Mechanical and Rheological Properties of Epoxidized Soybean Oil Plasticized Poly(lactic acid)

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ABSTRACT: Poly(lactic acid) (PLA) is a well known biodegradable thermoplastic with excellent mechanical properties that is a product from renewable resources. However, the brittleness of PLA limits its general applications. Using epoxidized soybean oil (ESO) as a novel plasticizer of poly (lactic acid), the composite blend with the twin-screw plastic extruder at five concentrations, 3, 6, 9, 12, and 15 wt %, respectively. Compared with pure PLA, all sets of blends show certain improvement of toughness to different extents. The concentration with 9 wt % ESO increases the elongation at break about 63%. The melt flow rates of these blends with respect to different ESO ratio have been examined using a melt flow indexer. Rheological behaviors about shear viscosity and melt strength analysis are discussed based on capillary rheology measurements. The tensile strength and melt strength of the blends with 6 wt % ESO simultaneity reach the maximums; whereas the elongation at break of the blends is the second highest level. ESO exhibits positive effect on both the elongation at break and melt strength. The results indicate that the blend obtained better rheological performance and melt strength. The content of 6 wt % ESO in PLA has been considered as a better balance of performance. The results have also demonstrated that there is a certain correlation between the performance in mechanical properties and melt rheological characterization for the PLA/ESO blends. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3185–3191, 2009

Key words: poly(lactic acid); plasticizer; epoxidized soybean oil; blends; melt

INTRODUCTION

The ecosystems are now considerably disturbed and are slowly being damaged as a result of the usage of nondegradable materials in disposable items. The development of biodegradable plastics can play a crucial role in helping to solve the waste disposal problems. Poly(lactic acid) (PLA) is a degradable thermoplastic polymer belonging to the family of aliphatic polyesters, with excellent mechanical properties and transparency which is now beginning to be produced on a large scale from fermentation of corn to lactic acid and subsequent chemical polymerization.[1–3] Unfortunately, the brittleness of PLA limits its general applications in extensive areas because it cannot provide high ductile performance in many case.[4,5]

PLA has received much attention in the research of alternative biodegradable polymers. The physical properties of PLA may be modified by blending with a plasticizer or a second polymer, and the flexibility of PLA can thereby be improved. The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. For packaging and hygiene applications, only nontoxic substances approved for food contact and personal care can be considered as plasticizing agents. The plasticizer should not be too volatile because this would cause evaporation to occur at the elevated temperatures used for processing. Furthermore, the plasticizer should not be prone to migration because this would cause contamination of the materials in contact with the plasticized PLA. As plasticizers for PLA, oligomeric lactic acid, glycerol,[3] PEG[6–8] and low molecular weight esters such as citrates[9,10] have been investigated.

Epoxidation of the unsaturated bonds that occur along the fatty acid chains of the seed oils produces the more reactive oxirane group. This three-member ring provides a more energetically favorable site for reaction and represents a chemical intermediate for the preparation of derivatives that would be difficult to obtain directly from the unsaturated bond. The epoxidation of vegetable oils is performed on an industrial scale with these materials used primarily for polymers, coatings, adhesives, and similar industrial products.[11,12]

Epoxidized soybean oil (ESO) has been used as plasticizer for polyvinyl chloride (PVC) compounds, chlorinated rubber, and polyvinyl alcohol (PVA)

emulsions.[13] Phenolic resin modified by ESO (ESO/PR) has also been prepared for laminate materials.[14] Eopxidized oil shows significant improvement of tougheness effect through grafting or blending modification.[10–12]

However, there is no report on PLA plasticized with ESO and its properties. The present study focuses on the use of ESO as plasticizer for PLA and its effects on the mechanical and rheological behavior. The aim of the study is to determine preferable concentration of ESO and establish the certain relationship between mechanical and rheological properties, building a platform for further research concerning better processability for plasticized PLA.

EXPERIMENTAL

Materials

A film grade PLA with a viscosity-average molecular weight molecular weight (M_w) of approximately 100,000 g/mol and a polydispersity of 2.4 was supplied by Guanghua, Shenzhen, China. The melting temperature (T_m) was 163°C and the glass transition temperature (T_g) was 65.5°C measured by DSC with 10°C/min.

Epoxidized soybean oil with oxirane oxygen more than 6.5% and purity more than 99.99% was purchased from Hairma, Guangzhou, China.

Sample preparation

Epoxidized soybean oil was added at five concentrations, 3, 6, 9, 12, and 15 wt %, based on 100 parts of PLA. The mixtures were fed in to the twin-screw plastic extruder TE-34 (screw length-diameter ratio is 25, made in China). The screw speed was 110 rpm. The temperature profile along the extruder barrel was 150,160, 170, 180, and 160°C (from feed zone to die).

Tensile test

Blends from the twin-screw extruder were compression with the Flat Sulfuration Machine at 180°C and 8 MPa for 10 min. The molded specimens with thickness of 4 mm were cooled to 65°C before removal from the mold and then preconditioned at 50% relative humidity and 25°C for 48 h before testing.

The tensile strength and elongation at break were determined with an Instron testing system (model 5566, UK) according to Chinese Standard GB1040 (Type I dumbbell-shaped sample) with crosshead speed of 50 mm/min and a 70-mm gauge length. Results from five specimens were averaged.

Melt flow index

Melt flow index (MFI) is the melt flow rate index, expressed in grams, extruded isothermally in 10 min under constant load through a die of standard dimensions.[15,16] MFI were measured using Melt Flow Indexer (at 190°C, load 2.16 kg) (MP993A, T.Olsen, USA). All samples were dried in a vacuum oven for 24 h at 85°C.

According to the definition of MFI, it is expressed as

$$\text{MFI} = \frac{600 \cdot W}{t} \tag{1}$$

where W is the extrudate weight in grams, and t is the test time in seconds.

Capillary rheology test

Capillary rheological measurements and melt strength characteristics were performed on Rheologic 5000 capillary rheometer (CEAST, Italy). The capillary viscometer consisted of a barrel into which material was loaded before being pushed by a plunger through a capillary was controlled by a surrounding heating unit. The diameter of capillary was 1 mm and length-diameter ratio was 30. The small pieces were placed into the barrel through a funnel and then packed down with the plunger until the first extrudate appeared at the capillary exit. The sample was allowed to come to temperature for 3–5 min, and was then forced through the capillary by the plunger at preselected velocities. The load on the plunger provided the total pressure drop through the barrel and capillary. Rheologic 5000 capillary rheometer was connected to a computer, with the use of the data acquisition program, real-time experimental data could be obtained for a detailed analysis.

Shear rate (γ) and shear stress (τ) were calculated by stand methods. To understand the processing properties and fluidity of PLA/ESO blends, the rheology experiments were performed 160, 170, and 180°C, which covered the processing temperature range.

The melting volumetric flow rate through the capillary is given as

$$Q = \frac{\pi R^3}{4} \gamma \frac{4n}{3n+1} \tag{2}$$

where R is capillary radius, γ is shear rate at the capillary wall, and n is flow index depending on the temperature. The term $\frac{4n}{3n+1}$ is the Rabinowitsch correction factor.

Pressures are monitored, and shear stress values are calculated using the following equation:

$$\tau = \frac{\Delta PR}{2L} \tag{3}$$

where ΔP is the pressure at the capillary entrance, R and L are radius and length of the die (mm), respectively.

According to Onteniente,[17] if a thermoplastic material obeys power-law behavior:

$$\tau = K\gamma^n \tag{4}$$

The apparent viscosity η is defined by eq. (5):

$$\eta = \tau/\gamma \tag{5}$$

where τ is shear stress; γ is shear rate at the capillary wall; K is consistency of the materials depending on the temperature, the structure and the formulation of the polymer.

Substituting eq. (4) for τ in eq. (5), it produces the following formula relating η and γ:

$$\eta = K\gamma^{n-1} \tag{6}$$

$$\log \eta = \log K - (1 - n) \log \gamma \tag{7}$$

If $\log \gamma$ and $\log \eta$ are substituted by x and y, respectively, then the linear fitting equation is as following:

$$y = \log K - (1 - n)x \tag{8}$$

RESULTS AND DISCUSSION

Tensile properties

Stress-strain curves of the PLA/ESO blends are shown in Figure 1. Neat PLA appeared very brittle and no yield point is observed. For the blends with ESO, the material showed yield point before damage, which representing toughness properties to some extent, different to that of pure PLA.

Tensile fracture energy (E_{TF}) is an important parameter characterized material tensile toughness, which is
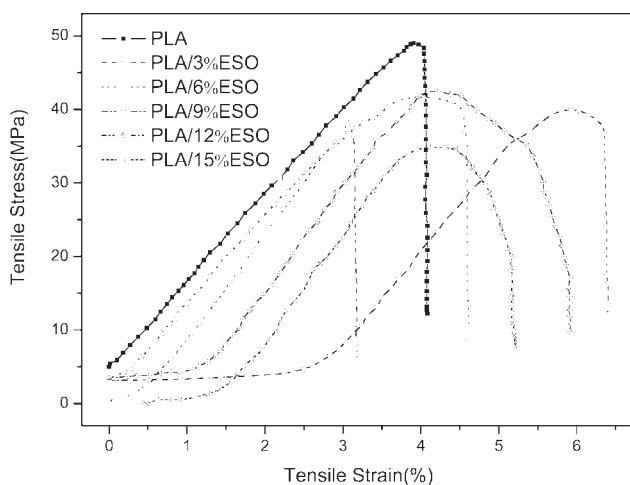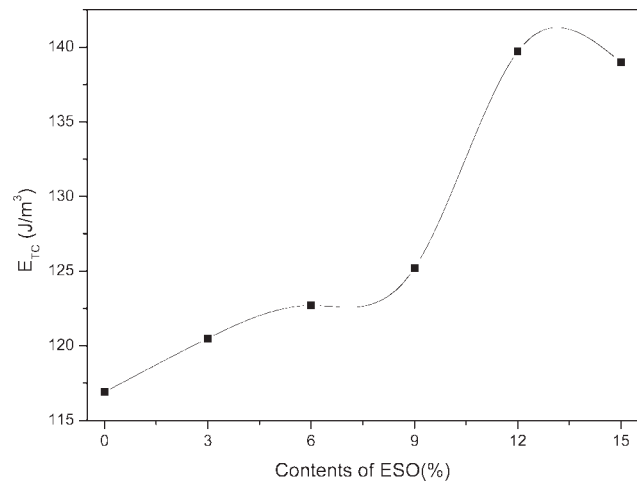

Figure 2 Effect of ESO contents on E_{TF} in the blends.

defined as area enclosed by stress-stain curve from tensile to fracture.[18] Trapezoid rules with a high accuracy are used to conveniently calculate E_{TF}.[19]

$$E_{TF} = \sum_{i=1}^{n} \frac{\sigma_{i-1} + \sigma_i}{2} \Delta\varepsilon \tag{9}$$

where σ is the tensile stress; $n = t_t/\Delta t$, t_t is the whole loading time; Δt is the time interval of stress value recorded; $\Delta\varepsilon$ is the strain increment on the recording moment.

Figure 2 shows E_{TF} curve with different ESO contents. With the increment of ESO content, E_{TF} increased slowly and then sharply. When the content of ESO exceeded 6 wt %, E_{TF} increased rapidly and reached maximum at 12 wt %, suggesting that the loading of ESO was beneficial to improving tensile toughness.

The variation of tensile strength, elongation at break and tensile modulus with the PLA loading of ESO is shown in Table I.

As expected, the tensile strength of the blends decreased with the incorporation of ESO. According to gelatin theory of plasticization, plasticizer is absorbed by matrices when blending with polymer,

Figure 1 Stress-strain curves of the PLA/ESO blends.

TABLE I
Tensile Properties of PLA/ESO Blends

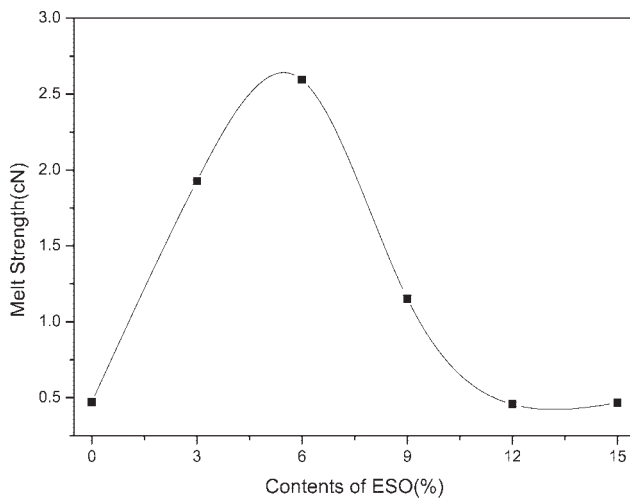| Sample	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
Neat PLA	57.68	3.98	1.71
PLA+3%ESO	40.02	3.96	1.53
PLA+6%ESO	45.58	5.35	1.34
PLA+9%ESO	41.96	6.5	1.32
PLA+12%ESO	37.67	5.73	1.33
PLA+15%ESO	35.46	5.42	1.31

Figure 3 Effect of ESO contents on melt strength at 160°C for the PLA/ESO blends.

which can dissolve the connection points of polymer macromolecule. As the connection points destroyed, the centers of force making polymer macromolecule move close together are masked, leading to weaken the attractive force between polymer macromolecule and tensile strength of polymer decreases.

Despite a small addition of ESO (3 wt %) slightly decreased elongation at break, ESO exhibited positive effect on elongation of blends, generally. For the concentration with 9 wt % ESO, the elongation at break increased by about 63.32% with respect to pure PLA.

The tensile modulus of the PLA/ESO blends was decreased as the loading of ESO increased. This was attributed to the toughening and elastomeric effect of ESO. It is speculated that ESO (containing epoxy group) could form favorable interaction with PLA (containing ester group), presumably via hydrogen bonding. A slight improvement in the tensile strength and elongation at break was achieved by the addition of 6 wt % ESO. This was due to the improvement of the interaction between PLA and ESO. It was believed that hydrogen bonding could form between the ester group of PLA and the oxirane group of ESO. From Table I, it could be seen that further addition of ESO (i.e., 9 wt %) resulted in a reduction of the tensile strength. It was interesting to note that the tensile modulus of PLA/ESO blends was not much affected by ESO content more than 6 wt %. An obvious reduction in tensile strength was observed at the loading of ESO in exceeded of 9 wt % in the systems. This could be attributed to interface slipping and separating under tension.

By comprehensive consideration on tensile properties, 6 wt % ESO possessed preferable tensile strength and the second highest level of the elongation at break. It obtained the best balance of tensile properties, elongation at break and tensile modulus.

Melt strength

The force at which the polymer melt strand breaks is called the melt strength. The melt strength test
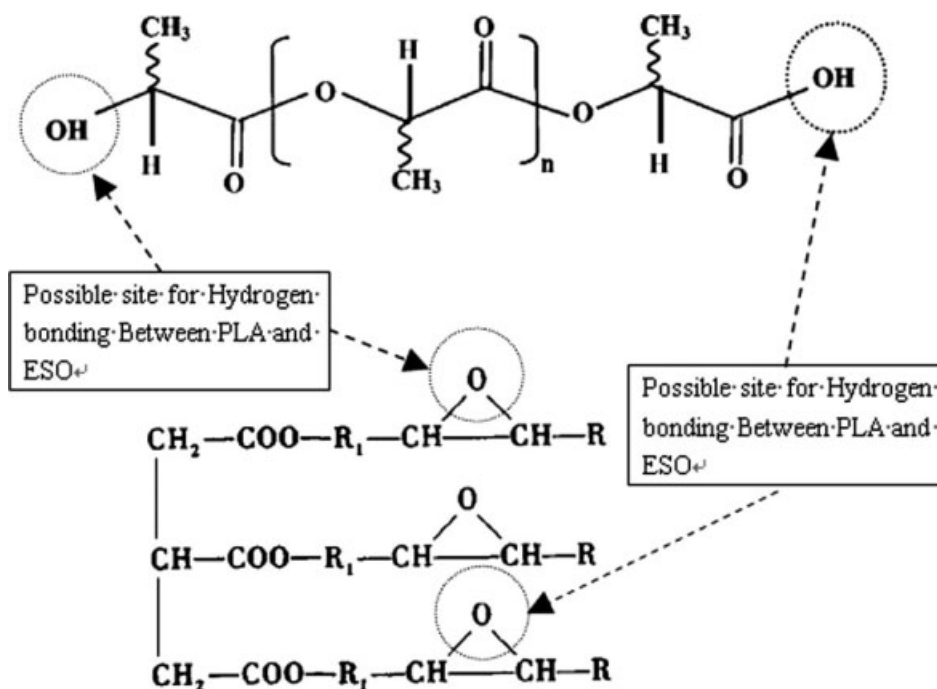

Figure 4 Proposed chemical interactions between PLA and ESO.

result for PLA/ESO blends at the temperature of 160°C is shown in Figure 3. Melt strength of the samples at 160°C (Fig. 3) increased at first and then decreased with the increase of ESO content, which almost reached stable value when the ESO dosage was more than 12 wt %. The melt strength reached a maximum with 6 wt % ESO, which was 5.5 times that of pure PLA.

The melt strength of blend was related to the presence of long chain branches in the PLA, which participated in forming intermolecular interactions in the melt during elongation, thus increasing the resistance to deformation. ESO was more effective in enhancing the melt strength value when content less than 6 wt %, because it promoted covering and bonding of long chain branching. These results were in agreement with tensile properties.

It was presumed that adhesion between PLA and ESO molecules existed; however, the interaction was not very strong. The interaction between PLA and ESO could be attributed to the possible hydrogen bonding that occurs between the carbonyl group (i.e., from ester linkage) in PLA and the epoxy group in ESO. A proposed possible site for interaction between PLA and ESO is shown in Figure 4. A small amount of hydroxyl group (—OH) in the PLA were used in this study. The —OH group came from the terminal hydroxyl groups in the PLA main chain. It was believed that hydrogen bonding could form between the ester groups of PLA and the epoxy groups of ESO. On the other hand, ESO was a plasticizer of PLA; ESO molecules might penetrate into PLA chains at a high level of addition, increasing fluidity and decreasing melt strength of the blends.

Melt flow index

It was observed that the values of MFI for all samples, except for 9 wt % ESO concentration, were higher than those of pure PLA (10.01 g per 10 min). Figure 5 is the MFI of PLA with different ESO contents. MFI of PLA/ESO blends raised first and felled later, which reached the lowest point (9.21 g per 10 min) at 9wt%, even lower than that of the neat PLA. In this work, ESO was not only a new type of plasticizer but also a lubricant of PLA. When lower concentration of ESO was added in PLA, the ESO molecule diffused into PLA matrix by penetrating, which would make matrix slip and flow easier. It indicated that the chain scission process was more severe as compared with branching and cross-linking. As ESO concentration increased, more and more ESO molecules got together and surrounded PLA matrix, which resisted slipping and flowing. Meanwhile, ESO played an important role in effectively lubricating between PLA macromolecule, which
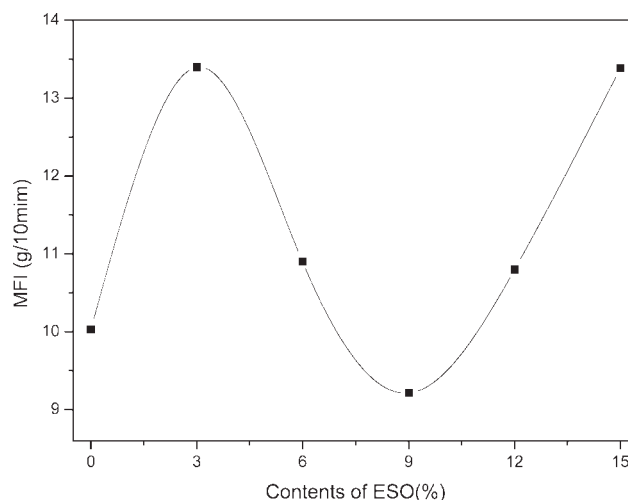

Figure 5 Effect of ESO contents on MFI in the blends.

finally caused the value of MFI increasing when loading ESO greater than 9 wt %.

Rheology curves analysis

The capillary rheological results are plotted using a double logarithmic scale (in Fig. 6), suggesting the effect of different ESO contents and temperature on the rheological behavior of PLA/ESO blends. With increasing shear rate, the viscosity of each blend decreased. Such flow behavior was called shear thinning. According to the linear fitting equations, the blends were prone to the flow along with the increasing temperature, and the apparent viscosity η of PLA/ESO blends decreased with increasing the content of ESO at the same temperature.

The flow index n and the constant K were obtained from the linear fitting analysis of the double logarithmic plots, respectively. According to eq. (8), $-(1-n)$ is the slope of linear fitting equation and $\log K$ is the interception. The constant K of PLA/ESO blends at 160, 170, and 180°C are listed in Table II. It could be seen from the Table II that the values of K decreased significantly with the increasing temperature. PLA blended with 6 wt % ESO at 160°C came to the peak value of K.

The curves of n at three different temperatures are shown in Figure 7. Compared with that of pure PLA, the values of n increased in all sets of blends and reached maximum at 9 wt % ESO, which could be ascribed to effective plasticization of ESO and gain better fluidity. When the concentration of the ESO was more than 9 wt %, the values of n decreased, because ESO molecules were easier to cover with PLA chains. At this level of content, the chain of PLA was disentangled under high temperature and shear. Moreover, the PLA blends with ESO improved the elastomeric behavior of matrix, which
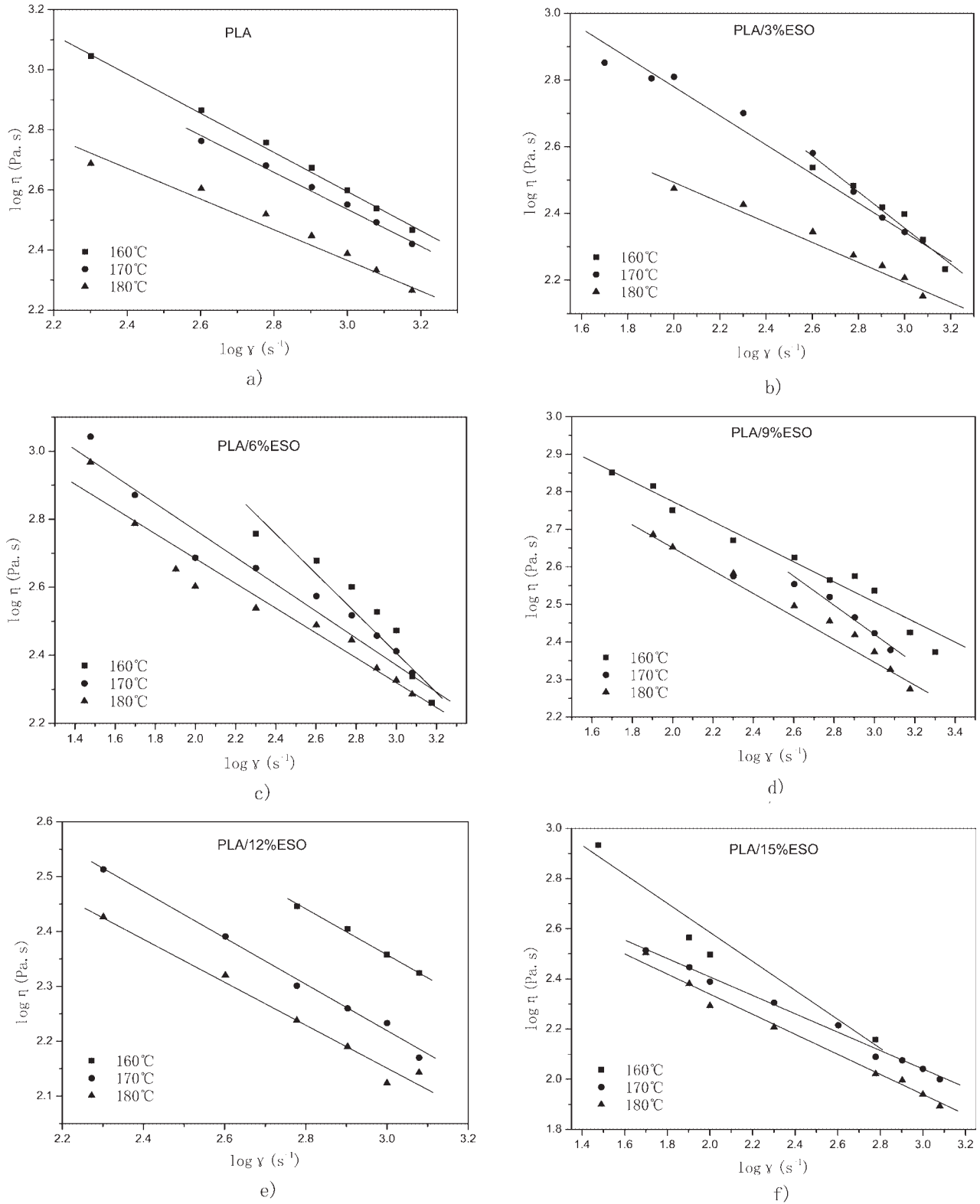
Figure 6 The rheological plots of PLA/ESO blends at 160, 170, and 180°C: (a) pure PLA, (b) PLA/3%ESO blends, (c) PLA/6%ESO blends, (d) PLA/9%ESO blends, (e) PLA/12%ESO blends, (f) PLA/15%ESO blends.

TABLE II
The Constant K (Pa s^n) of PLA/ESO Blends with Different ESO Contents

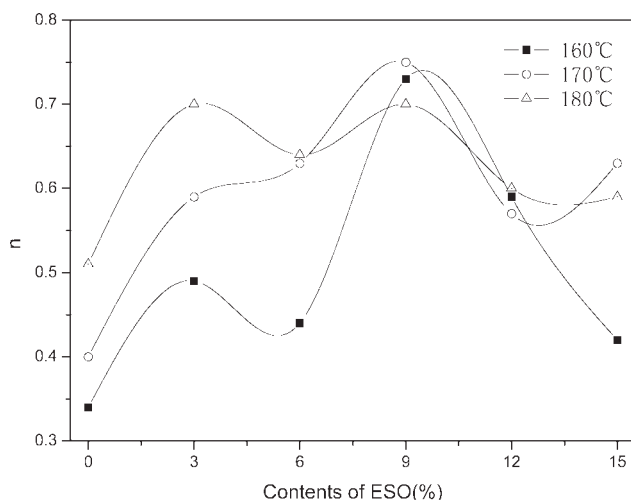| Temperature (°c)	0	3 wt %ESO	6 wt %ESO	9 wt %ESO	12 wt %ESO	15 wt %ESO
160	38.03×10^3	7.66×10^3	12.79×10^3	2.11×10^3	3.83×10^3	5.08×10^3
170	2.14×10^3	3.99×10^3	3.36×10^3	1.51×10^3	3.13×10^3	1.40×10^3
180	7.05×10^3	1.22×10^3	2.51×10^3	1.86×10^3	2.20×10^3	1.42×10^3

Figure 7 Relationship between n and contents of ESO in the blends.

would resist flow and make the value of n tend to decreased.

CONCLUSIONS

The mechanical and rheological investigation found that PLA could be effectively plasticized with ESO. Compared with pure PLA, all sets of blends possessed certain toughness to different extents. Properties analyses indicated that the blend could get better rheological performance and melt strength. ESO was effective for improving the elongation at break and melt strength. It was possible to obtain a significant increase in tensile and melt strength, which was attributed to adhesion between PLA and ESO molecules. The concentration with 9 wt % ESO increased the elongation at break about 63.32%. The blends with 6 wt % ESO reached the maximal melt strength, which was 5.5 times that of pure PLA. Better rheological properties were obtained between ESO content of 6–9 wt % for the larger values of n. In general, the optimum addition level of 6 wt %

ESO plasticized PLA could get a good performance balance.

It was the first time that a correlation between mechanical and rheological properties about PLA blends. The test had demonstrated quantitatively that there was a very strong correlation between the experimentally-measured melt rheological property of ESO blends and their performance in mechanical property, whereby higher melt strength (i.e., a larger resistance to elongation deformation) was associated with adding ESO into PLA. This correlation gave credence to the use of ESO improving properties of PLA.

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