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Additional Information

"The effect of maleinized linseed oil as biobased plasticizer in poly(lactic acid)-based formulations".

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Abstract

The use of maleinized linseed oil (MLO) as a potential biobased plasticizer for poly(lactic acid) (PLA) industrial formulations with improved toughness was evaluated. MLO content varied in the range 0 – 20 phr (parts by weight of MLO per hundred parts by weight of PLA). Mechanical, thermal and morphological characterizations were used to assess the potential of MLO as an environmentally friendly plasticizer for PLA formulations. Dynamic mechanical thermal analysis and differential scanning calorimetry revealed a noticeable decrease in the glass transition temperature of about 6.5 °C compared to neat PLA. In addition, the cold crystallization process was favoured with MLO content due to the increased chain mobility that the plasticizer provides. PLA toughness was markedly improved in formulations with 5 phr MLO, while maximum elongation at break was obtained for PLA formulations plasticized with MLO content in the range 15 – 20 phr. Scanning electron microscopy revealed evidence of plastic deformation. Nevertheless, phase separation was detected in plasticized PLA formulations with high MLO content (above 15-20 phr MLO), which had a negative effect on overall toughness.

1. INTRODUCTION.

The increasing concern about the environment and sustainable development is currently leading the search and development of new materials. Today, a wide variety of biobased and/or biodegradable polymers with potential use at an industrial scale can be obtained from renewable resources [1]. These polymers could be used as environmentally friendly solutions as against conventional petroleum-based and non-biodegradable polymers in blend formulations [2], disposable products [3, 4], medical devices [5], packaging [6, 7], green composites [8-13], etc. It is worth noting the increasing use of aliphatic polyesters [14], polysaccharides [15] and protein-derived polymers [16, 17]. Despite the wide variety of biobased polymers, poly(lactic acid) (PLA) is one of the most promising polymers due to its excellent balance between mechanical, barrier and processing properties, and an increasingly competitive price. It is obtained from lactic acid derived from several cereals and tubers, mainly from corn, wheat, beetroot, potato and other starch-rich products. Its biodegradability in natural media makes it the ideal choice for a wide range of disposable products that can undergo disintegration by hydrolysis and enzymatic degradation in controlled conditions (moisture, temperature, bacterial growth, etc.) [18-20]. Moreover, PLA is characterized by high biocompatibility and a good balance of mechanical properties, thus widening its uses in the medical sector [21], such as in resorbable interference screws and prostheses subjected to moderate mechanical stresses [22]. In addition to this, its relatively good resistance to moisture and fats, together with overall balanced barrier properties to flavours and odours, makes PLA a good candidate for the food packaging industry. One important drawback of PLA is its extremely high stiffness,

which leads to high fragility, and this fact restricts some engineering uses that require high toughness behaviour. To overcome this drawback, various approaches have been explored in the last few years. New flexible copolyesters have been investigated as toughened alternatives to brittle PLA formulations [23, 24]. In these works, the results showed increased elongation at break values and a marked improvement in ductile properties. A wide variety of conventional plasticizers have been reported to greatly increase PLA ductility [25], but the potential toxic risks associated to some of these plasticizers, restrict their use in some sectors such as food packaging, medical devices, toys, etc. For this reason, new plasticizers are continually being demanded by industry with the aim of reducing the toxic risk related to plasticizer migration [26, 27]. Vegetable oils such as those obtained from linseed, rape, soybean and cottonseed, among others, offer a natural source of chemicals for the polymer industry [28, 29]. They can readily be converted into their corresponding epoxidized oils by epoxidation, leading to materials with potential use as biobased plasticizers and matrices for green composites. Several epoxidized vegetable oils such as epoxidized linseed oil (ELO) [30], epoxidized soybean oil (ESBO), epoxidized castor oil (ECO), epoxy octyl stearate (EOS) [31] and epoxidized cottonseed oil (ECSO) [32-36] have been reported as environmentally friendly plasticizers for a wide variety of polymers [32, 37]. The use of monomeric and polymeric plasticizers has also been reported in the last decade. Monomeric plasticizers such as acetylbutyl ricinoleate (ABR), acetyltributyl citrate (ATBC) , ricinoleic acid, adipate 2-ethylhexyl (DOA), diisodecyl adipate (DIDA), octyl oleate, octyl trimellitate (TMO), methyl methacrylate (MMA) and glycidyl methacrylate (GMA), among others [14, 16, 38], have given interesting results in PLA plasticization. Also, several polymeric plasticizers such as aliphatic polyesters from dicarboxylic acids, polypropylene glycol adipate, thermoplastic starch (TPS),

polycaprolactone (PCL), etc., [2, 39-44] have proved their efficiency in plasticizing PLA formulations.

The use of plasticizers from vegetable oils is a cost-effective alternative [45, 46]. Unmodified vegetable oils are not suitable for most polymers due to the lack of compatibility. For example, the solubility parameter for soybean oil has been reported to be close to 16 MPa$^{1/2}$,[47] whilst some epoxidized compounds derived from soybean oil achieve a solubility parameter of 19-19.5 MPa$^{1/2}$ [48]. Considering that the solubility parameter of PLA is between 19.5 and 20.5 MPa$^{1/2}$ [49], chemically modified vegetable oils are preferable as their corresponding solubility parameters are closer compared to those of unmodified vegetable oils. For this reason, the majority of vegetable oil-based plasticizers consist of chemically modified vegetable oils with increased polarity to achieve improved interactions with polymers. The final performance of a vegetable oil can be tailored to specific properties by chemical modification [50]. Prempeh *et al.* studied the effect of epoxidized sunflower oil (ESFO) and ESBO on ductile properties of PLA [45]. Our previous study revealed that addition of 5 phr epoxy octyl stearate to PLA led to a marked increase in elongation at break by 300% compared to neat PLA; the toughness was also improved by 75% [31]. Finally, Chieng *et al.* [46] combined various epoxidized vegetable oils, i.e. epoxidized palm oil (EPO) and ESBO, and reported synergistic effects on ductile properties.

In addition to epoxidized vegetable oils, new plasticizers derived from vegetable oils are being investigated. Maleinization represents an interesting and easy way to chemically modify a vegetable oil. In such thermochemical process, maleic anhydride is chemically attached to a triglyceride by "ene" reactions, and, in some cases, by Diels-Alder condensation (in the case of conjugated unsaturations in a fatty acid) as it can be seen in **Fig. 1**. Maleinized vegetable oils and other petrochemical oils

are widely used in the field of cosmetics [51], detergents [52], cleaning products [53], lubricants [54], coatings [55], etc. [56, 57].

Figure 1

The reactivity of maleinized vegetable oils is much higher than that of unmodified vegetable oils due to maleic anhydride polarity. Recently, this has been reported to provide good compatibilizing and chain extension effects in immiscible polymer blends such as those from PLA and thermoplastic starch [58]. Wiyono *et al.* reported that chemical modification of pimaric rosins with maleic anhydride and fumaric acid led to materials with potential use as fruit coatings with good antioxidant and barrier properties [59]. In addition, maleinized vegetable oils offer high thermal stability and can be subjected to temperatures up to 300 °C without any degradation. The cyclic anhydride functionality can readily react with hydroxyl groups to form monoesters. This feature has been widely exploited in the paper industry to provide hydrophobizing properties by using various chemicals such as alkenyl succinic anhydrides [60]. This reaction could be conducted with polymers with terminal hydroxyl groups as is the case of biobased polyesters. Maleic anhydride could react with hydroxyl groups to provide a plasticization effect combined to a chain extension phenomenon due to the multifunctionality of maleinized vegetable oil as shown in Fig. 2.

Figure 2

The work presented here explored the potential of maleinized linseed oil (MLO) as a bio-derived plasticizer for PLA formulations with improved toughness. The effect

of MLO content on the mechanical properties of PLA formulations was evaluated using standard tests: tensile, impact and hardness. The thermal stabilization effect was assessed using thermal analysis: DSC and TGA. Dynamic properties were studied using dynamic mechanical thermal analysis (DMTA) and the morphology of the formulations was observed using field emission SEM (FESEM).

2. EXPERIMENTAL.

2.1. Materials.

PLA (commercial grade Ingeo™ Biopolymer 6201D) was supplied by NatureWorks LLC (Minnetonka, USA). This PLA grade contains around 2% D-lactic acid. Its density is 1.24 g cm^{-3} and its melt flow index is between 15 and 30 g (10 min)$^{-1}$ at 210 ºC. MLO (commercial grade Veomer Lin) was supplied by Vandeputte (Mouscron, Belgium). Its viscosity at 20 ºC is 10 dPa s and its acid value is 105-130 mg KOH g^{-1} as a consequence of the maleinization process. Typical acid values of unmodified linseed oil are lower than 1 mg KOH g^{-1} and this value is markedly increased in the corresponding maleinized oil due to presence of attached cyclic anhydride groups.

2.2. Preparation of PLA formulations plasticized with MLO.

Four different PLA formulations were manufactured with MLO as an environmentally friendly plasticizer (Table 1). The MLO content varied in the range 0-20 phr (parts by weight of MLO with respect to 100 parts by weight of PLA). As PLA is rather sensitive to moisture, it was dried overnight at 60 ºC in an air-circulating oven. The procedure for sample preparation was as follows. Initially, the required amounts of both PLA and MLO were weighed and mechanically pre-mixed in a zipper bag.

After this stage, the mixture was extruded in a twin-screw co-rotating extruder (with diameter D of 25 mm and L/D ratio of 24) from DUPRA SL (Castalla, Spain) with a temperature profile of 165 °C (feed), 170 °C, 172.5 °C and 175 °C (die), and subsequently pelletized after cooling. Further processing was carried out by injection molding with a Meteor 270/75 from Mateu & Solé (Barcelona, Spain) at an injection temperature of 175 °C and normalized samples for testing were obtained.

Table 1. Summary of compositions and labelling of PLA formulations plasticized with MLO.

Poly (lactic acid)-PLA, phr	Maleinized linseed oil (MLO), phr	Code
100	-	PLA
100	5	PLA/5MLO
100	10	PLA/10MLO
100	15	PLA/15MLO
100	20	PLA/20MLO

2.3. Mechanical characterization of PLA formulations plasticized with MLO.

The effect of MLO content on mechanical properties was studied using standardized tensile, flexural, hardness and impact tests. Tensile and flexural tests were conducted with an Ibertest ELIB 30 universal test machine from SAE Ibertest (Madrid, Spain) at room temperature. The load cell was 5 kN and the crosshead rate was set to 10 mm min^{-1} for both tests as recommended by the ISO 527-5 and ISO 178 standards for tensile and flexural characterization, respectively. Tests were carried out on five different specimens and the average values of the main parameters were

calculated. Additionally, for a correct determination of the Young's modulus, an axial extensometer was used. Shore D hardness values were obtained using a Shore D model 673-D durometer from Instrumentos J Bot SA (Barcelona, Spain) as recommended by the ISO 868 standard. The impact-absorbed energy was characterized using a 6 J Charpy pendulum from Metrotec SA (San Sebastián, Spain) on unnotched samples following the ISO 179:1993 standard. Five different measurements of each property were obtained and averaged.

2.4. Morphology of PLA formulations plasticized with MLO.

A high-resolution FESEM instrument (Zeiss ULTRA55 from Oxford Instruments, Oxford, UK) operated at an accelerating voltage of 2 kV was used to characterize the surface morphology. Fractured samples from impact tests were subjected to a metallization process in vacuum conditions with a high-vacuum sputter (EM MED020 from Leica Microsystems, Wetzlar, Germany).

2.5. Thermal analysis of PLA formulations plasticized with MLO.

Thermal transitions of PLA and PLA formulations plasticized with various MLO loads were obtained using DSC with a Mettler Toledo DSC 821 calorimeter (Schwerzenbach, Switzerland). The thermal programme consisted of a heating ramp from 30 to 350 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere with a constant flow rate of 66 mL min^{-1}. The percentage crystallinity of PLA and plasticized formulations was calculated with the following equation:

$$X_c \ (\%) = \frac{\Delta H_m - \Delta H_c}{w \ \Delta H_m^0} 100 \qquad \text{(Equation 1)}$$

where ΔH_m and ΔH_c represent the experimental melt and cold crystallization enthalpies, respectively, and w is the weight fraction of PLA. ΔH_m^0 is the melt enthalpy for a theoretical fully crystalline PLA structure, and was assumed to be 93 J g^{-1} as reported in the literature [20].

Thermal degradation/decomposition of PLA and PLA formulations plasticized with MLO was assessed using TGA with a TGA/SDTA 851 thermobalance from Mettler Toledo (Schwerzenbach, Switzerland). Samples with an average weight of 8-10 mg were subjected to a heating ramp from 30 to 500 °C at a heating rate of 20 °C min^{-1} in nitrogen atmosphere with a constant flow of 66 mL min^{-1}.

DMTA in torsion mode of neat PLA and plasticized PLA formulations was carried out in an AR G2 oscillatory rheometer from TA Instruments (New Castle, USA), equipped with a clamp accessory for solid samples. Rectangular samples of dimensions 40x10x4 mm^3 were subjected to a temperature ramp from 30 to 130 °C at a heating rate of 2 °C min^{-1}. The maximum deformation (γ) was 0.1% and all samples were tested at a constant frequency of 1 Hz.

3. RESULTS AND DISCUSSION.

3.1. Effect of MLO on mechanical properties of plasticized PLA formulations.

Figure 3 compares the infrared (IR) spectra of linseed oil and MLO with clear evidence of increased functionality through the cyclic anhydride. The IR spectrum of linseed oil is characterized by peaks at 3020, 1650 and 719 cm^{-1} which are attributed to the stretching vibration of C&bond;H bond of an sp2 carbon atom, stretching vibration of C&dbond;C and angular deformation of *cis*-CH&dbond;CH moieties, respectively [61]. On the other hand, Eren *et al.* reported a band located at 1708.5 cm^{-1} that corresponds to the carbonyl functional group. This peak can also be observed in the IR spectrum of MLO [62]. Moreover, as pointed out by Balsamo et al. in research work

concerning maleinized copolymers, two peaks located at 1780 and 1857 cm-1 can be assigned to carbonyl stretching [63].

Figure 3

Figure 4 shows the evolution of the tensile strength of plasticized PLA formulations as a function of MLO content. As expected, MLO provides improved ductile properties (with similar effect as some epoxidized vegetable oils) that lead to lower tensile strength. Tensile strength and tensile modulus decrease in all formulations with increasing MLO content. Specifically, the plasticized formulation containing 20 phr MLO (16.67 wt%) offers a decrease in tensile strength of 21.1% with regard to unplasticized PLA while the tensile modulus is slightly reduced (no clear percentage value can be set due to the deviation of the results, but possibly, this decrease could be close to 3%) for the same formulation in comparison to neat PLA. Similar findings were reported by Silverajah *et al.* [64]. They reported that 5 wt% EPO plasticizer in PLA formulations led to lower tensile strength values by 26.3% with regard to neat PLA. In a previous work, we reported a decrease of 37% in the tensile strength of neat PLA by the addition of 20 phr of octyl epoxy stearate [31]. In a similar way, Silverajah *et al.* reported a decrease in Young's modulus of EPO-plasticized PLA of 7% by adding 5 wt% EPO [31]. MLO facilitates crystallization [65], as it provides increased chain mobility and free volume. Increasing the crystallinity of a polymer also increases its rigidity, although in this case it is counteracted with the ductility offered by the MLO in PLA.

MLO has a positive effect on ductile properties. PLA is quite a brittle polymer with very low elongation at break (about 7%). This is noticeably improved by MLO addition. In a previous work, the elongation at break of neat PLA was improved up to

40.5% [31] by the addition of only 5 phr of octyl epoxy stearate, which was the highest elongation at break achieved with this plasticizer in the range 5-20 phr. Over 5 phr octyl epoxy stearate, phase separation occurs, and this results in lower elongation at break values. This phase separation has been reported for other plasticized systems [66]. Xu *and Qu* reported a marked increase in elongation at break of neat PLA using ESBO (36% increase on addition of 15 wt% ESBO) [67]. The PLA formulation plasticized with 20 phr MLO provides a high elongation at break value of 78.4% which represents an increase of 1020% with regard to neat PLA. This can be indicative of good compatibility between PLA and MLO, which can minimize the negative effects of phase separation. The plasticization effects that MLO provides to PLA are noticeable, increasing the ductility in the same way (or even a greater extent) as some other plasticizers from renewable resources. This can be explained by three different combined effects. Firstly, MLO exerts a lubricant effect which increases chain mobility. Secondly, the gel theory suggests that the plasticizer contributes to weaker polymer-polymer interactions (hydrogen bonds, Van der Waals or ionic forces, etc.) as MLO molecules are placed between PLA chains. This phenomenon also has a positive effect on chain mobility. Finally, the plasticizer increases the free volume and, subsequently, chain interactions decrease, thus leading to improved intermolecular mobility [68].

Figure 4

In a parallel way, Figure 5 shows a noticeable decrease in the flexural strength, even for formulations with low MLO content. As the MLO content increases, a decreasing tendency in flexural strength is detected. Nevertheless, the maximum decrease (24% with regard to neat PLA) is achieved by the addition of 5 phr MLO while no marked changes are obtained for higher MLO loads. In fact, flexural strength

tends to stabilize at MLO concentrations of 15-20 phr, which could be a sign of plasticizer saturation. Some authors have described an anti-plasticization effect once plasticizer saturation occurs [66]. This anti-plasticization phenomenon could lead to an increase in mechanical resistant properties. Anti-plasticization effects were observed by Gutierrez-Villarreal and Rodriguez-Velazquez when citrate esters were used to plasticize poly(methyl methacrylate) [69]. They reported this effect at a low plasticizer concentration of about 13 wt%. Vidotti *et al.* suggested that the anti-plasticization effect can be due to a free volume reduction [70]. When this free volume becomes full of plasticizer this effect may appear. The increase in tensile strength related to the anti-plasticization phenomenon can also be explained by taking into account crystallinity considerations, as plasticizer enhances chain mobility, and thus the crystallization tendency is clearly favoured. The anti-plasticization effect depends on molecular weight and concentration of the diluent and is specific for each polymer–plasticizer system [71]. The plasticization threshold for the PLA-MLO system could be located near the 15-20 phr MLO composition as no clear evidence of anti-plasticization is observed in the studied range. As can be seen in Figs 4 and 5, the evolution of mechanical resistance properties tends to stabilize to constant values for PLA formulations plasticized with 15-20 phr MLO. This fact is in accordance with plasticizer saturation as no further plasticization effects can be achieved with plasticizer contents over this range.

Figure 5

Another interesting technique for assessing the plasticization efficiency of MLO is the measurement of the impact-absorbed energy using Charpy's test. This is directly related to toughness. Table 2 summarizes the impact-absorbed energy of neat PLA and

formulations plasticized with MLO. The impact-absorbed energy of neat PLA (30.9 kJ m^{-2}) is relatively low due to intrinsic brittleness. The impact-absorbed energy depends on several factors, i.e. presence of stress concentrators, crack size and growth rate, phase separation, etc. All these factors can influence the overall deformation ability and, subsequently, the total energy absorbed during deformation and fracture. As it has been described previously, plasticization with MLO leads to a marked increase in elongation at break, whilst mechanical resistant properties, such as modulus and strength, are lower compared to neat PLA. The impact-absorbed energy results from the combination of two effects: on the one hand, the deformation ability that is directly related to mechanical ductile properties and, on the other hand, the fracture resistance that is linked to mechanical resistant properties. As evident from Table 2, the impact-absorbed energy is increased to twice the value of neat PLA (62.9 kJ m^{-2}) with the addition of 5 phr MLO. Above this value, the impact-absorbed energy decreases slightly, but the values are still much higher than that of unplasticized PLA. This behavior could indicate that plasticizer saturation occurs for MLO contents between 15 and 20 phr as reported by Mikus *et al.* for similar systems [66]. Phase separation is one of the main problems related to plasticizer saturation, with a clear negative effect on mechanical ductile properties due to stress concentration and the occurrence of microcracks at the interfaces. Xiong *et al.* manufactured PLA-starch blends by co-extrusion with ESBO as a reactive plasticizer/compatibilizer. By adding 10 wt% ESBO, the absorbed energy increased by 5.6%. MLO addition leads to toughened materials as the formulation with 10 phr MLO (9.09 wt%) offers an absorbed energy 81% higher than that of neat PLA. However, Xiong *et al.* reported a marked increase in toughness by previous starch maleinization, with an increase in absorbed energy of 140% with regard to neat PLA. They concluded the role of maleic anhydride as a compatibilizer between both polymers improving the absorbed energy. In that work, PLA-MLO

formulations with an MLO content in the range 5 – 10 phr offer the best balanced properties and optimized toughness. These formulations offer the maximum energy absorption ability. It is important to remark that MLO shows similar results to those observed with epoxidized vegetable oils in terms of ductility and energy absorption[2, 31].

Table 2. Variation of Charpy impact energy, Shore D hardness, Vicat softening temperature (VST) and heat deflection temperature (HDT) of PLA formulations with varous contents of MLO.

MLO content (phr)	Hardness Shore D	Charpy impact energy (kJ m^{-2})	VST (ºC)	HDT (ºC)
0	76.0±0.5	30.9±0.8	52.8	47.6
5	75.7±0.6	62.9±3.1	50.0	47.4
10	75.2±0.7	56.0±5.9	48.8	47.0
15	74.3±0.7	50.3±6.6	47.6	46.8
20	73.4±0.5	48.0±0.9	47.4	47.0

3.2.- Effect of MLO on thermal properties of plasticized PLA formulations.

Table 3 summarizes the main thermal parameters of PLA formulations plasticized with various MLO contents obtained using DSC. With regard to the glass transition temperature (T_g), a marked decrease with increasing MLO content can be observed. Neat PLA possesses T_g of 65.4 ºC and the addition of 5 phr MLO promotes a decrease of almost 5 ºC down to 60.5 ºC. This is due to the plasticization effect that MLO provides. MLO molecules accommodate between different PLA polymer chains with different effects. On the one hand, the intensity of secondary forces between

polymer chains is reduced. On the other hand, the free volume increases and, therefore, chain mobility is favoured along with the lubricity provided by MLO [70, 71]. Over 5 phr MLO, a slight decrease in T_g can be detected but the real change occurs for relatively low MLO content. These results differ slightly from those reported by Santos et al. with PLA formulations plasticized with mixtures of oligoesters obtained from sunflower oil biodiesel as a plasticizer. T_g decreased from 62 °C (neat PLA) to 44 °C for the blend with 20 wt% of plasticizer. Burgos *et al.* obtained PLA melt-blended with a bio-based oligomeric lactic acid plasticizer at various concentrations between 15 and 25 wt%. T_g decreased dramatically from 59.2 °C (neat PLA) to 25.8 °C (25 wt% oligomeric lactic acid). In contrast, Mauck *et al.* reported negligible changes in T_g of PLA formulations with acrylated ESBO as a plasticizer [72].

Table 3. Main thermal parameters of PLA formulations plasticized with various contents of MLO obtained using DSC.

MLO content (phr)	[I] T_g (°C)	[II] T_{cc} (°C)	[III] ΔH_c (J g^{-1})	T_m (°C)	[IV] ΔH_m (J g^{-1})	ΔH_m - ΔH_{cc} (J g^{-1})	[V] X_{PLA} (%)
0	65.4	102	26.71	168.3	40.19	13.48	14.5
5	60.5	96.1	21.73	173.3	38.44	16.71	18.9
10	60.1	91.0	19.09	172.1	38.01	18.92	22.4
15	60.8	87.1	19.16	174.3	40.49	21.33	26.4
20	59.0	87.2	18.75	171.5	40.34	21.59	27.9

[I] T_g is the glass transition temperature.
[II] T_{cc} is the cold crystallization temperature.
[III] ΔH_c is the crystallization enthalpy.
[IV] T_m is the melt peak temperature.
[V] ΔH_m is the melt enthalpy and X_{PLA} is the degree of crystallinity.

The cold crystallization peak also changes with the addition of MLO. The increased chain mobility due to a plasticization effect allows crystallization to occur with lower energy content, thus leading to lower crystallization temperatures as indicated by Li and Huneault [65]. They studied the effect of various nucleants and plasticizers on the crystallization process of PLA during cooling and the effects on the cold crystallization in a subsequent heating. They reported a crystallization peak in PLA plasticized with 5% poly(ethylene glycol) located at 110 $^{\circ}$C that was reduced to 95 $^{\circ}$C for a PEG content of 10%, showing that the increase in chain mobility was responsible for the slightly increased ability of PLA chains to crystallize after a previous cooling process. In the present work, the peak temperature for the cold crystallization process of neat PLA is around 102 $^{\circ}$C. This is markedly reduced to about 87 $^{\circ}$C for MLO contents of 15-20 phr. This indicates that the energetic barrier for crystallization is lower, and PLA polymer chains can form stable crystallites at lower temperatures [65]. In general, the degree of crystallinity is increased due to improved chain mobility as evident from Table 3. Neat PLA possesses a degree of crystallinity (X_{PLA}) of 14.5%, which is increased up to twice this value for plasticized PLA formulations containing 20 phr MLO. Silverajah *et al.* used EPO as plasticizer for toughened PLA formulations (up to 5 wt% plasticizer) and showed an increase in degree of crystallinity by 10% [64].

Regarding thermal stability, Table 4 gives some characteristic thermal parameters of the TGA thermograms for neat PLA and PLA formulations plasticized with various MLO contents. The characteristic thermal parameters are $T_{5\%}$, which stands for the temperature at which a 5% weight loss occurs, and maximum degradation temperature (T_{max}), which corresponds to the highest thermal degradation rate temperature.

Table 4.- Thermal parameters of degradation process of neat PLA and PLA formulations plasticized with various contents of MLO obtained using TGA[a].

MLO content (phr)	$T_{5\%}$ (°C)	T_{max} (°C)
0	336.9	363.5
5	333.5	363.6
10	331.8	362.5
15	330.0	361.9
20	328.3	362.2

[a]MLO values: $T_{5\%}$, 349.8°C; T_{max}, 424.4°C.

Thermal degradation of neat PLA, MLO and PLA-MLO formulations occurs in a one-step process, as can be concluded from their corresponding TGA and DTG results. As evident from Table 4, PLA has a significantly lower thermal stability than MLO. The PLA degradation peak is observed at 363.5 °C while the maximum degradation rate for neat MLO is located at 424.8 °C. As expected, the degradation peak temperatures of PLA-MLO formulations are located at about 362 °C which is very similar to that of neat PLA. Choi and Park reported an absence of interactions between poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] blended with ESBO and soybean oil and both components were degraded separately [73]. We can conclude that MLO also provides negligible effects on the thermal stability of PLA-MLO formulations.

3.4. Dynamical mechanical behaviour of PLA formulations plasticized with MLO.

Figure 6 shows the evolution of the storage modulus (G′) as a function of temperature. At room temperature, neat PLA possesses a storage modulus close to 1000 MPa and this value remains almost constant up to 65 °C. Then the storage modulus undergoes a decrease of three orders of magnitude to 1-2 MPa, which is

related to T_g. Above 80 °C the material behaves as a rubber plastic and then, at 90 °C, G′ increases again up to about 80-90 MPa. This last phenomenon represents the cold crystallization process. At this temperature, the energetic conditions are adequate for crystallization and polymer chains move to a packed structure, which improves elastic behaviour, thus leading to an increase in G′. With regard to the plasticized PLA formulations, it is possible to observe three main differences compared to neat PLA. Firstly, the initial storage modulus at room temperature is clearly lower for some formulations. Plasticized formulations with 10 and 15 phr MLO possess a storage modulus of 650 and 500 MPa respectively. This indicates the clear plasticization effect that MLO provides. The plasticized formulation with 5 phr MLO is characterized by a storage modulus of 1100 MPa at room temperature, thus indicating that very low plasticizer amounts do not affect the mechanical resistant properties to a great extent. Regarding the PLA formulation with 20 phr, a slight anti-plasticization phenomenon can be observed as the storage modulus is higher compared to formulations with lower MLO content [66]. The second important change is related to T_g. As has been described previously, MLO increases the free volume. In addition to this, the lubricity effect of MLO chains leads to improved chain mobility. This is evidenced by a decrease in T_g, which indicates that plasticized PLA chains can move with lower energy content than neat PLA chains. T_g is shifted by 10 °C to lower temperatures, indicating a clear plasticization effect of MLO. Finally, cold crystallization is also moved to lower temperatures as polymer chains can rearrange to a more packed form with less energy content. This decrease in the cold crystallization process is close to 10-15 °C. All these results are in total agreement with those obtained using DSC.

Figure 6

Figure 7 shows the evolution of the damping factor (tan δ) which represents the ratio between loss modulus (G") and storage modulus (G'). This ratio represents the lost energy (due to viscous behaviour) with regard to the stored energy (due to elastic behaviour). By considering the damping factor peak, T_g of neat PLA is close to 67 °C, and it is markedly decreased, as expected, to values of 61-62 °C for all plasticized formulations. Santos *et al.* observed a similar decrease in T_g with increasing plasticizer content in PLA formulations with oligoesters obtained from sunflower oil biodiesel. They reported a decrease in T_g from 62 °C (neat PLA) down to 52 and to 44 °C in formulations containing 10 and 20% plasticizer, respectively [29]. In the same way, Silverajah *et al.* reported a similar trend. T_g of neat PLA was reduced from 68 to 67 and 62 °C, for plasticized PLA formulations with 1 and 5 wt% of EPO, respectively [64].

Figure 7

3.5. *Morphology of PLA formulations plasticized with MLO.*

Figure 8 shows FESEM images of fractured surfaces from impact tests. Neat PLA (**Fig.8(a)**) offers typical brittle fracture with smooth surface which indicates absence (or very low) plastic deformation. With increasing MLO content, clear changes in the fractured surfaces can be observed. Presence of filaments is evident as the MLO content increases. Moreover, the typical smooth surface of brittle fracture changes to a rougher surface with increasing MLO. This rough surface is indicative of plastic deformation and is more intense for PLA formulations plasticized with high MLO content. Silverajah *et al.* confirmed that neat PLA undergoes brittle fracture, whereas the fractured surface of PLA with 1 wt% EPO was smooth and homogenous, indicating that no phase separation took place. No agglomerates or brittle crack behaviour were observed, which evidenced good interfacial adhesion between PLA matrix and EPO

plasticizer [64]. Nevertheless, some kind of plasticizer saturation for MLO contents of 5 phr and above can be observed, which leads to phase separation. It is possible to observe the presence of small cavities and holes that are filled with the excess plasticizer with a negative effect on PLA ductile properties as observed previously. Above 10 phr MLO, the absorbed energy in Charpy's test is noticeable whilst no marked increase in elongation at break can be detected. This agrees with plasticizer saturation and somewhat anti-plasticization effect.

Figure 8

4. CONCLUSIONS.

The present work assesses the effectiveness of a new environmentally friendly plasticizer derived from linseed oil, i.e. maleinized linseed oil (MLO) for poly(lactic acid), PLA with improved toughness. MLO content varied in the 5 – 20 phr range that corresponds to a weight percentage content comprised between 4.76 and 16.67 wt%. Although the plasticization effects of MLO was weak (the T_g decreases by 5 °C with 5 phr MLO, plasticizer saturation occurs at this content) it is worth to remark the great results for impact-absorbed energy with an increase of almost twice the value of neat PLA for formulations with 5 phr MLO. With regard to elongation at break, maximum values were obtained for plasticized formulations with 15 – 20 phr MLO. MLO leads to increased chain mobility due to reduced intermolecular forces, an increase in free volume and a lubricity effect. All these phenomena have a positive effect on chain mobility with the subsequent decrease in the glass transition temperature by 5-6 °C as well as the cold crystallization process. On the other hand, low MLO content (5 phr) showed a small effect on mechanical properties such as modulus and strength in comparison to other plasticizers thus showing its potential with both benefits on

toughness and plasticization. FESEM revealed clear plasticization with appearance of filaments and a rough surface typical of plastic deformation in contrast to the smooth surface typical of brittle PLA fracture. It is possible to conclude that maleinized linseed oil (MLO) is a cost-effective eco-friendly solution to PLA plasticization to overcome its low toughness with relative low plasticizer content.

Acknowledgments

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Figures legends

Figure 1.- Scheme of the maleinization process of linseed oil by Diels-Alder and "ene" reactions.

Figure 2.- Proposed mechanism for a chain extension effect that MLO could provide by reaction with hydroxyl terminal groups in PLA.

Figure 3.- Comparison of IR spectra of linseed oil (LO) and MLO.

Figure 4.- Plot of evolution of tensile mechanical properties of PLA formulations plasticized with various contents of MLO.

Figure 5.- Plot of evolution of flexural mechanical properties of PLA formulations plasticized with various contents of MLO.

Figure 6.- Plot of the evolution of storage modulus (G′) in terms of temperature for PLA formulations plasticized with various contents of MLO.

Figure 7.- Plot of evolution of damping factor (tan δ) in terms of temperature for PLA formulations plasticized with various contents of MLO.

Figure 8.- FESEM images of fractured surfaces from impact tests of PLA formulations plasticized with various contents of MLO: (a) neat PLA; (b) 5 phr MLO; (c) 10 phr MLO; (d) 15 phr MLO; (e) 20 phr MLO.

Table captions

Table 1.- Summary of compositions and labelling of PLA formulations plasticized with MLO.

Table 2. Variation of Charpy's impact energy, Shore D hardness, Vicat softening temperature (VST) and heat deflection temperature (HDT) of PLA formulations with varous contents of MLO.

Table 3.- Main thermal parameters of PLA formulations plasticized with different content of MLO obtained using DSC.

Table 4.- Thermal parameters of degradation process of neat PLA and PLA formulations plasticized with various contents of MLO obtained using TGA.