Properties Investigation of Epoxidized Sunflower Oil as Bioplasticizer for Poly (Lactic Acid)

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Research Article

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Abstract

This study aims to improve the ductility of poly (lactic acid) (PLA). For that purpose, bioblends based on PLA and epoxidized vegetable oils (EVO) as bioplasticizers were prepared. Commercial sunflower oil was epoxidized and epoxidized sunflower oil (ESO) was used as plasticizer for PLA. To investigate ESO potential as plasticizer for PLA, its plasticizing effect was compared with commercial epoxidized soya bean oil (ESBO). The plasticizers (ESO or ESBO) were respectively compounded with PLA at 10, 20, 30, and 40 wt%. Mechanical (tensile and Shore D hardness), thermal (differential scanning calorimetry (DSC), thermogravimetric analysis (TGA)) and morphological properties (optical microscopy and scanning electron microscopy (SEM)) were characterized. The results showed that the addition of ESO or ESBO to PLA decreased tensile strength and tensile modulus compared to neat PLA but increased elongation at break for which an optimum (9.02%, 15.55% and 33.67% for ESBO, ESO5.5% and ESO6.5% respectively) was reached at a content of 20 wt% of plasticizer. The structures of the obtained plasticized PLA were confirmed by FTIR spectroscopy. DSC showed a clear decrease in the glass transition temperature of PLA and SEM analysis proved successful modification on the PLA brittle morphology with addition of EVO. On the other hand, TGA results revealed significant increase in the thermal stability. Based on the results of this study, ESO exhibited promising results regarding

Introduction

Research in biodegradable polymers has received increased attention in recent years because of their wide application in environmental friendly packaging. The most popular and biodegradable polymers are aliphatic polyesters, such as poly(lactic acid) (PLA), polycaprolactone (PCL), poly (butylene adipate terephthalate) (PBAT) and polyhydroxybutyrate (PHB).

PLA is a polyester that can be produced from lactic acid derived from renewable resources. It is one of the most frequently used biodegradable polymers, especially in packaging applications because of its high strength, high modulus, good transparency, processability, and biocompatibility. However, PLA is quite brittle, which limits its applications. Considerable efforts have been carried out to improve the properties of PLA so as to compete with low cost and flexible commodity polymers. These attempts include blending PLA with other polymers [1], modifying PLA with plasticizers [2, 3], or blending with mineral fillers composites [4].

Enhancement of the flexibility could be achieved by blending it with low molecular weight plasticizers such as citrate esters [5], polyethylene glycol [6], polypropylene glycol [7] and oligomeric lactic acid [8]. Nowadays, there is increasing interest in the use of natural-based plasticizers that are characterized by low toxicity and low migration. This group includes epoxidized triglyceride vegetable oils from soybean oil [9], cottonseed oil [10], castor-oil [11], sunflower oil [12], and fatty acid esters (FAEs) [13]. Epoxidized vegetable oils have received much attention because they act as reactive plasticizers through the reactivity between epoxy functional groups and the −OH and −COOH groups of PLA [14-17].
Sunflower oil is a renewable resource which was modified by epoxidation [18]. Epoxidized sunflower oil was used as not toxic and environment-friendly additive (thermal stabilizer and plasticizer) in polymer formulations and specially poly vinyl chloride [19-22].

In this study, commercial sunflower oil was epoxidized. The plasticizing effects of epoxidized sunflower oil (ESO) on the properties of PLA were investigated. Performances of ESO on PLA are compared to those of epoxidized soya bean oil (ESBO) in the same conditions.

Experimental

2.1 Materials

PLA (Nature Works 2002D) with an MFI 6.18 g/10 min, density 1.23, T_g 63 °C and T_m 154 °C, as used. Sunflower oil is a commercial product from the company Cévital (Béjaia, Algeria). It was used as received. Epoxidized sunflower oil was especially prepared as described previously [10]. Its level of oxyrane oxygen (O.O) is 5.5% and 6.5%. A commercial epoxidized soya bean oil (ESBO) from Akdeniz Kimya A.S. (Turkey) with O.O of 5.9 % was used for comparison as plasticizer for PLA.

Formic acid (98%) was obtained from Panreac Química SA, hydrogen peroxide (30 wt%) and hydrogen bromide (40 wt%) were purchased from Biochem Chemophama, glacial acetic acid (99.9%) was purchased from ChemLab NV and chloroform analytical grade from Aldrich Co.

2.2 Sunflower oil characterization

Characterization of sunflower oil was carried out according to American Oil Chemists’ Society (AOCS) Official Method. The acid value (AV), saponification value (SV) and iodine value (IV) were determined according to the AOCS Official Method CD 3A-63, AOCS Official Method CD 3C-91 and AOCS Official Method CD 1D-92, respectively. The viscosity was determined according to dynamic viscosity test method (ASTM D 445–79) using a DV-II + Pro Viscometer, Brookfeld Engineering Labs. Inc. Middleboro at 100 rpm with S2, S1 spindles at different temperatures. The relative density was determined according to ASTM D891-09 Test Method B by means of a pycnometer, water content was measured by Karl Fischer titration. Characteristics of sunflower oil are given in Table 1.

Table 1 Main physicochemical properties of sunflower oil
### 2.3 Epoxidation of sunflower oil

Sunflower oil was used as received. The reaction of epoxidation was carried out according to C=C double bond/formic acid/hydrogen peroxide molar ratio of 1/0.5/1.5, the unsaturated compound is mixed with hydrogen peroxide and acetic acid, and the peracid is consumed as it is formed. Sunflower oil and formic acid were poured in a three-necked flask fitted with a mechanical stirrer; the flask was immersed in a water bath with water temperature of 40 °C ± 2 and moderate speed of 1500 rpm. To start the epoxidation, hydrogen peroxide solution (H₂O₂, 30 wt %) was charged dropwise over a period of 15 min to avoid overheating. The reaction continued for a further 4 hours. After that, the oil and aqueous phases were decanted; the organic phase was washed, rinsed and neutralized successively with heated distilled water. A succinct scheme, without taking into consideration the undesired consecutive reactions due to the attack (ring opening) is given in Scheme 1. Titration of oxirane groups (oxirane index) was determined using analytical method [23]; this operation was repeated three times. After the best conditions were determined, two samples of ESOs with 0.0 of 5.5 and 6.5% were prepared.

The characteristics of ESBO and ESO are listed in Table 2.

**Table 2** Properties of ESBO, ESO₅.₅% and ESO₆.₅%

| Sample composition          | ESBO       | ESO₅.₅%   | ESO₆.₅%   |
|-----------------------------|------------|-----------|-----------|
| Oxirane Oxygen (%)          | 5.9        | 5.5       | 6.5       |
| Acid value (mg KOH.g⁻¹)     | 6.2 ± 0.2  | 5.6 ± 0.1 | 5.1 ± 0.2 |
| Iodine value (g I₂/100g oil)| 82.5 ± 1.5 | 106.7 ± 0.2 | 105.3 ± 0.4 |

### 2.4 Preparation of plasticized poly (lactic acid)
Plasticized PLA films were prepared by solution casting method. PLA was first dried overnight in an oven at 40°C. Plasticized PLA films were obtained by dissolving the required amount of PLA in chloroform at room temperature in a stirred flask for 1 h, followed by the addition of the plasticizer, with a dropper and continued stirring for 3 at 4 hours. The PLA / plasticizer mixtures were poured into ceramic dishes with appropriate dimensions (50 x 100 x 60 mm$^3$). Chloroform was evaporated. The plasticizers (ESO (0.0 = 5.5 or 6.5 %) or ESBO) were respectively compounded with PLA at 10, 20, 30, and 40 wt %.

2.5 Plasticized PLA characterization

2.5.1 Tensile testing

Tensile properties were performed at room temperature using MTS Criterion Electromechanical Universal Test System, Model 41 Series 40. The 1 mm plasticized PLA sheets were cut into a dumbbell shape based on ASTM D638 (type V) standard. The test was conducted with a 1.0 kN load cell and a constant crosshead speed of 10 mm.min$^{-1}$. Tensile strength, tensile modulus, and elongation at break were measured. The results obtained represent the average of three measurements for each sample at least.

2.5.2 Hardness Shore D characterization

The shore D hardness test was carried out according to ISO 868 using a Bareiss Shore D Tester. Sheets of 4mm thickness were used for hardness measurements. Three measurements were made on each sample type.

2.5.3 Fourier transform infrared spectroscopy analysis

In order to identify the surface functional groups on the prepared samples, Fourier transform infrared spectroscopy was carried out on a Nicolet iS10 spectrophotometer at high resolution and over 32 scans in the wavelength range between 4000 and 400 cm$^{-1}$.

2.5.4 Differential scanning calorimetry analysis

Differential scanning calorimetry was conducted with a NETZSCH STA 409PC/PG instrument in nitrogen atmosphere; the heating program was from 20 to 200 °C at a heating rate of 10 °C.min$^{-1}$. OriginPro 2018 was used to analyze the curves.

2.5.5 Thermogravimetric analysis

Thermogravimetric analysis measurements were performed using a NETZSCH STA 409PC/PG instrument from 20 to 500 °C at a heating rate of 10 °C.min$^{-1}$ in nitrogen atmosphere.

2.5.6 Optical microscopy analysis

Samples were analyzed by optical microscopy with an OPTIKA® type apparatus piloted by a computer at a magnification of 100 times using a 10/0.40 compound lens and transmitted light.
2.5.7 Scanning electron microscopy analysis

The fracture surfaces of tensile failed sample were studied under a FEI Quanta 650 scanning electron microscopy (SEM) instrument.

Results And Discussion

3.1 Mechanical properties

Tensile properties are the most frequently used indicator of changes caused by plasticization. Results of the tensile measurements, including tensile strength, tensile modulus and elongation at break are displayed graphically in Figures 1, 2 and 3. Figure 1 shows that the addition of gradual amounts of ESBO, ESO\textsubscript{5.5\%} and ESO\textsubscript{6.5\%} plasticizers into PLA matrix improved the tensile strength of PLA. At 20 wt \%, the most efficient plasticizer is the ESO\textsubscript{6.5\%} that reduced tensile strength from 13.3 MPa to 8 MPa. At low loading of 10 wt \% as at high loading of 40 wt \%, there were no significant differences in tensile strength between plasticizers.

Tensile strength of plasticized PLA decreased with increasing amount of plasticizers. At higher plasticizer loading, only a part of the plasticizer was located in the interfacial area, while the rest is penetrated into the polymer mass, separating chains and thus reducing intermolecular forces between them and consequently reducing the tensile strength of the plasticized PLA \cite{24-25}.

The shape of tensile modulus curves is analogous to that of tensile strength. The decrease of tensile modulus indicates an increase in samples’ flexibility due to the diminution of chains interactions induced by the presence of plasticizers.

Neat PLA exhibited an elongation at break of 5 \% (Figure 3). The addition of plasticizers increased elongation at break of PLA. An optimum (9.02\%, 15.55\% and 33.67\% for ESBO, ESO\textsubscript{5.5\%} and ESO\textsubscript{6.5\%} respectively) is reached at a content of 20 wt \% of plasticizer. Beyond that, the addition of

An optimum is reached at a content of 20\% by weight of plasticizer.Un optimum est atteint à une teneur de 20\% en poids de plastifiant. Elongation at break is defined as the ability of film to deform before finally breaking. This parameter helps to determine the flexibility and stretch ability of films. Elongation of polymeric materials depends on the mobility of their molecular chains. The increasing in films elongation can be explained by the fact that plasticizers decrease the intermolecular bonds between polymer chains and substitute them with hydrogen bonds formed between plasticizer and polymer chains. Such disruption and reconstruction of polymer chains interactions reduce the rigidity and promote the flexibility of films by allowing more chains mobility \cite{26, 27}.

Figure 4 shows the evolution of Shore D hardness as a function of plasticizers contents (ESBO and ESO). The addition of plasticizers leads to softer materials with decreasing hardness as the plasticizer content increases. Nevertheless, the best efficiency can be observed for PLA/ESO\textsubscript{6.5\%} by a decrease from 71 to 46
at a level of 20 wt %. These results are in total agreement with previous mechanical characterization, thus indicating the high efficiency of ESO$_{6.5\%}$ versus ESO$_{5.5\%}$ and ESBO for PLA plasticization.

According to the results of mechanical characterization, the use of 20 wt.% EVO reduced the intermolecular interactions between the polymeric chains and increased their mobility improving the flexibility and plastic deformation of PLA.

The most efficient plasticizer is ESO$_{6.5\%}$ at 20 wt % due to more important intermolecular interactions with PLA. In the rest of this study the effect of plasticizers at 20 wt % was investigated.

### 3.2 FT-IR spectroscopy

FT-IR spectroscopy was used to control the known functional group interactions of PLA with epoxidized vegetable oils and compare different plasticized PLA. Yin et al. [28] stressed that when two or more substances are mixed, physical blends versus chemical interactions are reflected by changes in the characteristic spectral bands. **Figure 5** shows the FT-IR spectra of PLA in absence and presence of 20 wt % of ESBO, ESO$_{5.5\%}$ or ESO$_{6.5\%}$ from 500 to 4000 cm$^{-1}$.

Ester group of PLA exhibits characteristic peaks at 1748, 1187 and 1090 cm$^{-1}$ corresponding respectively to C=O stretching vibration, the asymmetrical valence vibrations of C-O-C and symmetrical valence vibrations of C-O-C of the aliphatic chain as Ristić and al. reported [29]. Changes in the position and intensity of these peaks were observed for the blends materials. The peak at 871 cm$^{-1}$ can be assigned to the amorphous phase, while the peak at 756 cm$^{-1}$ can be assigned to the crystalline phase as reported by Younes and Cohn [30]. Similar findings were reported by Auras and al. [31].

A relatively small peak at approximately 3500 cm$^{-1}$ is visible for neat PLA due to the presence of hydroxyl groups. The FTIR spectra indicate that there are interactions between PLA and plasticizers. The characteristic peak of PLA at 1748 cm$^{-1}$ has neutralized at 1752 cm$^{-1}$ with the incorporation of plasticizers, and the peak at 3465 cm$^{-1}$ was shifted to a broad peak at 3500 cm$^{-1}$. Hydrogen bonding could occur between the carbonyl group (from ester linkage) in PLA and the epoxy group in plasticizers [32, 33]. Proposed possible sites for interactions between PLA and ESO are shown in **Scheme 2**.

### 3.3 Differential scanning calorimetry investigation

DSC is a very useful technique to study the glass transition temperature, crystallization temperature, and melting behavior. DSC thermograms of neat and plasticized PLA are shown in **Figure 6**.

Neat PLA showed a clear $T_g$ at 71.81°C. The addition of 20 wt % of ESBO, ESO$_{5.5\%}$ and ESO$_{6.5\%}$ decreased $T_g$ to 69.07°C, 70.31°C and 68.45°C respectively indicating that these plasticizers are miscible with PLA. With similar loading of plasticizers incorporated, ESO$_{6.5\%}$ exhibited relatively the most important effect on $T_g$ which indicates the best plasticizing effect. This decrease in $T_g$ can be explained on the base of increased mobility of the soft segments because of the penetration of plasticizers molecules into PLA.
hard segments [35]. The incorporation of plasticizers at various loadings did not result in any trace of separate melting or crystallization of EVO, indicating that the phase separation of EVO did not occur.

Furthermore, cold-crystallization was chosen as a crystallization method because it leads to a more intense spherulite nucleation resulting in shorter crystallization time and smaller spherulite sizes [35]. Figure 6 shows that neat PLA present a cold-crystallization temperature (T<sub>cc</sub>) at about 124.11°C. T<sub>cc</sub> of PLA decreased by the addition of plasticizers, which suggests that plasticizer enhanced the ability to cold-crystallization of PLA. It is apparent that the (T<sub>cc</sub>) of PLA decreased with plasticizers addition, in parallel with the shift in T<sub>g</sub>. The T<sub>cc</sub> decreased to 113.40 °C, 115.06 °C and 108.43 °C for ESBO, ESO<sub>5.5</sub> and ESO<sub>6.5</sub> respectively. The significant drop of T<sub>cc</sub> and the decrease in T<sub>g</sub> indicates that the EVO are compatible with PLA. The decrease of Tcc and Tg of PLA occurred because of enhanced chains mobility with the plasticizer content [36]. Enhanced chain mobility increased the rate of crystallization, which allowed PLA to crystallize at lower temperature [37].

Neat PLA showed an endothermic peak of melting, T<sub>m</sub> = 145.68 °C. A minor decrease in the melting temperature (3.10 °C for PLA/ESBO, 1.57 °C for PLA/ESO<sub>5.5</sub>% and 0.95 °C for PLA/ESO<sub>6.5</sub>%) was observed, indicating that the melting temperature of PLA was not greatly affected by the addition of plasticizers.

### 3.4 Optical microscopy analysis

To give a clearer view of surface modification of PLA and PLA/EVO blends, surfaces were characterized by optical microscopy. Figures 7(a) to (d) show the optical images of neat PLA, PLA/ESBO, PLA/ESO<sub>5.5</sub>% and PLA/ESO<sub>6.5</sub>%.

Neat PLA (Fig. 10(a)) displays smooth surface as compared with PLA/EVO blends while morphology of plasticized samples is heterogeneous and displays a skin-core distribution. EVO plasticizers are located below PLA skin as droplets in the polymer as it is clearly showed in Figures 7(b) to 7(d). These droplets cause the improvement of the mechanical properties.

### 3.5 Scanning electron microscopy analysis

Scanning electron microscopy analysis shows the surface morphology of the fractured tensile specimens and the state of dispersion of the epoxidized vegetable oils in the PLA matrix. A typical fracture surface of PLA exhibits smooth, homogeneous and a flat surface, corresponding to brittle crack growth behavior [3]. The addition of 20 wt % of epoxidized vegetable oils to PLA results in a significant change in morphology with improved adhesion and interfacial dispersion (Figures 8(b) to (d)). The incorporation of 20 w% EVO didn’t create a brittle fracture, as observed in the neat PLA. Evident signs of plasticization were observed in EVO/PLA samples. However, the presence of fibrils and microvoids was observed indicating the formation of EVO rich phase in PLA matrix by phase separation [38].

### 3.6 Thermogravimetric analysis

The study of plasticized polymers must take into account the impact of the plasticizer on the thermal stability. The thermal degradation of plasticized PLA was investigated by thermogravimetric analysis.
Figures 9(a) and (b) illustrate, respectively, the weight loss and the weight loss derivative of PLA/EVO samples. The corresponding data are given in Table 3.

The thermal stability of a polymeric material depends on the inherent characteristics of the macromolecules as well as on the molecular interactions between the different molecules. The chain cleavage or the bond dissociation of the macromolecules takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective chemical bonds [34]. It is observed that the degradation onset temperatures of PLA/ESBO (290.70°C), PLA/ESO5.5% (292.20°C) and PLA/ESO6.5% (291.20°C) are higher than that of neat PLA (280.40°C). Hydrogen bonding between PLA and EVO increased the thermal stability of plasticized PLA. On the other hand, the weight loss of PLA in presence of ESO5.5% (88.39 %) or ESO6.5% (88.02 %) is similar to that of PLA (86.62 %) and lower than that of PLA in presence of ESBO (90.10 %).

Table 3 Thermogravimetric data of PLA in absence and presence of 20 wt% plasticizer.

|                | PLA     | PLA/ESBO | PLA/ESO5.5% | PLA/ESO6.5% |
|----------------|---------|----------|--------------|-------------|
| $T_{\text{max}}$ (°C) | 280.40  | 290.70°C | 292.20       | 291.20      |
| Weight loss (%) | 86.62   | 90.10    | 88.39        | 88.02       |

$T_{\text{max}}$: temperature of maximum weight loss

Conclusion

From the above results, the following conclusions can be derived:

Mechanical characterization of PLA/EVO samples showed a decrease in tensile strength and tensile modulus, but an increase in elongation at break. The optimum EVO loading with enhanced mechanical properties of PLA was 20 wt %. ESO6.5% was the most effective plasticizer due to more hydrogen bonds with hydroxyl groups of PLA. Furthermore, it exhibited the most important decrease of the glass transition temperature of plasticized PLA. SEM analysis showed successful modification of the PLA brittle morphology with addition of EVO. On the other hand, TGA results revealed significant increase in the thermal stability.

Globally, the results showed that the performances of the epoxidized sunflower oil are similar to those of epoxidized soya bean oil.

Based on the results of this study, ESO exhibited promising results regarding the improvement of the brittleness and overall properties of PLA and can therefore be considered as a potential plasticizer.

Declarations
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