The final publication is available at

http://dx.doi.org/10.1016/j.carbpol.2016.03.082

Additional Information

1   **"The effect of maleinized linseed oil (MLO) on mechanical performance of poly(lactic**

2   **acid)-thermoplastic starch (PLA-TPS) blends"**

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9

10   **Abstract**

11   In this work, poly(lactic acid), PLA and thermoplastic starch, TPS blends (with a fixed

12   content of 30 wt.% TPS) were prepared by melt extrusion process to increase the low ductile

13   properties of PLA. The TPS used contains an aliphatic/aromatic biodegradable polyester

14   (AAPE) that provides good resistance to aging and moisture. This blend provides slightly

15   improved ductile properties with an increase in elongation at break of 21.5% but phase

16   separation is observed due to the lack of strong interactions between the two polymers. Small

17   amounts of maleinized linseed oil (MLO) can positively contribute to improve the ductile

18   properties of these blends by a combined plasticizing-compatibilizing effect. The elongation at

19   break increases over 160% with the only addition of 6 phr MLO. One of the evidences of the

20   plasticizing-compatibilizing effect provided by MLO is the change in the glass transition

21   temperature (T_g) with a decrease of about 10 ℃. Field emission scanning electron microscopy

22   (FESEM) of PLA-TPS blends with varying amounts of maleinized linseed oil also suggests an

23   increase in compatibility.

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1.- Introduction.

Due to the high environmental impact, the use of conventional non-biodegradable plastics is being questioned and new environmentally friendly polymers are being demanded and introduced in several industrial sectors. Today, several polymers such as poly(lactic acid)-PLA, poly(hydroxybutyrate)-PHB and thermoplastic starch (TPS), among others, find new and attracting uses in different sectors such as automotive (Mulhaupt, 1996) and packaging (Arrieta et al., 2014, Arrieta et al., 2014) industries with increasing use. These polymers are characterized by high environmental efficiency along the whole life cycle as they are obtained from renewable resources (PLA is obtained from corn starch and sugar bagasse, PHB is obtained from bacterial fermentation and TPS combines different plant starches with plasticizers) and can be easily disintegrated in compost conditions (Vroman et al., 2009). In addition to these, some petroleum-based polymers such as poly(caprolactone)-PCL, poly(butylene succinate)-PBS, poly(ester amide)-PEA, etc. offer attracting properties as they can be easily processed and they can biodegrade in different media (Arrieta et al., 2014). Many of the so-called biobased polymers are obtained or derived from different types of starch which plays a key role in their synthesis (Pessione et al., 2014, Poomipuk et al., 2014, Bhatia et al., 2015, Liaud et al., 2015).

Poly(lactic acid), PLA is one of the most promising polymers to replace petroleum-based polymers in the packaging industry (Cheng et al., 2015, Sanyang et al., 2015). This is characterized by balanced mechanical properties, good chemical barrier behavior (Plackett et al., 2006), odorless, biocompatible, bio resorbable (Hutmacher et al., 2001) and, in the last years its cost has been remarkably reduced. The main synthesis route is ring-opening polymerization from lactides obtained from starch (wheat, corn, sugar bagasse, yucca, tapioca roots, among others) depending on its availability (Averous, 2004, Lasprilla et al., 2012). Some of the main drawbacks of PLA are its sensitiveness to moisture, low flexibility, low elongation at break and low toughness. To overcome these intrinsic properties, copolymers represent an interesting alternative. Nevertheless, copolymers are, in general, costly materials. A cost effective solution is the use of natural plasticizers which are interesting from an environmental point of view and

1   can be an alternative to traditional petroleum-based plasticizers. Some natural vegetable oils

2   (Yokesahachart et al., 2011) and epoxidized vegetable oils (EVOs) find increasing uses in the

3   plasticization industry (Mohammed et al., 2015, Narute et al., 2015). In addition to these, a wide

4   variety of monomeric (Shi et al., 2011, Tsui et al., 2013) and polymeric plasticizers have been

5   proposed in the last years (Averous, 2004, Ren et al., 2009, Oromiehie et al., 2013).

6   Plasticization mechanisms have been widely studied and the main phenomena are related to the

7   lubricant effect and to the free volume that the plasticizer can provide. Plasticizer molecules

8   placed between two different base polymer chains act as a lubricant with a positive effect on

9   chain mobility. Compatible plasticizers can move into the free volume around the polymer

10   chains. This phenomenon results in several effects: the space between two polymer chains is

11   increased and this reduces the intensity of polymer-polymer interactions. On the other hand,

12   compatibility between the plasticizer and the polymer chains allows entering the plasticizer and

13   this increases intermolecular distance which results in some swelling with a subsequent increase

14   in free volume. As a result of these two phenomena, the plasticizer acts as a lubricant with a

15   remarkable enhancement of polymer chain mobility. A wide variety of plasticizers have been

16   proposed to improve the low intrinsic toughness of neat PLA (Liu et al., 2011). In addition,

17   plasticizers can react with hydroxyl groups located at the end groups of PLA polymer chains

18   with a chain extension effect. This is based on the ability of hydroxyl, carbonyl, carboxyl or

19   other polar groups (Niazi et al., 2015) to chemically react with polymer chains to provide a

20   chain extension or a chemical bridge between two polymers in a blend (compatibilization).

21   Some vegetable oil plasticizers act as internal lubricants that allow chain motion and this leads

22   to improved processing conditions, high thermal stability and ductility.

23   Blending rigid polymers such as PLA with ductile polymers such as poly(caprolactone),

24   thermoplastic starch, polyethylene, etc. is an attracting alternative to overcome the fragility of

25   brittle polymers in a cost effective way. The main problem related to polymer blends is the

26   miscibility between the components. Thermoplastic starch-TPS, has been proposed as a ductile

27   component in different blends to provide toughness and reduce fragility of brittle polymers

28   (Averous, 2004, Boonprasith et al., 2013). TPS addition can lead to increased flexibility and

elongation at break (Sahari et al., 2013). Industrial TPSs are based on different starches (wheat, corn, sorghum, yucca, potato, etc.) (Sahari et al., 2013) and plasticizers (glycerol, sorbitol, maltose, glucose, etc. or a combination of these) (Chocyk et al., 2015, Mahieu et al., 2015) that enable easy processing and provide high ductile materials with improved elongation at break, reduced retrogradation effects and improved thermal stability (Zhang et al., 2014, Schmitt et al., 2015). Chemically, starch is constituted of two polysaccharides: amylose and amylopectin. Depending on the their ratio, mechanical properties can vary in a great extent (Raquez et al., 2008, Ren et al., 2009, Oromiehie et al., 2013, Clasen et al., 2015).

One of the main drawbacks of using TPS as co-component in polymer blends is its poor miscibility with polymers such as PLA (Teixeira et al., 2012, Mittal et al., 2015). For this reason, important efforts are being conducted to improve it by using compatibilizer agents. Maleic anhydride (MA) and other esterifying agents have been successfully used to improve compatibility of immiscible or very low miscible polymers (Raquez et al., 2008, Ren et al., 2009, Zhu et al., 2012, Oromiehie et al., 2013, Clasen et al., 2015, Detyothin et al., 2015). Maleinization of TPS with 20 wt.% glycerol by using reactive extrusion was revealed as a useful technique to increase the compatibility with a biodegradable polyester (Raquez et al., 2008). Same results were obtained with chemical modification of starch with an esterifying agent leading to improved blending with poly(lactic acid) (Shin et al., 2011). PLA-TPS blends containing 15 wt.% TPS showed improved elongation at break and impact absorbed energy with previous modification with maleic anhydride (Gao et al., 2011). Monomeric plasticizers can also provide compatibilization to immiscible or low miscible polymers. Glycidyl methacrylate was successfully used to modify TPS/PEO (TPEO) for improved formulations with poly(lactic acid) (Shi et al., 2011). High molecular weight polyethylene glycols have demonstrated to provide good compatibilization properties (Yu et al., 2015).

PLA/TPS blends and, in particular, the PLA/TPS blend with 30 wt.% TPS show balanced properties in terms of improved toughness but the restricted miscibility between the two components leads to a clear phase separation which gives low mechanical performance. As described previously, the highly reactive acid/anhydride groups in maleinized vegetable oils can

4

1   potentially provide a dual effect on PLA blends: a plasticizing and a compatibilizing/chain

2   extension effect. The aim of this work is the use of thermoplastic starch to provide improved

3   toughness to rigid-brittle poly(lactic acid). Due to the lack of miscibility of TPS and PLA,

4   maleinized linseed oil (MLO) is used as a natural-derived compatibilizer for PLA-TPS

5   immiscible blends. The influence of MLO on thermal, mechanical, morphological properties

6   and its effect on the compatibility of these two restricted miscibility polymers is evaluated.

7

8   **2.- Experimental.**

9   *2.1.- Materials.*

10   Poly(lactic acid), PLA Ingeo^{TM} Biopolymer commercial grade 6201D was supplied by

11   NatureWorks LLC (Minnetonka, USA). This grade contains 2% D-lactic acid; it is characterized

12   by a density of 1.24 g cm^{-3} and a melt flow index (MFI) in the 15-30 g/(10 min) range measured

13   at 210 ºC. Thermoplastic starch commercial grade Mater-Bi® NF 866 was obtained from

14   Novamont SPA (Novara, Italy) and it is produced from maize starch. It shows a melt flow index

15   of 3.5 g/(10 min) measured at 150 ºC, a density of 1.27 g cm^{-3} and a melt peak located in the

16   110 ºC – 120 ºC range. This thermoplastic starch is composed of about 15% of an

17   aliphatic/aromatic biodegradable copolyester (AAPE) (NOVAMONT, 2010). The material used

18   as plasticizer-compatibilizer was a maleinized linseed oil (MLO) VEOMER LIN supplied by

19   Vandeputte (Mouscron, Belgium) with a viscosity of 10 dPa s at 20 ºC and an acid value of 105

20   – 130 mgKOH g^{-1}.

21

22   *2.2.- Preparation and compatibilization of PLA-TPS blends.*

23   A constant TPS content of 30 wt.% was used to evaluate the plasticization

24   compatibilization effect provided by maleinized linseed oil (MLO). This composition has given

25   interesting results in terms of toughness improvement as observed by previous results and

26   reported in the literature (Li et al., 2011). 30 wt.% TPS also contributes to lower the cost of the

27   material as it is cheaper than PLA while maintaining the overall properties of PLA. PLA-30

28   wt.% TPS blends with different maleinized linseed oil (MLO) content as indicated in Table 1

1 were manufactured. The MLO range composition varied in the 0-8 phr (per hundred resin) as

2 previous studies with epoxidized vegetable oils and maleinized oils indicated saturation with

3 relatively low contents close to 10 phr. Initially, PLA and TPS were dried at 60 ºC for 24 hours

4 in an air circulating oven. After this, PLA and TPS pellets were mechanically mixed in a zip bag

5 together with the corresponding amounts of MLO. Subsequently, the mixtures were extruded in

6 a twin-screw co-rotating extruder at a rotating speed of 60 rpm. The temperature profile was set

7 to 167.5 ºC, 170 ºC, 172.5 ºC and 175 ºC from the hopper to the die. After cooling, the extruded

8 materials were pelletized and processed by injection molding in a Meteor 270/75 from Mateu &

9 Solé (Barcelona, Spain) at an injection temperature of 175 ºC. Standard samples for tensile tests

10 and rectangular shapes sizing 80x10x4 mm^3 for other characterizations were obtained.

11

12 **Table 1**

13

14 *2.3.- Mechanical characterization.*

15 Mechanical properties of the blends and individual materials were obtained with

16 standard tensile, flexural, hardness and impact tests. Tensile and flexural properties were

17 obtained in a universal test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain) at room

18 temperature with the guidelines of the ISO 527-5 and ISO 178 respectively. A 5 kN load cell

19 was used for all tests and the crosshead speed was set to a constant value of 10 mm min^{-1}. At

20 least five different samples were tested in both tensile and flexural tests to obtain average values

21 of the main parameters. In addition, a bi-axial extensometer from Ibertest was used to measure

22 the Young Modulus in a more accurate way.

23 Shore D hardness was measured in a Shore D durometer 673-D from Instrumentos J.

24 Bot S.A. (Barcelona, Spain) as recommended by the ISO 868. With regard to the energy

25 absorption, a Charpy pendulum (1 J) from Metrotec S.A. (San Sebastián, Spain) was used to

26 measure the absorbed energy in impact conditions as recommended by the ISO 179:1993. Five

27 different notched samples were tested and average values were calculated. The geometry of the

1 notch was type A with a background radius of 0.25 ± 0.05 mm; the remaining width of 8.0 ± 0.2

2 mm and the notch angle is $45º \pm 1º$.

3 *2.4.- Microstructural characterization.*

4 A high-resolution field emission microscope ZEISS ULTRA55 from Oxford

5 Instruments (Oxfordshire, United Kingdom) operated at 2 kV was used to observe the

6 microstructure of cryofractured surfaces. Samples were coated with an ultrathin platinum layer

7 in vacuum conditions in a high vacuum sputter EM MED020 from Leica Microsystems.

8

9 *2.5.- Thermal characterization.*

10 Thermal transitions were studied by differential scanning calorimetry (DSC) in a DSC

11 821 calorimeter from Mettler-Toledo Inc. (Schwerzenbach, Switzerland) with a heating program

12 from 30 ℃ to 350 ℃ in nitrogen atmosphere (66 mL min^{-1}) at a heating rate of 10 ℃ min^{-1}.

13 Degradation at high temperatures was studied by thermogravimetric analysis (TGA) in a

14 TGA/SDTA 851 thermobalance from Mettler-Toledo Inc. (Schwerzenbach, Switzerland). The

15 selected temperature ramp was from 30 ℃ to 500 ℃ in nitrogen atmosphere (66 mL min^{-1}) at a

16 heating rate of 20 ℃ min^{-1}.

17 Dynamic mechanical thermal analysis (DMTA) in torsion mode was done on

18 rectangular samples sizing 40x10x4 mm^3 in an oscillatory rheometer AR G2 from TA

19 Instruments (New Castle, USA) equipped with a special clamp system for solid samples. The

20 temperature program was from -80 ℃ to 130 ℃ at a heating rate of 2 ℃ min^{-1} at a frequency of

21 1 Hz and a maximum deformation (γ) of 0.1%.

22

23 **3.- Results and discussion.**

24 *3.1.- Effect of MLO on mechanical properties of PLA-TPS blends.*

25 Unblended PLA possesses a tensile strength of 64 MPa and a tensile modulus of 3590

26 MPa. These values are higher than most commodity plastics. Nevertheless, PLA is a quite brittle

27 polymer with an elongation at break of about 7%. Addition of a high ductile and flexible

polymer such as thermoplastic starch provides improved ductile properties but the lack of miscibility of them can lead to lower performance than expected. For this reason, maleinized linseed oil was added at different concentrations to provide plasticization and/or compatibilization effects. Fig. 1a shows the plot evolution of tensile properties of PLA-30TPS with varying maleinized linseed oil (MLO). PLA-30TPS blend offers a tensile strength of 41.5 MPa and a tensile modulus of 2475 MPa. With the only addition of 2 phr MLO the tensile strength suffers a decrease up to values of 35.7 MPa which represents a percentage decrease of 14%. Higher MLO content such as 8 phr MLO leads to tensile strength values of about 28.2 MPa (percentage decrease of almost 32%). With regard to the tensile modulus, it changes from 2475 for PLA-30TPS blend without MLO to values in the 2200 MPa – 2300 MPa range for MLO content in the 2 – 8 phr range. It is evident that mechanical resistant properties decrease with increasing MLO content. On the other hand, mechanical ductile properties are remarkably improved with MLO. PLA-30TPS is characterized by an elongation at break of 21.5% and we observe an increasing tendency up to 6 phr MLO with noticeable higher elongation at break values of 160%. For an MLO content of 8 phr, the elongation at break is still higher than raw PLA-30TPS blend but this value is lower than that obtained for 6 phr MLO. This could indicate that an optimum is achieved for phr contents close to 6 phr and higher MLO contents do not provide increased ductile properties. Miscibility of TPS in PLA is poor as referred by some authors (Teixeira et al., 2012, Mittal et al., 2015) and phase separation is the resulting microstructure. Nevertheless, finely rich TPS dispersed phase provides improved toughness and other ductile properties to PLA due to its high flexibility which enables some energy absorption and elongation but in general terms TPS does not act as a plasticizer when blended with PLA. As one can observe, MLO addition leads to a remarkable in elongation at break whilst no remarkable decrease is detected for both tensile strength and tensile modulus. This indicates that MLO provides a clear plasticization effect and the evidence is the noticeable increase in elongation at break. On the other hand, the tensile strength and modulus do not decrease in a great extent thus giving some evidences that in addition to plasticization, other phenomena could occur. It is expectable that maleic anhydride groups in MLO can react with some

1   hydroxyl groups in PLA end chains (and partially hydrolysed PLA chains during processing) to

2   give a chain extension effect and, on the other hand, MLO can also react with hydroxyl groups

3   in TPS thus leading to a compatibilization effect as observed by the evolution of the mechanical

4   properties.

5

6   **Figure 1**

7

8   Fig. 1b shows the evolution of the flexural properties as a function of the maleinized

9   linseed oil (MLO) content. The flexural strength and flexural modulus of unblended PLA is

10   116 MPa and 3273 MPa respectively. We observe a decrease in both flexural strength and

11   flexural modulus with minimum values in the 4 – 6 phr MLO range up to 45-50 MPa and 2100

12   MPa for flexural strength and modulus respectively. Over 6 phr MLO a decrease in both

13   mechanical resistant and ductile properties is observed and this could be related to a negative

14   effect due to phase separation (Mikus et al., 2014).

15   One of the main features of PLA-30TPS blends with MLO is the large increase in the

16   impact-absorbed energy as it can be observed in Table 2. Unblended PLA is characterized by a

17   relatively low energy absorption ability with a Charpy's impact energy of 1.6 ± 0.3 kJ m^{-2}.

18   Physical blend of PLA with TPS leads to a remarkable increase in the energy absorption up to

19   values of 5.3 kJ m^{-2}, which represents a percentage increase of about 230%. Despite this

20   remarkable increase, addition of MLO still improves more the energy absorption up to values of

21   about 9.5 kJ m^{-2} for MLO compositions comprised between 4 and 6 phr MLO, which represents

22   a percentage increase of almost 500% with regard to unblended PLA. For an MLO content of 8

23   phr we observe the same phenomenon described before with a decrease in the energy absorption

24   due to a negative effect as a consequence of MLO saturation and subsequent phase separation.

25

26   **Table 2**

27

1   With regard to the Shore D hardness, we observe similar decreasing tendency as other

2   mechanical resistant properties. The Shore D of unblended PLA is 76 and it is decreased up to

3   68 by blending with TPS but addition of MLO leads to softer materials due to the plasticization

4   effect clearly observable up to 6 phr MLO.

5   Evolution of Vicat softening temperature (VST) and heat deflection temperature (HDT)

6   follows typical tendency of a mechanical resistant property such as strength and modulus. The

7   VST and HDT values for unblended PLA are 52.8 ºC and 47.6 ºC respectively. A blend of PLA

8   with 30 wt.% TPS provides improved deformation properties thus leading to lower VST and

9   HDT values of 50.6 ºC and 49.4 ºC respectively. Once again, addition of MLO leads to

10   decreased VST and HDT values up to asymptotic values of 47 ºC and 44 ºC respectively.

11

12   *3.2.- Effect of MLO on thermal properties of PLA-TPS blends.*

13   Table 3 shows a summary of the main thermal parameters obtained by differential

14   scanning calorimetry (DSC) on PLA-30TPS blends with different amounts of maleinized

15   linseed oil (MLO).

16

17   **Table 3**

18

19   As it can be observed, the melt temperature does not vary in a significant way with

20   regard to the reference PLA-30TPS blend. The glass transition temperature slightly decreases

21   with MLO content due to increased polymer chain mobility. There are two possible effects that

22   MLO can provide: a lubricant effect and a decrease in the intensity between polymer chains.

23   Lubricity and gel theories have been extensively used to explain the effects of plasticizers on

24   polymeric structures. Lubricity theory proposes that the plasticizer can exert a lubricant effect

25   which leads to increased chain mobility as the distance between polymer chains increases thus

26   leading to decreased polymer-polymer interactions. On the other hand, the gel theory suggests

27   that the plasticizer contributes to lower polymer-polymer interactions (hydrogen bonds, van der

28   Waals or ionic forces, etc.) which has a positive effect on the overall chain mobility. These

1 phenomena could explain the observed decrease in Tg values as MLO is added. In addition,

2 MLO can readily react with hydroxyl groups in both PLA end chains and thermoplastic starch

3 chains leading to a combined effect of compatibilization and chain extension with a subsequent

4 decrease in crystallinity which can also contribute to lower polymer-polymer interactions

5 (Chieng et al., 2014). It is important to remark that the only addition of 30 wt.% TPS to PLA

6 leads to a decrease in the glass transition temperature from 65.4 ºC (unblended PLA) to 62.8 ºC

7 for the blend. Although these polymers are not fully miscible and phase separation is evident,

8 PLA is able to dissolve a very low amount of TPS chains resulting in a PLA rich phase but the

9 effect of the dissolved TPS chains promotes a decrease in the glass transition temperature. In

10 addition, the cold crystallization temperature follows similar tendency to that observed for T_g.

11 Unplasticized PLA shows a cold crystallization peak at 102 ºC and the blend with 30 wt.% TPS

12 leads to a decrease in the cold crystallization peak to values of 98.5 ºC. Addition of MLO to this

13 blend provides a slight decrease in the cold crystallization temperature up to values of 95.2 ºC

14 for an MLO content of 8 phr. This is directly related to increased chain mobility due to the

15 internal lubrication effect that MLO produces (Chieng et al., 2014).

16 With regard to the thermal stability of PLA-30TPS, Fig. 2 shows a comparative plot of

17 the TGA thermograms for neat PLA and its blends with 30 wt.% TPS (with and without MLO

18 compatibilizer). We can clearly observe a positive effect of MLO on overall thermal stability

19 with improved thermal degradation temperature as MLO content increases.

20

21 **Figure 2**

22

23 As we can observe, the PLA blend with 30 wt.% TPS offers improved thermal stability

24 with regard to unblended PLA and this thermal stability is still improved with the addition of

25 maleinized linseed oil (MLO) as observed in Fig. 2. Specifically, the degradation temperature

26 corresponding to 90% weight loss (T_{90}) is 380 °C, whereas for PLA/30TPS is 408 °C. A

27 significant increase in PLA stability is observed when adding TPS, but still it is higher when the

blends contains MLO. In fact, a high increase in T90 is observed with values of 415 ºC, 411.5

ºC, 416.6 ºC and 420.5 ºC for blends containing 2, 4, 6 and 8 phr MLO, respectively.

3.3.- Effect of MLO on dynamic mechanical thermal properties of PLA-TPS blends.

Fig. 3a &3b represent the evolution of the storage modulus (G') and the damping factor (tan δ) in terms of temperature for different maleinized linseed oil compositions. The storage modulus (G') at temperatures below T_g (Fig. 3a) decreases as the MLO content increases. By observing the curve corresponding to the evolution of G' for the PLA-30TPS blend with 6 phr MLO we see the best ductile properties with minimum G' values. Over 6 phr MLO a negative effect occurs thus leading to decreased flexibility as it can be seen by G' values higher than those obtained with an MLO content of 6 phr. This could be related to plasticizer saturation leading to phase separation (Mikus et al., 2014). In addition, a clear decrease in the cold crystallization process as previously detected by differential scanning calorimetry (DSC) can be observed. The only presence of TPS is responsible for a slight decrease in the cold crystallization temperature with onset values located at lower temperatures. Although PLA and TPS are not completely miscible a PLA rich phase with some TPS polymeric chains can be expected due to the partial (very low) interactions as evidenced by phase separation. This PLA rich phase is characterized by slightly higher mobility which is responsible for some decrease in both cold crystallization onset and glass transition temperature. Addition of MLO provides two phenomena that result in increased chain mobility. On the one hand, MLO acts as typical plasticizer with a lubricant effect and, on the other hand, MLO contributes to increase PLA-TPS interactions. These two phenomena have a positive effect on overall polymer chain mobility and this results in decreased cold crystallization onset temperature and glass transition temperature as observed in Fig. 3.

Figure 3

1   Fig. 3b shows the evolution of the damping factor (tan δ) for PLA and PLA-30TPS

2   blends with different MLO content. The peak is directly related to the glass transition

3   temperature ($T_{g\,PLA}$) and as it can be seen, this peak is moved to lower values thus indicating a

4   decrease in the glass transition temperature of the PLA rich phase. Once again, the initial

5   decrease that TPS provides is accentuated by the synergistic effect of MLO addition.

6   **3.4.- *Effect of MLO on morphology of PLA-TPS blends.***

7   Fig. 4 shows FESEM images of fractured samples corresponding to unblended PLA,

8   unblended TPS and the PLA blend with 30 wt.% TPS (PLA-30TPS) (Fig. 4e & 4f). These

9   pictures show the typical brittle fracture of PLA (Fig. 4a & 4b) with smooth fracture surface due

10   to inexistent or very low plastic deformation and a ductile fracture corresponding to a flexible

11   polymer, TPS (Fig. 4c & 4d) with flake formation. These flakes correspond to crystalline plane

12   growth or "*crystalline lamellae*" located at the amylopectin branches that are fold up because of

13   fracture. These flake structures form parallel-plane blocks and clusters of these blocks form

14   granules separated by porous of amorphous areas in which amylose and plasticizers can be

15   allocated (Hee-Young Kim, 2014). The blend with 30 wt.% TPS shows a clear phase separation

16   with a PLA rich phase as the matrix and the TPS rich phase as the dispersed component as

17   detected in Fig. 4e & 4f. This phase separation is related to the lack of affinity between TPS and

18   PLA and this leads for the need of somewhat compatibilization (Huneault et al., 2007). PLA is a

19   hydrophobic polymer whilst TPS is a highly hydrophilic polymer (in fact one of the main

20   drawbacks of TPS is its extremely high moisture sensitiveness). This different polarity is

21   responsible of the lack (or very low) affinity between these two polymers and this leads to a

22   phase separation. For this reason, a compatibilization strategy must be applied to PLA-TPS

23   blends to give materials with interesting properties. This effect is provided by MLO as

24   previously described.

25

26   **Figure 4**

27

1   The effect of maleinized linseed oil (MLO) can be observed in Fig. 5. The only addition

2   of 2 phr (Fig. 5a & 5b) leads to improved adhesion/interaction between the two main

3   components in the blend. As the MLO content increases, the compatibility or miscibility

4   between PLA and TPS is improved and it is difficult to observe the dispersed TPS rich phase.

5   As we have previously described, MLO provides a combined effect on these blends. On the one

6   hand, a clear plasticization effect can be observed by mechanical characterization as MLO

7   increases the free volume. This phenomenon has a positive effect on polymer chain mobility as

8   polymer-polymer interactions are lowered and additionally, the plasticizer provides a lubricant

9   effect. On the other hand, a compatibilization effect is achieved by MLO which can interact

10   with both poly(lactic acid) chain ends and hydroxyl groups in thermoplastic starch thus leading

11   to an overlapped compatibilization and chain extension effect which in turn, is responsible for

12   the observed increase in ductile-flexible properties of PLA-30TPS blends. As the MLO

13   increases the blend becomes saturated and phase separation occurs for MLO content over 6 phr.

14   Fig. 5h shows some voids that can be related to excess MLO.

15

16   **Figure 5**

17

18   **4.- Conclusions.**

19   Thermoplastic starch offers very restricted miscibility with PLA as evidenced by

20   FESEM. Addition of TPS leads to an improvement on toughness due to a microstructure

21   composed of a brittle PLA rich phase in which fine TPS rich microspheres are finely dispersed.

22   This particular microstructure results in improved toughness. The lack of strong PLA-TPS

23   interactions does not allow higher ductile properties. To achieve this, a plasticization strategy

24   with maleinized linseed oil (MLO) has been proposed in this research work. Addition of an

25   environmentally friendly plasticizer derived from vegetable oils, maleinized linseed oil (MLO)

26   at relatively low contents in the 2-6 phr leads to a remarkable increase in mechanical ductile

27   properties such as elongation at break and impact-absorbed energy due to a combination of

28   different phenomena. Maleinized linseed oil exerts a typical plasticization effect by increasing

the free volume and lowering polymer-polymer interactions and this results in increased chain mobility due to the lubricant effect provided by the plasticizer. On the other hand, the particular chemical structure of maleinized linseed oil, with maleic anhydride groups allows some reactions with hydroxyl groups in both PLA end chains and starch chains resulting in a chain extension and compatibilization effect respectively. With regard to the elongation at break, unblended and unplasticized PLA shows an elongation at break of about 7%. This value is increased by blending PLA with 30 wt.% TPS up to values of 21% but the addition of 4-6 phr MLO leads to an elongation at break of 140-160% respectively. Similar tendency is detected for energy absorption and other ductile properties. Nevertheless, it is important to note that plasticizer saturation occurs for relatively low MLO content. Over 6 phr MLO a decrease in ductility and ductile properties and an increase in mechanical resistant properties can be detected. This saturation can lead to phase separation which in turn is responsible for stress concentration phenomena thus leading to fracture. The plasticization effect of MLO is clearly evident by a decrease in the glass transition temperature (T_g) of the PLA rich phase as evidenced by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). On the other hand, MLO also provides a compatibilization effect that allows improving compatibility between PLA and TPS and this also has a positive effect on overall properties. In general terms, maleinized linseed oil (MLO) is an attractive additive to provide plasticization properties to brittle polymers and also improve compatibility in immiscible or partially miscible polymer blends. In addition is natural origin represents an environmental efficient solution to improve industrial formulations based on biopolymers and biopolymer blends.

Acknowledgements

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1   **Table captions**

2   **Table 1.-** Summary of the compositions and labelling of the PLA-TPS blends with varying

3   amounts of maleinized linseed oil (MLO).

4   **Table 2.-** Variation of Charpy's impact energy, Shore D hardness, VST and HDT of PLA-

5   30TPS blends with different amounts of maleinized linseed oil (MLO).

6   **Table 3.-** Main thermal parameters of the PLA-30TPS blend with different MLO contents

7   obtained by differential scanning calorimetry (DSC): glass transition temperature (T_g), cold

8   crystallization temperature (T_{cc}) and enthalpy (ΔH_{cc}) and melt temperature (T_m) and enthalpy

9   (ΔH_m).

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1 **Figure legends**

2 **Figure 1.-** Plot evolution of mechanical tensile (a) and flexural (b) properties of PLA-30TPS

3 blend with varying maleinized linseed oil (MLO) content.

4 **Figure 2.-** Comparative thermogravimetric curves for unblended PLA, PLA-30TPS and PLA-

5 30TPS with maleinized linseed oil (MLO).

6 **Figure 3.-** Comparison of the evolution of the storage modulus (G')(a) and damping factor (tan

7 δ)(b) for unblended PLA, PLA-30TPS and PLA-30TPS with different maleinized linseed oil

8 (MLO) content.

9 **Figure 4.-** FESEM images from cryofractured surfaces of a) PLA at 1000X, b) PLA at 5000X,

10 c) TPS at 1000X, d) TPS at 5000x, e) PLA-30 wt.% TPS at 1000X and f) PLA-30 wt.% TPS at

11 5000X.

12 **Figure 5.-** FESEM images of PLA-30TPS blends with different maleinized linseed oil (MLO)

13 content at different magnifications, a) 2 phr MLO at 1000X, b) 2 phr MLO at 10000X, c) 4 phr

14 MLO at 1000X, d) 4 phr MLO at 10000X, e) 6 phr MLO at 1000X, f) 6 phr MLO at 10000X, g)

15 8 phr MLO at 1000X, h) 8 phr MLO at 10000X.

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