

Poly(lactic acid) plasticized by biodegradable glyceryl lactate

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ABSTRACT: The esterification of glycerol with lactic acid was carried out to synthesize glyceryl lactate, which was used as a plasticizer with different contents and blended with poly(lactic acid) (PLA) to get a completely biodegradable material with potential applications because of its biodegradability. The structural, morphological, thermal, and mechanical properties of the plasticized PLA were studied to evaluate the plasticizing effects. The results show that the PLA plasticized with glyceryl lactate had a lower glass-transition temperature and a better ductility. With increasing plasticizer content, the crystallinity of PLA increased. The elongation at break reached 380%, and the impact strength was 1.7 times that of neat PLA. Simultaneously, the migration rate measurements showed that glyceryl lactate presented relatively low migration toward the surface compared with glycerol and citrate esters. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43460.

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INTRODUCTION

In the last few decades, as polymer science has developed rapidly, many issues concerning environmental and sustainable impacts have appeared at the same time. Therefore, degradable polymers have been increasingly attended to.^{1,2} Poly(lactic acid) (PLA) is one such polymer, with biodegradability, biocompatibility, good mechanical properties, processability, and extensive commercial applications.^{3,4} However, PLA also has some defects that limit its applications, such as in medical films and agriculture films. A high brittleness is one such defect, and it occurs because of the glass-transition temperature (T_g), which is close to 55 °C;^{5,6} this is a restriction in the film-extrusion industry.⁷ To overcome these defects and improve the possibility for widespread utilization, the modification of PLA to enhance its toughness and ductility is necessary.^{8–10} Considerable efforts have been made to obtain PLAs with improved properties; they include the blending of PLA with other polymers, the plasticizing of PLA with low-molecular-weight plasticizers, and copolymerization with other monomers.^{11,12}

The addition of plasticizer to modify PLA is a method that is used widely in the plastics industry.¹³ With respect to thermoplastic materials such as PLA, the addition of plasticizers to the matrix should meet several necessary requirements. In addition to improving the defects mentioned previously, it is essential to retain the primary positive properties. The compatibility of the plasticizers with polymers should be considered. In addition, they should hardly migrate toward the surface of the polymer matrix

to enhance the plastic effects and extend the longevity.^{2,14,15} A number of plasticizers have been applied to PLA plasticization with the aim of improving its flexibility and ductility. Typical examples of such plasticizers are citrate esters,^{16–18} triacetate, glycerol,¹⁹ oligomeric lactic acid,¹⁴ malonate oligomers,^{4,20} poly(ϵ -caprolactone),^{21–23} poly(ethylene glycol),^{20,24} poly(propylene glycol),²⁵ and epoxidized vegetable oils.^{8,26,27} In addition, diethyl bis(hydroxymethyl) malonate,⁴ oligomeric polyesters, and esteramides have also been used to plasticize PLA.²⁸

The plasticizers above all show certain plastic effects on PLA; these effects include a decrease in T_g , an increase in the elongation at break, and an improvement of ductility. However, the plasticizers show no permanence in the inside of the matrix and migrate toward the surface of the material. Studies have shown that increases in the molecular weight of the plasticizer decrease the migration.^{14,29} Another fact is that the plasticizers show a poor miscibility with matrix materials as their molecular weight increase to a certain value. As a result, it is important to base the choice of plasticizers on a consideration of equilibrium between the molecular weight and migration.

In this study, glyceryl lactate was synthesized to plasticize PLA, which was produced from renewable resources. It was obtained from the esterification between lactic acid and glycerin. Glyceryl lactate was used as a plasticizer and compatibilizer for poly(vinyl alcohol)/PLA blends by Li *et al.*³⁰ They found that the lactyl units of the plasticizer contributed to improvements in the compatibility between PLA and poly(vinyl alcohol), with its

Table I. Molar Contents and Molar Ratios of Lactic Acid and Glycerol

Lactic acid (mol)	Glycerol (mol)	Molar ratio
0.24	0.2	1.2
0.38	0.2	1.9
0.52	0.2	2.6
0.66	0.2	3.3

similar structure to that of PLA. We evaluated the effects on the structure and thermal and mechanical properties of PLA films plasticized with different contents of glyceryl lactate. The PLA plasticized with glyceryl lactate had a higher elongation at break and a better ductility. In addition, glyceryl lactate presented a certain extent of compatibility with PLA and a low migration over time compared with conventional plasticizers.

EXPERIMENTAL

Materials

A commercial PLA [4032D; number-average molecular weight = 207,000 g/mol, weight-average molecular weight/number-average molecular weight = 1.74, $T_g = 60^\circ\text{C}$, melting temperature (T_m) = 168°C] from NatureWorks, LLC (Minnetonka, MN) was used as polymeric matrix. Glycerol (analytical-reagent grade, Kelong Chemical Reagent Factory, Chengdu, China) and lactic acid (analytical-reagent grade, Kelong Chemical Reagent Factory, Chengdu, China) were used to synthesize glyceryl lactate. Dimethyl benzene, *p*-toluene sulfonic acid, ethyl acetate, and sodium chloride were purchased from Kelong Chemical Reagent Factory and were analytical-reagent grade. Solvents were used without further purification.

Preparation of the PLA/Glycerol Lactate Films

Different molar contents (shown in Table I) of lactic acid and glycerol were added to a three-necked boiling flask with a water separator. A 10 wt % content of dimethyl benzene and a 0.5 wt % content of *p*-toluene sulfonic acid were added as a water carrier and catalyst, respectively. The system was heated to a certain temperature and maintained with continuous stirring for 5 h. After the reaction, residual dimethyl benzene and lactic acid were removed by reduced-pressure distillation. A mixture of glyceryl lactate was obtained, and the reaction process is shown in Figure 1.

A purification step was conducted before we obtained the pure glyceryl lactate products.

The glyceryl lactate obtained previously was dissolved in saturated sodium chloride. The solution was poured into a separatory funnel with a certain amount of ethyl acetate to extract the residual glycerol and lactic acid from the solution (because of the better solubility of lactic acid in water than in ethyl acetate and the insolubility of glycerol in ethyl acetate). We separated the bottom sodium chloride solution and repeated the extraction step three times. All of the clear liquid of upper layer, which contained ethyl acetate and glyceryl lactate, was collected. Reduced-pressure distillation was carried out to remove the ethyl acetate and water from the clear liquid, and then, the pure glyceryl lactate was obtained.

Before mixing, PLA was dried at 80°C for 6 h to prevent PLA hydrolysis during processing. Glyceryl lactates with different degrees of esterification (D_s) were mixed with PLA in a torque rhe-

ometer (model XSS-300, Shanghai Kechuang Rubber Plastics SET Co., Ltd., China) at PLA/glycerol lactate ratios of 100:0 (0%), 95:5 (5%), 90:10 (10%), 85:15 (15%), 80:20 (20%), and 75:25 (25%). The mixtures were premixed at a rotational speed of 20 rpm for 1 min and then mixed at 80 rpm for 5 min. We took the start time as the point at which the rotational speed reached 80 rpm and recorded the changes in torsion over time. The samples of the mixed blends were processed into sheets with a thickness of 1 mm or 0.1 mm by compression molding at 180°C in a Gemini 200 curing press (Bohlin Co., United Kingdom). We preheated the materials at atmospheric pressure for 3 min to melt them. Then, we exhausted air three times and carried out heat pressing for 3 min when the pressure and temperature reached the expected values. The resulting product was cold-pressed for 3 min.

Material Characterization

$^1\text{H-NMR}$ Analysis. Lactic acid, glycerol, and glyceryl lactate were dissolved in D_2O . $^1\text{H-NMR}$ experiments were performed on a Bruker AV II 400-MHz instrument. The internal standard was tetramethylsilane.

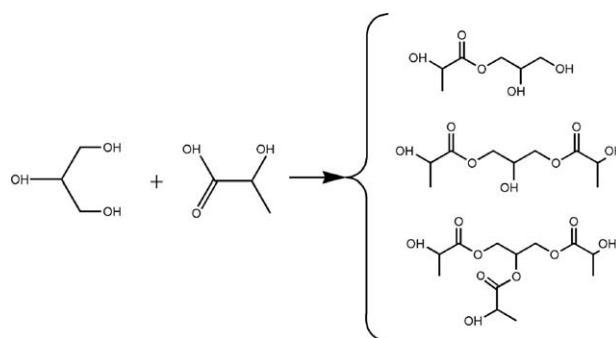
Mechanical Properties. Tensile tests were performed with a universal test machine (CMT4104, Shenzhen SANS Testing Machine Co., China) according to GB/T 1040-2006, type II, with a tensile speed of 10 mm/min at 24°C .

Impact tests were carried out on a XJU-22 impact tester (Beijing Jinshengxin Testing Instrument Co., China) at 24°C . Tests were performed according to GB/T 1843-2008, gap type A, with a gap reserved width of 8 mm.

Dynamic Thermomechanical Analysis. Dynamic thermomechanical analysis was carried out on a dynamic thermomechanical analyzer (Q800, Netzsch, GER) in double-cantilever mode. The samples ($50 \times 12 \times 2 \text{ mm}^3$) were scanned from 20 to 160°C at a heating rate of $3^\circ\text{C}/\text{min}$ and a fixed frequency and amplitude at 1 Hz and $20 \mu\text{m}$, respectively.

Scanning Electron Microscopy (SEM). A JSM-7500F scanning electron microscope (JEOL, Japan) operated at 5 kV was used to observe the morphologies of the samples. In liquid nitrogen, the samples were fractured to expose the cross sections. The cross sections were etched in water for 2 h, dried, and sputtered with gold for SEM studies.

Plasticizer Migration Tests. The rectangular samples ($10 \times 10 \times 1 \text{ mm}^3$) contained on watch crystals were put into two vacuum ovens at 125 and 150°C to test the migration rates of the plasticizers.

**Figure 1.** Synthetic map of glyceryl lactate.

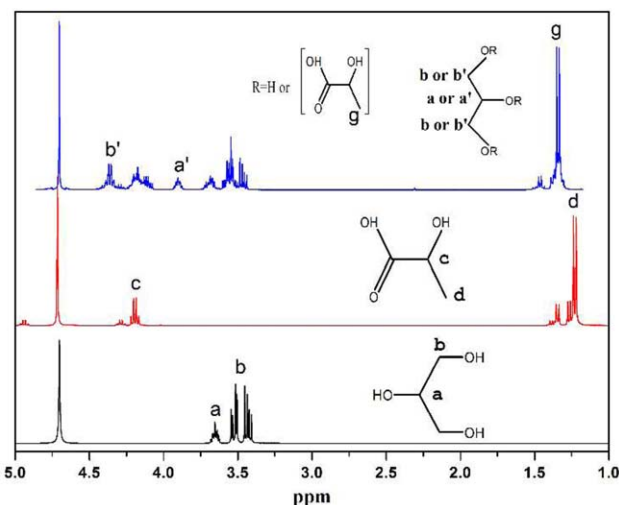


Figure 2. $^1\text{H-NMR}$ spectra of glycerol, L-lactic acid, and glyceryl lactate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The samples were taken out at regular intervals, wiped to clean the plasticizer that had moved to the surface, and then weighed on an analytical balance (FA1004N, Heng Ping Electronics Co., Ltd., China). The migration rates (ω s) were calculated by the following equation:

$$\omega = [(m_1 - m_2) / m_1] \times 100\% \quad (1)$$

where m_1 and m_2 are the masses of the sample before and after they were put into the vacuum oven, respectively.

Differential Scanning Calorimetry (DSC). DSC measurement was performed on a TA DSC 204 instrument (Netzsch, GER) under nitrogen gas. Samples (ca. 8 mg) with different plasticizer contents were sealed in aluminum pans, heated from 0 to 200 °C at 10 °C/min, and maintained for 3 min to erase their thermal histories. After the samples were cooled to 0 °C at 10 °C/min and maintained at that temperature for 3 min, the second heating was conducted under same conditions as used in the first heating scan. The data were obtained from the second heating scan.

Rheological Characterization. Rheological measurements were carried out on a rotational rheometer (Gemini 200 Bohlin Co., United Kingdom) with a parallel-plate geometry with a diameter of 25 mm. A transducer (200FRTN1) was introduced with a sensitivity of 0.02 g cm. Wafers of the plasticized PLA obtained from thermoforming with a diameter of 25 mm and a thickness of 1 mm were used for the measurements. A dynamic frequency sweep was performed at 180 °C with a strain of 5%. The range of the dynamic frequency was 0.1–100 rad/s. The storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) responses to the frequency were recorded.

RESULTS AND DISCUSSION

Preparation of Glyceryl Lactate

Compared with glycerol and lactic acid, the $^1\text{H-NMR}$ spectra of glyceryl lactate presented new chemical shifts at 3.8 and 4.3 (Figure 2). These two peaks were induced by the methine and meth-

ylene groups of the esterified glycerols with different degrees of esterification, respectively. In addition, D_e could be calculated by the following equation³⁰:

$$D_e = \frac{I_{1.3} \times 4}{(I_{4.1} + I_{3.5}) \times 3} \quad (2)$$

where $I_{1.3}$ is the representative intensity of the methyl groups of the lactic acid moieties and $I_{4.1}$ and $I_{3.5}$ are the representative intensities of the methylene groups of the glycerol moieties.

Effect of the Acid-to-Alcohol Ratio on the Product of Glyceryl Lactate

Figure 3 shows the effects of different acid-to-alcohol molar ratios on the average D_e and acid value of glyceryl lactate. The average degree of substitution (D_e) of glyceryl lactate increased with the acid-to-alcohol molar ratio and the acid value of the product. This indicated a controllable D_e of the product through the adjustment of the acid-to-alcohol molar ratio.

Effect of D_e on the Mechanical Properties of the Blends

Variations of the tensile strength and elongation at break of the PLA plasticized by glyceryl lactate with a 15 wt % glyceryl lactate content according to D_e are shown in Figure 4. With increasing D_e , the tensile strength of the plasticized PLA decreased gradually. When D_e increased from 0.42 to 2.16, the elongation at break of the plasticized PLA improved from 34 to 175%. However, the elongation at break decreased to 145% when D_e reached 2.76. On the basis of the comprehensive consideration of the tensile strength and elongation, in the following experiments, we chose the glyceryl lactate with D_e at 2.16 to examine the effects of different contents of glyceryl lactate on the structure and properties of PLA.

Morphological Analysis of the Blends

Figure 5 shows the SEM images of the fracture surfaces of the neat PLA and PLA modified by glyceryl lactate. A smooth surface morphology and a continuous phase were observed in the neat PLA. The modified PLA with the addition of glyceryl lactate contents from 5 to 25 wt % contained spherical particles and exhibited a sea-island structure. Moreover, with increasing glyceryl lactate content, the size of the separate phases increased. Overall,

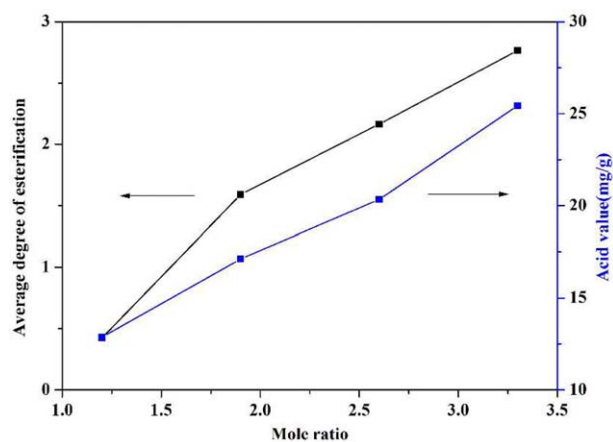


Figure 3. Effect of the molar ratio on the average D_e and acid value. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

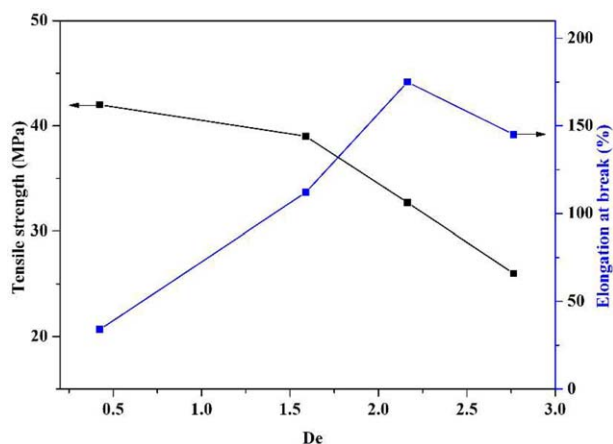


Figure 4. Effect of D_e on the tensile strength and elongation at break with 15 wt % glyceryl lactate content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the previous phenomena indicated that the PLA/glyceryl lactate blends belonged to a partly compatible system, and the glyceryl lactate dispersed steadily in the PLA matrix in a state of spherical droplets.

DSC of the Blends

Figure 6 shows the thermograms of PLA plasticized by different contents of glyceryl lactate. The thermal properties of the blends

were investigated by means of DSC. PLA has a slow crystalline rate; therefore, the products cooled from melts have a low crystallinity in general industry processes.^{31,32} The heating of semicrystalline PLA to the point above T_g leads to a cold crystallinity phenomenon. As shown in Figure 6, when PLA was cooled from 200 to 0 °C at a rate of 10 °C/min to eliminate the thermal history, no cold crystallinity phenomenon was observed in the secondary heating curves, although the melting peaks were strong. This indicated that the cooling of the PLA melts at a rate of 10 °C/min led to higher crystallinity in the products. The degree of crystallinity (X_c) of the blends could be calculated from the melting enthalpy in the secondary heating curves (ΔH_m) according to the following equation:

$$X_c = [\Delta H_m / (\omega_{\text{PLA}} \Delta H_m^0)] \times 100\% \quad (3)$$

where ω_{PLA} is the mass fraction of PLA in the blends and ΔH_m^0 is the standard melting enthalpy of the PLA crystalloid (93 J/g).³³ The T_m , ΔH_m , and X_c values of the blends and neat PLA are given in Table II. As shown in Figure 6 and Table II, the addition of glyceryl lactate improved X_c of PLA. This could be explained by the increased chain mobility of the plasticized PLA.^{34,35} With the increase in glyceryl lactate, X_c of PLA increased first and then tended to be stable, and the T_m decreased dramatically. Because the glass-transition platforms were not clear at the curves, a more sensitive method to measure T_g of the blends, such as dynamic mechanical analysis, was necessary. In addition, we also discovered

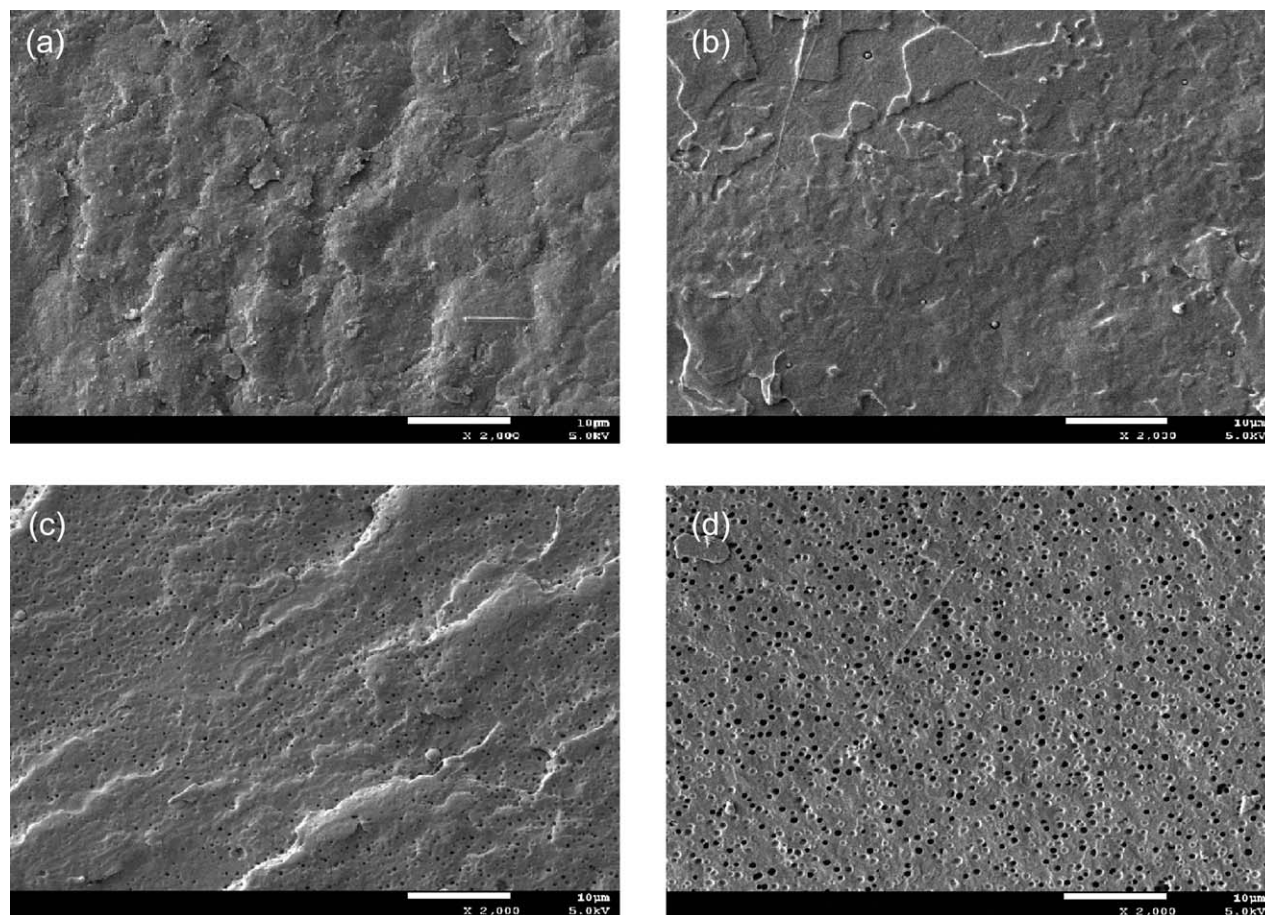


Figure 5. SEM pictures of the PLA plasticized with different glyceryl lactate contents: (a) 0, (b) 5, (c) 15, and (d) 25 wt %.

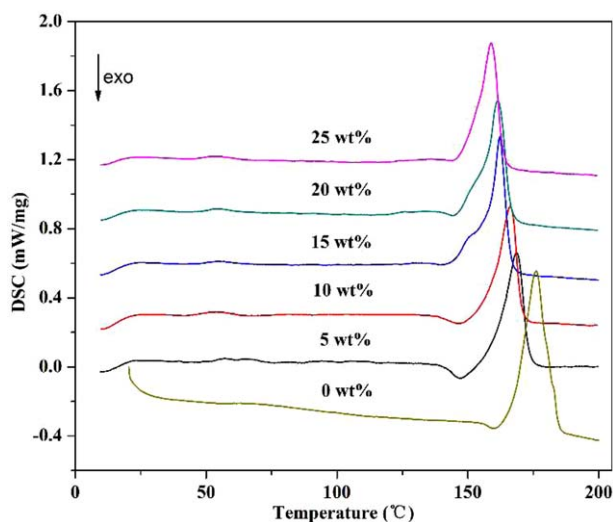


Figure 6. DSC curves of the plasticized PLA with different glyceryl lactate contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from Figure 6 that a small exothermic peak before the melting peak of the blends decreased until it disappeared gradually as the glyceryl lactate content increased; this indicated that glyceryl lactate could improve the completeness of the crystal structure.

Dynamic Mechanical Analysis of the Blends

Figure 7 shows the loss factor of the plasticized PLA by different glyceryl lactate contents. In this blend system, the loss factor peak corresponded to the T_g of PLA. As shown in the curves, the T_g value of PLA decreased with increasing content of glyceryl lactate. When the glyceryl lactate content increased from 0 to 25%, the T_g value of PLA decreased from 66.48 to 44.64 °C; this indicated that glyceryl lactate displayed an excellent plastic efficiency on PLA. Compared with epoxidized vegetable oils plasticized PLA with 5% content ($T_g = 60.12$ °C),²⁶ the glyceryl lactate resulted in a lower T_g (58.07 °C) at the same content.

G' represents the values of the storage energy caused by elastic deformation when a material is deformed. Figure 8 shows the effects of different plasticizer contents on the G' values of the blends. We observed that the neat PLA and the plasticized PLA with 5 wt % plasticizer had higher G' values under T_g , whereas the PLA chains were frozen and the samples presented a glassy state. As the temperature rose and approximated T_g , the PLA

Table II. DSC Data for the Plasticized PLA with Different Glyceryl Lactate Contents

Glyceryl lactate content (%)	T_m (°C)	ΔH_m (J/g)	X_c (%)
0	179.7	33.48	36
5	168.4	33.09	37
10	166.1	33.81	40
15	161.9	40.64	51
20	161.3	37.64	51
25	158.6	36.35	52

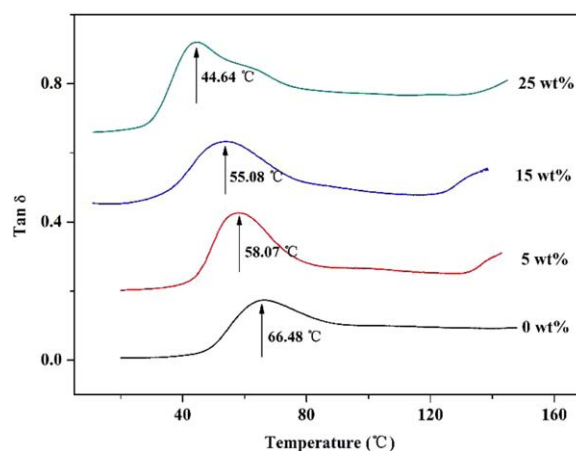


Figure 7. Tan δ curves of the plasticized PLA with different glyceryl lactate contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chain movement started, viscous deformation occurred, and G'' values declined sharply to the lowest values. As the temperature continued to rise to 70 °C, in the PLA molecular segments, cold crystallization appeared; this limited the movement of molecular segments. Also, the G'' values started rising and then reached approximate state values. Although the blend samples plasticized by 15 and 25 wt % glyceryl lactate had lower extents of the decline of G' with the increases in temperature, the G'' values under 110 °C were significantly larger than those of two previously mentioned samples. These phenomena could be explained by the fact that the glyceryl lactate at 15 and 25 wt % contents improved the crystalline characteristics of PLA because of the increased chain mobility; this was in agreement with the conclusions confirmed by DSC analysis.

Dynamic Rheology Analysis of the Blends

η^* is one of the major parameters for characterizing the rheological properties of polymer materials. The value of η^* reflects the speed of movement of the polymer molecule segments.³⁶ Figure 9 shows the η^* values of the neat PLA and the plasticized

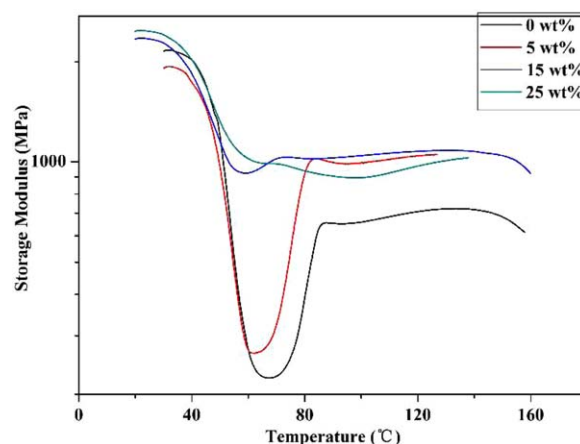


Figure 8. G' curves of the plasticized PLA with different glyceryl lactate contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

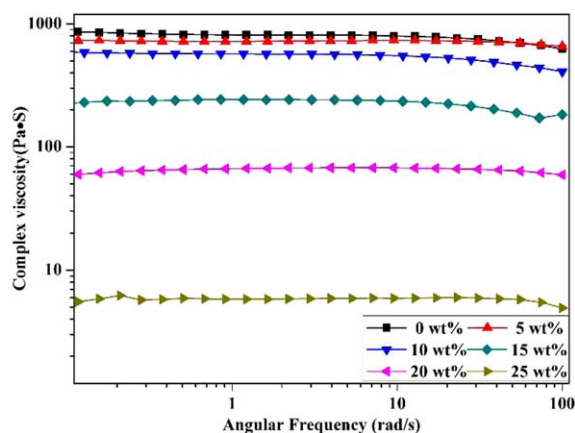


Figure 9. Angular frequency dependence of η^* of the plasticized PLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PLA with different glyceryl lactate contents against the angular frequency. We observed that the η^* 's of the plasticized PLA were significantly lower than those of the neat PLA, and the η^* 's of the plasticized PLA decreased successively with increasing glyceryl lactate content. The addition of glyceryl lactate contributed to improvements in the mobility of the PLA chains and, therefore, greatly decreased η^* . Moreover, we also found in the figure that η^* of the PLA was sensitive to the shear rate, and the PLA was a pseudoplastic fluid with a shear-thinning nature. In the mixture of the glyceryl lactate with PLA, a lower sensitivity of the mixtures to the shear rate was obtained. This indicated further that glyceryl lactate had a significant plasticization effect on PLA and decreased the chain entanglements of the PLA molecules.

Under alternating stress conditions, in the polymeric fluid, we found that the strain lag behind the stress because of its viscoelasticity. The work shear stress applied to the polymeric fluid, on the one hand, was used to change the conformation of polymer chains; on the other hand, it was used to provide essential energy to overcome friction caused by the segment movements. When the stretched molecular chains curled again, the moving segments also needed to overcome the internal friction resistance between segments. In a cycle, a part of the work was lost to conversion into thermal energy; the energy loss corresponded to G'' . Therefore, G'' generally characterized the energy loss of the polymer materials. The relationships of the G'' values of the neat PLA and plasticized PLA against frequency are illustrated in Figure 10. We observed that all of the G'' values improved as the shear frequencies increased. Moreover, neat PLA possessed a higher G'' than all of the modified PLAs because the plasticizer improved the mobility of the PLA chains and depressed the hysteresis of PLA. Also, the G'' values of the samples decreased as the glyceryl lactate content increased.

The dynamic G' is one of the vital parameters in dynamic rheological measurements to the elastic characterization of a macromolecular polymer. Its physical meaning is the elastic response value of the melt of the macromolecular polymer or its blend systems under a dynamic state, that is, the values of spring-

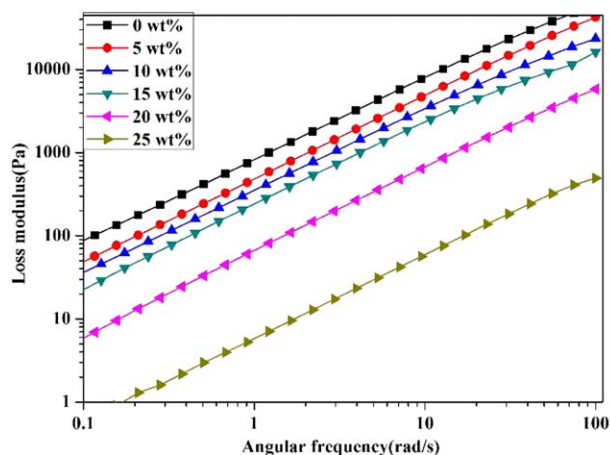


Figure 10. Frequency dependence of G'' of the plasticized PLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

back.³⁷ The relationships of the G' values of the neat PLA and plasticized PLA by different glyceryl lactate contents against frequency are illustrated in Figure 11. They were similar to the relationships between G'' and frequency, where all of the moduli of the neat PLA and plasticized PLA increased with increasing frequency. According to the theory of time-temperature superposition, an increase in the frequency corresponds to a shorter force time. Because of the increase in frequency, the mobility of the molecular chains was unable to keep pace with the changes in stress; they thus displayed a relatively high rigidity. Therefore, G' increased with increasing frequency, and the dynamic G' of neat PLA was higher than those of the plasticized PLA.

Mechanical Properties

It is well known that neat PLA has poor flexibility and presents a typical fragility macroscopically. PLA has a high tensile strength, a high modulus, and a low elongation at break. With the addition of glyceryl lactate, changes in the mechanical properties were identified by tensile tests. The tensile properties and

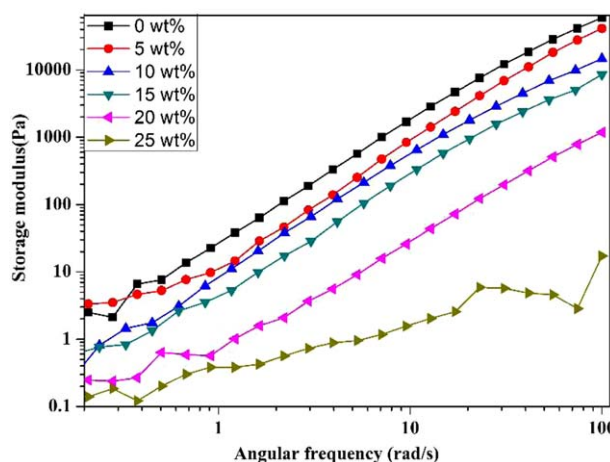


Figure 11. Frequency dependence of G' of the plasticized PLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

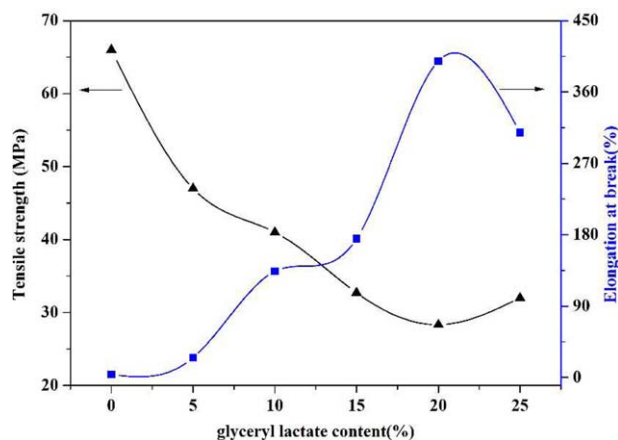


Figure 12. Tensile properties of the plasticized PLA with different glyceryl lactate contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress–strain curves of the PLA samples are shown in Figures 12 and 13, respectively. The tensile strength of the PLA plasticized by glyceryl lactate decreased, whereas the elongation at break improved dramatically. At the same content of plasticizer, such as 10%, the plasticization of glyceryl lactate led to a lower decrease in the tensile strength and a higher increase in the elongation at break compared with epoxidized palm oil.²⁶ The stress–strain curves at 15, 20, and 25 wt % contents of plasticizer displayed obvious yield and stress softness. A necking phenomenon was discovered in the tensile process. These all indicated that the brittle fracture of PLA was converted into ductile fracture. However, when the content of glyceryl lactate reached 25 wt %, the elongation at break of the blends decreased instead; this was the result of the oversized glyceryl lactate phase (SEM).

Figure 14 shows the impact strength curves of the neat PLA and PLA plasticized by glyceryl lactate. The plasticized PLA showed improved impact properties to some extent. Compared to neat PLA with a 3.9 kJ/m² impact strength, the PLA

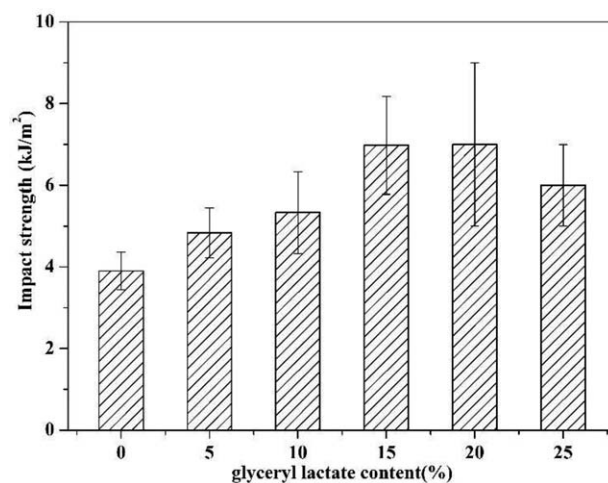


Figure 14. Impact strength of PLA with different glyceryl lactate contents.

plasticized by glyceryl lactate had the highest impact strength value, namely, 6.98 kJ/m², which was almost 1.7 times that of neat PLA. When the content of glyceryl lactate continued to increase, the impact strength decreased. This might have also

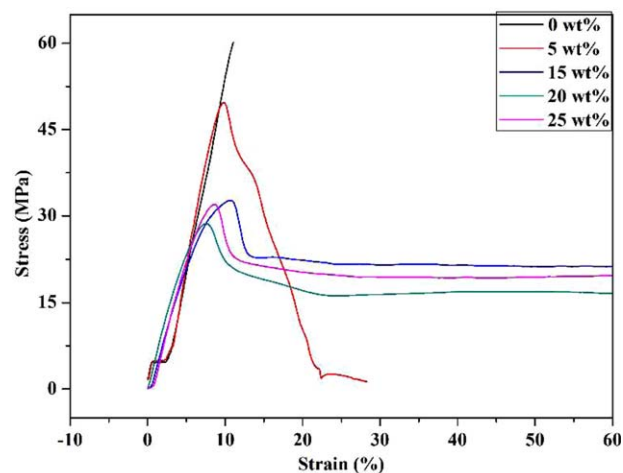


Figure 13. Stress–strain curves of the plasticized PLA with different glyceryl lactate contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

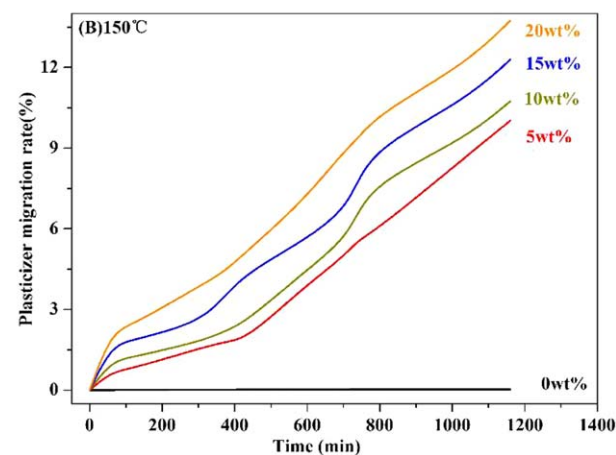
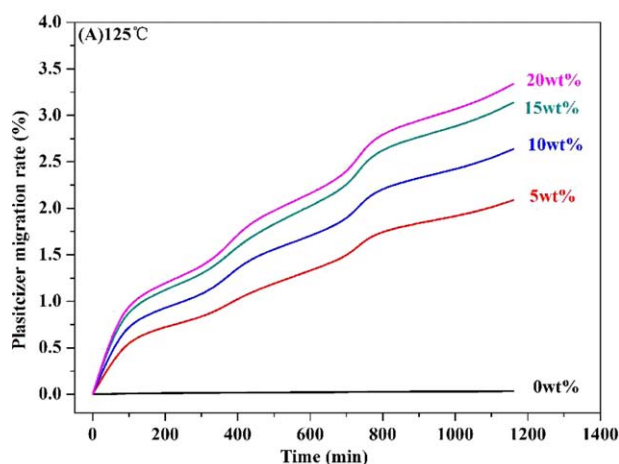


Figure 15. Migration rate of the plasticizer of the plasticized PLA at different temperatures: (A) 125 and (B) 150 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

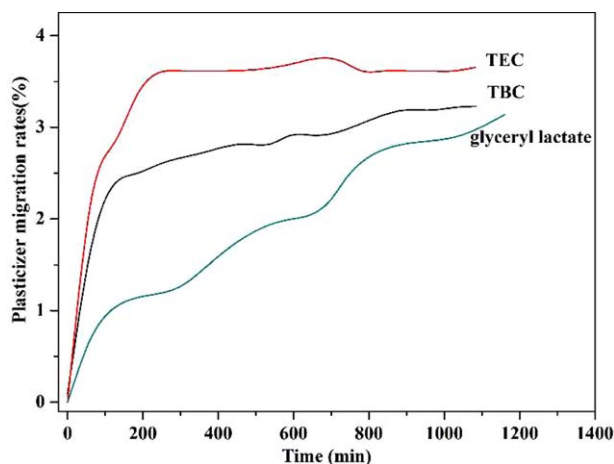


Figure 16. Comparison of the plasticizer migration rate at 125 °C for TEC, TBC, and lactic glyceride. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been due to the oversized glyceryl lactate phase and the increased crystallinity.

Migration of the Plasticizer

Figure 15 shows the plasticizer migration rate of the plasticized PLA as a function of the time at 125 °C [Figure 15(A)] and 150 °C [Figure 15(B)]. According to Figure 15(A), the migration rate of the plasticizer increased with time. Compared to the plasticized PLA at 125 °C, the plasticized PLA at 150 °C had a higher migration rate. This was close to the melting point of PLA at 150 °C; thus, the segmental motion of the PLA molecules was enhanced. Meanwhile, the interactions between the PLA molecules and the plasticizer were weakened, and the mobility of the plasticizer obviously improved. We also observed that the migration rate of glyceryl lactate increased as its contents increased at the same times at 125 and 150 °C.

Figure 16 shows a comparison of the plasticizer migration rate of PLA plasticized by triethyl citrate (TEC), tributyl citrate (TBC), and glyceryl lactate at the same content of 20 wt % at 125 °C. The three curves all indicated that the migration of the plasticizers increased over time. Among these plasticizers with similar molecular weights, glyceryl lactate had the lowest migration rate. In the early state of the migration, glyceryl lactate even presented an extremely lower migration rate than the others. These all suggested that PLA plasticized by glyceryl lactate had a better stability with the plasticizer.

CONCLUSIONS

The synthesized biodegradable glyceryl lactate was characterized by ¹H-NMR to verify its structure. The thermal, mechanical, and morphological properties of the PLA plasticized with different plasticizer contents were studied; this indicated that the glyceryl lactate was an efficient plasticizer. The results show an apparent decrease in the T_g of PLA and an increase in the elongation of break. The impact of the plasticized PLA was 1.7 times that of neat PLA. The main drawback of PLA at the time of application—brittleness—was overcome in this project. Simulta-

neously, the plasticizer was partly compatible with the PLA matrix and had a relatively low migration rate toward the material surface compared with glycerol and citrate esters.

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