

## Epoxidized soybean oil-plasticized poly(lactic acid) films performance as impacted by storage

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**ABSTRACT:** This study examined the effect of storage time at room temperature on the melt viscosity, thermal, and tensile properties of epoxidized soybean oil plasticized poly(lactic acid) (PLA) films manufactured through a cast extrusion process. Infrared results indicate that plasticizer migration to the surface of the film occurred after only 30 days of storage, which significantly affected the performance of plasticized films. While the melt viscosity, glass transition temperature, degree of crystallinity, tensile strength, and modulus increased, the elongation at break and energy to break decreased with storage time up to 30 days and all properties remained constant thereafter. However, the ability of stored plasticized film to cold crystallize remained unaffected since both the cold crystallization temperature and melting temperature were not affected during storage. Although plasticized film lost some flexibility after only 30 days of storage due to plasticizer migration to the surface of the film, sufficient plasticization performance still remained in plasticized PLA films for flexible packaging application even after a long storage period at ambient conditions. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43201.

**KEYWORDS:** biopolymers and renewable polymers; films; packaging; plasticizer; properties and characterization

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### INTRODUCTION

Bio-based plastics from sustainable resources such as biomass are the best alternative to petroleum-based polymers because they provide solutions for reducing the general dependency on oil availability and environmental concerns about the use of common petroleum-based plastics.<sup>1–7</sup> One bio-based plastic that has become an attractive alternative to petroleum-based polymers because of its physical properties and favorable degradation characteristics is poly(lactic acid) (PLA). PLA is a plastic that comes from fermented plant starch such as corn and sugar beets. It has gained interest because of its degradability, high stiffness, reasonable strength, excellent flavor, and aroma barrier.<sup>1–7</sup>

Despite these attractive properties, PLA has drawbacks preventing its widespread usage in flexible films for food packaging. PLA is more expensive, has a lower impact resistance, is significantly more brittle (less flexible) and has poor water barrier properties than most of the petroleum-based plastics such as polypropylene and polyethylene.<sup>2–7</sup> These factors severely hinder its use, particularly in packaging applications where production lines for flexible films cannot tolerate film cracking or tearing when folded or subjected to force during manufacture.<sup>4,6</sup> Therefore, it is of paramount importance to overcome these difficul-

ties in order to broaden the range of PLA commercial applications.

Over the past years, successful attempts have been made to enhance the flexibility and toughness of PLA through different approaches such as its blending with various other polymers<sup>4,8–11</sup> or its plasticization with petroleum-based<sup>12–15</sup> and natural resources-based<sup>2,16–23</sup> plasticizers. Recently, modified vegetable oils have gained a lot of interest as a renewable source of plasticizer for PLA.<sup>2,16–18,20–22</sup> Epoxidized soybean oil (ESO) is one such renewable source, which is produced on an industrial scale and is being used for polymers, coatings, adhesives, laminate materials, etc.<sup>2</sup>

Our recent study directed towards the use of vegetable oil-based plasticizers for biopolymers has reported ESO as an effective plasticizer for PLA due to its excellent efficiency of plasticization.<sup>2</sup> Plasticized PLA sheets and blown films with improved flexibility and toughness were manufactured by developing a single-step processing system for continuous and accurate incorporation of ESO into a PLA matrix. The impact strength and the ductility of plasticized PLA films increased significantly with the ESO content; and the brittle-to-ductile transition occurred in the range of 5–10 wt % ESO content. This toughening capacity of ESO as a plasticizer was attributed to its partial miscibility with the matrix.<sup>2</sup>

Despite these encouraging results, the permanency of the plasticizer in the film during storage remains one of the concerns of plasticized films. There was evidence in our laboratory that plasticized PLA films were not stable since they experienced slight property changes over time. Two issues could arise if the plasticizer leaches out from the film: (1) the film will lose its flexibility over time and (2) the plasticizer could migrate and potentially contaminate the packaged products. Thus, the objective of this study was to determine the permanency of ESO in the plasticized film. Particularly, this study was aimed at understanding the stability of ESO in the plasticized film over time by examining the effect of storage time on the rheological, mechanical, and thermal properties of ESO-plasticized PLA films. Additionally, infrared spectroscopy was performed to monitor plasticizer migration to the surface of plasticized film.

## EXPERIMENTAL

### Materials

Semi-crystalline PLA (2002D) from NatureWorks<sup>®</sup> LLC (Minnetonka, MN) was used in this study. The characteristics of the resin are: melt flow rate (MFR) of 3.4 g 10 min<sup>-1</sup>, density of 1.256 g cm<sup>-3</sup>, and melting temperature of 149°C.<sup>5</sup> The ESO (commercially known as Drapex<sup>®</sup> 6.8) supplied by Galata Chemicals (Southbury, CT) was used as plasticizer. It has a density of 0.992 g cm<sup>-3</sup>, flash point of 290°C, oxirane content of 7%, iodine value of 1.6, and is insoluble in water as described in previous work.<sup>2</sup>

### Film Manufacturing

Film manufacturing was performed by first compounding PLA with 10 wt % of plasticizer using a single-step processing system in which an extruder and a peristaltic injection pump attached in tandem was developed for a continuous and accurate incorporation of ESO into a PLA matrix.<sup>2</sup> Compounding of PLA and ESO was carried out in a co-rotating segmented twin screw extruder (TSE DSE 25) (C.W. Brabender Instruments, South Hackensack, NJ) with a screw diameter of 25 mm and a length-to-diameter ratio of 32:1. The extruder was fitted with a rod die (3.175 mm in diameter) and was powered by a 5.6 kilowatt (7.5 hp) Intelli-Torque Plasti-Corder Torque Rheometer<sup>®</sup> (C.W. Brabender Instruments, South Hackensack, NJ). Starting from the hopper to the die, the melt blending temperature profile was set at 180–175–175–170–165°C. A digital variable speed peristaltic injector pump (Omega<sup>®</sup>, Stamford, CT), which is an externally controllable pump, was used to accurately meter 10 wt % of plasticizer into the PLA blends. The extruded PLA/ESO rod was air-cooled and then pelletized. Details of blending PLA with the plasticizer were presented in our previous study.<sup>2</sup> It should be mentioned that PLA was dried in an oven at 55°C for at least 24 h prior to processing to remove residual moisture.

Following compounding, films were produced by extrusion casting technique. The pelletized PLA/ESO blend was fed into a 19 mm single-screw extruder (C.W. Brabender Instruments, South Hackensack, NJ) with a length-to-diameter ratio of 15:1. This extruder was fitted with a rectangular cast film die having dimensions of 90 mm (width) by 1 mm (thickness) and was powered by a 3.7 kilowatt (5 hp) driver with speed-control gearbox (Brabender Prep Center from C.W. Brabender Instru-

ments, South Hackensack, NJ). After leaving the die, the film was immediately cooled by the rollers with circulating water and then collected by the winder roller. The thickness of the films was controlled by the speed of winder rollers (25 rpm) with a target thickness of 90 μm. The extrusion parameters were kept constant with a barrel temperature profile from the hopper to the die set at 185–175–170°C and a rotation screw speed of 25 rpm. Neat PLA film was also prepared using the same conditions described above to eliminate the effect of thermal history and allow a proper comparison of properties between unplasticized and plasticized films. Different batches of specimens were cut from a roll of film after production and stored in a conditioning chamber at 23 ± 3°C and 50% relative humidity (RH) before testing. Samples were removed from the chamber at various intervals, tested, and discarded after analysis.

### Property Evaluation

**Infrared Spectroscopy.** Fourier transform infrared (FTIR) spectra of the samples were collected by attenuated total reflectance (ATR) infrared spectroscopy using a Shimadzu IR Prestige-21 infrared spectrometer fitted with a diamond ATR infrared spectroscopy accessory (Shimadzu Scientific Instruments, Columbia, MD), collecting 64 scans at a resolution of 4 cm<sup>-1</sup>. All spectra were recorded in absorbance unit in the 4000–400 cm<sup>-1</sup> range. Data analysis, including peak normalization and scale set to 1, was performed using WinFIRST software from Thermo Nicolet (Madison, WI). No baseline modification was done before performing data analysis of the spectra.<sup>24,25</sup>

**Melt Flow Rate and Melt Viscosity.** The melt flow rates (MFR) of plasticized PLA pellets conditioned at 23°C and 50% RH were measured according to the procedure outlined in ASTM D1238 (Procedure A) using a Melt Indexer (model LMI 4000) by Dynisco Polymer Testing (Franklin, MA). The melt temperature was 190°C and an applied dead load (D) of 2.16 kg (including the piston) was employed. Three replicates were performed.

There is an inverse relationship between MFR and zero-shear viscosity ( $\eta_0$ ) according to the following equation<sup>26</sup>:

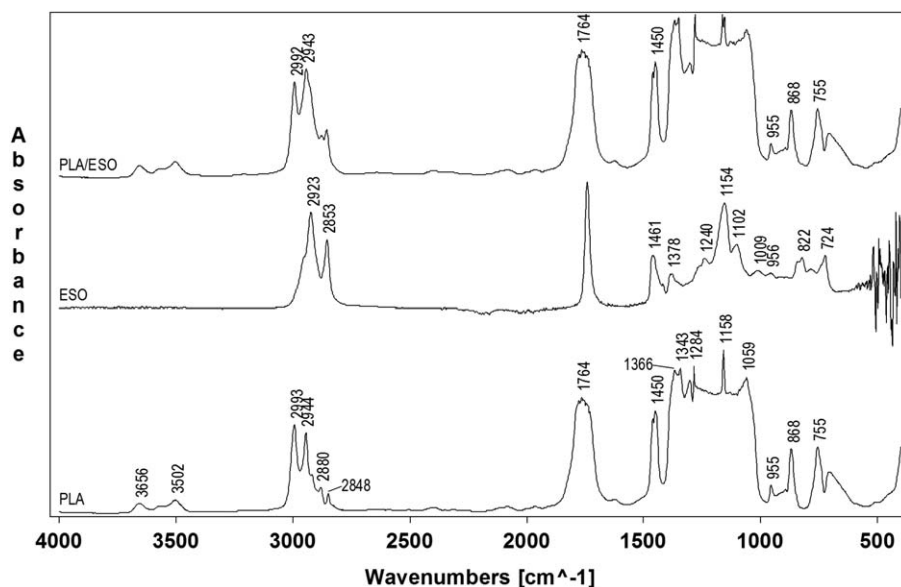
$$MFR = \frac{\rho \cdot D \cdot R^4}{8 \cdot \eta_0 \cdot L \cdot R_A^2} \quad (1)$$

where  $\rho$  is the melt density (g cm<sup>-3</sup>) of the polymer, R (1.0475 mm),  $R_A$  (4.775 mm), and L (8 mm) are the bore radius of the die, the bore radius of the cylinder where the polymer melts, and the length of the die, respectively. Therefore, for the prescribed flow geometry and efflux time of 10 minutes, the reciprocal relationship between melt index (MFR) and viscosity eq. (1) yields the following:

$$\eta_0 = 4.8547 \times \frac{\rho \cdot D}{MFR} \quad (2)$$

where  $\eta_0$  is expressed in Pa s, D in g, MFR in g 10 min<sup>-1</sup>, and the melt density in g cm<sup>-3</sup>.

It should be pointed out that procedures A and B of ASTM standard D1238 were also performed to simultaneously measure the melt flow rate (MFR) and melt volume rate (MVR) in order



**Figure 1.** Infrared spectra of plasticizer (ESO), neat PLA film, PLA films plasticized with 10 wt % ESO at zero storage date (as manufactured).

to determine the melt density of PLA as function of storage time, which is a required input in the calculation of zero-shear viscosity ( $\eta_0$ ) in eq. (1). This test was also performed at 190°C with a load of 2.16 kg and the melt density ( $\rho$ ) was calculated from the following equation:

$$\rho = \frac{MFR}{MVR} \quad (3)$$

**Thermal Analysis.** Thermal analysis of the film samples was carried out on a Q200 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE), with a quench cooling accessory. The samples (3 replicates for each set) with size between 2.1 and 4.5 mg were heated at 10°C min<sup>-1</sup>, between 20–180°C under nitrogen atmosphere with a flow rate of 40 mL min<sup>-1</sup>. The glass transition temperature ( $T_g$ ), the melt peak temperature ( $T_m$ ), the cold crystallization temperature ( $T_{cc}$ ), the enthalpy of the cold crystallization process ( $\Delta H_{cc}$ ), and the total enthalpy of the melting peaks ( $\Delta H_m$ ) were determined with help of the software Universal Analysis 2000, V4.5 (TA Instruments, Delaware). The percent crystallinity ( $\chi_c$ ) of PLA was determined from the first heat curve using the following equation<sup>5</sup>:

$$\chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100 \quad (4)$$

where  $\Delta H_m^0 = 93 \text{ J g}^{-1}$  is the enthalpy of fusion of a PLA crystal of infinite size.<sup>5</sup>

**Mechanical Properties.** The tensile properties of the films were characterized as function of storage time, including the strength at yield, tensile modulus, elongation at break, and energy to break. The tests were carried out in an Instron 5565 Universal Testing Machine using the Instron Bluehill 2 software (Norwood, MA), in accordance with the procedures outlined in ASTM standard D 882. Ten replicates were tested to obtain a reliable mean and standard deviation, using a crosshead speed of 12.5 mm min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Infrared Spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopy was used to monitor the changes that occurred on the surface of plasticized PLA films during storage. Infrared spectra of plasticizer (ESO), neat PLA film, and PLA films plasticized with 10 wt % ESO at zero storage date (as manufactured) are shown in Figure 1. Table I lists the wavenumbers of peaks found in these spectra, along with the assignments of corresponding functional groups.

Obviously, there are many similarities between the important peaks in the spectrum of PLA/ESO blend and those found in the spectra of both neat PLA and ESO. However, the peaks at 822 cm<sup>-1</sup> and 1240 cm<sup>-1</sup> characteristic of the epoxy group of the plasticizer (ESO) are not identified in the spectrum of PLA/ESO blend (Figure 1), indicating that the plasticizer may have reacted through the ring-opening reactions as reported by several investigators.<sup>21,27</sup> The disappearance of these two peaks that correspond to the C–O–C stretching from oxirane vibrations (epoxide ring) could be attributed to the interactions between the terminal hydroxyl groups in PLA and the epoxy groups of ESO through hydrogen bonding interactions, as shown in Figure 2.<sup>17,20,21,27</sup> However, it should be pointed out that the absorption peaks in the range of 3500–3600 cm<sup>-1</sup>, characteristic peaks of PLA, should have disappeared (or their relative intensity decreased) in the spectrum of ESO-plasticized film if the reaction had occurred through the mechanism illustrated in Figure 2 as reported by Al-Mulla *et al.*<sup>20</sup> The presence of hydroxyl groups in the spectrum of ESO-plasticized film may be due to the fact that the film had OH groups in excess from the matrix relative to the small amount of epoxy groups of ESO in the blend. The hydroxyl groups on the spectra of both neat PLA and ESO-plasticized PLA films could also be attributed to the absorbed moisture since the films were not dried before FTIR analysis.

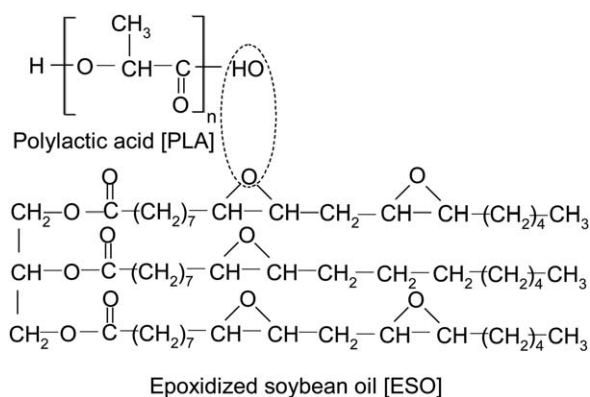
The FTIR spectra of ESO-plasticized PLA films revealed a strong effect of storage time on the surface properties of plasticized

**Table I.** FTIR Absorption Bands and Assignments for Neat PLA, ESO, and PLA/ESO Blend<sup>17,20,21,27,28</sup>

| PLA       | ESO      | PLA/ESO   | Peak assignments  |
|-----------|----------|-----------|---|
| 3656–3502 | -        | 3656–3502 | OH vibrations (hydroxyl stretching)                         |
| 2993–2880 | -        | 2992–2880 | CH stretching of CH <sub>2</sub> , CH <sub>3</sub>          |
| -         | 2923     | -         | CH asymmetric stretching of CH <sub>2</sub>                 |
| 2848      | 2853     | 2848      | CH symmetric stretching of CH <sub>2</sub>                  |
| 1764      | 1744     | 1764      | C=O stretching (ester carbonyl)                             |
| 1450      | 1461     | 1450      | CH bending (scissoring, CH <sub>2</sub> , CH <sub>3</sub> ) |
| 1366      | 1378     | 1366      | CH symmetric bending (CH <sub>3</sub> )                     |
| 1284      | -        | 1284      | C=O ketonic binding   |
| -         | 1240     | -         | C–O–C asymmetric stretching (oxirane)                       |
| 1158–955  | 1154–956 | 1158–955  | C–O and C–O–C stretching, OH deformation                    |
| 868       | -        | 868       | CH rocking vibration  |
| -         | 822      | -         | C–O–C symmetric bending (oxirane)                           |
| 755       | 724      | 755       | (CH <sub>2</sub> ) <sub>n</sub> rocking vibration           |

films as illustrated in Figure 3. Significant changes were observed in the region of 1000–1300 cm<sup>-1</sup>. The major differences between the FTIR spectra of unstored and stored plasticized films are seen at 1281, 1254, 1245, 1224, 1163, 1153, and 1060 cm<sup>-1</sup>.

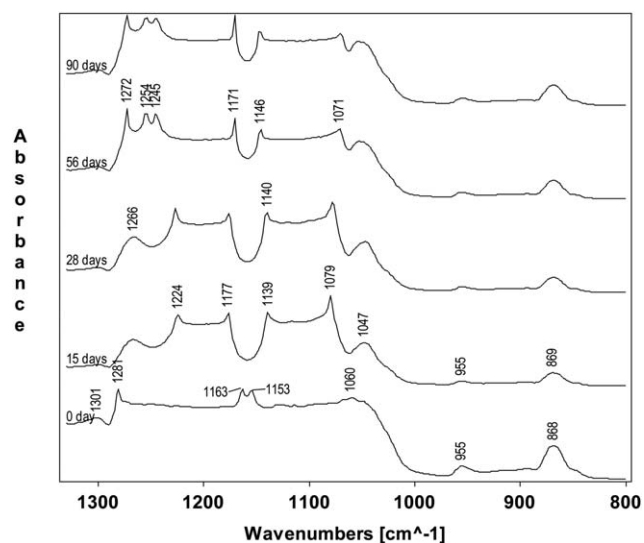
A sharp peak at 1281 cm<sup>-1</sup> in the spectrum of the unstored film (as manufactured) shifted to lower wavenumber value and formed a broad peak at 1266 cm<sup>-1</sup> after 15 and 28 days of storage, and then shifted back to 1272 cm<sup>-1</sup> with sharper and increased peak intensity with further storage time up to 90 days. The peak at 1163 cm<sup>-1</sup> in unstored film shifted to 1171–1177 cm<sup>-1</sup> in stored films, while the peak at 1153 cm<sup>-1</sup> of unstored film shifted to lower wavenumber values (1139–1146 cm<sup>-1</sup>) with storage time. The band at 1060 cm<sup>-1</sup> in the spectrum of unstored film also shifted to higher wavenumber values in the range of 1071–1079 cm<sup>-1</sup> for stored films. A small shoulder in the spectrum of unstored film at 1047 cm<sup>-1</sup> became an evident peak after 15 days storage and afterward.

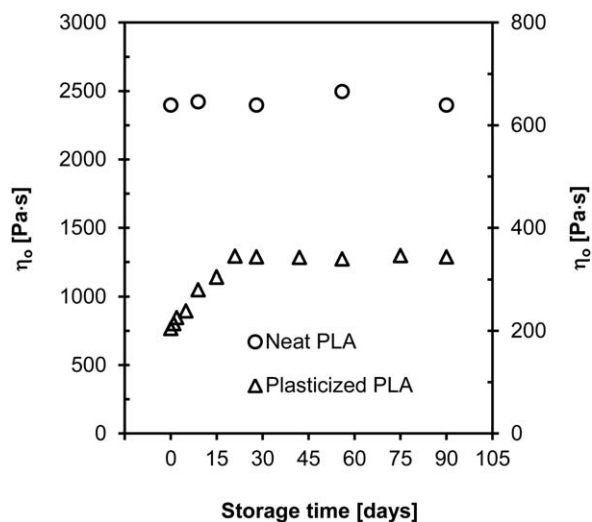
**Figure 2.** Scheme of the reaction of the epoxy ring (ESO) with the OH groups (PLA).

Notice that a new peak at 1224 cm<sup>-1</sup> was observed in the spectrum of plasticized film stored for 15 and 28 days but disappeared as the storage time increased to 56 days. All these changes indicate that interactions most likely took place between PLA and ESO that are affecting the surface of the films (Figure 3). Interestingly, as the storage time increased, new peaks related to epoxy groups in ESO appeared at 1245 cm<sup>-1</sup> and 1254 cm<sup>-1</sup> (Table I) in the spectra of the plasticized films stored for 56 and 90 days, indicating that some plasticizer migrated to the surface of the film.

#### Effect of Storage Time on the Flow Properties of Plasticized PLA

Plasticizers impart flexibility and play an important role in heat processing by reducing the viscosity of the molten material to

**Figure 3.** FTIR spectra of ESO-plasticized PLA films stored for 0 day (as manufactured), 15, 28, 56, and 90 days.

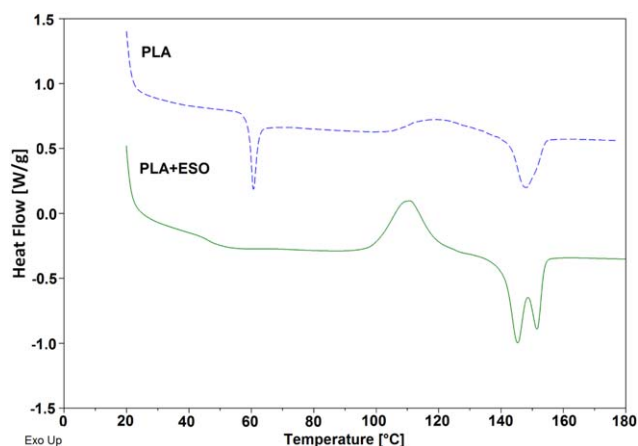


**Figure 4.** Effect of storage time on the zero shear viscosity ( $\eta_0$ ) of neat and plasticized-PLA films. The left Y-axis is for the viscosity of neat PLA film and the right one for plasticized PLA film. The error bars are not shown because of smaller standard deviations in the data (coefficients of variation in the range of 0.3–3.8%).

ensure good flow properties. In addition to the melt flow properties, the flexibility, extensibility, and rigidity of finish products at room temperature are influenced by the addition of plasticizers.<sup>29</sup> Figure 4 illustrates the effect of storage time on the zero shear viscosity of neat and plasticized-PLA films.

First, compared to unplasticized PLA and irrespective of the storage time, the zero shear viscosity of neat PLA decreased significantly from the range of 2395–2495 Pa s to 204–345 Pa s by adding ESO into the matrix as expected from the theory of plasticization.<sup>21,29</sup> Strong intermolecular forces reduce the mobility of polymer chains, thus preventing flow. In contrast, plasticizers reduce the intermolecular forces between the polymer chains, thus facilitating the flow of the polymer.<sup>29</sup> It is believed that as the PLA/ESO blend was heated up during processing, the plasticizer molecules diffused into the matrix segments and reduced the polymer-polymer interactive forces by acting as shields between polymer chains. This reduction in intermolecular forces along the polymer molecular chains could be the main contributor to the lower melt viscosity of the plasticized PLA. In other terms, the addition of plasticizer in PLA enhanced the chain mobility arising from an increase in free volume or decrease in molecular interaction.<sup>29</sup>

Second, the melt viscosity of plasticized PLA increased with the storage time up to 30 days and remained constant thereafter (Figure 4). The increased viscosity may be due, in appreciable part, to the loss of plasticizer in the matrix. Moreover, the FTIR spectra of various PLA samples shown in Figure 3 validate the occurrence of plasticizer migration to the surface of the film. During plasticization process, ESO was forced to diffuse into the intermolecular chains of the matrix by the shear force generated by the screws of extruder. Conversely, after processing, a small amount of ESO leached out slowly from the intermolecular chains of the matrix since the shear force stopped. As a



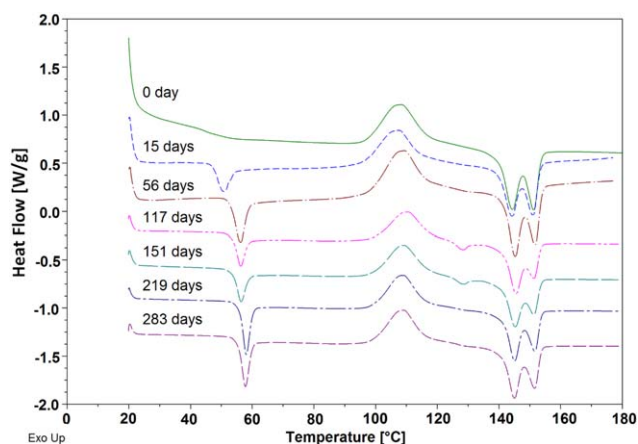
**Figure 5.** DSC heating thermograms of neat PLA and ESO-plasticized PLA films at zero storage date (as manufactured). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

result, the loss of plasticizer increased with the storage time up to 30 days but a dynamic equilibrium could have been reached in the PLA/ESO blend as the storage time increased, thus ending the plasticizer loss.

Although the zero shear viscosity of plasticized PLA increased with the storage time, the plasticized PLA still exhibited significantly lower melt viscosity than unplasticized counterparts even after 90 days of storage.

#### Effect of Storage Time on Thermal Properties

First, consider the effect of plasticization on the thermal properties of PLA. Figure 5 illustrates the DSC heating thermograms of neat PLA and ESO-plasticized PLA films at zero storage date (as manufactured). As expected, the  $T_g$  of PLA decreased from 60.9°C to 45.8°C by adding ESO plasticizer into the matrix, suggesting increased segmental mobility of the PLA chains due to plasticization,<sup>2,18,21</sup> which also resulted in increased degree of crystallinity from 1.52% (neat PLA) to 3.13% (plasticized PLA) as expected.<sup>15</sup> The cold crystallization temperature ( $T_{cc}$ ) of neat



**Figure 6.** DSC thermograms of plasticized PLA recorded at various storage times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

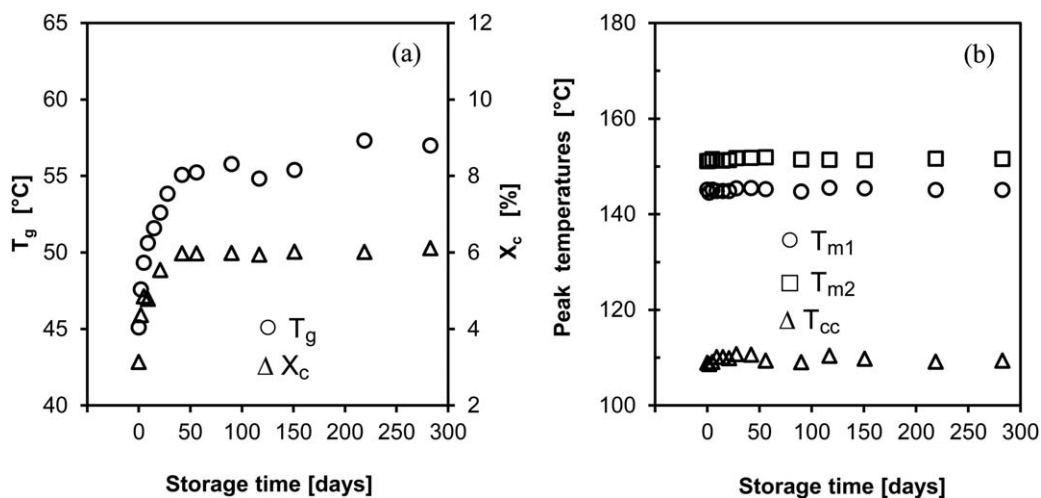


Figure 7. Effect of storage time on the (a)  $T_g$ ,  $X_c$  and (b)  $T_{cc}$ ,  $T_m$  of plasticized-PLA films.

PLA was also affected by plasticization, which decreased the  $T_{cc}$  of neat PLA to lower temperature (from  $\sim 121.2^\circ\text{C}$  to  $110.7^\circ\text{C}$ ) and significantly increased the intensity of the cold crystallization peak as seen in Figure 5. This result implies that ESO increases the ability of PLA to cold crystallize. It can be noted that the cold crystallization temperature of PLA decreased in parallel with the shift in  $T_g$  due to the enhanced segmental mobility of the PLA chains by plasticization as expected for plasticized PLA systems. Other investigators have reported similar trend for PLA blended with various types of plasticizers.<sup>18,21,30–32</sup> Melting of PLA crystals began around  $135^\circ\text{C}$  in all materials but two distinct trends were observed for the melting endotherms. A single melting peak, centered at around  $148^\circ\text{C}$  was observed for the unplasticized film. In contrast, two melting peaks ( $T_{m1}$ ,  $T_{m2}$ ) centered at around  $145$  and  $151^\circ\text{C}$ , respectively, developed in plasticized PLA films, in agreement with the results reported by other investigators for PLA/ESO blends,<sup>18,21</sup> PLA/poly(ethylene glycol) blends,<sup>30</sup> PLA/poly(propylene glycol) blends,<sup>31</sup> and PLA/poly(ethylene oxide) blends.<sup>32</sup> The presence of two melting peaks on thermogram of plasticized PLA has

been related to the rearrangement of crystal structure, i.e., to the formation of crystallites with different sizes and perfection which is arisen by lamellar reorganization during crystallization of PLA.<sup>18,21,30–32</sup> The thermal history of the films during preparation was also reported to contribute to this phenomenon.<sup>33</sup>

Next, consider the effect of storage time on the thermal properties of plasticized PLA films. DSC traces recorded for ESO-plasticized PLA films stored for up to 283 days are shown in Figure 6. An increase in both  $T_g$  and  $X_c$  was observed as the storage time increased up to around 30–40 days and leveled off as the storage time further increased [Figure 7(a)]. The dependence of both  $T_g$  and  $X_c$  of plasticized films on the storage time followed a similar trend as the zero shear viscosity (Figure 4). The increased  $X_c$  in parallel with the increase in  $T_g$  with storage time could also be attributed to the segregation and migration of the plasticizer as reported by Wang and coworkers.<sup>15</sup> Notice that, although the  $T_g$  of plasticized PLA increased with the storage time, plasticized PLA films still exhibited significantly lower  $T_g$  values than unplasticized counterparts ( $60.9^\circ\text{C}$ ) even after 283 days of storage, implying that they remained more flexible than the unplasticized film. The changes of

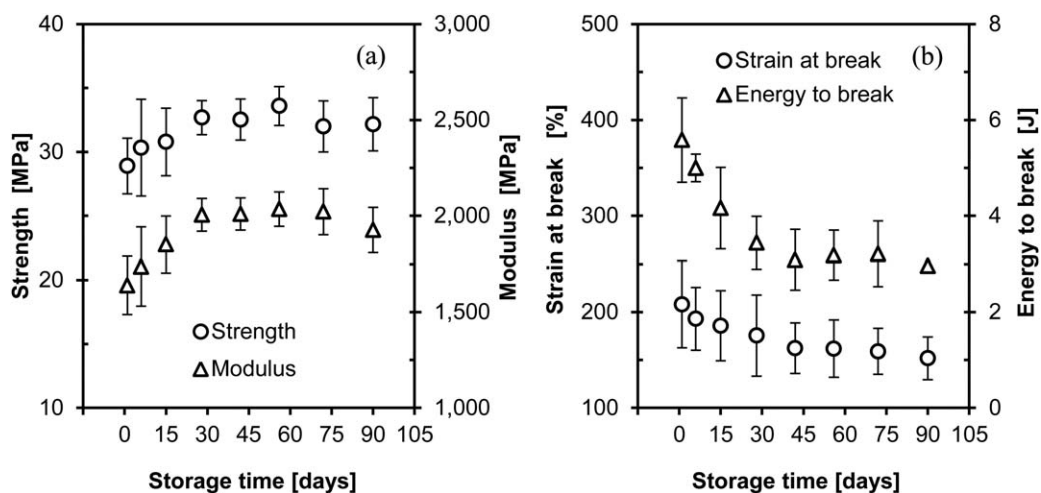


Figure 8. Changes in (a) yield strength and tensile modulus and (b) elongation at break and energy to break of plasticized PLA film with storage time.

both  $T_{cc}$  and  $T_m$  of plasticized films with storage time are shown in Figure 7(b). Unlike  $T_g$  and  $X_c$  of plasticized films that changed over time, both the  $T_{cc}$  and  $T_m$  of plasticized films remained almost constant during storage, indicating that the ability of plasticized PLA to cold crystallize was unaffected during the storage.

#### Effect of Storage Time on Tensile Properties

The tensile properties of plasticized films were measured as a function of time over a span of 90 days to understand the effect of storage on the properties of the films stored under normal environmental conditions. The changes in yield strength and modulus of plasticized PLA films on the storage time [Figure 8(a)] followed a similar trend as the  $T_g$  of the films [Figure 7(a)]. Both properties increased as the storage time increased up to around 30 days and leveled off as the storage time further increased [Figure 8(a)]. As expected, the loss of plasticization during the first 30 days (increased  $T_g$  as seen in Figure 7(a)) also affected the elongation at break and the energy to break [Figure 8(b)], by causing a significant decrease in both properties. As the storage time increased, plasticized PLA films became less flexible, as indicated by the increased  $T_g$ , as well as less extensible and tougher, resulting in reduced elongation at break and the energy to break.

Nevertheless, it should be mentioned that the changes in tensile properties occurred within the first 30 days of storage and then they remained constant as the storage time further increased. While the storage time led to strength and modulus losses, the flexibility of the plasticized PLA films was still greater than that of unplasticized counterpart even after 90 days of storage.

#### CONCLUSIONS

The effect of storage on the performance of ESO plasticized PLA films manufactured through a cast extrusion process was investigated. Films plasticized with 10 wt % ESO were stored in a desiccator at room temperature and the melt viscosity, thermal, and tensile properties were measured over a minimum of 90 days of storage. Additionally, infrared spectroscopy was used to monitor plasticizer migration to the surface of plasticized film. Plasticizer migration occurred within the first 30 days of storage, which significantly affected the properties of plasticized films. While the melt viscosity, glass transition temperature, degree of crystallinity, tensile strength, and modulus increased, the elongation at break and energy to break in contrast decreased with the storage time up to around 30 days and all properties remained constant thereafter suggesting that the films lost some flexibility during storage. However, the ability of stored plasticized film to cold crystallize was unaffected since both the cold crystallization temperature and melting temperature were not affected during storage. Although the storage time led to property changes, plasticized PLA films still remained more flexible than the unplasticized counterpart even after 90 days storage. This result indicates that sufficient plasticization performance still remained in ESO-plasticized PLA films for flexible packaging application even after a long storage period at ambient conditions. Nevertheless, the exudation of ESO may not be desirable for films used in contact with packaged products. Therefore, future investigations are needed to

understand the migration mechanisms of ESO-plasticized PLA films in order to develop strategies to overcome exudation.

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