, from the values of the solubility parameters (Table 1) it could be predicted that GTA and Glyp3 could lead to more important plasticizing effects in PLA when compared to DOA or Glyp7. On one hand, it is considered that components with close solubility parameters in relation to the polymer matrix will lead to miscible blends. On the other hand, the compatibility of a plasticizer depends on both components (polymer and plasticizer) and for such a system it can be described in terms of polymer–liquid miscibility by using the thermodynamic properties of polymer–liquid systems [31]. It is reasonable to precise that these theoretical predictions are relative because the solubility parameter may only be representative for a given polymer since variations in compositions, crystallinity, polarity, etc. can lead to changes in the values of the interaction parameters. However, there is not enough information about the molecular nature of polymer–plasticizer interactions to explain why certain plasticizers are superior to others.

The efficiency of low molecular weight esters (GTA, DOA) and polymeric adipates (Glyp3 and Glyp7) has already been considered in different PLA matrices containing high amount of plasticizer, i.e., 15–20 wt% [15,29]. Often, at high percentage of plasticizer, the PLA compositions are characterized by low tensile strength properties with respect to the neat PLA, evolution of the tensile strength that can be also expected by their addition in PLA–AII compositions. In this context, in order to preserve the performances of the highly filled PLA–AII compositions (40 wt% filler), the percentage of plasticizer was limited to 10 wt% in this study.

Another consideration to be aware of is that these compositions can be potentially interesting for processing by extrusion where an important residence time at high temperature is required, and in such context, addition of high amount of plasticizer characterized by high volatility can lead to an important decrease of the thermal stability and low performances of the end-use products. In other words, it is believed that the choice of the most adequate processing conditions (residence time, temperature, etc.) and of thermally stable PLA compositions could lead to improved end-use characteristics. In relation to the thermal stability, the utilization of less volatile polymeric adipates can be a solution (the stability of Glyp3 is slightly lower than those of Glyp7). Indeed, the TGA traces of plasticizer shown in Fig. 1 revealed that the thermal stability (under air) of the low molecular weight (and therefore volatile) plasticizers selected for this study (GTA and DOA) is lower than those of the polymeric adipates. Another point is that the polymeric plasticizers can extend considerably the life of polyester (PLA) end-products compared to low molecular weight plasticizers since they also exhibit low migration and extraction (the comparative aging studies will be the object of a future contribution).

Finally, it is important to point out that the rheological parameters recorded during melt-mixing confirm the assumption that addition of plasticizer into PLA–AII compositions can facilitate the melt-compounding/processing by important reduction of the torque values with respect to the compositions without plasticizer.

3.2. Modification of PLA molecular characteristics by plasticizer/filler addition

PLA, as most of polyesters, is sensitive to its environment during processing (especially water, shear and temperature). Indeed, in many cases, the mixing of PLA with additives and/or plasticizers is followed by an important decrease of the molecular weights, with negative impact on the thermo-mechanical properties of the polymer matrix. On one hand, minimizing moisture content by intensively drying all components represents a first step to reduce the losses by hydrolysis and to preserve the polyester molecular weights as high as possible. On the other hand, the degradation of PLA during processing in the presence of plasticizers with ester groups can be also due to potential transesterification reactions leading to an overall decrease of PLA molecular weights.

Table 2 shows the effect of plasticizer and/or filler addition on PLA molecular weight parameters after melt-blending under moderate mixing conditions as determined by SEC. As a remark, the neat PLA is a thermally stable high molecular weight polymer for which the processing conditions only slightly affect the number average molar mass. The number average molecular weight (M_n) decreases from 74,500 to 64,000 in the worst case (entry 2). From Table 2, it comes out that as it was already reported [8], addition of AII into PLA does not detrimentally affect molar mass and molar masses distribution, at least within experimental errors which can be estimated to 15% taking into account size exclusion chromatography accuracy but also PLA

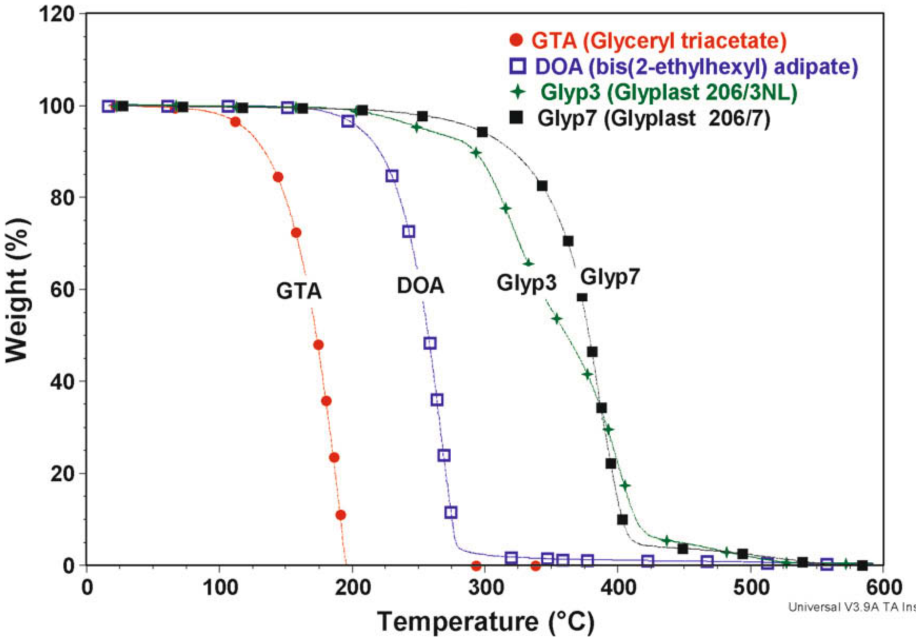

Fig. 1. TGA under air flow of GTA, DOA, Glyp3 and Glyp7 (ramp of 20 °C/min).

Table 2
Evolution of PLA molecular weights and polydispersity indices upon melt-blending

Entry	Sample composition (%, by weight)	Polydispersity index	$M_{n\ (PLA)}$ (g mol^{-1})
1	PLA (granules)	2.1	74,500
2	PLA-processed	2.2	64,000
3	PLA–40% AII	2.2	63,000
4	PLA–40% AII–10% DOA	2.2	69,000
5	PLA–40% AII–10% GTA	2.1	63,000
6	PLA–40% AII–10% Glyp3	2.5	53,000
7	PLA–40% AII–10% Glyp7	1.8	60,000

extraction and purification steps (see Section 2). On the other hand, only addition of Glyp3 into PLA (entry 6) seems to lead to a slightly more pronounced decrease in M_n and increase in M_w/M_n, attesting for some undesirable reactions between the aliphatic polyester chains and this plasticizer. Clearly, many assumptions can be proposed to take into account such an observation, including reactions between the reactive groups of Glyp3 and PLA ester functions or terminal end groups, acidity, presence of catalysts or some impurities, etc.

The molecular characterization allows concluding that, under adequate processing conditions, melt-blending of highly filled PLA–AII compositions with DOA, GTA or Glyp does not induce any dramatic drop of PLA molar masses by thermal degradation or hydrolysis of the polyester chains, while the polydispersity index is poorly affected by the nature of the plasticizer.

3.3. Thermal characterizations: ternary compared to binary compositions

Plasticizer effect has been evaluated by studying the changes of T_g, T_m and crystallization ability of the performed composites.

From the first DSC scanning cycle, recorded on the samples used for mechanical testing, it comes out that unfilled PLA and PLA-40 wt% AII specimens are characterized by low crystallinity (4% and 6%, respectively), whereas the plasticizer addition leads to increased values, i.e., between 10% and 15%. In addition, the thermal characteristics acquired from the second heating scan, i.e., for the specimens with defined cooling history conferred by DSC technique, confirm once again the poor ability of neat PLA matrix (4% content of D isomer) and PLA–AII composite to crystallize, both materials revealing only a tiny melting endotherm at 153 °C of 0.1 and 0.4 J g^{-1}, respectively (Table 3). On the contrary, the ternary compositions obtained by addition of plasticizer are in all cases characterized by an important crystallization exotherm upon heating (cold crystallization) with enthalpy of cold crystallization (ΔH_c) varying from 7.7 to 24.3 J g^{-1} (Table 3). More specifically this phenomenon appears to be more important when DOA or Glyp are used. This means that the additives, particularly plasticizers, enhance the ability of the PLA matrix to crystallize, behavior clearly affected by the nature of the plasticizer. It is important to precise that the percent of crystallinity can be directly related to many of the key-properties exhibited by PLA (brittleness, toughness, stiffness or modulus, thermal stability, barrier resistance, etc.) and this parameter is critical in many applications such as injection molded components, plates, monofilaments, etc.

All these ternary blends are characterized by T_g values between 39 and 45 °C, significantly decreased by comparison to the neat PLA matrix (T_g = 62 °C). The lowest decrease in T_g (by only 17 °C) is observed for the ternary composite containing 10 wt% DOA. This is due to the limited miscibility of DOA in PLA: it has been effectively shown in a previous paper [15] that, above 5 wt%, DOA undergoes segregation in the PLA matrix. Such phenomenon likely occurs in the AII-filled PLA, as clearly observed by SEM analysis in Section 3.4.

From TGA measurements, we have already established [8,9] that PLA–AII composites are characterized by similar (or even better) thermal stability under air with respect to the neat polymer. This is a key-property in the perspective of the practical application of such materials.

Furthermore, to allow the observation of possible interactions between the components of PLA–AII blends and the consequences on the thermal stability of the polyester matrix, the curves of weight difference (obtained by subtracting the theoretical from experimental TG results) have been calculated and interpreted as described elsewhere [32]. It is worth pointing out that positive or negative values of the weight difference are associated, respectively, to stabilization or destabilization effects from the point of view of thermal stability.

Fig. 2A shows the TGA curves of neat PLA, AII and PLA-40 wt% AII (experimental and theoretical). The AII filler is stable in the temperature range of interest and it seems that the thermal mechanism of PLA decomposition is not significantly modified in its presence. Moreover, from the curve of weight difference plotted for PLA-40 wt% AII

Table 3
Comparative DSC data of different PLA compositions with/without plasticizers (second heating from −10 to 220 °C with a ramp of 10 °C/min)

Sample (%, by weight)	T_g (°C)	T_c (°C)	ΔH_c (J g^{-1})	Crystallinity from cold crystallization* (%)	T_m (°C)	ΔH_m** (J g^{-1})
PLA reference	62	–	–	–	–	–
PLA processed	62	–	–	–	153	0.1
PLA–40% AII	62	–	–	–	153	0.4
PLA–40% AII–10% DOA	45	104	24.3	14.8	148	29.1
PLA–40% AII–10% GTA	39	113	7.7	8.3	144	9.5
PLA–40% AII–10% Glyp3	40	120	17.5	18.8	149	21.3
PLA–40% AII–10% Glyp7	41	116	22.4	24.1	149	27.1

* Increase due to cold crystallization.

** Initial crystallinity of ternary compositions before second DSC heating was less than 5.2% as calculated by substracting ΔH_c from ΔH_m.

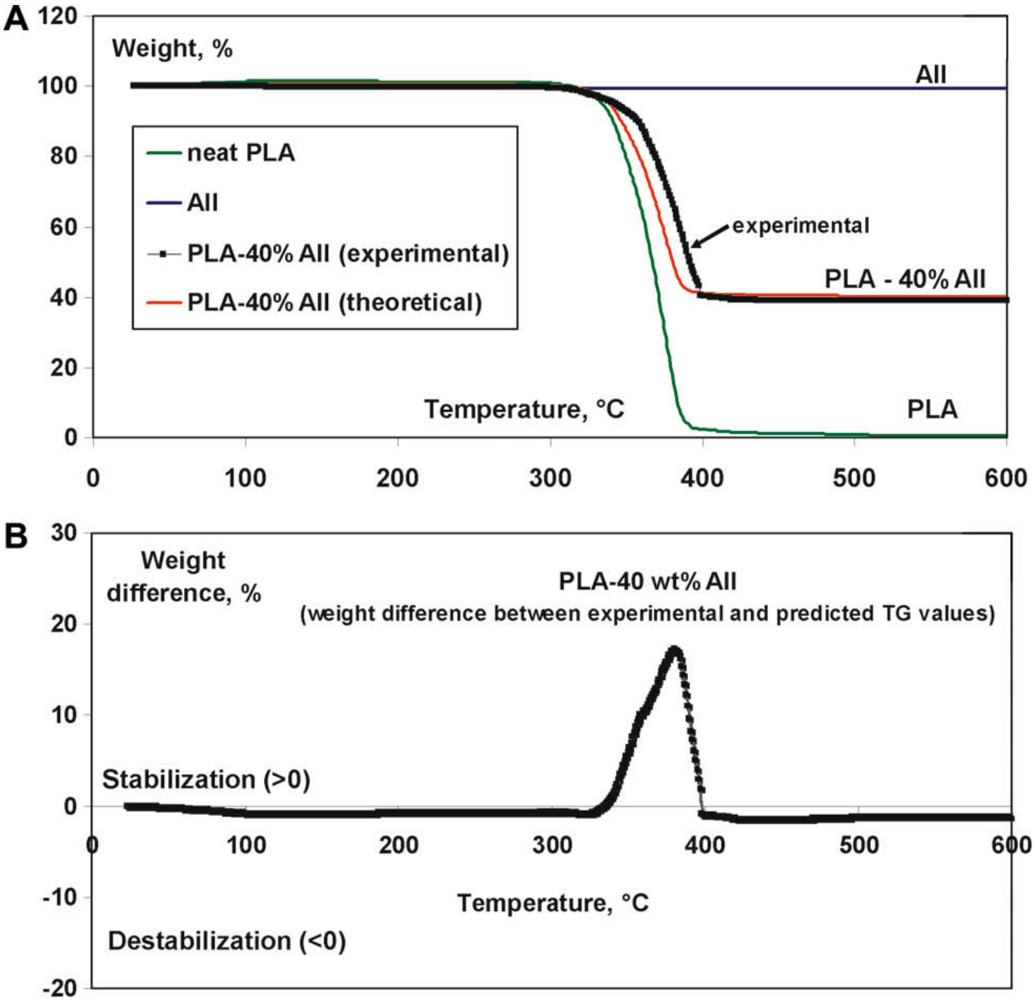

Fig. 2. Evaluation of the stabilization effect by filler addition for PLA–AII composites: (A) TGA traces under air flow (20 °C/min) of neat PLA, AII and PLA-40 wt% AII composites (experimental and theoretical traces); (B) temperature dependence of weight differences between the experimental and predicted TG values for composite.

composites (Fig. 2B), it comes out that addition of AII clearly leads to a delay in the degradation of PLA matrix and to a significant stabilization effect, which can be quite well distinguished in the interval of temperature 340–400 °C. An increase of the maximum decomposition temperature was observed by dispersing AII in PLA [8,9]. Actually and as will be reported in a forthcoming paper, the morphology of the considered microfiller has a crucial importance. Fillers characterized by platelet-like primary particles, e.g., AII particles, are much more favorable for improving the polyester thermal stability when compared to fillers of same chemical composition characterized by more isotropic geometry (e.g., spherical primary particles).

Concerning the ternary compositions (Fig. 3), due to the volatility of the low molecular weight plasticizers, a deterioration of the thermal properties of plasticized formulations compared to the compositions without plasticizer is not surprising. Because GTA and DOA are characterized by a relatively higher volatility when compared to Glyp, a higher decrease in the thermal stability of the compositions performed using these low molecular weight plasticizers can be expected. Actually, this assumption is confirmed for these materials by a lower value of the temperature at which 5 wt% weight loss takes place (Table 4). Particularly, the highest decrease of this parameter for the PLA–AII–DOA composition is observed. This behavior might reasonably be ascribed to the presence of segregated domains of DOA in PLA matrix due to limited miscibility and related higher diffusivity of this plasticizer out of the material. Surprisingly, the maximum degradation temperature (from DTGA) is higher for the ternary composites containing DOA or GTA (404 or 425 °C, respectively) than for the composites plasticized with Glyp7 or Glyp3 (376 or 391 °C, respectively). The former effect can be explained by a better dispersion of AII filler within PLA matrix plasticized with the plasticizer of lower viscosity (DOA, GTA and even Glyp3). This is actually confirmed via SEM observation (Section 3.4.).

It is relevant to point out that the PLA–AII–Glyp compositions do not exhibit any significant loss under 300 °C (Fig. 3), result that allows their processing at higher temperature. From the point of view of the thermal stability and considering the usual extrusion temperatures of PLA, the composites plasticized with Glyp3 and Glyp7 seem to present better properties than those of the composites plasticized with low molecular weight GTA, and in this

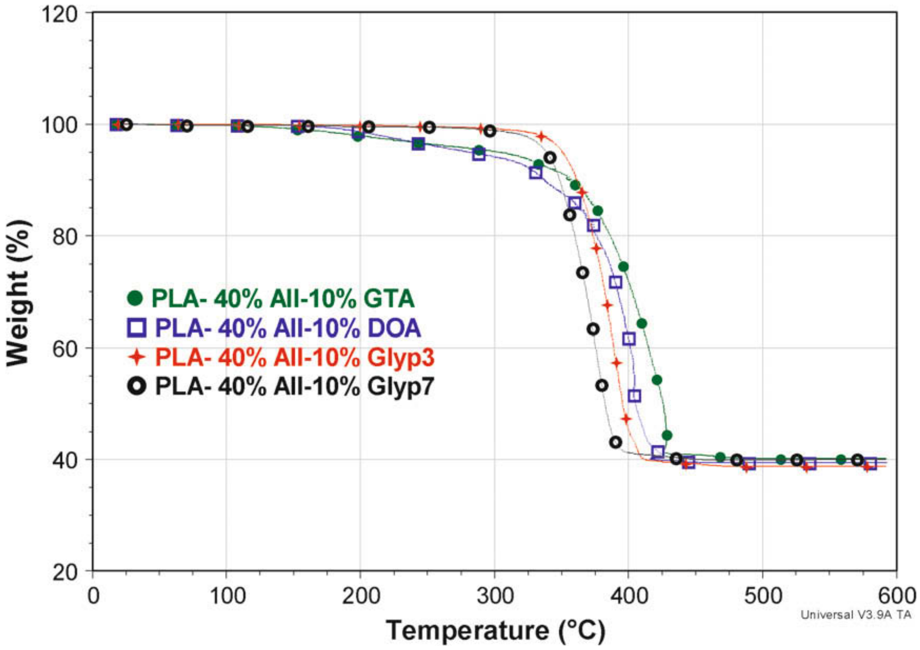

Fig. 3. TGA of ternary compositions (PLA-40 wt% AII-10 wt% plasticizer): low molecular weight *vs.* polymeric plasticizers (under air flow, ramp 20 °C/min).

Table 4
Thermal properties of different PLA compositions from TGA measurements

Compositions (%, by weight)	Temperature for 5% weight loss (°C)	Temperature of the maximum rate of degradation (°C) (from D-TGA)
PLA–40% AII	340	385
PLA–40% AII–10% GTA	303	425
PLA–40% AII–10% DOA	281	404
PLA–40% AII–10% Glyp3	351	391
PLA–40% AII–10% Glyp7	339	376

context, they are more indicated for applications that are requiring improved resistance at higher temperature and/or residence time in processing conditions.

3.4. SEM of the fractured surfaces of PLA composites

With the aim of assessing the extent of filler dispersion within the (plasticized) polyester matrix, SEM images recorded over cryofractured surfaces have been performed using scattered electrons (SE) or back scattered electrons (BSE) to get a higher phase contrast. At low magnification, well dispersed AII particles with various geometries and quite broad size distribution are evidenced at the surface of all cryofractured composites. For example, Fig. 4 shows representative SEM images in BSE mode of PLA-40 wt% AII composite without plasticizer (A) compared to plasticized compositions (B) with polymeric adipates, i.e., Glyp3. From these SEM pictures, it is rather difficult to compare the dispersion state of AII, which seems anyway quite correct, knowing the large weight fraction of filler (40 wt%) and the absence of any previous surface treatment of $CaSO_4$ particles to make them more compatible with the PLA matrix.

Figs. 5A–D display SEM–SE images of PLA–AII–plasticizer composites at high magnification (3000×). From SEM pictures of fractured PLA samples, the micrometric AII filler particles – even with a dimension of 1–2 μm or less, seem to be quite well dispersed. The great majority of AII particles are featured by irregular shape. The

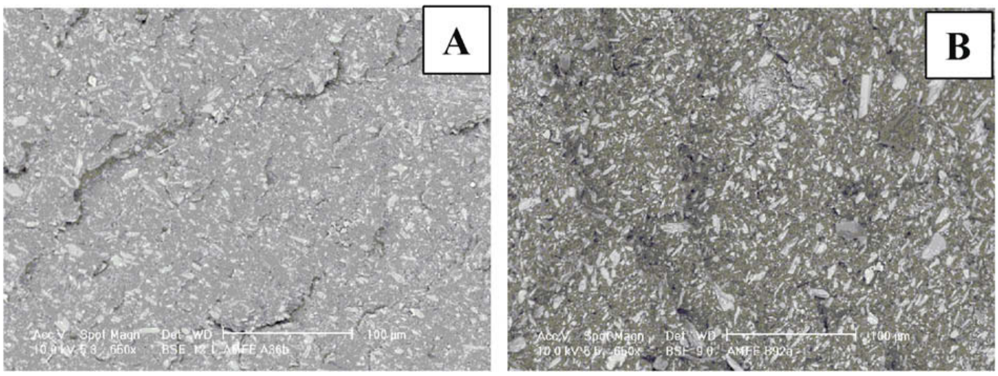

Fig. 4. SEM pictures at low magnification (650×, BSE mode) of the fractured surface of PLA-40 wt% AII (A) and PLA-40 wt% AII-10 wt% Glyp3 compositions (B).

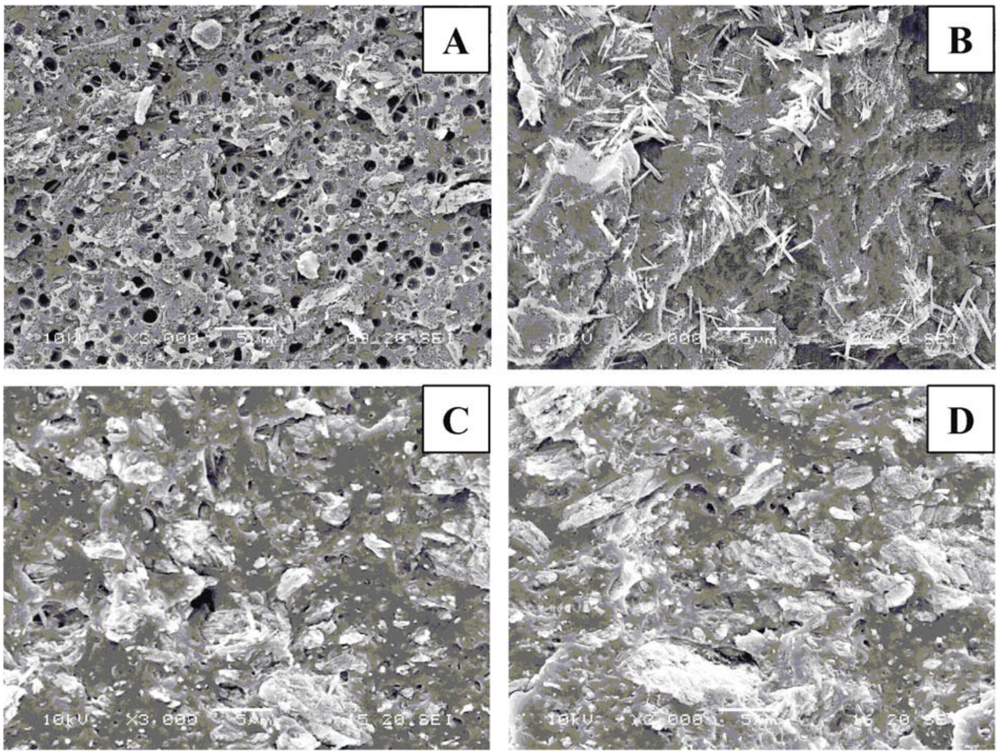

Fig. 5. SEM pictures at high magnification (SE mode) of the fractured surfaces of PLA-40 wt% AII-10 wt% plasticizer (A, DOA; B, GTA; C, Glyp3; D, Glyp 7).

compositions with polymeric adipates contain larger aggregates than in the blends performed using low molecular weight plasticizers – in which case, particles with lower dimension are generally observed. Interestingly enough, the presence of elongated rods assumed to be individual lamellar particles of AII (Fig. 5A and B) – approx. 2–5 μm long, are better evidenced in the SEM images of the compositions with low molecular weight plasticizers. This observation seems to indicate that the low molecular weight plasticizers tend to further improve the dispersion state of AII in the related composition, when compared with the polymeric plasticizers.

From the SEM pictures of the cryofractured surfaces of the ternary blend (PLA–AII–DOA) phase separation of plasticizer from the matrix is clearly stressed out (Fig. 5A). It is evidenced by the presence of regular small spherical voids (initially droplets of DOA which have been expulsed during sample preparation) with diameter of 1–2 μm or less throughout the whole composite. Thus, it can be assumed that for PLA–DOA blends the PLA matrix became saturated with this plasticizer at a certain concentration (about of 5 wt% [15]) and above it, a phase separation occurred. Another point is that the presence of immiscible or partially miscible phase into PLA–AII composites can negatively affect their mechanical properties.

The SEM analyses of the phase structure of the composites will be useful for the interpretation of the mechanical properties discussed in the following section.

3.5. Mechanical properties of the ternary compositions (PLA–AII–plasticizer)

The toughness of a polymer blend/composite is generally assessed via two methods, tensile and impact testing. Sometimes, a material that shows a significant improvement in impact strength may show only minor improvements in elongation at break. Therefore, as reported in a recent review article [13], the toughening approach for a particular application should be selected based on the expected stress state and how that relates to the impact testing and tensile testing methods. In terms of mechanical properties, the highly filled PLA–AII composites are typically characterized at room temperature by low impact values (Fig. 6), low ultimate elongation associated with high tensile strength and Young's modulus values (Table 5). More precisely, concerning the tensile properties, the neat PLA matrix presents a maximum tensile strength of 66 MPa, whereas the highly filled composition (PLA-40 wt% AII) is characterized by an attractive tensile strength of 57 MPa and high rigidity (Young's modulus of 1600 MPa).

The results shown in Table 5 indicate that addition of plasticizer (10 wt%) into PLA–AII compositions leads to a decrease of both tensile strength and Young's modulus. Because the plasticizer behaves like a solvent when mixed with a polymer, the macromolecular chains cohesion is decreased and tensile strength properties are thus reduced. It is interesting to stress that the maximum tensile strength values of PLA–AII compositions containing 10 wt% plasticizer are obtained using polymeric plasticizers (31 MPa) instead of low molecular weight plasticizers such as GTA or DOA. On the other hand, it is worth noting that the tensile strength of composites containing GTA (26 MPa) is attractive enough for applications where good tensile strength is required. Another point is that the more important decrease of tensile strength recorded using DOA is not surprisingly due to its limited miscibility with PLA and to presence of DOA inclusions that should weaken this com-

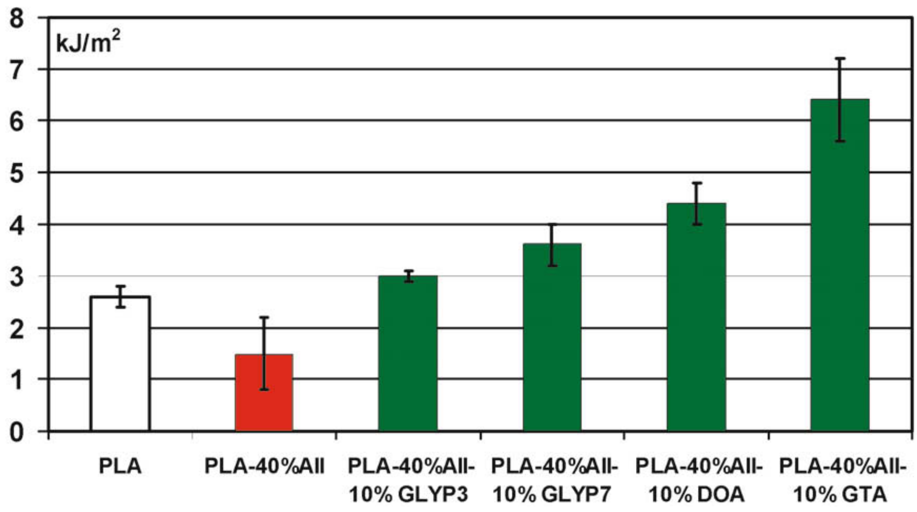

Fig. 6. Notched impact strength-Izod measurements of different PLA compositions with/without plasticizer (%, by weight).

Table 5
Tensile properties of different PLA compositions (standard deviations are given in brackets)

Compositions (%, by weight)	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Young's modulus (MPa)	Nominal strain at break (%)*
PLA	66 (2)	65 (3)	1000 (100)	11 (3)
PLA–40% AII	–	57 (3)	1600 (150)	6 (1)
PLA–40% AII–10% DOA	18 (1)	15 (1)	1150 (300)	8 (3)
PLA–40% AII–10% GTA	26 (1)	14 (1)	700 (50)	75 (34)
PLA–40% AII–10% Glyp3	31 (2)	27 (2)	960 (60)	6 (1)
PLA–40% AII–10% Glyp7	31 (1)	27 (3)	950 (60)	7 (1)

* Gauge length of 25.4 mm.

position. As a consequence, above a certain content in DOA (about 5 wt%), one can assume that saturation in the partially miscible plasticizer is reached in the polyester matrix, which may explain the decrease of tensile strength properties. It is also important to point out that the highest ultimate elongation for an amount of 10 wt% plasticizer is obtained for the plasticizer with the best solubility parameter in relation to PLA (GTA), and in this context, these composites are potentially interesting for applications requiring high ductility. Moreover, the stress-strain diagrams indicates that only GTA leads to a large increase of the nominal strain at break (mean value of 75%), whereas using the other plasticizers, the great majority of specimens are characterized only by minor modifications of the strain at break with respect to the non plasticized PLA–AII composition.

Concerning the decrease of rigidity, the PLA–AII blends modified with 10 wt% DOA are characterized by a slightly higher Young's modulus when compared to the compositions with Glyp or GTA (Table 5). This confirms that PLA can incorporate only a given amount of DOA as plasticizer. The highest decrease of Young's modulus is obtained for the plasticizer presenting the lowest molecular weight (GTA).

In relation to the impact strength, the incorporation of high amount of mineral fillers usually triggers a significant decrease in performances for the polymer materials. At higher loading of AII (e.g., at 40 wt%), the dispersion of the particles is critical in these composites and it may become difficult to avoid aggregates. In such a case, sharp decrease in impact strength was reported [8] (Fig. 6). This behavior is generally considered to be due to the poor interfacial adhesion between the filler (and its aggregates) and the polymer matrix leading to crack debonding. Therefore, as the filler content increases, impact strength tends to reduce gradually due to presence of more heterogeneous (mechanically weak) regions, e.g., remaining filler aggregates poorly dispersed within the matrix.

The addition of plasticizer into PLA–AII rubbed off the negative behavior of the composite and excellent impact strength performances are obtained even for highly filled compositions. More specifically, the impact strength values obtained using polymeric adipates – Glyp3 or Glyp7, i.e., 3.0 and 3.6 kJ/m^2, respectively, represent an attractive increase of the impact performances. Moreover, addition of low molecular weight plasticizers into PLA–AII compositions, i.e., DOA and GTA, leads to a spectacular increase of impact strength (values of 4.4 and 6.4 kJ/m^2, respectively).

To summarize the mechanical properties results, it appears that the addition of GTA and Glyp to PLA–AII composites leads to the most attractive compromise of both impact and tensile strength properties and these ternary compositions seem to be the most adaptive for packaging/technical applications where toughness is a critical requirement.

4. Conclusions

In response to the demand for enlarging PLA applications range while reducing its production cost, we have emphasized in this study that commercially available PLA can be effectively melt-blended with selected plasticizers and previously dehydrated gypsum-β-anhydrite II form (AII), actually a by-product issued from the lactic acid fabrication process.

To reduce the brittle behavior of PLA–AII composites and to improve their processing, plasticizers from the low molecular weight (DOA and GTA) and polymeric (polyadipates with different molecular weights) categories were selected and mixed with a specific PLA grade for extrusion (high molecular weight, L/D isomer ratio of 96/4) and AII. The effect of the plasticizer addition in highly filled composites (40 wt% AII) in terms of molecular, thermal and mechanical properties has been evaluated. Processing and filler dispersion are facilitated by addition of up to 10 wt% plasticizer, without any important decrease of PLA molecular weights. The notched impact strength is also significantly improved. The best impact performances – up to fourfold increase of impact strength (Izod), were obtained by addition of low molecular weight plasticizers (GTA), whereas the polymeric plasticizers lead to PLA composites characterized by better thermal stability and higher tensile strength properties.

DSC analysis allowed the evaluation of the plasticizer effect on the T_g value of the PLA matrix (initial temperature: 62 °C) and its influence on thermal properties in relation to the material composition. Contrary to non-plasticized polyester (PLA and PLA–AII samples), all ternary compositions (PLA–AII–plasticizer) are characterized by cold crystallization properties (with intensity dependent on the plasticizer nature) and a distinct decrease of the T_g to about 40 °C. As evidenced by SEM and thermal analyses, the composites plasticized with DOA displayed phase-separation and therefore limited decrease of T_g.

Finally, it is believed that optimized compositions can be targeted to achieve the desired end-use product characteristics by adequate preparation of the filler and a perfect correlation between the chemical nature of the plasticizer, its relative content and the type of PLA used as polymer matrix. In future works, migration/ageing tests will be carried to outline the comparative properties of PLA plasticized with low molecular weight and polymeric ester-like plasticizers.

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