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Additional Information

# “PLA films with improved flexibility properties by using maleinized cottonseed oil”

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## Abstract

This work assesses the potential of maleinized cottonseed oil – MCSO as plasticizer in poly(lactic acid) – PLA films with improved ductile behaviour. The effects of MCSO are compared with commercially available maleinized oil, *i.e.* maleinized linseed oil – MLO in terms of mechanical, thermal and barrier properties, as well as morphology changes. Plasticized PLA formulations were obtained with a maleinized oil content in the 0 – 10 wt% range. Addition of both maleinized vegetable oils leads to a slight decrease in the glass transition temperature ( $T_g$ ) of neat PLA from 63 °C to 60 – 61 °C. Nevertheless, MCSO provides better overall properties. Addition of 7.5 wt% MCSO increases the elongation at break by 292%. Regarding the barrier properties, both maleinized vegetable oils increase the oxygen transmission rate – OTR. Nevertheless, this increase is less pronounced in the case of MCSO thus indicating its higher efficiency compared to MLO. On the other hand, addition of both maleinized vegetable oils do not compromise the overall disintegration of the obtained PLA formulations, thus positioning

these additives as environmentally friendly solutions to increase ductile properties in PLA-based films.

**Keywords:** poly(lactic acid) – PLA; cottonseed oil; maleinization; mechanical properties; thermal properties; barrier properties.

## **1.- Introduction.**

The growing awareness about the ongoing environmental pollution, together with the, still distant but increasingly close, problematics of petroleum depletion, are leading the research on obtaining materials from renewable resources and, potentially, biodegradable. This situation is particularly accentuated in the packaging industry due to the huge amounts of wastes that are generated worldwide. For these reasons, new polymers and industrial formulations are continuously being developed with the main aim of lowering their environmental impacts. Today, a wide variety of polymers can be obtained from renewable resources. Polysaccharides are a promising source of polymers due to their worldwide abundance. Different starches *e.g.* maize, potato, rice, etc. can be converted into industrial plastic formulations by using appropriate plasticizers such as glycerol, water, sorbitol, etc. leading to the so called “thermoplastic starches” – TPS [1, 2]. A new range of materials have been successfully synthesised from chitin which is the Earth’s second most abundant polysaccharide, surpassed only by cellulose. Chitin can be found in the exoskeleton of crustaceans [3]. Proteins are another important source of polymers. It is worthy to note the use of vegetable proteins such as gluten or soy protein in the field of polymers and composites, as well as animal proteins such as collagen, casein, ovalbumin, etc. widely used in the food industry [4, 5]. Aliphatic polyesters represent a promising solution to environmentally friendly polymers. Although some of

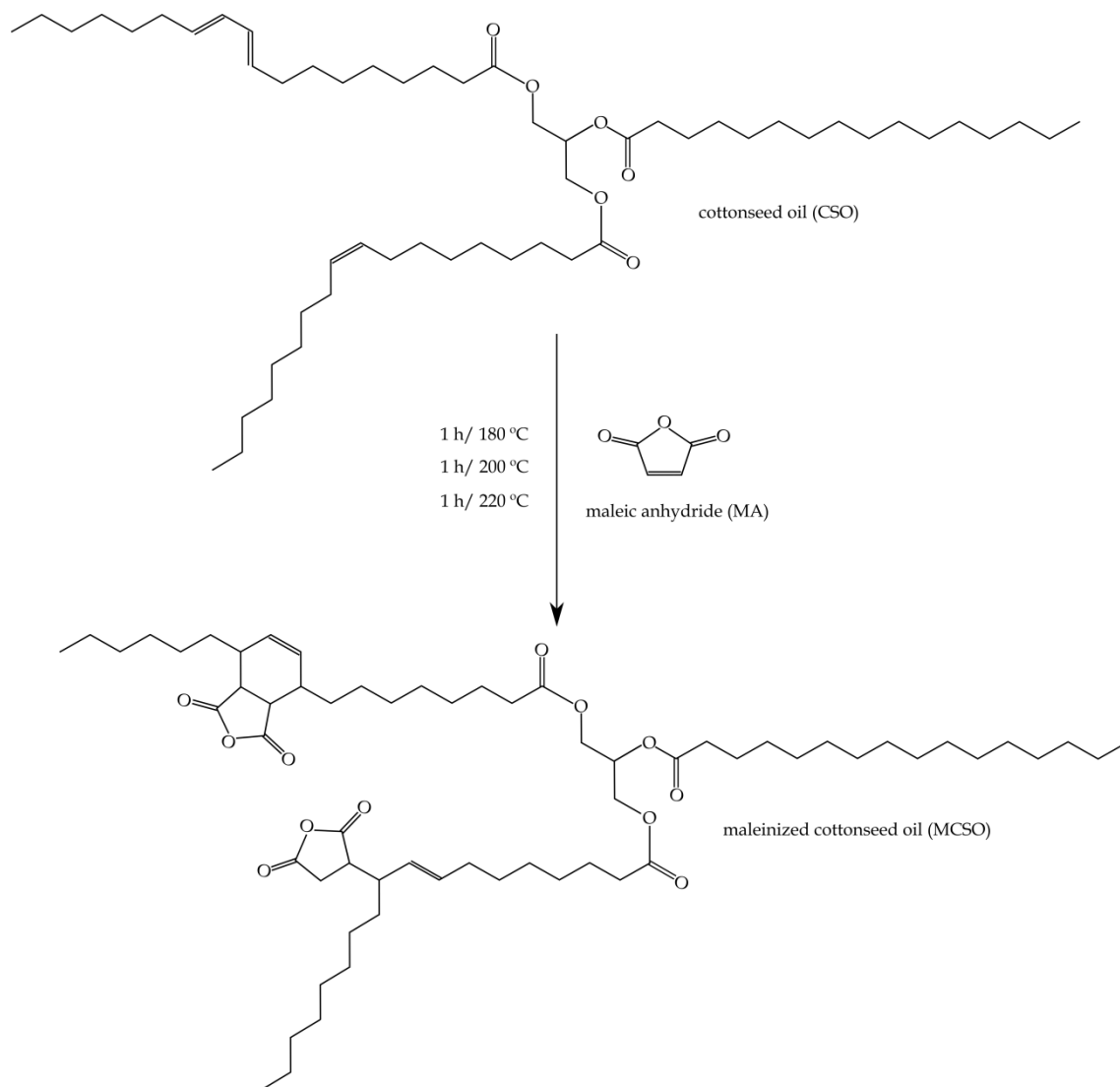
them are obtained from petroleum derivatives, e.g. poly(butylene succinate) – PBS, poly( $\epsilon$ -caprolactone) – PCL, poly(butylene succinate – *co* – adipate) – PBSA, etc. some polyesters can be obtained from renewable resource and could represent a full solution to both petroleum depletion and environmental impact as all these polyesters can be disintegrated in controlled soil [6, 7]. These high environmental efficiency polyesters include several bacterial polyesters (polyhydroxyalkanoates – PHAs) such as poly(hydroxybutyrate) – PHB, poly(hydroxybutyrate – *co* – hydroxyvalerate) – PHBV, among others [8, 9]. Although PHAs are very promising due to an excellent balance between mechanical, thermal and barrier properties, their cost is still high and their offer a very narrow processing window which limits a massive use in [10]. Other aliphatic polyester that has owned a privileged position in the last years is poly(lactic acid) – PLA which can be synthesised from ring-opening polymerization (ROP) of lactic acid obtained from starch fermentation [11, 12]. In addition, PLA offers balanced mechanical and barrier properties, it is transparent, brilliant and shows excellent resistance to fats. All these features have led PLA to a wide variety of sectors such as medical, automotive, textile, packaging, etc. [13-16]. However, not all are advantages; PLA is quite fragile and this fact restricts its use in some industrial sectors [17]. To overcome this fragility, different strategies have been proposed. One interesting solution is blending PLA with flexible polymers such as thermoplastic starch – TPS, poly( $\epsilon$ -caprolactone) – PCL, poly(butylene succinate – *co* – adipate) – PBSA, or others, with a remarked increase in toughness and other ductile properties [18-22]. Although physical blending is a cost-effective solution to overcome this drawback, the lack of miscibility between the components restricts the improvement on toughness. For this reason, some authors have proposed the use of compatibilizer agents. Ferri *et al.* reported PLA/TPS blends with a clear phase separation due to immiscibility. They suggested the use of maleinized linseed

oil – MLO as compatibilizer agent with a noticeable increase in the elongation at break [2].

Modified vegetable oils – MVOs represent an interesting alternative to petroleum-based plasticizers. In the last years, different modified vegetable oils (epoxidized, maleinized, acrylated, hydroxylated, etc.) have been successfully used as renewable plasticizers with a positive contribution on environmental efficiency. Some epoxidized vegetable oils are commercially available. This is the case of epoxidized soybean oil (ESBO) [23, 24] and epoxidized linseed oil (ELO) [25] which are widely used in the poly(vinyl chloride) – PVC industry as secondary plasticizers with additional thermal stabilization effects on PVC. Other research works have focused on the plasticization efficiency of other epoxidized vegetable oils derived from palm oil [26] and sunflower oil [27]. Mauck SC *et al.* reported the use of acrylated epoxidized soybean oil – AESO as plasticizer in toughened PLA formulations [28] and Ferri *et al.* reported the potential of maleinized linseed oil – MLO as plasticizer for PLA with a remarkable increase in the elongation at break higher than 1000% with addition of 20 phr MLO. They also reported a decrease of 6 °C in the glass transition temperature ( $T_g$ ) [29].

Cottonseed oil – CSO has shown its potential in the polymer industry in several fields such as thermosetting resins [30], PVC plasticizer [31] and PLA plasticization, with promising results. Cottonseed oil can be considered a by-product of the cotton industry whose main product is the cotton fiber. Approximately, 5.12 million tons cotton is produced annually worldwide and the main by-products are the oil and the cottonseed meal. Cottonseed oil can be converted into its corresponding maleinized oil by a conventional procedure [32]. This reaction can follow several paths, being the “ene” addition the most favourable path. Nevertheless, in some cases, when conjugated double bonds are present in the fatty acid chain, the Diels-Alder condensation can also take place

as it is shown in **Fig. 1**. Tarek *et al.* reported that over 200 °C, maleic anhydride is bonded to the triglyceride in an allylic position in the unsaturated fatty acid [33]. **Fig. 1** shows a schematic representation of the maleinization process of cottonseed oil.



**Figure 1.-** Schematic representation of the maleinization process of cottonseed oil

This work assesses the potential of cottonseed oil as natural-based plasticizer for PLA films. Optimum maleinization process are described and the effect of maleinized cottonseed oil – MCSO on mechanical, thermal and barrier properties as well as

morphology is evaluated and compared with a commercially available maleinized oil: maleinized linseed oil – MLO.

## **2.- Experimental.**

### **2.1.- Materials.**

A PLA commercial grade Ingeo Biopolymer 6210D from NatureWorks LLC (Minnetonka, USA) was used in pellet form as base material for films. It shows a melt flow index of 15 – 30 g/(10 min) at 210 °C and a density of 1240 kg m<sup>-3</sup>. Cottonseed oil was purchased from Sigma Aldrich España (Madrid, Spain) and used without further purification. Its density is 920 kg m<sup>-3</sup> and its iodine value is comprised in the 109 – 120 range. Its acid number is 0.25 mg KOH g<sup>-1</sup> as obtained following ISO 660:2009.

Maleinized linseed oil, commercial grade VEOMER LIN was purchased from Vandeputte (Mouscron, Belgium) with an average acid number of 105-130 mg KOH g<sup>-1</sup>. Maleic anhydride (Purity>98) was supplied by Sigma Aldrich (Madrid, Spain).

### **2.2.- Maleinization of cottonseed oil.**

A three neck round flask with a capacity of 500 mL equipped with a heating mantle was used to synthesize maleinized cottonseed oil. A reflux condenser was placed in the central neck. A digital thermometer was connected to a second neck and was used to measure the temperature during the reaction. Finally, the third neck was used to add maleic anhydride, simple extraction for evaluation and provide an inert atmosphere with nitrogen gas. A typical batch production is summarized as follows: 300 g of cottonseed oil were placed in the round flask and subjected to magnetic stirring and heating until the first temperature step was reached. The process was carried out in three temperature steps at 180 °C, 200 °C and 220 °C. At each temperature step, the same portion of maleic

anhydride (9 g of maleic anhydride per 100 g cottonseed oil) was dropped into the flask and subjected to magnetic stirring while temperature was maintained constant for 1 additional hour. To evaluate the extent of the maleinization reaction, samples were extracted from the flask every 30 min (for the temperatures of 180 °C and 200 °C) and every 20 min for the maximum temperature step at 220 °C. Finally, the mixture was cooled down to room temperature and subjected to centrifugation at 4000 rpm to allow full separation.

The maleinization extent was followed through the measurement of the acid number as indicated in ISO 660:2009 with the following equation:

$$\text{Acid number} = \frac{56.1 \times V \times C}{m} \quad (1)$$

Where  $V$  stands for the volume of the KOH standard solution (mL),  $C$  represents the exact concentration of the KOH standard solution ( $\text{mol L}^{-1}$ ) and  $m$  is the mass of the maleinized oil used in the analysis (g).

### ***2.3.- Manufacturing of PLA films with maleinized vegetable oils.***

**Table 1** summarizes the compositions and codes used for the different plasticized PLA formulations with maleinized cottonseed oil – MCSO and maleinized linseed oil – MLO. PLA was dried at 60 °C for 24 h. Initially, the appropriate amounts of PLA and the corresponding maleinized oil, were mechanically mixed in a zipper bag and subjected to a compounding process in a twin-screw co-rotating extruder ( $D= 30 \text{ mm}$ ;  $L/D = 20:1$ ) by DUPRA (Alicante, Spain), at a rotating speed of 60 rpm. The following temperature program was programmed: 167.5 °C (feeding), 170 °C, 172.5 °C, 175 °C (die). The obtained compounds were cooled down to room temperature, subsequently pelletized and



dried at 50 °C for 24 h. Films with an average thickness 100 µm were obtained in a cast-roll machine from Eurotech S.A.S. (San Marino in Riu, Italy). The extrusion rate was set to 55 rpm and the calendaring process was 2 m min<sup>-1</sup>.

**Table 1.-** Composition and labelling of the plasticized PLA formulations with different maleinized vegetable oils.

<b>Reference</b>	<b>wt% PLA</b>	<b>wt% MCSO</b>	<b>wt% MLO</b>
PLA	100	0	0
2.5 % MCSO	97.5	2.5	0
5 % MCSO	95.0	5.0	0
7.5 % MCSO	92.5	7.5	0
10 % MCSO	90.0	10.0	0
2.5 % MLO	97.5	0	2.5
5 % MLO	95.0	0	5.0
7.5 % MLO	92.5	0	7.5
10 % MLO	90.0	0	10.0

#### **2.4.- Mechanical characterization.**

Mechanical characterization of films was carried out by testing five different standard tensile samples (type 2) as indicated in ISO 527-3, with a total length of 160 mm, a width of 10 mm and a thickness of 100 µm. The different sample films were tested in a universal testing machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain) using specific pneumatic clamps at a crosshead rate of 5 mm min<sup>-1</sup>.

### **2.5.- Morphology characterization.**

The morphology of transversal cross sections of the obtained films was observed and characterized in a field emission scanning electron microscope – FESEM model ZEISS ULTRA from Oxford Instruments (Oxfordshire, United Kingdom) using an acceleration voltage of 2 kV. A sputtered metal coating with platinum was used to increase the electrical conductivity of the samples prior to observation as well as to work with low acceleration voltage and avoid sample damage. The sputter-coater equipment was an EM MED020 from Leica Microsystems (Wetzlar, Germany).

### **2.6.- Thermal characterization.**

The main thermal transitions of plasticized PLA films were studied by differential scanning calorimetry – DSC in a 821e calorimeter from Mettler Toledo Inc. (Schwerzenbach, Switzerland) using a dynamic temperature program from 25 °C to 300 °C at a constant heating rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere (66 mL min<sup>-1</sup>). The degree of crystallinity (%X<sub>c</sub>) was calculated by using Equation 2:

$$\%X_c = 100 \times \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m(100\%)}} \times \frac{1}{w} \quad (2)$$

Where  $\Delta H_m$  stands for the melt enthalpy,  $\Delta H_{cc}$  represents the cold crystallization enthalpy,  $\Delta H_{m(100\%)}$  indicates the melt enthalpy of theoretically 100% crystalline PLA (93 J g<sup>-1</sup>) [34] and  $w$  represents the weight fraction of PLA in plasticized formulations.

Degradation at high temperatures was followed by thermogravimetric analysis – TGA in a TGA/SDTA 851 thermobalance from Mettler-Toledo Inc. (Schwerzenbach, Switzerland). A dynamic thermal program from 25 °C up to 700 °C at a heating rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere (66 mL min<sup>-1</sup>).

### **2.7.- Barrier properties. Oxygen transmission rate – OTR.**

The oxygen transmission rate – OTR was obtained in triplicate using an oxygen permeation analyser Systech model 8500 from Metrotec S.A. (San Sebastián, Spain) with pure oxygen (99.9%). Samples were cut in circular shapes with a diameter of 14 cm and average thickness of 100  $\mu\text{m}$ . A Mitutoyo digimatic micrometer model 293-832 (Illinois, USA) was used to calculate the average thickness –  $h$  of the samples all around their perimeter. The oxygen flow rate was monitored until a stationary state was reached. The product  $OTR \cdot e$  for each film was calculated and compared.

### **2.8.- Contact angle measurements.**

The contact angle ( $\theta$ ) was obtained in a goniometer model FM140 from Krüss GmbH (Hamburg, Germany). Samples with an average thickness of 100  $\mu\text{m}$  were dried at 40 °C for 24 h before testing. Five different water drops ( $\sim 100 \mu\text{l}$ ) were placed into the film surface and ten different measurements were obtained for each water drop and averaged. The static contact angle was measured after 30 s.

### **2.9.- Disintegration in controlled compost soil.**

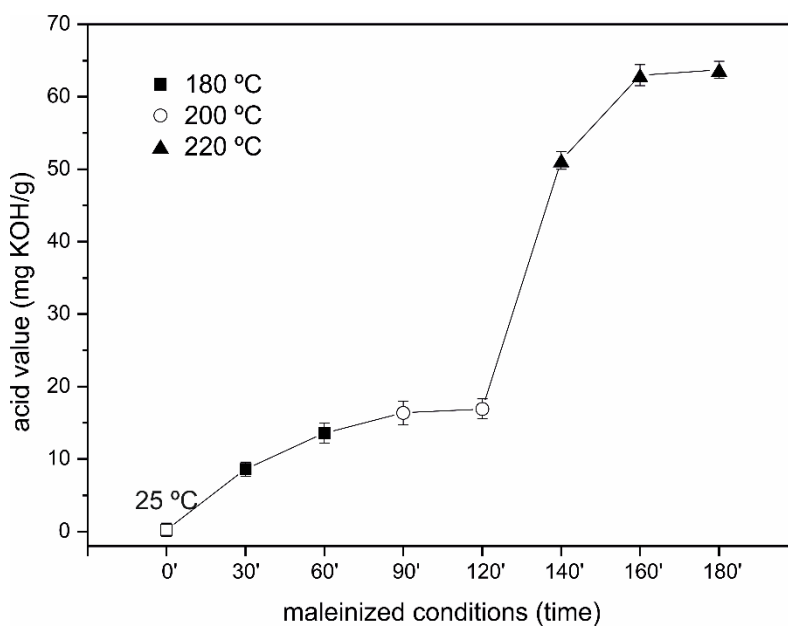
The disintegration test in controlled compost conditions was carried out by following the guidelines of ISO 20200 in triplicate. Samples sizing 25x25  $\text{mm}^2$  with an average thickness of 100  $\mu\text{m}$  were placed in a compost reactor (300x200x100  $\text{mm}^3$ ). Samples were dried at 40 °C for 24 h before they were dug into the synthetic compost soil. The synthetic soil was composed of sawdust, feed for rabbits, mature compost, corn starch, saccharose, corn oil and urea in the proportions indicated in the ISO 20200. All samples were initially weighed and immersed in water before placing them into the mixture. Samples were extracted from the reactor at 6, 8, 9, 10, 11 and 13 days, washed

with distilled water and dried for 24 h before weighing. In addition, optical images of the samples were collected at these disintegration periods.

### **3.- Results and discussion.**

#### **3.1.- Synthesis of maleinized cottonseed oil – MCSO.**

**Fig. 2** shows the evolution of the acid number along the three temperature steps at 180 °C, 200 °C and 220 °C. At the beginning of the reaction, cottonseed oil shows an acid number of 0.25 mg KOH g<sup>-1</sup>. After the first two hours, an important increase is detected thus indicating that maleinization has taken place. At the end of the second temperature step at 200 °C, the acid number reaches 16.9 mg KOH g<sup>-1</sup>. Nevertheless, it is in the third temperature step at 220 °C when the maleinization process takes place in a high extent. After 20 min at 220 °C, the acid number has reached 51.2 mg KOH g<sup>-1</sup> due to the high availability of maleic anhydride which can be readily attached to an allylic position in the unsaturated fatty acid which is specially favoured above 200 °C [33]. As the reaction time increases while maintaining the temperature at 220 °C, the acid number tends to stabilize at about 63.7 mg KOH g<sup>-1</sup>. These results are in total agreement with other reported maleinization processes. A.I. Aigbodion *et al.* maleinized rubber seed oil with similar conditions and obtained an acid number of 75.8 mg KOH g<sup>-1</sup> [35].



**Figure 2.-** Effect of temperature and time on the efficiency of the maleinization process of cottonseed oil with maleic anhydride.

An important change in colour was also obtained as a consequence of the maleinization process. During the first temperature step at 180 °C, the colour was yellow as most of the vegetable oils. As the maleinization takes place, a change in colour from yellow to reddish was observed as it can be seen in Fig. 3. Ernzen J.R *et al.*, reported a similar change in colour during the maleinization of soybean oil with an intense reddish colour at the end of the reaction [36].

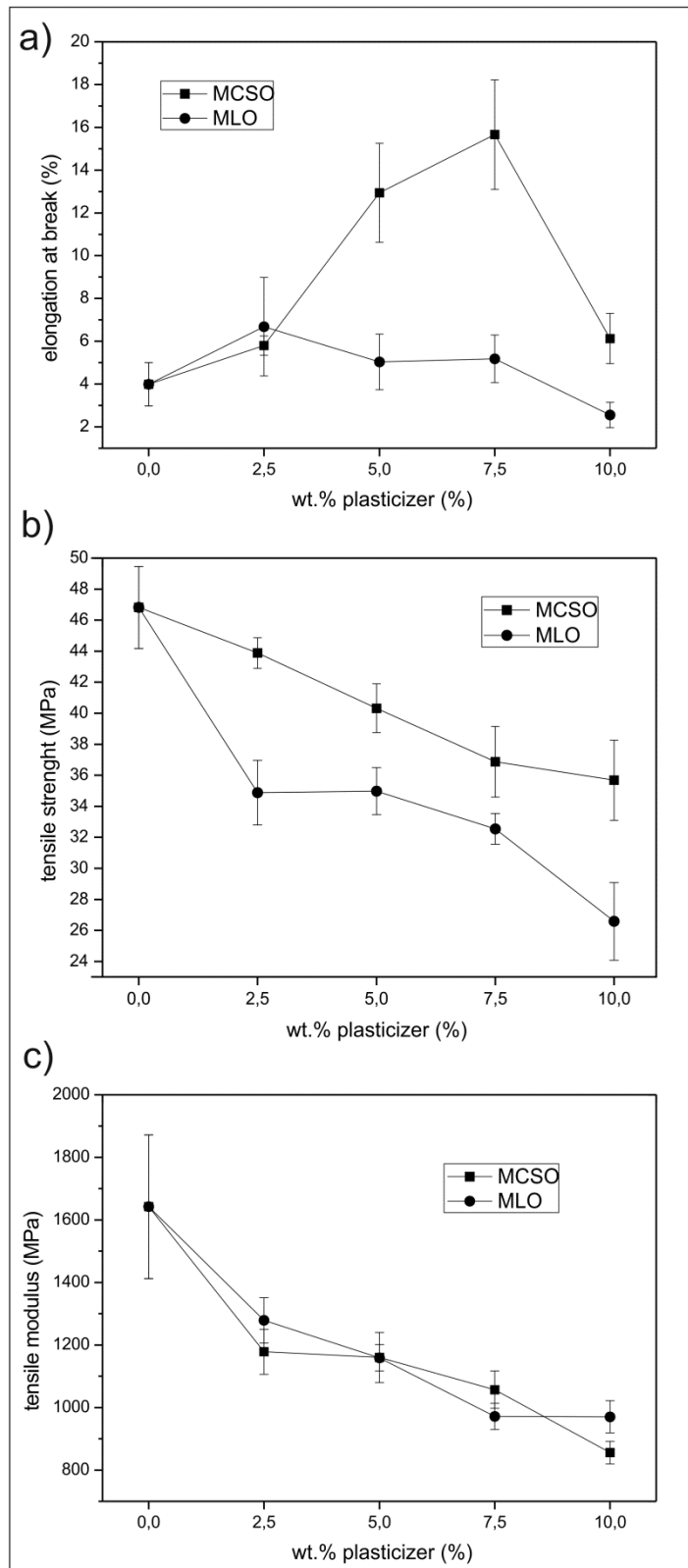


**Figure 3.-** Influence of the reaction temperature and time on the colour during maleinization process of cottonseed oil, a) 180 °C – 60 min, b) 200 °C – 60 min, c) 220 °C – 60 min.

### **3.2.- Mechanical properties of plasticized PLA with MCSO.**

The efficiency of MCSO as biobased plasticizer for PLA films was assessed by comparing with a commercial MLO. **Fig. 4** shows the results obtained in the tensile test. Unplasticized PLA film shows the maximum tensile strength and Young's modulus with values of 46.8 MPa and 1.64 GPa respectively. Regarding the elongation at break, unplasticized PLA shows a remarkably low value close to 4% thus leading to a fragile behaviour. The plasticization effect that MCSO provides is evident by seeing the evolution of mechanical properties. The only addition of 2.5 wt% MCSO gives an improvement on elongation at break up to values of 5.8% whilst the tensile strength and modulus decrease to 43.9 MPa and 1.18 GPa respectively. As the MCSO content increases, the elongation at break increases up to values of 12.9% and 15.7% for plasticized PLA films with 5.0 wt% and 7.5 wt% MCSO. These results are in total agreement with those reported by Sheli C. Mauck with similar elongation at break value on PLA plasticized with epoxidized soybean oil – ESBO [28]. Despite this increasing tendency, it seems that plasticizer saturation occurs at a relatively low MCSO content of 5.0-7.5 wt%. In fact, the elongation at break for the plasticized PLA film with 10 wt% MCSO decreases due to a phase separation process as reported by Balart JF *et al.* [37]. These results suggest a slight plasticizing effect of MCSO. As it has been reported, small amounts of modified vegetable oils have a positive effect on PLA ductile properties. Despite this, as Ferri JM *et al.* have also reported, plasticizer saturation occurs at relatively low oil content and phase saturation occurs over this threshold with a subsequent decrease in ductile properties [14]. The good performance of MCSO as plasticizer for PLA films is evident by comparing its effects with MLO. In this way, although addition of 2.5 wt% MLO to PLA leads to an elongation at break of 6.9%, which is slightly higher than the obtained with the same MCSO content, this is the maximum value that MLO can achieve.

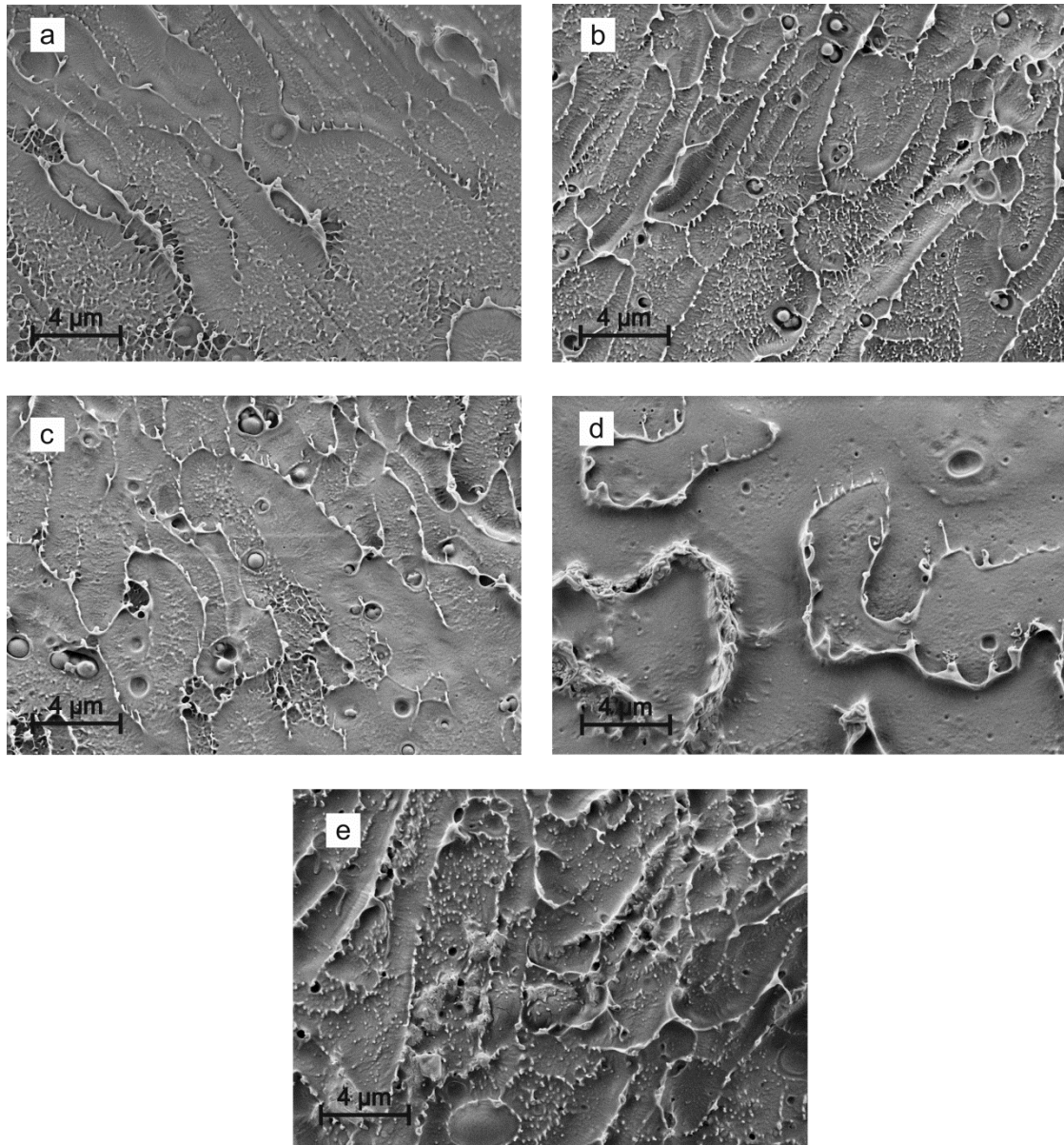
In fact, plasticized PLA films with 5.0 – 7.5 wt% give lower elongation at break values close to 5% and the plasticized formulation with 10 wt% MLO gives even lower elongation at break the unplasticized PLA films. Regarding mechanical resistant properties, the decrease in tensile strength is more pronounced by using MLO as it can be seen in **Fig. 4b** with values of 26.6 MPa for the plasticized PLA film with 10 wt% MLO. Buong Woei Chieng *et al.* also observed this dramatic decrease in tensile strength in formulations of PLA plasticized with epoxidized palm oil – EPO from 60 MPa (neat PLA) down to 30 MPa with addition of 10 wt% EPO [38]. With regard to the Young's modulus, MLO provides similar behaviour to MCSO as it can be seen in **Fig. 4c**. In fact, the minimum value is 0.97 GPa and 0.86 GPa for plasticized PLA films with 10 wt% MLO and MCSO respectively. These results agree with some other works that use modified vegetable oils as plasticizers in polymers [23].



**Figure 4.-** Plot evolution of mechanical properties of plasticized PLA films as a function of the wt% of MCSO and MLO, a) elongation at break, b) tensile strength and c) Young's modulus.



The plasticization effect can be seen by observing FESEM images in **Fig. 5**. Although there are not pronounced differences between the FESEM images of PLA plasticized with MLO (**Fig. 5b** and **Fig. 5c**) compared to unplasticized PLA, plasticized PLA films with MCSO (**Fig. 5d** and **Fig. 5e**) show slightly higher differences. Ferri *et al.* reported a restricted miscibility between PLA and MLO with a clear phase separation when plasticizer saturation occurred [29]. As it has been described previously, the results of mechanical properties, suggest better behaviour of MCSO compared to MLO. This could be related to slightly higher miscibility of MCSO with PLA than that of MLO. Unplasticized PLA film (**Fig. 5a**) shows a cross section image typical of a fragile polymer with a smooth surface topography. The morphology of plasticized PLA films with MLO (**Fig. 5b** and **Fig. 5c** with 5 wt% and 7.5 wt% MLO respectively) is similar, but small spherical shapes can be distinguished, which correspond to excess MLO. This is typical of a phase separation process and is responsible for low elongation at break values as previously seen. Conversely, the cross section of plasticized PLA films with MCSO shows more plastic deformation areas, which are in accordance with the abovementioned increased ductility. In a similar way, there is a direct relationship between the MCSO content and the presence of spherical shapes. Voids indicate a better dispersion of MCSO into the PLA matrix and this has a positive effect on elongation at break and other ductile properties.



**Figure 5.-** FESEM images (5000x) of the cross section of plasticized PLA films with different maleinized vegetable oils, a) unplasticized PLA, b) PLA with 5 wt% MLO, c) PLA with 7.5 wt% MLO, d) PLA with 5 wt% MCSO and e) PLA with 7.5 wt% MCSO.

### ***3.3.- Thermal properties of plasticized PLA with MCSO.***

Both maleinized oils, MCSO and MLO, have a direct effect on thermal properties of plasticized PLA formulations as it can be seen in **Table 2**. The main thermal transition of unplasticized PLA are: the glass transition temperature ( $T_g$ ) located at 63 °C, the cold crystallization temperature peak ( $T_{cc}$ ) located at 117.3 °C and the melt temperature peak

at 171.7 °C. Both plasticizers have a clear effect on the glass transition temperature and cold crystallization process, thus indicating a more or less intense plasticizing effect. In fact, both plasticizers, MCSO and MLO, give lower  $T_g$  and  $T_{cc}$  temperatures due to increased chain mobility [2]. The very low decrease in  $T_g$  obtained for both MCSO and MLO with values of 60 – 61 °C, indicates limited plasticizing effect due to restricted miscibility. Nevertheless, although the plasticization effects are not so high in terms of thermal properties, the particular morphology of plasticized PLA formulations with MCSO and, in a less extent, with MLO, is responsible for a toughening phenomenon on PLA with a positive effect on ductile properties, mainly with MCSO. Regarding the melt temperature peak, DSC thermograms do not show any additional peak or a noticeable change in the peak shape. The melt temperature peak remains at values of 170 – 171 °C. Nevertheless, slight changes can be observed for the melt enthalpy and its components. The melt enthalpy is directly related to two crystal fractions: one obtained after cooling after injection moulding and a second one achieved during the cold crystallization process. The degree of crystallinity ( $\%X_c$ ) is representative for the crystal fraction obtained during processing while the second crystal fraction is obtained during the cold crystallization. The most relevant changes can be observed for the cold crystallization enthalpy (important decrease) whilst the melt enthalpy does not change in a remarkable way. This indicates that MCSO contributes to increase the degree of crystallinity after injection moulding due to increased chain mobility. For this reason, the cold crystallization enthalpy decreases in a greater extent than the melt enthalpy. With regard to the cold crystallization temperature range, once again both maleinized vegetable oils, lead to a remarkable decrease in the characteristic temperature peak. In the case of MCSO,  $T_{cc}$  falls down to values around 110 °C while the decrease is still higher for MLO with  $T_{cc}$  values located at about 105 °C. This decrease is directly related to the plasticization

effect that both maleinized oils provide. Modified triglyceride molecules are placed between PLA polymer chains with a subsequent increase in the free volume. This phenomenon allows PLA chains to arrange towards a packed/ordered structure at lower temperatures [39]. In agreement with this, the degree of crystallinity (% $X_c$ ) also increases with both maleinized plasticizers. Unplasticized PLA offers a crystallinity of 6.2%. By using MCSO in plasticized PLA films, the crystallinity increases up to 10.6% for MCSO contents of 2.5-5.0 wt%. It is important to remark that plasticized PLA films with 10 wt% MCSO show 19% crystallinity. Similar findings can be observed by using MLO, while it is true that the maximum crystallinity is close to 15%. These results give support to the mechanical properties as PLA films with MCSO showed higher tensile strength values than those obtained with MLO. This phenomenon could be related to the higher crystallinity that MCSO provides versus MLO. As it has been shown, plasticizer saturation with MLO occurs at lower concentrations regarding MCSO and this can also affect the crystallinity [37].

**Table 2** also summarizes the influence of MCSO on the thermal degradation of plasticized PLA films. In particular, the temperatures at which a weight loss of 5% and 50% are given ( $T_{5\%}$  and  $T_{50\%}$  respectively). As per the results, it is worth to note that the thermal stability of PLA is not remarkably affected by MCSO. Maleinized vegetable oils seem to provide lower thermal stabilization than epoxidized vegetable oils which have been widely used as thermal stabilizers in poly(vinyl chloride) – PVC formulations as well as in other polymer based formulations. Chieng *et al.* reported a remarkable increase in the thermal stability of PLA by using modified vegetable oils, e.g. epoxidized palm oil (EPO) and a mixture of epoxidized palm oil and soybean oil (EPSO). Specifically, the onset degradation temperature changed from 274.26 °C (neat PLA) up to values of 313.54 °C and 330.40 °C for plasticized PLA formulations with 5 wt % EPO and EPSO

respectively [38]. Maleinized vegetable oils still contain unsaturations; for this reason, they show lower thermal stabilization effects than the epoxidized counterpart oils. Ferri *et al.* reported negligible effects of MLO on the thermal stability of PLA formulations with MLO content comprised in the 5 – 20 phr range. In fact they report a decrease in the  $T_{5\%}$  from 336.9 °C (neat PLA) down to 331.8 °C for the plasticized formulation with 10 phr MLO [29]. The obtained results suggest that MCSO does not increase in a remarkable way the thermal stability of PLA which remains unaffected by MCSO content.

**Table 2.-** Summary of the main thermal properties of neat PLA and plasticized PLA films with maleinized oils, obtained by differential scanning calorimetry – DSC and thermogravimetric analysis – TGA.

Sample code	DSC						TGA	
	$T_g$ (°C)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$X_c$ (%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)
PLA	63.0	117.3	32.3	171.7	38.1	6.2	329.4	358.5
2.5 % MCSO	61.7	109.8	26.9	170.6	36.5	10.6	323.5	351.3
5 % MCSO	61.6	113.1	25.2	171.0	34.6	10.6	334.2	363.7
7.5 % MCSO	61.6	110.4	24.6	170.5	37.4	15.0	327.3	361.9
10 % MCSO	61.1	109.7	22.5	170.3	38.5	19.1	333.1	361.0
2.5 % MLO	61.7	108.9	23.3	171.6	35.1	13.0	322.4	355.5
5 % MLO	60.9	104.5	22.6	170.3	36.2	15.4	329.6	359.1
7.5 % MLO	60.4	105.5	23.8	170.5	34.6	12.5	329.7	361.6
10 % MLO	60.6	106.2	23.1	170.7	32.8	11.6	320.68	356.94

### **3.4.- Barrier properties and surface wetting properties of plasticized PLA with MCSO.**

Barrier properties are directly related to the free volume, therefore, it is not expectable an improvement on the barrier properties, since thermal analysis has suggested an increase in the free volume due to a slight plasticization effect. PLA is characterized by moderate barrier properties. In fact, PLA has high OTR compared to ethylene-vinyl alcohol copolymer (EVOH) but it offers lower OTR values than highly oxygen permeable polymer such as LDPE [40-42]. As reported by Auras *et al.* the OTR of oriented PLA is ten times lower than oriented poly(styrene) – PS but six times higher than poly(ethylene terephthalate) – PET, which is widely used due to its excellent barrier properties against oxygen [43]. **Table 3** summarizes the product  $OTR \cdot e$  to compare the effects of both MCSO and MLO, at different concentrations, in plasticized PLA films. As it was expected, both plasticizers offer worse barrier properties than unplasticized PLA. The  $OTR \cdot e$  value for unplasticized PLA is close to  $19 \text{ cm}^3 \text{ mm m}^{-2} \text{ day}^{-1}$ ; the plasticized formulation with 5 wt% MCSO increases this up to  $20.63 \text{ cm}^3 \text{ mm m}^{-2} \text{ day}^{-1}$  which represents a percentage increase of 8.23%. In the case of MLO, addition of 5 wt% to PLA leads to an  $OTR \cdot e$  value of  $26.67 \text{ cm}^3 \text{ mm m}^{-2} \text{ day}^{-1}$  which represents almost a 40% increase. Obviously, the  $OTR \cdot e$  product is still increased as the plasticizer content increased due to its effects on the global free volume. These results were observed by Burgos N. *et al.* in PLA formulations plasticized with oligomeric lactic acid – OLA. They reported a clear increasing tendency in the  $OTR \cdot e$  parameter with increasing the plasticizer content. Specifically, the  $OTR \cdot e$  value increased from  $33 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  up to values over  $70 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  for plasticized formulations with 25 wt% OLA [39]. Martino VP *et al.* also reported the same phenomenon in plasticized PLA formulations with di-2-ethylhexyladipate – DEHA or DOA, with a percentage increase in the  $OTR \cdot e$  parameter of 54.58% with regard to neat PLA films. In particular, the  $OTR \cdot e$  rate increased from  $29.5 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  (neat PLA) up to  $66.4 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  for

PLA formulations with 20 wt% DOA [44]. Armentano *et al.* reported similar results with PLA/PHB blends plasticized with 20 wt% OLA. They observed that the  $OTR \cdot e$  for neat PLA ( $22.9 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ ) increased up to  $25.5 \text{ cm}^3 \cdot \text{mm} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  by the addition of 20 wt% OLA plasticizer [13].

**Table 3.-** Barrier properties against oxygen measured as the product between the oxygen transmission rate – OTR and the average thickness ( $OTR \cdot e$ ) and water contact angle ( $\theta_{\text{water}}$ ) measurements for plasticized PLA formulations with maleinized oils.

Sample code	$OTR \cdot e$ ( $\text{cm}^3 \text{ mm m}^{-2} \text{ day}^{-1}$ )	Water contact angle, WCA ( $^\circ$ )
PLA	19.06±0.99	63.5±3.6
5 % MCSO	20.63±0.09	74.1±1.5
7.5 % MCSO	23.39±0.52	74.5±2.7
5 % MLO	26.67±0.92	77.8±0.8
7.5 % MLO	28.57±0.76	77.6±1.4

Maleinized oils also have an effect on the surface properties of plasticized PLA films as it can be seen in **Table 3**. Unplasticized PLA film shows a  $\theta_{\text{water}}$  of  $63.5^\circ$  which is lower than other highly hydrophobic polymer films such as polyolefins. Both maleinized oils provide increased hydrophobicity which could possibly be related to the increase in crystallinity as Arrieta MP *et al.* have suggested [11] and the intrinsic nature of hydrophobic fatty acid segments. The  $\theta_{\text{water}}$  increases up to values of  $74^\circ$  and  $77^\circ$  for plasticized PLA films with MCSO and MLO respectively which could have a positive effect on restricting of water permeation. Darie-Nita *et al.* evaluated the influence of several plasticizers, e.g. ESBO, OLA and PEG on the water contact angle of plasticized PLA formulations. They observed a decrease in the water contact angle for all three

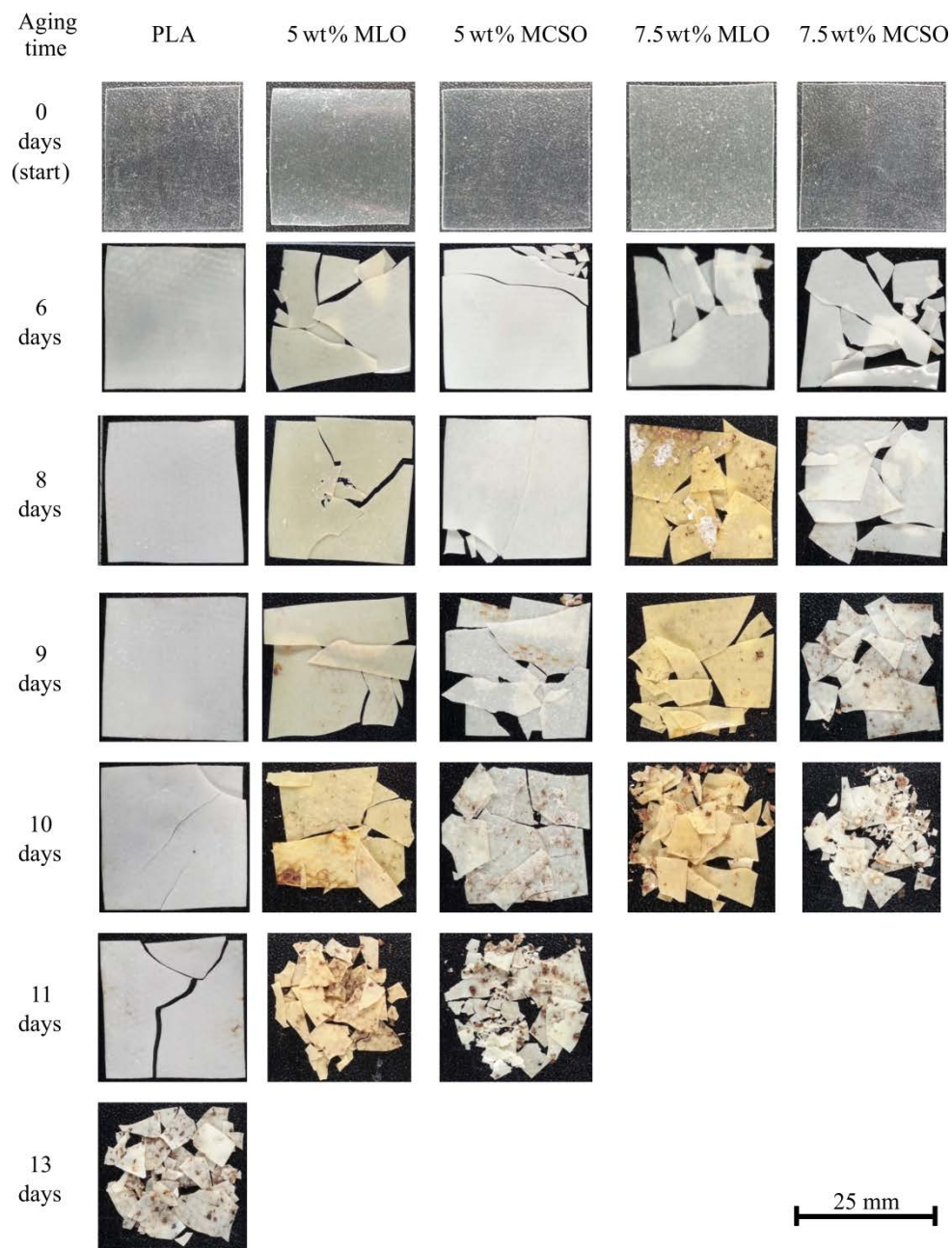
plasticizers thus giving evidences of increased hydrophilicity with a positive effect on biocompatibility but negative effects on water barrier properties. The plasticizer with the strongest effects on surface hydrophilicity was PEG [45]. Ljungberg *et al.* evaluated the effect of the storage time on the water contact angle on plasticized PLA films. They observed an initial increase in the water contact angle by adding triacetine – TAc (15 wt%) as plasticizer but this decreased after 45 days due to migration thus indicating that although some hydrophobic properties can be obtained initially with some plasticizers, migration with time could lead to increased hydrophilicity [46].

### ***3.5.- Disintegration of plasticized PLA films with MCSO in controlled compost soil.***

**Fig.6** gathers different images corresponding to different disintegration times of unplasticized PLA and plasticized PLA films with 5 wt% and 7.5 wt% MCSO and MLO. With only a disintegration time of 6 days, the effects are clearly detectable. In fact, all films become translucent and opaque due to the increase in crystallinity during the initial stages of the degradation which are particularly favoured by moisture and temperature inside the compost reactor [6]. Nevertheless, unplasticized PLA shows different behaviour than that observed for all plasticized formulations. As a matter of fact, PLA does not become fragile until 10 days which is evidenced by the appearance of cracks. Nevertheless, plasticized PLA films with MCSO and MLO become highly fragile for an aging time of 6 days and this fragility is much more evident with increasing the aging time. As suggested by these images, plasticized PLA formulations with both MCSO and MLO seem to accelerate the disintegration process in controlled compost soil. In fact, while PLA requires almost 14 days to disintegrate, plasticized films with 5 wt% of both MCSO or MLO, need only 11 days to achieve the same disintegration level and plasticized films with 7.5 wt% of MCSO or MLO reach the same disintegration level after



an aging period of 10 days. Similar findings have been reported by Arrieta MP *et al.* with plasticized PLA and PLA/PHB blends with acetyl tri-n-butyl citrate – ATBC [11].



**Figure 6.-** Visual aspect of plasticized PLA films with maleinized oils in terms of the oil content and disintegration time (the initial size of all films was 25 x 25 mm<sup>2</sup>).

#### 4.- Conclusions.

This research work assesses the usefulness of maleinized cottonseed oil – MCSO as plasticizer for PLA films. In addition, a comparison of the potential of the synthesised MCSO and a commercially available maleinized vegetable oil, maleinized linseed oil – MLO, shows better performance of MCSO versus MLO. A slight plasticization effect was observed by differential scanning calorimetry, with an associated decrease in the glass transition temperature –  $T_g$  of 2 °C. In a similar way, the cold crystallization process was advanced by 7 °C for MCSO and 10 °C for MLO, thus indicating increased chain mobility with the subsequent increase in PLA crystallinity. This phenomenon is much more pronounced in the case of plasticized PLA films with MCSO and this has a positive effect on their mechanical properties. Although the plasticizing effect of MCSO is poor, mechanical ductile properties are remarkably improved. The very low elongation at break of neat PLA (around 4%) is increased up to almost 16% in formulations containing 7.5 wt% MCSO. FESEM analysis revealed a particular morphology on plasticized PLA films, which is composed of micro-spherical oil particles dispersed in the PLA matrix, which could positively contribute to increase ductile properties. Although the barrier properties are not improved with MCSO addition, the  $OTR \cdot e$  changes from 19.06 cm<sup>3</sup> mm m<sup>-2</sup> day<sup>-1</sup> for neat PLA up to 20.63 cm<sup>3</sup> mm m<sup>-2</sup> day<sup>-1</sup> in plasticized films with 5 wt% MCSO, thus showing good enough barrier properties. The results with MLO were worse. Finally, MCSO does not compromise the disintegration; as the MCSO increases, the disintegration process is noticeably accelerated. It is possible to conclude that MCSO is a highly efficient plasticizer for PLA films with high interest from both technical and environmental standpoints.

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### **Table Captions**

**Table 1.-** Composition and labelling of the plasticized PLA formulations with different maleinized vegetable oils.

**Table 2.-** Summary of the main thermal properties of neat PLA and plasticized PLA films with maleinized oils, obtained by differential scanning calorimetry – DSC and thermogravimetric analysis – TGA.

**Table 3.-** Barrier properties against oxygen measured as the product between the oxygen transmission rate – OTR and the average thickness ( $OTR \cdot e$ ) and water contact angle ( $\theta_{\text{water}}$ ) measurements for plasticized PLA formulations with maleinized oils.

## **Figure Legends**

**Figure 1.-** Schematic representation of the maleinization process of cottonseed oil

**Figure 2.-** Effect of temperature and time on the efficiency of the maleinization process of cottonseed oil with maleic anhydride.

**Figure 3.-** Influence of the reaction temperature and time on the colour during maleinization process of cottonseed oil, a) 180 °C – 60 min, b) 200 °C – 60 min, c) 220 °C – 60 min.

**Figure 4.-** Plot evolution of mechanical properties of plasticized PLA films as a function of the wt% of MCSO and MLO, a) elongation at break, b) tensile strength and c) Young's modulus.

**Figure 5.-** FESEM images (5000x) of the cross section of plasticized PLA films with different maleinized vegetable oils, a) unplasticized PLA, b) PLA with 5 wt% MLO, c) PLA with 7.5 wt% MLO, d) PLA with 5 wt% MCSO and e) PLA with 7.5 wt% MCSO.

**Figure 6.-** Visual aspect of plasticized PLA films with maleinized oils in terms of the oil content and disintegration time (the initial size of all films was 25 x 25 mm<sup>2</sup>).