J Mater Sci (2010) 45:1942–1946
DOI 10.1007/s10853-009-4185-1

Properties of epoxidized palm oil plasticized polytlactic acid

**Emad A. Jaffar Al-Mulla · Wan Md. Zin Wan Yunus ·
Nor Azowa Bt Ibrahim · Mohd Zaki Ab. Rahman**

Received: 1 October 2009 / Accepted: 28 December 2009 / Published online: 9 January 2010

Abstract In this study, epoxidized palm oil (EPO) was utilized as a plasticizer for polylactic acid (PLA) using chloroform as a solvent by solution casting process at six weight ratios of PLA/EPO, 95/05, 90/10, 80/20, 70/30, 60/40, and 50/50, respectively. Fourier-transform infrared (FTIR) spectroscopy was used to identify the functional groups of PLA, EPO, and PLA/EPO blends. Thermal stability, mechanical, and morphological properties of the blends were investigated by thermogravimetric analyzer (TGA), tensile properties measurements, and scanning electron microscope (SEM) technique, respectively. The FTIR spectra indicate that there are some molecular interactions by intramolecular hydrogen bond between PLA and EPO. All sets of PLA/EPO blends show high thermal stability and significant improvement of mechanical properties compare to pure PLA. The highest elongation at break (about 210%) was obtained when the ratio of PLA/EPO blend was 80/20. Morphological results of PLA/EPO blends show that ESO was good miscible with PLA.

Introduction

Biodegradable polyesters have attracted much attention due to their biodegradability and biocompatibility which offer clear advantages for both customers and environment. Polylactic acid (PLA) is one of the most promising candidates as partial alternative of petrochemical polymers because it is biodegradable and produced from renewable resources [1].

In addition to its application in textile industries, automotive and clinical uses, PLA represents a good candidate to produce disposable packaging due to its good mechanical properties and processability [2–4]. However, high tensile, high modulus, low elongation at break, and high price limit its application. Therefore, the tailoring of its properties to reach end-users demands is required.

Attempts have been made to enhance the flexibility and other mechanical properties by blending of PLA with other polymers such as polycaprolactone, polybutylene succinate, or polyetherurethane [5–8]. Low molecular weight plasticizers such as polyethylene glycol, polypropylene glycol, and citrate esters were also used to improve of the mechanical properties of PLA [9–12].

Epoxidized palm oil (EPO) is an epoxidized derivative of a mixture of esters of glycerol with various saturated and unsaturated fatty acids. It is important for many chemical industries as they are derived from renewable, biodegradable, environmental friendly and easily available raw materials.

The inherent low iodine value of the oil and the low compatibility of epoxidized oil with polymers have some shortcomings which restrict applications of EPO as plasticizer [13]. On the contrast, other epoxidized oils such as soybean oil are widely utilized as plasticizers. Ali et al. reported that epoxidized soybean oil was used as a plasticizer for PLA to improve flexibility [14]. They found that thermal and SEM analysis revealed that epoxidized soybean oil is partially miscible with PLA. Rheological and mechanical properties of PLA/epoxidized soybean oil blends were studied by Xu et al. [15]. Epoxidized soybean oil exhibits positive effect on both the elongation at break and melt rheological characterization.

E. A. J. Al-Mulla (✉) · W. Md. Z. W. Yunus ·
N. A. B. Ibrahim · M. Z. Ab. Rahman
Department of Chemistry, Faculty of Science, Universiti Putra
Malaysia, 43400 UPM Serdang, Selangor, Malaysia
e-mail: emadaalmulla@yahoo.com

In present study, EPO was used as a plasticizer for PLA via solution casting process using chloroform as a solvent. The aim of this study is to investigate the effects EPO on thermal stability, mechanical, and morphological properties of PLA as well as investigation of interaction between PLA and EPO in the blend.

Experimental

Materials

EPO was provided by Advanced Oleochemical Technology Division (AOTD), Malaysia. PLA and chloroform were purchases through local suppliers from Nagoya, Japan and Merck, Germany, respectively.

Preparation of PLA/EPO blends

The required amounts of PLA and EPO were dissolved in 50 mL chloroform separately. The EPO solution was then transferred into the PLA solution with a dropper and continuous stirring. After all the EPO solution was transferred into the PLA solution, the resultant mixture was then stirred for 1 h. After that, the mixture was refluxed for 2 h. The PLA/EPO blend was poured into a Petri dish and left to dry. The amount of PLA to EPO used in this study is listed in Table 1.

Viscometery measurement

Measurement of viscosity was performed by an Ubbelohde type viscometer. According to Huggin's equation (1), the reduced viscosity values (η_{red}) was calculated and plotted versus concentration of PAL/EPO blend in the solution [16].

$$\eta_{\text{red}} = \frac{t - t_{\text{o}}}{t_{\text{o}} C}, \qquad (1)$$

where t is the flow time of the PLA/EPO blend solution, t_o is the flow time of the pure solvent, and C is the concentration of PAL/EPO blend in the solution.

Table 1 The amount of the PLA/EPO blends

Sample identity	Weight of PLA (g)	Weight of EPO (g)
Neat PLA	5.00	0.00
95PLA 05EPO	4.75	0.25
90PLA 10EPO	4.50	0.50
80PLA 20EPO	4.00	1.00
70PLA 30EPO	3.50	1.50
60PLA 40EPO	3.00	2.00
50PLA 50EPO	2.50	2.50

Fourier-transform infrared (FTIR) spectroscopy

The FTIR spectra of the blends samples were recorded by the FTIR spectrophotometer (Perkin Elmer FT-IR-Spectrum BX, USA) using KBr disc technique.

Tensile properties

The tensile strength, tensile modulus, and elongation at break were measured by using Instron Universal Testing Machine 4301 at 5 mm/min of crosshead speed in accordance to ASTMD638 [17]. Seven samples were used for the tensile test and an average of five results was taken as the resultant value.

Scanning electron microscopy (SEM)

The morphology of tensile fracture surface of the blend was observed by SEM at room temperature. A JEOL (model JSM-6300F) SEM with field emission gun and accelerating voltage of 5 kV was used. A gold coating of a few nanometres in thickness was coated on tensile fracture surfaces.

Thermogravimetric (TG) analysis

The thermal stability of the samples was studied by using Perkin Elmer model TGA 7. Thermogravimetric analyzer (TGA) was used to measure the weight loss of the samples. The samples were heated from 30 to 800 °C with the heating rate of 10 °C min^{-1} under nitrogen atmosphere at the flow rate of 20 mL min^{-1}.

Results and discussion

The FTIR spectra of PLA, EPO, and PLA/EPO blends are shown in Fig. 1. The peaks located at 2,984, 2,926, and 1,744 cm^{-1} of PLA and 2,906, 2,845, and 1,733 cm^{-1} of EPO were assigned to the stretching vibration of $-\text{CH}_2$ and vibration of $-\text{C{=}O}$ bonds, respectively; while in the blend materials these peaks were found in the neutralized regions of 2,910, 2,848, and 1,741 cm^{-1}. This result is in agreement with Kim and Choi that shows the peaks of infrared were shifted due to the interaction between polymethyl methacrylate and phenoxy in their blend [18]. In addition, it could be observed that with the increasing content of EPO, the relative strength of peaks 1,910 and 2,848 cm^{-1}, which belongs to PLA content decreased.

The FTIR result indicates that there are some molecular interactions between PLA and EPO. It was believed that hydrogen bonding could form between the ester group of PLA and the oxirane group of EPO [15]. The interaction

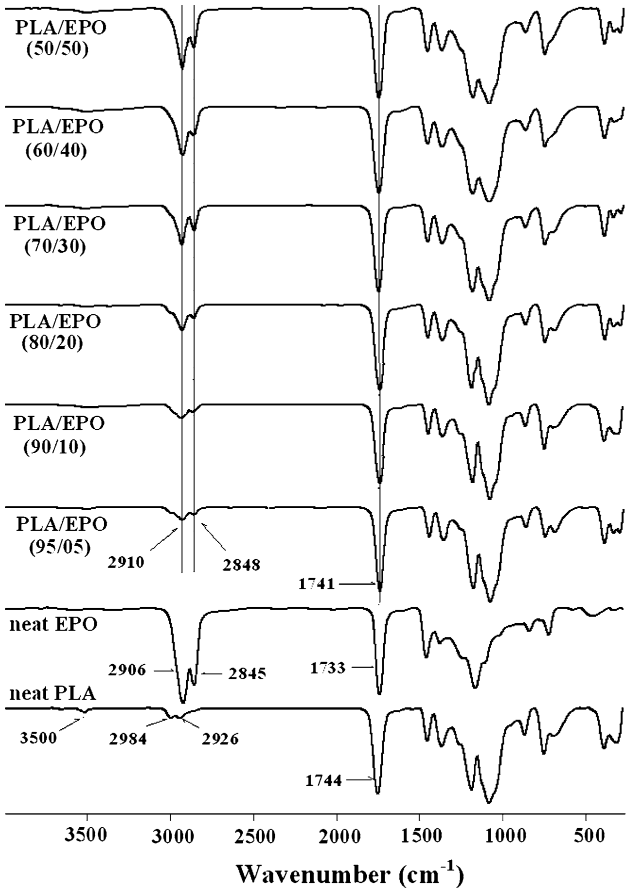
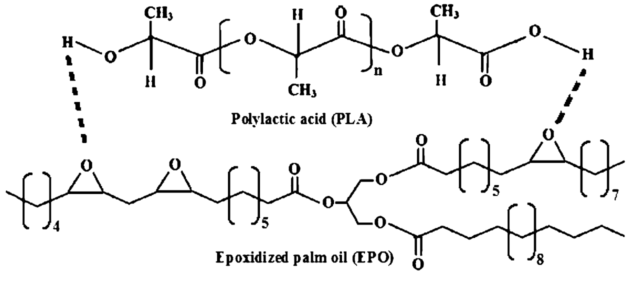


Fig. 1 The FTIR spectra: PLA EPO and PLA/EOP blends

between PLA and EPO may also be attributed to the possible hydrogen bonding that occurs between the oxirane group in EPO and the small amount of terminal hydroxyl groups in the PLA main chain [19]. A proposed possible site for interaction between PLA and EPO is shown in Scheme 1. FTIR spectrum of the neat PLA supports this claim which shows peak at 3,500 cm^{-1} (hydroxyl group stretching). It was observed that this characteristic peak of PLA has disappeared with the incorporation of EPO.

Neat PLA sample exhibits a tensile strength of approximately 25 MPa. The addition of 5% EPO to PLA caused a reduction in tensile strength for the blend of PLA/EPO to around 23 MPa. The tensile strength of plasticized PLA decreased with increasing amounts of plasticizer; eventually losing about 72% of its initial strength with 50% plasticizer (Fig. 2a).



Scheme 1 Proposed chemical interactions (intramolecular hydrogen bonding) between PLA and EPO

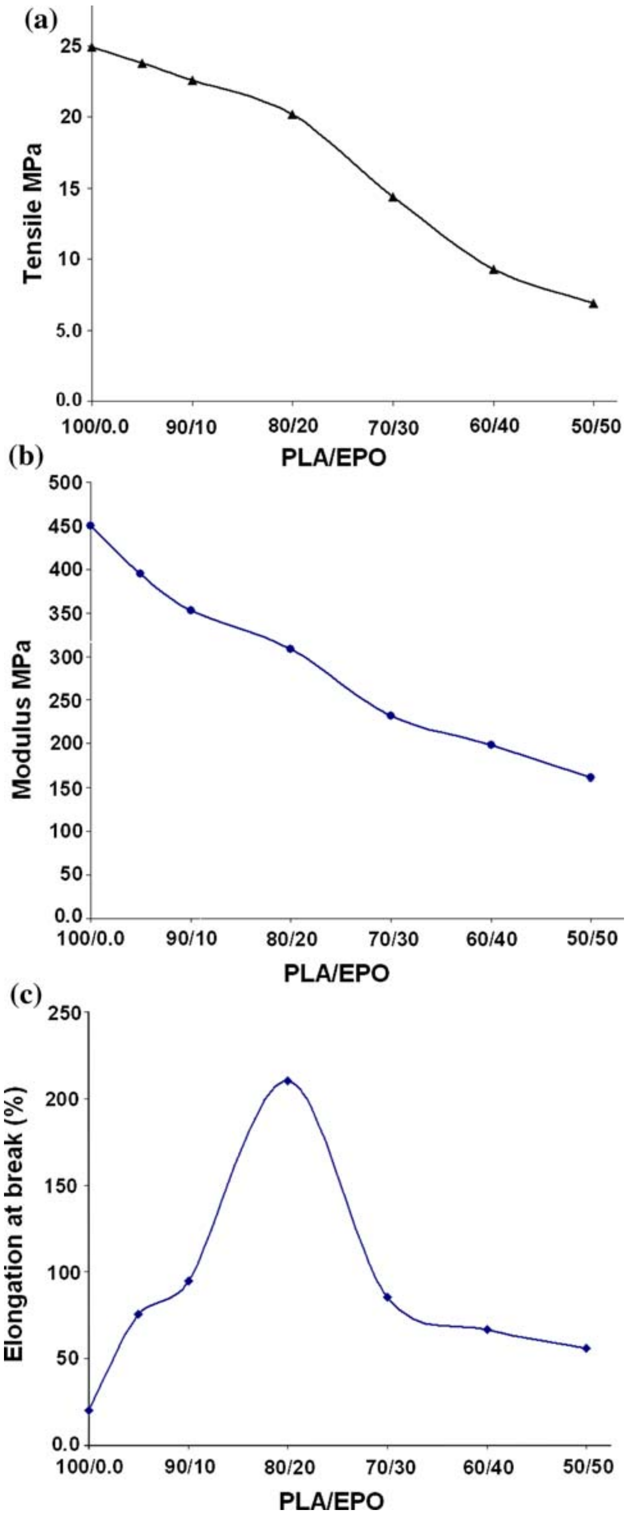


Fig. 2 Mechanical properties of PLA/EPO blends: **a** tensile strength, **b** modulus strain, and **c** elongation at break

Measuring the slope of Young's modulus curve is the common method of determining the stiffness [20]. Figure 2b shows Young's modulus curve of pure PLA and PLA/EPO blends. Neat PLA exhibits a modulus value of 450 MPa, and the addition of EPO significantly decreases the stiffness. It was evident that the increase of EPO from 5 to 50% leads to the decrease of the modulus value to 390 and 160 MPa, respectively.

Figure 2c shows the elongation at break as a function of neat PLA and amount of EPO in the blend. Neat PLA exhibits an elongation at break value of 43%. It increases with the addition of EPO. The highest elongation at break (210%) is observed with 20% EPO. Further addition of EPO causes the decrease of elongation at break which made the blend to be more brittle.

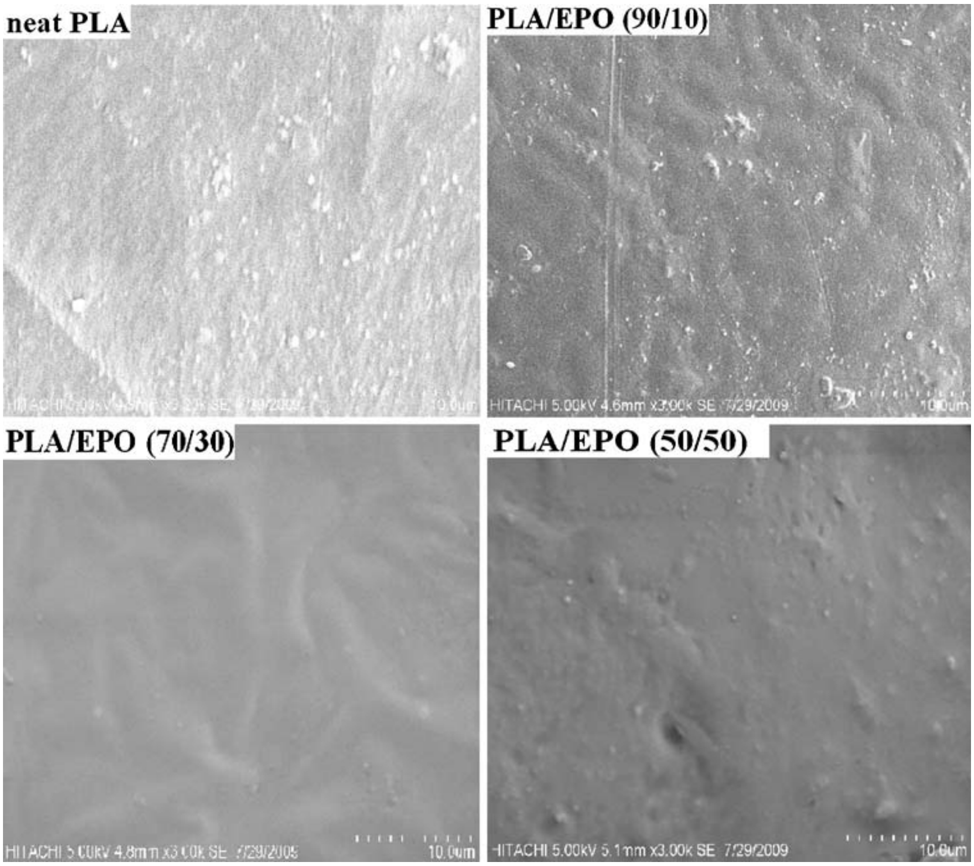
It is known that the mechanical properties of immiscible polymer blends are dependent on their morphologies [21]. The relation between mechanical properties and morphology for the blend of PLA and epoxidized soy bean oil was investigated [14]. Phase morphology of the neat PLA and PLA/ESO blends were assessed by SEM. The SEM image of the neat PLA and PLA/ESO blends are shown in Fig. 3. SEM of PLA/EPO blends micrographs show very good compatible morphologies without the edge, cavity, and holes resulting from poor interfacial adhesion. It is possible that the good adhesion of these blends is due to molecular interactions between PLA and EPO that could create hydrogen bonds.

Different phase morphology was observed in PLA/epoxidized soybean oil blends in which low molecular weight epoxidized soybean was accumulated during phase separation and form microvoids in the PLA matrix [14].

The typical plot of reduced viscosities as a function of PLA/EPO blends concentrations in solutions are presented in Fig. 4 which shows the effects of EPO on viscosity of PLA. It can be observed that the increase of EPO percentage in PLA solution causes decrease of reduced viscosity. The figure also shows a lower reduced viscosity with increase the concentration in all sets of EPO/PLA blends.

Thermogravimetric analysis was used to study the thermal stability of PLA/EPO blends by measuring their thermal decomposition temperature at the onset and end of weight loss. Higher decomposition temperature means better thermal stability for the blends. The thermal decomposition temperature at the onset and end of weight loss for PLA/EPO blends was shown in Fig. 5. With the addition of EPO, the thermal stability of PLA component was increased. For example, the onset of PLA increased from 236.41 to 283.32 °C and the end of decomposition

Fig. 3 SEM micrographs of fracture surfaces of neat PLA and PLA/ESO blends



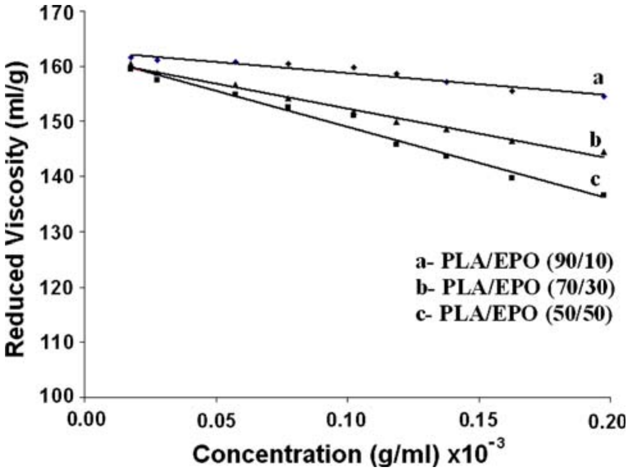


Fig. 4 Reduced viscosities plot of PLA/EPO blends as a function of concentration for the blend in the solution

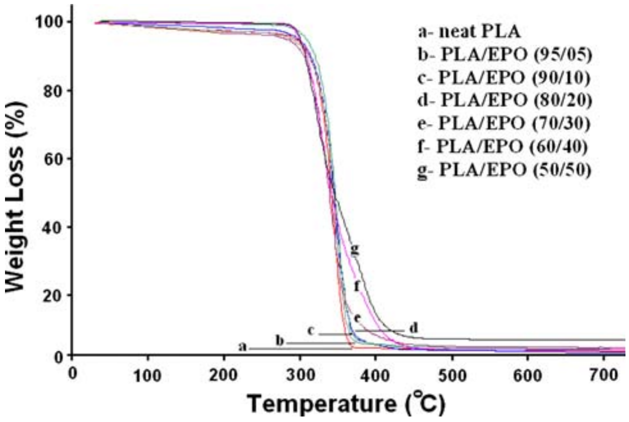


Fig. 5 TGA thermograms of neat PLA and PLA/EPO blends

process increased from 369.87 to 455.25 °C when the weight component of EPO increased from 0.0 to 30% (Fig. 5c). The increase of thermal stability of PLA came from the effect of EPO. With the addition of EPO, the molecular chain of PLA was restricted, which would increase the thermal stability of PLA due to reducing its heat sensitivity [22].

Conclusion

This article describes plasticization of PLA by new plasticizer (EPO) via solution casting process using chloroform as a solvent. The results indicate that improved flexibility could be achieved by incorporation of EPO. FTIR spectroscopy shows some molecular interactions by intramolecular hydrogen bond between PLA and EPO. High thermal stability and significant enhancement of mechanical properties were observed for PLA/EPO blends compare to pure PLA. SEM micrographs of PLA/EPO blends show good compatible. Due to viscometery measurements, reduced viscosities of the blends were decrease with increase amount of EPO.

Acknowledgements All the technical staffs in the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia are greatly acknowledged for their assistance.

References

1. Lemmouchi Y, Murariu M, Santos AMD, Schacht AJAE, Dubois P (2009) Eur Polym J 45:2839
2. Murariu M, Ferreira AS, Pluta M, Bonnaud L, Alexandre M, Duboi P (2008) Eur Polym J 44:3842
3. Auras RA, Singh SP, Singh JJ (2005) Packag Technol Sci 18:207
4. Auras RA, Harte B, Selke S, Hernandez R (2003) J Plast Film Sheeting 19:123
5. Nijenhuis AJ, Colstee E, Grijpma DW, Pennings AJ (1996) Polymer 37:5849
6. Liu LJ, Li SM, Garreau H, Vert M (2000) Biomacromolecules 1:350
7. Lopez-Rodriguez N, Lopez-Arraiza A, Meaurio E, Sarasua JR (2006) Polym Eng Sci 46:1299
8. Li Y, Shimizu H (2007) Macromol Biosci 7:921
9. Baiardo M, Frisoni G, Scandola M, Rimelen M, Lips D, Ruffieux K, Wintermantel E (2003) J Appl Polym Sci 90:1731
10. Ogata N, Sasayama H, Nakane K, Ogihara T (2003) J Appl Polym Sci 89:474
11. Kulinski Z, Piorkowska E (2005) Polymer 46:10290
12. Ren Z, Dong L, Yang Y (2006) J Appl Polym Sci 101:1583
13. Gan LH, Ooi KS, Goh SH, Gan LM, Leong YC (1995) Eur Polym J 31:719
14. Ali F, Chang Y, Kang SC, Yoon JY (2009) Polym Bull 62:91
15. Xu Y, Qu J (2009) J Appl Polym Sci 112:3185
16. Ovejero G, Perez P, Romero MD, Guzman Dıez E (2004) Eur Polym J 43:1444
17. ASTM D638-03 (2004) Standard test method for tensile properties of plastics
18. Kim BK, Choi CH (1996) Polymer 37:807
19. Yew GH, Yusof AMM, Ishak ZAM, Ishiaku US (2005) Polym Degrad Stab 90:488
20. Finkenstadt VL, Liu CK, Cooke PH, Liu LS, Willett JL (2008) J Polym Environ 16:19
21. Dell'Erba R, Groeninckx G, Maglio G, Malinconico M, Migliozzi A (2001) Polymer 42:7831
22. Lee SN, Lee MY, Park WH (2002) J Appl Polym Sci 83:2945