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Additional Information

“Processing and characterization of high environmental efficiency composites based on PLA and hazelnut shell flour (HSF) with biobased plasticizers derived from epoxidized linseed oil (ELO)”

J.F. Balart¹, V. Fombuena, O. Fenollar, T. Boronat, L. Sánchez-Nacher

Instituto de Tecnología de Materiales (ITM)

Universitat Politècnica de València (UPV)

Plaza Ferrandiz-Carbonell, s/n, 03801 Alcoy, Alicante, Spain

Abstract

Different amounts of epoxidized linseed oil (ELO) have been added to poly(lactic acid)-PLA composites with hazelnut shell flour (HSF) to provide a plasticizing effect and improve the low intrinsic ductile properties of PLA/HSF composites. Mechanical, thermal, thermo-mechanical and dynamic mechanical properties have been studied in terms of the weight percentage ELO. Mechanical resistant properties in both tensile and flexural tests decrease with wt.% ELO while a remarkable increase with wt.% ELO is obtained. These results reveal a clear plasticization effect of ELO but, in addition, internal structure of PLA/HSF/ELO composites shows good PLA-HSF (matrix-particle) interactions so that indicating that ELO also provides a coupling effect between PLA matrix and HSF filler. ELO addition leads to a decrease in storage modulus (G') obtained by dynamic mechanical thermal analysis (DMTA) in torsion mode thus giving clear evidence of the plasticization effect of ELO. Overall, the use of ELO in PLA/HSF composites is an attracting way to improve the low intrinsic fragility of these green

¹ Corresponding author: J.F. Balart, tel.:+34 966528424, fax: +34 966528433, e-mail: jfbalart@dimm.upv.es

composites; furthermore, ELO provides an improvement on thermal stability and a coupling effect between the polymer matrix and the surrounding lignocellulosic filler.

Keywords: A. Particle-reinforcement; B. Interface/interphase; D. Mechanical testing; E. Injection moulding.

1.- Introduction.

In the last years, a remarkable increase in the development of high environmentally friendly materials has been detected in the field of polymers and polymer composites. The high concern of society about environment protection has promoted the development of new “eco”, “bio” or “green” materials. One of the main features of these new materials is their natural origin and/or potential biodegradability. So that, substitution of commodity plastics from petrochemical origin by biobased polymers is a challenge for the plastics and polymer composite industries as they do not generate harmful wastes at the end of the life cycle. With regard to polymer composites, the use of natural reinforcements (fibers, particulates, flours) such as vegetable fibers (jute, hemp, flax, sisal, *Posidonia oceanica*, etc.) or lignocellulosic particles (sawdust, peanut shell, almond shell, rice husk, spend coffee ground, etc.) [1-6] and other cellulose particles, contributes to obtain high environmentally friendly composite materials with new and attracting uses. These new uses include applications of conventional wood plastic composites (WPCs) in the building industry (outdoor deck floors, fences, window and door frames, railings, etc.) as well as in some technologic sectors such as automotive (parcel shelves, front and rear door linens, seat backs, headliners, etc.) [7].

Poly(lactic acid), PLA is one of the most widely used biopolymer in the field of plastics (packaging) and green composites. Poly(lactic acid) is obtained by

polymerization of lactic acid which is a natural monomer obtained by fermentative processes from sugar-rich compounds such as cellulose and starches (potato, corn, wheat, sugarcane, etc.) [8, 9]. PLA is a fragile thermoplastic with good mechanical resistance similar to polystyrene, PS. The molecular chain structure is similar to most thermoplastics and it can be manufactured by conventional processing techniques. In the last years, some researches have focused on the development of fully biobased composites with natural reinforcements, mainly natural fibers or woof flours. Hazelnut shell is a byproduct of the food industry. It is an industrial waste, so that it is cost effective and upgrading it is an interesting challenge. This filler can be grinded to give a lignocellulosic flour that can provide wood like appearance to polymer composites. It can be used as reinforcement/filler with a wide variety of polymeric matrices to give wood-like materials that contribute to preserve forestry resources [10-21]. Although these composites are attractive for some technical uses, one important drawback is their excessive fragility, which results from the high intrinsic account the relatively low hydrophilic nature of PLA and the extremely high hydrophilic nature of the lignocellulosic filler, poor matrix-particle interactions are achieved thus leading to stress concentration phenomena that also contributes to fragility. For this reasons, research on how to reduce fragility of PLA-based composites is being investigated. One approach is focused on the use of compatible plasticizers for PLA and another approach considers the use of compatibilizer agents to act as a bridge between the hydrophobic PLA matrix and the highly hydrophilic surrounding particles.

In general terms, the use of plasticizers lead to a decrease in the PLA glass transition temperature (T_g PLA); they also favor cold crystallization and the resulting material is more flexible. Yu *et al.* concluded that poly(ethylene glycol), PEG is an effective plasticizer for PLA and contributes to a remarkable improvement on the impact

strength of PLA. On the other PEG-plasticized PLA shows very low migration levels. Oligomeric lactic acid (OLA) gives excellent plasticizing properties to PLA as reported by Burgos *et al.* with a noticeable improvement on PLA ductile properties. Other research works focus on monomeric plasticizers (lactic acid, citrate esters, low-molecular weight ester-type, etc.), oligomeric and polymeric plasticizers such as commercial adipates (DOA - (bis(2-ethylhexyl) adipate), lactic-acid derived polymers, poly(ethylene glycol), poly(propylene glycol), etc.[8, 22-29].

On the other hand, the use of coupling agents or compatibilizers provides intense PLA matrix-lignocellulosic filler interactions that contribute to decrease fragility. Chemical coupling agents such as N,N-(1,3-phenylene dimaleimide) and 1,1-(methylenedi-4,1-phenylene) bismaleimide contribute to improved adhesion between PLA and dispersed lignocellulosic fillers thus leading to a remarkable increase in overall mechanical performance[10, 30]. Other successful coupling systems include silane-based coupling agents, alkali soaking, maleic anhydride treatment. All these coupling systems have demonstrated their usefulness in improving PLA-cellulosic particle interactions, with a considerable increase in elongation at break of PLA/cellulosic composites as well as reducing their impact behavior[31-37]. Other researchers analyzed the effectiveness of acrylic core-shell rubbers, coconut oil, sodium-montmorillonite, ionic liquids, etc. as coupling agents with a noticeable reduction of fragility [38-41].

Epoxidized linseed oil (ELO) is a vegetable obtained by an epoxidation process of industrial oil coming from flax seed. Its main features are null volatility, extremely low migration tendency and high resistance to extraction in aqueous media or hydrocarbons (natural or biobased). Some authors have proved the efficiency of epoxidized vegetable oils as plasticizers for PLA and other polymers such as poly(vinyl chloride), PVC. Ali *et al.* concluded that epoxidized soybean oil (ESBO) offers good plasticizing effect to PLA

with a remarkable increase in flexibility. Epoxidized palm oil (EPO) was tested by Silverajah *et al.* as plasticizer for PLA with an optimum amount of 1 wt.% with a noteworthy improvement of mechanical and thermal properties. Prempeh *et al.* used epoxidized sunflower oil (ESFO) to give high elongation at break to PLA (four times higher than unplasticized PLA)[23-25, 42-47].

The main aim of this study is to reduce the high intrinsic fragility of poly(lactic acid), PLA – hazelnut shell flour (HSF) by using a biobased plasticizer from epoxidized linseed oil (ELO). Mechanical, thermal and thermomechanical properties of PLA – HSF green composites are evaluated in terms of the epoxidized linseed oil (ELO) load in the 0 – 22.5 wt.% range.

2.- Experimental.

2.1.- Materials.

Poly(lactic acid), PLA commercial grade Ingeo 6201D was supplied by NatureWorks LLC (Minnesota, USA). This grade is characterized by a melt flow index in the 15 – 30 g/10 min range and a density of 1.24 g cm⁻³.

Hazelnut shell waste (*Corylus avellana*) was obtained from the food industry and subjected to a grinding process to an average particle size of 63 μm to give a homogeneous flour (hazelnut shell flour, HSF). Hazelnut shell was grinded in an ultra centrifugal mill from Retsch GmbH (Hann, Germany) at a rotating speed of 10000 rpm.

Epoxidized linseed oil (ELO), CAS number 8016-11-3 was used as plasticizer in PLA – HSF green composites. ELO with an oxyrange oxygen content of 8% and a iodine value of 5% was supplied by Traquisa S.L. (Barcenola, Spain). This epoxidized oil is characterized by a molecular weight of about 1037 g mol⁻¹, a density of 1.05-1.06 g cm⁻³ at 20 °C and a viscosity of 8-11 p at 25 °C. It shows high thermal stability with a

flammability temperature of 287 °C and it is not water-soluble. The average fatty acid profile is: 3-5% stearic acid, 5-7% palmitic acid, 14-20% linoleic acid, 18-26% oleic acid and 51-56% linolenic acid.

2.2.- Manufacturing of PLA – HSF composites with different ELO loads.

Initially, both poly(lactic acid) pellets and hazelnut shell flour were dried at 60 °C for 24 h to remove moisture. After this, PLA, HSF and ELO were weighed according to the compositions defined in Table 1.

Table 1

All four compositions were extruded in a twin screw co-rotating extruder from DUPRA S.L. (Castalla, Spain). The temperature profile in the extruder was set to 176 °C, 180 °C, 185 °C and 192 °C (from the hopper to the die) and the rotating speed was set to 40 rpm. After extrusion, the different compositions were pelletized for further processing by injection molding in a Meteor 270/75 from Mateu & Solé (Barcelona, Spain). The injection temperature was set to 190 °C, the cavity filling time was 1 second and the cooling time was set in 10 seconds. Standard samples for different tests were obtained with a thickness of 4 mm.

2.3.- Testing and characterization.

Mechanical Testing.

Tensile properties of ELO modified PLA – HSF composites were obtained as indicated in the UNE-EN-ISO 527-1 standard in a universal test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain). The selected load cell was 5 kN. Samples with a total length of 150 mm and a cross section of 10x4 mm² (type 1A) were subjected to tensile

tests at a crosshead speed was set to 10 mm min^{-1} . The same machine was used for flexural characterization of composites by following the guidelines of the ISO 178 with a crosshead rate of 5 mm min^{-1} . The impact strength was tested in a 1 J Charpy pendulum from Metrotec S.A. (San Sebastián, Spain) as suggested by ISO 179. Finally, Shore D hardness of PLA – HSF with different ELO content was measured in a Shore D durometer mod. 673-D from J. Bot S.A. (Barcelona, Spain) following the UNE-EN ISO 868. At least five different samples were tested for each mechanical property and average values were calculated.

Microscopic characterization.

Fractured surfaces from impact tests and cryofractured surfaces of PLA – HSF with different ELO content were observed by field emission scanning electron microscopy (FESEM), mod. Zeiss Ultra 55 de Oxford Instruments (Abingdon, United Kingdom) at an acceleration voltage of 2 kV. Samples were covered with a thin platinum layer in a high vacuum sputter coater EM MED20 from Leica Microsystem (Milton Keynes, United Kingdom).

Thermal and thermo-mechanical characterization.

Thermal transitions of PLA – HSF composites with varying ELO content were obtained by differential scanning calorimetry (DSC) in a DSC calorimeter mod. 821 from Mettler Toledo Inc. (Schwerzenbach, Switzerland). Samples with an average weight of 7-10 mg were subjected to a three step program with an initial heating cycle from $30 \text{ }^{\circ}\text{C}$ to $200 \text{ }^{\circ}\text{C}$ at $10 \text{ }^{\circ}\text{C min}^{-1}$ to remove thermal history followed by a cooling to $-50 \text{ }^{\circ}\text{C}$ at a heating rate of $-10 \text{ }^{\circ}\text{C min}^{-1}$. Finally, a second heating cycle from $-50 \text{ }^{\circ}\text{C}$ up to $350 \text{ }^{\circ}\text{C}$ at

10 °C min⁻¹ was used to evaluate all thermal transitions. All thermal cycles were performed in presence of a nitrogen atmosphere at 66 mL min⁻¹.

Thermogravimetric analysis (TGA) was used to evaluate thermal stability of PLA – HSF composites at high temperatures. The heating program was from 30 °C to 700 °C at a heating rate of 20 °C min⁻¹ in nitrogen atmosphere (66 mL min⁻¹). TGA characterization was carried out in a TGA/SDTA 851 thermobalance from Mettler Toledo Inc. (Schwerzenbach, Switzerland).

Vicat softening temperature (VST) was obtained as described in ISO 306 by using a load of 5 kg and a heating rate of 50 °C h⁻¹. Additionally, the heat deflection temperature (HDT) was obtained following the guidelines of the ISO 75 and ASTM D 648 with a load of 296 g and a heating rate of 120 °C h⁻¹. Both VST and HDT values were determined in a VICAT-HDT station from Metrotec S.A. (San Sebastián, Spain). Dimensional stability was studied by determining the coefficient of linear expansion (CLTE) of PLA – HSF composites with varying ELO content in a thermomechanical analyzer Q400 from TA Instruments (Delaware, USA). The heating program was comprised between 0 °C and 140 °C with a constant heating rate of 2 °C min⁻¹ and a constant load of 0.02 N.

Dynamic Mechanical Analysis, DMA, in torsion mode were carried out in an oscillatory rheometer AR-G2 (TA Instruments, New Castle, EEUU) equipped with an environmental test chamber (ETC) with a rectangular torsion clamp system for solid samples. Samples sizing 40x10x4 mm³ were subjected to a dynamic temperature program ramp from 30 °C to 120 °C at a heating rate of 2 °C min⁻¹, with the following conditions: maximum deformation (γ)=0.1% and constant frequency of 1 Hz.

3.- Results and discussion.

3.1.- Effect of biobased plasticizer (ELO) content on the mechanical properties of the PLA – HSF composites.

Mechanical behavior of PLA – HSF containing 20 wt.% HSF is characterized by high fragility (see Table 2). The elastic modulus is relatively high, with values around 1019 MPa, thus indicating it is a rigid material with high tensile strength but low elongation at break (3%). The inherent fragility of poly(lactic acid) together with the poor matrix-particle interaction lead to a pronounced fragility on this composite.

Table 2

The change in mechanical behavior of PLA – HSF composites with ELO content is a clear evidence of the plasticization effect that ELO provides. As the ELO content increases, we observe a clear decreasing tendency on both tensile strength and elastic modulus while the elongation at break increases with ELO content. Unmodified PLA – 20 wt.% HSF composite possesses an elastic modulus of 1019 MPa and this decreases up to values of 751 MPa and 590 MPa (a percentage decrease of 26% and 42% respectively) for composites containing 15 wt.% and 22.5 wt.% ELO thus indicating a clear plasticizing effect. Same behavior can be observed for tensile strength with an initial value of 45 MPa (unmodified PLA – 20 wt.% HSF composite) and a reduction up to 15.3 MPa for the composite containing 22.5 wt.% ELO which represents a percentage decrease of about 66%. The remarkable decrease in tensile strength is representative for inappropriate PLA-ELO interactions. The plasticizer excess can appear as a dispersed phase in the PLA matrix with a negative effect on homogeneity that promotes a decrease in tensile strength. High plasticizer contents produce intense plasticizer-plasticizer interactions that lead to a phase separation[47]. Chieng *et al.* concluded that for high

plasticizer contents, only a small part is directly in contact among the interface area while the excess is dispersed in the polymeric matrix. This phenomenon highly affects homogeneity and a decrease in tensile strength on PLA – 20 wt.% HSF composite with varying ELO content[23-25, 46].

On the other hand, the elongation at break is highly increased with ELO content. Unmodified PLA – 20 wt.% HSF composite is characterized by a relatively low elongation at break value of about 3%. Composites containing 7.5 wt.% ELO are characterized by slightly higher elongation at break with average values of 4.2% but we can clearly see the plasticizing effect in PLA – 20 wt.% HSF composites containing 15 wt.% and 22.5 wt.% ELO with elongation at break close to 11% and 17% respectively. This means that ELO provides a clear plasticizing effect to PLA – 20 wt.% HSF composites. Presence of ELO promotes less intense intermolecular forces between PLA macromolecular chains thus leading to improved chain mobility which is responsible for the abovementioned decrease in stiffness as well as the clear improvement of ductile properties[22, 26, 42].

The effect of ELO content on flexural properties can be explained by observing data in Table 2. In a similar way to tensile properties, the flexural modulus and strength (mechanical resistant properties) are reduced with increasing ELO content. With regard to flexural modulus, it is reduced by 10% in PLA – 20 wt.% HSF composites containing 7.5 wt.% ELO. The flexural modulus is reduced to the half for composites containing 22.5 wt.% ELO. As indicated previously, epoxidized linseed oil (ELO) molecules enable polymer chain mobility so that the material is less stiff. If we observe the evolution of the flexural strength it changes from 83.7 MPa (unmodified PLA – 20 wt.% composite) up to minimum values of 29.5 MPa for composites containing 22.5 wt.% ELO, which represents a percentage decrease of about 65%. Similar tendency can be observed for

Shore D hardness of PLA – 20 wt.% HSF composites with varying ELO content as abovementioned for other mechanical resistant properties.

3.2.- Effect of biobased plasticizer (ELO) content on morphological of PLA – HSF composites.

FESEM technique was used to study the effect of different ELO content on morphology of cryofractured surfaces to show in a qualitative way the internal structure and give evidence of the potential interactions. Fig. 1 shows FESEM images of PLA – 20 wt.% HSF composites with varying ELO content.

Figure 1

Fig. 1a & 1b correspond to unmodified PLA – 20 wt.% composite. We can clearly see the lack of interaction between the lignocellulosic particles and the surrounding PLA matrix. This is evidenced by a small gap between the particle and the matrix, which is responsible for material discontinuity. This phenomenon does not allow optimum load transfer between particle and the matrix leading to stress concentration phenomena which has a consequence the fragility of the material as it has been observed in the previous section. In addition, the fracture surface is very smooth and homogenous due to the intrinsic fragility of poly(lactic acid) polymers.

Nevertheless, composites containing 7.5 wt.% ELO show a remarkably different surface fracture morphology as observed in Fig. 1c & Fig. 1d for different magnifications. Improved particle-polymer interaction can be observed by a reduction of the gap between the dispersed lignocellulosic particle and the surrounding PLA matrix and the overall discontinuity is remarkably reduced. This interaction allows load transfer between PLA

matrix and dispersed HSF particles and this leads to improved ductile properties such as elongation at break. PLA can be plasticized with relatively low amounts of epoxidized vegetable oils as reported by other authors and PLA is not absolutely miscible with epoxidized vegetable oils[23, 24, 44, 47]. This lack of complete miscibility is evidenced by observation of fractured surfaces. The fractured surfaces of composites with high ELO content are less homogeneous and we can find round shape irregularities and/or microvoids uniformly dispersed in the PLA matrix. This rounded shapes correspond to ELO-rich phase that has not mixed with poly(lactic acid) polymer chains due to this partial miscibility which leads to a phase separation[43, 46]. For composites with higher ELO content, the fractured surface morphology is similar but the particle-polymer interactions are pronounced. For example, the composite containing 15 wt.% ELO (Fig. 1e & Fig. 1f) shows more intense adhesion phenomena between the lignocellulosic filler and the surrounding matrix. These strong interactions contribute to lowering the intrinsic fragility thus leading to increased elongation at break (around 11%). Fig. 1g & Fig. 1h correspond to PLA – 20 wt.% HSF composite with 22.5 wt.% ELO and show good particle-matrix adhesion. The gap between the HSF particles and the surrounding area is very small so that the composite offers higher ductility[31, 33, 36].

This remarkable change in surface morphology is due the double action that ELO provides to PLA – 20 wt.% HSF composites; on the one hand the plasticizing effect of ELO leads to improved chain mobility but on the other hand, ELO provides a coupling effect between lignocellulosic HSF particles and plasticized PLA matrix thus leading to a synergistic effect. It is important to take into account that epoxidized linseed oil is characterized by high polarity due to the oxirane groups. The oxiranic oxygen content (OOC) of ELO is close to 8% which is higher compared to other commercial epoxidized vegetable oils such as epoxidized soybean oil (ESBO). The epoxide group can react with

the hydroxyl groups in lignocellulosic filler to form strong interactions. These reactions (see Fig. 2) are favored by temperature during manufacturing (extrusion + injection molding)[23, 24, 42]. Wang *et al.* concluded that this mechanism decreases the overall polarity of lignocellulosic particles which favors good particle dispersion in hydrophobic (or low hydrophilic) polymeric matrices such as PLA. On the other hand, epoxide groups in ELO can react with terminal hydroxyl groups in poly(lactic acid) macromolecular chains as proposed in Fig. 2. The high oxiranic oxygen content of ELO enables different reaction points with PLA[23, 24, 29, 41, 44, 47]. These two combined effects: PLA-ELO interactions and HSF-PLA interactions allow ELO to act as a coupling agent between poly(lactic acid) and hazelnut shell flour with a remarkable increase in polymer-particle adhesion as described previously. This interactions are optimum for ELO contents over 7.5 wt.%. For relatively low ELO amounts (7.5 wt.%) ELO does not fully wet lignocellulosic particles due to the high surface area of HSF particles; so that, ELO-HSF interactions are not optimum (Fig. 1d) and the corresponding composite is characterized by relatively low ductility (see Table 2).

Figure 2

3.3.- Effect of biobased plasticizer (ELO) content on thermal and thermo-mechanical properties of PLA – HSF composites.

Fig. 3 shows a comparative plot of the DSC thermograms of PLA – 20 wt.% HSF composites with varying ELO content. We can see a decrease in the glass transition temperature (T_g) with increasing ELO content. The glass transition temperature of unmodified PLA – 20 wt.% HSF is located at about 66.5 °C and this is moved to lower temperatures in the 60 °C range for composites with 7.5 wt.% ELO. Higher ELO contents

(i.e. 22.5 wt.%) lead to glass transition temperatures of 58 °C. This is due to the plasticization effect of ELO as ELO presence promotes chain mobility. Epoxidized linseed oil molecules are placed between poly(lactic acid) macromolecules thus allowing polymer chain motions due to the internal lubricant effect. On the other hand, only one glass transition temperature can be observed so that indicating good compatibility between ELO and PLA in this range of compositions[22-24, 42, 45].

Figure 3

The cold crystallization temperature (T_{cc}) does not change in a great extent (1 – 2 °C) with increasing ELO content. With regard to the melt temperature (T_m) it changes from 170 °C (unmodified PLA – 20 wt.% HSF) up to 167 °C for composites containing 22.5 wt.% ELO. So that, we can conclude that presence of ELO in PLA – HSF composites does not affect in a great extent the melt process[23, 24].

Another important thing is that poly(lactic acid) is a semicrystalline polymer, so that the influence of ELO on PLA crystallinity degree ($X_{c\text{ PLA}}$) has also been studied by using the following equation:

$$X_{c\text{ PLA}} (\%) = \left[\frac{|\Delta H_m| - |\Delta H_{cc}|}{|\Delta H_{100\%}| \cdot w_{\text{PLA}}} \right] \cdot 100 \quad \text{Eq. 1}$$

Where ΔH_m is the melt enthalpy (negative value due to the endothermic process), ΔH_{cc} is the cold crystallization enthalpy (positive value due to the exothermic process), $\Delta H_{100\%}$ is the melt enthalpy for theoretical 100% crystalline PLA (-93.7 J g^{-1}) and finally, w_{PLA} is the weight fraction of PLA in PLA – 20 wt.% HSF composites with different ELO content[8, 14, 27, 35, 48-50].

Table 3

Table 3 shows a summary of the main thermal parameters in terms of the wt.% ELO in PLA – 20 wt.% HSF. Normalized enthalpy values (ΔH_{cc} and ΔH_m) have been corrected by considering the wt.% PLA (excluding the dilution effect of HSF and ELO as these two components do not show thermal transitions in the typical melt and cold crystallization temperature range of PLA). If we observe the evolution of the corrected cold crystallization enthalpy (ΔH_{cc}), we see a slight increase with ELO content, which is directly related to the crystallinity increase as the plasticizer allows more intense polymer chain motion. The crystallinity of PLA in unmodified PLA – 20 wt.% HSF composites is close to 15% due to the nucleating effect of cellulose in hazelnut shell flour particles[9, 14, 35]. The presence of ELO plasticizer allows chain mobility and this has a positive effect on crystallinity as polymer chains can rearrange to ordered/packed structures. The highest crystallinity value is detected for the composite with 7.5 wt.% ELO ($X_c = 19\%$). Higher ELO contents lead to slightly lower crystallinity. This could be related to a phase separation between PLA and excess plasticizer as observed in FESEM images (Fig. 1)[25, 46, 47]. The melt temperature is not highly affected by presence of ELO but a slight decrease from 169.9 °C up to values in the 167-168 °C range can be observed.

With regard to the thermal stability of PLA – 20 wt.% HSF composites with varying ELO percentages, Fig. 4 shows a plot comparison of the thermogravimetric curves (TGA). We can observe an increase in the thermal stability with increasing ELO content. The TGA curve of the unmodified PLA – 20 wt.% HSF composite is placed to the left if compared to the TGA curves of composites containing different ELO contents. This means that degradation of unmodified composite occurs at lower temperatures. The

degradation onset for unmodified composite is about 317 °C and the degradation temperature range is relatively narrow. As the ELO content increases, the onset degradation temperature is moved to higher temperatures of about 335 °C, 337 °C and 339 °C for composites containing 7.5, 15 and 22.5 wt.% ELO respectively[23, 24, 43, 44]. With regard the degradation endset temperature, it changes from 365 °C for unmodified composite to 381 °C for composite containing 22.5 wt.% ELO. It is important to remark that the main uses of epoxidized vegetable oils are as plasticizer and thermal stabilizers mainly for poly(vinyl chloride), PVC so that, ELO presence in PLA – 20 wt.% HSF composites, contributes to improved thermal stability. Prempeh *et al.* concluded that this stabilizing effect could be attributed to formation of hydrogen bonds between poly(lactic acid) polymer chains and the plasticizer which can lead to improved thermal stability[45]. In addition ELO rich phase embedded in the PLA matrix also contributes to act as an oxidation barrier which also restricts permeation to degradation volatile compounds and promotes a delay in degradation process[46]. Regarding to the weight loss, similar residual weights are obtained with a main degradation step of about 90 – 91%. This is due to the fact that all composites contain 20 wt.% HSF and the residual weight is associated to the ashes generated by the combustion of the lignocellulosic filler.

Figure 4

In addition to the thermal transitions by DSC and degradation by TGA study, the coefficient of linear thermal expansion (CLTE) was determined by thermomechanical analysis (TMA) as it is representative for the dimensional stability. The main parameters (CLTE below and over glass transition temperature, T_g) from TMA characterization of PLA – 20 wt.% HSF composites with different ELO content are summarized in Table 4.

If we compare the CLTE below the T_g we can see that the initial value of the unmodified PLA – 20 wt.% HSF composite is close to $64 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ while composites with different ELO content offer remarkably higher values of $87 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ and $102 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ for composites with 7.5 wt.% HSF and 22.5 wt.% HSF respectively. This is in total accordance with the plasticization effect provided by ELO as it allows chain mobility, which is more pronounced with temperature.

Table 4

The evolution of the CLTE over T_g follows similar tendency with a change from $157.7 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ (unmodified composite) up to values of 175.8 for the composite with 22.5 wt.% ELO. As we have observed, the CLTE is characterized by lower values below T_g as the chain mobility is restricted. On the other hand, CLTE values are higher over T_g due to a remarkable increase in chain mobility which is also more pronounced by the plasticization effect provided by ELO.

In addition to dimensional stability by TMA analysis, other thermo-mechanical properties have been evaluated. Fig. 5 shows the plot evolution of the Vicat softening temperature (VST) and heat deflection temperature (HDT) of PLA – 20 wt.% HSF composites with varying ELO content. As these two thermal parameters are directly related to mechanical resistant properties we observe the same tendency of that observed for strength and modulus. The initial VST and HDT values for unmodified composite are $54.5 \text{ }^\circ\text{C}$ and $53.1 \text{ }^\circ\text{C}$ respectively which indicate that moderate temperatures lead to material softening. Regarding the VST evolution in terms of wt.% ELO, plasticization provided by ELO leads to more soft and flexible materials so that, VST values decrease with increasing ELO content up to values of $51.1 \text{ }^\circ\text{C}$, $50.5 \text{ }^\circ\text{C}$ and $48.3 \text{ }^\circ\text{C}$ for an ELO

content of 7.5 wt.%, 15 wt.% and 22.5 wt.% respectively. Epoxidized linseed oil acts as a plasticizer which leads to a clear softening effect which is more pronounced by the application of external loads at lower temperature values. Sliding of polymer chains is easier in the presence of epoxidized linseed oil molecules since these diminish the intermolecular attraction forces between individual poly(lactic) acid macromolecules[42]. The evolution of the heat deflection temperature (HDT) is similar to that observed for VST. The HDT of unmodified composite (51.6 °C) is reduced up to 49 °C for composites containing 22.5 wt.% ELO.

Figure 5

Figure 6

The plasticization effect of ELO can also be detected by dynamic mechanical thermal analysis (DMTA). Fig. 6 shows a plot evolution of the storage modulus (G'). We can see that all DMTA curves for composites containing different ELO amounts are located below the curve for unmodified composite. Below the glass transition temperature (T_g), the storage modulus (G') is high due to an elastic-vitreous behavior. In this first section the maximum G' values are obtained for unmodified PLA – 20 wt.% composite with a value around 1952 MPa. As one can see, the initial storage modulus decreases as the ELO content increases with values of 1705 MPa, 1352 MPa and 1049 MPa for composites containing 7.5 wt.%, 15 wt.% and 22.5 wt.% respectively. Once the glass transition temperature is overpassed, we observe a remarkable decrease in G' due to an elastic-viscous behavior. The temperature range of this softening process is remarkably lower for composites with high wt.% ELO content. This softening temperature range

changes from [64 °C – 85 °C] for unmodified composite up to [50 °C – 65 °C] for composites with an ELO content of 22.5 wt.%. This is in total accordance with previous results as ELO enhances polymer chain motion, which leads to a softer material. So that, at 60 °C, the storage modulus (G') of unmodified composite is close to 1081 MPa while this is remarkably reduced up to values of 467 MPa for composites with 7.5 wt.% ELO due to the plasticizing-softening effect provided by ELO. These values are even extremely lower for composites containing 15 wt.% and 22.5 wt.% ELO with G' values of 6.2 MPa and 3.4 MPa respectively [43, 47]. Over 90 °C, unplasticized composite from PLA and 20 wt.% HSF shows an increase in the storage modulus which is directly related to the cold crystallization process. As we can see, presence of ELO in PLA-HSF composites leads to a remarkable decrease in the cold crystallization onset temperature with values of about 85 °C, 70 °C and 65 °C for composites containing 7.5 wt.%, 15 wt.% and 22.5 wt.% ELO. This behavior is related to increased chain mobility over the glass transition temperature, which allows chain rearrangement to ordered/packed structures at lower temperatures. During the cold crystallization process, both density and stiffness increase to the highly packed structure [16, 28]. Once the crystallization process is completed, the evolution of the storage modulus (G') follows similar tendency as observed in the initial stages with maximum values for unmodified composites and decreasing values with higher ELO content.

Figure 7

With regard to the damping factor ($\tan \delta$) Fig. 7 shows its evolution with temperature for PLA – HSF composites. As the ELO content increases, the damping peak is moved to lower temperature. This peak is related to the glass transition due to a change

in behavior from elastic to viscous material. By taking the damping peak as a representative value of the glass transition temperature (T_g) we can see that unmodified PLA – HSF composite is characterized by a T_g of 75 °C and this is remarkably reduced with increasing ELO content up to values of 72 °C, 60 °C and 57 °C for PLA – HSF composites containing 7.5 wt.%, 15 wt.% and 22.5 wt.% ELO respectively. As indicated previously, ELO provides good plasticizing effect on PLA – HSF composites and is evidenced by a decrease in the damping peak that is representative of a decrease in the glass transition temperature[22-24, 42, 45, 51].

The evolution of the storage modulus and the damping factor indicate that low ELO content gives similar behavior to unmodified composite with a rigid behavior. For these compositions, the plasticization effect is not important and some coupling effect can be achieved by ELO. On the other hand, when high contents of ELO are used flexible materials are obtained with a clear plasticization effect evidenced by a decrease in the glass transition temperature and, furthermore, optimum coupling effects are provided by ELO thus leading to composites with improved overall properties. In addition to mechanical properties, ELO provides a lubricant effect that enables manufacturing of PLA-based composites with a remarkable decrease in viscosity even with presence of filler particles[16, 47].

4.- Conclusions

The effect of varying epoxidized linseed oil (ELO) content on overall properties of poly(lactic acid), PLA composites with constant 20 wt.% hazelnut shell flour (HSF) has been studied. The obtained results have revealed a dual effect provided by ELO: on the one hand it contributes to plasticize PLA with a noticeable decrease in the glass transition temperature and on the other hand, ELO acts as coupling agent with potential

interactions with hydroxyl groups from both lignocellulosic filler and terminal groups in poly(lactic acid) macromolecular chains. A synergistic effect is provided by ELO which enhances overall properties of PLA – HSF composites.

With regard to mechanical properties, presence of ELO leads to lower resistant properties such as tensile and flexural strength, elastic and flexural modulus and Shore D hardness but a remarkable increase in ductile properties is achieved with increasing amounts of ELO. The elongation at break changes from 3.1% for the unmodified PLA – 20 wt.% HSF composite up to values of 17% for the composite containing 22.5 wt.% ELO in its composition. ELO provides a clear plasticizing effect, particularly for ELO content over 7.5 wt.%. Epoxidized linseed oil (ELO) molecules are placed between individual poly(lactic acid) macromolecules and contribute to diminish intermolecular attraction forces between polymer chains and this enhances chain mobility with a positive effect on deformation mechanisms. In addition, the coupling effect of ELO has been evidenced by field emission electron scan microscopy (FESEM) with a remarkable decrease of the gap among the filler-matrix interface area.

Regarding thermal properties of PLA – 20 wt.% HSF it is important to note an important decrease in the glass transition temperature by differential scanning calorimetry, DSC (about 8 °C lower for the composite with 22.5 wt.% ELO) and dynamic mechanical thermal analysis, DMTA (about 15 °C lower for the same composition)

In general terms, attractive synergistic plasticization and coupling effects can be obtained by adding epoxidized linseed oil (ELO) to green composites based on poly(lactic acid) matrix and hazelnut shell flour (HSF) without further modifications. The resulting materials offer improved ductile properties and easy manufacturing due to the plasticization effect of ELO and overall mechanical properties are obtained due to the coupling effect between the lignocellulosic filler and polylactic acid.

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Tables

Table 1.- Composition (in weight %) of poly(lactic acid), PLA – hazelnut shell flour (HSF) composites with varying epoxidized linseed oil (ELO) content.

Sample	PLA content (wt.%)	Hazelnut shell flour (HSF) content (wt.%)	ELO content (wt.%)
0-ELO	80	20	0
7.5-ELO	72.5	20	7.5
15-ELO	65	20	15
22.5-ELO	57.5	20	22.5

Table 2.- Mechanical properties of PLA – HSF composites with varying epoxidized linseed oil (ELO) content.

Sample	Tensile			Flexural		Hardness Shore D
	Elastic modulus (MPa)	Strength (MPa)	Elongation at break (%)	Modulus (MPa)	Strength (MPa)	
0-ELO	1019±53	45.0±4.9	3.1±0.4	3932±92	83.7±1.9	75.6±0.5
7.5-ELO	965±42	34.4±1.4	4.2±0.4	3523±152	59.6±0.9	71.2±0.4
15-ELO	751±81	22.1±0.7	11.2±1.8	2702±287	42.1±0.8	67.8±0.8
22.5-ELO	590±58	15.3±0.9	17.1±1.8	2118±143	29.5±0.9	59.6±0.5

Table 3.- Thermal properties of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content, obtained by differential scanning calorimetry (DSC).

Samples	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J g ⁻¹)	ΔH_{cc} corrected * (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	ΔH_m corrected * (J g ⁻¹)	X_c (%)
0-ELO	66.5	104.8	20.99	26.24	169.9	-32.43	-40.53	15
7.5-ELO	60.1	105.3	22.84	31.5	168.8	-35.85	-49.45	19
15-ELO	59.4	103.1	18.50	28.46	167.5	-29.76	-45.78	18
22.5-ELO	58.7	102.4	16.97	29.51	167.5	-25.42	-44.21	16

*ΔH_{cc} corrected and ΔH_m corrected correspond to normalized crystallization and melt enthalpies by considering the real wt.% PLA in composites.

Table 4.- Coefficient of linear thermal expansion (CLTE) of PLA – 20wt.% composites with varying wt.% of epoxidized linseed oil (ELO) content, obtained by thermomechanical analysis (TMA).

Samples	CLTE below T_g (μm m ⁻¹ °C ⁻¹)	CLTE after T_g (μm m ⁻¹ °C ⁻¹)
0-ELO	64.1	157.7
7.5-ELO	87.0	164.9
15-ELO	102.6	171.4
22.5-ELO	102.7	175.8

Figures

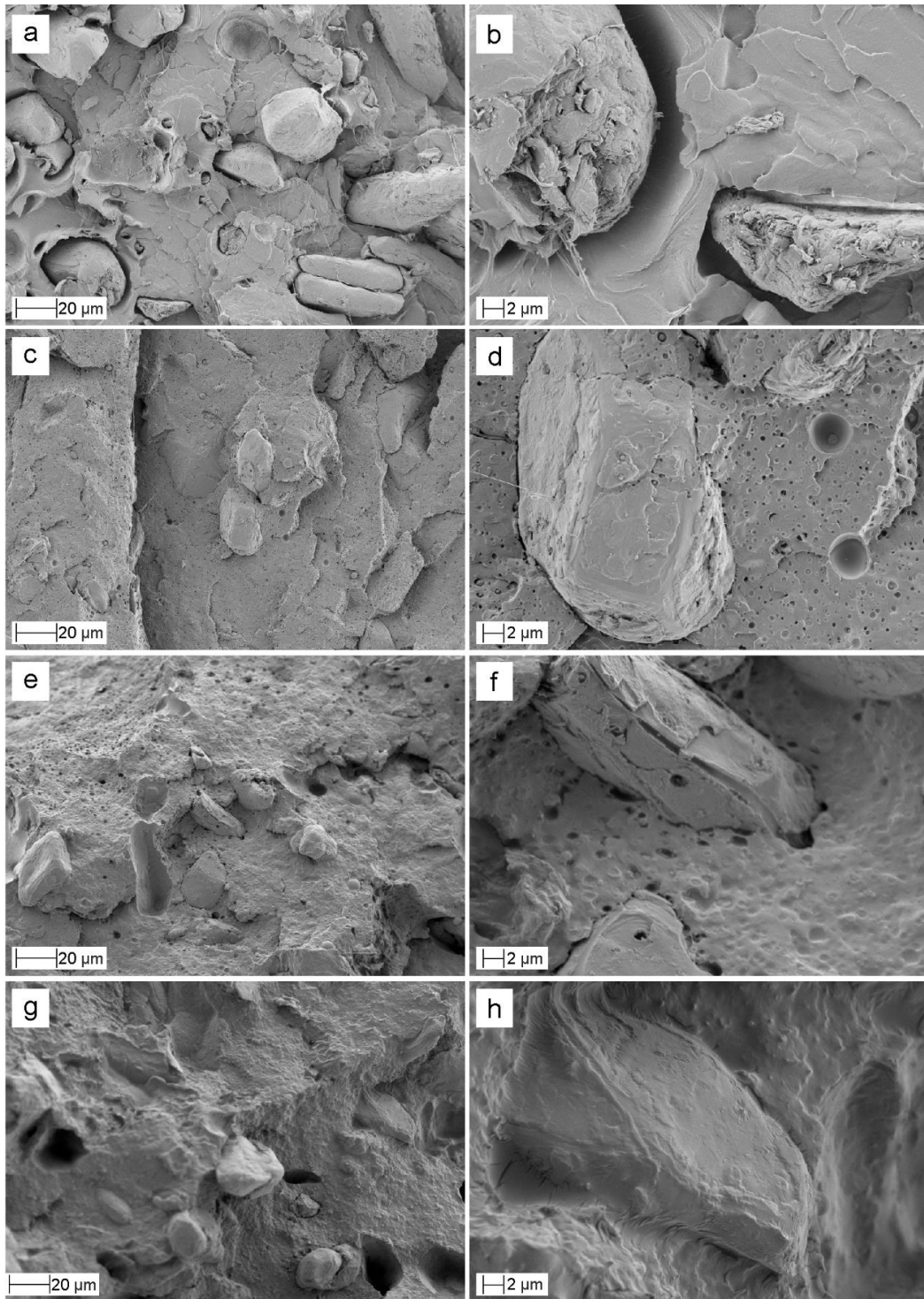


Figure 1.- FESEM images Corresponding to cryofractured surfaces from PLA – 20 wt.% HSF and varying ELO content: a) 0 wt.% ELO (500x); b) 0 wt.% ELO (2500x); c) 7.5 wt.% ELO (500x); d) 7.5 wt.% ELO (2500x); e) 15 wt.% ELO (500x); f) 15 wt.% ELO (2500x); g) 22.5 wt.% ELO (500x); h) 22.5 wt.% ELO (2500x).

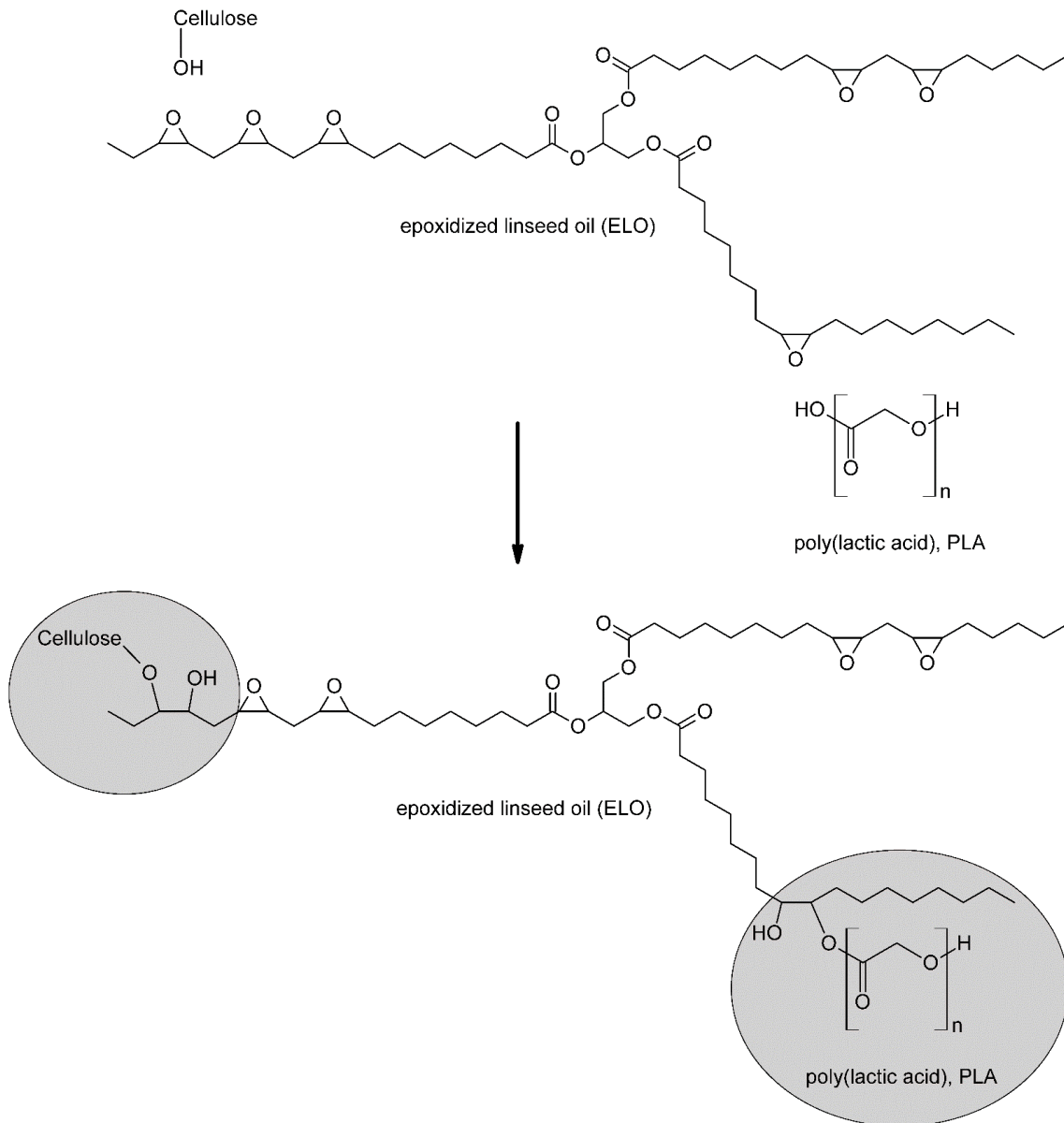


Figure 2.- Proposed chemical interactions between epoxidized linseed oil (ELO) and lignocellulosic particles from hazelnut shell flour (HSF) and ELO with poly(lactic acid) polymer chains.

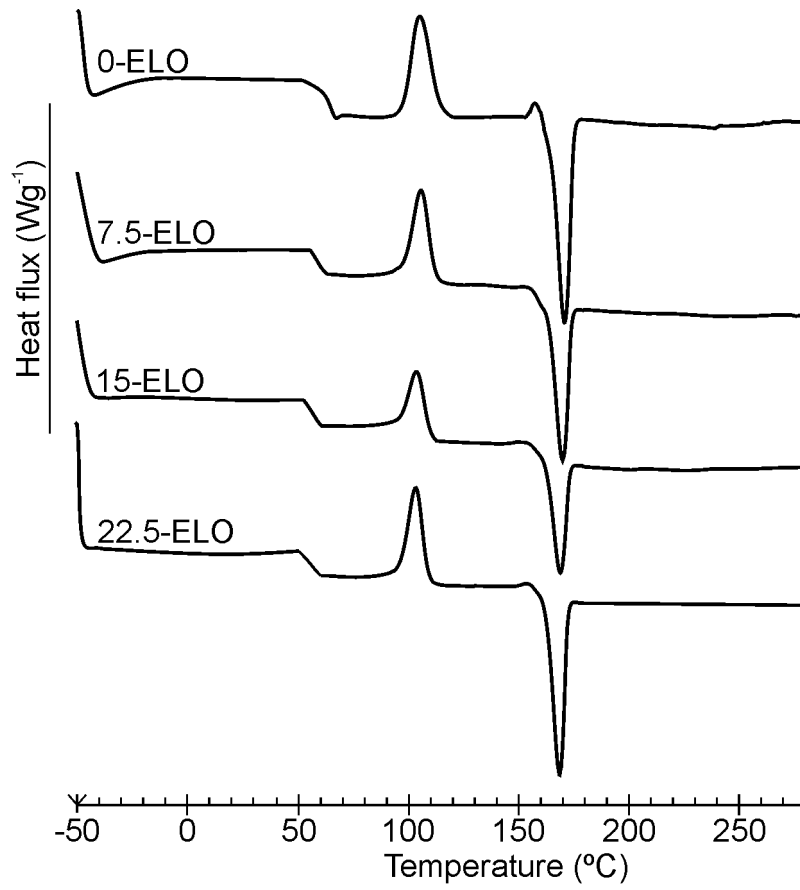


Figure 3.- Comparative plots of differential scanning calorimetry (DSC) curves of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content.

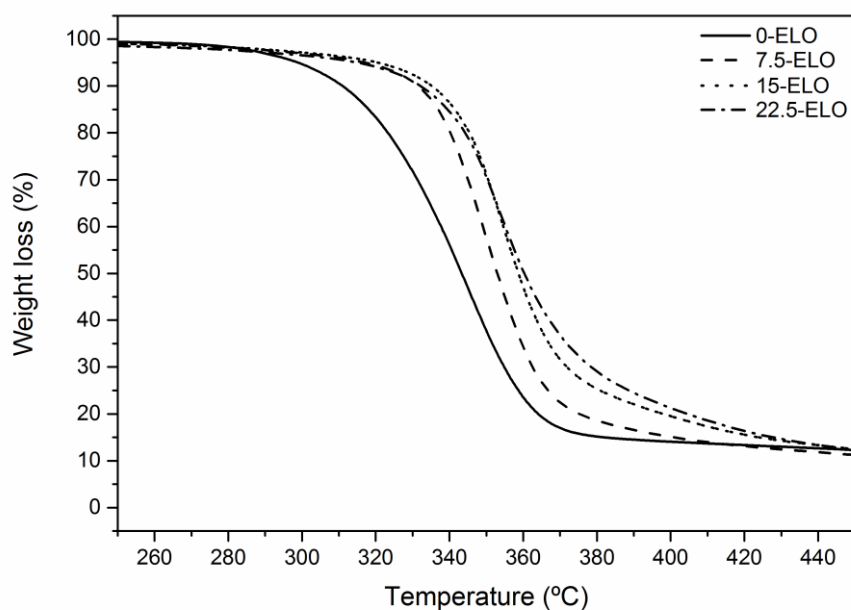


Figure 4.- Comparative plots of thermogravimetric degradation (TGA) curves of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content.

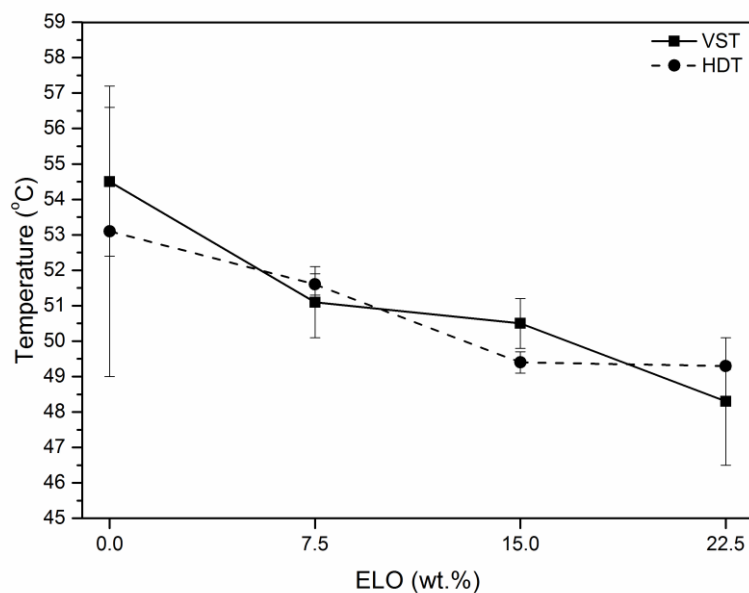


Figure 5.- Plot evolution of the Vicat softening temperature (VST) and heat deflection temperature (HDT) of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content.

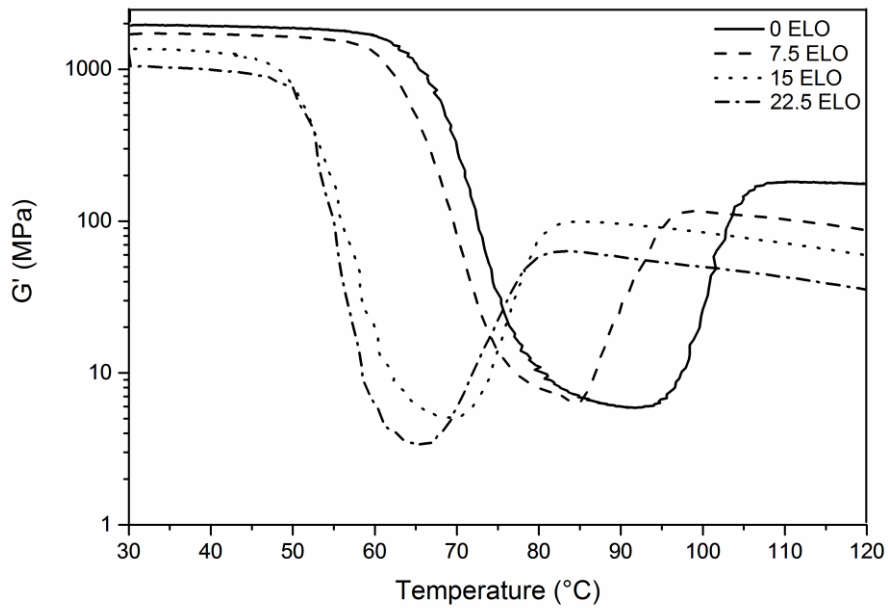


Figure 6.- Comparative plot of the storage modulus (G') of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content.

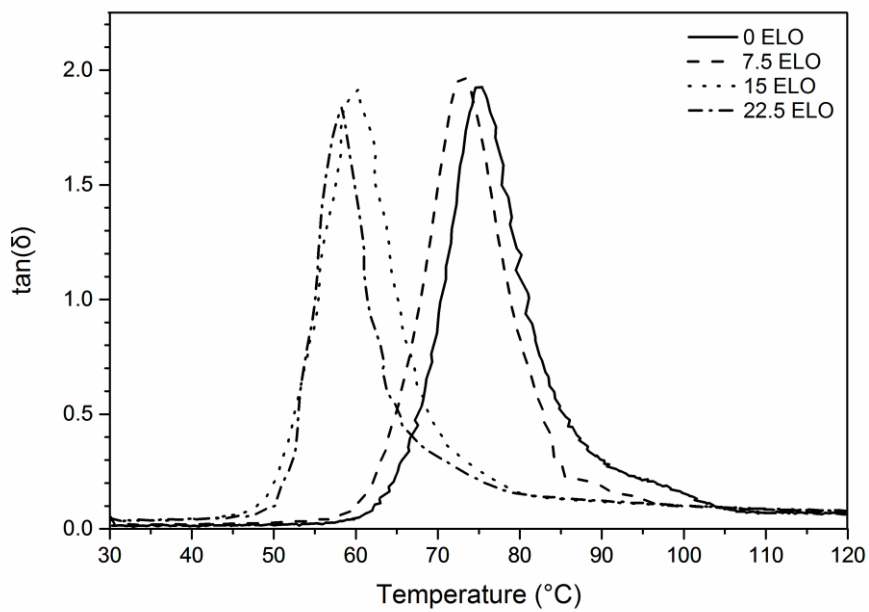


Figure 7.- Comparative plot of the damping factor ($\tan \delta$) of PLA – 20 wt.% HSF composites with varying wt.% of epoxidized linseed oil (ELO) content.