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Additional Information

“High toughness poly (lactic acid) (PLA) formulations obtained by ternary blends with poly (3-hydroxybutyrate) (PHB) and flexible polyesters from succinic acid”

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Abstract

This work reports the development of poly(lactic acid) (PLA) formulations with improved toughness by ternary blends with poly(3-hydroxybutyrate) (PHB) and two different flexible polyesters derived from succinic acid, namely poly(butylene succinate) (PBS) and a copolymer, poly(butylene succinate-co-adipate) (PBSA). The main aim of this work is to increase the low intrinsic toughness of PLA without compromising the thermal properties by manufacturing ternary blends using epoxidized vegetable oils (EVOs) as compatibilizer agents. The ternary blends were manufactured by reactive extrusion in a co-rotating extruder and were subjected to mechanical, thermal, thermos-mechanical and morphology characterization. The obtained results confirm that these two succinic acid-derived polymers, i.e. PBS and PBSA positively contribute to increase ductile properties in ternary blends with PLA and PHB with a subsequent improvement on impact toughness. In addition, both epoxidized vegetable oils, ELO and ESBO are responsible for somewhat compatibilization between all three polyesters in blends which gives improved ductile properties with regard to uncompatibilized ternary blends. In addition, the temperature range in which these materials can be used is broader than ternary blends with other flexible polyester such as poly(ϵ -caprolactone), as both PBS and PBSA melt at about 100 °C. These PLA-based materials with improved impact properties offer interesting applications in the packaging industry.

Keywords: poly(lactic acid) – PLA; impact toughness; ternary blends; mechanical properties; morphology.

1. Introduction

Poly(lactic acid) (PLA) owns a privileged position in the field of biopolyesters due to an excellent combination of mechanical, thermal and barrier properties together with a cost-competitive price. For these reasons, PLA is widely used in several sectors such as packaging [1-3], medical devices [4, 5], 3D printing [6, 7], disposable cutlery and tableware [8], automotive [9-11], construction and building [12, 13], wood plastic composites [14, 15], and so on. Despite this, industrial formulations of PLA have important challenges since PLA is a brittle polymer with low impact toughness and this must be improved [16]. This is a key factor in some applications which require good balanced properties (mechanical, thermal, chemical barrier, etc.) together with good resistance to impacts.

There are several approaches to overcome or minimize this drawback. It has been reported a wide variety of PLA-based copolymers with improved properties [17, 18]. Nevertheless, this is an expensive process and despite it is technically viable at laboratory scale, it is not the best solution at industrial scale due to costs.

A second approach is the use of plasticizers to reduce the glass transition temperature (T_g). A wide range of plasticizers have been proposed, including citrate and adipate esters (acetyl tributyl citrate - ATBC [19, 20], triethyl citrate - TEC [21], bis(2-ethylhexyl) adipate - DEHA, diisodecyl adipate - DIA [22]), polyglycols: (poly(ethylene glycol) - PEG [23, 24] and poly(propylene glycol) (PPG) [25, 26]), lactic acid oligomers (OLAs) [27, 28], and so on. Recently, it has

been reported plasticization properties that modified vegetable oils (epoxidized and maleinized) can provide to PLA with a remarkable increase in toughness [29]. The use of plasticizers is a cost-effective solution to the above-mentioned drawback, but in general, mechanical resistant properties are highly reduced.

The third approach consists of physical blends with flexible (or even, rubber like) polymers which can contribute to improve PLA performance at a cost-competitive way. A wide variety of PLA-based binary blends have been proposed to improve toughness of PLA. It is worthy to note the interesting properties of PLA blends with poly(ϵ -caprolactone) - PCL [30-33], poly(hydroxybutyrate) - PHB [1, 34], poly(hydroxybutyrate-*co*-valerate) - PHBV [35-37], thermoplastic starches - TPSs [38, 39], poly(butylene adipate-*co*-terephthalate) - PBAT [40], poly(butylene succinate) - PBS [41-43] - PBSA, poly(butylene succinate-*co*-adipate) [44] and so on. As indicated previously, rubber or rubber-like polymers have been proposed as impact modifiers in polymer and composites systems with remarkable positive effects on overall toughness[45].

Another approach is the use of functionalized nanoparticles on PLA or PLA blends. It is worthy to note the increasing use of multiwalled carbon nanotubes (MW-CNTs)[46], sepiolite needles[47], halloysite nanotubes (HNTs)[48], montmorillonite clays[49], among others. All these functionalized nanoparticles provide chemical groups that are able to react (or interact) with the components of an immiscible polymer blend or directly with PLA, providing improved toughness with relatively low nanoparticle loading.

The most relevant problem related to these binary blends is the poor (or lack of) miscibility between PLA and most of these polymers which leads to poor mechanical properties [50]. This leads to the use of compatibilizers that interact with both polymers in the binary blend to give a rise on overall properties. A wide variety of compatibilizers have been proposed [51, 52]. Epoxy-styrene acrylic oligomers (ESAO) and ethylene/acrylate copolymers give good compatibilizing effects combined with a chain extension effect [53]. Recently, epoxidized and maleinized vegetable oils have been successfully used as compatibilizers in flexible polymer blends due to the high reactivity of both epoxy and maleic anhydride groups towards hydroxyl terminal groups in polyester chains [54, 55]. This high reactivity allows using reactive extrusion with PLA to overcome and/or minimized its low intrinsic toughness [16, 56]. Also, ternary blends have been proposed to reach tailored properties, *e.g.* PLA/PHBV/PBS [57], PLA/PCL/TPS [58], PLA/PCL/cellulose acetate butyrate (CAB) [59], among others.

In previous works, it was assessed the suitability of poly(ϵ -caprolactone) in ternary blends of PLA and PHB, modified with modified vegetable oils as flexible compatibilizers [60]. PCL has an important effect on increasing ductile properties of ternary blends and, subsequently, improving impact toughness. Nevertheless, PCL is a low melt temperature polyester (around 60 °C) and, although it contributes to improved toughness, the service temperature range is highly reduced due to the softening (or melting) of PCL at moderate temperatures. For this reason, the main aim of this work is the use of high melt

temperature flexible polyesters to improve the toughness of PLA blends with PHB. In particular, two bio-sourced polyesters are used, namely poly(butylene succinate) - PBS and poly(butylene succinate-*co*-adipate), with a melt temperature around 100 °C. Additionally, the effect of two epoxidized vegetable oils, namely epoxidized linseed oil - ELO and epoxidized soybean oil - ESBO, on overall toughness properties of ternary PLA/PHB/PBS and PLA/PHB/PBSA blends is addressed.

2. Experimental

2.1. Materials

The base polymer for ternary blends was a commercial poly(lactic acid) (PL) Ingeo™ Biopolymer 6201D supplied by NatureWorks (Minnetonka, USA). Regarding poly(3 hydroxybutyrate) (PHB), a commercial grade P226 supplied by Biomer (Krailling, Germany). Two succinic acid-derived polymers, poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-adipate)(PBSA) were supplied by Showa Denko Europe GmbH (Munich, Germany). The chemical structure of all four polyesters is shown in **Figure 1**. **Table 1** shows a summary of the main properties of the above-mentioned polymers.

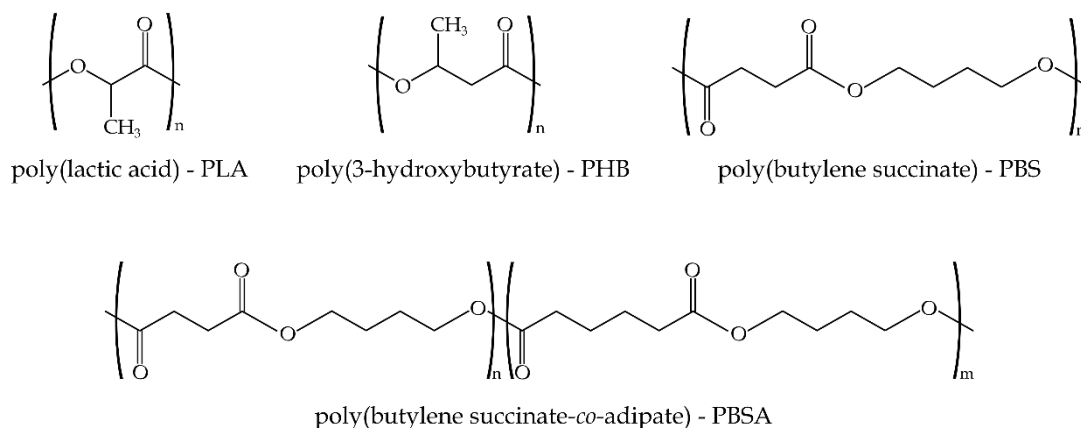


Figure 1 Schematic representation of the chemical structure of the polyesters used for ternary blends.

Two different compatibilizers were used, both derived from vegetable oils (see **Figure 2**): epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO), supplied by Traquisa S.A. (Barcelona, Spain).

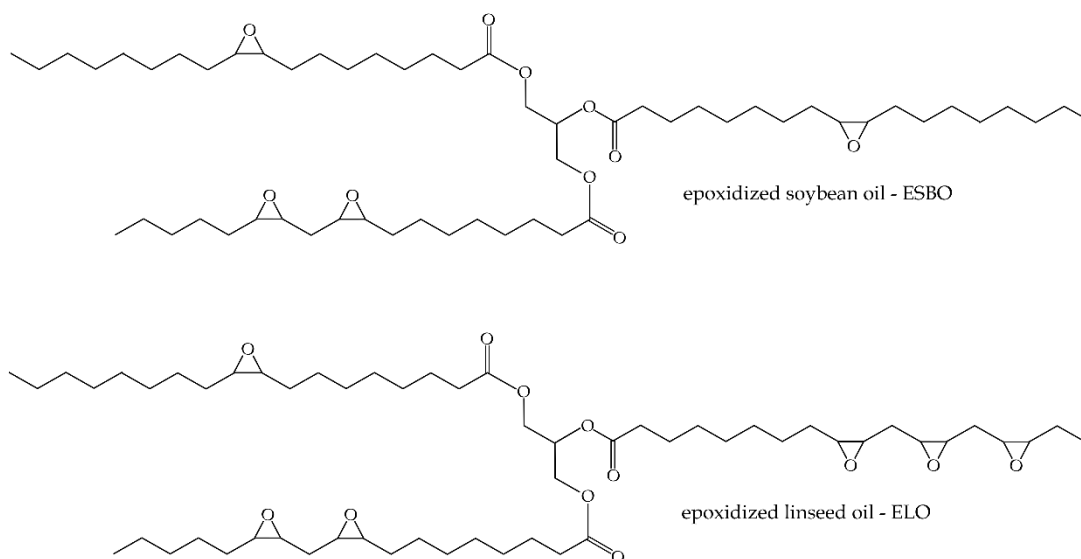


Figure 2 Schematic representation of the chemical structure of the epoxidized vegetable oils used as compatibilizers in ternary blends.

2.2. Manufacturing of ternary blends

All materials were previously dried in a MDEO dehumidifier from Industrial Marsé (Barcelona, Spain). The selected drying cycles were 60 °C/24 h for PHB, PBS, PBSA and PLA. Previous drying of polyesters is a key factor for further processing as polyesters are highly sensitive moisture which promotes hydrolysis, and, consequently, a decrease in overall properties. ELO and ESBO were stored in a vacuum desiccator and, heated at 40 °C for 30 min to reduce their viscosity and enhance the pre-mixing process with polyesters.

Ternary blends with and without compatibilizers (see **Table 2**) were extruded in a twin-screw co-rotating extruder from Construcciones Mecánicas DUPRA S.L. (Alicante, Spain). This extruder is equipped with standard screws with a diameter of 25 mm and a length to diameter ratio (L/D) of 24. The extrusion rate was set to 24 rpm and the thermal profile was defined as follow: 165 °C (hoper), 170 °C, 175 °C and 180 °C (extrusion die). After extrusion, the obtained blends were pelletized for further processing by injection molding in a Sprinter 11 from Erinca S.L. (Barcelona, Spain). The temperature profile for the injection molding process was set to 165 °C (hoper), 170 °C, 175 °C and 180 °C (injection nozzle).

2.3. Morphological characterization

The morphology of the fractured samples from impact tests were atudied by field emission scanning electron microscopy (FESM) in a ZEISS ULTRA microscope from Oxford Instruments (Oxfordshire, United Kingdom). To avoid

charging during observation, all samples were covered with a thin metallic alloy (Au-Pd) in a high vacuum sputtering process with a Emitech SC7620 sputter coater from Quorum Technologies Ltd. (East Sussex, United Kingdom). The acceleration voltage was 2 kV.

2.4. Thermal characterization

Thermal characterization was carried by differential scanning calorimetry (DSC) in a 821 calorimeter from Mettler-Toledo (Schwerzenbach, Switzerland). An average sample weight of about 5-6 mg was subjected to the following thermal program: first heating from -50 °C to 200 °C; cooling from 200 °C to -50 °C and a second heating program from -50 °C up to 300 °C. The first heating cycle did not exceed 200 °C to avoid possible degradation of polyesters. The second heating cycle was conducted until degradation up to 300 °C to see potential degradation processes. The heating rate was 10 °C min⁻¹ for all three stages and the atmosphere was nitrogen (66 mL min⁻¹). Standard sealed aluminum crucibles with a volume of 40 mL were used. The thermal stability of the developed ternary blends was evaluated by means of thermogravimetric analysis (TGA) in a TGA/SDTA 851 thermobalance from Mettler-Toledo (Schwerzenbach, Switzerland). Samples with a weight ranging from 5 to 6 mg were placed in standard alumina crucibles (70 µL) and were subjected to a dynamic heating program from 30 °C to 700 °C. The selected atmosphere was air and the heating rate was 20 °C min⁻¹.

2.5. Mechanical characterization

Mechanical properties, *i.e.* tensile modulus (E_t), elongation at break ($\% \epsilon_b$) and tensile strength (σ_t) were obtained in a universal test machine ELIB 50 from S.A.E. Ibertest (Madrid, Spain) following the guidelines of ISO 527-1:2012. All the tests were carried out using a 5 kN load cell and the crosshead speed was set to 5 mm min⁻¹. On the other hand, Shore D hardness values were obtained in a mod. 676-D durometer from J. Bot Instruments (Barcelona, Spain) as recommended by ISO 868:2003. The impact strength was obtained by the Charpy method in a 1 J pendulum from Metrotec on notched samples ("V" type notch and a radius of 0.25 mm) as indicated in ISO 179:2010. At least five samples were tested and the average values and standard deviation of the corresponding parameters were calculated. All mechanical tests were carried out at room temperature.

2.6. Thermomechanical characterization

Mechanical-dynamical thermal analysis (DMTA) was carried out in DMA1 from Mettler-Toledo (Schwerzenbach, Switzerland). Samples with a size of 10x7x1 mm³ were subjected to a temperature sweep from -90 °C up to 80 °C working in single cantilever mode with a maximum deformation of 10 μm. The selected frequency was 1 Hz and the heating rate was set to 2 °C min⁻¹.

In addition, the Vicat softening temperature (VS) and the heat deflection temperature (HDT) were obtained in a VHDT 20 dual (VST/HDT) station from Metrotec S.A. (San Sebastián, Spain). VST tests were carried out following ISO 306. The applied method was the B50 method by using a load of 50 N and a

heating rate of 50 °C h⁻¹. With regard to the HDT, the heating rate was set to 120 °C h⁻¹ as specified in ISO 75-1. Samples with dimensions 80x10x4 mm³ were subjected to three point conditions with a distance between support of 60 mm and a load of 320 g.

Finally, the dimensional stability was studied by thermomechanical analysis (TMA) in a Q400 thermoanalyzer from TA Instruments (Delaware, USA). Samples with dimensions of 10x10x4 mm³ were subjected to a heating program from -90 °C up to 80 °C with a constant heating rate of 2 °C min⁻¹. The supported load was 20 mN. The coefficient of linear thermal expansion (CLTE) was calculated from the dimensional change as a function of temperature (slope of TMA curves).

3. Results and discussion

3.1. Mechanical properties of PLA/PHB blends with PBS or PBSA and different vegetable oil-based compatibilizers

The main results regarding tensile tests are gathered in **Table 3**. As expected, both PBS and PBSA lead to a remarkable improvement on ductile properties with regard to neat PLA. Neat PLA (as described in previous works)[61] has a very low elongation at break of 7.87% while its tensile modulus is relatively high (around 3.6 GPa). Its tensile strength is located at 58.2 MPa. As reported previously, the ternary blend with PHB and PCL (PLA₆₀PHB₁₀PCL₃₀) gives a remarkable increase in elongation at break up to values of 15.3% With regard to the tensile modulus, it goes down to 2.0 GPa

and the tensile strength also drops down to 48.4 MPa [60]. This previous work also reported the excellent compatibilizing effect that epoxidized soybean oil (ESBO) can give to this ternary blend. The most important effect of ESBO is an increase in elongation at break up to values of 130.0%. This plasticization effect of ESO has been previously reported for PLA with a subsequent improvement on toughness [62]. Nevertheless, the service temperature range in which these ternary blends can find applications is relatively narrow due to the low melt temperature of PCL. As it can be seen in Table 3, both PBS and PBSA have a positive effect on elongation at break of ternary PLA/PHB/PBS blends up to values of 49.3% and 62.9%, respectively. These values are remarkably higher than typical values of neat PLA and, even more, they are higher than those offered by the PLA ternary blend with PHB and PCL. These findings are interesting since from a mechanical point of view, ternary blends containing PBS and PBSA are comparable to similar blends with PCL but with the advantage of the melt temperature of both PBS and PBSA which is close to 100 °C. Another important finding is the clear compatibilizing effect that both epoxidized vegetable oils can provide. For example, the ternary blend PLA₆₀PHB₁₀PBS₃₀ shows an elongation at break of 49.3% and this is noticeably increased up to values of 115.2% and 160.4% by the addition of 5 phr ELO or ESBO respectively. The same tendency can be observed for the ternary blend with PBSA. Nevertheless, as expected, PBSA is more flexible than PBS and this contributes to higher elongation at break values. Another important conclusion is the better compatibilizing effect of ESBO compared to ELO. This could be

related to the number of reactive points present in ELO and ESBO. ELO possesses an average number of epoxide rings per triglyceride of 6 while ESBO is characterized by a lower number of oxirane groups per molecule (about 4). This could be a key issue to explain the better performance of ESBO-compatible blends. ELO, with more reactive points can establish more interactions with all three polyesters thus leading to a combined effect of chain extension, plasticization and compatibilization, all these, having a positive effect on increased elongation at break and other ductile properties. With regard to ESBO, it shows less reactive points so that, its interactions with all three polyesters are similar to ELO but lower in number. Therefore, ESBO-compatible blends show more flexibility.

Regarding mechanical resistant properties, as expected, both PBS and PBSA are responsible for a decrease in both tensile strength and tensile modulus. This decrease is more pronounced in ELO- and ESBO-compatible blends. Nevertheless, these mechanical properties are still similar or even higher to most commodity plastics. Therefore, these ternary blends can clearly compete with commodity plastics in terms of mechanical performance.

The study of the morphology of the developed ternary blends with PBS and PBSA can be useful to support the previous results. **Figure 3** gathers the FESEM images corresponding to the uncompatibilized and compatibilized ternary blend PLA/PHB/PBS. Although it has been reported some miscibility between PLA and PHB (especially with low molecular weight PHB), **Figure 3a** and **Figure 3b** show a clear phase separation thus indicating poor miscibility.

As PLA and PBS are the main components (they represent 90 wt%), it can be inferred that the matrix is a PLA-rich phase in which PBS-rich spherical domains are finely dispersed. It has been reported the poor miscibility between PLA and PBS with clear phase separation which is improved by addition of compatibilizers [42, 63]. PHB could also appear as a dispersed phase but it seems that its partial miscibility towards PLA and, possible towards PBS leads to the observed spherical shapes with a high number of small holes. It can be detected an important gap between the PLA-rich phase and the dispersed spherical domains which is representative for poor miscibility. Addition of 5 phr ELO (PLA₆₀PHB₁₀PBS₃₀/ELO₅) leads to significant changes in morphology as it can be seen in **Figure 3b** and **Figure 3c**. The dispersed spherical domains seem to be wetted by the surrounding matrix although phase discontinuity is still detectable. This increase in the wetting behavior could due by the reaction of epoxy groups in ELO with hydroxyl terminal groups in all three polyesters thus leading to compatibilization thorough several mechanisms such as chain extension, branching, crosslinking, among others [64]. All these phenomena have been reported by reactive extrusion with dicumyl peroxide in a binary PLA/PBAT blend [65]. Despite interesting effects of ELO on elongation at break, ESBO provides better compatibilization to the ternary blend as it can be observed in **Figure 3e** and **Figure 3f**. Although full continuity is not detected, the morphology of the fractured surface shows that dispersed phase is embedded into the PLA-rich matrix which indicates more intense interactions between all three polyesters. Despite full miscibility is not detected, ESBO

increases the wettability of the dispersed phase and this has a positive effect on load transfer and subsequently, the cohesive properties are improved.

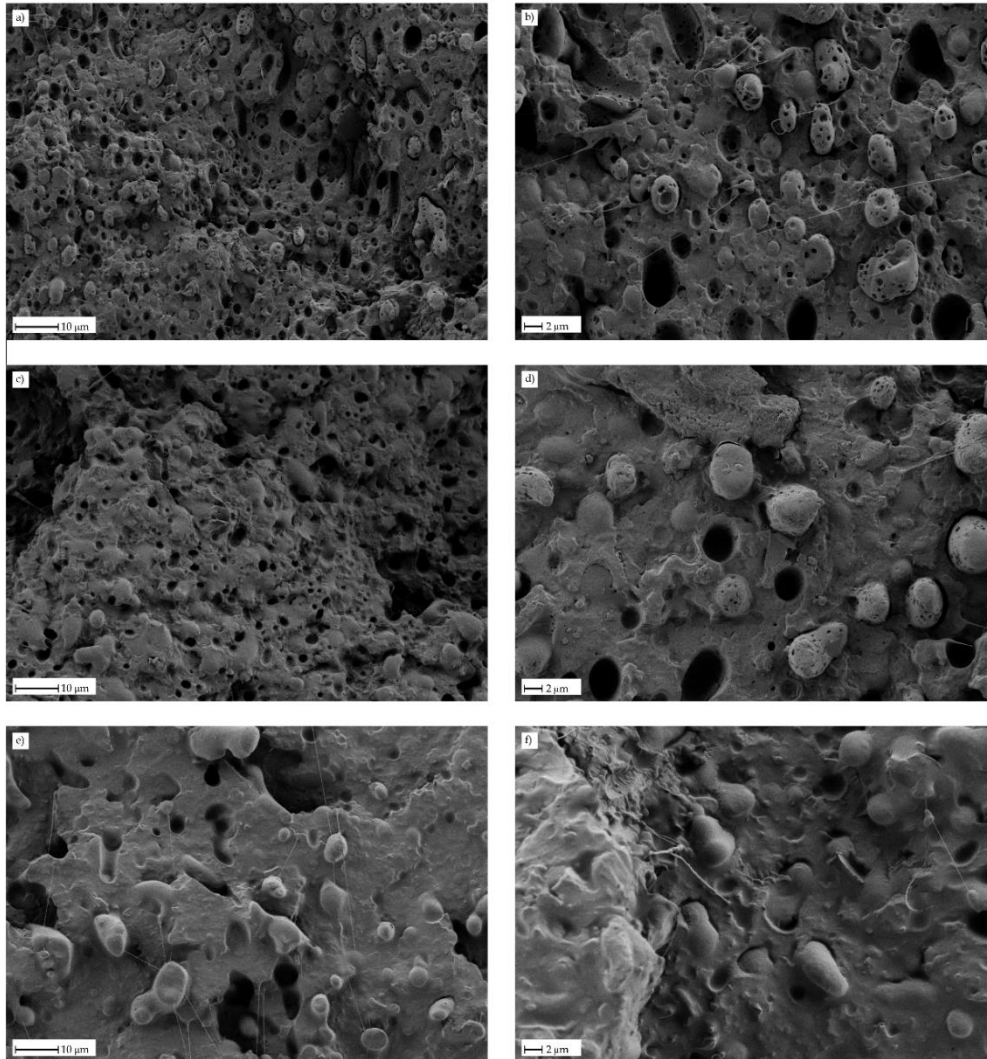


Figure 3 Field emission scanning electron microscopy (FESEM) images at different magnifications (left column - 1000x; right column - 2000x) corresponding to poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) with different epoxidized vegetable oils (EVOs), a) & b) PLA₆₀PHB₁₀PBS₃₀, c & d) PLA₆₀PHB₁₀PBS₃₀/ELO₅, e & f) PLA₆₀PHB₁₀PBS₃₀/ESBO₅.

The PLA ternary blend with PHB and PBSA shows important differences in morphology. As it has been reported, PLA and PBSA are immiscible [66], but the spherical domains are lower in size than those observed in the ternary PLA/PHB/PBS blend (**Figure 3**) as it can be seen in **Figure 4a** and **Figure 4b**, which correspond to the uncompatibilized PLA₆₀PHB₁₀PBSA₃₀ blend. This particular morphology could be directly related to the higher ductile properties achieved with PBSA in comparison to PBS as above-mentioned. The effects of ELO are not as evident as in ternary blends (**Figure 4c** and **Figure 4d**) with PBS but in a similar way, ELO reacts with all three polyesters to form a compatibilized structure with improved elongation at break. The best mechanical response of ternary blends with PBSA was obtained with ESBO as compatibilizer agent. As it can be seen in **Figure 4e** and **Figure 4f**, the morphology of the fractured surface shows high continuity. In fact, the drop-like structure almost disappears thus leading to improved cohesion, which in turn, is responsible for the high elongation at break values observed.

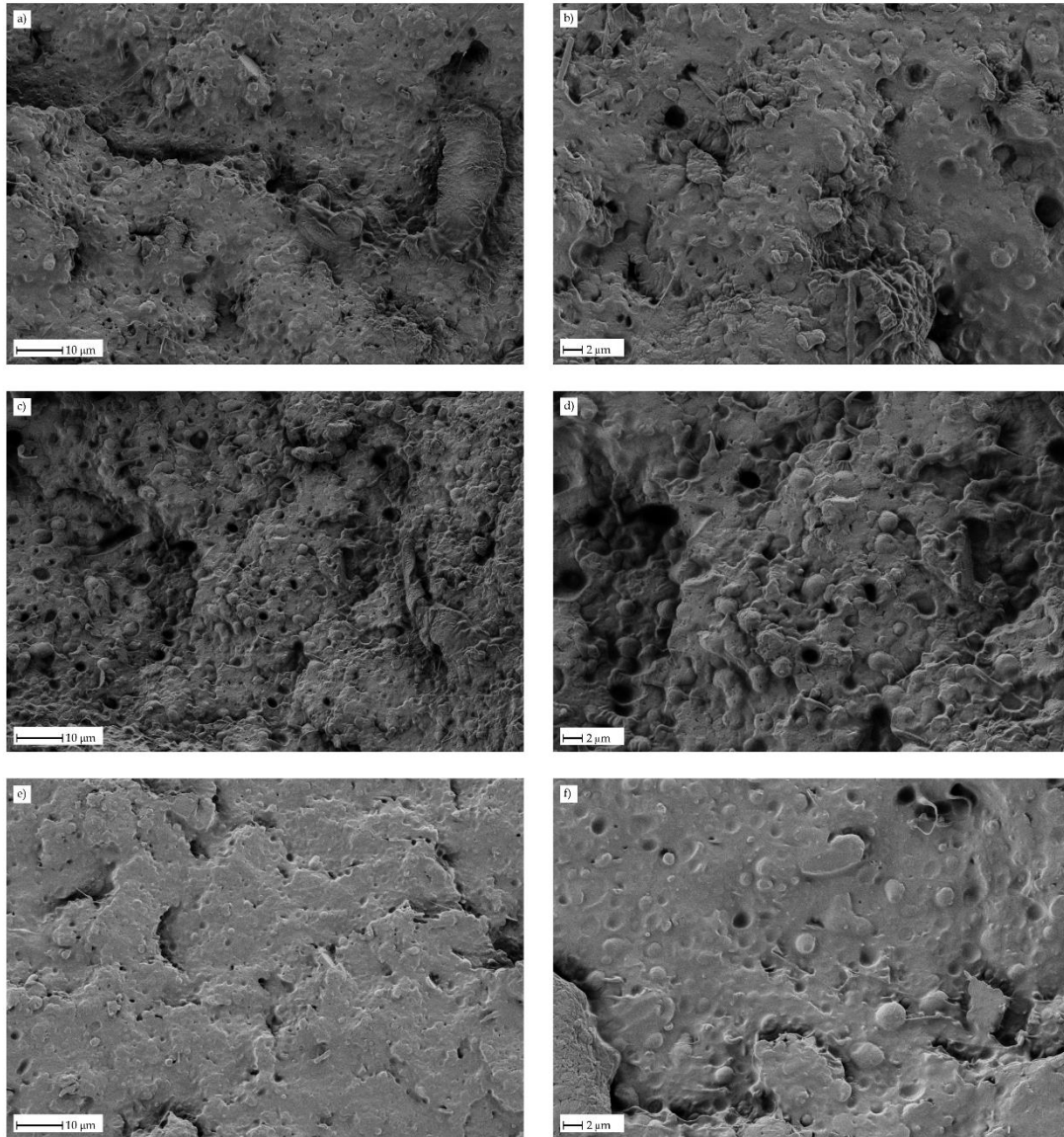


Figure 4 Field emission scanning electron microscopy (FESEM) images at different magnifications (left column - 1000x; right column - 2000x) corresponding to poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate-co-adipate) (PBSA) with different epoxidized vegetable oils (EVOs), a) & b) PLA₆₀PHB₁₀PBSA₃₀, c & d) PLA₆₀PHB₁₀PBSA₃₀/ELO₅, e & f) PLA₆₀PHB₁₀PBSA₃₀/ESBO₅

The impact toughness is directly related to the energy absorption during the deformation/fracture process. This property is highly sensitive to the cohesion of the material and, in turn, it depends on both ductile and resistant properties. Neat PLA is characterized by an extremely low impact strength value (Charpy test on notched samples) of about 1.63 kJ m⁻². In previous works, a remarkable increase in impact strength was observed on PLA ternary blends with PBH and PCL. In fact, the blend with a composition PLA₆₀PHB₁₀PCL₃₀ showed an impact strength of 5.06 kJ m⁻². This value was increased up to twice by using a compatibilizer agent [60]. Substitution of PCL by PBS leads to similar impact strength values of about 5.94 kJ m⁻² (see **Table 4**). The presence of the compatibilizer increases the impact strength up to values of 8.63 kJ m⁻² and 9.41 kJ m⁻² for ELO- and ESBO-compatible blends respectively. Although it seems ESBO gives higher impact strength values in comparison to ELO, it is important to remark that the standard deviation is approximately 0.6 kJ m⁻², so that, the difference is not significant and fits within the standard deviation, so that, both ELO and ESBO give a qualitative improvement on impact strength up to values of about 9 kJ m⁻². With regard to ternary blends with PBSA, the uncompatibilized blend (PLA₆₀PHB₁₀PBSA₃₀) gives a noticeably high impact strength of 8.40 kJ m⁻² which is in accordance with the morphology observed by FESEM as ternary blends with PBSA seem to offer more cohesion than blends with PBS (in addition, PBSA is remarkably much flexible than PBS due to the long adipate chain segments). Addition of compatibilizers improves the impact strength to values of 12.58 kJ m⁻² and 10.40 kJ m⁻² for the ELO- and ESBO-

compatibilized ternary blends respectively. It is evident both modified oils give increased impact strength values but the obtained results suggest ELO contributes to higher impact strength values as even considering the standard deviation, it gives higher values than the ESBO-compatible system. Despite the use of ESBO as compatibilizer gives the highest elongation at break, the higher number of interactions that ELO can contribute to a slightly higher tensile strength. As the impact strength combines both mechanical ductile and resistant properties, it seems that the ELO-compatible ternary blend gives the best results in terms of impact energy absorption. With regard to Shore D hardness, the slight changes are almost negligible but it can be observed the same tendency, i.e. PBSA gives more flexible materials and ESBO-compatible blends offer the lowest values in the corresponding blend.

3.2. Thermal and thermomechanical properties of PLA/PHB blends with PBS or PBSA and different vegetable oil-based compatibilizers

Figure 5 gathers the DSC thermograms. Conventional DSC is helpful to see the main thermal properties. Nevertheless, as it does not use a modulated signal, it cannot separate some overlapped processes. Two clear melting peaks can be identified in each DSC curve. The melt peak located at about 170 °C corresponds to the melting process of the crystalline PLA and remains at this temperature in all the ternary blends thus indicating that the different co-blending materials do not affect its melt peak temperature. It is important to remark that this melt peak overlaps with the melt process of PHB. Nevertheless, as PHB represents only a 10 wt%, its contribution is highly diluted and does not

affect the overall melting process of PLA. A second melt peak can be identified in all the ternary blends at lower temperatures. This peak is located at about 95 °C and 116 °C and corresponds to the melt of the crystalline regions in PBSA and PBS, respectively. The peak corresponding to the melting process of PBSA is remarkably smaller than that of the PBS. This is directly related to their chemical structure. PBS can reach a maximum crystallinity of 45% while PBSA shows a degree of crystallinity comprised between 20 and 35%. It is important to note that the melt peak of both PBS and PBS overlaps with the cold crystallization process of PLA. In fact, the cold crystallization of PLA is restricted by the presence of PHB [67]. With regard to the glass transition temperatures (T_g), it can be identified that corresponding to PLA at about 55 °C but it cannot be clearly seen in all ternary blends. Regarding the T_g of PBS and PBSA, located at -35 °C and -45 °C respectively, as indicated in the technical datasheet, although some evidences of their presence is detectable, these T_{gs} cannot be resolved appropriately by DSC. The most relevant information that DSC thermograms provide is the temperature range in which these ternary blends could be used. In fact, although a softening occurs at 55-60 °C (T_g of PLA), these materials can be used up to 85-90 °C without any melting.

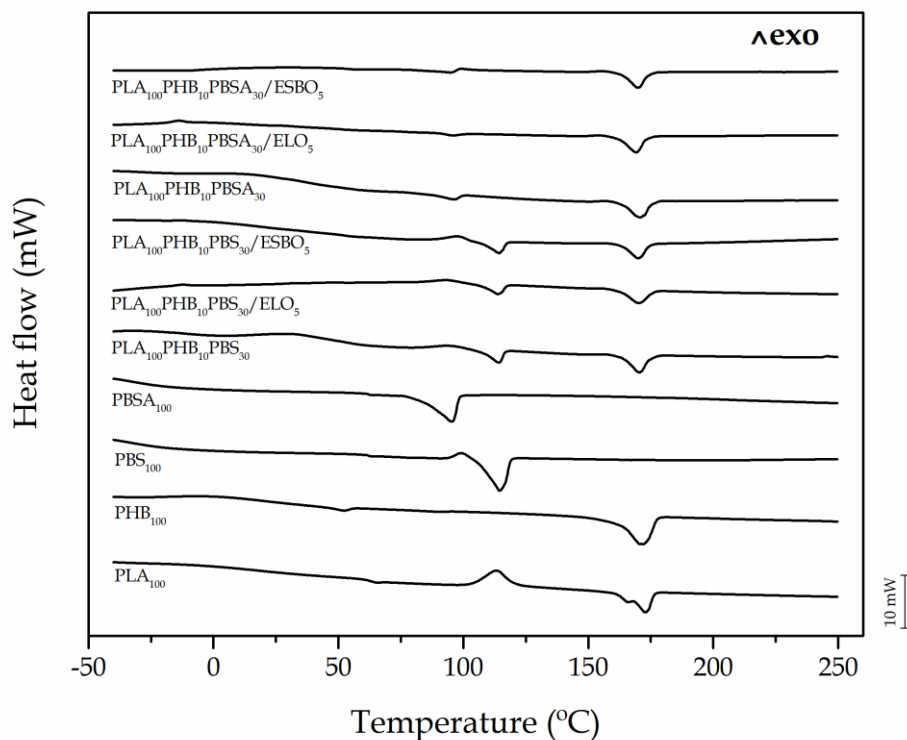
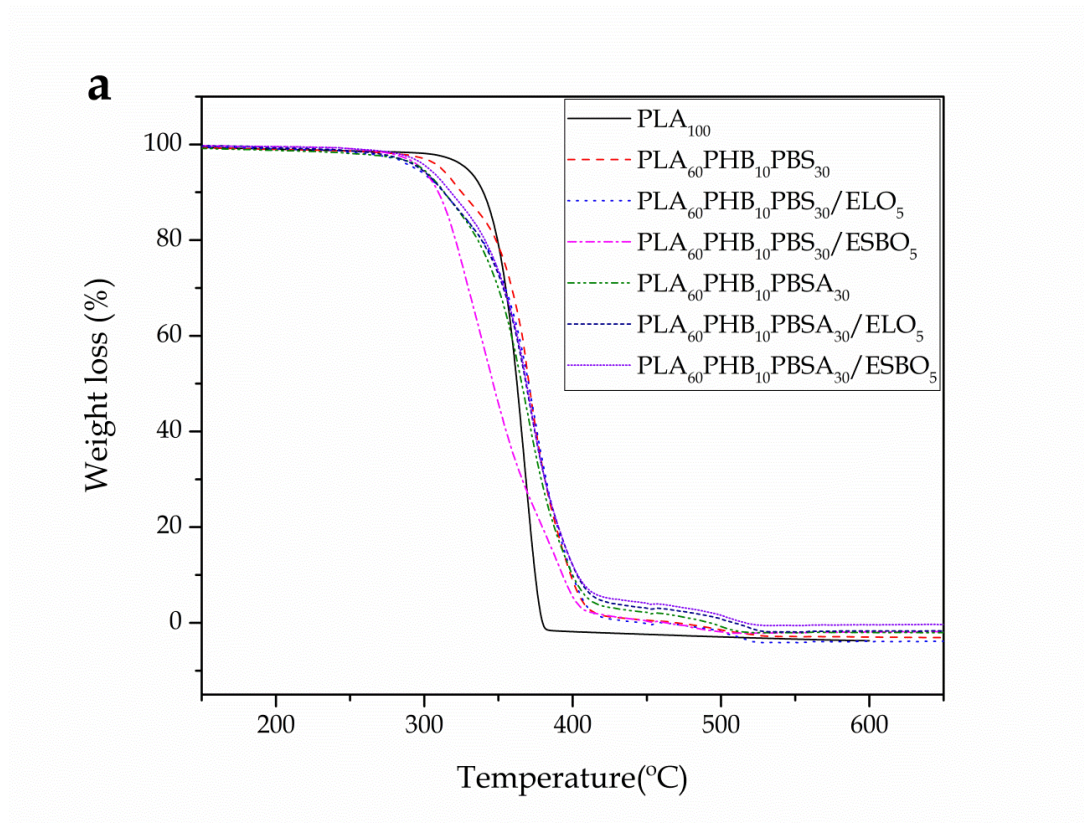


Figure 5 Differential scanning calorimetry (DSC) thermograms corresponding to ternary poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).

With regard to the thermal stability at high temperatures (decomposition conditions), TGA shows interesting findings. **Figure 6** gathers the TGA curves (**Figure 6a**) and the first derivative (DTG) curves (**Figure 6b**). The first important finding is that PBS provides more thermal stability than PBSA to ternary blends. The onset degradation temperature, measured at a weight loss percentage of 5% is 312 °C for the uncompatibilized PLA₆₀PHB₁₀PBS₃₀ blend while the onset for the uncompatibilized PLA₆₀PHB₁₀PBSA₃₀ blend is lower,

around 298 °C. The effect of the compatibilizers, ELO and ESBO shows different tendency depending on the presence of PBS or PBSA on ternary blends. On ternary blends with PBS, addition of both ELO and ESBO leads to slightly lower onset degradation temperatures of 296 °C and 298 °C respectively. On the other hand, the effect of ELO and ESBO on ternary blends with PBSA is different with onset degradation values of 298 °C and 303 °C for ELO and ESBO respectively. This is related to the lower thermal stability of PBSA compared to that of PBS. Anyway, these ternary blends show similar thermal stability than ternary blends of PLA, PHB and PCL as PCL is characterized by a similar degradation onset to PBS [60].



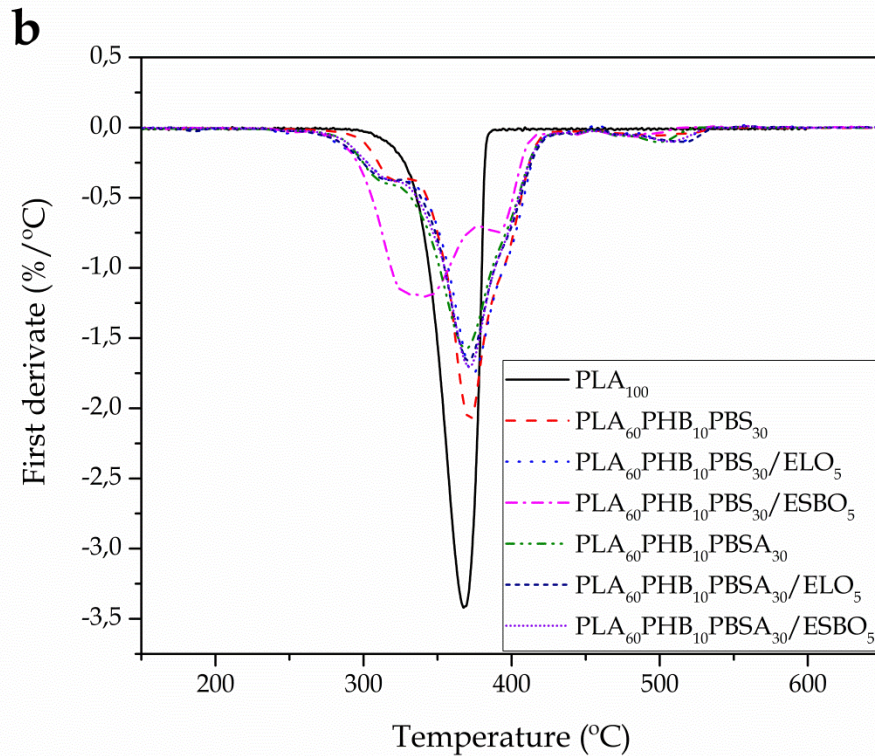


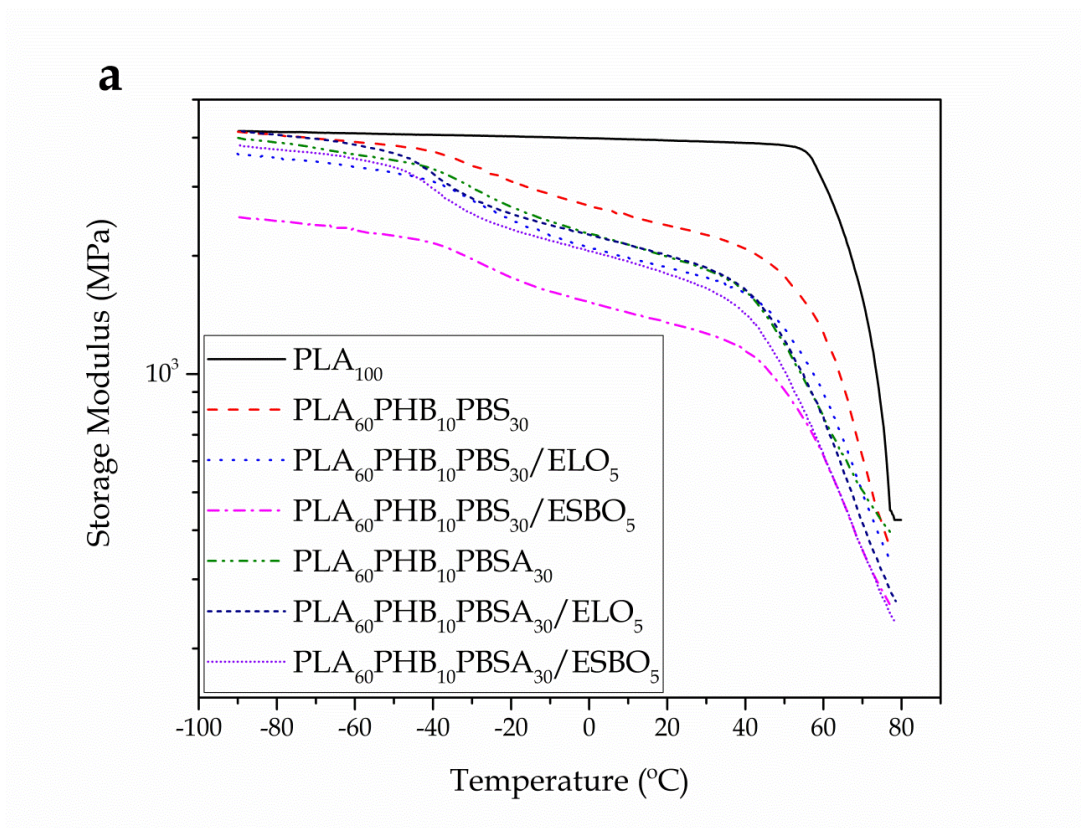
Figure 6 a) Thermogravimetric (TGA) curves and b) first derivative (DTG) of ternary poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).

Dynamic-mechanical thermal analysis (DMTA) gives simultaneous information about the mechanical performance as a function of temperature in dynamic conditions. In particular, the evolution of the storage modulus (E') and the damping factor ($\tan \delta$) are useful to identify the effects of PBS and PBSA on ternary blends as well as the effects of the vegetable oil-based compatibilizers. **Figure 7a** gathers the DMTA curves for all ternary blends containing PBS or PBSA. The uncompatibilized blend with PBS (PLA₆₀PHB₁₀PBS₃₀) shows the highest storage modulus, E' which is in total accordance with the previous

results on mechanical properties. The effect of both ELO and ESBO is a flexibilization that can be observed by a shift of the characteristic curve towards lower E' values. These results agree with those obtained by tensile tests which showed the maximum elongation with ESBO addition. For this reason, the ternary blend with PBS compatibilized with ESBO shows the lowest E' values, compared to ELO-compatibilized and uncompatibilized ternary blend. Similar tendency can be found for the PBSA-based ternary blends. As indicated previously, PBSA is more flexible than PBS, therefore, the PBSA-based ternary blend shows its characteristic storage modulus below that of the PBS-based ternary blend. The effects of both ELO and ESBO are similar as those observed for the PBS-based ternary blend.

An observation of the damping factor (**Figure 7b**) allows to clearly identify the characteristic glass transition temperatures of the main components, PLA and PBS or PLA and PBSA, since PHB only represents a 10 wt% and its contribution to the damping factor is very low. The T_g value of the PLA-rich phase in uncompatibilized ternary blend (PLA₆₀PHB₁₀PBS₃₀) with PBS is 71 °C and is slightly moved to 69 °C with the addition of 5 phr ESBO. Addition of ELO gives the same T_g for PLA-rich phase. This is representative for low miscibility between the three polyesters. With regard to the PBSA-based ternary blend (PLA₆₀PHB₁₀PBSA₃₀), uncompatibilized blend shows a T_g of 67 °C, thus corroborating somewhat more miscibility as shown by FESEM characterization. This T_g value is slightly moved to 68 °C with presence of both ELO or ESBO. The effect of ELO and ESBO on the T_g values of PBS and PBSA is

also negligible. In fact, the T_g of the PBS-rich phase is maintained at about $-27\text{ }^\circ\text{C}$ while the T_g for the PBSA-rich phase is close to $-38\text{ }^\circ\text{C}$. These values are slightly higher to those observed in the technical datasheet thus indicating slight miscibility with PHB and/or PLA which moves T_g to upper values. It is important to remark that the damping factor represents the ratio between the stored energy and the lost energy as observed in composite materials[68, 69]. Neat PLA is a highly stiff polymer and this gives a narrow damping factor peak with high values due to the high stored energy. Nevertheless, all PLA blends show a broader damping factor peak with lower values which means energy dissipation (loss) due to friction between different immiscible phases. This means ternary blends do not store as energy as neat polymer. The fact of blending promotes energy dissipation instead of energy storage.



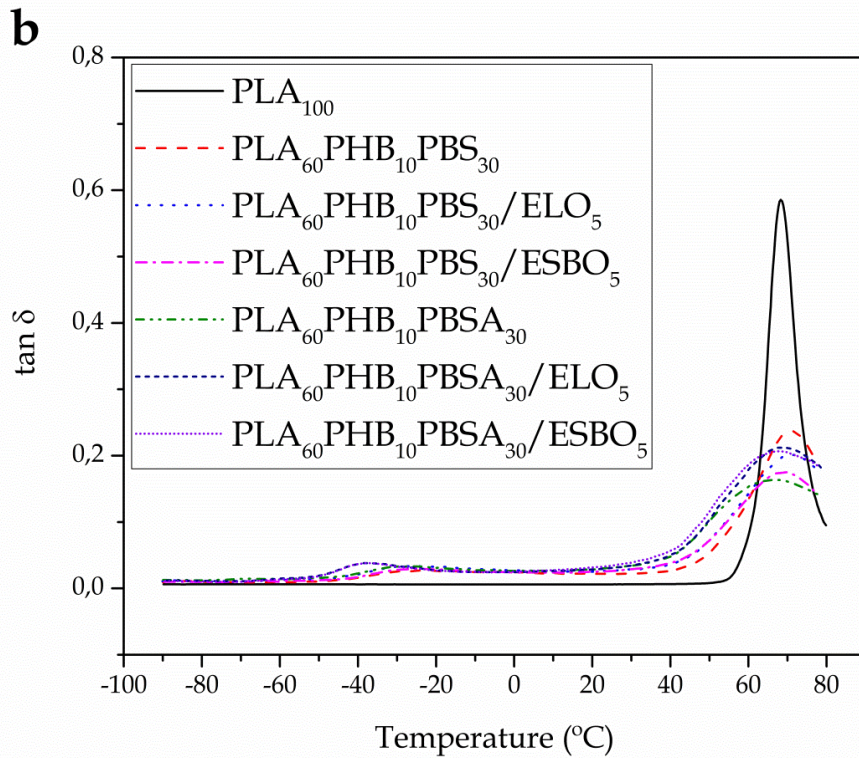


Figure 7 Mechanical-dynamical thermal (DMTA) properties, a) storage modulus (E') and b) damping factor ($\tan \delta$) of ternary poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).

In addition to dynamic-mechanical properties, other thermomechanical properties have been tested. Table 5 gathers information about the Vicat softening temperature (VST), heat deflection temperature (HDT) and the coefficient of linear thermal expansion (CLTE) at different temperature ranges comprised between several T_{gs} . With regard to VST, once again it is possible to see the same tendency as observed in mechanical tests. Uncompatibilized blend

with PBS (PLA₆₀PHB₁₀PBS₃₀) shows a VST value of 60.5 °C which is higher than the corresponding value for the uncompatibilized blend with PBSA (PLA₆₀PHB₁₀PBSA₃₀), located at 57.4 °C. The effect of ELO and ESBo on both ternary systems is the same. A slight decrease in the corresponding VST values can be detected. This decrease is in the 2 - 3 °C range. The same tendency is observed for HDT values. With regard to the CLTE, the same tendency can be detected in all three temperature ranges considered for calculations. Obviously, the CLTE increases with increasing the temperature range. So that, the PBS-based ternary blend (PLA₆₀PHB₁₀PBS₃₀) shows a CLTE of 93.5 $\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ below T_{g1} and increases to values of 113.8 $\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ at the temperature range comprised between T_{g1} and T_{g2} . Finally, above T_{g2} , its CLTE is 242.4 $\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$. As PBSE is more flexible than PBS, the corresponding CLTE values for the uncompatibilized PBSA-based ternary blend (PLA₆₀PHB₁₀PBSA₃₀) are 95.4; 131.1 and 329.0 for the temperature ranges below T_{g1} ; between T_{g1} and T_{g2} and above T_{g2} , respectively. The effects of both ELO and ESBO can be clearly seen by an increase in the corresponding CLTE values. This is specifically pronounced above T_{g1} since below this temperature, the material is completely glassy.

4. Conclusions

Ternary blends with constant content of poly(lactic acid) (PLA) - 60 wt%, poly(3-hydroxybutyrate) (PHB) - 10 wt% were manufactured with two different linear polyesters derived from succinic acid, *i.e.* poly(butylene

succinate) (PBS) and poly(butylene succinate-*co*-adipate) (PBSA) with a constant content of 30 wt%. Uncompatibilized ternary blends based on PBS and PBSA showed a remarkable increase in elongation at break with regard to neat PLA and other ternary blends, thus showing the potential of both PBS and PBSA to obtain highly toughened PLA-based formulations. These ternary blends show a clear phase separation as revealed by field emission scanning electron microscopy (FESEM) with PLA-rich phase in which, the other main component (PBS or PBSA) is fine dispersed with the typical drop-like structure. FESEM also revealed more compatibility in ternary blends with PBSA. Although these uncompatibilized blends offer interesting properties, the poor interaction hinder the reach of even more improved mechanical properties. For this reason, two commercially available epoxidized vegetable oils, i.e. epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO) were used. In general, both modified vegetable oils contribute to a remarkable increase in elongation at break and impact toughness and do not compromise in a great extent other mechanical properties. In addition, PBS and PBSA represent an alternative to poly(ϵ -caprolactone) (PCL) which is another flexible polyester, widely used to improve PLA toughness. PBS and PBSA offer an interesting advantage versus PCL as their melt peak temperature are higher (around 100 °C) to that of PCL which is close to 60 °C.

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Tables

Polymer	Density, (g cm ⁻³)	Melt flow index, MFI (g/10 min)	Glass transition temperature, T _g (°C)	Melt temperature, T _m (°C)
Poly(lactic acid) (PLA)	1.24	15-30 @210 °C	60	170
Poly(3-hydroxybutyrate) (PHB)	1.25	10 @180 °C	-5	170
Poly(butylene succinate) (PBS)	1.26	20-34 @190 °C	-32	114
Poly(butylene succinate-<i>co</i>- adipate) (PBSA)	1.23	20-34 @190 °C	-45	94

Table 1. Summary of the main properties of poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (PHB), poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-adipate) (PBSA), used for ternary blends.

Code	Blend composition (wt%)				Compatibilizer content (phr)	
	PLA	PHB	PBS	PBSA	ELO	ESBO
PLA ₁₀₀	100	-	-	-	-	-
PLA ₆₀ PHB ₁₀ PBS ₃₀	60	10	30	-	-	0
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ELO ₅	60	10	30	-	5	-
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ESBO ₅	60	10	30	-	-	5
PLA ₆₀ PHB ₁₀ PBSA ₃₀	60	10	-	30	-	-
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ELO ₅	60	10	-	30	5	-
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ESBO ₅	60	10	-	30	-	5

Table 2. Composition and coding of poly(lactic acid) (PLA) ternary blends with poly(3-hydroxybutyrate) (PHB) and succinic acid-derived polyesters, poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-adipate) (PBSA).

Code	E (MPa)	σ_t (MPa)	ϵ(%)
PLA ₁₀₀	3514 ± 64	57.6 ± 1.2	7.6 ± 0.5
PLA ₆₀ PHB ₁₀ PBS ₃₀	1902 ± 87	53.4 ± 1.5	49.3 ± 17.8
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ELO ₅	1792 ± 34	43.3 ± 1.1	115.2 ± 35.8
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ESBO ₅	1816 ± 46	42.5 ± 2.2	160.4 ± 36.4
PLA ₆₀ PHB ₁₀ PBSA ₃₀	1715 ± 53	42.7 ± 2.5	62.9 ± 5.7
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ELO ₅	1660 ± 99	35.6 ± 2.1	132.1 ± 39.8
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ESBO ₅	1701 ± 115	35.1 ± 1.7	168.8 ± 8.2

Table 3. Summary of mechanical properties obtained by tensile tests on ternary poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).

Code	Impact strength (kJ m ⁻²)	Shore D hardness
PLA ₁₀₀	1.59 ± 0.29	75.6 ± 1.3
PLA ₆₀ PHB ₁₀ PBS ₃₀	5.94 ± 0.44	75.5 ± 1.4
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ELO ₅	8.63 ± 0.65	75.1 ± 1.2
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ESBO ₅	9.41 ± 0.59	74.3 ± 1.9
PLA ₆₀ PHB ₁₀ PBSA ₃₀	8.40 ± 0.68	73.9 ± 1.9
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ELO ₅	12.58 ± 0.57	74.6 ± 0.7
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ESBO ₅	10.40 ± 0.44	72.9 ± 1.8

Table 4. Summary of mechanical properties obtained by Charpy impact test and Shore D hardness of poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).

Code	VST (°C)	HDT (°C)	CLTE ($\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$) by TMA		
			Below T _{g1}	Above T _{g1}	Above T _{g2}
PLA ₁₀₀	60.9 ± 0.4	54.9 ± 0.3	-	95.7 ± 0.7	148.5 ± 0.6
PLA ₆₀ PHB ₁₀ PBS ₃₀	60.5 ± 0.5	47.4 ± 0.5	93.5 ± 0.3	113.8 ± 0.4	242.4 ± 0.5
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ELO ₅	56.6 ± 0.6	45.9 ± 0.4	89.9 ± 0.8	131.0 ± 0.6	266.9 ± 0.9
PLA ₆₀ PHB ₁₀ PBS ₃₀ /ESBO ₅	58.8 ± 0.5	46.3 ± 0.5	87.8 ± 1.3	133.5 ± 0.9	253.4 ± 0.5
PLA ₆₀ PHB ₁₀ PBSA ₃₀	57.4 ± 0.3	46.8 ± 0.4	95.4 ± 0.9	131.1 ± 0.7	329.0 ± 0.6
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ELO ₅	55.6 ± 0.5	45.6 ± 0.4	83.7 ± 1.2	140.8 ± 1.5	355.3 ± 0.9
PLA ₆₀ PHB ₁₀ PBSA ₃₀ /ESBO ₅	56.2 ± 0.4	46.5 ± 0.3	94.5 ± 0.9	129.0 ± 1.3	262.8 ± 1.6

Table 5. Summary of thermomechanical properties obtained by thermomechanical analysis (TMA) on ternary poly(lactic acid) (PLA) blends with poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) or poly(butylene succinate-*co*-adipate) (PBSA) with different epoxidized vegetable oils (EVOs).