

Manufacturing and compatibilization of PLA/PBAT binary blends by cottonseed oil-based derivatives

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Abstract. This research work aims at the compatibilization of poly(lactic acid)/poly(butylene adipate-co-terephthalate), PLA/PBAT binary blends by using cottonseed oil derivatives, *i.e.* epoxidized (ECSO) and maleinized (MCSO) cottonseed oil. The potential of these vegetable oil-based compatibilizers are compared versus the effects of a conventional styrene-acrylic oligomer. The base PLA/PBAT binary blend composition was 80 wt% PLA/20 wt% PBAT and the amount of compatibilizer was set to 1 and 7.5 wt%. The effects of the different compatibilizers were evaluated on PLA/PBAT films in terms of mechanical and thermal properties as well as blend's morphology by field emission scanning electron microscopy (FESEM). Complementary, biodegradation tests in controlled compost soil and surface properties were evaluated to assess the effects of the compatibilizers. Addition of 1 wt% ECSO and MCSO led to a remarkable increase in the elongation at break up to values over 100% with regard to neat PLA. Despite this, maximum elongation at break was obtained for the compatibilized PLA/PBAT blend with 7.5 wt% MCSO, reaching values of about 321.2% respect neat PLA keeping mechanical resistant properties, such as Young's modulus and tensile strength, at high levels. Therefore, vegetable oil-derived compatibilizers stand out as environmentally friendly additives for PLA/PBAT binary blends with improved properties.

Keywords: biopolymers, biocomposites, poly(lactic acid), cotton seed oil, maleinization

1. Introduction

Poly(lactic acid), PLA is currently considered as one of the most promising polymers from renewable resources, due to an excellent balance between mechanical properties and a competitive price day by day [1]. Nevertheless, it is intrinsically quite brittle, its chemical barrier behavior is not optimum compared to other widely used polymers, its thermal stability is also restricted and its resistance to external agents (UV radiation, moisture, etc.) are issues to overcome. For this reason, industrial PLA and other polymer formulations usually contain several additives with different purposes thus widening its use in sectors such as agriculture [2], packaging [3, 4],

medical devices [5], 3D printing, textile fibers [6]. With the aim of a sustainable development and a low environmental impact, biobased additives are been searched, *i.e.* antioxidants, plasticizers, fillers, etc. [7–10]. With the increasing development of nanotechnology, many research works have been focused of using nanostructures to improve the properties of PLA-based materials [11–13] and interactions.

Typical PLA materials are characterized by low toughness and this is one of the main drawbacks in a massive use of this biopolyester. A broad range of approaches has been observed in the last decade to minimize this effect Xu *et al.* [14] reported a new

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injection molding technology (oscillating shear) to improve all properties of PLA, including its toughness. One of the easiest methods to overcome the intrinsic brittleness of PLA is by physical blends with ductile polymers [15]. A wide variety of binary and ternary blends with PLA have been proposed as a technical solution to improve toughness. Among others, it is worthy to note some interesting PLA-based blends with poly(ϵ -caprolactone)(PCL) [16], thermoplastic starch (TPS) [17], poly(butylene succinate) (PBS) [18], poly(butylene succinate-*co*-adipate) (PBSA) [19], poly(glycolic acid) (PGA) [20], poly(hydroxybutyrate) (PHB) [21], poly(hydroxybutyrate-*co*-valerate) (PHBV) [22], poly(butylene adipate-*co*-terephthalate) (PBAT) [23], etc. Ternary blends allow obtaining tailored properties in PLA-based blends [24, 25]. Despite some increase in mechanical ductile properties are achieved with these blends, most of PLA-based blends show partial or total immiscibility, being this an important drawback to obtain synergistic effects. To improve compatibility between immiscible or partially miscible polymers, different approaches have been proposed. Reactive extrusion stands out as a cost effective alternative to copolymerization [26]. Reactive extrusion with PLA considers chemical reactions with some additives such as triphenyl phosphite, adimides (*e.g.* Bioadimide[®]), epoxy-based styrene-acrylic oligomers (*e.g.* Joncryl[®]), glycidyl copolymers [27], etc. with the hydroxyl terminal groups present in PLA and other biobased polyesters. This allows chain extension and/or branching with a positive effect on compatibilization of both polymers in the blend with a subsequent improvement in toughness. Ojijo *et al.* [28] developed PLA/PBSA blends with 2% triphenyl phosphite (TPP). They reported an increase in elongation at break of 37% and the energy absorption changed from 6.76 kJ·m⁻² (neat PLA) up to 16.4 kJ·m⁻² for the PLA blend with 10% PBSA and 2% TPP. Over 2% TPP, over-crosslinking occurs and properties are not improved. Al-Itry *et al.* [29] studied the effect of Joncryl ADR-4368 (an epoxidized styrene-acrylic oligomer) on PLA/PBAT blends. In fact, they reported a percentage increase in the elongation at break of 900% with regard to neat PLA. In addition, the other mechanical properties were not affected to a great extent, since the effect of this oligomer is not only chain extension, but also branching and/or crosslinking as reported by Torres-Giner *et al.* [30].

Similar results have been reported with reactive extrusion by generating free radicals during the extrusion process, which can be achieved by using organic peroxides. This leads to a combination of chain extension, branching and crosslinking. Bureepukdee *et al.* [31] compared the compatibilizing effect of di(*tert*-butylperoxy isopropyl) benzene (DTBP) and 2, 5-dimethyl-2, 5-(*t*-butylperoxy) hexane (DTBH). They reported a continuous phase by using 0.1 phr DTBP on a binary PLA blend with 40% PBSA with a remarkable increase in ductility.

With the aim of obtaining high environmentally friendly PLA formulations, the use of vegetable-oil (VO)-derived additives is increasing as vegetable oils can be chemically modified to tailor some particular functionalities which can react with PLA and other biopolyesters. Currently, epoxidized vegetable oils (EVOs) are widely used in the new generation of environmentally friendly plasticized PVC formulations [32, 33] and thermosetting resins [34]. Their use in the packaging industry is attracting due to low migration rates towards the food [35]. A new generation of biobased poly(urethanes) has been developed by using vegetable oil-derived polyols [36]. Modified vegetable oils could potentially act as compatibilizers in binary and ternary blends. Some vegetable oils (those with unsaturated fatty acids such as oleic, linoleic, linolenic, etc.) can be subjected to a wide variety of chemical modifications such as epoxidation, acrylation, hydroxylation, maleinization, etc. among others. With these processes, oxirane rings, acrylic groups, hydroxyl groups and maleic anhydride, and other functional groups can be added to the vegetable oil structure thus increasing their reactivity towards terminal hydroxyl groups in PLA and other biopolyesters.

In previous works, cotton seed oil (CSO) was chemically modified by conventional epoxidation process [35] to obtain epoxidized cotton seed oil (ECSO). Moreover, CSO was subjected to a maleinization process with maleic anhydride [37] to give maleinized cotton seed oil (MCSO). Both CSO-derivatives showed a clear plasticization effect on PLA. Specifically, the addition of 10 wt% ECSO led to a noticeable increase in elongation at break up to values of 110% of PLA, characterized by an elongation at break close to 9%. Similar findings were obtained with MCSO. Ferri and coworkers [38, 39] studied the effect of maleinized linseed oil (MLO) as compatibilizer in PLA/TPS blends. Two different phenomena

were attributed to MLO: on one hand, a clear plasticization effect was observed but on the other hand, MLO also acted as a compatibilizer with a remarkable improvement on miscibility on such binary blends. Furthermore, MLO contributed to improve the processing of PLA/TPS blends.

The main aim of this research work is to assess the potential of cottonseed oil derivatives, *i.e.* epoxidized cottonseed oil (ECSO) and maleinized cottonseed oil (MCSO) as compatibilizers in PLA/PBAT binary blends. The effect of these two vegetable oil-derived compatibilizers is compared with a conventional epoxy styrene-acrylic oligomer in terms of mechanical properties, thermal stability, thermomechanical properties and blend's morphology. The novelty of this work is the assessment of cottonseed oil as potential base material for blend compatibilization with comparable features to other commercially available modified-vegetable oils. This widens the use of cottonseed wastes in industrial applications and contributes to high biobased content materials.

2. Experimental

2.1. Materials

The PLA grade used was Ingeo™ Biopolymer 2003 D supplied by NatureWorks LLC (Minnetonka, USA) in pellet form with a density of $1.24 \text{ g}\cdot\text{cm}^{-3}$ and a melt flow index of $6 \text{ g}/(10 \text{ min})$ measured at 210°C . A PBAT commercial grade Biocosafe™ 2003 F was supplied by Xinfu Pharmaceutical Co. Ltd. (Zhejiang, China) and it is characterized by a density of $1.25 \text{ g}\cdot\text{cm}^{-3}$ and a melt flow index $<6 \text{ g}/(10 \text{ min})$ at 190°C . PBAT has been selected because of its flexibility (an average tensile strength of 14 MPa and an elongation at break of 525%) which can contribute to improve toughness of PLA.

Two cottonseed oil derivatives, *i.e.* epoxidized cottonseed oil (ECSO) and maleinized cottonseed oil (MCSO) were used as compatibilizers, and compared with an epoxy styrene-acrylic oligomer, *i.e.* Joncryl®. The cottonseed oil (CSO) was supplied by Sigma Aldrich Spain (Madrid, Spain). Its main properties are a density of $0.92 \text{ g}\cdot\text{cm}^{-3}$ and an iodine index comprised in the $109\text{--}120$ range, which allows chemical modification. Joncryl® ADR-4368 was supplied by BASF S.A (Barcelona, Spain) and is characterized by a T_g of 54°C , an epoxy equivalent weight of $285 \text{ g}\cdot\text{mol}^{-1}$ and a molecular weight, M_w of $6800 \text{ g}\cdot\text{mol}^{-1}$. The cottonseed oil was subjected

to epoxidation [40] and maleinization as reported in previous works [37]. The most relevant parameters obtained after the corresponding chemical processes are as follows. With regard to ECSO, the oxirane oxygen index was 5.32 after 8 h . Regarding MCSO an acid value of $63.72 \text{ mg KOH g}^{-1}$ was obtained after 3 h reaction. Figure 1 shows a schematic representation of the base polymers and the compatibilizer additives.

2.2. Manufacturing of PLA/PBAT films

PLA/PBAT blends were manufactured with different compositions as summarized in Table 1. The amount of Joncryl® was set to $1 \text{ wt}\%$ as the manufacturer recommends an additive load comprised between $0.25\text{--}2 \text{ wt}\%$. With regard to the cottonseed oil derivatives, two different loads were used, *i.e.* 1 and $7.5 \text{ wt}\%$ as previous results have suggested [35, 37]. PLA was dried for 24 h at 60°C while PBAT was dried overnight at 40°C . All materials were processed by extrusion in a DSM Xplore MC 15 micro compounder at 180°C . The pre-mixing time inside the plasticization chamber was set to 3 min at a rotating speed of 100 rpm . After this time, the compounded material was forced to exit the plasticization chamber and extruded through a nozzle connected to a chill-roll system to obtain a continuous film, 30 mm width and $30 \mu\text{m}$ thick films at 15 rpm and a controlled force of 700 N .

2.3. Mechanical characterization

Mechanical characterization was carried out as indicated according to the ISO 527-3 standard in a universal test machine LLOYD 30 K (Hampshire, England). Samples (type 2) were tested at a crosshead speed rate of $5 \text{ mm}\cdot\text{min}^{-1}$ with a load cell of 500 N . The samples sized 160 mm in length, 20 mm width and an average thickness of $30 \mu\text{m}$. Special grips for thin films supplied by LLOYD (TG series) were used to appropriate characterize films avoiding premature fracture due to the clamp force. These grips are used for tensile testing of thin materials such as paper, rubber, thin plastic films, woven and non-woven textiles. At least five parallel samples were tested at room temperature and average values of the main parameters were calculated.

2.4. Morphological characterization

The fracture surface obtained by cryofracture (longitudinal to the extrusion direction) was observed in

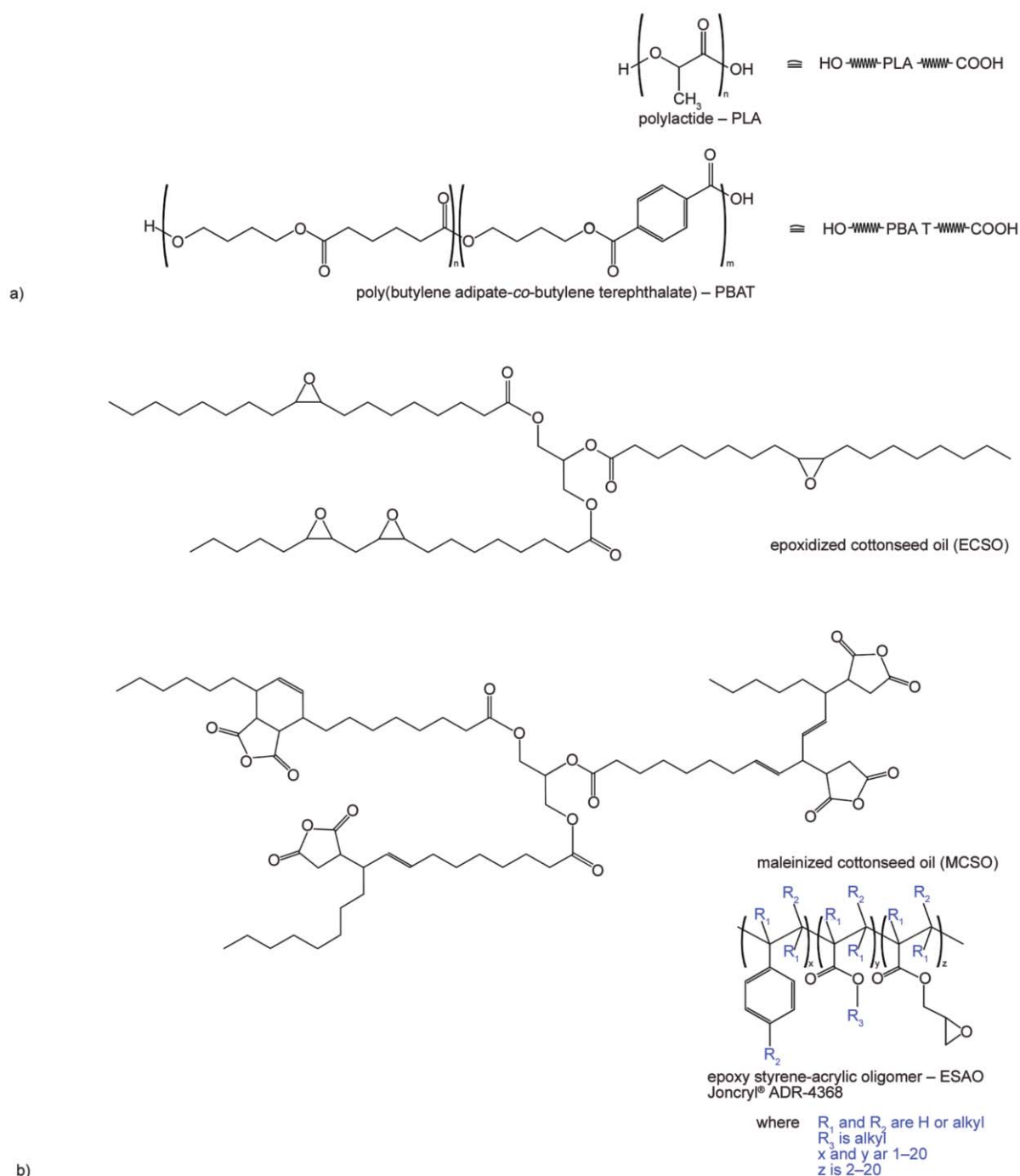


Figure 1. Schematic representation of the chemical structure of a) base polymers, *i.e.* poly(lactic acid) – PLA and poly(butylene adipate-co-terephthalate) – PBAT and b) epoxidized cottonseed oil – ECISO, maleinized cottonseed oil – MCSO and epoxy styrene-acrylic oligomer Joncryl® (generic structure).

a field emission scanning electron microscope, FESEM Zeiss Ultra from Oxford Instruments at an acceleration voltage of 2 kV. An ultrathin metallic layer of platinum was sputtered on the fractured films in a sputter coater EM MED020 from Leica Microsystems.

2.5. Thermal and thermomechanical characterization of PLA/PBAT films

The most relevant thermal transitions were obtained by differential scanning calorimetry (DSC) in a Mettler–Toledo DSC mod. 821 (Schwerzenbach, Switzerland). The DSC runs were programmed into three

Table 1. Composition and coding of PLA/PBAT binary blends compatibilized with cottonseed oil derivatives.

Code	PLA [wt%]	PBAT [wt%]	Joncryl® [wt%]	ECSO [wt%]	MCSO [wt%]
PLA	100.0	–	–	–	–
PBAT	–	100.0	–	–	–
PLA/PBAT	80.0	20.0	–	–	–
PLA/PBAT/1 ECSO	79.2	19.8	–	1.0	–
PLA/PBAT/7.5 ECSO	74.0	18.5	–	7.5	–
PLA/PBAT/1 MCSO	79.2	19.8	–	–	1.0
PLA/PBAT/7.5 MCSO	74.0	18.5	–	–	7.5
PLA/PBAT/1 Joncryl®	79.2	19.8	1.0	–	–

stages: first a heating from -25 to 200 °C; then a cooling process down to -25 °C and a final heating stage up to 200 °C again. All three stages used the same heating rate of 10 °C·min $^{-1}$ and were run under nitrogen atmosphere (66 mL·min $^{-1}$). The degree of crystallinity (χ_c [%]) was calculated from the second DSC heating runs using Equation (1):

$$\chi_c [\%] = 100 \cdot \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m (100\%)} \cdot \frac{1}{W_{PLA}} \quad (1)$$

where ΔH_m and ΔH_{cc} stand for the melt and cold crystallization enthalpies respectively [$J \cdot g^{-1}$]. On the other hand, $\Delta H_m (100\%)$ represents the melt enthalpy of a theoretical fully crystalline PLA ($93 J \cdot g^{-1}$) [21] and W_{PLA} is the wt% PLA in the blend. With regard to the glass transition temperature, ISO 11357-2:2015 was used. From the methods described in this standard, the inflection point was considered as the T_g value of all developed materials. In this method, the T_g value is assigned to the maximum of the derivative DSC curve or the temperature with the maximum slope in the glass transition area.

Thermal degradation at high temperatures was followed by thermogravimetric (TGA) analysis. Samples with an average weight of about 5 – 7 mg were placed in standard alumina pans and subjected to a heating program from 30 up to 660 °C at a heating rate of 20 °C·min $^{-1}$ in a Mettler-Toledo TGA/SDTA851e/SF/1100 thermobalance in nitrogen atmosphere. In addition to the TGA thermograms, two representative temperatures, were calculated: $T_{5\%}$ and $T_{50\%}$ which correspond to temperatures at which a 5 and a 50 wt% loss occurs, respectively.

Thermomechanical characterization of PLA/PBAT films was carried out in an oscillatory rheometer AR G2 from TA Instruments equipped with a special clamp system for solid samples working in a

combined shear-torsion mode. Samples of 10×20 mm 2 with an average thickness of 30 μ m, were subjected to a temperature sweep from -40 up to 100 °C at a heating rate of 2 °C·min $^{-1}$. The selected frequency was 1 Hz and the normal force was 0.02 N while the maximum deformation was maintained at 1% ($\% \gamma$).

2.6. Surface characterization of PLA/PBAT films

The wetting properties of the developed blends were obtained by contact angle measurements in a Krüss goniometer model FM140 from KRÜSS GmbH (Hamburg, Germany). Five water droplets were deposited onto the film surface and the corresponding contact angle was measured after 30 s to obtain stabilized values. Prior to contact angle characterization, sample films were dried at 40 °C for 24 h.

In addition, the color properties of the developed films were characterized in a Hunter Mod. CFLX-DIF-2 colorimeter from Hunterlab (Murnau, Germany). Although the apparatus can provide different measurements, only the luminance (L^*) was measured to evaluate the change in transparency.

2.7. Disintegration in controlled compost soil of PLA/PBAT films

Disintegration tests were conducted on squared samples (25×25 mm 2) with an average thickness of 30 μ m under the recommendations of the ISO 20200. Samples were placed into an aerobic reactor with a synthetic waste manufactured as indicated in ISO 20200. Before placing samples into the reactor, all films were dried at 40 °C for 24 h. Then, the films were buried into the compost soil and extracted at 6 , 8 , 9 , 10 , 11 , 14 , 16 , 21 and 23 days, washed with distilled water and dried at 40 °C for a day. Finally, optical images were taken to follow the disintegration process.

3. Results and discussion

3.1. Effect of compatibilizers on mechanical properties of PLA/PBAT films

Figure 2 shows the main results obtained with the herein-developed PLA/PBAT blends. As it can be seen, neat PLA is quite brittle with a modulus of 3145 MPa and a tensile strength of 54.5 MPa. Regarding its ductility, its elongation at break is close to 29.2% (in film form).

These features limit the use of PLA in the packaging industry in which flexible films are required. On the other hand, PBAT is an extremely ductile polymer with a modulus of 96.4 MPa and a tensile strength of 26.2 MPa. In contrast, its elongation at break reaches values of 307.6% thus giving clear evidences of its flexibility. For this reason, blends of PLA with PBAT are expected to be more flexible. As it can be seen in the above-mentioned figures, the uncompatibilized PLA/PBAT blend containing 20 wt% PBAT shows an increased elongation at break of 59.0% with interesting mechanical resistant properties, *i.e.* a Young modulus of 2079 MPa and a tensile strength of 39.9 MPa. The addition of 1 wt% Joncryl[®] gives similar mechanical resistance properties (modulus and tensile strength) while the elongation at break is remarkably improved up to 83.7% compared to the uncompatibilized blend. These results give clear evidences of the compatibilization effects that Joncryl[®] can provide to polyesters. Specifically, the compatibilization is achieved by the reaction of the epoxy

groups in Joncryl[®] oligomers and the hydroxyl terminal groups in polyesters (See Figure 3a) leading to chain extension and potential crosslinking. Racha Al-Itry *et al.* [29] reported similar results with a PLA/PBAT blend with an elongation at break of 50% which was increased up to 135% with the addition of 0.5 wt% Joncryl[®]. Addition of 1 wt% of both ECSO and MCSO leads to an increase in elongation at break with values of 70.0 and 60.5% respectively but this increase is not as high as that observed with Joncryl[®]. Nevertheless, it is worthy to note that both 1 wt% ECSO and MCSO provide improved mechanical resistant properties with tensile strength values of 52.9 and 45.0 MPa respectively which are noticeable higher than those of Joncryl[®] (39.9 MPa). This suggests that both ECSO and MCSO (even at very low concentrations) provide a plasticizing effect but due to the triglyceride structure, not only chain extension but also branching and somewhat crosslinking, can occur as shown in Figure 3b. It has been reported that small amounts of modified vegetable oils can slightly plasticize PLA and other polyesters. Nevertheless, the efficiency of vegetable oil-based plasticizers is very poor as, in general, a very slight decrease on the glass transition temperature is achieved. Nevertheless, the highly reactive groups in modified vegetable oils (mainly epoxy, acrylate, maleic anhydride groups, among others) can react with hydroxyl groups present in the end chains of polyesters thus leading to additional reactions that could lead to

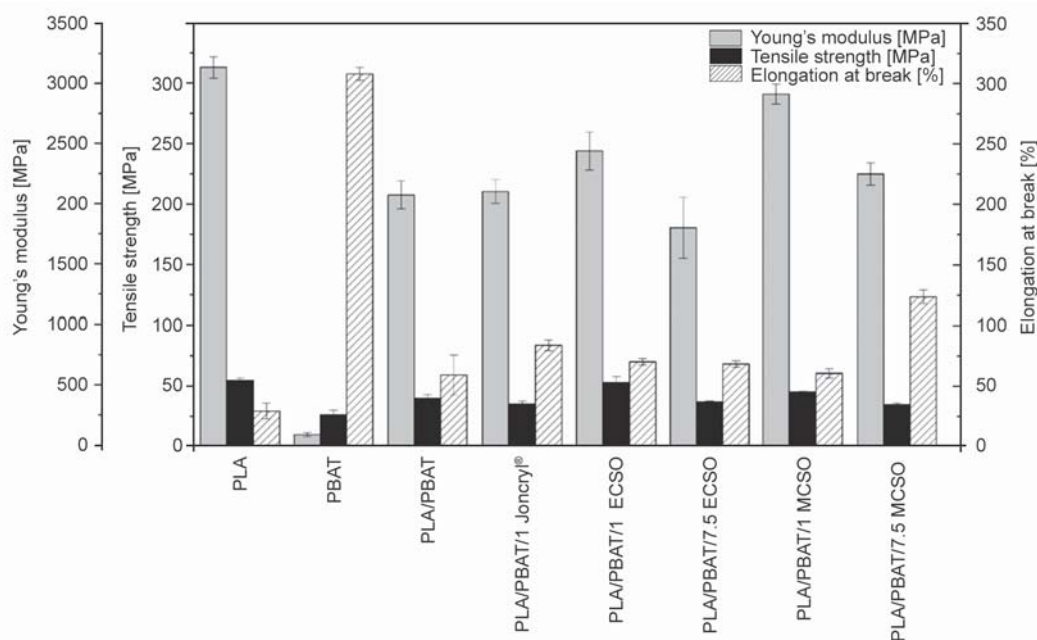


Figure 2. Comparative bar plot of tensile properties, *i.e.* Young's modulus, tensile strength and elongation at break, of neat PLA, neat PBAT and PLA/PBAT blends with and without compatibilizers.

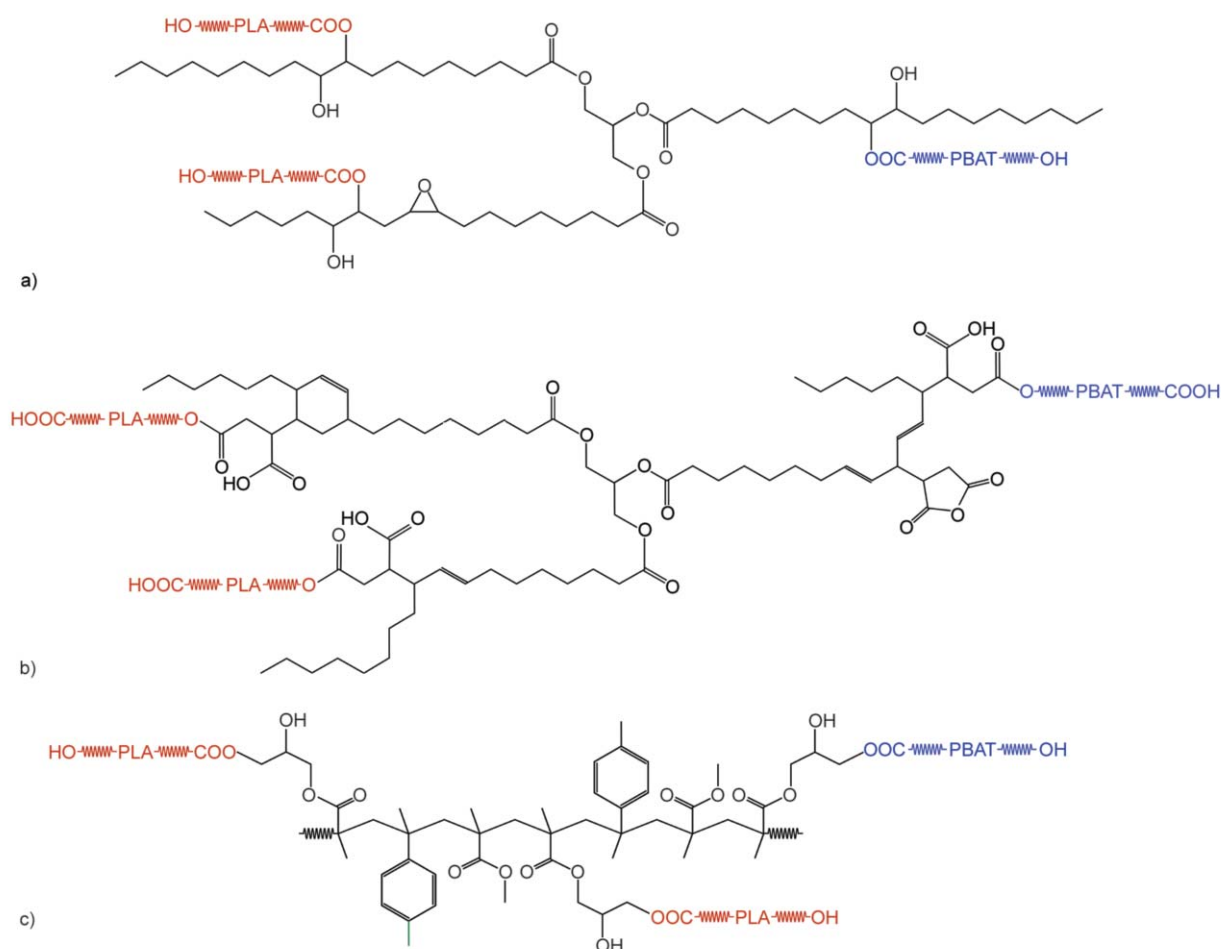


Figure 3. Schematic representation of a) ECSO compatibilized PLA/PBAT blend, b) MCSO compatibilized PLA/PBAT blend and c) Joncryl[®]-compatibilized PLA/PBAT blend.

chain extension, branching and crosslinking simultaneously as reported by Quiles-Carrillo and coworkers [41–43] in several works. With regard to Joncryl[®], typical amounts of 1 wt% are recommended by suppliers to avoid gel formation by crosslinking. So that, it is expectable a more intense overlapping of chain extension, branching and crosslinking when using ECSO and MCSO than in the case of Joncryl[®] (Figure 3c). A FTIR study carried out by Quiles-Carrillo *et al.* [43] on poly(lactic acid) with lignocellulosic fillers demonstrated the reaction between maleinized linseed oil (MLO) and hydroxyl groups in PLA end chains and cellulose particles therefore giving clear evidences of reactive extrusion.

3.2. Effect of compatibilizers on the morphology of PLA/PBAT films

The addition of 7.5 wt% ECSO does not provide any improvement on mechanical ductility nor mechanical resistance. Nevertheless, PLA/PBAT blend compatibilized with 7.5 wt% MCSO offers the maximum elongation at break of all developed formulations,

reaching values of 123.0% without compromising in a remarkable way other mechanical resistance properties such as modulus and tensile strength. Figure 4 shows some evidences of the compatibilizing effect of the different additives used in this study. It has been reported that PLA/PBAT system can show miscibility, partial miscibility or even, immiscibility [44] with 20 wt% PBAT. As it can be observed in Figure 4b, PLA/PBAT does not show the typical droplet-like structure of immiscible polymer blends but DSC and DMA results suggest poor miscibility as it will be discussed later. It is possible to expect that PBAT-rich domains are very small. On the other hand, neat PLA (Figure 4a) shows a smooth surface typical of a brittle fracture. Addition of 1 wt% of the different compatibilizers provides some differences. The PLA/PBAT blend compatibilized with 1 wt% ECSO (Figure 4d) shows a smooth fracture surface similar to that of the PLA/PBAT blend and some small spherical domains can be detected, while PLA/PBAT blends compatibilized with Joncryl[®] or MCSO show presence of cavities/voids and filaments in the longitudinal

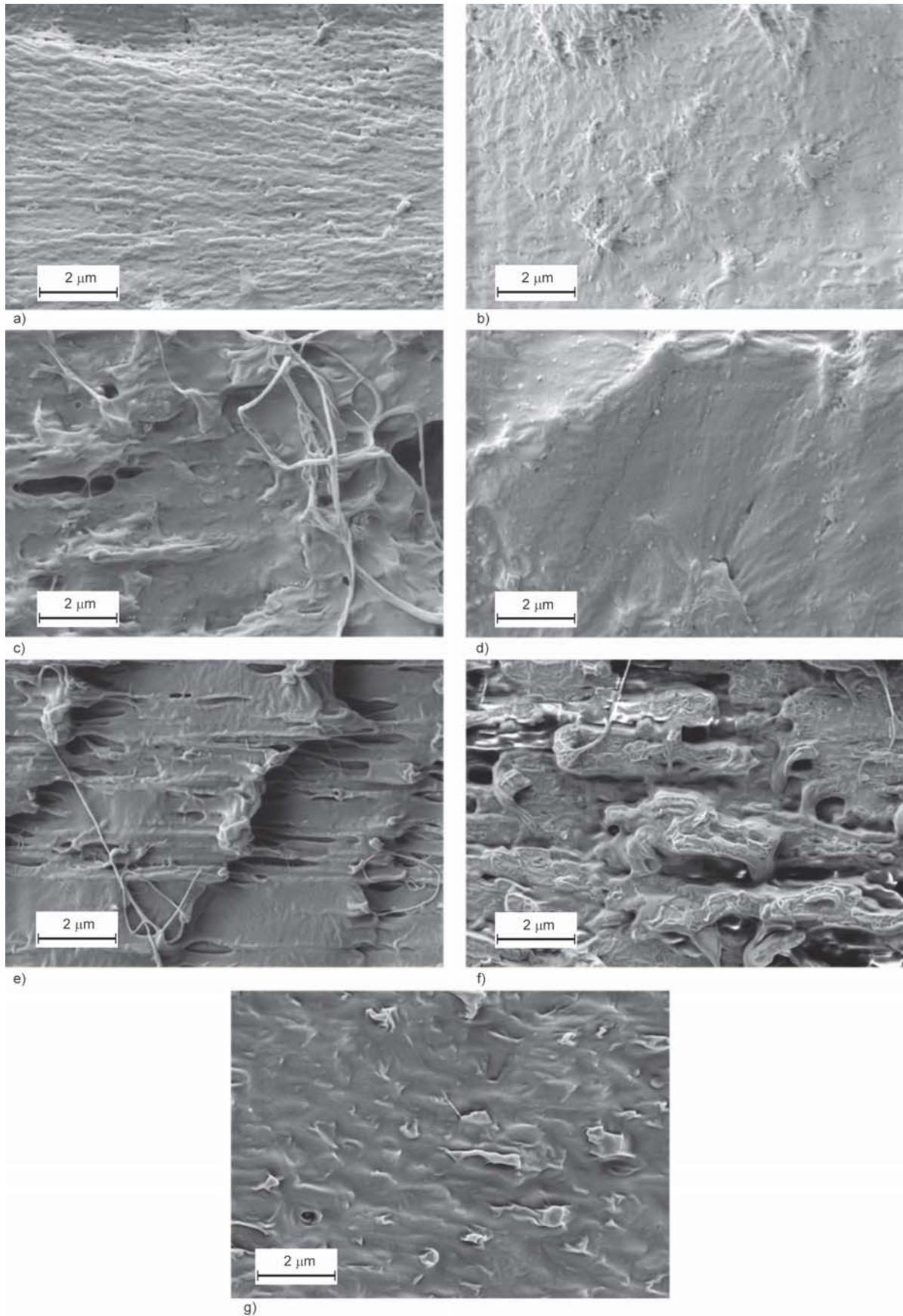


Figure 4. FESEM images of the cryofractured films at 10000 \times , a) neat PLA b) uncompatibilized PLA/PBAT c) PLA/PBAT (80/20 wt/wt) compatibilized with 1 wt% Joncryl[®], d) PLA/PBAT (80/20 wt/wt) compatibilized with 1 wt% ECSO e) PLA/PBAT (80/20 wt/wt) compatibilized with 1 wt% MCSO, f) PLA/PBAT (80/20 wt/wt) compatibilized with 7.5 wt% ECSO and g) PLA/PBAT (80/20 wt/wt) compatibilized with 7.5 wt% MCSO.

(extrusion) direction. Phase separation has been reported for vegetable oil-derived additives over 5 wt% as small spherical domains due to excess plasticizer/compatibilizer [45]. Nevertheless the PLA/PBAT system shows a heterogeneous fracture surface, even for the ECSO- and MCSO-compatible blends with 7.5 wt% compatibilizer (Figure 4f and 4g) which suggests phase separation as well. Despite this, the fracture surface of the ECSO-compatible PLA/PBAT blend (Figure 4f) shows strong heterogeneity which can be related to phase separation while the MCSO-compatible blend (Figure 4g), offers a more homogeneous fracture surface which could be responsible for the maximum elongation at break achieved.

3.3. Effect of compatibilizers on thermal properties of PLA/PBAT films

Figure 5 shows the DSC profiles of the neat polymers, namely PLA and PBAT during the second heating stage, while Figure 6 gathers the comparative DSC thermograms of PLA/PBAT blends without and with several compatibilizers.

The glass transition temperature (T_g) of neat PLA can be clearly observed in Figure 5 as a step in the base line located at 59.1 °C. The glass transition temperature of PBAT cannot be observed in the temperature range covered by the DSC temperature program as it is located below room temperature. With regard to the melt peak temperature, PLA and PBAT melt at 147.8 and 123.1 °C respectively. In addition, PLA shows a cold crystallization (endothermic peak) between the T_g and the melt process, with a peak temperature (T_{cc}) located at 117.7 °C. The glass transition

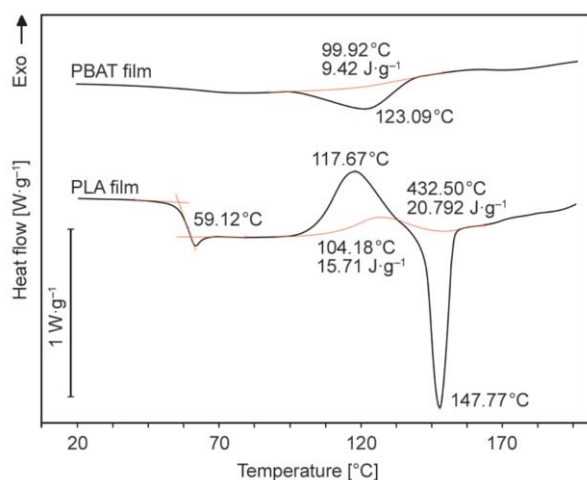


Figure 5. Differential scanning calorimetry (DSC) thermograms for neat PLA and PBAT.

temperature for PBAT was determined by DMA and was -22.9 °C.

Some miscibility between PLA and PBAT polymer chains can be expected as the T_g for the uncompatibilized blend is slightly lower (58.8 °C). In a similar way, the study by Abdelwahab *et al.* [46] revealed poor miscibility between these two polymers as indicated by DSC characterization. In particular, they only observed a decrease in the T_g of neat PLA of 0.25 °C for a PLA/PBAT blend containing 30 wt% PBAT. The addition of all three compatibilizers, whatever their amount, led to an additional decrease in T_g . In the case of Joncryl[®], addition of 1 wt% to the PLA/PBAT blend led to a decrease of almost 1.3 °C as obtained by DSC. Abdelwahab *et al.* [46] reported negligible changes in T_g in PLA/PBAT blends with 20 wt% organosolv lignin (OL) and different Joncryl[®] loading. With regard to the vegetable oil-derived compatibilizers, it has been proved that their plasticization effects are not as pronounced as typical primary plasticizers. Nevertheless, vegetable-oil derived compatibilizers exert a dual function: on one hand, they promote chain extension due to reaction of epoxide rings or maleic anhydride groups with hydroxyl terminal groups in both PLA and PBAT polyesters. On the other hand, they contribute to compatibilization as they can react with both PLA and PBAT polymeric chains, acting as a bridge between the two immiscible (or low miscibility) polymers. Vegetable oil derivatives, with the triglyceride structure, provide increased free volume and this has a positive effect on chain mobility [35, 37]. It is, in fact, the

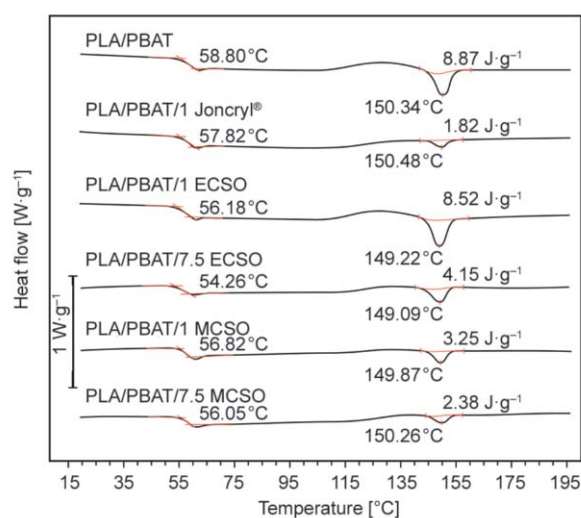


Figure 6. Comparative plot of the DSC thermograms of uncompatibilized PLA/PBAT blend (80/20 wt/wt) and the same blend compatibilized with different amounts of Joncryl[®], ECSO and MCSO.

PLA/PBAT blend with 7.5 wt% MCSO which reaches the lowest T_g values among all the formulations in this study (56.1 °C). The main advantage of vegetable oil-derived compatibilizers/plasticizers is that the elongation at break is remarkably increased but, in contrast, other mechanical resistance properties are not reduced in a great extent.

With regard to the crystallinity, it is worthy to note that neat PLA possesses a χ_c % of 5.46%. Although it seems that the cold crystallization process decreases in the blend, it is important to remark that both the cold crystallization of PLA and the melt process of PBAT occur in a similar temperature range (see Figure 5). As these two energetically opposite processes are overlapped, it is not appropriate to calculate the degree of crystallinity of PLA in the uncompatibilized and compatibilized blends. It could be possible to separate these processes by using modulated signal.

PLA/PBAT films were also characterized by dynamic mechanical thermal analysis (DMA). This is a more sensitive technique to obtain the T_g values and measure mechanical properties, *i.e.* storage modulus (G') and damping factor ($\tan\delta$) in dynamic conditions. Figure 7 gathers the DMA of neat PLA, PBAT and their blend (80/20 wt/wt) without and with different compatibilizers. As it can be seen, the uncompatibilized PLA/PBAT blend shows a slight decrease in T_g from 66.3 °C (neat PLA) down to 65.0 °C. This is representative for very low miscibility between the two blend components. Al-Itry *et al.* [47] observed similar decrease in T_g when 20 wt% PBAT was added to PLA. Specifically, the T_g was reduced by 1 °C with regard to unblended PLA. Addition of 1 wt% of the three compatibilizers used in this study led to a slight decrease in T_g of about 2 °C which indicates some compatibilizing/plasticization behavior but these two phenomena are overlapped. Once again, the highest reduction in the T_g is obtained with high vegetable oil-derived compatibilizer. In particular, the T_g decreases down to 62.2 and 62.6 °C in blends with 7.5 wt% ECSO and MCSO respectively. Nevertheless, the most relevant information regarding the effect of all used compatibilizers can be observed by following the evolution of the storage modulus, G' . Neat PLA is the stiffer material with a G' value of about 2500 MPa. Obviously, neat PBAT is an extremely flexible polymer with a very low G' value at 30 °C of about 100 MPa. With regard to the uncompatibilized PLA/PBAT blend, the G' at 30 °C

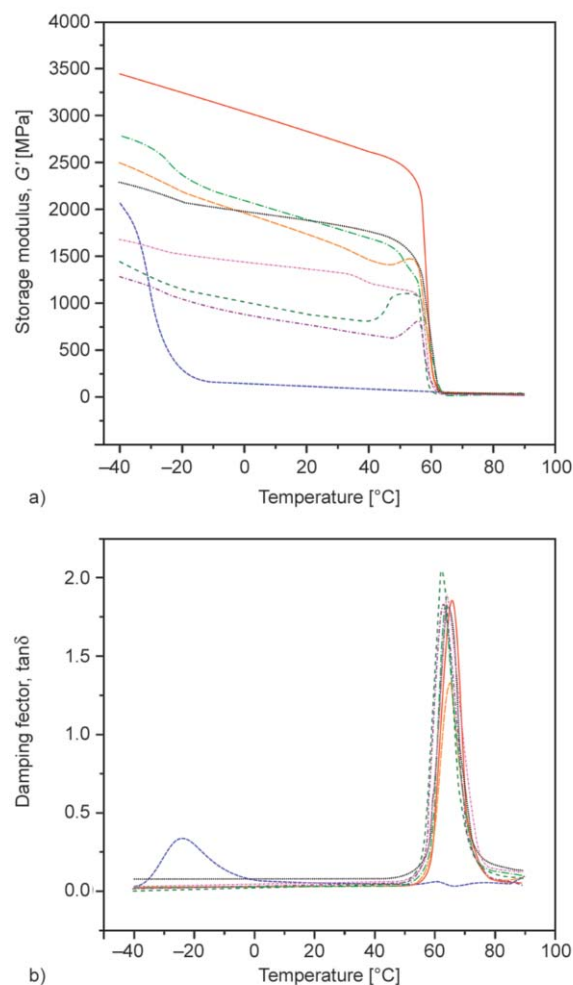


Figure 7. Plot comparison of a) storage modulus, G' and b) damping factor, $\tan\delta$ of neat PLA, PBAT and PLA/PBAT blend (80/20 wt/wt) without and with different compatibilizers.

is close to 1650 MPa thus showing the flexibilization effect of PBAT on PLA/PBAT blends. ECSO seems to be more reactive as the corresponding compatibilized blend with 1 wt% ECSO shows a G' value of 1750 MPa at 30 °C which is similar to the Joncryl-compatibilized blend (1800 MPa). MCSO seems to give more flexible materials with G' values at 30 °C of 1300 and 950 MPa for 1 and 7.5 wt% MCSO content in PLA/PBAT blends. All these results are in total agreement with the previous mechanical properties. Although G' suggests the T_g of the PBAT rich phase (decrease in G' at about -20 °C), the corresponding damping factor peaks are not detectable. It is important to take into account that G' is plotted in

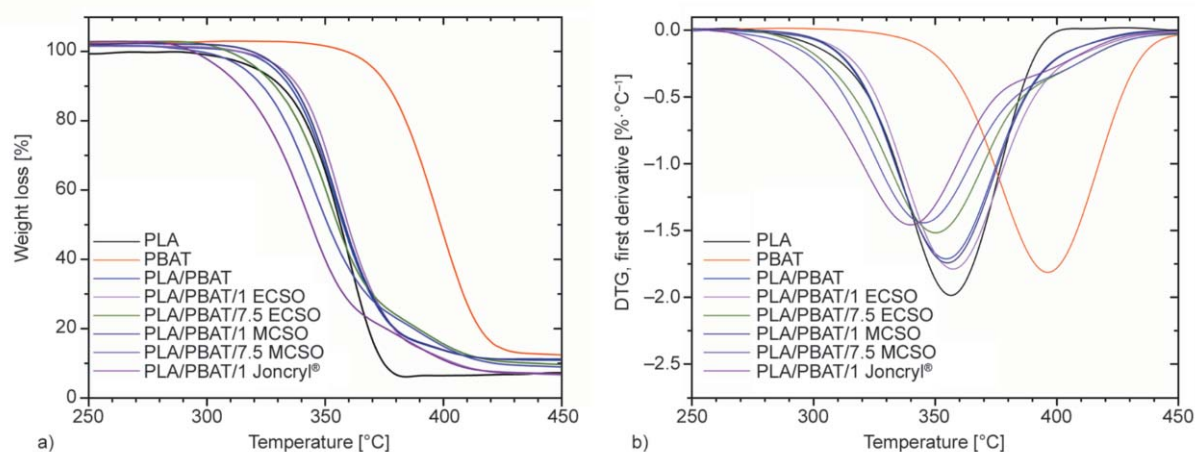


Figure 8. Comparative plot of the TGA thermograms of neat PLA, PBAT and PLA/PBAT blend (80/20 wt/wt) without and with different compatibilizers, a) TGA and b) first derivative DTG.

a decimal scale (not logarithmic) and this change is less pronounced in a logarithmic scale.

One important issue to take into account in these formulations is their thermal stability. As it can be seen in Figure 8, both vegetable oil-derived additives contribute to an improvement on overall thermal stability while Joncryl® does not provide any relevant increase in thermal stability. This could be related to the particular thermal stability of vegetable oils and the flexibility they provide to the compatibilized structure. In fact, one of the main uses of modified vegetable oils, is as secondary plasticizers in poly (vinyl chloride) – PVC industrial formulations as these can act as free radical scavengers thus leading to increased thermal stability. In fact, PVC is extremely sensitive to thermal degradation and presence of modified vegetable oils leads to improved thermal stability [8]. As suggested by TGA analysis, Joncryl seems to slightly decrease the thermal stability as it probably, cannot act as a free radical scavenger.

The main parameters obtained by TGA analysis are summarized in Table 2 with the temperature values corresponding to 5 and 50 wt% loss, $T_{5\%}$ and $T_{50\%}$ respectively.

As it can be seen, the simple addition of PBAT in the uncompatibilized blend, gives increased thermal stability. The onset degradation temperature, measured at 5 wt% loss, changes from 321.2 up to 328.2 °C. Similar findings were reported by Lu *et al.* [48] that observed an increase of 11.2 °C in thermal stability of PLA with addition of 30 wt% PBAT. It is also worthy to note the additional stabilization that ECSO and MCSO provides with $T_{5\%}$ values over 330–331 °C with 1 wt% ECSO or MCSO while higher ECSO or

Table 2. Summary of the main results of the thermal degradation of neat PLA, PBAT and PLA/PBAT blend (80/20 wt/wt) without and with different compatibilizers.

Code	TGA	
	$T_{5\%}$ [°C]	$T_{50\%}$ [°C]
PLA	321.2	356.6
PBAT	370.9	398.7
PLA/PBAT	328.2	357.8
PLA/PBAT/1 ECSO	331.7	359.8
PLA/PBAT/7.5 ECSO	321.5	355.3
PLA/PBAT/1 MCSO	330.5	358.3
PLA/PBAT/7.5 MCSO	315.7	351.3
PLA/PBAT/1 Joncryl®	305.9	344.1

MCSO content leads to a small decrease in thermal stability, probably due to a plasticizer excess. This behavior has been reported previously with other vegetable oil-derived compatibilizers/plasticizers [49, 50]. Similar trend can be seen for $T_{50\%}$. With regard to Joncryl®, it leads to small decrease in thermal stability.

3.4. Effect of compatibilizers on surface and disintegration properties of PLA/PBAT films

The wetting properties of the herein developed materials was determined by contact angle measurements. Table 3 shows the water contact angle obtained on PLA, PBAT and their compatibilized and uncompatibilized blend. PLA shows an average contact angle of 66.4° which is lower than typical polyolefins, *i.e.* poly(ethylene) – PE, poly(propylene) – PP, with contact angles close to 90° [51, 52]. With regard to PBAT, due to its chemical structure, its water contact angle

is located at 53.9°. Addition of all three compatibilizers at a fixed composition of 1 wt%, provides increased hydrophobicity as the water contact angle increases up to values of about 71° for Joncryl® and 75° for ECSO and MCSO. Hydrophobicity is an interesting property in films so that, all three compatibilizers at 1 wt% give good results. Nevertheless, blends with 7.5 wt% of both ECSO and MCSO show a decrease in hydrophobicity (lower water contact angle values of about 63 and 56° respectively). This could be related to phase separation at high vegetable oil content. Finely dispersed droplets of ECSO and MCSO could play an important role in reducing hydrophobicity due to their functionality [53]. Table 3 also summarizes the luminance (L^*) which is a direct measurement of the transparency. Neat PLA film shows the highest transparency, with a L^* of 99.4%. All the developed formulations show high luminance, thus indicating very low effects on transparency. Disintegration in controlled compost soil gives interesting information about the effect of the different compatibilizers on the biodisintegration process. Figure 9 shows in a qualitative way the evolution of the disintegration process of neat PLA, PBAT and their uncompatibilized and compatibilized blend (1 wt% Joncryl®, ECSO, MCSO). After an induction period of 11 days, relevant changes appear. Very smooth changes take place during this induction period. First changes are related to a change in PLA crystallinity due to hydrolysis as reported by Xu *et al.* [54] The luminance is directly related to the transparency. Neat PLA film shows the highest transparency while the uncompatibilized PLA/PBAT shows decreased transparency (and decreased luminance as seen in Table 3). Both ECSO and MCSO contribute to slightly lower transparency and, consequently, the

Table 3. Summary of some surface properties, *i.e.* water contact angle and luminance (L^*) for neat PLA, PBAT and PLA/PBAT blend (80/20 wt/wt) without and with different compatibilizers.

Code	Water contact angle, θ_w [°]	Luminance, L^*
PLA	66.4±1.6	99.4±0.1
PBAT	53.9±1.1	98.7±0.1
PLA/PBAT	66.2±3.4	98.0±0.3
PLA/PBAT/1 ECSO	75.6±2.6	98.1±0.1
PLA/PBAT/7.5 ECSO	62.7±1.4	98.9±0.1
PLA/PBAT/1 MCSO	74.2±2.8	98.3±0.2
PLA/PBAT/7.5 MCSO	56.3±4.0	97.9±0.1
PLA/PBAT/1 Joncryl®	71.6±4.1	99.1±0.1

change in luminance is very small. Although Joncryl compatibilized film could seem to be less transparent than ECSO and MCSO compatibilized blend films, it is important to remark that luminance values were obtained as average values of a series of measurements in different parts while images in Figure 9 are individual pictures.

It can be seen that PBAT delays the disintegration process since first signs of disintegration appears at 14 days whilst neat PLA is highly degraded at the same period. PBAT degradation rate is much higher than that of PLA. Tabasi *et al.* [55] reported an incubation time of 45 days on PBAT films which is noticeably higher than that of PLA. It is worthy to note that PLA is almost disintegrated at 16 days and all other formulations (uncompatibilized and compatibilized PLA/PBAT blends) degrade at 26 days. Although it has been reported that MCSO can lead to a reduction of the induction time in neat PLA [37], the herein developed blends show higher induction time due to presence of PBAT and a combination of different reactions with the compatibilizers, *i.e.* chain extension, branching and crosslinking, all those having an effect on delaying the disintegration time.

4. Conclusions

This work assesses the potential of vegetable oil-derived additives as compatibilizers in PLA/PBAT blends containing 20 wt% PBAT. The only addition of PBAT to PLA gives increased elongation at break due to the high flexibility of PBAT. Nevertheless, poor miscibility between PLA and PBAT was observed by FESEM and confirmed by a very low decrease in the glass transition temperature of neat PLA. Compatibilization with epoxidized cottonseed oil (ECSO) and maleinized cottonseed oil (MCSO), gave a remarkable increase in elongation at break without compromising other mechanical resistance properties, even better than those provided by an epoxy styrene-acrylic oligomer (Joncryl®) widely used as chain extender and/or compatibilizer. The plasticization effect of the different compatibilizers is restricted as the glass transition temperature, T_g , is not reduced in a great extent. Besides, the transparency of the films is not highly affected by the presence of the different additives. With regard to the disintegration process, PBAT delays the overall disintegration period due to its low

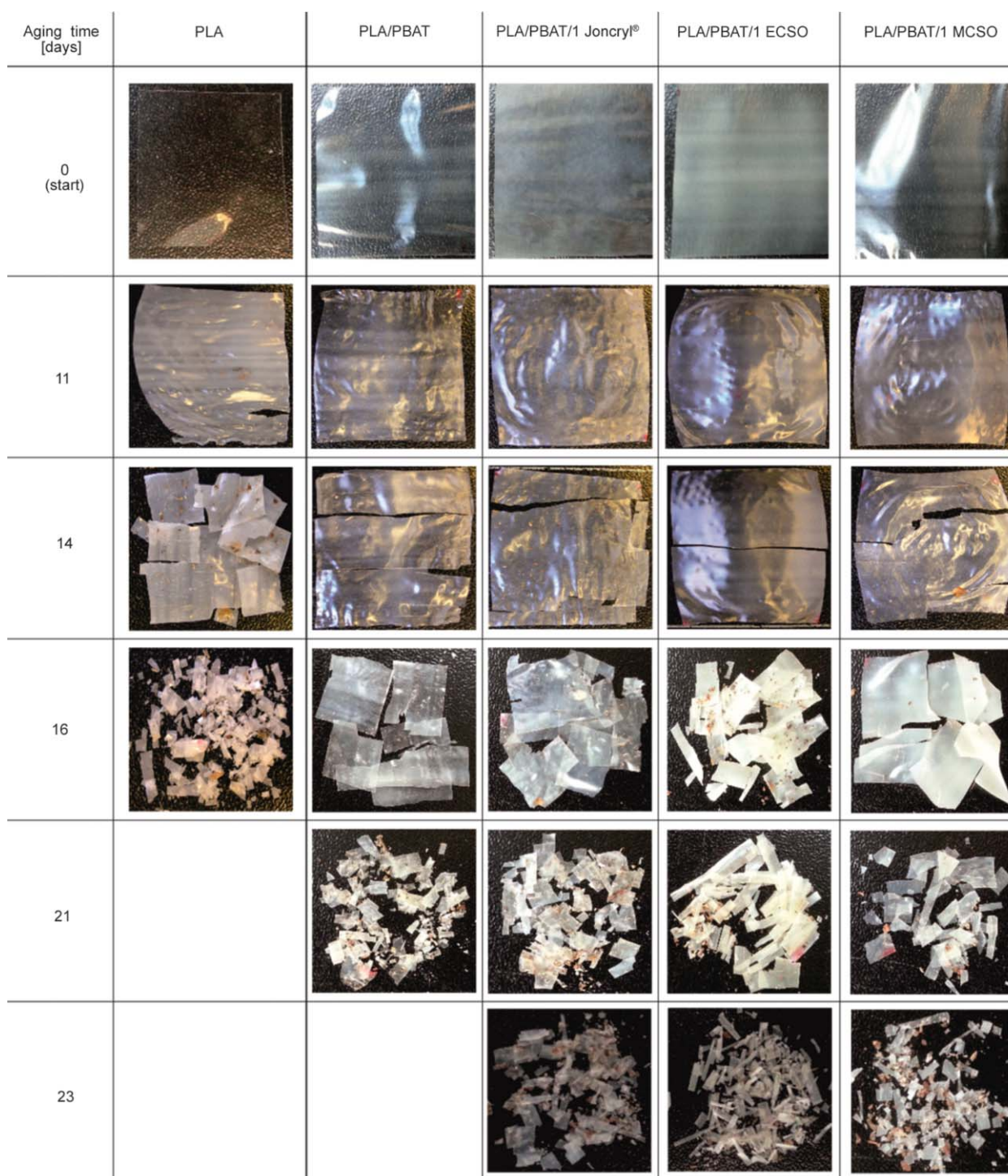


Figure 9. Qualitative assessment of the disintegration in controlled compost soil of neat PLA, PBAT and PLA/PBAT blend (80/20 wt/wt) without and with 1 wt% different compatibilizers.

disintegration rate. Both ECSO and MCSO do not have a relevant effect on overall disintegration but they contribute positively to improve the thermal stability as revealed by thermogravimetry. Use of vegetable oil-derived compatibilizers (epoxidized and maleinized vegetable oils) stands out as an environmentally friendly solution to improve miscibility of

polyester-type blends with excellent balance on mechanical and thermal properties.

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