The final publication is available at

http://dx.doi.org/10.1002/pi.5164

Additional Information

"Plasticization effects of epoxidized vegetable oils on mechanical properties of poly(hydroxybutyrate), PHB"

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Abstract

The effect of different epoxidized vegetable oils (EVOs) as potential plasticizers for poly(3-hydroxybutyrate), PHB was evaluated in terms of changes in mechanical and thermal properties and morphology. PHB is a biodegradable aliphatic polyester obtained from bacterial fermentation. High stiffness and fragility are two of its main drawbacks. To overcome this behavior PHB was plasticized with various amounts of two different epoxidized vegetable oils: epoxidized linseed oil (ELO) and epoxidized soybean oil (ESBO). The total ELO and ESBO content varied in the 5 phr (per hundred resin) − 20 phr range and plasticized PHB materials were obtained by melt extrusion and compounding followed by injection molding. The results show that the plasticizing effect provided by ELO is more efficient than ESBO with balanced properties at a concentration of 10 phr ELO. ELO addition leads to an improvement on mechanical ductile properties with a noticeable increase in elongation at break and impact absorbed energy. With regard to thermal properties, both the addition of ELO and ESBO leads to a remarkable increase in thermal stability of PHB. All these findings suggest that addition of 10 phr ELO leads to optimized PHB formulations with potential uses in technical applications.

Keywords: Poly(hydroxybutyrate) (PHB); epoxidized soybean oil (ESBO); epoxidized linseed oil (ELO); plasticization; biodegradable.

INTRODUCTION

Recent decades have witnessed a remarkable increase in the production and consumption of plastic materials, mainly from petroleum origin such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), etc. that

covers a wide range of properties that make them useful for diverse industrial sectors. Nevertheless one important weakness of these petroleum-based polymers is that most of them are not biodegradable. Packing and packaging industries use large amounts of plastic materials and their products are characterized by a relatively short life cycle and consequently, a huge amount of non-biodegradable plastics is continuously generated with the subsequent environmental impact. The increase in environmental concerns related to waste generation has led to an increased interest on the study and development of polymers that can undergo total degradation/decomposition in appropriate temperature and moisture conditions. This has a positive effect on environment as it avoids generation of harmful and potentially toxic wastes.[1] These polymers, also known as biopolymers, can be classified into four different groups depending on the production process and the origin of the base material or monomer. One group includes all polymers obtained directly from biomass such as cellulose, starch, alginate, gluten, etc. Another groups considers all polymeric materials obtained by chemical synthesis from monomers derived from renewable resources as it is the case of poly(lactic acid), PLA. A third group is represented by those polymers that although they are obtained from fossil and no renewable resources can undergo degradation/decomposition due to their particular chemical structure as it is the case of some petroleum-derived polyesters: i.e. poly(caprolactone)-PCL, poly(butylene succinate)-PBS, poly(butylene adipate-co-terephthalate)-PBAT, etc. Finally, some biodegradable polymers can be obtained from bacterial fermentation such as poly(hydroxyalkanoates) (PHAs).[2] Therefore, the use of biodegradable polymers is one of the main alternatives to reduce the large amounts of wastes with a subsequent reduction of their environmental impact.[3, 4]

Poly(hydroxybutyrate), PHB is one of the best known poly(hydroxyalkanoates), PHAs.[5] PHB is an aliphatic polyester obtained from controlled bacterial fermentation characterized by its intrinsic biodegradability and biocompatibility.[6, 7] PHB is readily biodegradable in such environments where the combination of nitrogen, phosphates, salts, moisture and temperature allow microorganism growth.[8, 9] These microorganisms use PHB polymer chains as nutrients. For this reason, PHB degradation can occur in different environments such as soil,[10, 11] compost [12-14] and marine sediments.[15, 16] Otherwise, PHB can remain almost intact for long periods. PHB biodegradation depends on several factors such as microbial activity of the environment, moisture, temperature, pH, initial molecular weight of polymer chains, crystallinity, etc.[17, 18] In the case of PHB, biodegradation in compost at temperatures around 60 ºC and a moisture content in the 50-55% range has been reported.[19, 20]

The excellent combination of its properties makes it ideal for biodegradable packing products and resorbable medical devices.[21] Despite this, up to now there is not a large production of PHB products because of its cost and some weaknesses in comparison to commodities and other technical plastics.[22] One of the main drawbacks of PHB is its intrinsic fragility due to its high crystallinity, which can be higher than 55%. This leads to low elongation at break and deformation ability which limits its field of applications.[23, 24] Another important drawback of PHB is its relatively low resistance to thermal degradation which leads to a remarkably narrow processing window. The melt temperature of PHB is located at about 180 ºC and it can be processed at about 190 ºC as higher temperatures (or longer residence times) promote chain scission with the subsequent decrease in molecular weight.[25] These problems can be overcome by using several techniques such as internal [26] or external plasticization [23, 25, 27] as well as physical blending with other polymers.[28-30]

Among the different options to prepare industrial PHB formulations, external plasticization represents an interesting, simple and cost-effective route to improve mechanical and thermal properties of raw PHB.[31] Generally, addition of plasticizers promotes a decrease in both the glass transition temperature (T_g) and the melt temperature (T_m) and this allows processing at lower temperatures thus reducing the risk of thermal degradation. Furthermore, plasticizers increase PHB ductility while its brittleness is noticeably reduced as a consequence of lower crystallinity degree.[32] Petroleum-based plasticizers such as phthalates, trimellitates, dicarboxylates, adipates, etc. are widely used at industrial level and some of them offer potential toxicity problems associated to plasticizer migration.[33] For this reason, new environmentally friendly plasticizers are continuously being investigated and tested. It has been shown that epoxidized vegetable oils are a viable alternative as a replacement of petroleum-based conventional plasticizers. Epoxidized vegetable oils (EVOs) are obtained by epoxidation of vegetable oils (VOs) obtained from different plants and seeds.[34] The chemical structure of vegetable oils is based on a triglyceride structure with different fatty acids.[35, 36] Presence of carbon-carbon unsaturations allows epoxidation by conventional processes. These unsaturations appear in conventional fatty acids such as oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids with one, two and three carbon-carbon double bonds respectively. Soybean oil (SBO) is characterized by high content of unsaturated fatty acids, mainly oleic (20-26%), linoleic (48-57%) and linolenic (6-10%) and linseed oil (LO) is highly rich in linolenic acid (51-46%) and other unsaturated fatty acids such as oleic (18-26%) and linoleic (14-20%). In addition, both soybean oil and linseed oil are commercially available as byproducts of other industries and can be easily epoxidized with cost effective processes; therefore, both

epoxidized vegetable oils are also commercially available.[3] Some research works report the successful use of epoxidized vegetable oils as plasticizers for thermoplastic matrices both biodegradable and non-biodegradable.[3, 4, 37-43] It has been reported the use of epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO) as plasticizers for poly(3-hydroxybutyrate-*co*-valerate), PHBV. M. Ö. Seydibeyoğlu *et al.*[44] reported that addition of 10 wt% ELO and ESBO leads to a slight increase in elongation at break with a subsequent reduction of the tensile strength and Young's modulus. In addition, a slight decrease in the melt temperature was observed. Similar behaviour was confirmed by J. S. Choi *et al.*[45] by the addition of 30 wt% ESBO to PHBV with a remarkable increase in both the impact resistance and the elongation at break. Plasticizer interaction is directly related to the chemical structure of both the base polymer and the plasticizer as well as other external processing parameters related to mixing and homogenization. It has been reported that PHBV and PHB possess similar solubility parameters due to similar chemical structure.[46] Nevertheless, it is possible that differences in chain length, crystallinity, amount of hydroxyvalerate co-monomer and other slight differences between PHB and PHBV polymers could have an important effect on plasticization. Plasticizer saturation promotes phase separation and this has a negative effect on overall properties of plasticized formulations. As indicated by B. W. Chieng *et al.*[47], Y. Q. Xu *et al.*[48] and J.M. Ferri *et al.*[49], plasticization of polyester-type polymers such as poly(lactic acid)-PLA occurs at relatively low plasticizer content. This behaviour was also observed by Y. Zhao *et al.*[38] for polybutylene succinate-PBS plasticized with ESBO. As indicated by J. S. Choi *et al.*[45], PHBV plasticized formulations admit a relatively high plasticizer (ESBO) content. On the other hand, M. Ö. Seydibeyoğlu *et al.*[44], reported interesting results for intermediate plasticizer content with a different PHBV grade and different valerate content. By taking into consideration these studies,

the main aim of this work is to assess the plasticization effect of both ELO and ESBO on PHB and determine the optimum plasticizer content before plasticizer saturation occurs. In this work, the effectiveness of two cost effective and commercially available epoxidized vegetable oils: ELO and ESBO as potential plasticizers for poly(hydroxybutyrate) is evaluated. The effect of different plasticizer content (in the 0 – 20 phr: per hundred resin) and type (ELO, ESBO) on mechanical and thermal properties of PHB is described.

EXPERIMENTAL

Materials

Poly(3-hydroxybutyrate), P3HB pellets, commercial grade P226 were supplied by Biomer (Krailling, Germany). This PHB grade has an average molecular weight of 426,000 g mol^{-1}, a density at 23 ℃ of 1.25 g cm^{-3} and a melt flow index (MFI) of 10 g/10 min tested at 180 ℃ and 5 kg loading. Epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO) were used as PHB plasticizers. Epoxidized linseed oil (ELO) has a density at 20 ℃ between 1.05-1.06 g cm^{-3}, an EEW (epoxide equivalent weight) of 178 g equiv^{-1} and an acid value below 1 mg KOH/g. Epoxidized soybean oil (ESBO) has a density at 20 ℃ between 0.990-0.997 g cm^{-3}, an EEW of 238 g equiv^{-1} and an acid value below 0.75 mg KOH/g. Both of them were supplied by Traquisa S.L. (Barcelona, Spain) and were used as received without any other treatment. The hydroxyl and peroxide values of both epoxidized vegetable oils is almost negligible as indicated by the supplier.

Sample preparation

PHB pellets were vacuum dried at 70 ºC for 24 h before blending to remove moisture. After this, PHB and the corresponding amounts of ELO or ESBO were mechanically mixed in a zipper bag. The total plasticizer content varied in the 0 – 20 phr. All PHB plasticized formulations were processed in a twin-screw co-rotating extruder with D= 25 mm and L/D ratio= 24. The temperature profile was accurately selected to avoid thermal degradation and was set to 170 ºC (hopper), 170 ºC, 175 ºC and 180 ºC (die). All materials were obtained at a screw speed of 40 rpm. After extrusion, the material was cooled and pelletized in a mill. After this, standard samples for tensile tests and rectangular samples sizing 80x10x4 mm^3 were obtained by injection molding in an injection molding machine mod. Meteor 270/75 (Mateu & Solé, Barcelona, Spain) at a temperature of 180 ºC. PHB processing leads to a decrease in molecular weight due to the its high sensitiveness to thermal degradation.[50] The percentage decrease in molecular weight of unplasticized PHB after the extrusion process was around 11.6% whilst this reduction was still more accentuated after the injection moulding process with a percentage decrease of about 34.2% with regard to unprocessed PHB pellets. This noticeable decrease in the PHB average molecular weight is directly related to thermal degradation and affects in a remarkable way to the overall mechanical and thermal features of PHB-derived materials.[51] Nevertheless, this work is focused on the effect of different plasticizers (type and amount) on final properties of plasticized PHB and all formulation were subjected to the same processing conditions to give comparable results.

Viscosity molecular weight

Intrinsic viscosity (η) of PHB before processing and after extrusion and extrusion+injection moulding was obtained by using an Ubbelohde viscometer type 1C

at room temperature following the guidelines of the ISO 1628. All samples were dissolved in chloroform with three different concentrations for each sample. The viscosity molecular weight (M_v) for each sample was obtained by using the Mark-Houwink equation with K and a values of 1.18 x 10^{-2} and 0.780 respectively for PHB as reported elsewhere.[52]

$$[\eta] = K \times M_V^a \qquad\qquad \text{Eq.1}$$

Mechanical properties

Tensile tests of neat PHB and ELO/ESBO plasticized-PHB formulations were carried out at a rate of 5 mm min^{-1} in an electromechanical universal test machine Ibertest ELIB 30 (S.A.E. Ibertest, Madrid, Spain) with a 5 kN load cell at room temperature, following ISO 527. A set of five different samples was tested and average values were calculated. In addition, an axial extensometer was used to obtain the Young's modulus in a more accurate way.

Impact test was done using a 1 J Charpy's impact pendulum (Metrotec S.A., San Sebastian, Spain) according to ISO 179 standard. At least five different notched samples ("V" type at 45º with a radius of 0.25 mm) were tested and the average value of the absorbed energy was calculated.

Shore D hardness values of ELO/ESBO plasticized PHB were obtained with a Shore D hardness durometer model 676-D (J. Bot Instruments, Barcelona, Spain)

following the ISO 868. At least five different measurements were taken and average values were calculated.

Thermal properties

The melting and crystallization behaviour of neat PHB and ELO/ESBO plasticized PHB was studied in a differential scanning calorimeter (DSC) from Mettler-Toledo mod. 821 (Mettler-Toledo Inc., Schwerzenbach, Switzerland). The sample weight was approximately in the 7 – 9 mg range. All samples were subjected to a four-step thermal program to remove thermal history. 1st step: dynamic heating from -50 ℃ to 180 ℃ at a heating rate of 10 ℃ min^{-1}, 2nd step: isothermal program at 180 ℃ for 2 min, 3rd step: dynamic cooling from 180 ℃ to -50 at a cooling rate of 10 ℃ min^{-1}, 4th step: dynamic heating from -50 to 300 ℃ at 10 ℃ min^{-1}. All the tests were conducted in nitrogen atmosphere at a constant flow rate of 66 mL min^{-1}. Both the melt temperature (T_m) and the melt enthalpy (AH_m) were obtained from the second heating program to eliminate the influence of the material processing. The crystallinity percentage of PHB ($X_{c, PHB}$) was calculated by using the following equation:

$$X_c\ (\%) = 100\ \times\ \left[\frac{\Delta H_m}{\Delta H_0 \cdot w}\right] \qquad\qquad \text{Eq.2}$$

Where ΔH_m in the melt enthalpy, ΔH_0 is the melt enthalpy for a theoretical 100% crystalline PHB and it was assumed to be 146 J g^{-1} [20] and w is the weight fraction of PHB in all tested formulations.

The thermal stability of the samples was studied by thermogravimetric analysis in a thermobalance TGA/SDTA 851 (Mettler-Toledo Inc., Schwerzenbach,

Switzerland). Samples with an average weight of 8 mg were heated from 25 ºC to 600 ºC at a heating rate of 10 ºC min^{-1}. All tests were carried out in nitrogen atmosphere with a constant nitrogen flow rate of 66 mL min^{-1}. The onset degradation temperature (T_0) was taken as the temperature for a mass loss of 5% and the maximum degradation rate (T_{max}) for each degradation stage was determined thorough de peaks in the first derivative from TGA curves (DTG).

Field emission scanning electron microscopy (FESEM)

Morphology of fractured surfaces from impact tests of neat PHB and ELO/ESBO plasticized PHB was observed by field emission scanning electron microscopy (FESEM) ZEISS ULTRA55 (Oxford instruments), with an acceleration voltage of 2 kV. Prior to FESEM test, all surfaces were sputter coated with a thin layer of platinum in a high vacuum sputter EM MED020 (Leica Microsystems) in order to make the samples electrically conductive.

Dynamic Mechanical Analysis (DMTA)

Mechanical dynamical thermal analysis (DMTA) in torsion mode of neat PHB and plasticized PHB was evaluated between –50 to 80 ºC at a heating rate of 2 ºC min^{-1} using an oscillatory rheometer AR G2 (TA Instruments, New Castle, USA). Samples sizing 40x10x4 mm^3 were subjected to the abovementioned thermal program at a frequency of 1 Hz and a maximum deformation (γ) of 0.1%. The storage modulus (G') and the damping factor (*tan δ*) were measured in terms of increasing temperature and the glass transition temperature (T_g) was taken at the point in which the *tan δ* peak reaches its maximum value.

RESULTS AND DISCUSSION

Mechanical properties of ELO/ESBO plasticized PHB

The effect of the plasticizer type (ELO or ESBO) and content (in the 0 – 20 phr range) can be observed in Fig. 1. The evolution of tensile mechanical properties is one of the most used indicator to assess plasticization. As it can be seen, as the plasticizer content (both ELO and ESBO) increases, both tensile strength and Young's modulus decrease. Some authors have reported similar tendency with regard to the tensile strength and Young's modulus in several plasticized polymers with ELO and ESBO.[38, 44, 48] On the other hand, we observe a slight increase in elongation at break when PHB is plasticized with ELO. As evidenced in Fig. 1, the maximum decrease in tensile strength is obtained for the PHB-ESBO system; in particular, the tensile strength of unplasticized PHB changes from 24.1 MPa up to values of 15.4 MPa for an ESBO increase of 16.6 wt% (from 0 phr to 20 phr) which represents a percentage decrease of about 36% in tensile strength. Regarding the PHB-ELO system, the tensile strength reduces up to 16.2 MPa for an ELO content of 20 phr (representing a percentage decrease of 33%). With regard to the elongation at break, it can be observed as the plasticized PHB has different behavior depending on the plasticizer type and content. In the case of the ELO plasticized PHB a slight increase from 9.7% (unplasticized PHB) to 13.6% for an ELO content of 10 phr can be observed which represents a percentage increase of about 40%. Higher ELO contents leads to lower elongation at break values thus indicating that maximum plasticization properties can be achieved for an ELO content around 10 phr as observed in Fig. 1c. This could be related to plasticizer saturation at this composition, so that, higher plasticizer load leads to phase separation with a remarkable effect on

ductile properties. M. Ö. Seydibeyoğlu *et al.*[44] also demostrated that the optimum epoxy soyate (the esterified form of epoxidized soybean oil) concentration in a PHBV matrix was located at around 10 wt%. The PHB-ESBO system follows different behavior and although some plasticization effect can be observed through the evolution of tensile strength (Fig. 1a), the elongation at break is not improved; in fact, a very slight decrease in elongation at break is detected with a change from 9.7% for unplasticized PHB up to values of about 8.5 - 9.0%. This behavior is different to that observed in previous works in which, an increase in flexibility is achieved with ESBO addition and, subsequently, elongation at break is improved in different polymers such as PHBV, PLA or PBS. J. S. Choi *et al.*[45] reported a slight increase in elongation at break in PHBV by addition of 30 wt% ESBO plasticizer. Similar trend was observed by Y. Q. Xu *et al.*[48] that achieved 63% higher elongation at break values by addition of 9 wt% ESBO while Y. Zhao *et al.*[38] achieved remarkably high values of elongation at break of 1400% by the addition of 5 wt% ESBO to PBS. With regard to the Young's modulus, it is important to note that it follows the same tendency as tensile strength for both systems; as the plasticizer content increases (ELO and ESBO), the Young's modulus decreases. It is worth to note that the Young's modulus represents the ratio between the stress and the elongation in the linear region. As indicated, the tensile strength decreases in a remarkable way with the plasticizer content while the elongation at break follows different behavior: slight increase for PHB-ELO system for 10 phr ELO and a very slight decrease for the PHB-ESBO system. As the Young's modulus represents the stress to elongation ratio, its value is lower due to lower stress values and slightly higher (or equal) elongation values. The Young's modulus of unplasticized PHB is located at about 1872 MPa and the only addition of both ELO and ESBO leads to lower values located at 1550 MPa and 1400 MPa respectively. Increasing ELO and ESBO load up to 20 phr leads to

values around 1350 MPa for both systems. By observing mechanical properties, we can conclude that the ESBO system is not as good as ELO for PHB plasticization as, even with a decrease in tensile strength and Young's modulus, the elongation at break is not improved. With regard to ELO, it also provides a decrease in tensile strength and modulus with increasing load but the most important parameter is the 40% increase in elongation at break for 10 phr ELO. The higher effectiveness of ELO versus ESBO as plasticizer for PHBV was assessed by M. Ö. Seydibeyoğlu et al.[44]
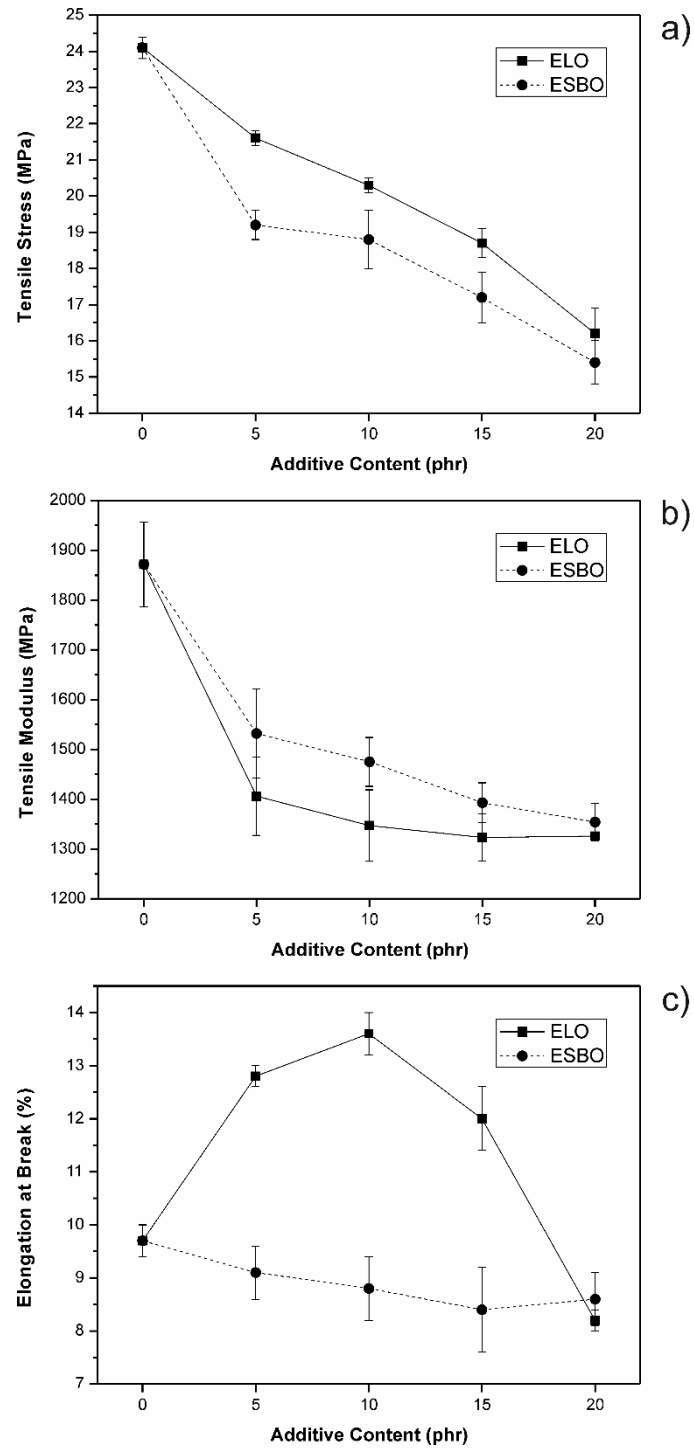
Figure 1. Effect of biobased plasticizers, ELO and ESBO content on mechanical

properties of poly(hydroxybutyrate), PHB: (a) tensile strength, (b) tensile modulus and

(c) elongation at break.

Fig. 2 shows the plot evolution of the impact absorbed energy (Charpy) and Shore D hardness values for both PHB-ESBO and PHB-ELO systems. Impact results (Fig. 2a) confirms the efficiency of ELO as plasticizer for PHB with a slight increase in the absorbed energy in the 5-10 phr ELO range from 2.1 J m^{-2} to values around 3 J m^{-2} (percentage increase of about 40%). Once again, over 10 phr ELO, the impact energy decreases thus indicating that plasticizer saturation occurs. Nevertheless, M. Ö. Seydibeyoğlu et al.[44] showed that addition of 10 wt% ELO to PHBV matrix did not affect the impact absorbed energy that remained almost constant. With regard to the PHB-ESBO system, the impact energy remains almost constant as observed in Fig. 2a. Low plasticizer content up to 5 phr ESBO provides a very slight increase in impact energy but in general terms, ESBO addition leads to invariable impact energy values. J. S. Choi et al.[45] reported that the highest impact absorbed energy for PHBV was reached after addition of 30 wt% ESBO. Similar findings were reported by M. Ö. Seydibeyoğlu et al.[44] by using 20 wt% epoxy soyate to achieve maximum impact absorbed energy values on PHBV. Regarding Shore D hardness values, Fig. 2b shows the evolution in terms of the plasticizer type (ELO and ESBO) and content. As it can be seen, both the addition of ELO and ESBO leads to softer materials with decreasing hardness as the plasticizer content increases. Nevertheless, best efficiency can be detected for ELO as the Shore D hardness values are under those obtained with ESBO for each composition. These results are in total agreement with previous mechanical characterization thus indicating the high efficiency of ELO versus ESBO for PHB plasticization.
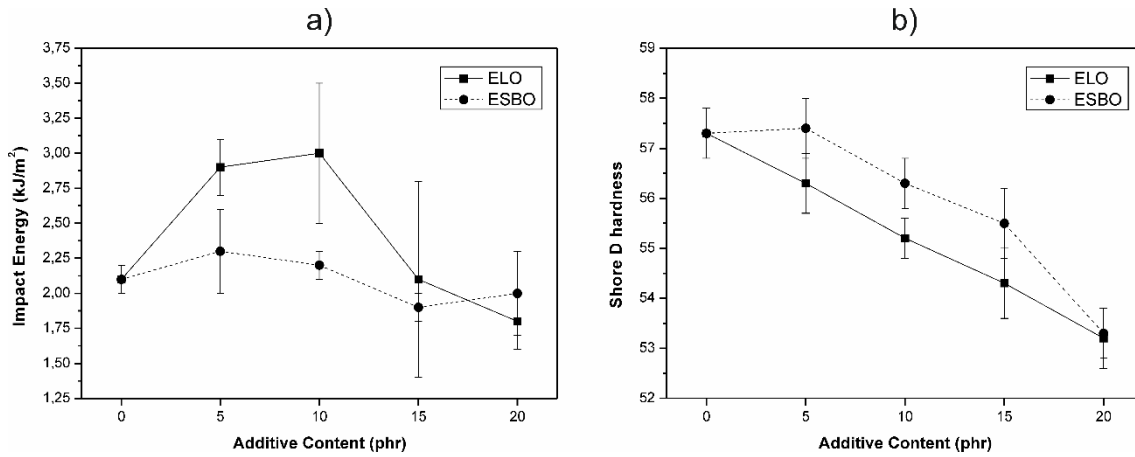
Figure 2. Effect of biobased plasticizers, ELO and ESBO content on (a) impact energy and (b) Shore D hardness of PHB.

Thermal properties of ELO/ESBO plasticized PHB

The influence of both biobased plasticizers, ELO and ESBO, on thermal properties of poly(hydroxybutyrate) was carried out by differential scanning calorimetry (DSC). Table 1 shows a summary of the melt enthalpies (ΔH_m) and the percentage crystallinity (X_c) for different plasticizer formulations. The melt peak of unplasticized PHB is located at 174.8 ºC; a very small peak can also be detected at 52.3 ºC which can be attributed to a low molecular weight additive in the commercial PHB formulation.[53] On the other hand, the glass transition temperature (T_g) of PHB is located at -2.2 ºC approximately and it could not be detected in a clear way by differential scanning calorimetry so that, it was determined by dynamic mechanical thermal analysis (DMTA). With regard to DSC behavior of ELO/ESBO plasticized PHB formulations we observe the same melt peaks described before for neat PHB but it is worth to note a slight decrease in the corresponding values with a change from 174.8 ºC (neat PHB) up to 171.2 ºC (PHB with 10 phr ELO) and 172.2 ºC (PHB with 10 phr ESBO). This is related to an increase in chain mobility with the plasticizer. This same behavior has been reported by different authors that employed epoxidized vegetable oils as

The normalized melt enthalpy (ΔH_m) values of the different plasticized PHB formulations was used to calculate the percentage crystallinity of each formulation as the crystallinity plays an important role in mechanical properties. As it can be seen in Table 1, addition of both ELO and ESBO leads to a slight decrease in crystallinity from 51.9% (unplasticized PHB) up to values of about 46-47% for ELO-plasticized PHB and 47-48% for ESBO-plasticized PHB. The decrease in crystallinity is directly linked to a decrease in mechanical resistant properties as observed previously with tensile strength, Young's modulus and Shore D hardness. Once again, it is evident the best performance of ELO versus ESBO as plasticizer for PHB as the melt peak and the crystallinity provided by ELO are slightly lower than ESBO.

Table 1. Thermal parameters of ELO/ESBO plasticized PHB obtained by differential scanning calorimetry (DSC).

Samples (PHB-Plasticizer type-phr plasticizer)	DSC Parameters			
	$T_{m\ PHB}$ (ºC)	$\Delta H_{m\ PHB}$ (J g^{-1})[a]	$\Delta H_{m\ PHB}$ (J g^{-1})[b]	$X_{c\ PHB}$ (%)
PHB	174.8	-75.8	-75.8	51.9
PHB-ELO-5	172.5	-65.3	-68.6	47.0
PHB-ELO-10	171.2	-61.4	-67.5	46.3
PHB-ESBO-5	172.7	-66.1	-69.4	47.5
PHB-ESBO-10	172.2	-63.3	-69.6	47.7

[a] Values obtained directly from DSC.

[b] Normalized values respect to the real polymer mass weight.

Thermal degradation of unplasticized PHB and ELO/ESBO plasticized PHB was studied by thermogravimetry (TGA). Fig. 3 shows a comparative plot of the TGA curves and derivative curves (DTG) for ELO and ESBO plasticized PHB for 5 and 10 phr as this is the range that can provide attracting plasticized properties as observed in the previous characterization. The main thermal degradation parameters such as onset degradation temperature (T_0), first stage maximum degradation rate temperature (T_{max1}) and second stage maximum degradation rate temperature (T_{max2}) are summarized in Table 2. As it can be observed in Fig. 3a, PHB thermal degradation occurs in two main steps which can be clearly identified in the DTG curves by the presence of two different peaks. This is due to the fact that commercial PHB contains a complex formulation to make it useful at industrial level so that it contains small amounts of plasticizers, nucleating agents, fillers and stabilizers.[53] The addition of both ELO and ESBO plasticizers leads to a noticeable improvement in the thermal stability. This improvement is achieved by the interaction of the epoxidized vegetable oils molecules and the polymer chain thus leading to formation of a thin physical barrier on the surface which obstructs permeability of volatile products towards the exterior and this has a positive effect on thermal degradation delaying.[55] In addition, it is important to remark that epoxidized vegetable oils confer improved thermal stability as they are able to scavenge acid groups by catalytic degradation during degradation thus leading to improved thermal stability as well as light and heat stability.[4, 37, 56]

In the case of ELO-plasticized PHB we observe that the onset degradation temperature (T_0) of neat PHB increases in a remarkable way with the plasticizer content, changing from 246.7 ºC (unplasticized PHB) to 272.3 ºC and 274.7 ºC for an ELO content of 5 phr and 10 phr respectively. With regard to the ESBO-plasticized system

the maximum thermal stabilization is observed for an ESBO content of 5 phr with a degradation onset temperature of 277 ºC. In accordance with this, the maximum degradation rate temperatures are also moved to higher values of both degradation stages. By using ELO/ESBO plasticizers the maximum degradation rate temperatures (T_{max1} and T_{max2}) are moved from 272.3 ºC and 380 ºC to values of 293 ºC and 410 ºC respectively (T_{max1} and T_{max2}) for both ELO and ESBO with very slight changes with the total plasticizer content.
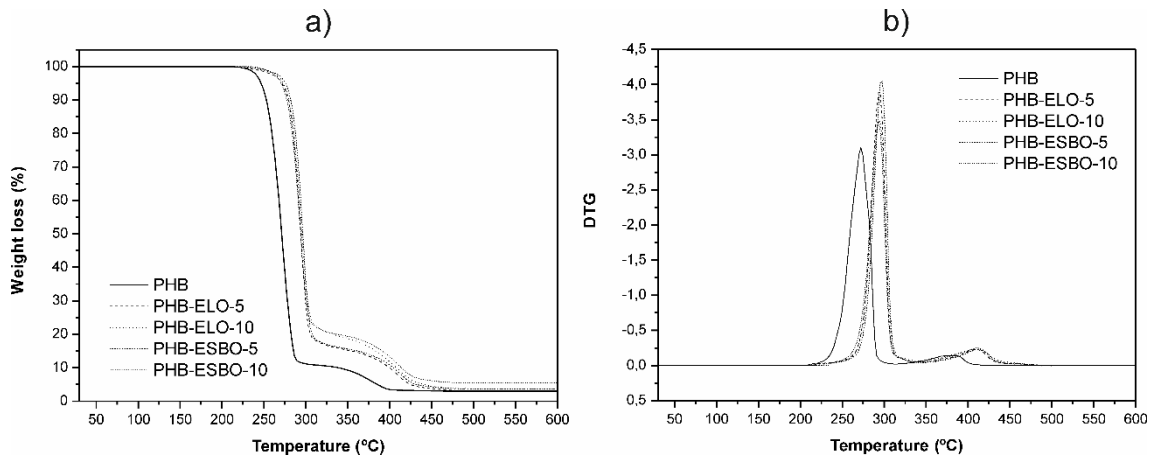

Figure 3. (a) thermogravimetric, TGA curves and (b) differential TG curves (DTG) of PHB formulations plasticized with biobased plasticizers, ELO and ESBO.

Table 2. Characterization of the thermal degradation process of ELO/ESBO plasticized PHB obtained by thermogravimetric analysis (TGA).

Samples (PHB-Plasticizer type-phr plasticizer)	TGA Parameters		
	T_0[a] (ºC)	$T_{max\ 1st}$ (ºC)	$T_{max\ 2nd}$ (ºC)
PHB	246.7	272.3	382.0
PHB-ELO-5	272.3	293.3	410.0
PHB-ELO-10	274.7	293.3	410.0
PHB-ESBO-5	277.0	295.7	412.3
PHB-ESBO-10	272.3	293.3	410.0

[a] T_0, calculated at 5% mass loss.

Morphology of ELO/ESBO plasticized formulations

Field emission scanning electron microscopy (FESEM) was employed to characterize the morphology of PHB formulations plasticized with biobased ELO and ESBO. As it can be seen in Fig. 4a, PHB shows an irregular fracture surface with high roughness areas typical of a brittle behaviour in addition to a porous morphology with many voids. In addition it is possible to observe different immiscible formations due to the chemical formulation of industrial PHB as observed in the thermal degradation.[53] Addition of 10 phr of both ELO and ESBO plasticizers promote a slight change in surface morphology. FESEM images corresponding to PHB with 10 phr ELO (Fig. 4b) and PHB with 10 phr ESBO (Fig. 4c) show a softer topography with less pronounced fracture edges. Furthermore, all the voids seem to have disappeared and the plasticized structures have filled them leading to a more homogeneous fracture surface. It is not detectable phase separation as these compositions (mainly in the case of ELO plasticizer) have given optimum results in terms of mechanical and thermal properties. EVOs containing epoxy groups, which are able to react with terminal hydroxyl groups (OH) of PHB through hydrogen bonds.[3, 56] The high ductile properties that can be achieved by ELO versus ESBO can be related to the more intense interactions that ELO can exert with PHB chains and end groups.
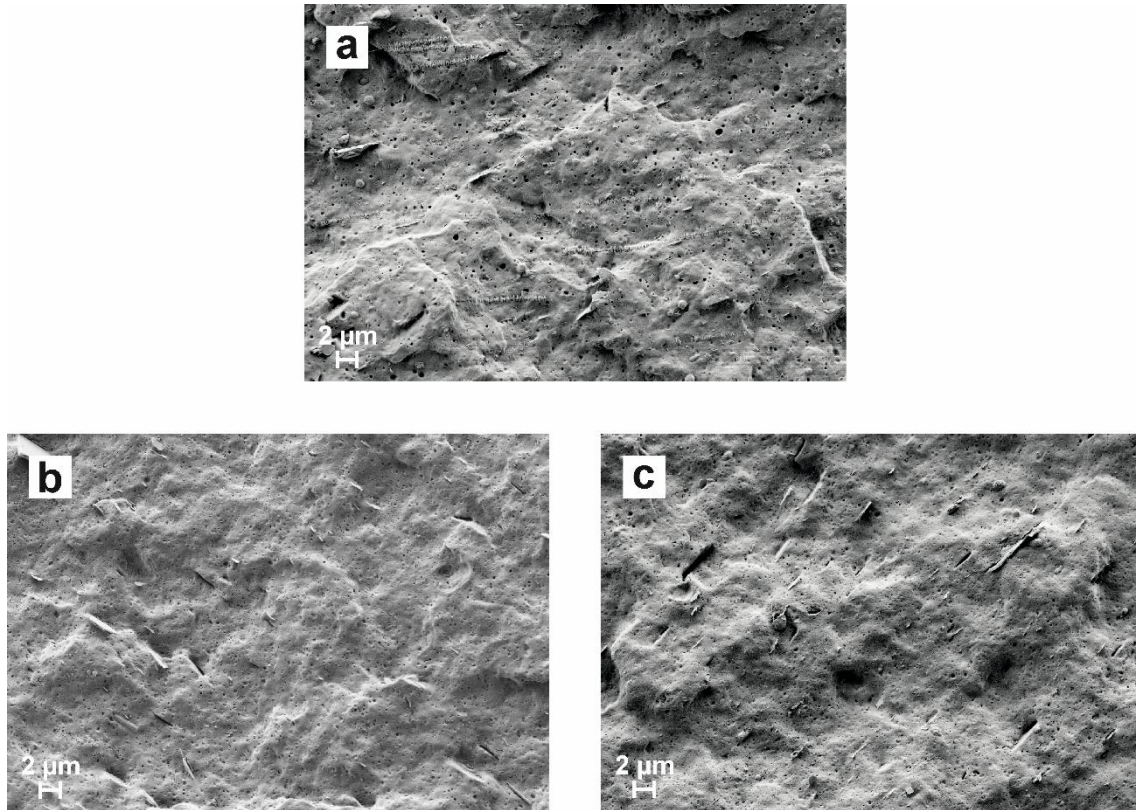
Figure 4. FESEM photographs 2000X of fractured surface of ELO/ESBO plasticized

PHB formulations: (a) unplasticized PHB, (b) PHB with 10 phr ELO and (c) PHB with

10 phr ESBO.

Dynamic mechanical behaviour of ELO/ESBO plasticized PHB formulations

As the best plasticization system is obtained with epoxidized linseed oil (ELO),

dynamic mechanical properties of ELO-plasticized PHB formulations were obtained.

Fig. 5 shows the evolution of the storage modulus (G') and the damping factor (*tan δ*)

of unplasticized PHB and ELO-plasticized PHB with 5 and 10 phr ELO. As it can be

seen, the storage modulus (G') decreases by the addition of ELO plasticizer thus

indicating the clear plasticization effect that ELO provides to the PHB matrix. The

plasticizer promotes chain mobility and this has a positive effect on ductility and

flexibility. In addition the evolution of the storage modulus (G') shows a small step in

the -5 ºC – 0 ºC range which is attributed to the glass transition temperature (T$_g$) of

PHB. The glass transition value can be more accurately determined through the peak of the damping factor (*tan δ*) as it can be seen in Fig. 5b. A clear evidence of the plasticization effect of a particular plasticizer is the reduction of the glass transition temperature toward lower values. The plasticizer increases the free volume and this makes polymer chain interactions of less intensity and promote chain mobility with the subsequent reduction on T_g. As we can see the T_g of unplasticized PHB is close to -2.2 ºC and it is reduced up to values of almost -7 ºC for an ELO content of 10 phr thus indicating good miscibility with PHB in this range composition.[55] This decrease in the glass transition temperature was previously observed by different authors that used epoxidized vegetable oils as biobased plasticizers for biodegradable polymers.[38, 44, 45, 54]
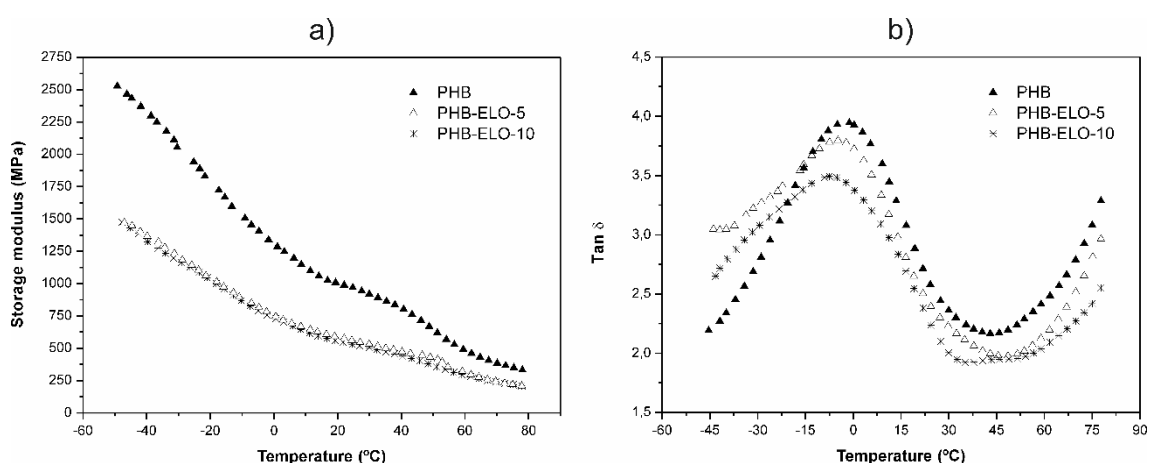

Figure 5. Dynamic mechanical thermal analysis (DMTA) of ELO-plasticized PHB formulations with different plasticizer content. Plot evolution of a) storage modulus (G') and b) damping factor, (*tan δ*) as a function of temperature.

CONCLUSIONS

In this work, new PHB industrial formulations were developed by the addition of biobased plasticizers from vegetable oils. Epoxidized linseed oil (ELO) and epoxidized

soybean oil (ESBO) were added at different loads in the 0 − 20 phr range to PHB to improve its low intrinsic ductility. Fragility and brittleness are two of the main weaknesses of PHB but this work has stated that addition of 10 phr ELO leads to a remarkable increase in elongation at break (percentage increase of about 40%) with regard to neat/as-supplied PHB and this can widen industrial applications of PHB. Although ESBO plasticizer leads to a remarkable decrease in stiffness and tensile strength it does not provide improved elongation at break so that it is not as efficient as ELO for PHB plasticization. Dynamic mechanical thermal analysis also reveals that ELO addition promotes a decrease of the glass transition temperature from -2 ºC to -7 ºC for an ELO content of 10 phr. Even though ESBO does not provide clear and evident plasticization properties, both ELO and ESBO provide an intense thermal stabilization effect with a remarkable increase in the onset degradation temperature from 246 ºC up to values over 270 ºC for ELO and ESBO plasticized PHB formulations and this has a positive effect on processing/manufacturing as PHB is highly sensitive to thermal degradation even at moderate temperatures. So that, we can conclude that addition up to 10 phr of epoxidized linseed oil (ELO) is an environmentally friendly, cost effective and technical solution to overcome the high intrinsic fragility of poly(hydroxybutyrate), PHB and widen its industrial applications.

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TABLE CAPTIONS

Table 1. Thermal parameters of ELO/ESBO plasticized PHB obtained by differential scanning calorimetry (DSC).

Table 2. Characterization of the thermal degradation process of ELO/ESBO plasticized PHB obtained by thermogravimetric analysis (TGA).

FIGURE LEGENDS

Figure 1. Effect of biobased plasticizers, ELO and ESBO content on mechanical properties of poly(hydroxybutyrate), PHB: (a) tensile strength, (b) tensile modulus and (c) elongation at break.

Figure 2. Effect of biobased plasticizers, ELO and ESBO content on (a) impact energy and (b) Shore D hardness of PHB.

Figure 3. (a) thermogravimetric, TGA curves and (b) differential TG curves (DTG) of PHB formulations plasticized with biobased plasticizers, ELO and ESBO.

Figure 4. FESEM photographs 2000X of fractured surface of ELO/ESBO plasticized PHB formulations: (a) unplasticized PHB, (b) PHB with 10 phr ELO and (c) PHB with 10 phr ESBO.

Figure 5. Dynamic mechanical thermal analysis (DMTA) of ELO-plasticized PHB formulations with different plasticizer content. Plot evolution of a) storage modulus (G') and b) damping factor, (*tan δ*) as a function of temperature.