Polylactide (PLA) and Highly Filled PLA – Calcium Sulfate Composites with Improved Impact Properties

*M. Murariu, A. Da Silva Ferreira, E. Duquesne, L. Bonnaud, Ph. Dubois**

Summary: Starting from gypsum as by-product of lactic acid fabrication process, novel high performance composites have been produced by melt-blending PLA and this filler after a previous specific dehydration performed at 500 °C for min. 1h. Due to PLA sensitivity towards hydrolysis, the utilization of β-anhydrite II (AII) as filler is a prerequisite. Characterized by attractive mechanical and thermal properties due to good filler dispersion throughout the polyester matrix, these composites are interesting in biodegradable rigid packaging or technical applications. Interestingly, tensile strength of PLA – AII composites proved remarkably high, e.g. higher than 35 MPa at 50 wt-% filler content. However a decrease of impact properties has been recorded. To increase the toughness of these composites while preserving high stiffness an impact modifier based on ethylene copolymer has been mixed with both the polymer matrix and AII by melt-compounding. The effectiveness of the impact modifier was confirmed in both neat PLA and AII-based composites. Addition of 5-10 wt-% impact modifier into highly filled composites (30 to 40 wt-% filler) leads to an attractively threefold increase of impact strength with respect to the compositions without modifier, remarkable thermo-mechanical performances and good filler dispersion.

Keywords: calcium sulfate anhydrite; composites; compounding; impact resistance; poly(lactic acid)

Introduction

Biodegradable polymers have already found applications in many market areas and polylactide (PLA) seems to be one of the most promising candidates for future developments; it is not only biodegradable but is also produced from non fossil renewable natural resources by fermentation of polysaccharide or sugar, e.g., from corn and beet, therefore allowing the biological cycle to come full circle with PLA biodegradation as well as the photosynthesis process.[1–6]

Center of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, University of Mons-Hainaut & Materia Nova Research Center, Place du Parc 20, 7000-Mons, Belgium
Fax: (+32)65373484;
E-mail: philippe.dubois@umh.ac.be

Because PLA has been recently considered as an alternative in replacing petrochemical polymers, there is a strong demand to extend the range of PLA properties. For applications where the property of transparency is not strictly needed, the use of PLA with mineral fillers can be an interesting solution to reduce its global cost and to improve some specific properties such as rigidity, heat deflection temperature, processability, etc. Thus, various types of mineral fillers, surface-modified or not, can be incorporated into PLA in order to obtain either nanocomposites or microcomposites, where the filler has dimensions from nanometers to several microns or more, respectively.[7–10]

The basic constitutional unit of PLA, lactic acid (2-hydroxypropanoic acid), can be produced through chemical synthesis as a racemic mixture while lactic acid

enantiomers are obtained by carbohydrate fermentation using appropriate bacterial strains. The fermentation broth containing lactate products is filtered to remove cells, carbon treated, evaporated and acidified with sulfuric acid to get lactic acid. Further steps involve esterification, e.g., by using methanol, distillation and hydrolysis to obtain a purified lactic acid.[11] Such a procedure results in the formation of large amounts of calcium sulfate (gypsum) as main by-product, i.e., for each kilogram of lactic acid produced, about one kilogram of gypsum is formed as by-product.[12]

In response to the demand for extending PLA applications range while reducing its production cost, it has been recently demonstrated by some of us[10,13] that commercially available PLA can be effectively melt-blended with previously dehydrated gypsum (so called anhydrite II form), thus a by-product directly issued from the lactic acid fabrication process. These two products from the same source as origin can lead by melt-mixing to polymer composites characterized by remarkable mechanical performances. For instance, the tensile strength proved to be maintained at a level higher than 35 MPa at filler content as high as 50 wt-% without any filler treatment.[10] Unfortunately, at filler amount higher than 20% (by weight), the filled composites are characterized by low impact strength properties that become poorer with increasing $CaSO_4$ (anhydrite II form) content.

Because for some potential applications such as packaging or technical parts these composites do not have the required impact resistance, they need to be impact modified in order to fulfill the industry requirements. Like for other mineral 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 one of alternatives for the increasing of impact strength performances. Among the different commercially available impact modifiers shown to work well for improving PLA toughness (functionalized elastomers, grafted rubber resin

blends as styrene/acrylonitrile or methyl methacrylate grafted polybutadiene, acrylate rubber products, etc.), some specific ethylene copolymers represent a category of products very recently considered as most suited for PLA impact modification.[14–16]

This communication aims at reviewing some new strategic pathways in the preparation and characterization of PLA-based composites filled with calcium sulfate issued from the lactic acid production process. With the main goal of preparation of highly filled composites characterized by improved impact strength properties, a selected modifier based on ethylene copolymer (Biomax® Strong 100- DuPont, noted BS) has been mixed with PLA and $CaSO_4$ (anhydrite II). The effectiveness of the additive was firstly evaluated by blending with the PLA matrix. In a second step, various amounts of AII and BS were mixed together with PLA via melt-compounding technology and then, the performed composites were fully characterized to evidence the improvements obtained by impact modification.

Preparation of PLA-BS and PLA–CaSO₄(AII)-BS Compositions

Like other aliphatic polyesters, PLA is stable in the molten state provided that it is adequately stabilized and intensively dried[17] before processing, with a maximum acceptable water content of 250 ppm according to the supplier information. Therefore, it is of prime importance to dry the polyester resin but also to dehydrate the filler prior to melt-compounding. In this context, the polylactide (PLA- supplied by Galactic s.a. under the tradename: Galastic, number average molar mass = 74,500, residual monomer content = 0.18%, L/D isomer ratio of 96/4, MFI (190 °C, 2.16 kg) = 6.6 g/10 min) was dried 4 h at 110 °C under vacuum just before use.

Within the same goal, the filler, i.e., β-calcium sulfate hemihydrate ($CaSO_4 \times 0.5\,H_2O$), actually recovered as a by-product
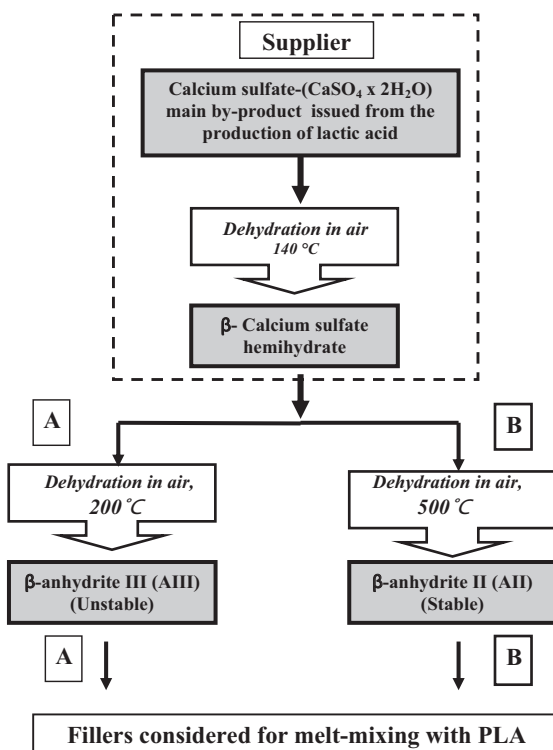
Figure 1.

Schematic representation of the experimental routes considered for the preparation of the filler: (A) β-anhydrite III route; (B) β-anhydrite II route.

issued from the lactic acid fabrication process (with mean particle diameter of 9 μm; supplied by Galactic s.a.) was dehydrated at 500 °C for min. one-hour, as shown in Figure 1 - route B, to obtain β-calcium sulfate anhydrite II (AII).

It is important to point out that the recovered $CaSO_4$ anhydrites, i.e., AIII or AII, can react very quickly or very slowly with water,[10] respectively and, hence, the name soluble anhydrite and insoluble anhydrite are also given to these forms of anhydrite. Calcium sulfate hemihydrate can be found in different forms, α- and β- forms, in function of the production method:[18] α-hemihydrate is obtained by wet dehydration of gypsum dihydrate in an autoclave (temperature > 100 °C, under pressure), β-hemihydrate is formed by dry dehydration (usually at temperatures above 100 °C, under air). For this study, as illustrated in Figure 1, the dry-dehydration technology

has been applied, thus the filler used as raw material for production of anhydrites is β-calcium sulfate hemihydrate. Further dehydration at higher temperature leads to diverse anhydrite forms[18,19] characterized by different stability to moisture absorption. For achieving high performance PLA composites and for preventing polyester degradation by hydrolysis, it has been demonstrated by some of us that it is important to use the β-anhydrite AII form, i.e., calcium sulfate hemihydrate dried at temperature of min. 500 °C, which proved to be much better suited for melt-blending with PLA with respect to AIII. Indeed, AIII is by far too much sensitive to atmospheric water absorption[10] (β-anhydrite III form reabsorbs rapidly ambient moisture forming back calcium sulfate hemihydrate in less than one-hour).

Concerning the impact modifier, i.e., Biomax® Strong 100 (BS) kindly supplied

by DuPont, it is designed with special chemistry to improve PLA impact strength and flexibility. Typical characteristics of BS are as follows:[15] melting point (DSC): 72 °C; glass transition temperature: −55 °C; MFI (190 °C/2.16kg): 12 g/10 min, and elongation at break = 950%.

It is very important to point out that according to some US patents, for successful action in PLA, an impact modifier can have a complex composition: for instance, an ethylene copolymer obtained by copolymerizing ethylene and more olefins (e.g., butyl acrylate, glycidyl methacrylate, vinyl acetate,…), one or more ionomers, grafting catalysts (e.g., stannous octanoate), etc.[16]

PLA-BS and PLA-AII-BS composites were obtained by melt-compounding at a temperature of 200 °C under moderate mixing (3 min. premixing at 30 rpm, followed by mixing up to 6 min. at 70 rpm) using a Brabender bench scale kneader equipped with cam blades. 3-mm thick plates were then prepared by compression molding at 190 °C using an Agila PE20 hydraulic press (low pressure for 240 s with three degassing cycles, followed by a high-pressure cycle at 150 bars for 150 s and cooling by tap water at 50 bars). Specimens for tensile and Izod impact testing were cut from plates by using a milling-machine in accordance to ASTM D 638-02a norm (type V specimens) and ASTM D 256-A norm (notched specimens, 60x10x3 mm), respectively.

In many cases the mixing of PLA with additives and fillers is followed by an important decrease of the molecular weights, with negative impact on the thermo-mechanical properties. Minimizing moisture content by intensive drying of all components (PLA, AII and BS) represents a first step to reduce the losses by hydrolysis and to preserve the polyester molecular weight as high as possible.

PLA molecular weight parameters (number average molar mass, M_n, and polydispersity index, M_w/M_n) were determined by size exclusion chromatography (SEC) using a previously described procedure.[10] Table 1 shows the effect of AII and/or BS addition on PLA molecular weights and polydispersity indices as determined by SEC on selected compositions. First of all, it is worth mentioning that under the investigated processing conditions, it has been found that the polydispersity index is poorly affected by the filler and/or impact modifier addition. It could be observed that kneading of PLA with AII and/or BS does not induce additional drop of PLA molar masses (more likely due to some unavoidable hydrolysis of polyester chains in melt-processed PLA), at least within the experimental errors that could be estimated to 15% taking into account SEC accuracy but also PLA extraction and purification steps. On the contrary, it is worth pointing out that the simple addition of 5 wt-% BS into PLA and PLA-AII compositions can lead to slightly higher molecular weights compared to the compositions without modifier. Indeed, M_n values of 68,000 and 69,000 are recorded for PLA chains in presence of 5 wt-% BS (entry 3) and 40 wt-% AII/5 wt-% BS (entry 5), respectively, compared to 64,000 for simply processed PLA (entry 2). Clearly, many assumptions can be proposed

Table 1.
Dependence of PLA molecular parameters upon composite formation.

Entry	Sample	M_n (PLA)	Polydispersity index
1	PLA (granules)	74,500	2.1
2	PLA processed	64,000	2.2
3	PLA − 5% BS	68,000	2.1
4	PLA − 40% AII[*]	63,000	2.2
5	PLA − 40% AII- 5% BS	69,000	2.1
6	PLA − 40% AII- 10% BS	64,000	2.0

[*]Reported in [10].

to take into account such an observation, including reactions between the reactive groups of BS and PLA ester functions or terminal end groups, reactions due to presence of catalysts, etc. More detailed information about the impact modifier composition is needed to draw any further conclusions.

Evaluation of Thermo-Mechanical Properties of PLA-BS Compositions

Differential scanning calorimetry (DSC) measurements have been carried out to determine the thermal behavior of PLA compositions, with/without BS as impact modifier (Figure 2). DSC analyses were performed with a DSC Q200 (TA Instruments) under nitrogen flow using a particular experimental procedure (first heating ramp of 10 °C/min from 0 to 220 °C to eliminate any different thermal history after the processing by compression molding, cooling ramp of 10 °C/min down to −10 °C to give to samples a similar thermal history, second heating with ramp

of 10 °C/min from −10 to 220 °C to record the events of interest and to compare polymer crystallization properties). Glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating cycle.

DSC analyses on composites containing 5–10 wt-% BS confirm the poor ability of PLA (4% content of D isomer) to crystallize. In fact, from these measurements, it could be pointed out that addition of BS into PLA (5–10 wt-%) does not lead to significant modifications of principal thermal parameters (e.g., increase of crystallinity). Moreover, since the recorded values of T_g are similar ($T_g \sim 61$ °C), it could be concluded that contrary to the use of plasticizers, the addition of 5 to 10 wt-% BS into PLA does not change the glass transition temperature of the amorphous PLA matrix. On the other hand, it is important to precise that the peak corresponding to the typical melting temperature of BS ($T_m \sim 72$ °C) is more easily detectable at higher percentage of BS into PLA, e.g. 10 wt-% BS (first DSC scan,
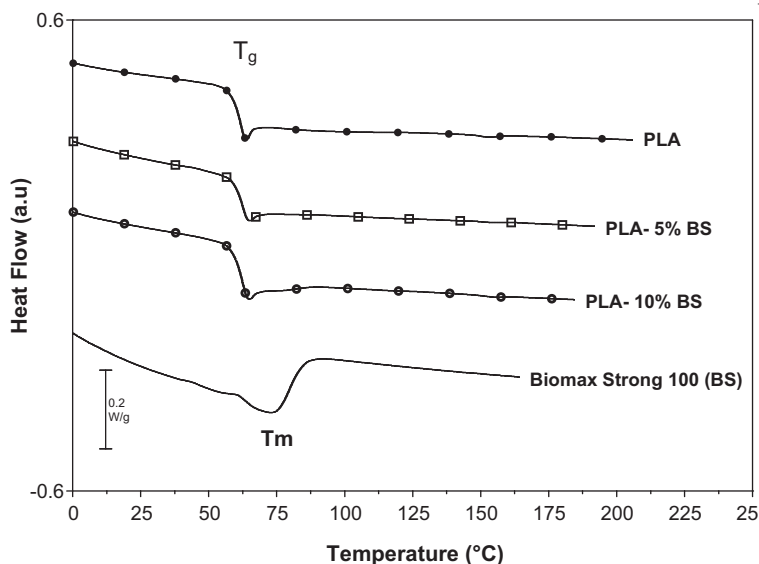

Figure 2.
DSC measurements on various PLA samples with/without BS and of BS (second heating from −10 to 220 °C with a ramp of 10 °C/min).

thermogram not shown here). In this context, one can assume that the PLA–BS blends are partially immiscible. This assumption is confirmed by the presence of BS-based microgels as identified during filtration-extraction steps in presence of different solvents such as chloroform, heptane or THF, according to the SEC characterization procedure.[10]

By comparison to PLA, BS seems to be characterized by a higher thermal stability under air as evidenced by the thermally induced weight loss recorded by TGA (TGA Q50 from TA Instruments) (Figure 3). Therefore it is expected that in relation to the utilization of plasticizers, addition of BS in the polyester matrix will not decrease the thermal stability of the blend. Indeed, Figure 4 shows comparative thermogravimetry results for PLA and PLA–(2.5 or 5 wt-%) BS blends, which confirm that the investigated PLA-BS compositions are characterized by similar thermal stability with respect to the composition involving non-modified PLA.

As far as the mechanical properties are concerned, addition of BS modifier remarkably improves the impact properties of PLA, i.e., the notched Izod impact strength

is increased from 2.6 kJ/m^2- value recorded for the unfilled PLA, to 4.6 kJ/m^2 by addition of 5 wt-% BS or even to more than 12 kJ/m^2 by addition of 10 wt-% BS into PLA (Figure 5). Regarding the tensile properties (comparative results are presented in the next section), addition of BS into PLA leads to a slight decrease of rigidity and tensile strength performances, but improves ductility as illustrated by the increase of the nominal strain at break (Figure 8).

To obtain information about modifier dispersion, scanning electron microscopy (SEM) analyses were performed on previously fractured samples using a scanning electronic microscope Philips XL equipped for both secondary electron (SE) and back scattered electron (BSE) imaging, at accelerated voltage up to 30 kV and various magnitudes. It is well-known that the polymer blends and copolymers are viable approaches in formulating polymeric materials with enhanced toughness. To allow the rubber impact modifier to confer toughness to PLA or to other polymers, specific conditions are required:[14,20] the rubber must be distributed as small domains (usually 0.1–1.0 μm) in the polymer matrix,
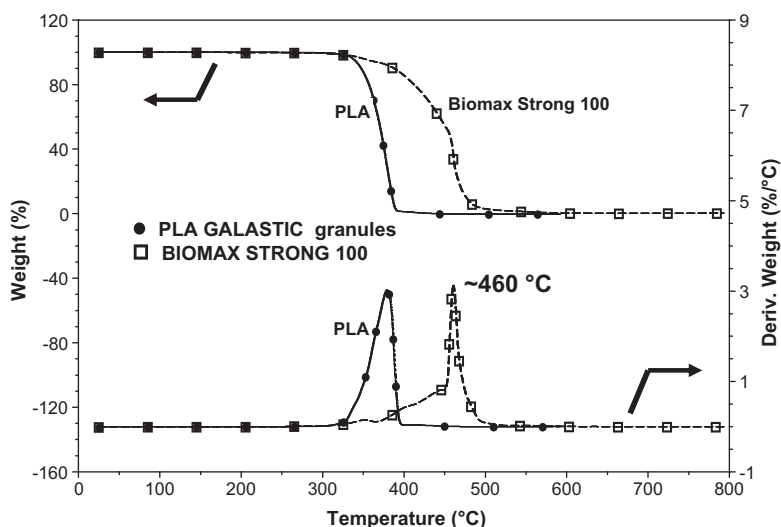

Figure 3.
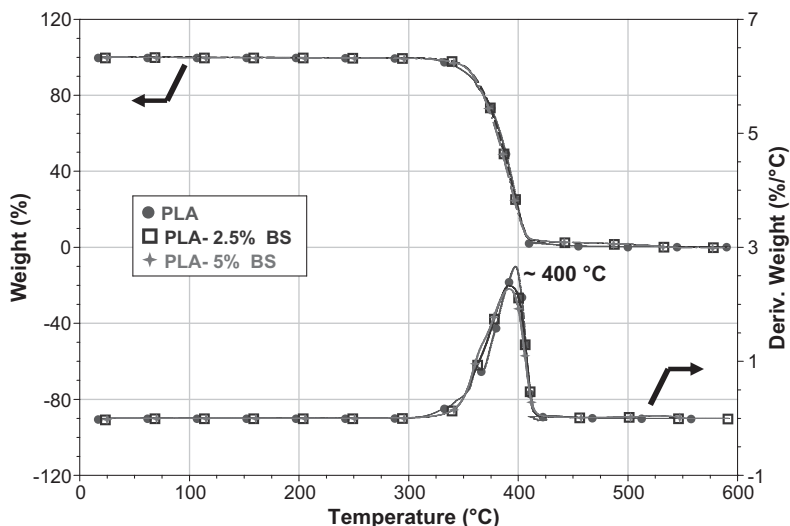TGA and d-TGA measurements on PLA and BS (under air, ramp of 20 °C/min).

Figure 4.
TGA measurements on PLA and PLA with 2.5 and 5 wt-% impact modifier (under air, ramp of 20 °C/min).

must have low value of T_g and good interfacial adhesion, should not be miscible with the polymer matrix, stable at polymer processing temperatures, etc. It is important to point out that these factors will allow the modifier to induce energy dissipation mechanisms in PLA, which will retard crack initiation and propagation, leading finally to an improved toughness of the brittle matrix. In this context, the main issue in producing toughened plastics is the adequate dispersion of the elastomer- as small domains, which will initiate the plastic

deformation and will absorb the impact mechanical energy.

Indeed, from SEM images of PLA–BS samples fractured during impact testing (Figure 6A and B), it can be assumed that the small micrometric nodules (see arrows) represent the additive, i.e., BS, and it is therefore reasonable to suppose that the well dispersed phase can have a dampening action in the brittle PLA matrix, capable to absorb energy and stop craze propagation. At this stage of the study it is preferred to perform some more detailed SEM
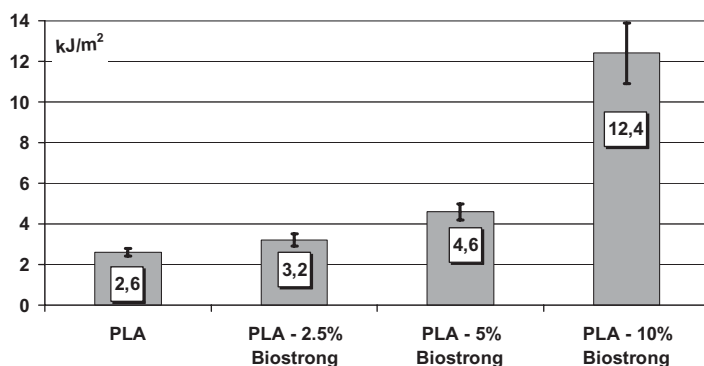

Figure 5.
Notched impact strength (Izod) of various PLA compositions with/without BS (ASTM D256-A, 3.46 m/s impact speed, hammer 0.668 kg).
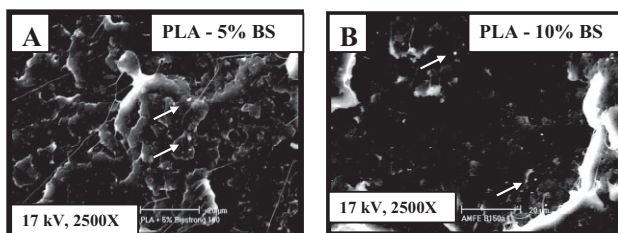
Figure 6.
SEM pictures (SE mode) at high magnification on fractured surfaces of PLA–BS blends with 5 wt-% (A) and 10 wt-% impact modifier (B).

investigations before drawing any conclusions concerning the major driving forces responsible for these remarkable improvements of the impact performances.

Highly Filled PLA-AII Composites with Improved Impact Properties

In a second experimental step, the impact modifier (up to 10 wt-%) has been added into the highly filled PLA-AII compositions (30–40 wt-% filler) and these composites were characterized with particular attention paid to the impact strength properties.

Most of the time, the incorporation of high amount of mineral fillers triggers a significant decrease in the toughness or impact strength of the polymer materials. At higher loading of AII (30–40 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.[10] This behaviour 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.

By addition of BS into PLA-AII compositions this negative behaviour is remarkably rubbed off and excellent impact strength performances are obtained even for highly filled compositions (Figure 7). Indeed, the impact strength values, i.e.,
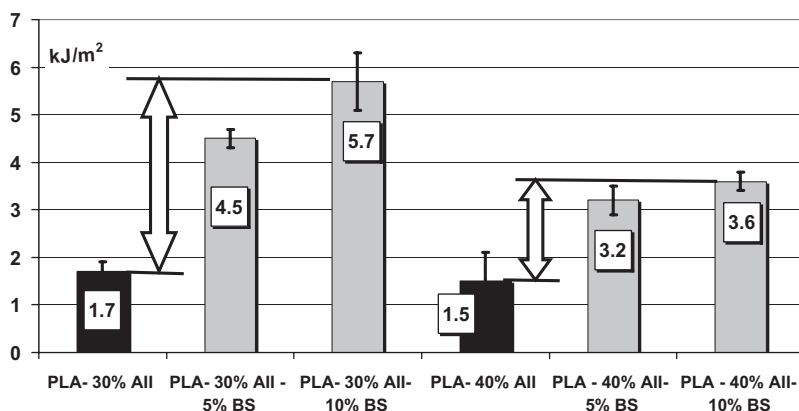

Figure 7.
Notched impact strength (Isod) of PLA-AII compositions with/without impact modifier (ASTM D256-A, 3.46 m/s impact speed, hammer 0.668 kg).

4.5 and 5.7 kJ/m², respectively obtained by addition of 5 and 10 wt-% BS in the PLA-AII (30 wt-%) represent a spectacular increase of the impact performances (of 2.6 and 3.3 times, respectively). Further increase of the filler content (up to 40 wt-%) decreases the impact strength values but, they remain more than 2 times higher than for the composites without modifier. It is also very interesting to notice that the impact resistance of those highly filled composites remains well higher than for the neat PLA (2.6 kJ/m²; Figure 5).

Generally, addition of mineral filler into the polymer matrix leads to increased rigidity (e.g., high Young's modulus value), while the elongation at break and impact strength decrease with increasing filler loading. A similar trend was observed for PLA–AII composites.[10] Usually, addition of a rubber component into a polymeric matrix improves the toughness but can also lead to a decrease of tensile strength performances in correlation to modifier percentage. In this context it is important to find the optimal formulations where tensile strength performances are maintained at the level needed for a required application. Indeed, Figure 8 shows that the increase of BS content into PLA matrix slightly

decreases the tensile strength properties while the strain at break values increase with additive amount. A similar trend is recorded for highly filled PLA-AII composites for which in all cases addition of a high amount of BS, i.e., 10 wt-%, leads to an important decrease of tensile strength performances. The most important difference is recorded at relatively high amount of filler, i.e., 40 wt-%, for which the composition without BS yielded a tensile strength of 48 MPa to be compared to values of 30 MPa and 22 MPa, obtained by addition of 5 and 10 wt-% BS, respectively.

The remarkable stress performances of the PLA-AII compositions have already been explained[10,13] by the existence of favourable inherent polymer/filler interactions and fine particle dispersion even without the use of compatibilizing agents. Addition of a third component in high amount (e.g. 10 wt-% BS) leads to composites more heterogeneous and can change the level of interaction between components (PLA and AII). This point is clearly evidenced in Figure 8 by a significant decrease of tensile strength performances. In this context, it is believed that for further developments, addition of 5 wt-% BS into PLA or PLA-AII (30-40 wt-%)
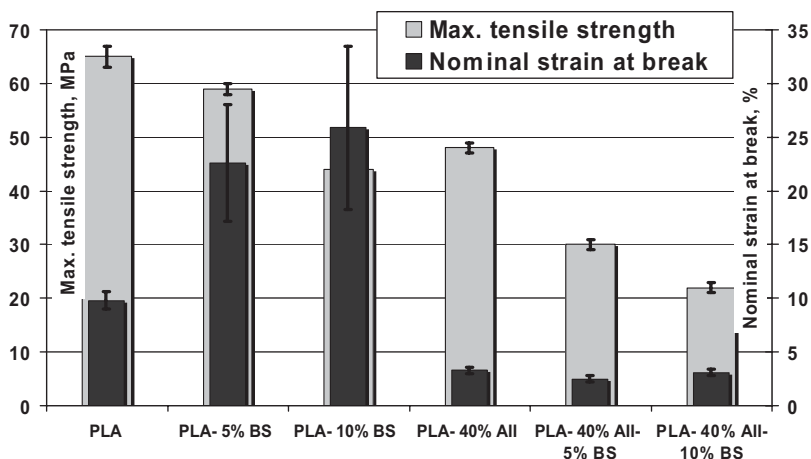

Figure 8.
Tensile properties of PLA and PLA-BS compositions with/without AII filler (ASTM 638, specimens type V, v = 1 mm/min, distance between grips of 25.4 mm).

compositions represents an interesting choice that can lead to composites characterized by attractive values of both impact and tensile strength properties.

SEM images have been performed especially for highly filled composites using back scattered electrons (BSE) - to get higher phase contrast, and to detect the most important differences conferred by co-addition of impact modifier and filler.

At low magnification, the compositions with 40 wt-% AII show even in presence of 10 wt-% BS, a rather good dispersion of the filler (Figure 9A). These observations allow concluding that by addition of BS, the filler remains homogeneously dispersed into PLA matrix without detectable larger aggregated particles or related associations.

At higher magnification (Figure 9B), SEM images give more information and details about the presence of particles with different shape and higher/smaller dimensions than the mean diameter (9 microns). Well dispersed β-anhydrite II particles with various geometries and quite broad size distribution are clearly evidenced at the surface of cryofractured composites. On the other hand, due to high filler content, the SEM images of these composites do not allow clearly the identification of the impact modifier, which can be dispersed into PLA matrix as third phase, can partially encapsulate the filler particles, etc. From SEM images it is important to point out that highly loaded compositions with well-dispersed filler particles are easily obtained

and the compounding of PLA-AII-BS blends even at relatively low shear (by using an internal mixer) allows to reach a surprisingly efficient aggregate breakdown. One may expect that an improved mixing, e.g., using twin-screw extruders, could lead to more advanced filler dispersion.

In relation to the thermal stability, mineral fillers can produce either pro-degrading or stabilizing effects in thermoplastic polymers. The reasons for this behavior are varied and complex, with factors such as adsorption (and lost) of the stabilizers, the presence of detrimental impurities (incl. metal residues), form of primary particles, etc.

As far as TGA measurements are concerned, it has been already reported by some of us[10] that by dispersing up to 50 wt-% AII, no decrease in thermal stability of PLA is induced by the presence of the filler. On the other hand, it was demonstrated by our additional experimental work that addition of a third component, e.g., a plasticizer, can lead to a dramatically decrease of the thermal stability of these composites.

Usually, the good filler dispersion was considered as source of key-performances that can explain the thermal stability or remarkable mechanical performances of PLA–AII composites. Interestingly enough, the comparative TGA results (not shown here) of PLA-AII and PLA-AII-BS compositions with up to 10 wt-% of impact modifier show an excellent thermal
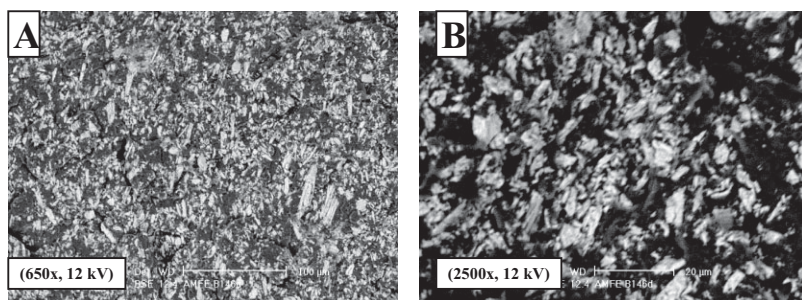
Figure 9.
SEM pictures (BSE mode) of cryofractured surfaces of PLA-40% AII-10% BS composites at low (A) and high magnifications (B).
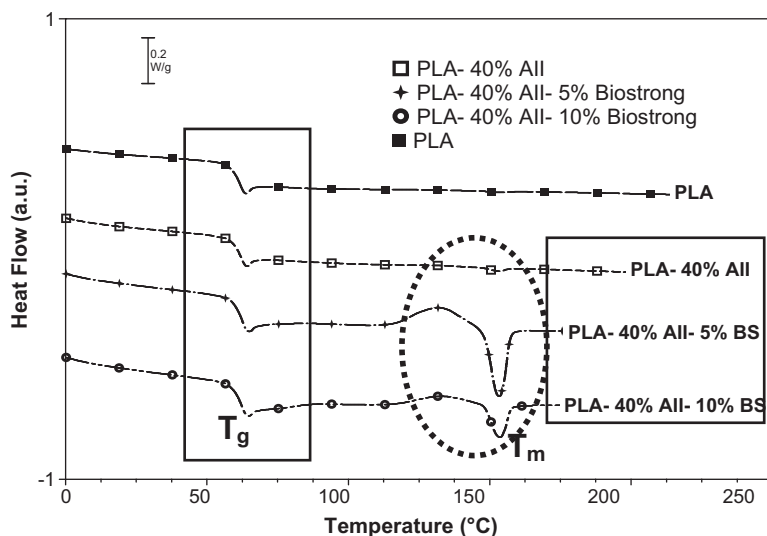
Figure 10.
DSC measurements on various PLA samples with/without impact modifier (second heating from −10 to 220 °C with a ramp of 10 °C/min).

stability for the ternary compositions, even some time slightly higher compared to the compositions without modifier.

Finally, as for PLA-BS blends, DSC measurements confirm again that addition of 5–10 wt-% BS in PLA compositions with 40 wt-% filler does not decrease the T_g value of the polyester matrix (Figure 10), a main property that is needed for many technical applications. Since the ''AII-BS'' co-addition leads to some interesting cold crystallization properties that are not evidenced for PLA or PLA-AII compositions, it is important to precise that these effects are under intensive investigation not only for PLA based on a L/D lactic acid isomer ratio of 96/4, but also semi-crystalline P(L)LA (with 100% L isomer).

Conclusion

In response to the demand for enlarging PLA applications range while reducing its production cost, this study has emphasized that commercially available PLA can be effectively melt-blended with selected additives and previously dehydrated gypsum, actually a by-product issued from the lactic

acid fabrication process. To preserve PLA molecular weights, dehydration of calcium sulfate hemihydrate to form β-anhydrite II (AII) is a prerequisite. The effectiveness of an ethylene copolymer as impact modifier, i.e., Biomax® Strong 100 (BS) from DuPont, and its influence on molecular, thermal and tensile properties of PLA and PLA-AII composites has been investigated. Addition of impact modifier did not negatively affect the principal molecular/ thermal parameters and improved significantly the notched impact strength. Accordingly, adding up to 10 wt-% BS in highly filled PLA-AII composites (with 30 to 40 wt-% filler) leads to a surprising threefold increase of impact strength (Izod), excellent thermal stability and typically good filler dispersion. A more detailed investigation to outline the impact mechanisms and some typical properties of both binary and ternary compositions is under current investigation and will be the object of a future contribution.

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