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Additional Information

1 **Reactive Toughening of Injection-molded Polylactide Pieces by Maleinized**
2 **Hemp Seed Oil**

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11

12

1 **Abstract.**

2 The present study describes the effect of maleinized hemp seed oil (MHO) on the
3 physical performance of polylactide (PLA) pieces. To this end, PLA pieces with varying
4 MHO contents in the 0 - 10 wt% range were manufactured by twin-screw extrusion
5 (TSE) followed by injection molding. The resultant pieces were characterized in terms of
6 their mechanical, thermal, and thermomechanical properties. The obtained properties
7 suggested that, unlike typical plasticizers, MHO does not only induce an increment in
8 elongation at break and impact strength but it also enhances both elastic modulus and
9 tensile strength. In addition, it was observed a moderate decrease in the glass transition
10 temperature (T_g). This was ascribed to a linear chain extension and/or branching
11 phenomenon due to the reaction of the multiple maleic anhydride (MAH) groups
12 present in MHO with the hydroxyl groups of the PLA terminal chains. Furthermore,
13 morphology characterization revealed that, though certain phase separation occurred at
14 its highest content, MHO was finely dispersed as submicron droplets within the PLA
15 matrix contributing to improving toughness. The use of multi-functionalized reactive
16 oils thus represents a highly sustainable solution to reduce the intrinsic brittleness of
17 PLA materials without compromising their mechanical resistance and the toughened
18 biopolymer pieces described herein can find interesting applications in, for instance,
19 rigid packaging.

20

21 **Keywords:** *PLA; vegetable oils; maleinization; mechanical properties; packaging*

22

23

1 **1. Introduction.**

2 The use of biopolymers is gaining interest and relevance due to an increasing
3 environmental concern. Some petroleum-derived polymers are being currently
4 employed due to their ability to disintegrate in a controlled compost soil such as poly(ϵ -
5 caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(butylene succinate-*co*-
6 adipate) (PBSA), etc. [1-3]. More interestingly, other biopolymers can be obtained from
7 renewable resources as it is the case of polylactide (PLA), prepared by starch
8 fermentation, and polyhydroxyalkanoates (PHAs), obtained from bacterial fermentation
9 [4-7]. Among them, PLA is nowadays the most close-to-market biopolymer from both
10 technical and economical standpoints [8]. PLA can be processed by conventional
11 manufacturing techniques at industrial scale with an annual volume of 140,000 t [9].
12 Currently, PLA finds several applications for rigid applications in the packaging
13 industry [10]. In particular, PLA offers an unusual range of physical properties that can
14 be tailored by the processing conditions, molecular weight (M_w), and type of isomers
15 [11].

16 However, one of the main drawbacks of PLA is its extremely low toughness. For
17 this reason, plasticization and blending with flexible and rubber-like polymers are
18 currently being investigated as economical and technical solutions to obtain toughened-
19 PLA industrial formulations [12-15]. Plasticizers represent a well-known strategy as they
20 can increase elongation at break by reducing the glass transition temperature (T_g) and
21 improving elongation at break, but mechanical resistant properties usually decrease in
22 a great extent. For this reason, other alternatives such as reactive extrusion by means of
23 functionalized oligomers or copolymers are preferred as the technical solution to
24 improve toughness. For instance, Wang *et al.* [16] proposed the use of an epoxy-
25 functionalized rubber copolymer with excellent performance on both toughness and

1 mechanical resistant properties. A wide variety of plasticizers for PLA have been
2 proposed. Oligomeric lactic acid (OLA) has proved its high compatibility with PLA,
3 showing a remarkable decrease in T_g and a high increase in elongation at break in the
4 biopolymer, as reported by Burgos *et al.* [17]. It is also worthy to note the efficiency of
5 citrate-derived plasticizers, such as acetyl tri-*n*-butyl citrate (ATBC), triethyl citrate
6 (TEC), among others [18-20]. Another important family of PLA plasticizers are derived
7 from polymeric glycols, such as poly(ethylene glycol) (PEG), poly(propylene glycol)
8 (PPG), etc. By selecting the appropriate M_w and/or type of copolymers, the properties
9 of PLA formulations can be tailored [18, 21, 22].

10 In the last years, vegetable oils (VOs) have acquired a relevant role in polymer
11 synthesis and modification [23-25]. VOs, obtained from plants, offer a great potential to
12 partially or fully substitute petroleum-derived materials in the polymer industry [26-28].
13 These consist on a glycerol base skeleton in which three different fatty acids are linked
14 through ester bonds, thus leading to the typical triglyceride structure. Fatty acids consist,
15 generally, on aliphatic long-chains made of 13 to 21 carbon atoms. The fatty acid
16 composition varies with the plant, crop, and growing conditions. Some fatty acids (*e.g.*
17 oleic, linoleic, linolenic, etc.) are characterized by the presence of one, two or more
18 degrees of unsaturation, *i.e.* highly reactive points, which make fatty acids and
19 triglycerides suitable for a wide variety of chemical modifications. In general, this
20 chemical modification is necessary to induce certain reactivity to the VOs and to achieve
21 good interactions with the PLA chains [29, 30]. Epoxidized vegetable oils (EVOs) and
22 epoxidized fatty acid esters (EFAE) have been successfully used as PLA plasticizers,
23 however certain saturation occurs at relatively low contents [31-33]. Although the
24 plasticizing efficiency of EVOs is lower to that reported for citrates, adipates, and
25 polymeric glycols, their main benefit when adding to PLA is a considerable toughness
26 improvement and a noticeable increase in thermal stability [34].

1 Hemp seed oil (HO) is an interesting vegetable oil obtained from *Cannabis sativa*
2 L. with a high potential in the polymer industry due to its typical lipid profile (wt%):
3 55.3% linoleic acid, 20.3% α -linolenic acid, 9.0% oleic acid, 5.9% palmitic acid, 4.4% γ -
4 linolenic acid, 2.2% stearic acid, and 1.7% arachidic acid [35]. HO can be easily obtained
5 by cold-press processing the hemp seeds [36] and possesses high oxidative stability [37].
6 It is worthy to note that an important fraction of the HO comes from the crops of hemp
7 plants for the textile industry, so that, it can be considered a by-product (or co-product)
8 of this industry, leading to a cost-effective raw material for chemical modification. Its
9 high unsaturation content (similar or slightly lower to linseed oil, which is widely used
10 in polymer synthesis and additives) allows a wide variety of modifications (e.g.
11 epoxidation, acrylation, hydroxylation, etc.) that makes it interesting for polymer
12 synthesis, modification, and composite manufacturing [38-42]. Shuttleworth *et al.* [43]
13 have recently reported the fabrication of flexible bio-based nanocomposites from
14 epoxidized hemp seed oil (EHO) as thermosetting resin with halloysite nanotubes
15 (HNTs). Manthey *et al.* [40] reported interesting green composites based on EHO
16 thermosetting matrix and hemp fiber reinforcement. The main use of modified HO has
17 been so far focused on thermosetting resins. In particular, both EHO and acrylated
18 epoxidized hemp seed oil (AEHO) have been proposed as bio-derived thermosetting
19 resins for uses in polymer composites. The works of Francucci *et al.* [44] reported the
20 cure mechanism of these bio-based thermosets with interesting uses at industrial scale.

21 Cyclic anhydrides, *i.e.* itaconic, phthalic, maleic anhydride, and derivatives, are
22 readily reactive groups towards hydroxyl groups. Marsilla *et al.* [45] reported the
23 grafting of itaconic anhydride to improve the overall properties of PLA. In fact,
24 maleinized copolymers have been widely used to compatibilize polymer blends and
25 polymers with cellulosic fillers [46]. Maleinization is a straightforward chemical
26 modification carried out on VOs that proceeds mainly by “ene” reaction or allylic

1 addition of maleic anhydride (MAH) and, in some cases, by Diels-Alder condensation
2 when conjugated carbon-carbon double bonds are present [47]. Depending on
3 stoichiometry, maleinization reaction can be performed to a partial extent, thus leading
4 to tailored functionality [48, 49]. The application of maleinized vegetable oils (MVOs) as
5 additives in PLA and other bio-based polyesters has proved to provide increased
6 ductility and toughness. For instance, Ferri *et al.* [50] reported the efficiency of
7 maleinized linseed oil (MLO) for toughening PLA formulations by the only addition of
8 4.3 wt% MLO. Despite this, the efficiency of MLO on poly(3-hydroxybutyrate) (PHB)
9 was not as high as that reported for PLA [51]. Carbonell-Verdu *et al.* [52] also reported
10 the usefulness of maleinized cottonseed oil (MCSO) as another green alternative to MLO,
11 showing a good plasticizing effect on PLA films. MVOs can also contribute to a
12 compatibilization effect, as previously described by Xiong *et al.* [53]. Depending on both
13 the maleinization degree and the particular chemical profile of the base vegetable oil,
14 different plasticization properties can be achieved.

15 This work focuses on the maleinization process of HO to produce maleinized
16 hemp seed oil (MHO) and its use, for the first time, as an environmentally friendly
17 additive for toughening PLA pieces obtained by twin-screw extrusion (TSE) and
18 followed by injection molding.

19

20 **2. Experimental.**

21 **2.1. Materials.**

22 PLA Ingeo™ Biopolymer 6201D grade was supplied by NatureWorks
23 (Minnetonka, USA). This is a commercial grade with a density of 1.24 g cm⁻³ and a melt
24 flow index (MFI) of 15-30 g/10 min (190 °C, 2.16 kg), which is suitable for injection
25 molding. HO, obtained from hemp seeds by a cold-press process, was provided by

1 Suministros Agropecuarios Jordà (Concentaina, Spain). MAH was obtained from Sigma-
2 Aldrich S.A. (Madrid, Spain).

3

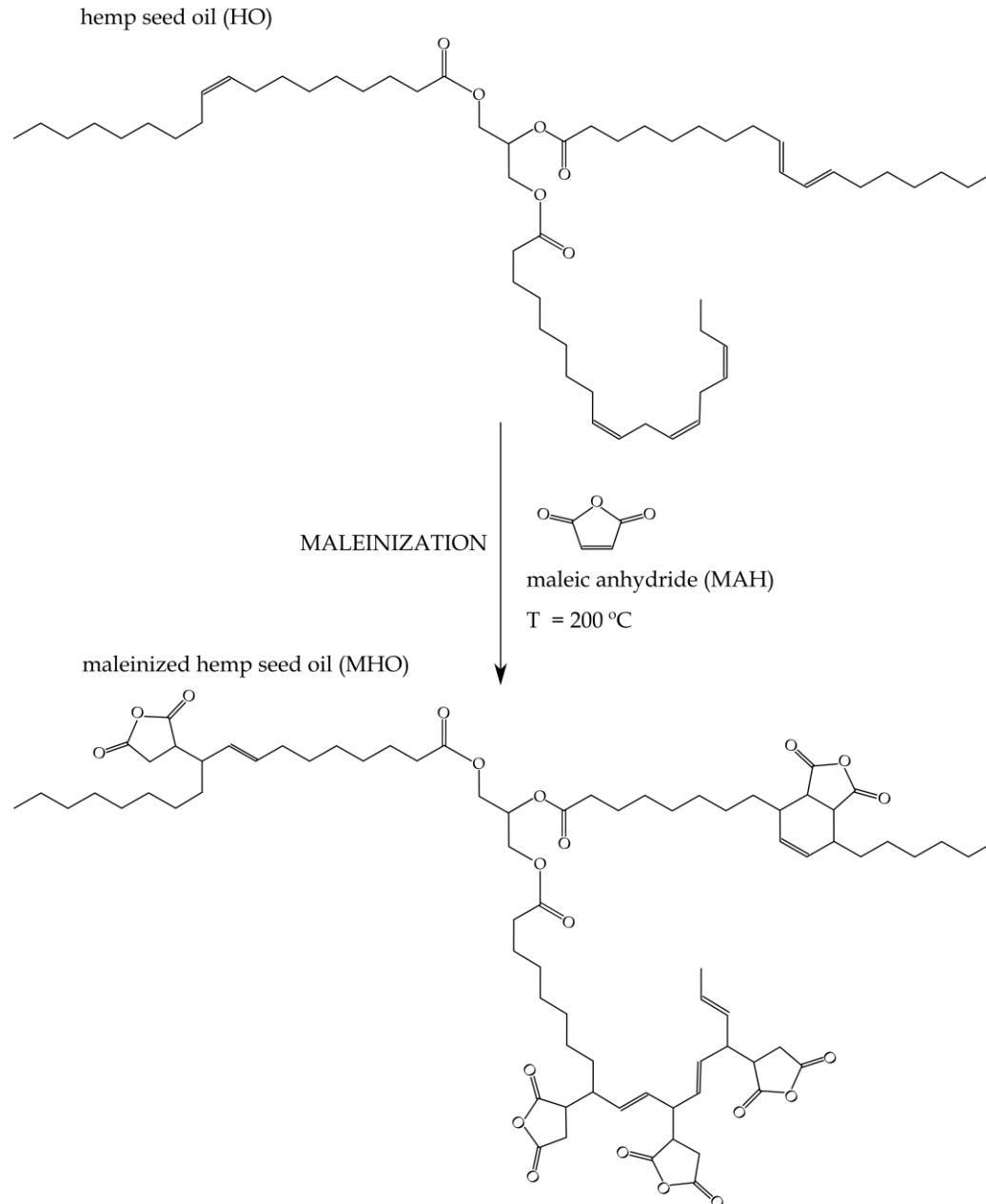
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5 *2.2. Maleinization of hemp seed oil.*

6 The extracted HO was subjected to a maleinization process with MAH. To this
7 end, a three-necked round bottom reactor equipped with a magnetic stirrer-heating
8 mantle was used. In the first neck, a digital thermometer was introduced to control the
9 temperature of the process. In the second neck, a nitrogen gas dispenser with a flow-rate
10 of 1.5 L min⁻¹ was added to achieve an inert atmosphere. A reflux condenser was coupled
11 in the third neck to minimize the MAH loss during the process.

12 The production consisted on introducing into the reactor 20 g of MAH per 100 g
13 of HO to achieve a stoichiometric ratio. For this, taking into account the most abundant
14 fatty acids present in HO [35], it was considered that each molecule of linolenic acid,
15 linoleic acid, and oleic acid, will react with an average of 2.5, 2, and 1 molecules of MAH,
16 respectively. The mixture was heated at 200 °C and allowed to react for four hours under
17 constant stirring, maintaining the nitrogen atmosphere to avoid oil oxidation. **Fig. 1**
18 shows a schematic representation of the process.

19



1

2 **Figure 1.-** Schematic representation of the maleinization process of hemp seed oil (HO)
 3 by maleic anhydride (MAH).

4

5 **2.3. Manufacturing of injection-molded pieces.**

6 Prior to processing, all materials were dried for 36 h in a dehumidifier model
 7 MDEO provided by Industrial Marsé (Barcelona, Spain). The selected temperature was
 8 60 °C. Then, different PLA formulations with MHO contents of 2.5, 5, 7.5, and 10 wt%

1 were prepared by a melt compounding process in a co-rotating twin-screw extruder
2 from Dupra S.L. (Castalla, Spain). The two screws had a diameter of 25 mm and a length
3 to diameter ratio (L/D) of 24. All raw materials were fed into the main hopper, being
4 previously pre-homogenized in a zipper bag. The temperature profile for the extrusion
5 process was, from hopper to die, 180 °C, 185 °C, 190 °C, and 195 °C while the rotation
6 speed was 20 rpm. The compounded materials were pelletized using an air-knife unit
7 and subsequently processed by injection molding in a Sprinter 11 t injection machine
8 from Erinca S.L. (Barcelona, Spain). The pelletized materials were fed at 165 °C and
9 injected at 180 °C into a mirror-finishing steel mold with standard shapes for sample
10 characterization. Pieces with a thickness of 4 mm were obtained for characterization.

11

12 ***2.4. Mechanical characterization.***

13 Tensile tests were carried out in a universal test machine Elib 50 from S.A.E.
14 Ibertest (Madrid, Spain) following the guidelines of ISO 527-1:2012. The selected load
15 cell was 5 kN and the cross-head speed was 5 mm min⁻¹. Shore D hardness values were
16 measured with a 676-D durometer from J. Bot (Barcelona, Spain) as indicated in ISO
17 868:2003. The improvement in toughness was estimated by standard Charpy's test with
18 a 6 J pendulum from Metrotec (San Sebastián, Spain) as suggested by ISO 179-1:2010. To
19 obtain reliable values, at least five different samples were subjected to each mechanical
20 test and the values were averaged. All tests were performed at room temperature.

21

22 ***2.5. Morphology characterization.***

23 Fractured samples from Charpy's tests were used to observe the morphology of
24 the MHO-containing PLA pieces using a field emission scanning electron microscope
25 (FESEM) model ZEISS ULTRA 55 from Oxford Instruments (Abingdon, United
26 Kingdom). All fracture surfaces were coated with an ultrathin metallic layer (Au-Pd

1 alloy) to provide electrical conductivity. This process was conducted in vacuum
2 conditions inside a sputter chamber EMITECH mod. SC7620 provided by Quorum
3 Technologies (East Sussex, United Kingdom).

4

5 **2.6. Thermal characterization.**

6 Thermal characterization was carried out by differential scanning calorimetry
7 (DSC) and thermogravimetric analysis (TGA). The main transition temperatures and
8 enthalpies were obtained by dynamic DSC in a Mettler-Toledo 821 calorimeter
9 (Schwerzenbach, Switzerland) with a temperature program consisting on three stages: a
10 first heating process from 30 °C to 200 °C, followed by a cooling process from 200 °C
11 down to 0 °C, and finally a second heating process from 0 °C to 350 °C. The
12 heating/cooling rate was 10 °C min⁻¹ for all three stages. The main thermal parameters
13 were obtained from the second heating program. The sample size ranged from 5 to 7 mg
14 and it was placed in standard aluminium crucibles (40 µL). All the DSC runs were carried
15 out in nitrogen (N₂) atmosphere with a flow-rate of 66 mL min⁻¹. The degree of
16 crystallinity (X_c) was calculated by means of **Equation 1**.

17

$$18 \quad X_C = \left[\frac{\Delta H_m - \Delta H_{CC}}{\Delta H_m^0 \cdot (1-w)} \right] \cdot 100 \quad \text{Eq. 1}$$

19

20 ΔH_m Melt enthalpy (J g⁻¹)

21 ΔH_{CC} Cold crystallization enthalpy (J g⁻¹)

22 ΔH_m^0 Melt enthalpy of a theoretical 100% crystalline PLA (J g⁻¹) [54]

23 w Weight fraction of MHO

24

1 Thermal stability was studied in a TGA/SDTA 851 thermobalance also from
2 Mettler-Toledo using a weight sample of 5 – 7 mg and standard alumina crucibles (70
3 μL). The thermal program was set from 30 °C to 700 °C at a constant heating rate of 20
4 °C min^{-1} in air.

5

6 ***2.7. Thermomechanical characterization.***

7 Thermomechanical properties were obtained by standard Vicat softening
8 temperature (VST) and heat deflection temperature (HDT) tests following the
9 recommendation of ISO 306 and ISO 75-1, respectively. Both VST and HDT values were
10 obtained in a Vicat/HDT station model VHDT 20 from Metrotec S.A. (San Sebastián,
11 Spain). VST values were obtained using the B50 method, which stands for an applied
12 force of 50 N and a heating rate of 50 °C h^{-1} . Regarding HDT values, samples with
13 dimensions 4x10x80 mm^3 , were subjected to a load of 320 g (three-point bending with a
14 distance between supports of 60 mm) and a heating rate of 120 °C h^{-1} . Three different
15 measurements of VST and HDT values were carried out and averaged.

16 Dimensional stability was studied by thermomechanical analysis (TMA) in a
17 Q400 TMA analyser from TA Instruments (Delaware, USA). Squared samples with
18 parallel faces (4x10x10 mm^3) were subjected to a constant load of 0.02 N and to a
19 temperature sweep from 0 °C to 140 °C at a constant heating rate of 2 °C min^{-1} . The
20 coefficient of linear thermal expansion (CLTE) was calculated below and above T_g . All
21 measurements were done in triplicate.

22 The effect of temperature on the thermomechanical properties was also followed
23 by dynamic mechanical thermal analysis (DMTA) in an oscillatory rheometer AR-G2
24 from TA Instruments (Delaware, USA). This device was equipped with a special clamp
25 system for solid samples, working in torsion-shear conditions. Rectangular samples
26 (4x10x40 mm^3) were subjected to a dynamic heating program from 30 °C to 140 °C using

1 a heating rate of 2 °C min⁻¹ at a constant frequency of 1 Hz. The maximum deformation
2 (γ) was set to 0.1%. Both the storage modulus (G') and the damping factor ($\tan \delta$) were
3 recorded as function of increasing temperature.

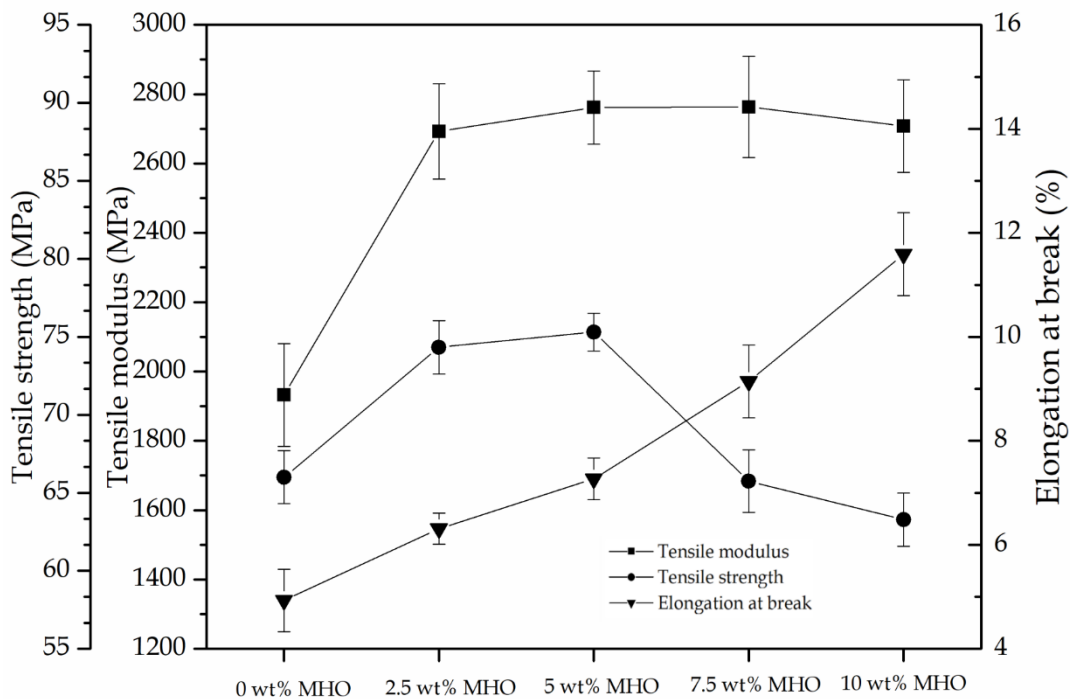
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5 **3. Results and discussion.**

6 *3.1. Mechanical properties of PLA pieces containing MHO.*

7 In Fig. 2 it can be observed the effect of MHO on the tensile properties of the
8 injection-molded PLA pieces. As a plasticizer, an increase in the ductile properties was
9 expected and results showed that the elongation at break was remarkably improved
10 from 4.97%, for the neat PLA piece, up to 11.6%, for the PLA pieces containing 10 wt%
11 MHO. In addition, it was also observed an increase in both the tensile modulus and
12 strength, which is an effect that differs from conventional plasticizers. In particular, the
13 tensile modulus of the neat PLA piece was close to 2.0 GPa and addition of MHO led to
14 an increase up to values of 2.7 GPa, which represents a percentage increase of about 35%.
15 Similar tendency was observed for the tensile strength, which increased from 66.0 MPa,
16 for the neat PLA piece, up to 75 MPa, for the PLA pieces containing MHO at 2.5-5.0 wt%.
17 However, for higher MHO contents than 5.0 wt%, the tensile strength started to
18 decrease, which can be ascribed to a saturation phenomenon of the in the PLA matrix.

19



1

2 **Figure 2.-** Plot evolution of the mechanical properties for the injection-molded
 3 polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content.

4

5 Whereas typical plasticizers habitually produce an increase in the mechanical
 6 ductile properties, such as elongation at break and impact resistance, they also produce
 7 a decrease in the mechanical resistant properties, such as modulus and strength. For
 8 instance, Xiong *et al.* [53] reported that the addition of 5 wt% maleinized tung oil (MTO)
 9 led to a decrease in tensile strength with no remarkable improvement of elongation at
 10 break. The main benefit of MTO was as compatibilizer in immiscible PLA/starch blends.
 11 Ferri *et al.* [50] also showed interesting plasticizing effects of MLO on PLA with a
 12 remarkable increase in elongation at break from values below 15%, for neat PLA, up to
 13 almost 80%, for a MLO content of 13 wt%. However, they also reported the typical
 14 decrease in both tensile modulus and tensile strength. In this study, interestingly, it was

1 observed that MHO exerted a different effect on PLA. This behavior can be related to a
2 chain extension effect provided by MHO. The MAH groups present in MHO are
3 expected to react with the hydroxyl (-OH) terminal groups of the PLA chains, generating
4 a macromolecule of higher M_w based on a linear, branched or even cross-linked structure
5 and, thus, with an improved molecular entanglement to resist mechanical deformation.
6 **Fig. 3** illustrates the here-described possible chemical reactions between the biopolymer
7 molecules with the reactive VO.

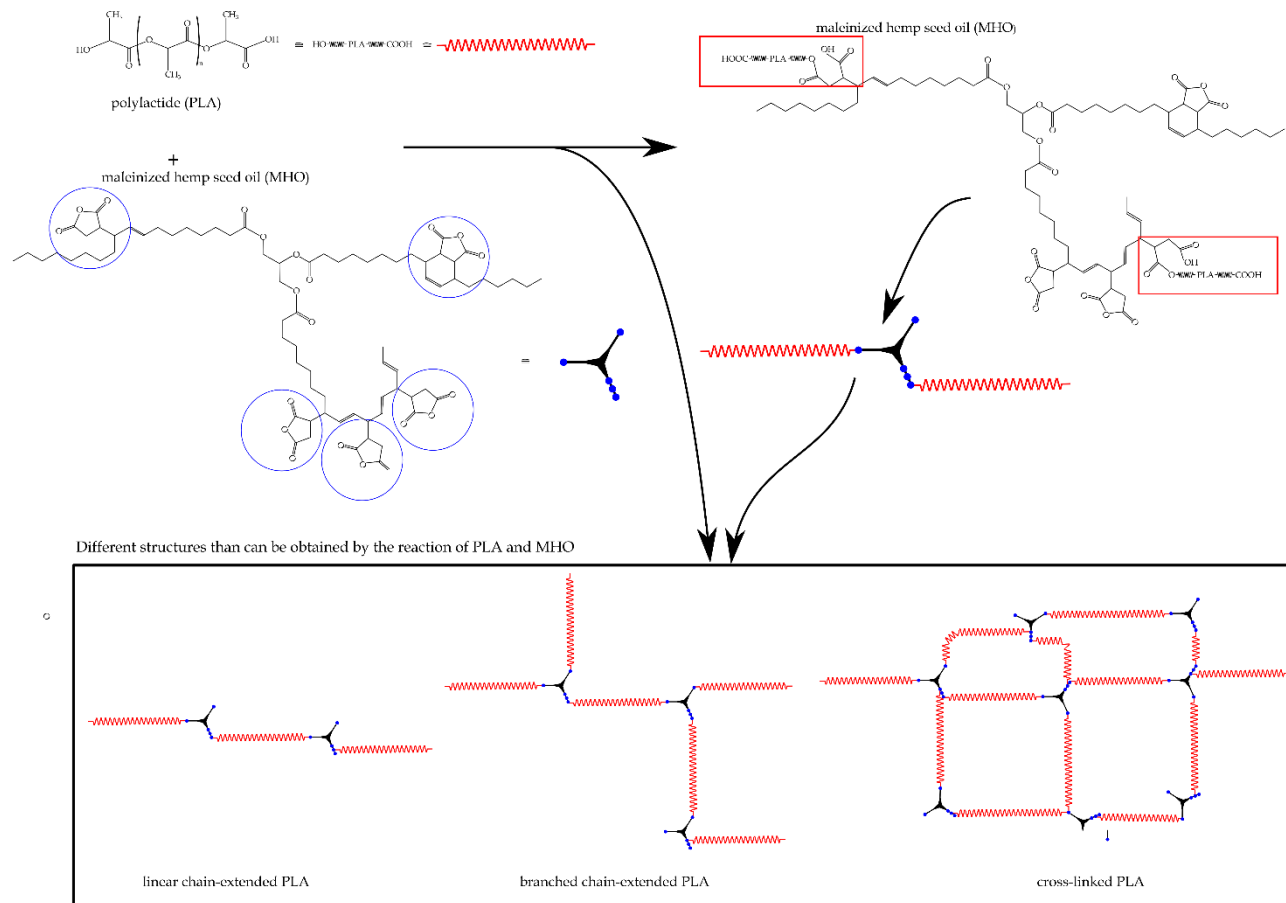


Figure 3.- Schematic representation of the proposed linear chain extension (left) or branching (right) process of polylactide (PLA) by maleinized hemp seed oil (MHO).

1 As a result, depending on the number of MAH groups in MHO, *i.e.* the number
2 average functionality (f), a combined effect of different processes such as linear chain
3 extension, branching and/or cross-linking can be achieved. A similar effect was
4 observed by Mauk *et al.* [55] who suggested that by using acrylated epoxidized soybean
5 oil (AESO) and a thermal initiator, reactive extrusion of PLA was achieved. The work
6 developed by Yuryev *et al.* gave clear evidences of certain toughness improvement on
7 PLA by using reactive extrusion with an acrylic-co-glycidyl copolymer [56]. Due to the
8 multi-functionality of MHO and the tendency of the MAH groups to react with hydroxyl
9 groups at the PLA terminal chains, the above-described simultaneous phenomena are
10 considered to take place, which can contribute to an increase in mechanical resistance.
11 This effect is then proposed to occur in combination with the typical plasticization
12 process due to the interactions of MHO individual molecules with PLA chains, being
13 responsible for the observed increase in the elongation at break.

14 The above-mentioned behavior can be also observed by analysing the Shore D
15 and the Charpy's impact resistance, as shown in **Table 1**. All the MHO-containing PLA
16 pieces showed higher hardness values compared to the neat PLA piece. It is worthy to
17 note the remarkable increase in the impact-absorbed energy that was obtained by the
18 Charpy's test. While the neat PLA piece was characterized by an absorbed-energy of 19.5
19 kJ m⁻², the only addition of 2.5 wt% MHO led to an absorbed-energy of 32.1 kJ m⁻². This
20 property even increased further up to values of 43.4 kJ m⁻² for the PLA piece additivated
21 with 10 wt% MHO, which represents an increase of 122.6% with regard to the
22 unmodified PLA piece. In this sense, it is important to take into account that the impact
23 resistance is highly dependent on both mechanical ductile and resistant properties.
24 Therefore, for the PLA pieces containing MHO it is expectable to have a higher
25 contribution of the improved tensile strength (resistant property) in the overall
26 toughness improvement, compared to the increase in elongation (ductile property).

1 Although similar improvements of toughness have been previously reported by means
2 of other chemically modified VO_s (e.g. MLO), their main contribution was related to an
3 increase in elongation at break since mechanical resistant properties usually decrease
4 with the plasticizer addition [31, 50, 53].

5

6 **Table 1.-** Shore D hardness and Charpy's impact strength for the injection-molded
7 polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content.

MHO content (wt%)	Shore D hardness	Charpy's impact resistance (kJ m ⁻²)
0	79.0 ± 0.6	19.5 ± 2.6
2.5	83.1 ± 0.5	32.1 ± 1.5
5.0	84.4 ± 0.9	34.0 ± 1.9
7.5	83.3 ± 0.8	37.1 ± 1.7
10.0	82.1 ± 0.7	43.4 ± 1.9

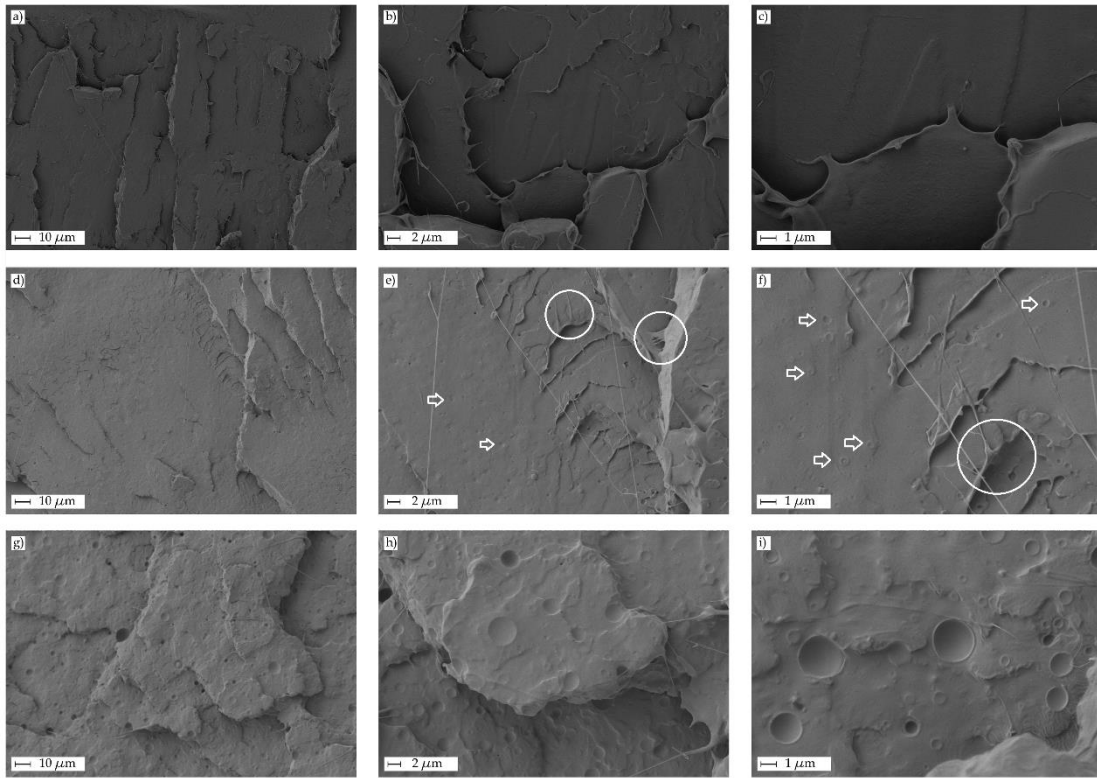
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9

10 **3.2. Fracture surfaces of PLA pieces containing MHO.**

11 As it can be observed in the FESEM micrographs of the fracture surfaces included
12 in **Fig. 4**, PLA and MHO are not fully miscible. Indeed, these images suggest that phase
13 separation occurred at a relative low MHO content. In **Fig. 4a-4c**, one can observe that
14 neat PLA showed the typical brittle fracture with several crack growths and a very soft
15 surface. This was mainly observable at higher magnification (**Fig. 4c**). This fracture
16 morphology is representative for a material with a low deformation during the impact
17 test, leading to lower impact-absorbed energy values.

18



1

2 **Figure 4.-** Field emission scanning electron microscopy (FESEM) images of the injection-
 3 molded polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content
 4 at different magnifications: a), b), and c) neat PLA at 500x, 2000x, and 5000x; d), e), and
 5 f) PLA with 5 wt% MHO at 500x, 2000x, and 5000x; g), h), and i) PLA with 10 wt% MHO
 6 at 500x, 2000x, and 5000x.

7

8 The fracture surface of the injection-molded PLA piece containing 5 wt% MHO,
 9 as it can be seen from **Fig. 4d** to **4f**, showed clear evidences of plastic deformation. This
 10 is emphasized with white circles in the images taken at 2000x and 5000x. At these
 11 magnifications, shown in **Fig. 4e** and **Fig. 4f**, respectively, some evidences of phase
 12 separation can be detected due to the presence of small spherical shapes, which can be
 13 ascribed to MHO, that appeared finely dispersed in the PLA-rich phase (marked with
 14 white arrows). At higher magnification (5000x, **Fig. 4f**) these spherical shapes were more
 15 evident with a diameter of 0.5 μm , *i.e.* in the submicron scale. Presence of filaments gives

1 support to the higher elongation at break of the PLA pieces with 5 wt% MHO. With
2 regard to the PLA pieces with the highest plasticizer content, *i.e.* 10 wt% MHO, phase
3 separation was evident even at low magnifications (**Fig. 4g**). At magnifications of 2000x
4 and 5000x (**Fig. 4h** and **4i**, respectively), the MHO droplets were clearly distinguishable
5 with diameters ranging from hundred nanometres to 1 – 2 μm . This submicron MHO
6 domains within the biopolymer matrix are expected to exert a positive effect on energy
7 absorption in a similar way that, for instance, a rubber phase that is finely dispersed in
8 a brittle polymer matrix [50, 52].

9

10 **3.3. Thermal properties of PLA pieces containing MHO.**

11 The DSC curves of the neat and MHO-containing PLA pieces are included in **Fig.**
12 **5. Table 2** summarizes the main thermal parameters obtained from the DSC analysis.
13 The baseline step in the 55 - 65 $^{\circ}\text{C}$ range corresponds to T_g of the biopolymer. The typical
14 cold crystallization process of PLA, due to the rearrangement of the biopolymer chains
15 in a packed way, was observed for neat PLA in the temperature range between 80 - 110
16 $^{\circ}\text{C}$. Finally, the melting process can be identified as an endothermic peak in the 160 - 175
17 $^{\circ}\text{C}$ range. All these three thermal transitions were clearly identified for neat PLA. Its T_g
18 was 62.8 $^{\circ}\text{C}$, cold crystallization temperature (T_{cc}) was located at 96.3 $^{\circ}\text{C}$ and, finally,
19 melting temperature (T_m) was around 169.6 $^{\circ}\text{C}$.

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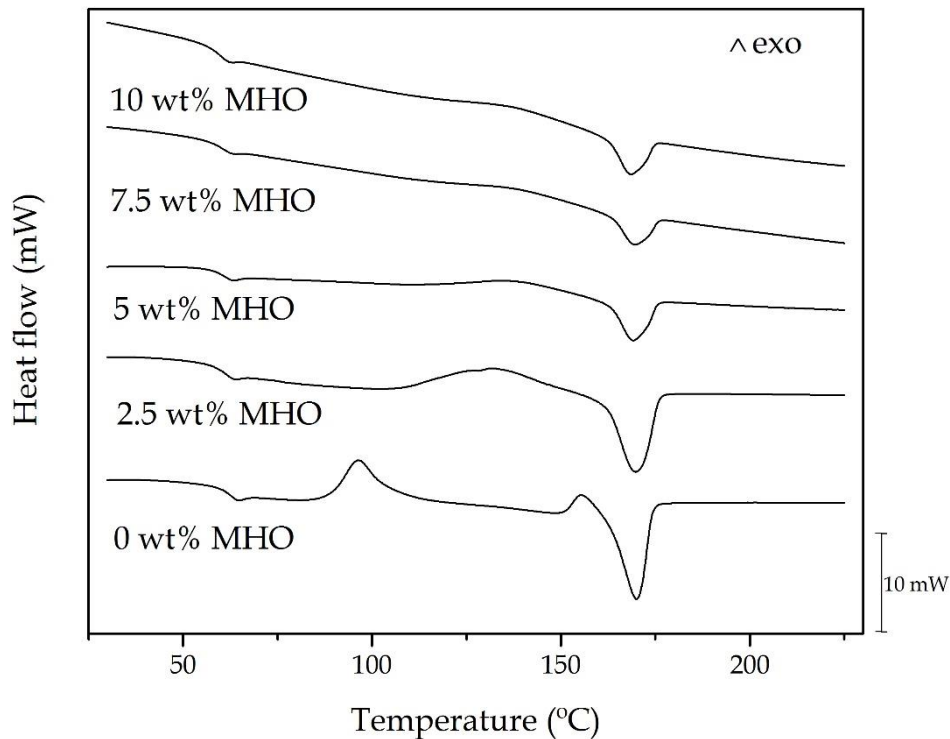


Figure 5.- Differential scanning calorimetry (DSC) thermograms of the injection-molded polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content.

The plasticization efficiency of a given additive is directly related to the T_g decrease it provides. Many studies have reported a remarkable decrease in T_g for PLA-based materials, particularly down to values in the range of 25-35 °C, by using common plasticizers such as ATBC, TEC, OLA, PEG, PPG, etc. [17, 20-22, 30]. As it can be seen in the DSC runs, a slight decrease of 2 - 3 °C in T_g was produced after incorporation of MHO, thus giving evidences of a low plasticization. As described above, MHO could induce certain chain extension, branching or cross-linking to the PLA chains by which it promoted a moderate increase in elongation at break in combination to a significant improvement of the mechanical resistant properties (both tensile modulus and strength).

1 **Table 2.-** Thermal values in terms of glass transition temperature (T_g), cold
 2 crystallization temperature (T_{CC}), enthalpy of crystallization (ΔH_{CC}), melting
 3 temperature (T_m), enthalpy of melting (ΔH_m), and degree of crystallinity (X_c) for the
 4 injection-molded polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO)
 5 content.

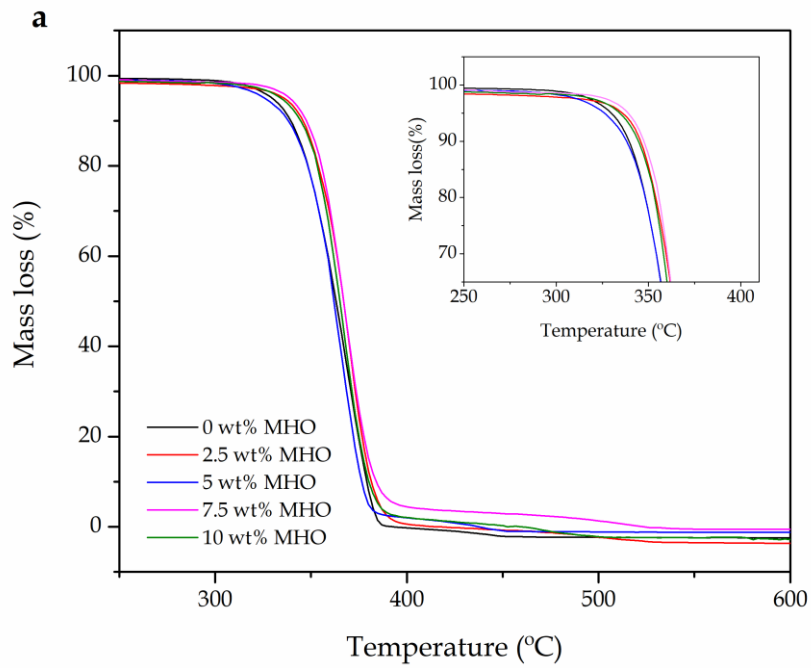
MHO content (wt%)	T_g (°C)	T_{CC} (°C)	ΔH_{CC} (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	X_c (%)
0	62.8 ± 0.26	96.3 ± 0.62	12.5 ± 0.29	169.6 ± 0.66	34.5 ± 0.37	23.6 ± 0.75
2.5	61.4 ± 0.54	132.6 ± 0.76	11.7 ± 0.67	169.5 ± 0.48	28.8 ± 0.52	18.9 ± 0.85
5.0	60.6 ± 0.36	137.1 ± 0.46	3.0 ± 0.58	168.9 ± 0.67	13.7 ± 0.47	12.1 ± 0.77
7.5	60.6 ± 0.34	137.1 ± 1.03	1.7 ± 0.37	169.1 ± 0.52	9.3 ± 0.62	8.8 ± 0.95
10.0	59.8 ± 0.42	135.8 ± 1.24	1.4 ± 0.42	168.0 ± 0.72	7.9 ± 0.64	7.8 ± 0.64

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 8 This macromolecular change can be reflected based on the fact that the cold
 9 crystallization peak was broader or even vanished as the MHO content increased and
 10 the melting peak slightly shifted to lower temperatures whereas the crystallization
 11 degree was noticeably reduced. In particular, T_{CC} of PLA formulations with 2.5 and 5.0
 12 wt% MHO moved up to 132.6 °C and 137.0 °C, respectively. Similar T_{CC} of PLA was
 13 observed for formulations with 7.5 wt% MHO and 10 wt% MHO with values of 137.1 °C
 14 and 135.8 °C, respectively. In addition, neat PLA showed a X_c of 23.6% and this value
 15 presented a decreasing tendency down to values of 7.8% for formulations containing 10
 16 wt% MHO. As it can be observed in Table 2, ΔH_{CC} changed from 12.5 J g⁻¹, with a narrow
 17 and well defined peak (see Fig. 5), for the unmodified PLA piece, down to values of 1-2
 18 J g⁻¹, for the PLA formulations with 7.5-10 wt% MHO, showing a broader and poorly

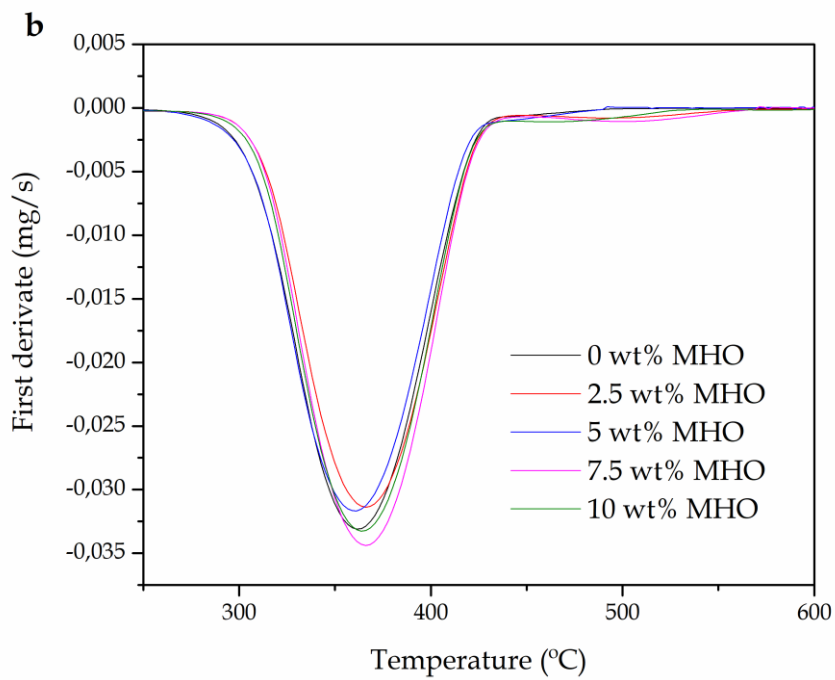
1 defined peak. This suggests a rupture of the crystalline structure in PLA. A similar effect
2 was previously observed for PLA-based formulations cross-linked with acrylic
3 monomers, as reported by Kaczmarek *et al.* [57]. They also observed a T_m decrease due
4 to the PLA crystallites were less perfect in the cross-linked structure. Yang *et al.* [58]
5 reported a similar thermal behavior for PLA cross-linked with triallyl isocyanurate
6 (TAIC) and dicumyl peroxide (DCP) as the thermal initiator. It was concluded that the
7 shift in the cold crystallization process was related to the network formation of PLA
8 molecules of high M_w that inhibits chain motion during the packed rearrangement.

9 With regard to thermal stability, PLA degraded in a one-stage decomposition
10 process, which can be seen in **Fig. 6**. As it was formerly reported by Carrasco *et al.* [59,
11 60], PLA degradation proceeds with a typical chain-scission reaction through breakage
12 of its ester groups. One can observe that MHO provided enhanced thermal stability as it
13 delayed the degradation/decomposition process at elevated temperatures. As shown in
14 **Table 3**, both the onset temperature of degradation ($T_{5\%}$), measured at a constant weight
15 loss of 5 wt%, and the degradation temperature (T_{deg}) slightly moved up to higher values
16 with increasing the MHO content. This increase was more evident in the case of $T_{5\%}$ for
17 which it changed from 331.2 °C, in neat PLA, up to values around 338 °C, for the PLA
18 compositions containing 7.5 – 10 wt% MHO. In this sense, it is well known that, due to
19 the high thermal stability of VOs and their chemically modified ones, some of them are
20 used as thermal stabilizers in poly(vinyl chloride) (PVC) formulations [61]. Recently, it
21 has been reported the efficiency of EVOs and other vegetable oil-derived materials as
22 thermal stabilizers for PLA formulations [62-64].

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4 **Figure 6.-** Comparative plot of the injection-molded polylactide (PLA) pieces varying
5 the maleinized hemp seed oil (MHO) content in terms of: a) Thermogravimetric analysis
6 (TGA) curves; b) Derivative thermogravimetric (DTG) curves.

1 **Table 3.-** Thermal degradation parameters in terms of onset temperature of degradation
 2 ($T_{5\%}$), degradation temperature (T_{deg}), and residual mass at 700 °C for the injection-
 3 molded polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content.

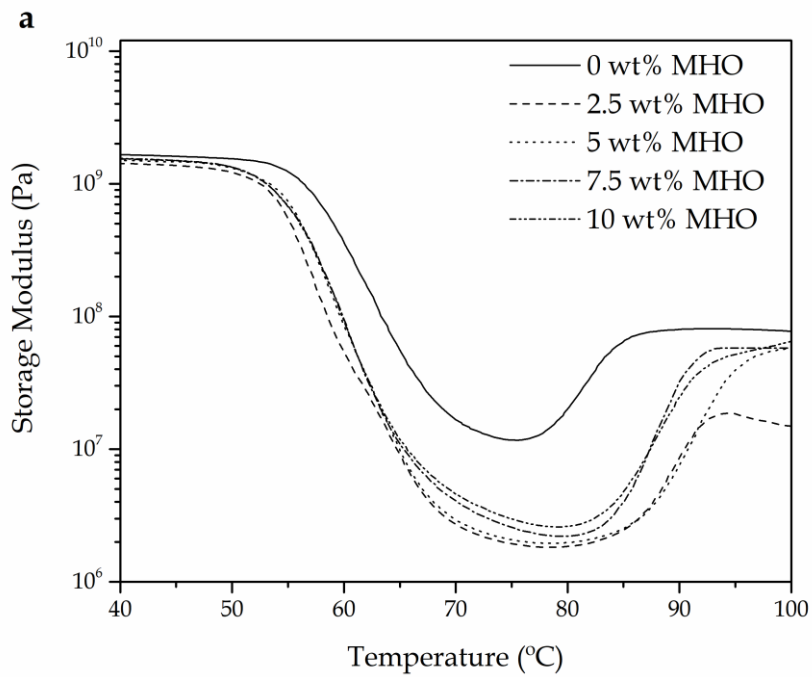
MHO content (wt%)	$T_{5\%}$ (°C)	T_{deg} (°C)	Residual mass (%)
0	331.2 ± 1.13	361.7 ± 1.74	0.81 ± 0.10
2.5	334.5 ± 0.96	366.4 ± 1.63	0.51 ± 0.09
5.0	335.0 ± 1.32	365.9 ± 1.55	1.42 ± 0.12
7.5	338.7 ± 1.08	365.9 ± 1.82	1.96 ± 0.23
10.0	337.9 ± 1.41	363.4 ± 1.77	0.91 ± 0.15

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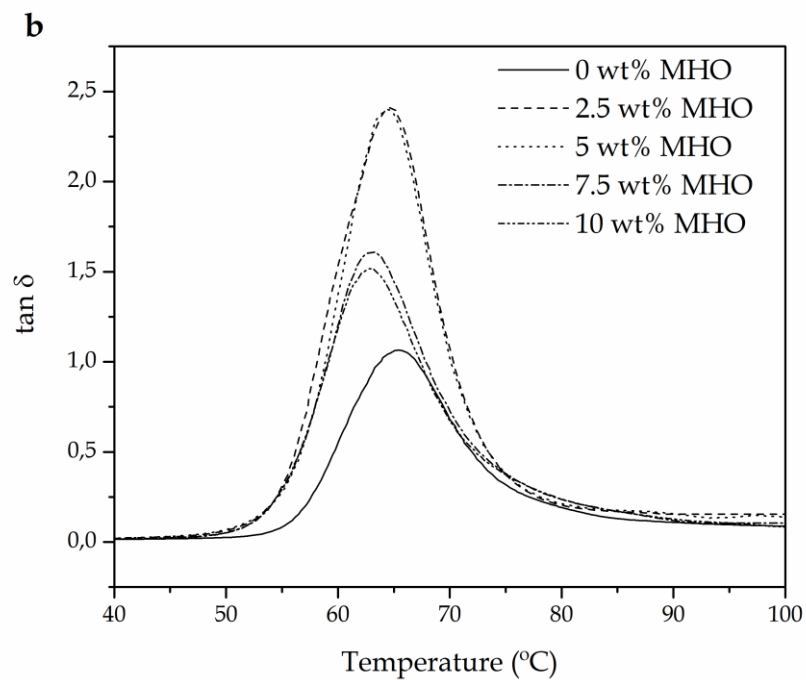
The present results suggest that the linear chain extension, branching and/or, even more intensely, cross-linking effect of MHO are responsible for the achieved thermal stabilization. This is related to the fact that this phenomenon is considered to counteract chain scission, potentially leading to a more branched structure. In this sense, Carrasco *et al.* [65] and Torres-Giner *et. al* [66] also reported similar findings on the thermal stability of PLA and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) ((P(3HB-co-4HB))), respectively, by reactive extrusion (REX) with a multi-functional epoxy-based styrene-acrylic oligomer (ESAO), which provided a chain extension effect by which a branched structure with a higher thermal stability was generated.

1 3.4. Thermomechanical properties of PLA pieces containing MHO.

2 Fig. 7 gathers the dynamic behavior, obtained from DMTA in torsion mode, of
3 the neat and MHO-containing PLA pieces corresponding to the evolution of storage
4 modulus (G') and damping factor ($\tan \delta$) vs. temperature. In the case of G' , this is
5 representative for the elastic behavior of these PLA materials. As it has been described
6 in the previous section, DSC revealed a slight T_g decrease and a T_{CC} shift until it
7 disappeared for increasing MHO contents. Both the glass transition and cold
8 crystallization processes can be clearly detected by DMTA. In particular, T_g for neat PLA
9 was detected by a G' drop of 2 orders of magnitude in the 52 – 75 °C range. With regard
10 to the MHO-containing PLA pieces, this reduction in G' was even more accentuated, *i.e.*
11 almost 3 orders of magnitude, and moved to a lower temperature range, *i.e.* 47 – 72 °C,
12 thus indicating a clear decrease in T_g as previously observed by DSC. The cold
13 crystallization process can be assessed by observing the rise in G' with increasing
14 temperature due to the crystallinity increase achieved, which leads to a stiffer material.
15 For the neat PLA piece, the cold crystallization process ranged from 75 to 90 °C. This can
16 be also observed for all toughened-PLA pieces by MHO but it is worthy to note that cold
17 crystallization occurred at higher temperature values, which is in accordance with the
18 above-mentioned behavior observed by DSC analysis. A similar effect on the cold
19 crystallization process was observed by Yang *et al.* [58] for PLA materials cross-linked
20 with TAIC and DCP. Even more, they also reported a remarkable change in the melt
21 behavior. Another relevant property that can be observed in Fig. 6b is the slight decrease
22 of the $\tan \delta$ peak. This indicates that the α -relaxation of the biopolymer, which is related
23 to its T_g , shifted down from 65 °C, for the neat PLA piece, to 62 °C, for the PLA pieces
24 containing 7.5 – 10.0 wt% MHO.



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2

3 **Figure 7-** Dynamic mechanical thermal analysis (DMTA) curves of the injection-molded
 4 polylactide (PLA) pieces varying the maleinized hemp seed oil (MHO) content: a)
 5 Storage modulus (G'); b) Damping factor ($\tan \delta$).

6

1 As it can be seen in **Table 4**, similar values were observed in the VST and HDT
 2 values after the incorporation of MHO into PLA. Only a slight reduction in the
 3 thermomechanical properties occurred for the highest MHO contents, *i.e.* 7.5 and 10
 4 wt%.

5

6 **Table 4.-** Thermomechanical values in terms of Vicat softening temperature (VST), heat
 7 deflection temperature (HDT), and coefficient of linear thermal expansion (CLTE) below
 8 and above glass transition temperature (T_g) for the injection-molded polylactide (PLA)
 9 pieces varying the maleinized hemp seed oil (MHO) content.

MHO content (wt%)	VST (°C)	HDT (°C)	CLTE ($\mu\text{m}/\text{m } ^\circ\text{C}$) by TMA	
			Below T_g	Above T_g
0	56.3 ± 0.5	55.4 ± 1.6	94.4 ± 0.42	146.9 ± 0.39
2.5	57.2 ± 2.4	57.2 ± 2.6	80.7 ± 0.65	160.3 ± 0.56
5.0	55.6 ± 1.3	55.2 ± 2.2	85.6 ± 0.59	160.4 ± 0.79
7.5	54.6 ± 2.5	54.6 ± 2.6	90.8 ± 0.67	168.6 ± 0.52
10.0	54.6 ± 2.4	54.2 ± 1.9	91.4 ± 0.62	172.8 ± 0.62

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11

12 However, these changes were comprised within the typical error associated to
 13 these two techniques. In relation to the dimensional stability, all PLA formulations
 14 presented higher CLTE values above T_g since the biopolymer chains can more readily
 15 move. However, MHO provided certain changes in the CLTE values. Specifically, below
 16 T_g , these values decreased from 94.4 $\mu\text{m}/\text{m } ^\circ\text{C}$ to 80.7 $\mu\text{m}/\text{m } ^\circ\text{C}$ after the only addition
 17 of 2.5 wt% MHO. The CLTE values then increased with further increasing the MHO
 18 content up to values close to the neat PLA piece. This effect can be ascribed to the

1 formation of a long-chained, branched, and/or cross-linked (or even a combination of
2 all three possible mechanisms) structure. Nevertheless, a positive dimensional
3 stabilization was observed for all MHO contents above T_g . The CLTE values increased
4 from $146.9 \mu\text{m}/\text{m } ^\circ\text{C}$, for the neat PLA piece, to $172.8 \mu\text{m}/\text{m } ^\circ\text{C}$, for the PLA piece
5 containing 10 wt% MHO. This is an indication of the formation of a more compacted
6 structure, indicating an extraordinary thermomechanical response.

7

8 **4. Conclusions.**

9 In the present study, MHO has been assessed as an environmentally friendly and
10 cost-effective reactive additive for producing injection-molded PLA pieces with
11 improved toughness. PLA pieces containing 2.5-7.5 wt% MHO offered a more balanced
12 combination of mechanical and thermomechanical properties whilst the thermal
13 properties remained nearly constant. As opposite to typical plasticizers, MHO generated
14 PLA pieces with not only higher mechanical ductility, in terms of improved elongation
15 at break and impact strength, but also enhanced mechanical strength. As suggested by
16 the obtained results, the MAH groups present in MHO react with the hydroxyl groups
17 of the PLA terminal chains to form a linear chain-extended, branching and/or cross-
18 linking structure with improved energy absorption. Morphological observation
19 performed on the fracture surface revealed good miscibility at low MHO concentrations.
20 However, over 5 wt% MHO, saturation of MHO in PLA occurred and some MHO-rich
21 domains appeared as finely dispersed submicron droplets, which were also considered
22 to positively improve toughness of the biopolymer. Therefore, the here-obtained
23 materials represent an environmentally friendly solution to overcome the high
24 brittleness of PLA articles with interesting applications in, for instance, the rigid

- 1 packaging industry or as parts or components for the automotive and building and
- 2 construction industries, etc.
- 3

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