"Plasticization effect of epoxidized cottonseed oil (ECSO) on poly(lactic acid)"

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ABSTRACT

In this work, the use of an environmentally friendly plasticizer derived epoxidized cottonseed oil (ECSO) for poly(lactic acid) (PLA) is proposed. Melt extrusion was used to plasticize PLA formulations with different ECSO contents in the 0 - 10 wt.%. PLA formulation with 10 wt.% shows a remarkable increase in mechanical ductile properties with a percentage increase in elongation at break of more than 1100% and a noticeable increase in the impact absorbed energy. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) revealed a clear decrease in the glass transition temperature of neat PLA as the ECSO content increased. Field emission scanning electron microscopy (FESEM) of fractured surfaces from impact tests showed an improvement of ductility with typical rough and porous topographies. Migration tests in *n*-hexane at different temperatures revealed very low migration properties thus leading to new interesting plasticizers for improved PLA industrial formulations.

Keywords: poly(lactic acid)-PLA; epoxidized cottonseed oil (ECSO); mechanical properties; thermal properties; migration.

1.- Introduction.

One of the most promising biopolymers as alternative to conventional petroleum-based polymers is poly(lactic acid)-PLA with an annual production of more than 140,000 tons (Grande et al., 2015). PLA is an aliphatic polyester obtained by polymerization of lactic acid (hydroxyl propionic acid) obtained from renewable and sustainable starch rich materials such as corn and sugarcane (Al-Mulla et al., 2011; Blanco and Siracusa, 2013; Sansone et al., 2012) . In the last years PLA has become an industrial alternative to some petroleum-based polymers because of its relatively low price (Gordobil et al., 2015) and overall balanced mechanical properties such as high tensile strength and Young's modulus with similar values of those of poly(ethylene terephthalate), PET (Chieng et al., 2014) which is widely used in plastic bottle manufacturing due to its excellent barrier properties. PLA possesses acceptable barrier properties, and additionally it can be transparent due to the low crystallization rate (Chieng et al., 2014). It is also shiny and offers low flammability; all these features, together with a relatively easy processing conditions, similar to many commodities, make PLA a good candidate for a wide variety of products in the packaging industry, automotive parts, textile fibers, prostheses and medical devices, etc. among others (Morelli et al., 2015; Murariu et al., 2008) . Nevertheless, PLA is characterized by high fragility, which is drawback for some technical applications in which some flexibility is required (Wang et al., 2015). For these reasons, different approaches have been explored to overcome this high intrinsic fragility by increasing ductile properties such as elongation at break, impact resistance, etc. while maintaining its environmentally friendly nature. A typical approach has been blending PLA with other ductile polymers. In this field, PLA was blended with chitosan, which is able to form films but the mixtures resulted in immiscible blends due to their different polarity and poly(vinyl alcohol), PVA was necessary to provide somewhat compatibility (Grande et al., 2015). Thermoplastic starch (TPS) also showed immiscibility with PLA and several compatibilizers such as maleic anhydride and methylene diphenyl diisocyanate (MDI) were needed to improve the overall properties (Clasen et al., 2015; Mittal et al., 2015; Yang et al., 2015). Blends with poly(hydroxybutyrate), PHB gave an interesting improvement on barrier properties of neat PLA but resulting blends were characterized by high fragility so that, different plasticizers such as acetyl(tributyl citrate), ATBC (Arrieta et al., 2015) and poly(ethylene glycol), PEG (Courgneau et al., 2011) were needed to overcome this drawback. PLA has also been blended with biodegradable petroleum-based polymers to give fully biodegradable blends. Among these petroleum-based polymers interesting results have been obtained with poly(caprolactone)-PCL biodegradable polyester. Although both PLA and PCL are polyester-type polymers, they show restricted miscibility but the high flexibility of PCL is enough to reduce the intrinsic fragility of PLA (Carmona et al., 2015; Ferri et al., 2016a; Tabasi et al., 2015) . Other petroleum-based polymers such as poly(butylene succinate)-PBS (Deng and Thomas, 2015) , poly(butylene succinate-*co*-adipate)-PBSA (Pivsa-Art et al., 2015), poly(butyl acrylate)-PBA (Meng et al., 2012) and poly(butylene adipate-*co*-terephthalate)-PBAT (Arruda et al., 2015; Kumar et al., 2010) have been successfully blended with PLA with remarkable increase in flexibility.

Another way to improve the flexibility of neat PLA is by using plasticizers. Among the wide variety of commercial plasticizers, most of them derived from petroleum, epoxidized vegetable oils (EVOs) represent an interesting alternative as they are cost-effective materials with high performance as plasticizers and are obtained from renewable resources, mainly from vegetable oils with non-food purposes. Epoxidized oils are used in the PVC industry as secondary plasticizers and thermal stabilizers due to their free radical scavenging properties (Carbonell-Verdu et al., 2016; Fenollar et al., 2009; Mehta et al., 2014). In the last years, the potential of different epoxidized vegetable oils has been explored. Some epoxidized oils such as epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO) are commercially available at a relatively low cost and, consequently, they can be readily employed in industrial applications. Epoxidized soybean oil (ESBO) contains an oxirane oxygen content comprised in the 6.5 – 8% range and it has been reported as an interesting plasticizer for PLA. The study developed by Yu-Qiong Xu et al. revealed that addition of 6 wt.% ESBO to PLA increased the elongation at break from 3.98% for neat PLA to values of 6.50%. Similar findings were reported by Shalini Vijayarajan et al. They evaluated the influence of ESBO content (up to 20 wt.%) on ductility, measured as the ratio between the failure to yield strain. They found the best overall ductile properties for ESBO contents in the 5-10 wt.% range (Vijayarajan et al., 2014; Xu and Qu, 2009) . With regard to epoxidized linseed oil (ELO), which contains more average number of oxirane groups per triglyceride than ESBO, Javed Alam et al. reported the plasticizing effect provided by ELO with a remarkable increase in elongation at break and a subsequent decrease in tensile strength. Addition of carbon nanotubes contributed to balanced mechanical ductile and resistant properties (Alam et al., 2014). Interesting results with low oxirane oxygen content epoxidized oils have also been reported. Buong Woei Chieng et al. reported the potential of epoxidized palm oil (EPO) with an oxirane oxygen content of 3.23% and a mixture of epoxidized palm oil and epoxidized soybean oil with an average oxirane oxygen content of 3.58%, showing that 5 wt.% of the epoxidized oil leads to a remarkable increase in ductile properties. Furthermore, the mixture with higher oxirane oxygen content led to the highest elongation at break values (Chieng et al., 2014).

Cottonseed oil (CSO) is considered a by-product of the cotton industry with a total production around 5.12 million tons in 2014/15 (Trade, March 2016), being China and India the major world producers with 1.396 and 1.320 million tons respectively. Although some uses in the food industry are common, its generalized use is restricted because of some drawbacks: on the one hand, it is worth to note that the main product of the cotton industry is cotton fiber so that, cotton crops are not subjected to the severe controls and regulations regarding the use of pesticides and other chemicals. On the other hand, cottonseed oil contains high amounts of free gossypol which has been reported as a potentially toxic substance (Gadelha et al., 2014). The particular lipid profile of cotton seed oil, with approximately 75% of unsaturated fatty acids makes this oil an interesting candidate for chemical modification such as epoxidation (Carbonell-Verdu et al., 2015). The oxirane oxygen content of epoxidized cottonseed oil (ECSO) is located between low values typical of epoxidized palm oil (EPO) and high values typical of epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO). For this reason, this work aims to study the potential of epoxidized cottonseed oil (ECSO) with an intermediate oxirane oxygen content as environmentally friendly plasticizer for poly(lactic acid), PLA. The effect of the epoxidized oil content on mechanical, thermal and migration properties of PLA were tested.

2.- Material and methods.

2.1.- Materials.

Poly(lactic acid), PLA commercial grade Ingeo TM Biopolymer 6201D was supplied by NatureWorks LLC (Minnetonka, USA) in pellet form with a density of 1.24 g cm^{-3}. Its melt flow index is in the 15-30 g/10 min range measured at a temperature of 210 ºC. The base oil for plasticizer synthesis was cottonseed oil (CSO). This was supplied by Sigma Aldrich (Sigma Aldrich, Madrid, Spain). This oil is characterized by a density 0.92 g cm^{-3} at 25 ºC and an iodine number of 107. This vegetable oil was subjected to an epoxidation process as indicated elsewhere with hydrogen peroxide and acetic acid (Carbonell-Verdu et al., 2015). After epoxidation, the oxirane number of the synthesized epoxidized cottonseed oil was 5.32% and its iodine number was 1.79. **Fig. 1** shows an schematic representation of the chemical structures of poly(lactic acid) and epoxidized cottonseed oil.

Figure 1.- Schematic representation of the chemical structure of a) poly(lactic acid)-PLA and b) epoxidized cottonseed oil (ECSO).

2.2.- Manufacturing of plasticized poly(lactic acid).

Firstly, PLA pellets were dried at 60 ºC for 24 h. PLA pellets and the corresponding amounts of the liquid plasticizer (see **Table 1**) were mechanically mixed in a zip bag until homogenization. After this stage, the mixtures were extruded in a twin screw extruder at a constant speed of 40 rpm. The temperature profile ranged from 170 ºC (feeding zone) to 180 ºC (die). Then the extrudate was pelletized and subsequently shaped into standard samples in an injection molding machine Meteor 270/75 (Mateu & Solé, Barcelona, Spain) at an injection temperature of 180 ºC.

Tabla 1.- Composition of ECSO plasticized PLA materials and labelling.

2.3.-Mechanical characterization of ECSO plasticized PLA.

Mechanical characterization was conducted with standard tensile, flexural and impact tests. Tensile and flexural characterization was carried out in a universal test machine Ibertest Elib 30 (Ibertest S.A.E., Madrid, Spain). A minimum of five different samples were tested using a 5 kN load cell. Tensile tests were carried out at a crosshead speed of 10 mm min^{-1} as recommended by the ISO 527 standard. An axial extensometer from Ibertes was used to give accurate values of the Young's modulus. Regarding the flexural test, the crosshead speed was set to 5 mm min^{-1} as suggested by the ISO 178. The impact absorbed energy was measured in a 6 J Charpy's pendulum (Metrotec S.A., San Sebastián, Spain) following the guidelines of the ISO 197:1993.

2.4.- Morphology of ECSO plasticized PLA.

Fractured surfaces from impact tests were observed by field emission scanning electron microscopy (FESEM) in a Zeiss Ultra microscope 55 (Oxford Instruments, Oxfordshire, United Kingdom) with an accelerating voltage of 2 kV. Fractured surfaces were previously coated with a thin platinum layer in a sputter coater EM MED020 (Leica Microsystems)

2.5.- Thermomechanical characterization of ECSO plasticized PLA.

Thermomechanical characterization was conducted by measuring the Vicat softening temperature (VST), heat deflection temperature (HDT). VST and HDT values were determined in a DEFLEX 687-A2 station (Metrotec S.A., San Sebastián, Spain). VST was measured according to ISO 306 (B method) at a constant heating rate of 50 ºC h^{-1} and a load of 50 N. Regarding HDT values, they were obtained as recommended by the ISO 75 (A method) at a fixed heating rate of 120 ºC h-1 and a constant load of 1.8 MPa. Additionally, dynamic mechanical thermal analysis (DMTA) was used to evaluate changes in storage modulus (G') and damping factor. Samples sizing 40x40x4 mm^3 were tested in torsion mode in an oscillatory rheometer AR G2 (TA Instruments, New Castle, USA) equipped with an accessory clamp for solid samples. Samples were subjected to a thermal program from 25 ºC to 130 ºC at a heating rate of 2 ºC min-1. The frequency was set to 1 Hz and the maximum deformation (γ) was 0.1%.

2.6.- Thermal characterization of ECSO plasticized PLA.

Thermal behavior of ECSO plasticized PLA samples was tested by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Differential scanning calorimetry tests were carried out in a Mettler-Toledo calorimeter 821e (Mettler-Toledo Inc., Schwerzenbach, Switzerland). Samples with an average weight in the 7-8 mg range were subjected to the following thermal program: initial heating from 30 ºC to 210 ºC at a heating rate of 10 ºC min^{-1} in nitrogen atmosphere with a nitrogen flux of 66 mL min^{-1}. The glass transition temperature (T_g), cold crystallization peak (T_{cc}) and the melt peak temperature (T_m) were obtained for each plasticized PLA formulation. The degree of crystallinity (X_c %) was calculated by Equation 1:

$$X_c\ (\%) = 100\ \times \frac{|\Delta H_{cc} + \Delta H_m|}{\Delta H_m(100\%)} \times \frac{1}{W_{PLA}} \qquad (1)$$

Where ΔH_{cc} is the cold crystallization enthalpy, ΔH_m is the melt enthalpy, ΔH_m (100%) is the theoretical melt enthalpy for a fully crystalline PLA structure (93 J g^{-1}) (Arrieta et al., 2014) and W_{PLA} is the PLA weight fraction.

The initial heating step was applied to remove the previous thermal history of the materials. Thermogravimetric analysis was carried out in a TGA/SDTA 851 thermobalance from Mettler-Toledo (Mettler-Toledo Inc., Schwerzenbach, Switzerland).

Samples with an average weight of 10 mg were subjected to a heating program from 30 ºC to 700 ºC at a heating rate of 20 ºC min^{-1} and constant nitrogen flux (66 mL min^{-1}).

2.7.- Plasticizer migration by the solvent extraction test.

Plasticizer migration was studied by solvent extraction with n-hexane. Samples were immersed in n-hexane and placed in an air circulating oven mod. Selecta 2001245 (JP Selecta S.A., Barcelona, Spain) working at different temperatures, between 30 ºC and 60 ºC during 8 hours. Finally, the samples were removed from n-hexane to measure weight loss.

3.- Results and discussion.

3.1.- Mechanical properties of ECSO plasticized PLA formulations.

The study of the effect of the epoxidized cottonseed oil (ECSO) on mechanical properties of PLA-based formulations is a good method to assess the plasticization that ECSO provides. PLA is a brittle polymer with relatively high tensile and flexural strength values, high modulus and very low elongation at break. **Table 2** summarizes the main results obtained by tensile and flexural tests. Neat PLA possesses a tensile strength of 63.7 MPa with very low elongation at break values around 9%. As the elastic modulus is defined by the ratio strength to elongation in the linear region, high strength with very low elongation give high modulus of 3.6 GPa. The plasticization effect is evident by observing the changes in both mechanical resistant and ductile properties. Plasticized PLA with 2.5 wt.% ECSO is characterized by slightly higher elongation at break values of 13.5% and a subsequent decrease in both tensile strength and Young's modulus with values of 58.5 MPa and 3.3 GPa respectively. As the total plasticizer content in PLA formulations increases it is clearly detectable a remarkable improvement in ductile properties by a dramatic change in elongation at break up to values of 110.5% for PLA formulations containing 10 wt.% ECSO which is approximately eleven times higher than the elongation at break of unplasticized PLA (9%). This represents an overall percentage increase of around 1128% regarding to neat PLA, calculated as the percentage ratio of the variation in elongation at break (110.5% - 9%) to the elongation at break of neat PLA (9%). These results are in accordance with previous works regarding PLA plasticization with epoxidized vegetable oils. Buong Woei Chieng *et al.* reported a percentage increase in elongation at break of more than 2000% with the only addition of 5 wt.% epoxidized palm oil (EPO) to PLA formulations. In fact, the elongation at break changed from 5.3% (neat PLA) up to 114.4% for the corresponding EPO-plasticized formulation. Even better results were obtained in PLA formulations plasticized with a mixture of epoxidized palm and soybean oil (EPSO) with an elongation at break of 220.5%. They also reported a noticeable drop on tensile strength values from values close to 60 MPa for neat PLA up to values of 35 MPa for plasticized PLA formulations with an epoxidized palm oil (EPO) content between 5 – 10 wt.%. This dramatic drop in tensile strength is directly related to polymer-plasticizer interactions. The epoxy groups contained in the epoxidized vegetable oil can interact with the hydroxyl groups located in the end chains of PLA. As they suggest, these interactions are stronger as the oxirane oxygen content increases (Chieng et al., 2014). Their findings are in total accordance with the plasticizing effect that epoxidized cottonseed oil (ECSO) provides. ECSO is characterized by a medium oxirane oxygen content (5.32%) compared to epoxidized palm oil (EPO) with low values (3.23%) and epoxidized linseed oil (ELO) with high values around 10%. As it can be observed in **Table 2**, the tensile strength of neat PLA (63.7 MPa) is reduced to values close to 50 MPa with the maximum ECSO content. This drop in tensile strength is lower than that observed by Buong Woei Chieng *et al.* with epoxidized palm oil (EPO). The higher oxirane oxygen content in ECSO can interact more strongly with PLA chains leading to intense polymer-plasticizer interactions that provide balanced tensile strength and elongation at break values. Regarding the Young's modulus, the initial value corresponding to unplasticized PLA is 3.6 GPa and this is slightly reduced up to values of 3.3 GPa for plasticized formulations with varying ECSO content. Although the plasticization effect of ECSO and other epoxidized vegetable oils is evident through a remarkable increase in elongation at break values. It has been reported that once the optimum plasticizer content has reached, a plasticizer excess leads to lower elongation at break values due to a possible phase separation (Ferri et al., 2016b). Although the values are not summarized in **Table 2**, a plasticized PLA formulation was also prepared with 15 wt.% ECSO. The elongation at break of this formulation was similar to that obtained for the plasticized PLA formulation with 5 wt.% thus giving a clear evidence of plasticizer saturation which has a negative effect on ductile properties due to phase separation.

Table 2. – Summary of mechanical properties from tensile and flexural tests of plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Similar behaviour has been found for flexural tests. As it can be observed in Table 2 the flexural strength of neat PLA (116.3 MPa) is progressively reduced up to values of 78.6 MPa and 53.3 MPa for plasticized PLA formulations containing 5 wt.% and 10 wt.% ECSO respectively. Although slight changes can be produced on flexural modulus, these changes are in the typical error range so that, no clear tendency can be observed.

As above mentioned, the addition of ECSO provides a clear plasticizing effect on PLA with a remarkable increase in mechanical ductile properties such as elongation at break. Besides this, ECSO plasticized PLA formulations are remarkably toughened as it can be seen in **Fig. 2**. The high intrinsic brittleness of neat PLA is reduced due to the toughening and elastomeric effect provided by the ECSO plasticizer. An increasing tendency of impact absorbed energy can be seen in **Fig. 2**. Neat PLA possesses an impact energy of 30.8 kJ m^{-2} and this is progressively increased up to values of 38.42 kJ m^{-2} for the plasticized PLA formulation with 10 wt.% ECSO which represents a percentage increase of 25% regarding neat PLA. As shown by tensile and flexural tests, addition of ECSO promotes a remarkable increase in elongation and this has a positive effect on energy absorption.

Figure 2.- Plot evolution of the impact absorbed energy measured by the Charpy's test for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

The effect of epoxidized cottonseed oil (ECSO) on the morphology of plasticized PLA formulations can be observed in **Fig. 3** which shows FESEM images of fractured surfaces from impact tests samples. **Fig. 3a** shows the typical fracture surface of a brittle polymer with a flat and smooth surface and no evidence of plastic deformation. For low ECSO plasticizer content of 2.5 wt.% (**Fig. 3b**) a homogeneous surface can be observed which is representative for good compatibility between PLA and ECSO plasticizer that is uniformly distributed in the PLA matrix. In addition to this, other plasticization signs can be detected in the form of fibrils resulting from plastic deformation during a sudden impact. This phenomenon is in total accordance with the previous mechanical properties. Plasticized PLA formulations with very low amounts of ECSO plasticizer are characterized by a relative low increase in elongation at break. This fact could be related to strong interactions between PLA polymer chains and the epoxidized cottonseed oil. These strong interactions occur because no phase separation occurs as observed in **Fig. 3b**. As the weight % of ECSO increases some spherical cavities/voids can be observed. These are produced by a cavitation process caused by debonding. The empty microvoids indicate presence of an epoxidized cottonseed oil rich phase dispersed in the PLA matrix that becomes more evident with increasing ECSO content. Presence of fibrils is less evident as the ECSO content increases. In general, FESEM reveals good miscibility between PLA and ECSO plasticizer for very low plasticizer content as observed by V. S. Giita Silverajah et al (Giita Silverajah et al., 2012). By increasing the plasticizer content, phase separation is more evident but elongation at break is highly improved until plasticizer saturation occurs. Over 10 wt.% ECSO, plasticizer saturation occurs and mechanical properties are not improved.

Figure 3.- FESEM images of fractured surfaces from impact tests corresponding to plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO) at 2000x: a) neat PLA, b) 2.5 wt.% ECSO, c) 5.0 wt.% ECSO, d) 7.5 wt.% ECSO and e) 10 wt.% ECSO.

3.2.- Thermal properties of ECSO plasticized PLA formulations.

Effective plasticization promotes important changes in thermal transitions, mainly the glass transition temperature (T_g) due to increased polymer chain mobility. **Fig. 4 and Fig. 5** show the effect of the ECSO plasticizer on dynamic mechanical response of plasticized PLA formulations. As it can be seen in **Fig. 4**, the storage modulus (G’) shows a flat plot from room temperature up to 50 ºC. Then the storage modulus undergoes a drops of nearby three orders of magnitude and tends to stabilize at about 70 ºC. This abrupt drop is directly related to the glass transition temperature (T_g) (Chieng et al., 2014). As the temperature raises and reaches values comprised in the 80 – 90 ºC range, a new increase in storage modulus can be detected which is related to the cold crystallization process. Regarding samples with different loads of ECSO plasticizer, the storage modulus curves are identical in shape but the typical values are shifted to lower temperatures thus indicating a decrease in both the glass transition temperature and cold crystallization process. The storage modulus of neat PLA below the glass transition temperature is close to 1.4 GPa. All plasticized formulations show a slight decrease in the storage modulus in this initial stage with typical values of 1.1 GPa thus indicating a clear plasticization effect. Plasticizer increases chain mobility and this has a positive effect on lowering both glass transition temperature and cold crystallization. The cold crystallization represents the realignment of PLA chains to form a more packed structure. It is evident that the plasticizer enables this rearrangement as it increases polymer chain mobility. The cold crystallization temperature changes from 81.7 ºC for neat PLA to values of 78 ºC for ECSO plasticized PLA formulations.

Figure 4.- Plot evolution of the storage modulus (G’) as function of temperature for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

By observing the evolution of the damping factor (tan δ) it is possible to detect two relaxations located at 50-70 ºC and 80-90 ºC which are attributed to the glass transition (T_g) and the cold crystallization (T_{cc}) temperatures respectively. The efficiency of the ECSO plasticizer can be assessed by measuring the changes in the glass transition temperature (T_g) (Liu and Zhang, 2011). Although the glass transition occurs in a temperature range, maximum values of the damping factor were taken as representative values (see **Fig. 5**). The T_g of neat PLA is 66.2 ºC. As the ECSO content increases, a decreasing tendency in T_g values can be observed up to values of 63.4 ºC and 62.5 ºC for plasticized PLA formulations with 2.5 wt.% and 10 wt.% ECSO respectively.

Figure 5.- Plot evolution of the damping factor (tan δ) as function of temperature for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

The plasticizing effect is also evident by observing the evolution of the Vicat softening temperature (VST) and heat deflection temperature (HDT) as seen in **Table 3**. Neat PLA is characterized by a HDT value of 47.6 ºC and this is reduced up to values in the 43 - 44 ºC range for all compositions. With regard to the Vicat softening temperature (VST) it changes from 52.8 ºC for neat PLA up to values of 43 ºC for the plasticized formulation with 10 wt.% ECSO thus indicating a clear plasticization effect related to increased polymer chain mobility.

Table 3.- Summary of thermomechanical properties, Vicat softening temperature (VST) and heat deflection temperature (HDT) of plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

As indicated previously, both the storage modulus (G’) and the damping factor (tan δ) obtained by dynamic mechanical thermal analysis revealed a decrease in the glass transition temperature (T_g) of neat PLA with increasing the ECSO plasticizer content. Differential scanning calorimetry (DSC) is a powerful technique that provides information not only about the glass transition and cold crystallization processes but also about the melt process. **Fig. 6** shows a comparative plot of the DSC heating thermograms of neat PLA and plasticized PLA formulations with different ECSO content. The glass transition temperature of neat PLA is 66.75 ºC. The cold crystallization process is clearly evident as an exothermic peak located in the 86 ºC – 114 ºC range with a maximum crystallization rate located at 97 ºC. Finally, the endothermic process between 156 ºC – 177 ºC corresponds to the melting of the crystalline phase in PLA. By observing the DSC heating thermograms of the plasticized PLA formulations with different weight % of ECSO plasticizer it is clearly evident a decrease in both the glass transition temperature (T_g) and the cold crystallization temperature range (and its representative temperature peak, T_{cc}). Thus, the plasticized formulation with low plasticizer content (2.5 wt.% ECSO) possesses a glass transition and cold crystallization temperatures of 63.8 ºC and 91.2 ºC respectively. These values are still lower for PLA plasticized formulations with higher plasticiser content. Therefore, PLA formulation with 10 wt.% ECSO is characterized by a glass transition temperature of 60.7 ºC and a cold crystallization peak located at 86.95 ºC. The decrease in the temperature range of the cold crystallization process is directly related to the plasticizing effect that ECSO provides. The plasticizer molecules, characterized by low molecular weight compared to polymer chains, diffuse inside the polymer matrix and are placed between polymer chains. This situation leads to an increase in the free volume that allows polymer chain motions to occur at lower temperatures. Additionally, the polymer-polymer interactions are less strong because the distance between polymer chains is increased by the plasticizer. Furthermore, in addition to the dilution effect that ECSO provides on the cold crystallization enthalpy (ΔH_{cc}), these values are lower because of the increased free volume that allows easy packing of the plasticized structure. Similar findings were reported by V. S. Giita Silverajah et al. with plasticized PLA with epoxidized palm oil (EPO). They concluded that good miscibility/compatibility between PLA and EPO was obtained for very low EPO content of 1 wt.%. They also reported a decrease in the glass transition of neat PLA for EPO contents of 5 wt.% but they observed clear phase separation for these formulations (Giita Silverajah et al., 2012). By taking into account the melt and cold crystallization enthalpies, it is possible to assume that PLA possesses a degree of crystallinity (X_c %) of 20.5%. The presence of plasticizer enables chain mobility and this has a positive effect on crystallization as polymer chains can move to a packed structure. The only addition of 2.5 wt.% ECSO leads to a degree of crystallinity of about 31.3% and similar values around 32.3% are obtained for plasticized PLA formulations with 10 wt.% ECSO. Similar findings were reported by Ferri et al. with plasticized PLA formulations with epoxidized fatty acid esters (Ferri et al., 2016b).

Figure 6.- Comparative plot of the DSC heating thermograms of neat PLA and plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Epoxidized vegetable oils also provide improved stability. The oxirane rings are able to scavenge acid groups by catalytic degradation and this has a positive effect on both thermal and light stabilization. In fact, one of the main commercial uses of epoxidized vegetable oils is as secondary plasticizers and thermal and light stabilizers (Mohammed et al., 2015).

Table 4 shows the typical degradation temperatures for neat PLA and plasticized PLA formulations with varying ECSO content. The onset degradation temperature has been assessed by the temperature with a wt.% loss of 5% ($T_{5\%}$). In addition, the temperature for a 50 wt.% loss has been assessed ($T_{50\%}$). The thermal stabilization effect that epoxidized cottonseed oil provides can be seen by observing the evolution of the onset degradation temperature. Neat PLA is characterized by a T5% of 335.5 ºC and this is upward shifted to almost 340 ºC for PLA formulations containing 10 wt.% ECSO.

Table 4.- Main degradation parameters obtained by thermogravimetric analysis (TGA) for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

3.3.- Plasticizer migration assessment on plasticized PLA formulations with ECSO.

The potential migrants from poly(lactic acid) include lactic acid, the cyclic dimer of lactic acid (lactide), the linear dimer of lactic acid (lactoyl lactic acid) and other oligomers. Several studies have assessed PLA as a safe substance for food-contact and lactic acid has been declared as a generally recognized as safe (GRAS) substance (Conn et al., 1995). Nevertheless, most industrial PLA formulations include plasticizers and other additives to tailor properties. For this reason, it is important to know the potential plasticizer migration levels as it can restrict some uses in the food packaging industry. The solvent extraction test is a quite aggressive test to measure to total migrated plasticizer and gives interesting results about the potential use of plasticizers at industrial scale. **Fig. 7** shows a comparative plot of the total plasticizer migrated in terms of increasing temperature (all migrated amounts are referred at a migration time of 8 h). As it can be observed, PLA does not show any relevant migration at 8 h in the temperature range comprised between 30 ºC and 60 ºC with weight % migration values less than 0.02%. Regarding PLA formulations with epoxidized cottonseed oil (ECSO) the lowest migration levels are obtained, as expected, at the lowest temperature considered in this study (30 ºC) with typical values of 0.03% and 0.06% for PLA formulations with 2.5 wt.% and 10 wt.% ECSO respectively. As temperature increases, the total amount of migrated plasticizer increases as well but the maximum migration levels achieved are less than 0.12% which indicates a very low plasticizer migration. It is important to note that epoxidized vegetable oils are characterized by a molecular weight comprised between 850 g mol^{-1} to 950 g mol^{-1}. Although these values are extremely lower compared to poly(lactic acid) molecular weight, other monomeric plasticizers for PLA have lower molecular weight, i.e. acetyl tributyl citrate, ATBC (402.5 g mol^{-1}) (Dobircau et al., 2015), tributyl citrate, TbC (360.44 g mol^{-1}) (Tanrattanakul and Bunkaew, 2014), di-2-etylhexyladipate, DOA (371 g mol^{-1}) (Martino et al., 2009). For this reason, the migration levels with epoxidized vegetable oils is extremely low compared to other monomeric plasticizers. As expected, migrated plasticizer amounts increase with temperature with similar values for all plasticized PLA formulations. These relative low migration levels indicate good plasticizer compatibility as indicated previously. Interaction of epoxy groups present in epoxidized cottonseed oil (ECSO) with hydroxyl groups in poly(lactic acid) leads to a plasticization effect and potential chain extension phenomenon. These strong interactions positively contribute to low migration levels thus indicating the feasibility of using these plasticized formulations at industrial scale.

Figure 7.- Plasticizer migration levels by the solvent extraction test on plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

4.- Conclusions.

New environmentally friendly plasticized PLA formulations were obtained with epoxidized cottonseed oil (ECSO). The low intrinsic elongation at break of PLA (9%)

was improved up to values of 110.5% for plasticized formulations with 10 wt% ECSO. Field emission scanning microscopy (FESEM) revealed good miscibility at low ECSO concentrations (lower than 2.5 wt%) while slight phase separation occurred over this composition. Despite this, a remarkable increase in toughness was observed for compositions over 2.5 wt.% due to the particular morphology defined by a PLA matrix with finely dispersed spherical ECSO domains. The glass transition temperature was reduced by around 5-6 ºC for plasticized formulations with 7.5 – 10.0 wt.% ECSO. This decrease in T_g gave evidences of increased free volume with a positive effect on chain mobility, so that both the glass transition and the cold crystallization temperature were moved to lower values. Very low migration levels were assessed by the solvent extraction test with *n*-hexane with a maximum migration of 0.12% at 50-60 ºC while very low plasticizer migration (<0.06%) was observed at 30 ºC. The results obtained in this work suggest that high environmentally friendly toughened PLA formulations can be obtained by using epoxidized cottonseed oil (ECSO) in the 5 – 10 wt% range. Over 10 wt% ECSO, plasticizer saturation occurs and this has a negative effect on overall properties.

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Figure captions

Figure 1.- Schematic representation of the chemical structure of a) poly(lactic acid)-PLA and b) epoxidized cottonseed oil (ECSO).

Figure 2.- Plot evolution of the impact absorbed energy measured by the Charpy's test for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Figure 3.- FESEM images of fractured surfaces from impact tests corresponding to plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO) at 2000x: a) neat PLA, b) 2.5 wt.% ECSO, c) 5.0 wt.% ECSO, d) 7.5 wt.% ECSO and e) 10 wt.% ECSO.

Figure 4.- Plot evolution of the storage modulus (G') as function of temperature for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Figure 5.- Plot evolution of the damping factor (tan δ) as function of temperature for plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Figure 6.- Comparative plot of the DSC heating thermograms of neat PLA and plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).

Figure 7.- Plasticizer migration levels by the solvent extraction test on plasticized PLA formulations with different weight % of epoxidized cottonseed oil (ECSO).