Polymer Bulletin 62, 91–98 (2009)
DOI 10.1007/s00289-008-1012-9

Polymer Bulletin

Thermal, mechanical and rheological properties of poly (lactic acid)/epoxidized soybean oil blends

Fathilah Ali,[1] Young-Wook Chang (✉),[1] Shin Choon Kang,[1] Joon Yong Yoon[2]

[1] Department of Chemical Engineering, Hanyang University Ansan, Kyunggi-Do, Korea
[2] Department of Mechanical Engineering, Hanyang University Ansan, Kyunggi-Do, Korea

Received: 7 July 2008 / Revised version: 6 October 2008 / Accepted: 6 October 2008

Summary

Poly(lactic acid) (PLA) was melt blended with epoxidized soybean oil (ESO) in an internal mixer and thermal, mechanical and rheological properties of the blends were investigated by means of differential scanning calorimetry, dynamic mechanical analysis, tensile test and small amplitude oscillatory shear rheometry. ESO lowered glass transition temperature and increased the ability of PLA to cold crystallization. The blend exhibited improved elongation-at-break along with a plastic deformation. The plasticization effect by ESO was also manifested by the lowering of dynamic storage modulus and viscosity in the melt state of the blends compared with neat PLA.

Introduction

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester derived from lactic acid, which can be obtained from the fermentation of renewable resources. Since the development of an effective process for the mass production of PLA by Cargill Dow, it has received considerable attention as a promising environmentally friendly material suitable for replacing commodity polymers, particularly in disposable packaging applications [1-3]. In spite of many attractive properties of PLA such as high strength, high modulus, biodegradability and processibility, their engineering applications have been limited due to its brittleness and high price. Considerable efforts have been conducted to modify the properties of PLA. Blending of PLA with other polymers such as polycaprolactone, polybutylene succinate or polyetherurethane has been attempted to improve the flexibility of PLA [4-8]. Enhancement of the flexibility could also be achieved by blending it with low molecular weight plasticizers such as citrate esters, polyethylene glycol, polypropylene glycol and oligomeric lactic acid [9-16]. The plasticization effects were also manifested by a shift of glass transition to lower temperature and an increase in ability of PLA to cold crystallization.

Epoxidized soybean oil (ESO) is an epoxidized derivative of a mixture of esters of glycerol with various saturated and unsaturated fatty acids. It originates from a renewable resource and therefore is biodegradable. ESO has mainly been used as a plasticizer for polyvinyl chloride (PVC) compounds and chlorinated rubbers to improve stability and flexibility.[17] Recently, Choi reported that ESO is an effective plasticizer for a biodegradable bacterially synthesized poly(3-hydroxy butyrate-co-3-

hydroxyvalerate) (PHB-HV) by depressing glass transition temperature as well as increasing elongation at break and impact strength of the polymer [18].
In this study, we prepared PLA/ESO blends by melt blending and examined their thermal, mechanical and rheological properties.

Experimental

Materials and Preparation of Blends

PLA, with a molecular weight (M_w) of approximately 148,000 g/mol and a poly dispersity index of 1.9, was procured from Cargill-Dow, and epoxidized soybean oil (ESO, epoxide content=6.9 wt %) was procured from Shindongbang Co, Korea. Prior to blending, both the PLA and ESO were dried overnight at 40°C in vacuum. The PLA was melt-blended with various amounts of ESO (5, 10, 20 and 30 parts per hundred (phr) of PLA) in a Haake internal mixer at 180°C with a rotor speed of 60 rpm. The blends were then compression-molded using a hot press at 180°C for further characterizations.

Characterizations

DSC analysis was carried out using a TA 2010 thermal analyzer in the temperature range of 0°C -200°C at a heating rate of 10°C/minute. Dynamic mechanical tests were performed by using a dynamic mechanical analyzer (TA instrument 2980). Samples were subjected to a dual cantilever with an amplitude of 0.2% at a frequency of 1 Hz. The temperature was increased at a heating rate of 2°C/min over a range from 0°C to 140°C. Tensile properties were measured using a Universal testing machine (United Co, STM 10E) at 25°C at a crosshead speed of 5 mm/min according to ASTM D638. We tested several samples to achieve good error reduction. The blend morphology was examined by SEM (JEOL JSM-630F). The sample was prepared by fracturing the compression molded specimen cryogenically. Melt rheological properties were examined using small amplitude oscillatory shear rheometer (RMS 800 instrument). The dynamic oscillatory shear measurement was performed at 180°C using a set of 25 mm diameter parallel plates and a sample of 1-2 mm thickness. Dynamic strain sweep experiments were performed to determine the limits of linear viscoelastic properties of the melts at a frequency of 10 rad/s. The frequency sweep experiments were also carried out within the frequency range of 0.1-100 rad/s at a strain of 5% (it is well within the linear viscoelastic range) to determine frequency dependence of storage modulus, $G'(\omega)$, and complex viscosity, $\eta^*(\omega)$ of the melts.

Results and discussion

Figure 1 illustrates the DSC thermograms of neat PLA and PLA/ESO blends resulted from heating scan of sample which was obtained by cooling non-isothermally from its melt state. We observed glass transition, cold crystallization and melting transition in the thermograms. The various DSC parameters are summarized in Table 1. It can be seen that a single glass transition (T_g) appeared for PLA/ESO blend at a lower temperature than that for the neat PLA and it gradually decreased to lower temperature with the increasing ESO content in the blend. The T_g decreased from 60.3°C of neat PLA to 51.3°C for PLA/ESO (100/30) blend. But, there was no more

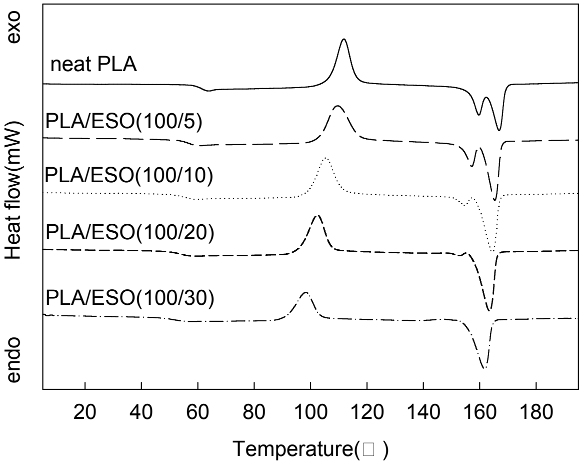


Figure 1. DSC thermograms of neat PLA and PLA/ESO blends.

Table 1. Thermal properties of neat PLA and PLA/ESO blends

Samples	T_g * (°C)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
neat PLA	74.2	60.4	111.9	39.5	159.6	166.8	37.4
PLA/ESO(100/5)	70.8	56.2	109.5	39.1	157.2	165.4	36.9
PLA/ESO(100/10)	69.7	54.3	105.4	38.5	154.7	164.5	35.0
PLA/ESO(100/20)	68.0	52.1	102.4	37.1	152.9	163.5	33.3
PLA/ESO(100/30)	67.4	51.3	99.8	34.4	-	161.8	31.2

*Obtained from DMA measurement

decrease in T_g with the higher ESO content. This indicates that ESO is partially miscible with PLA. Thermoplastic polyesters bearing carboxyl end groups have indeed reported to be miscible with epoxy resins when they are mixed at high temperature [19,20]. It can also be seen from the DSC thermograms that the cold crystallization temperature (T_{cc}) of PLA gradually decreased by the addition of ESO, which suggests that ESO enhances the ability to cold crystallization of PLA. It is apparent that the cold crystallization temperature of PLA decreases in parallel with the shift in T_g. Such decreases in T_g and an enhanced cold crystallization process are commonly observed for plasticized PLA systems and are due to the increased segmental mobility of the PLA chains by plasticization [14,15].

Two melting endotherms were found in neat PLA and PLA/ESO blends in the DSC thermograms. This behavior is attributed to the formation of crystallites with different sizes and perfection which is arised by lamellar rearrangement during crystallization of PLA [4, 15]. It can be noted from the thermograms that the melting temperature of the lower peak and its size gradually decreased with the increased ESO content in the blend, which indicates that ESO made crystallization of PLA more easy and complete.

Variations of dynamic storage modulus (E′) and tan δ of the samples with temperature are shown in Figure 2 and Figure 3, respectively. The lower storage modulus of the PLA/ESO blends compared to neat PLA can be seen in Figure 2, indicating an increase in the flexibility of PLA imparted by the ESO. And, the storage modulus of the blends decreased with increased ESO content below 80°C. There was a large drop of the storage modulus around 60-80°C corresponding to the glass transition region, and then it started to rise around 90°C. Such a rise in E′ is due to crystallization on heating (cold crystallization), and the temperature at which E′ starts to rise decreased with the ESO content in the blends. Figure 3 also shows that T_g determined from the tan δ peak were shifted to a lower temperature with an increasing ESO content in the blends (Table 1). These results are consistent with the DSC results.

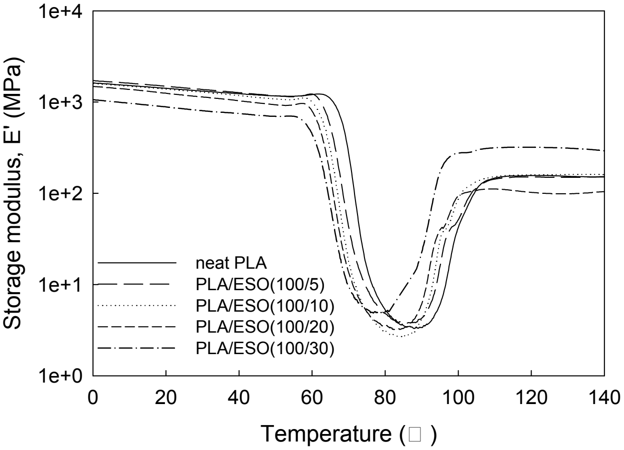


Figure 2. Dynamic storage modulus of neat PLA and PLA/ESO blends as a function of temperature.

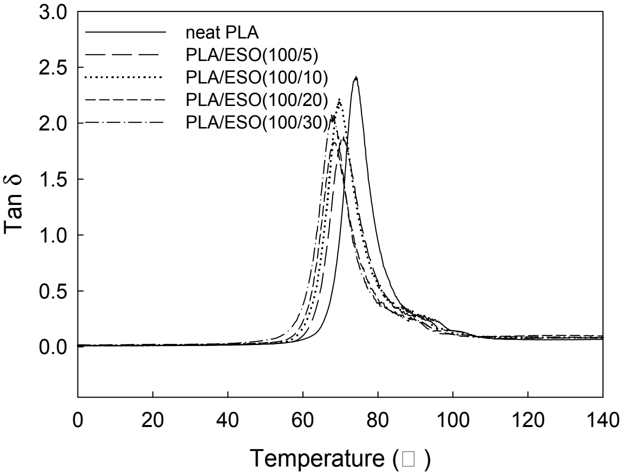


Figure 3. Tan δ of neat PLA and PLA/ESO blends as a function of temperature.

Phase morphology of the PLA/ESO blends was examined by SEM, and the SEM image of the PLA/ESO blends is shown in Figure 4. Empty microvoids were observed in the blends indicating a formation of ESO rich phase in PLA matrix by phase separation. Similar phase separated morphology was also observed in PLA/PPG

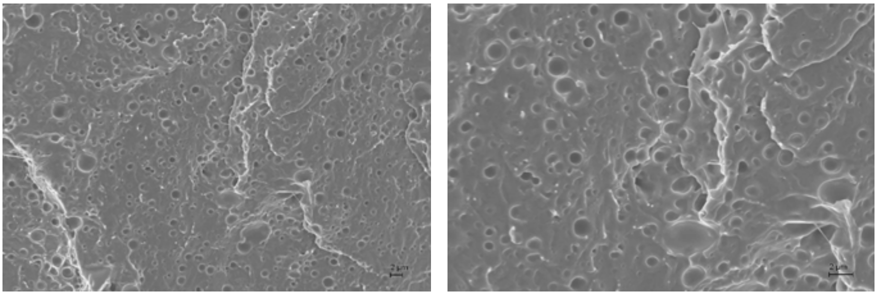

(a) (b)

Figure 4. SEM micrographs of fracture surfaces of PLA/ESO blends: (a) 100/10 (b) 100/20.

blends in which low molecular weight PPG was accumulated during phase separation and form microvoids in the PLA matrix [15].

The stress-strain curves of neat PLA and PLA/ESO blends are shown in Figure 5. It can be seen that neat PLA is fractured at low strain before a yielding, whereas the blends exhibited a ductile behavior with yielding and a subsequent plastic deformation. And, the blends exhibited a stress-whitening during tensile deformation (Figure 6). This stress whitening has also been observed in other plasticized PLAs and is originated from the void formation due to crazing [10,14]. The elongation-at-break was increased to 38% with 20 phr of the ESO. Such a neat increase in elongation-at-break of PLA/ESO blends despite of their relatively high T_g is believed to be due to the local plasticization by microdroplets of low molecular weight ESO dispersed in PLA matrix, as discussed by Piorkowska et al to explain the tensile behavior of PLA plasticized by PPG of 1000 g/mol [15].

The increased flexibility of the PLA/ESO blends was accompanied with a decrease in tensile strength, yield stress, and modulus. The yield stress, for example, decreased from 60 MPa for neat PLA to 26 MPa for the blend containing 20 phr ESO. The

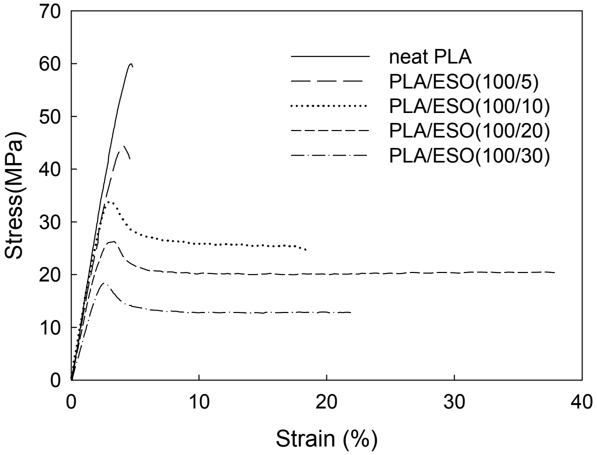
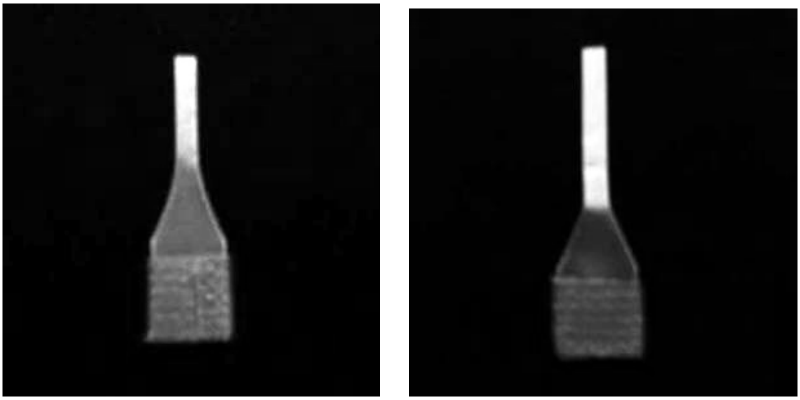


Figure 5. Stress -strain curves of neat PLA and PLA/ESO blends.



(a) PLA/ESO(100/10) (b) PLA/ESO(100/20)

Figure 6. Visualization of deformed samples under tensile test.

increase of ESO content to 30 phr further decreased the yield stress to about 18 MPa, but the elongation-at-break become smaller. Results on these thermal and tensile properties suggest that ESO is compatible with the semicrystalline PLA and act as a plasticizer.

Dynamic melt rheological properties of neat PLA and PLA/ESO blends were also investigated to see the microstructure and melt processibility of the blends. Dynamic strain sweep measurements were conducted first at 180°C and a frequency of 10 rad/s to determine the linear viscoelastic region of PLA and PLA/ESO blends. The results are displayed in Figure 7. It can be seen that storage modulus decreases with the addition of ESO, and the linear viscoelastic limit is about 30% for neat PLA melt and it is extended to higher deformation in the blends. Therefore, the linear melt rheological analysis was conducted at a strain of 5%.

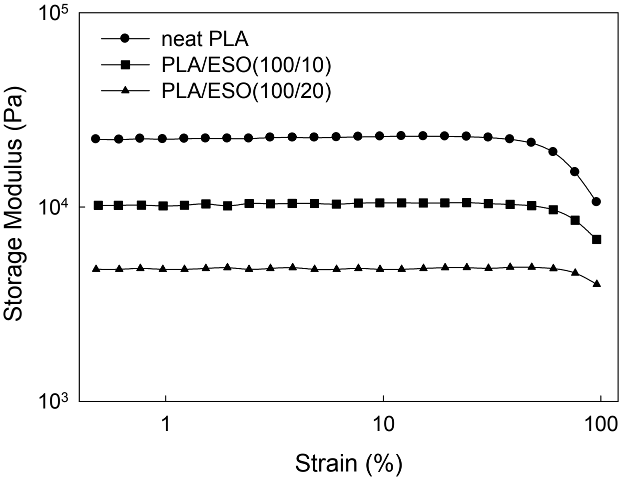
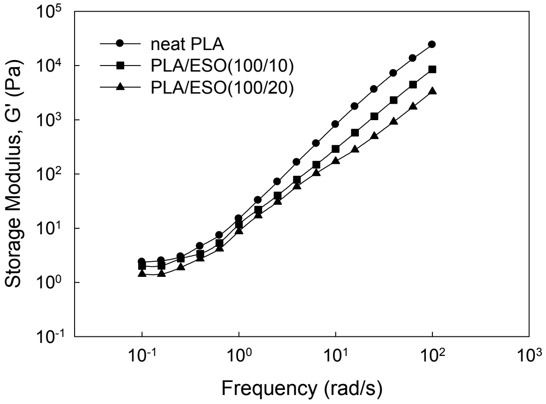
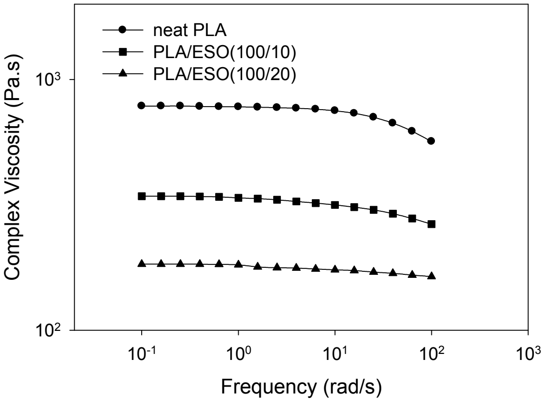


Figure 7. Dynamic strain sweep tests of neat PLA and PLA/ESO blends in molten state at 180°C.

Figure 8(a) and (b) present the frequency dependences of dynamic storage modulus (G') and complex viscosity(η*) of neat PLA and PLA/ESO blends in the molten state, respectively. The terminal zone slope of neat PLA melt at lower frequency region, less than 10 rad/s, obtained from Figure 8(a) is about 1.72, which is in consistency with the value reported by other researchers [21,22]. G' of the blends shows lower values compared with that of neat PLA over the entire frequency range, but the terminal zone slopes of the blends are more or less same as that of neat PLA. The lower storage modulus of the blends is supposed to be originated from the decrease in molecular entanglements in the blends. The dynamic complex viscosity of neat PLA and PLA/ESO blends, as presented in Figure 8(b), exhibits that the melt viscosity of the blends are substantially lower than that of neat PLA. For example, at 10 rad/s, the melt viscosity of the PLA/ESO (100/10) was reduced by about 77% compared to that of neat PLA. And, neat PLA melt showed non-Newtonian behavior at large frequency region. The blend exhibits a more pronounced Newtonian response with an extended Newtonian plateau compared with neat PLA. The decreased melt viscosity of the blend can be related to an increased free volume due to the plasticization by ESO.



(a)



(b)

Figure 8. Frequency dependence of (a) dynamic storage modulus, G' and (b) complex viscosity, η*, of neat PLA and PLA/ESO blends.

Conclusions

We demonstrated that improved flexibility of PLA could be achieved by incorporating epoxidized soybean oil using melt blending. Thermal, dynamic mechanical and SEM analysis revealed that ESO is partially miscible with PLA, which is manifested by decrease in T_g along with the facilitation of cold crystallization process of PLA as well as by the formation of ESO rich microdomains in PLA matrix. Due to the plasticization effect by ESO, there occurred plastic deformation and lowering of dynamic storage modulus as well as lower complex viscosity of the blends in the molten state compared with neat PLA.

Acknowledgement. This work was supported from Sustainable Building Research Center of Hanyang University which is supported by the SRC/ERC program of MEST (Grant R11-2005-056-04006-0).

References

1 Drumright RE, Gruber PR, and Henton DE (2000) Adv Mater 12: 1841.
2 Sodergard A and Stolt M (2002) Prog Polym Sci 27: 1123.
3 Auras R, Harte B, and Selke S (2004) Macromol Biosci 4: 835.
4 Nijenhuis AJ, Colstee E, Grijpma DW and Pennings AJ (1996) Polymer 37: 5849.
5 Liu LJ, Li SM, Garreau H, and Vert M (2000) Biomacromol 1: 350.
6 Lopez-Rodriguez, Lopez-Arraiza A, Meaurio E, and Sarasua JR (2006) Polym Eng Sci 46: 1299.
7 Shibata M, Inoue Y, and Miyoshi M (2006) Polymer 47: 3557.
8 Li Y and Shimizu H (2007) Macromol Biosci 7: 921.
9 Labrecque LV, Kumar RA, Dave V, Gross RA, McCarthy SP (1997) J Appl Polym Sci 66: 1507.
10 Jacobsen S and Fritz HG (1999) Polym Eng Sci 39: 1303.
11 Baiardo M, Frisoni G, Scandola M, Rimelen M, Lips D, Ruffieux K, Wintermantel E (2003) J Appl Polym Sci 90: 1731.
12 Ogata N, Sasayama H, Nakane K, Ogihara T (2003) J Appl Polym Sci 89: 474.
13 Ljungberg N and Wesslen B (2005) Biomacromolecules 6: 1789.
14 Kulinski Z and Piorkowska E (2005) Polymer 46: 10290.
15 Piorkowska E, Kulinski E, Galeski A, Masirek R (2006) Polymer 47: 7178.
16 Ren Z, Dong L, and Yang Y (2006) J Appl Polym Sci 101: 1583.
17 Ishiaku US, Shaharum A, Ismail H, Ishak ZA (1997) Polym Inter 45: 83.
18 Choi JS and Park WH (2003) Macromol Symp 197: 65.
19 Kim S, Jo W, Kim J, Lim SH, and Choe CR (1999) J Mater Sci 34: 161.
20 Li X, Kang T, Cho WJ, Lee JK, and Ha CS (2001) Macromol Rapid Commun 22: 1306.
21 Sinha Ray S and Okamoto M (2003) Macromol Mater Eng 288: 936.
22 Gu SY, Zhang K, Ren J, and Zhan H (2008) Carbohydrate Polym 74: 79.