

Plasticizing Effects of Epoxidized Sun Flower Oil on Biodegradable Polylactide Films: A Comparative Study¹

Nana Prempeh, Jinlei Li, Dagang Liu, Kunal Das, Sonakshi Maiti, and Ying Zhang

Department of Chemistry, Nanjing University of Information Science and Technology, Nanjing, China

e-mail: dagangliu@gmail.com, dagang@nuist.edu.cn

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Abstract—Polylactide (PLA) is one of the most promising materials among the renewable source-based biodegradable plastics. However, high inherent stiffness and brittleness of the pure PLA is often insufficient for wide range of engineering applications. One of the best ways to improve the processability, toughness and flexibility of PLA is to plasticize with epoxidized plant oils. In this work, epoxidized sun flower oil (ESFO) was incorporated into PLA matrix. The thermal, mechanical, biodegradation, optical transmission properties and fracture morphology of ESFO plasticized PLA were investigated to make a comparison with that of PLA plasticized by commercial epoxidized soya bean oil (ESO). Results show that a remarkable improvement of elongation at break was observed in the case of ESFO incorporated PLA. Although a slightly decrease the T_g of PLA was resulted from the plasticizing effects of ESFO, the thermal stability of the plasticized PLA was improved. On the other hand, the ESFO plasticized PLA showed a higher level of UV adsorption but a lower level of biodegradation ratio. After all, ESFO exhibited similar effects on the biodegradable PLA films to ESO, which is anticipated to be a good candidate for plasticizing biodegradable polymer materials.

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INTRODUCTION

Poly(lactide) (PLA) or poly(lactic acid) is a linear aliphatic thermoplastic polyester and produced from renewable resources like corn, sugar beets, wheat, and other starch-rich products. Nowadays PLA possesses enormous capability to replace synthetic materials in last few decades, and is widely used in the fields of textile, medical, packaging, and automotive industries [1–3]. However, inherent brittleness and stiffness of neat PLA are not sufficient enough for wide range of applications. A number of techniques have been evaluated to improve the mechanical properties of PLA, e.g., blending of PLA with other polymers such as polycaprolactone, polybutylene succinate or polyether urethane to improve the flexibility of PLA [4–8]. Enhancement of the ductility could also be achieved by incorporation of plasticizers with low molecular weight, such as citrate esters, polyethylene glycol, polypropylene glycol, or oligomeric lactic acid [9–16].

Petroleum-derived plasticizers are subject to several significant limitations. Increasing environmental concerns have made plant oils an attractive alternative for the production of epoxy-based materials, since plant oils are bio-renewable resources that can be used to reduce the stress from synthetic chemical industries on the environmental pollution and petroleum shortage. It was demonstrated by a world annual industrial

production of epoxidized soybean oils (ESO) of greater than 200000 tons. The rapid development of the plastics industry has made the demand for plasticizer rise tremendously; however, the application of these seed oils in industry at a large scale is impossible due to limited sources. Notably, some natural seed oils, including the oil from *Vernonia galamensis*, and *Euphorbia lagascae* containing epoxy groups in their fatty acids [8–10]. Therefore, current commercial epoxidized oils are chemically produced from unsaturated plant oil through Prilezhaev epoxidation. In Prilezhaev epoxidation, a short-chain peroxy acid, preferably peracetic acid is prepared by an in situ reaction of acetic acid with hydrogen peroxide (H_2O_2) and is used as a catalyst [11]. However, Prilezhaev epoxidation produces highly corrosive waste, and chemical epoxidation also leads to undesirable epoxy-ring opening as well as the polymerization of the product under acidic conditions. The plasticization effects were also manifested by a shift of glass transition to lower temperature and an increment in ability of PLA to cold crystallization. ESO has been used as a plasticizer for polyvinyl chloride (PVC) compounds, chlorinated rubber, and polyvinyl alcohol (PVA) emulsions. Phenolic resin modified by ESO (ESO/PR) has also been prepared for laminate materials [17]. Use of epoxidized oil in thermoplastic polymers shows significant improvement of toughness through grafting or blending modifications.

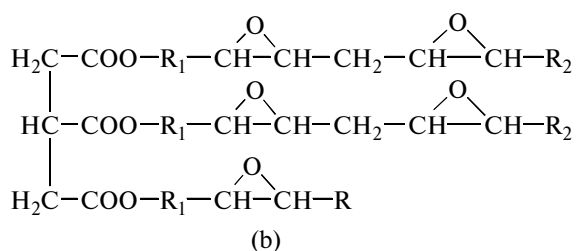
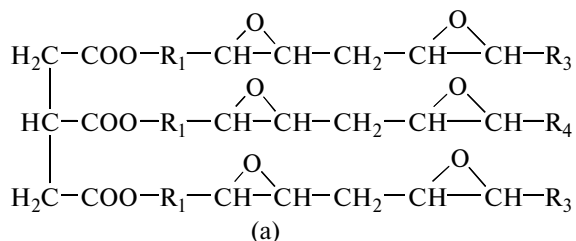
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Unsaturated sun-flower oil with a good oxidative stability finds many applications in the food market mainly as salad oil and cooking oil. Similar to ESO, Sun-flower oil after epoxidization is a good candidate plasticizer and has been reported to be an effective stabilizer and plasticizer for polyvinyl chloride film [18]. However, as far as we know no detailed reports about plasticizing effects of ESFO in comparison to ESO on biodegradable PLA has been done. In this work, we aimed to evaluate the behavior of ESFO as plasticizers for PLA by means of thermal, structural, mechanical, morphological and biodegradation investigations, and hope to provide some basic information for further-more industrial application of PLA film plasticized by ESFO.

EXPERIMENTAL

Materials

PLA used in the work is of commercial grade (PLA 2002D), obtained from Nature works LLC, USA. It has a D-isomer content of about 4 wt%; $M_w = 235000$; density = 1.24 g/cm³; melting temperature (T_m) is around 153°C. ESO, Per acetic acid, hydrogen peroxide, chloroform were obtained from sigma Aldrich. Sunflower oil (SFO) was obtained from Aura Cacia and Rein Oil, South Africa respectively. Epoxidation of the SFO was self-prepared by per acetic acid method [19]. The crude product was confirmed by FTIR shown in the supporting information according to the Infrared absorption band at around 845 cm⁻¹ attributed to the epoxy group [20]. The molecular structures of ESO and ESFO are illustrated below.



Plasticization of PLA

Plasticized PLA films were prepared by simple solution casting method in a glass plate. Firstly, a calculated amount of PLA was dispersed in chloroform and stirred at 25°C for 1.5 h to avoid any agglomeration. Then calculated amounts of ESO and ESFO were added to it and again stirred for another 1 h. This

was done in a closed flask to prevent evaporation. The liquor ratio of the PLA and chloroform was 1 : 10. Films were made by taking 30 wt % of all plasticizers (ESO or ESFO) with respect to dry weight of the PLA. Desired blends of PLA/(ESO/ESFO) were vacuum dried and immediately sealed in plastic bags and kept in a dessicator. Resultant films were designated as PLA, PLAESO30, and PLAESFO30, respectively.

Compost and Biodegradation

The composition of the compost was (dry weight): 40.8% cow dung, 11.4% sawdust, 15.8% newspaper and computer paper, 2% white bread, 7.8% shredded leaves, 19.2% food waste (dry milk, potato, carrot, banana, and other vegetables), and 3.0% urea [21]. The composting bin was filled with the above mentioned compost. The moisture content was maintained by spraying water at regular time intervals (150 mL/day). The duration of the test was 30 days and the ambient temperature range was from 30 to 34°C. The composting temperature varied with the temperature of the surrounding atmosphere. The films were cut into 20 × 20 mm² size and the samples were subjected to degradation at about 4 cm beneath the surface. The biodegradability was determined by measuring the weight loss of composted samples after thorough washing with distilled water and vacuum drying until constant weight. Three samples for each composition were picked up from the compost at regular time intervals and were investigated for their change in properties. The compost and biodegradation experiment was performed only once. Weight loss of the samples on biodegradation was measured following the equation,

$$\bar{W} = \frac{w_0 - w_t}{w_0} 100, \quad (1)$$

where \bar{W} is the average weight loss percent, w_0 is the weight of the sample before biodegradation and w_t is the weight of the sample after biodegradation at time t . The change in weight was measured for each time interval. The mean weight was recorded and the error bar corresponds to the standard deviation value. At the same time, the molecular weight of the samples after biodegradation for 5 days were determined in chloroform with a Shimadzu LC-3A GPC, using polystyrene standards for calibration.

Characterizations

FTIR analysis was done in the range 400–4000 cm⁻¹ with an FTIR-8300, SHIMADZU. Differential scanning calorimeter (DSC) measurements were carried out on a DSC Q2000 instrument (TA Instruments) under nitrogen atmosphere (flow rate 50 mL/min). The thermal properties of neat polymer and plasticized polymer (approximately 5 mg) were investigated by initially heating the samples at

10°C/min from room temperature (25°C) to 190°C with isothermal holding at 190°C for 5 min to destroy the previous thermal histories. Thereafter, cooling was carried out at the same rate. Enthalpies of melting (ΔH_m) were evaluated using TA Universal software by integrating the area of the melting peaks. The T_m was calculated from the deflection of the DSC curve from the baseline in the second heating cycle. Dynamic mechanical thermal analysis (DMTA) of neat PLA and plasticized PLA was carried out using a Perkin–Elmer DMA 8000 analyzer in the dual cantilever bending mode. The temperature dependence of loss modulus (E'') and $\tan\delta$ were measured at a frequency of 1 Hz. The strain amplitude was 0.05% and the heating rate was 2°C/min in the temperature range of –20 to 100°C. The thermal stability of samples was determined by means of thermo gravimetric analyzer using a TGA Q500 (TA Instruments) at a heating rate of 10°C from room temperature to 700°C under air atmosphere.

Tensile properties such as modulus, strength, and elongation at break of neat PLA and composites, were determined using Instron 5966 tester (Instron Engineering Corporation, USA) with a load cell of 10 kN. This was carried out under tension mode at a single strain rate of 50 mm/min at room temperature. To study the fracture surface morphology, the fractured samples from tensile testing were sputter-coated with gold using a Hitachi S 3400 N instrument under a flow of argon and observation of surface morphology was carried out an accelerated voltage of 10 kV.

The light barrier properties of PLA film and plasticized PLA film were determined by measuring their light transmittances at wavelengths ranging from 200 to 700 nm using Perkin-Elmer ultraviolet-visible spectrometer (Lambda 3B model). The transparency of the films was calculated by the equation A_{600}/T , where A_{600} is the absorbance at 600 nm and T is the average film thickness (mm).

RESULTS AND DISCUSSION

Thermo-Mechanical Properties

The visco-elastic and visco-plastic behavior of the plasticized PLA materials was investigated by DMTA. Dependence of $\tan\delta$ on temperature was plotted and presented in Fig. 1. Temperature at α relax transition denoted as T_α was 63, 62 and 60°C, corresponding to neat PLA, PLAESO30, and PLAESFO30, respectively, that is, the damping peak of plasticized PLA showed a slightly decreased magnitude of T_α in comparison to neat PLA. This might be explained that epoxidized oil at liquid state penetrated into an amorphous phase and broke the intrinsic joint force between LA molecules, thus leading to the rigidity chain moving freely after plasticization. However, plasticization effects were dependent on thermal properties of the oil as well as the interaction between oil and PLA, that is

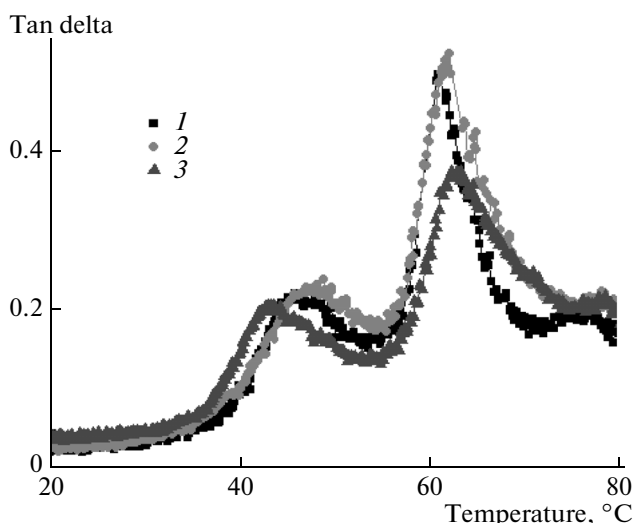


Fig. 1. Loss factor ($\tan\delta$) as a function of temperature for (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30.

why the PLA plasticized by epoxidized plant oil based plasticizers exhibited different T_α .

Mechanical Properties

Figure 2 shows tensile strength (Fig. 2a) and elongation at break of the PLA and plasticized PLA (Fig. 2b). Stiffness, brittleness and limited extensibility are the main features of PLA based materials [22], however, PLA modified with epoxydized oil in this work demonstrated markedly improved ductility, e.g. the elongation at break of PLAESFO30 was 4 times higher than that of neat PLA, and 3.6 times higher than PLAESO. However, tensile strength of PLAESFO30 was lower than that of neat PLA (38.1 MPa) and was at around 20 MPa. PLAESFO30 exhibited higher flexible mechanical properties than that of PLA modified by ESO, probably due to strong interaction between PLA and ESFO.

Morphology of Fracture Surface

Morphology of the fractured surface of neat PLA and plasticized PLA was elucidated by SEM and is shown in Fig. 3. Based on the tensile curve of the neat PLA (not shown), we observed that the sample broke rapidly after yielding, indicating a brittle failure which could be evidenced from Fig. 3a. There is a drastic change of crack growth behavior from brittle to ductile while epoxidized plant oil was incorporated into PLA, and also an orientation change generated in plasticized samples. It is very interesting that a clearly and well patterned nodular fracture surface was observed in Fig. 3c indicating good flexibility during the process of stretching orientation. On the other hand, it is suggesting that ESFO exhibited a good compatibility with

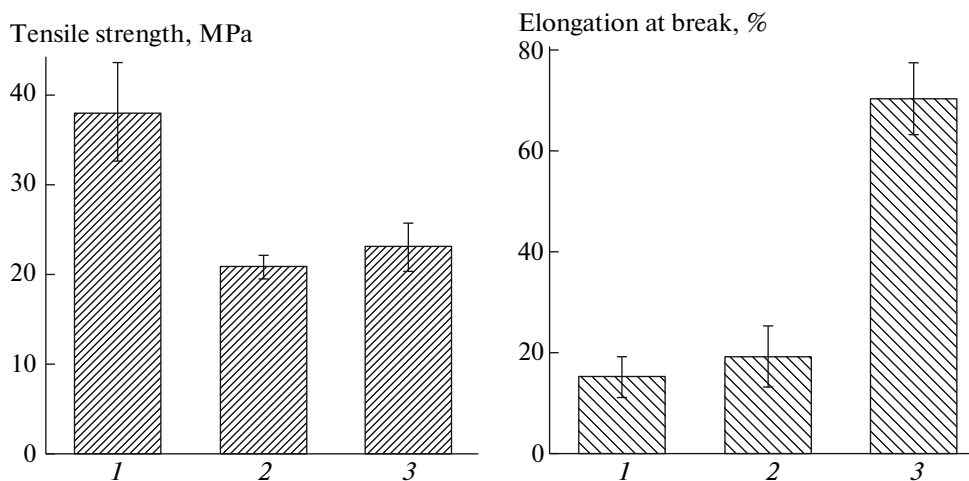


Fig. 2. (a) Tensile strength and (b) elongation at break of (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30.

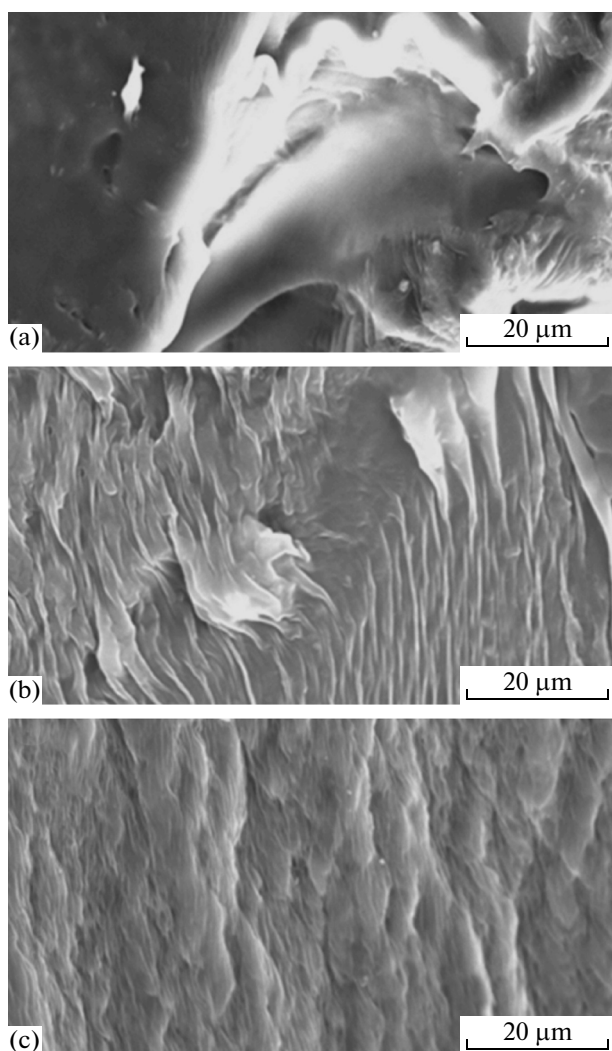


Fig. 3. SEM micrographs of the fracture surface of (a) neat PLA, (b) PLAESO30, and (c) PLAESFO30.

PLA and also a well dispersion of ESFO in the matrices, therefore, the fracture morphology is a good corroborate to illustrate the above mentioned mechanical properties.

Thermal Properties

DSC thermograms of neat PLA and plasticized PLA are shown in Fig. 4. A bimodal nonisothermal crystallization curve was observed in neat PLA, which could be related to hindrance of crystal growth. Meanwhile, neat PLA exhibited a very slow crystallization rate and a very insignificant melting enthalpy possibly because of high amount of D-isomer in the neat PLA. Bimodal crystallization curves were further observed in plasticized PLA samples, indicating impossible pene-

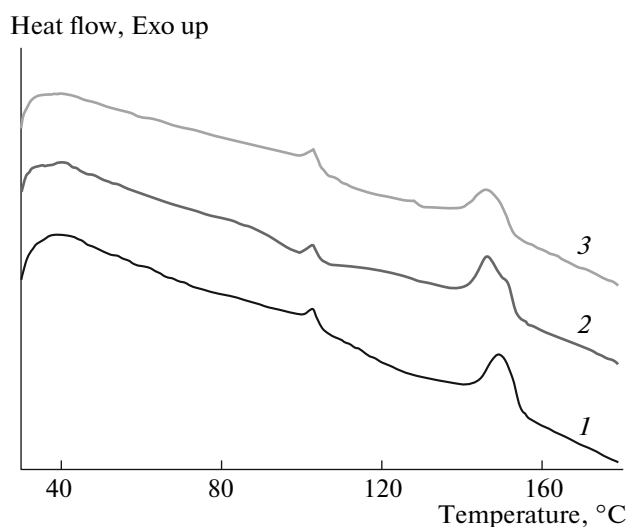


Fig. 4. DSC thermograms of (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30.

tration of plasticizers into crystalline-rich regions of PLA. That is to say, the crystallization behavior of PLA samples was insignificantly affected by plasticizers.

The degree of crystallinity (χ) was calculated using the equation presented below [16].

$$\chi = \frac{\Delta H_m}{f\Delta H^\circ} 100 \quad (2)$$

The degree of crystallinity of neat PLA, PLAESO30 and PLAESFO30 were 39.4, 36.1, and 35.0, respectively. The effect of decreasing crystallinity should be responsible for the reduction of the tensile strength in the plasticized PLA. This well corroborates our SEM and tensile observation.

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 polymeric materials takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective chemical bonds. TGA of the PLA and plasticized PLA are graphically presented in Fig. 5. It is generally considered that incorporation of oil always improve the thermal stability of the virgin polymer. It was observed that the degradation peak of the plasticized PLA especially PLAESFO30 shifted from 322 to 335°C and char residue improved significantly. We hypothesized that the possible inter component hydrogen bonding between PLA and plasticizers was responsible for the increment of the thermal stability.

The activation energy for thermal degradation was also calculated based on the equation derived by Broido [23]. The calculation is provided as follows:

$$\begin{aligned} & \ln[\ln(1/y)] \\ &= \ln\left[\ln\left(\frac{w_0 - w_\infty}{w_T - w_\infty}\right)\right] = -\frac{E_\alpha}{RT} + C, \end{aligned} \quad (3)$$

where w_0 and w_∞ are the initial and final weights; w_T is weight remaining at particular temperature T ; R is universal gas constant; T is temperature in Kelvin scale and C is the constant. The plots were followed a linear line as shown in Fig. 6a, whose slope express the activation energy E_α for the thermal degradation process. The variation of the activation energies of the PLA and plasticized PLA are shown in Fig. 6b. In the case of PLAESFO30, the activation energy was higher than neat PLA and PLASEO30, supporting that the higher stability of ESFO plasticized composites.

Light Transparency

Figure 7 shows the light transmittance of the PLA and plasticized PLA at selected wavelengths from 200 to 700 nm and also the transparency of the concerned film. All the films have an excellent transmittance in the visible light region. Normally, the thinner films were simply more transparent [24], that's why the

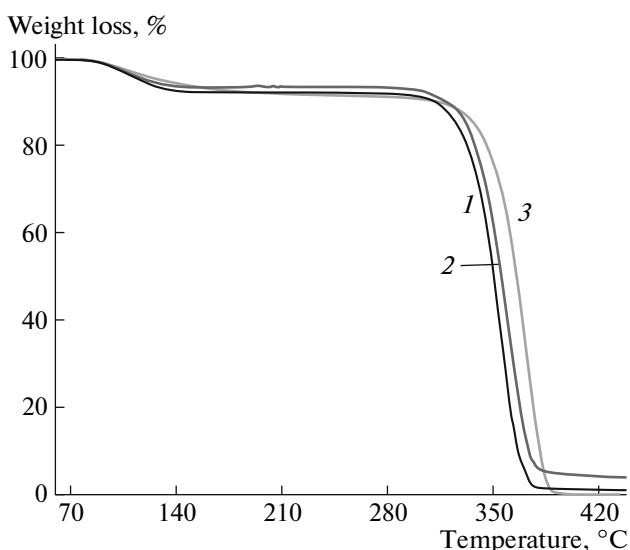


Fig. 5. TGA thermograms of (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30.

thickness of the film should be considered in the calculation of transparency. Results shows that the transparency of the film PLAESFO30 at $\lambda = 600$ nm was higher than the others. This phenomenon probably was connected with well dispersion of plasticizer in the matrix and also high level of well oriented morphological pattern which was observed from SEM. It is interesting that the plasticized film have a strong adsorption in the violet region.

Biodegradation

As far as biodegradability is concerned, it has been confirmed that PLA is naturally degraded in soil or compost. Biodegradation of PLA was usually done by esterases, proteases and lipases secreted from microorganisms in the compost. As shown in Fig. 8, the rate of biodegradation in the case of neat PLA was significantly higher than that of PLAESO30 and PLAESFO30 since PLA is highly biodegradable material and epoxidized plasticizers are partly hydrophobic. However, we observed that all samples fully degraded before our experimental tenure (30 days), e.g., neat PLA were broken down into small pieces after 10 days, while PLAESO30 and PLAESFO30 samples were completely broken down after 20 days. That is to say, PLA shows a higher rate of biodegradation. Plenty of holes and bacteria were presented in PLA samples observed by using SEM (Fig. 9). Furthermore, the absence of bacteria in the surface of PLAESO30 and PLAESFO30 in the SEM images confirms the reluctant biodegradation behavior of those oil-plasticized samples. After 5 days, the molecular weight of PLA, PLAESO30 and PLAESFO30 decreased from 235000 into 187000, 219700 and 219200, respectively. During the degradation process,

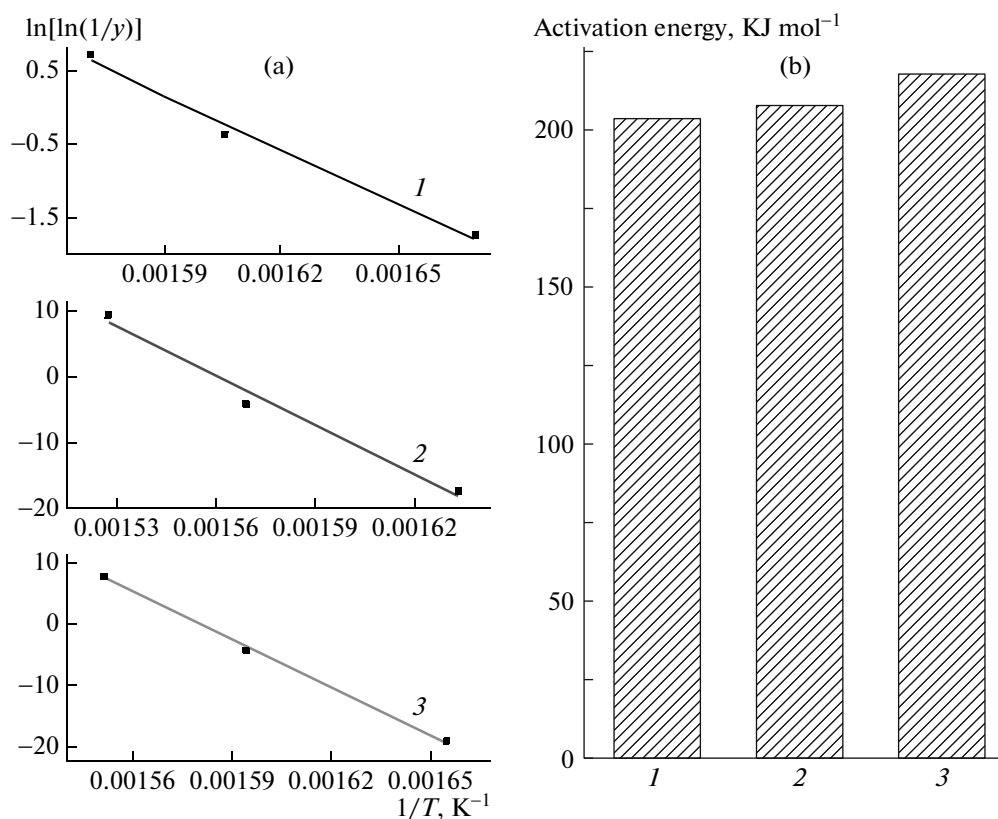


Fig. 6. (a) Plots of $\ln\{\ln(1/y)\}$ vs. $1/T$ and (b) activation energy of (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30.

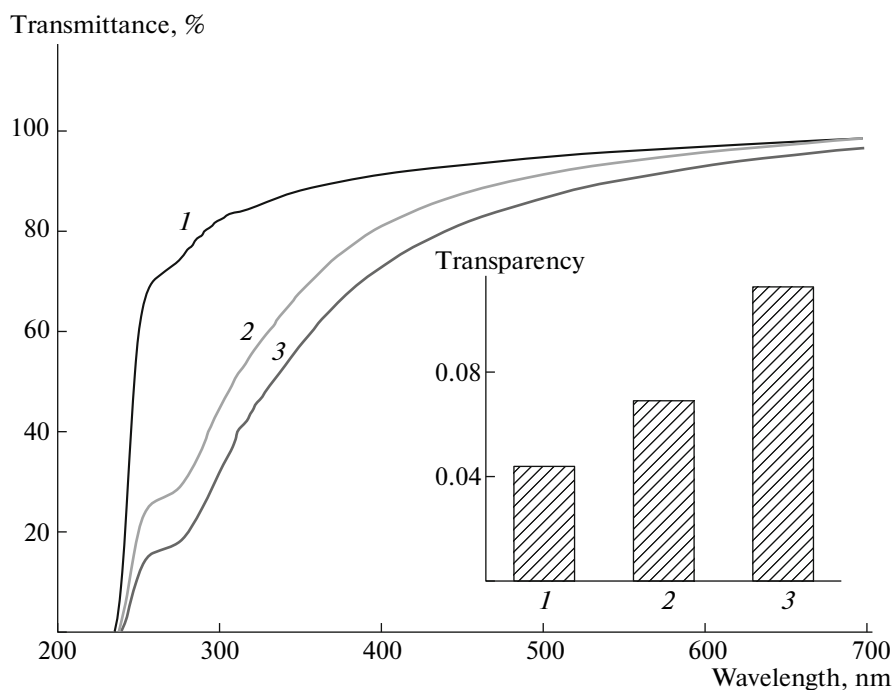


Fig. 7. UV-Vis spectra of (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESO30. The inset picture shows transparency of all films at $\lambda = 600$ nm.

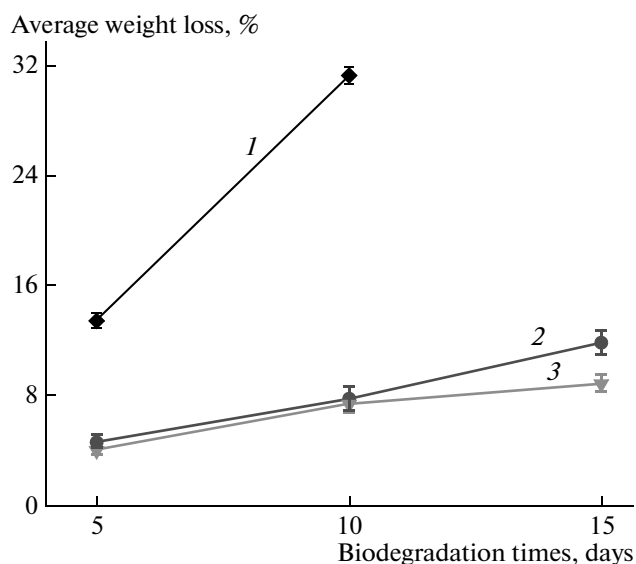


Fig. 8. Weight loss of the biodegraded samples: (1) neat PLA and plasticized PLA: (2) PLAESFO30 and (3) PLAESFO30 after a specific intervals.

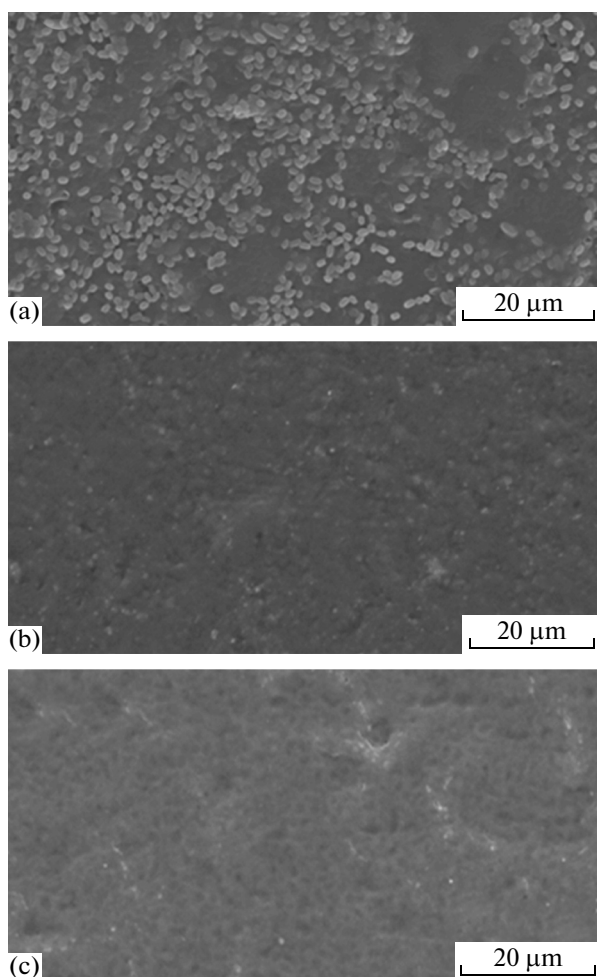


Fig. 9. SEM micrographs of (a) neat PLA and (b) PLAESFO30 and (c) PLAESFO after degradation for 5 days.

PLA polymer chain allowed a hydrolytic degradation which cause a decrease of molecular weight [25]. Moreover, it was thought that 30% epoxidized plant oil should be responsible for the retarded biodegradation behavior of PLA.

CONCLUSIONS

This work was devoted to make a comparative research to determine the plasticizing effects of ESFO on the structural, morphological, biodegradation and thermal behavior of PLA film. New plasticizer-ESFO could markedly improve the ductile mechanical properties, since the elongation at break could be about 4 times higher than that of neat PLA. Moreover, the T_g was reduced, and the thermal stability of PLA was elevated because of the incorporation of ESFO, indicating that well dispersion of plasticizer and good interaction between ESFO and PLA. On the other hand, biodegradation and film transparency behavior were also significantly influenced. Based on the comparative study, ESFO was demonstrated to be a candidate for commercial ESO and anticipated to be widely used as filler, stabilizer, or plasticizer in industrial products of PLA.

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