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"Plasticizing effect of biobased epoxidized fatty acid esters on mechanical and thermal properties of poly(lactic acid)"

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ABSTRACT

Poly(lactic acid)-PLA is a polyester that can be produced from lactic acid derived from renewable resources. This polymer offers attracting uses in packaging industry due to its biodegradability and high tensile strength. However, PLA is quite brittle, which limits its applications. To overcome this drawback, PLA was plasticized with epoxy-type plasticizer derived from a fatty acid, octyl epoxy stearate (OES) at different loading (1, 3, 5, 10, 15 and 20 phr). The addition of OES decreases the glass transition temperature and provides a remarkable increase in elongation at break and impact absorbed energy. Plasticizer saturation occurs at relatively low concentrations of about 5 phr OES; higher concentration leads to phase separation as observed by field emission scanning electron microscopy (FESEM). Optimum balanced mechanical properties are obtained at relatively low concentrations of OES (5 phr) thus indicating the usefulness of this material as environmentally friendly plasticizer for PLA industrial formulations.

Keywords: Plasticized, PLA, EVO, fatty acid esters.

1. Introduction.

Poly(lactic acid), PLA is a linear aliphatic polyester that is produced from lactic acid derived from renewable resources through a fermentation process of corn starch, wheat starch, sugar bagasse and other starch-rich products. This biobased polymer possesses attracting properties such as biodegradability, biocompatibility, easy processing and overall good mechanical properties. For these reasons, it is the selected candidate for a wide variety of applications as, in addition, it is shiny and transparent, moisture and fat resistant and offers similar flavor and odor barrier properties to poly(ethylene terephthalate), PET. All these features makes PLA highly useful for food packaging [1,2]. Furthermore, due to its high UV stability and low flammability it is widely used in non-discoloring textiles and fabrics for uses in agricultural applications [3,4]. PLA is also biocompatible and resorbable so that it finds increasing applications in the medical sector for controlled drug delivery [5] and tissue engineering [6-10].

Nevertheless, its high stiffness and brittleness restrict some uses in engineering applications. To overcome this, several environmentally friendly approaches have been proposed. One of this approaches is blending PLA with other polymers such as poly(hydroxy butyrate), PHB [11,2,12,13], poly(caprolactone), PCL [14], acetylated thermoplastic starch [15], etc. which can lead to tailored properties in terms of mechanical response, biodegradation rate, etc. Another interesting approach is the use of environmentally friendly and non-toxic plasticizers such as poly(ethylene glycol), PEG [16-18], poly(propylene glycol), PPG [19], oligomeric lactic acid, OLA [20], citrates such as acetyl tributyl citrate (ATBC) [21-23] or tributyl citrate (TBC) [22,24-26].

Vegetable oils are cost effective products (or in some cases, by-products) characterized by high availability; in addition, they can be chemically modified to improve some properties or attach selected functionalities. Raw or modified vegetable

oils find new and attracting uses as plasticizers or raw materials for polymer synthesis. Vegetable oils can be converted into epoxidized oils (EVOs) by conventional epoxidation processes. These epoxidized vegetable oils can be successfully used as high environmentally friendly epoxy resins [27-30] as well as plasticizers for poly(vinyl chloride), PVC industrial formulations due to its high compatibility with PVC resins [31-35]. Epoxidized vegetable oils also have been used as plasticizers for PLA. Chieng B.W *et al.* used epoxidized palm oil (EPO) and a mixture of epoxidized oils (palm-EPO and soybean-ESBO) as plasticizers for PLA and both plasticizers systems contributed to a remarkable increase in elongation at break and a parallel decrease in stiffness [36]. Prempeh N. *et al.* compared the effectiveness of epoxidized sunflower oil (ESFO) with regard to epoxidized soybean oil (ESBO) as plasticizers for PLA formulations. ESFO gave a remarkable increase in elongation at break. In addition, the glass transition temperature (Tg) was decreased by 3 ºC and the overall thermal stability of PLA was improved [37]. The results reported by Santos E.F. *et al.* showed a remarkable increase in mechanical ductile properties of PLA together with a decrease in Tg, by using 20% plasticizer coming from biodiesel derived from sunflower oil. This was attributed to an increase in polymer chain mobility due to the internal lubricating effect provided by the plasticizer [38]. Finally, Alam J. *et al.* studied the effect of epoxidized linseed oil (ELO) on mechanical performance of PLA with addition of carbon nanotubes; addition of ELO led to an increase in elongation at break, a reduction of the Tg and a thermal stabilization effect [1].

The aim of this work is to improve the ductile properties of PLA by using an epoxy plasticizer derived from a fatty acid, octyl epoxy stearate (OES). The work has focused on the effect of this plasticizer on thermal and mechanical performance of PLA with

different amounts of OES to obtain balanced properties and overcome the intrinsic fragility of PLA polymers.

2. Materials and Methods.

2.1. Materials.

Poly(lactic acid) resin commercial grade, Ingeo^{TM} Biopolymer 6201D was supplied by NatureWorks LLC (Minnetonka, USA). Its density is 1.24 g cm^{-3} and contains about 1.5% D-isomer. The selected plasticizer was an octyl epoxy stearate (OES) with tradename "plasticizer 201", supplied by Traquisa S.L. (Barcelona, Spain). It is characterized by an epoxide oxygen content in the 3.1%-3-3% range, a viscosity of 20-30 cP at 20 ºC and a molecular weight of 408 g mol^{-1}. A schematic representation of the chemical structure of OES is shown in Fig. 1 and presence of one epoxide ring per molecule can be observed.

Figure 1

2.2. Processing of OES plasticized PLA.

Initially, PLA pellets were dried at 60 ºC for 24 h for further processing operations. After this, PLA pellets and the corresponding amounts of OES plasticizer were mechanically mixed in a zipper bag. Table 1 summarizes all the compositions tested in this work as well as their labelling. PLA-OES mixtures were melt blended in a twin screw co-rotating extruder at a rotating speed of 60 rpm and temperature profile in the 172 ºC (hopper) – 180 ºC (die) range and subsequently pelletized. After this, plasticized PLA pellets were molded by injection molding in a Meteor 270/75 from Mateu & Solé (Barcelona, Spain) at an injection temperature of 180 ºC and standard samples for tensile tests and rectangular samples sizing 80 x 10 x 4 mm^3 were obtained. The formulation

with best-balanced properties was selected for film formation by using a cast film equipment from EuroTech S.A.S (San Martino in Riu, Italy). The extrusion temperature was set to 210 ºC and film 200 mm wide and 200 μm thick were obtained.

Table 1

2.3. Mechanical characterization of OES plasticized PLA.

Mechanical characterization was carried out with tensile and impact tests. Tensile tests were done in a universal test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain) at room temperature according to the ISO 527 standard. A 5 kN load cell and a crosshead speed of 10 mm min^{-1} were used. At least five different samples were tested and average values were calculated. In addition, an axial extensometer from Ibertest was coupled to the longitudinal section to obtain the Young's modulus in a more accurate way.

To evaluate the ability of the PLA-OES materials to absorb energy, the Charpy impact test was carried out in a Charpy pendulum (6 J) from Metrotec S.A. (San Sebastián, Spain) following the guidelines of the ISO 197:1993. At least five different specimens of each sample were tested and average values were calculated.

Surface characterization of the fractured samples from impact tests was carried out by field emission scanning electron microscopy (FESEM) in a Zeiss ULTRA microscope at an accelerating voltage of 2 kV. Samples were previously covered with a thin platinum layer in a high vacuum sputter EM MED020 from Leica Microsystems.

2.4. Thermo-mechanical characterization of OES plasticized PLA.

The effect of temperature on mechanical properties was studied by conventional heat deflection temperature (HDT) and Vicat softening temperature (VST) tests. In

addition, dynamic mechanical thermal analysis (DMTA) was carried on PLA-OES materials.

Dynamic-mechanical thermal analysis (DMTA) was carried out in rectangular torsion mode in an oscillatory rheometer AR G2 from TA Instruments (New Castle, USA), equipped with a torsion clamp system for rectangular solid samples. Samples sizing 40x10x4 mm^3 were subjected to a temperature sweep program from 20 ºC up to 130 ºC at a constant heating rate of 2 ºC min^{-1} in air atmosphere. The selected frequency was 1 Hz and the maximum deformation (γ) was set to 0.1%.

The heat deflection temperature (HDT) was determined by the A method according to ISO 75 which recommends a load of 1.8 MPa and a heating rate of 120 ºC h^{-1}. Vicat softening temperature (VST) was done using the B method as recommended by the ISO 306 with a load of 50 N and a heating rate of 50 ºC h^{-1}. Both tests were carried out in a VICAT/HDT station DEFLEX 687-A2 from Metrotec S.A. (San Sebastián, Spain).

2.5. Thermal characterization of OES plasticized PLA.

Thermal properties of PLA and PLA plasticized with octyl epoxy stearate (OES) were obtained by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Thermogravimetric (TGA) tests were carried out in a TGA/SDTA 851 thermobalance from Mettler-Toledo Inc. (Schwerzenbach, Switzerland) with a heating program from 30 ºC to 500 ºC at a heating rate of 20 ºC min^{-1} in nitrogen atmosphere (66 mL min^{-1}). Differential scanning calorimetry (DSC) was conducted in a Mettler-Toledo 821 calorimeter (Schwerzenbach, Switzerland) in nitrogen atmosphere (66 mL min^{-1}); the heating program was from 30 ºC to 190 ºC at a heating rate of 10 ºC min^{-1}.

3. Results and discussion.

3.1. Mechanical properties of OES plasticized PLA.

Mechanical properties are very sensitive to presence of plasticizers. Fig. 2 shows the evolution of the tensile strength and Young's modulus. We can see a clear plasticization effect as the tensile strength of unplasticized PLA (64.0 MPa) is reduced

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up to values of 61.3 MPa, 55,2 MPa and 43 MPa (a percentage decrease of 33%) for PLA-OES compositions containing 1, 3 and 5 phr OES respectively. With regard to the maximum OES content, the tensile strength is reduced up to 40.5 MPa (percentage decrease of 37%). This could be related to formation of a separated phase structure. Regarding to the Young's modulus, no significant changes are observed. The modulus of unplasticized PLA is close to 3600 MPa. Low amounts of OES plasticizer leads to a slight increase up to values of 3829 MPa and 3729 MPa for OES plasticized PLA containing 1 and 3 phr respectively. However, an increase of OES plasticizer leads to a decrease in Young's modulus to values of 3473 MPa and 3445 MPa for samples containing 5 and 10 phr OES respectively. Higher OES contents leads to slightly increased modulus in the 5-7% range (probably due to a decrease in elongation at break).

Figure 2

Regarding mechanical ductile properties, Fig. 3 shows the plot evolution of the elongation at break from tensile tests and the impact absorbed energy from Charpy's tests. We can see that for low OES plasticizer content (1 and 3 phr OES), both elongation at break and impact absorbed energy are slightly increased. However, an increase in the plasticizer content up to 5 phr OES clearly enhances both properties. The elongation at break of unplasticized PLA is close to 8.6% and this is increased up to values of 40.6% (a percentage increase of almost 300%) for PLA-OES formulations containing 5 phr OES. Similar tendency can be found for impact absorbed energy as unplasticized PLA is characterized by a relatively low value around 30.9 kJ m^{-2} and this is increased up to (54.2 kJ m^{-2}) which represents a percentage increase of about 75%. OES contents higher than 5 phr, leads to a decrease in both ductile properties to constant values of about 15% for elongation at break and 38 kJ m^{-2} for impact absorbed energy. This fact could be

related to a plasticizer saturation close to 5 phr OES. Higher OES plasticizer content can lead to a phase separation that is responsible for a decrease in ductile properties.

Figure 3

Surface analysis of fractured samples from impact tests was carried out by field emission scanning electron microscopy (FESEM). Fig. 4a shows the fracture surface of unplasticized PLA, which is mainly smooth and homogeneous with some voids related to porosity. In general, this is the typical surface appearance of a fractured brittle material. If we observe Fig. 4b, the appearance is different; this corresponds to OES plasticized PLA with 1 phr OES. We can see typical fracture surface of a ductile material characterized by a rough surface, presence of filaments due to plastic deformation and presence of voids (probably due to phase separation between the base polymer and excess plasticizer). Figs. 4c, 4d, 4e, 4f and 4g correspond to fractured surfaces of OES plasticized PLA with 3, 5, 10, 15 and 20 phr OES respectively. As the amount of OES increases, we can clearly see increased presence of voids in the surface, especially over 5 phr OES. This indicates that PLA is saturated with the plasticizer and phase separation occurs. The excess plasticizer appears in the form of spherical shapes and this has a negative effect on overall mechanical properties as described previously (mainly in ductile properties).

Figure 4

3.2. Thermo-mechanical properties of OES plasticized PLA.

Fig. 5 shows the plot evolution of the storage modulus (G') and the phase angle (δ) as a function of temperature for unplasticized PLA and OES plasticized PLA with

different plasticizer content. PLA is a semicrystalline polymer and as it can be observed in Fig. 5b, it shows relatively high G' values around 1.3 GPa. In the glass transition temperature range the storage modulus is remarkably reduced up to values of about 1.4 MPa and at about 84 ℃ the storage modulus increases again (up to 60 MPa) due to the cold crystallization process. OES plasticized materials show similar behavior but both the glass transition temperature (T_g) and the cold crystallization (T_{cc}) are moved to lower temperatures as the plasticizer enables chain mobility. The storage modulus (G') of the OES plasticized PLA samples starts at about 1.2 GPa and after the glass transition (a few degrees lower than in unplasticized PLA) decreases to 2 MPa. The cold crystallization in OES plasticized PLA samples starts before than unplasticized PLA; in particular, the cold crystallization process for samples containing 1 and 3 phr OES start at about 82 ℃ but when the OES content increases (samples with 5, 10, 15 and 20 phr of OES) the cold crystallization starts at lower temperatures of about 73-74 ℃. The glass transition was estimated as the phase angle peak (or tan δ peak). As we can see in Fig. 5a the T_g changes from 65.9 ℃ for unplasticized PLA up to slightly lower values of 65.2 ℃ (1 phr OES), 62.4 ℃ (3 phr OES). As the OES content increases the T_g is still lower with values of 60.4 ℃ (5 phr OES), 60.1 ℃ (10-15 phr OES) and 59.7 ℃ (20 phr OES). This decrease in Tg is a clear evidence of the plasticizing effect that OES provides; nevertheless, no important changes are observed with increasing OES content over 5 phr thus indicating that PLA gets saturated with relatively low plasticizer contents.

Figure 5

Octyl epoxy stearate plasticizer has also effects on thermo-mechanical properties as observed in Table 2 that summarizes the values of the heat deflection temperature

(HDT) and Vicat softening temperature (VST). The VST of unplasticized PLA (52.8 ºC) decreases up to values of 47.2 ºC for a plasticizer content of 1 phr and minimum values of 46 ºC are obtained for a plasticizer content of 20 phr. Variation of HDT is less accentuated with values of 47.6 ºC for unplasticized PLA and values in the 46.0 – 46.8 ºC for OES plasticized PLA.

Table 2

3.3. *Thermal properties of OES plasticized PLA.*

Differential scanning calorimetry (DSC) thermograms show three different thermal transitions as expected. The glass transition temperature (T_g) located between 55 ºC and 65 ºC; the exothermic peak located between 80 ºC and 100 ºC corresponds to the cold crystallization process and finally, the endothermic peak located at 170 ºC – 175 ºC which corresponds to PLA melting. The decrease in T_g is a clear evidence of the plasticization effect. OES plasticizers allows chain mobility due to the free volume and reduced chain interactions [39]. In good agreement with previously described DMTA behavior, DSC shows a clear decrease in T_g with OES plasticizer. The glass transition temperature of the unplasticized PLA is close to 64.2 ºC as obtained by DSC. This value decreases up to values of 55.5 ºC for OES plasticized PLA with 5 phr OES which is in total accordance with previous results. This also indicates that plasticizer saturation occurs for relatively low plasticizer content. Regarding the cold crystallization process, we observe a decrease in its typical temperatures (onset, peak and endset). This indicates that OES plasticizer allows chain motion, which has a positive effect on cold crystallization [38]; these results are in total agreement with DMTA results which show a decrease of about 10 ºC in the cold crystallization process. In addition, if we compare

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the cold crystallization enthalpy (ΔH_{cc}) and the melt enthalpy (ΔH_m) we observe that ΔH_m is much higher than ΔH_{cc} thus indicating the semicrystalline nature of PLA at room temperature. Presence of OES plasticizer leads to increased enthalpy difference (ΔH_m-ΔH_{cc}) thus indicating higher crystallinity.

Thermal stability of raw PLA and OES plasticized PLA was evaluated by means of thermogravimetric analysis (TGA). Table 3 also shows some parameters related to the thermal degradation. In particular, the temperature at which a 5% weight loss occurs ($T_{5\%}$) and the maximum degradation rate temperature (T_{max}), are summarized. Although slight decrease in $T_{5\%}$ can be detected, in general, the thermal stability is not highly affected by presence of OES plasticizer. In fact, as we can observe, a slight increase in T_{max} is detected but in both cases, the change is not significative.

Table 3

3.4. Oxygen permeability measurement of OES plasticized PLA films.

As optimum balanced properties were obtained for an OES content of 5 phr, this formulations was selected for an in depth study in the film form. The oxygen transmission rate (OTR) of neat is around $44.4 \pm 0.9 \ cm^3 \cdot mm \cdot m^{-2} \cdot d^{-1}$ [40,41] while the OTR for the OES plasticized PLA film is $23.2 \pm 0.2 \ cm^3 \cdot mm \cdot m^{-2} \cdot d^{-1}$. The lower oxygen transmission rate is due to increased crystallinity. As we have previously observed by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC), presence of plasticizer leads to increased polymer chain mobility and this leads to increased crystallinity. In general, the addition of plasticizers to polymers leads to an increase in gas permeability due to the free volume they provide. However, in this case,

this phenomenon is overlapped with the decreased gas permeability effect because of the increased crystallinity being the overall result a decrease in gas permeation properties.

3.5. Surface wettability of OES plasticized PLA films.

The surface wetting properties of 5 OES plasticized PLA films containing 5 phr OES was investigated by water contact angle measurement. By adding 5 phr OES into the PLA matrix, the water contact angle increased from 58º to approximately 66º showing an increase in hydrophobicity. It is evident that the contact angle of plasticized PLA is higher than neat PLA as the plasticizer is an oil type with remarked hydrophobicity. Therefore, PLA films containing 5 phr OES are also expected to have higher resistance to water adsorption than neat PLA film. For these reasons PLA films plasticized with OES can offer attracting uses in the packaging industry.

4. Conclusions.

In the present work, thermal and mechanical properties of PLA plasticized with octyl epoxy stearate (OES) were evaluated. Samples with 5 phr of octyl epoxy stearate showed the best results in terms of ductile properties such as elongation and impact properties. If compared to unplasticized PLA, OES addition leads to a percentage increase in elongation at break of about 300% and 75% regarding impact-absorbed energy. This behavior validated by surface analysis of fractured samples by FESEM images with clear evidences of plastic deformation in OES plasticized PLA materials. Moreover, DSC results showed that OES causes a decrease in the T_g of the PLA; in particular, the sample containing 5 phr of OES showed a T_g of 55.5 ºC while unplasticized PLA shows a T_g located at 64.2 ºC. Additionally, the cold crystallization process moves to lower temperatures when OES is added to PLA, more than 10 ºC for the plasticized samples

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with 5 phr OES. From DMTA results, a decrease in T_g and cold crystallization is also observed, which is consistent with the DSC results. Furthermore, oxygen permeability and wettability tests on PLA films plasticized with 5 phr OES showed attracting properties for the packaging industry as the oxygen transmission rate (OTR) changed from 44.4 $cm^3 \cdot mm \cdot m^{-2} \cdot d^{-1}$ for neat PLA to 23.2 $cm^3 \cdot mm \cdot m^{-2} \cdot d^{-1}$ for sample of PLA plasticized with 5 phr OES. In addition, OES plasticized PLA is more hydrophobic than neat PLA which has a positive effect on water resistance.

We can conclude that octyl epoxy stearate (OES) can be used as an effective plasticizer for PLA and good results are obtained for relatively low OES load of about 5 phr. This fact could be related to a plasticizer saturation close to 5 phr OES. Higher OES plasticizer content can lead to a phase separation that is responsible for a decrease in ductile properties due to an antiplasticization process. Octyl epoxy stearate represents an environmentally friendly material that can positively contribute to obtain high environmental efficient PLA formulations for industrial applications.

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Table legends

Table 1.- Summary of the compositions and coding of poly(lactic acid), PLA with different amounts of octyl epoxy stearate (OES) plasticizer.

Code	Plasticizer amount (phr – per hundred PLA resin)
PLA	-
PLA-1 OES	1
PLA-3 OES	3
PLA-5 OES	5
PLA-10 OES	10
PLA-15 OES	15
PLA-20 OES	20

Table 2.- Results of the heat deflection temperature (HDT) and Vicat softening temperature (VST) of OES plasticized PLA with different OES loads.

Sample	VST (ºC)	HDT (ºC)
PLA	52.8	47.6
PLA-1 OES	47.2	46.8
PLA-3 OES	47.6	46.6
PLA-5 OES	47.8	46.4
PLA-10 OES	47.0	46.0
PLA-15 OES	46.6	46.6
PLA-20 OES	46.0	46.6

Table 3. Thermal parameters of unplasticized PLA and OES plasticized PLA obtained by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in terms of the plasticizer content.

| OES (phr)	DSC						TGA	
	T_g (ºC)	T_{cc} (ºC)	ΔH_{cc} (Jg^{-1})	T_m (ºC)	ΔH_m (Jg^{-1})	ΔH_m-ΔH_{cc} (Jg^{-1})	$T_{5\%}$ (ºC)	T_{max} (ºC)
0	64.2	98.4	18.2	175.0	40.8	22.6	336.9	363.5
1	64.5	98.5	15.9	174.3	40.2	24.3	338.3	373.4
3	61.9	94.0	22.6	174.3	47.9	25.3	336.7	373.3
5	55.5	85.9	14.2	173.6	41.5	27.3	329.2	368.4
10	57.0	83.9	11.1	171.2	37.9	26.8	333.2	371.7
15	57.5	83.8	9.2	173.6	37.7	28.5	327.5	366.6
20	56.4	81.5	10.7	170.4	41.9	31.2	331.9	368.3

<u>Figure legends</u>

**Figure 1.-** Schematic representation of the chemical structure of octyl epoxy stearate (OES) plasticizer.
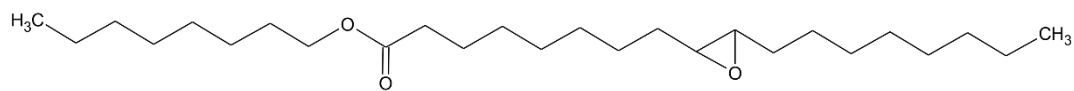
Figure 2.- Variation of tensile strength and Young's modulus of OES plasticized PLA.
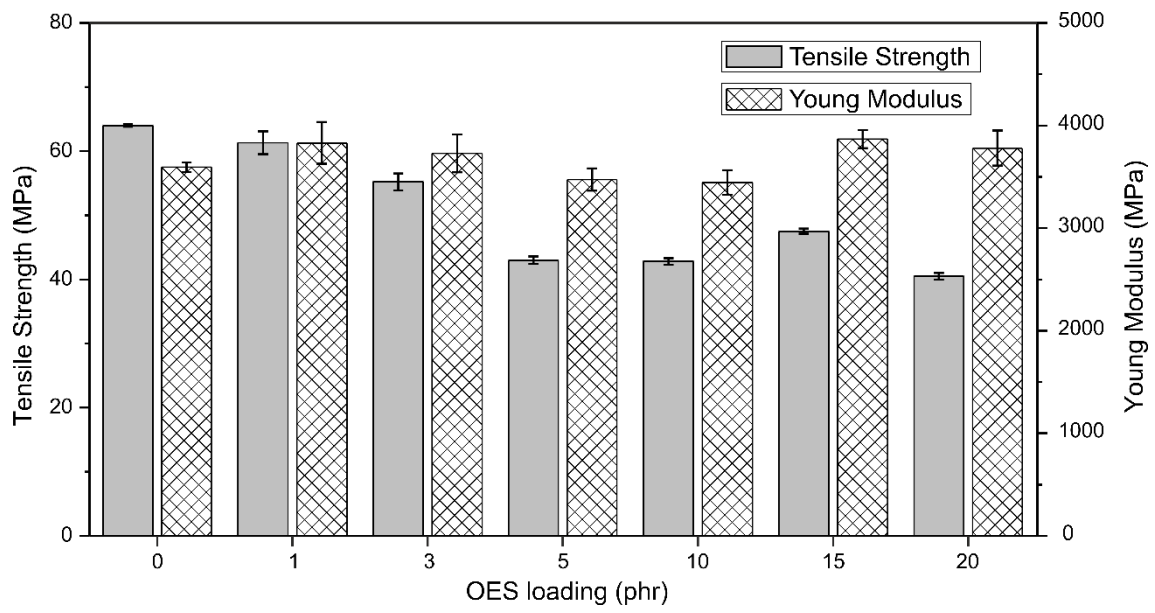
Figure 3.- Variation of elongation at break and impact absorbed energy of OES plasticized PLA.
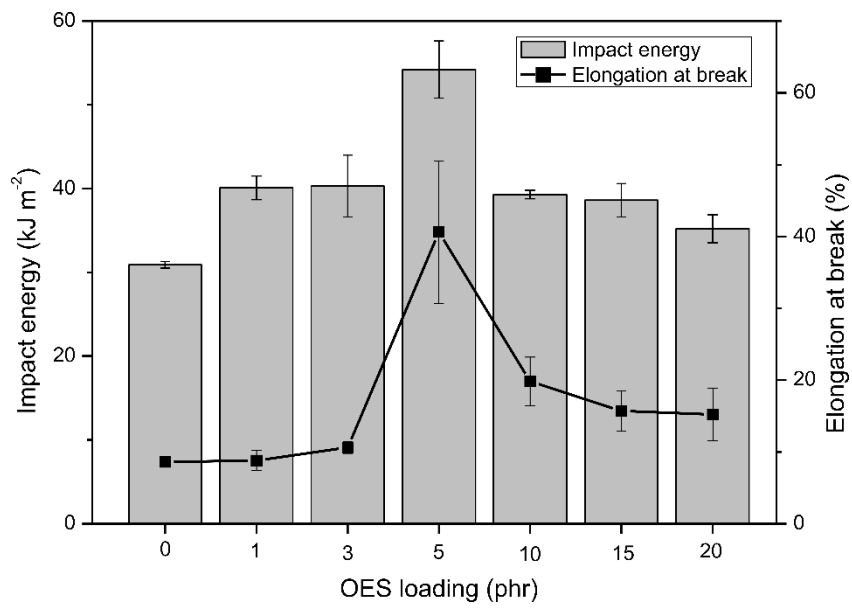
Figure 4.- FESEM images at 5000x of fractured samples from impact tests corresponding to a) unplasticized PLA, b) OES plasticized PLA with 1 phr OES, c) OES plasticized PLA with 3 phr OES, d) OES plasticized PLA with 5 phr OES e) OES plasticized PLA with 10 phr OES, f) OES plasticized PLA with 15 phr OES and g) OES plasticized PLA with 20 phr OES.
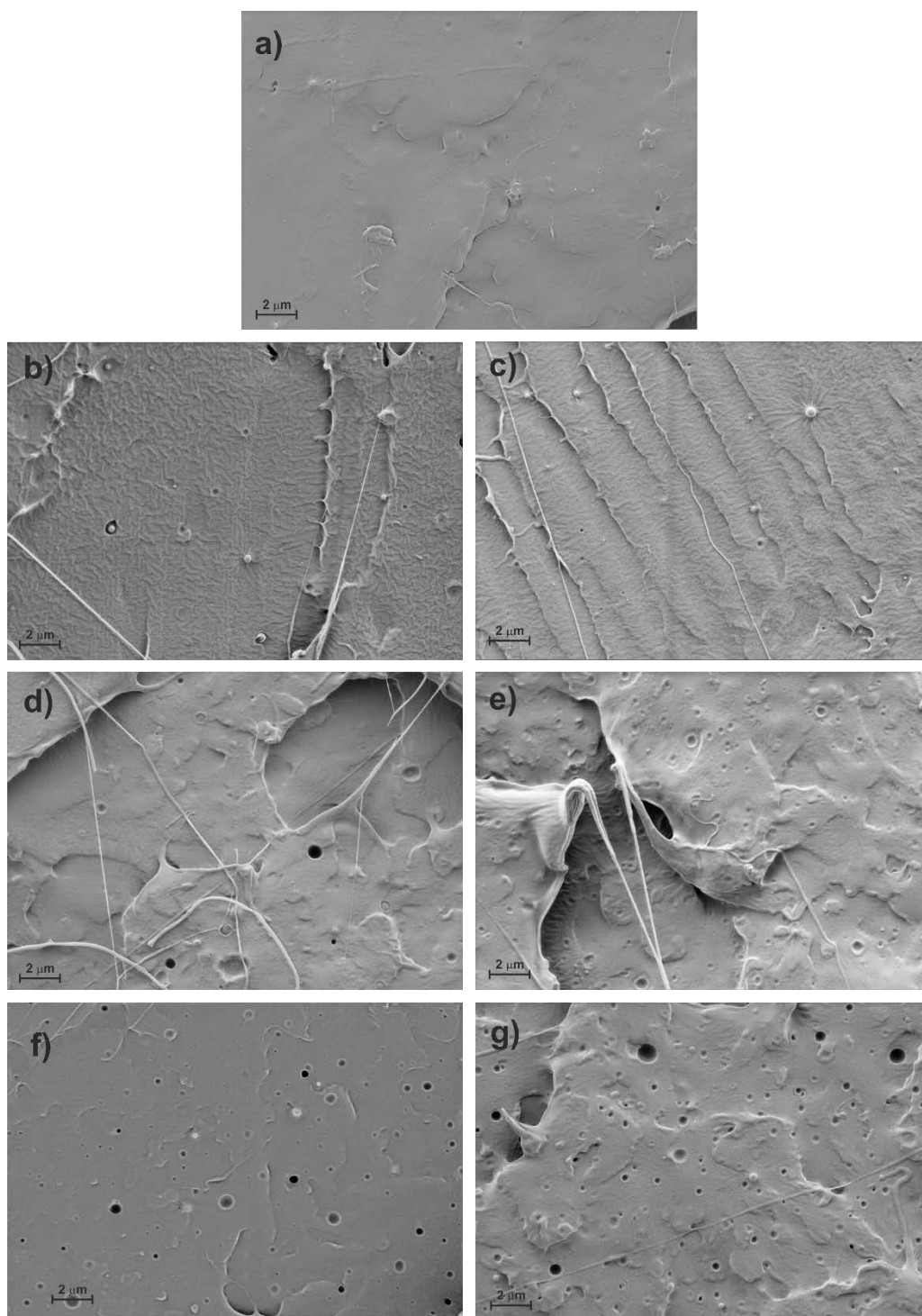
Figure 5.- Plot evolution of a) the phase angle (δ) and b) storage modulus (G') in terms of temperature for unplasticized PLA and OES plasticized PLA with different OES load.