

Plasticizing effect of poly(ethylene glycols) with different molecular weights in poly(lactic acid)/starch blends

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ABSTRACT: Binary and ternary blends composed of poly(lactic acid) (PLA), starch, and poly(ethylene glycols) (PEGs) with different molecular weights (weight-average molecular weights = 300, 2000, 4000, 6000, and 10,000 g/mol) were prepared, and the plasticizing effect and miscibility of PEGs in poly(lactic acid)/starch (PTPS) or PLA were intensively studied. The results indicate that the PEGs were effective plasticizers for the PTPS blends. The small-molecule plasticizers of PEG300 (i.e., the M_w of PEG was 300 g/mol) and glycerol presented better plasticizing effects, whereas its migration and limited miscibility resulted in significant decreases in the water resistance and elongation at break. PEG2000, with a moderate molecular weight, was partially miscible in sample PTPS3; this led to better performance in water resistance and mechanical properties. For higher molecular weight PEG, its plasticization for both starch and PLA was depressed, and visible phase separation also occurred, especially for PTPS6. It was also found that the presence of PEG significantly decreased the glass-transition temperature and accelerated the crystallization of the PLA matrix, depending on the PEG molecular weight and concentration. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41808.

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INTRODUCTION

Growing ecological concerns have resulted in the emergence of biodegradable plastics as alternative materials to petroleum-based polymers. Poly(lactic acid) (PLA), as one of the most promising biodegradable polymers, has exhibited vast appeal in recent decades because of its excellent performance in the biocompatibility, biodegradability, renewability, and mechanical properties; this leads to great potential in biomedical, agricultural, and packaging applications.^{1,2} Nevertheless, PLA is relatively expensive in comparison with petroleum-based polymers. To reduce the cost and enhance the biodegradability, starch, as a common and inexpensive biopolymer, is an attractive candidate as a filler for PLA. Meanwhile, thermoplastic starch (TPS), produced by native starch in the presence of plasticizers (e.g., glycerol, water, sorbitol), also becomes an attractive material in the utilization of biodegradable plastic items, such as agricultural foils, packaging materials, and garbage bags. Thus, poly(lactic acid)/starch (PTPS) may be an ideal material for biodegradable packaging and other consumer products.^{3–5}

Earlier research has shown that PLA is similar to polystyrene, with a low ability of deformation, and its stiffness greatly limits its applications. Native starch has a rigid granular structure with different particle diameters (from 2 to 100 μm) that vary with

the source, component, and technique of production.^{6–8} The introduction of native starch into PLA usually deteriorates the water and impact resistance of the blend. Many strategies have been developed to improve the flexibility and compatibility of PTPS; these include plasticization, copolymerization, and blending with a variety of flexible polymers. A plasticizer is used not only to improve the processability of polymers but also to enhance the flexibility and ductility of glassy polymers.^{8–10} Several plasticizers, such as poly(ethylene glycol) (PEG),¹¹ citrate esters,¹² and glycerol⁵ have been researched for PTPS blends.

However, small-molecule plasticizers usually evaporate during melt processing and also have a strong tendency to migrate toward the surface during storage.⁸ The addition of a small-molecule plasticizer to starch may decrease its melting temperature (T_m), but the limited mechanical properties, higher moisture sensitivity, and release of small-molecule plasticizer from matrix are also the main challenges in its applications.^{13–15} The common way to reduce the migration and evaporation of plasticizers is to increase the molecular mass of the plasticizer to an upper limit where migration will be minimized and the miscibility with the matrix will still be retained.¹⁶

Recently, PEG, as a nontoxic polymer with a molecular weight that varies from 200 to 20,000 g/mol, has been found to be an

Table I. Formulations of the Binary and Ternary Blends

Sample	Molecular weight of PEG	Starch/plasticizers (g)				Starch/plasticizers (wt %)	PLA (wt %)
		Dried starch	Water	Glycerol	PEG		
PLA	-	-	-	-	-	0	100
PTPS1	-	100	10	40	0	50	50
PTPS2	300	100	10	0	40	50	50
PTPS3	2000	100	10	20	20	50	50
PTPS4	4000	100	10	20	20	50	50
PTPS5	6000	100	10	20	20	50	50
PTPS6	10,000	100	10	20	20	50	50
PLA/PEG-a	2000	-	-	-	10	6.3	93.7
PLA/PEG-b	2000	-	-	-	20	11.8	88.2
PLA/PEG-c	2000	-	-	-	30	16.7	83.3

-a, -b, -c represent the different concentrations of PEG2000 in PLA/PEG blend.

effective plasticizer for PLA and starch.^{17–21} Previous studies have shown that PEG blending with PLA or starch presents different plasticization and miscible behaviors, which depend on the composition and molecular weight of the PEGs.^{22–24} Younes and Cohn²⁵ reported that microphase separation in a PLA blend occurred at a given composition; this depended on the molecular weight of PEG (from 1500 to 35,000 g/mol). Baiardo *et al.*²⁶ revealed that the lower molecular weight PEG showed better miscibility and plasticizing efficiency in the PLA matrix. On the other hand, Kim and coworkers^{27,28} showed that the starch chain conformation changed when the molecular weight of PEG was less than 8000 and PEG of proper molecular weight could effectively stabilize the interface of the starch/PCL blend. The miscible poly(ethylene oxide) (PEO)/starch blend prepared by a solution-casting method was also reported.²⁹ Furthermore, PEG was also used as a compatibilizer for PTPS, and the flexibility and interaction between two phases were obviously improved after the incorporation of PEGs.^{30,31}

To the best of our knowledge, few have focused on the plasticizing effect of PEGs with different molecular weights on both PLA and starch simultaneously. In this study, a simple route for preparing the PTPS blends plasticized by PEGs was carried out in a Haake mixer. In comparison with PTPS, PEG with the molecule weight of 2000 (PEG2000) was also chosen to prepare PLA/PEG binary blends based on its good performance in PTPS. The influence of the plasticizers with different molecular weights or concentrations on the blend properties (thermal, morphology, crystallization, water sorption, and mechanical) was then investigated.

EXPERIMENTAL

Materials

PLA 2003D was purchased from NatureWorks and consisted of 96% L-lactide and 4% D-lactide units. The cassava starch was supplied by Santa Ark Starch Co., Ltd. (Gansu, China) with the granule size ranging from 5 to 20 μm , and the apparent amylose content of starch was about 27.8%; this was determined by the iodine adsorption method according to ISO6647-1:2007. Glycerol and PEG were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The molecular weight of PEG

(ranging from 300 to 10,000 g/mol) was chosen on the basis of a previous study.²⁷

Preparation of the Blends

PLA and starch were dried in a vacuum oven for 4 h at 80 and 200°C, respectively. Glycerol, water, and the PEGs were blended (2000 rpm for 2 min) with starch and then stored overnight. The mixtures of PLA and starch/plasticizers were fed manually into a Haake mixer operating at 80 rpm and 180°C for 7 min. The samples were compression-molded at 180°C and then quenched through a cold compression process with a cooling rate of around 90°C/min with a flat sulfuration machine into sheets 1 and 4 mm in its thickness for subsequent tests. The formulation of the sample is shown in Table I, and the specimens of PLA/PEG for dynamic mechanical thermal analysis (DMA) and wide-angle X-ray diffraction (WAXD) measurements were annealed at 50°C for 60 min after the cold compression process.

Mechanical Testing

The blends were pressed by a flat sulfuration machine into a sheet, and mechanical property measurements were performed at room temperature. The tensile strength, Young's modulus, and elongation at break (EB) were measured on a mechanical tensile tester (WSM-20KN, Changchun Testing Machine Co., China) according to ASTM D 638 with a tensile speed of 10 mm/min. The impact strength was performed by a JJ-20 impact tester (Changchun Testing Machine Co., China) according to ASTM D 256. Each sample's width and thickness were measured before testing, and the data were averaged over six specimens.

Differential Scanning Calorimetry (DSC)

Thermal analysis of samples was carried out on a Netzsch DSC 200PC calorimeter (Bayern, Germany). The samples were sealed in aluminum pans (6–9 mg), heated from 25 to 200°C at a rate of 10°C/min, held at that temperature for 5 min, and then cooled to -20°C (10°C/min) before the second heating scan from -10 to 200°C at 10°C/min. The glass-transition temperature (T_g), T_m , crystallization temperature (T_c), and degree of crystallinity (X_c) were determined from the second heating scan.

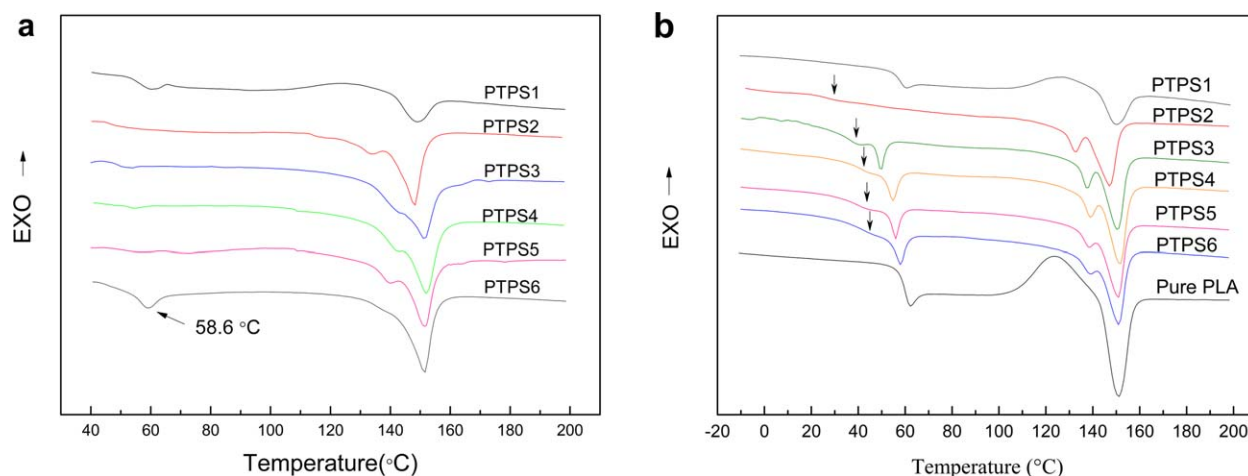


Figure 1. DSC thermograms of PTPS: (a) first heating scan and (b) second heating scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

When multiple endothermic peaks were found, the peak temperature of the main endotherm was taken as T_m . X_c of the modified PLA was determined as shown in eq. (1):

$$X_c(\%) = \frac{(\Delta H_m - \Delta H_c)}{X_{PLA} \Delta H_f} \times 100 \quad (1)$$

where ΔH_m , ΔH_c , and X_{PLA} are the enthalpy of melting, enthalpy of crystallization, and weight fraction of PLA, respectively. ΔH_f is the heat of fusion, defined as the melting enthalpy of 100% crystalline PLA, which is 93 J/g.³²

DMA

The blends for DMA were stored at room temperature for 1 week (at 30% relative humidity). DMA was carried out on a DMA E4000 (UBM, Rheology, Japan) in three-point bending mode. The temperature ranged from -100 to 130°C with a heating rate of $3^\circ\text{C}/\text{min}$ and the frequency of 11 Hz. The storage modulus (E') and loss modulus (E'') were recorded as a function of the temperature.

Scanning Electron Microscopy (SEM)

SEM was performed on the PTPS blends with a Hitachi S-3400N scanning electron microscope (Japan). The blend samples were cooled in liquid nitrogen for 2 min and then broken in half, and the surfaces were subsequently treated with hydrochloric acid (HCl; 6N) for 12 h to selectively dissolve the starch phase.

WAXD

The extruded blend strips were pressed at 10 MPa with a flat sulfuration machine, and the slices were placed in a sample holder for X-ray diffractometry. The cassava starch powder was tightly packed into a sample holder. X-ray diffraction patterns were recorded in the angular range $3\text{--}50^\circ$ (2θ) by D/MAX 2550 VB/PC X-ray diffractometer (Rigaku Corp., Japan). It was operated at 40 kV and 100 mA with Cu $K\alpha$ radiation. All of the experiments were carried out at ambient temperature with a scanning speed of $3^\circ/\text{min}$ and a step size of 0.02° .

Water Absorption

The samples ($10 \times 10 \times 4 \text{ mm}^3$) were immersed in water at 35°C . The weight of the sample was recorded at specific

intervals and repeated at several time intervals. The water absorption ratio (X) was calculated with eq. (2):

$$X(\%) = [(M_i - M_0)/M_0] \times 100\% \quad (2)$$

where M_i is the weight of the sample at day i and M_0 is the initial weight of the sample.

RESULTS AND DISCUSSION

Thermal Properties

The thermal characteristics of the blends were determined by DSC, and the thermograms of PTPS are given in Figure 1. From the first heating scan, the T_g and T_m values of PLA in sample PTPS1 were around 60 and 150°C , respectively, whereas no melting peak of PEG was observed for PTPS2 to PTPS5; this was due to the good miscibility between the PLA and PEGs. When the weight-average molecular weight (M_w) of PEG increased to $10,000 \text{ g/mol}$, a visible melting endotherm peak of PEG was observed at 58.6°C . This might have been due to the detachment between PLA and PEG10000, although it was reported earlier³³ that PLA was miscible in the melt up to at least 30 wt % PEG10000.

The results of the second heating scan are presented in Figure 1(b) and Table II. Neat PLA presented cold crystallization at 124°C , whereas the crystallinity degree was only 6.3%. PTPS1 showed similar thermal behavior, and this indicated that a limited interaction between PLA and gelatinized starch. Compared with that of PTPS1, the ΔH_m value of PTPS was greatly improved after the addition of the PEGs. This suggested that the PEGs significantly accelerated the crystallization of the PLA matrix. The crystallinity degrees of the blends plasticized by the PEGs increased obviously, and the crystallinity of PTPS3 achieved a maximum value of 33.5% (Table II). When the glycerol in PTPS1 was substituted by PEGs, there was no cool crystallization peak, and double melting peaks of PLA appeared; this might have been due to lamellar rearrangement during PLA crystallization.³⁴ When M_w of PEG increased from 300 to 10,000, the shoulder or low-temperature peaks ebbed, and T_g of PTPS was increased from 29.0 to 46.9°C . This indicated a decrease in the plasticization of PEG accordingly. TPS had little

Table II. T_x and DSC Data from the Second Heating Scan

Sample	T_x (°C)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	ΔH (J/g)	Crystallinity of PLA (%)
Neat PLA	75.8	62.0	150.9	19.7	13.8	6.3
PTPS1	73.6	60.3	149.9	7.0	4.0	6.3
PTPS2	51.8	29.0	147.2	14.4	-	30.9
PTPS3	61.9	41.1	150.6	15.6	-	33.5
PTPS4	64.9	44.9	151.6	15.6	-	33.5
PTPS5	65.8	46.0	150.7	15.0	-	32.3
PTPS6	68.9	46.9	150.9	15.3	-	32.9
PLA/PEG-a	67.1	47.8	151.6	25.0	19.6	6.2
PLA/PEG-b	63.8	-	152.7	13.9	-	17.0
PLA/PEG-c	77.8	-	151.8	24.0	-	31.0

ΔH , cold crystallization enthalpy.

influence on the thermal behavior of the PLA matrix, and starch gelatinization did not significantly affect the crystallization of PLA.³⁵ Thus, the high crystallinity of the PLA matrix and the depressed T_g could be attributed to the effective plasticization of PEGs. Moreover, the melting endotherm peaks of PEGs are shown in Figure 1(b); this was associated with the separation of the PEGs during the cooling step. This was because that the mobility gained by the PLA chains in the plasticized blends yielded crystallization, which is the driving force for various scale phase separations.²² However, no melting peak of the PEGs, except for PEG10000, was obtained, as shown in Figure 1(a). All of these results indicate that the phase separation of PEG10000 was evident, whereas the segments of the PLA and PEGs were partially miscible for PEGs with moderate molecular weights, despite the phase separation induced by crystallization afterward.

To further explain the miscibility and plasticizing effect of PEG in the PLA matrix, PLA/PEG blends with different ratios of PEG2000 were prepared, and the DSC results are given in Figure 2. For the first heating scan of DSC, as shown in Figure 2(a), pure PLA showed an obvious T_g around 60°C, and the T_g

of PLA shifted to low temperature when the concentration PEG increased. However, there was no melting peak of PEG for PLA/PEG-a and PLA/PEG-b. As the concentration of PEG increased further, a visible melting peak at 50.3°C was observed for PLA/PEG-c. This could be explained by the detachment between PLA and PEG. This was similar to the behavior of PTPS6. Moreover, the crystallization enthalpy and T_c of the PLA matrix decreased with increasing concentration of the plasticizers; this was consistent with the fact that PLA crystallized with more ease at lower temperature because of the enhanced chain mobility as the plasticizer content increased. When the concentration of PEG2000 increased to 16.7 wt %, the crystallization peak of PLA/PEG-c disappeared, and it was also in accordance with the DSC results of PTPS; this suggested that the PEGs were effective plasticizers for the PLA matrix. Compared with the first heating scan, the melting peak of PEG in PLA/PEG-b at 51.5°C was then detected from the second heating scan [Figure 2(b)]. This corresponded to the increasing phase separation of PEG because of the driving force of crystallization. However, with increasing concentration of PEG, both the crystallinity of PLA/PEG and the melting enthalpy of the shoulder peak increased. Meanwhile,

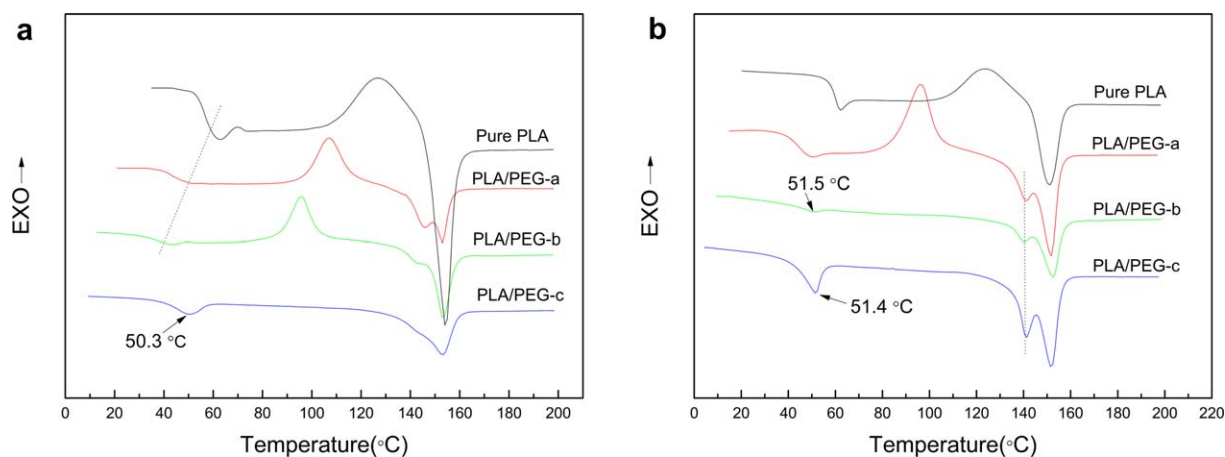


Figure 2. DSC thermograms of PLA/PEG: (a) first heating scan and (b) second heating scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

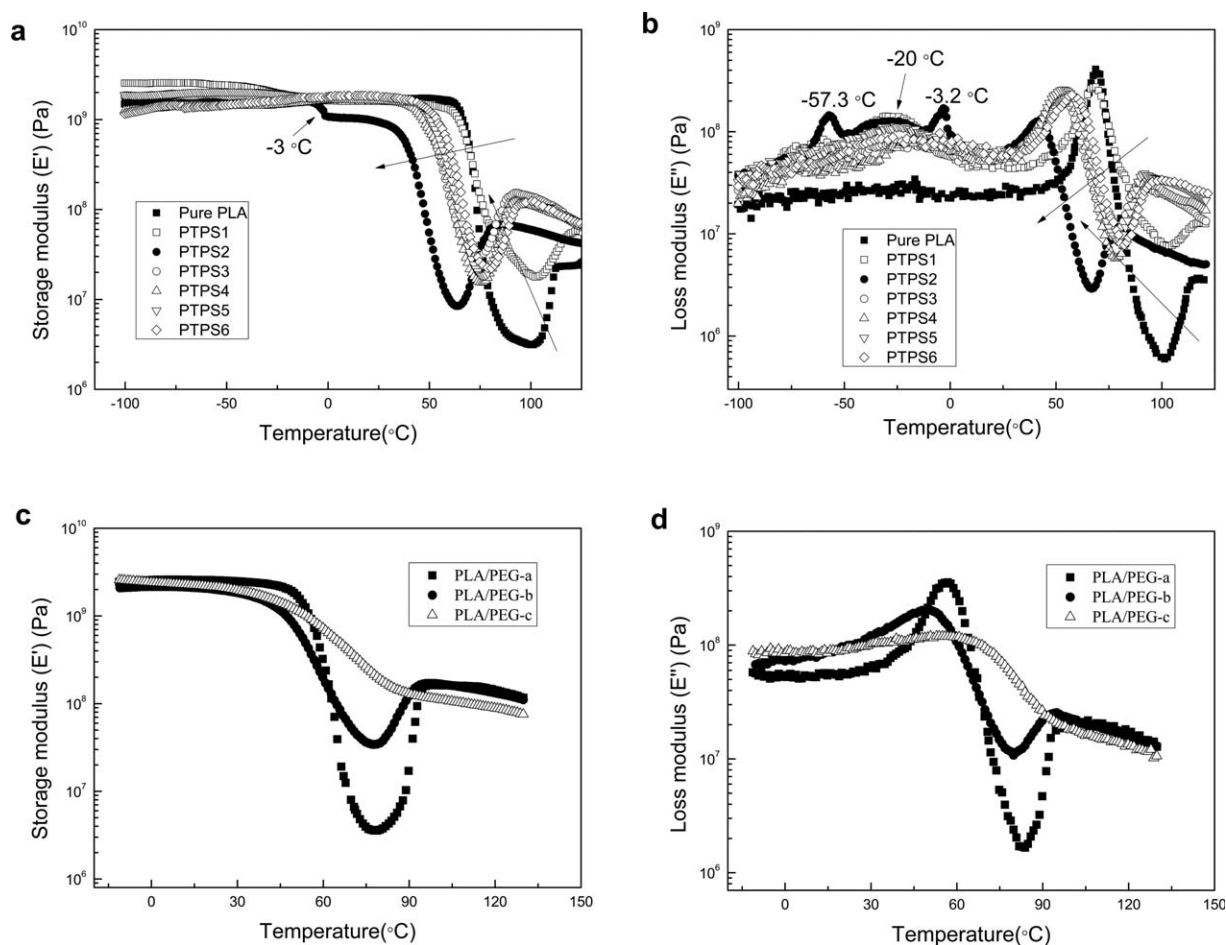


Figure 3. DMA traces of the binary and ternary blends: E' and E'' as a function of the temperature.

the cool crystallization peak of PLA/PEG-b also disappeared, and these results indicate the more effective plasticization of PEG at higher concentrations.

Thermomechanical Properties

The efficiency of the plasticizers was also appraised through DMA. Figure 3 presents the temperature dependence of E' and E'' for the ternary and binary blends, and the α -relaxation temperatures ($T_{g,s}$) of the blends recorded by DMA are listed in Table II. The DMA curve of PLA showed a marked drop in E' around 70°C [Figure 3(a)]; this corresponded to its dynamic T_g , which was higher than the T_g value detected by DSC. For the PTPS blends, as the temperature increased above 100°C, E' increased; this was the consequence of the crystallization of PLA. When the M_w of PEG in PTPS decreased, both T_g and T_c of the blend shifted to a low temperature accordingly (Table II). We concluded that the plasticizing effect of PEG to PLA was improved with decreasing M_w of PEG. The same trend is shown in Figure 3(b), where the T_g and T_c values of the blends also shifted to a low temperature with decreasing M_w of PEG, whereas there was only a slight decrease in T_g for PTPS1 plasticized by glycerol. Meanwhile, the E' values of PTPS2 and PTPS1 abruptly dropped around -3 and -30 °C, respectively; this indicated that the phase separation of PEG300 and glycerol occurred below room temperature. It is worth noting that T_g of

PEG was reportedly in the range -55 to -70 °C, depending on the molecular weight.²³ Two obvious peaks on the E'' thermogram of PTPS2 were obtained at -57.3 and -3.2 °C, which values corresponded to the T_g and T_m values of PEG300, respectively. This suggested the phase separation of PEG300. Furthermore, PTPS1 to PTPS6 displayed diffuse peaks around -20 °C; this was also associated with the partial phase separation of the plasticizers.¹⁶

The DMA behaviors of PLA/PEG with different contents of PEG2000 were detected, as shown in Figure 3(c,d). The samples were annealed at 50°C before testing, as mentioned when we discussed the ample preparation. We observed that E' of PLA/PEG-a was higher than that of pure PLA; this was also attributed to the crystallization of PLA with the plasticization of PEG. As the concentration of PEG increased, E' first decreased and then increased slightly at the low temperature. The decrease in E' was due to the increased plasticization,³⁶ and the latter increase in E' might have been due to a significant increase in the crystallinity of PLA. This was proven by the WAXD results afterward. As expected, the E' and E'' values of the blend with more PEG were significantly increased as the temperature ranged from 50 to 100°C. This could have been due to the increase in the crystallinity of PLA, which greatly restricted the chain mobility of PLA.

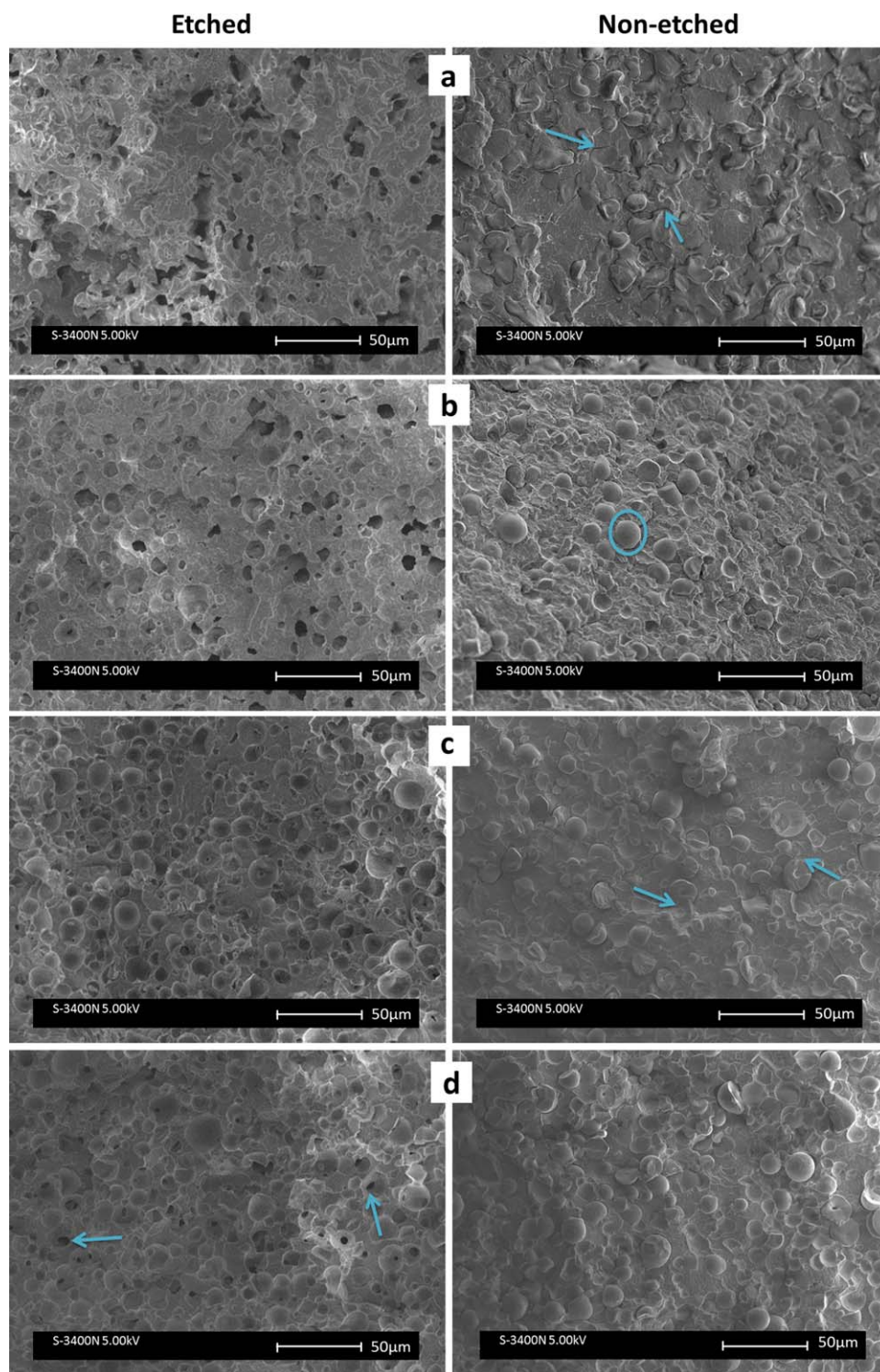


Figure 4. SEM micrographs: (a) PTPS1, (b) PTPS2, (c) PTPS3, and (d) PTPS6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphological Analysis

The SEM images of the PTPS/PEG blends are presented in Figure 4. The starch in the blends was selectively dissolved before observation, as shown in Figure 4 in the left column (Etched). For PTPS1, a very coarse dispersion of TPS in the PLA matrix

was obtained. The unusual shape of TPS might have been related to the retarded droplet coalescence caused by the high viscosity of TPS and the high melt-viscosity differentials between PLA and TPS. Consequently, the starch in PTPS1 was destroyed and well plasticized by glycerol; this might have been

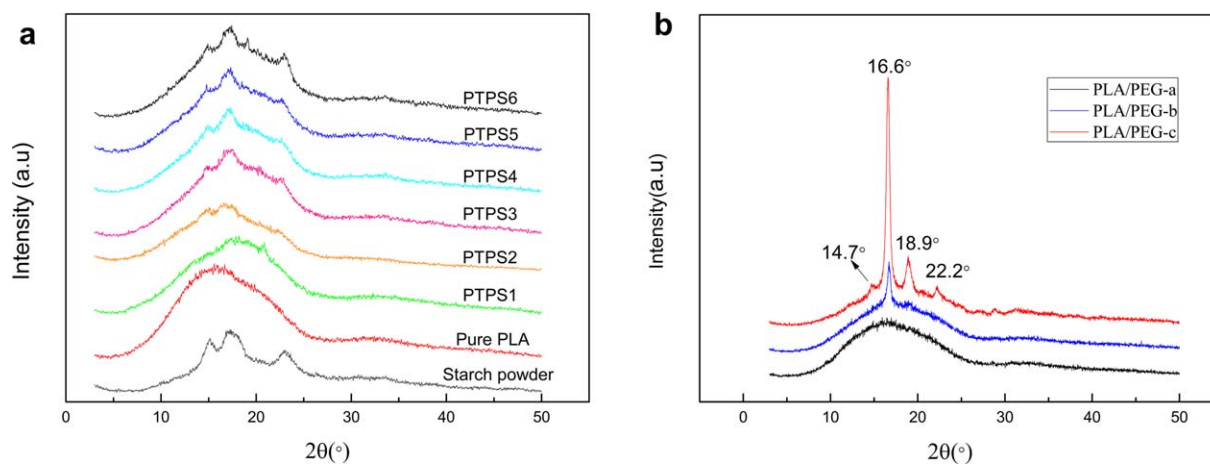


Figure 5. X-ray diffraction patterns: (a) PTPS/PEG and (b) PLA/PEG after annealing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the strong hydrogen-bond interaction between the glycerol and starch. However, the phase interface between TPS and PLA was visible [Figure 4(a)]; thus, the lack of affinity between TPS and PLA in PTPS1 was concluded.

As the glycerol was substituted by PEG300, the starch granules were dispersed in the PLA matrix [Figure 4(b)]. Although the starch particles (ranging from 10 to 20 μm) in PTPS2 were not broken, the crystalline structure of starch was also destroyed; this was also proven by the WAXD results. Furthermore, the detachment of the starch particles from the PLA matrix at the fracturing process of specimens was observed; this suggested that the interaction between starch and PLA in PTPS2 was even worse than that of PTPS1. As M_w of PEG increased to 2000 g/mol, the interface of the PLA and starch granules became blurry. The starch particles were broken in half and left in the PLA matrix in the fracturing process; this suggested that the interaction between PLA and starch was significantly improved by the presence of PEG2000 [Figure 4(c)]. As M_w of PEG increased to 10,000 g/mol, some small dark regions were observed around the groove of the etched starch [Figure 4(d)]. This was the PEG10000 phase etched by HCl.

Crystalline Structure of Blends

The X-ray diffraction measurements were also carried out to research the plasticizing effect of the PEGs, and the results are presented in Figure 5. In this study, the specimens were cooled from the melt to room temperature, and an amorphous PLA matrix was obtained. The spectrum of the native starch powder showed sharp peaks at $2\theta = 15.1, 17.3,$ and 23.0° [Figure 5(a)]; this corresponded to the C pattern crystallization in starch.³⁷ As discussed previously, the plasticizers of low molecular weight exhibited a better plasticizing effect to the PLA matrix. Here, the spectra of PTPS1 and PTPS2 displayed a broad, diffuse peak around 17° ; this implied the crystalline structure of starch was almost destroyed by both glycerol and PEG300. As M_w of PEG increased to 2000 g/mol, the three main peaks at 15.1, 17.3, and 23.0° were obtained for PTPS3, but the intensity of the peaks was much weaker than that of starch powder. When M_w of PEG increased further, the intensity of the peaks increased, especially

for PTPS6. In summary, the plasticizing effect of the PEGs to starch also decreased with increasing M_w of PEGs.

The WAXD patterns of the PLA/PEG blends are shown in Figure 5(b). PLA/PEG-c, with the highest concentration of PEG, presented four strong diffraction peaks around 14.7, 16.6, 18.9, and 22.2° ; these peaks were ascribed to the (010), (110/200), (203), and (015) reflections, respectively.³⁸ With decreasing PEG proportion, the intensity of the peaks for PLA/PEG-b was significantly decreased, which indicated the decrease in the crystallinity of PLA matrix. Furthermore, there was only a diffuse peak for PLA/PEG-a, because of the proverbial slow crystallization rate of PLA³⁹ and the sudden decrease in chain mobility by the cool compression. Therefore, the addition of PEG markedly accelerated the crystallization of the PLA matrix, and we concluded that the higher weight percentage of PEG in the studied range exhibited a greater plasticizing effect to the PLA matrix.

Water Absorption

Water sensitivity is an important criterion for many practical applications of starch-based materials. In this study, the concentration of starch in the PTPS blends approached 50 wt %; thus, it was worth investigating the water resistance of the PTPS blends. The results of water absorption for ternary blends are presented in Figure 6. Compared with the pure PLA, the PTPS blend exhibited improved water absorption because of the incorporation of hydrophilic starch. Among the blends, the water absorption value of PTPS1 plasticized by glycerol was the highest, reaching 13.6%, and the shortest time was required to reach equilibrium, although the crystalline of starch in PTPS2 was also destroyed; this could be explained by the greater plasticizing effect of glycerol to starch compared with PEG300. The similar plasticizing efficiency of glycerol to starch has also been reported by previous studies.^{40,41} On the other hand, the water absorption of PTPS2 was significantly higher than that of PTPS3 (11.3 vs 4.5%), although the dispersion of plasticized starch was all discontinuous for the PEG plasticized blends; this was attributed to the efficient plasticization of low-molecule PEG to starch and limited interaction between the two phases, as discussed previously. Thus, the water molecules penetrated

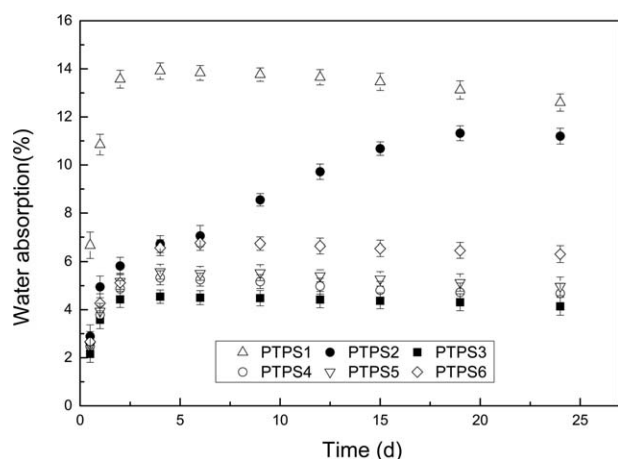


Figure 6. Water absorption of PTPS with different plasticizers.

into the PTPS2 blend easily; this resulted in a high water absorption value. On the contrary, PEG2000 not only showed better stability and miscibility with PLA but also presented strong hydrogen bonding with starch, which confined the interactions between starch and water molecules; thus, PTPS3 exhibited good performance in water sensitivity. This was also consistent with the SEM observation (Figure 4) and a previous study⁴² about the molecular weight of plasticizers. However, when M_w PEG increased further, the value of water absorption increased gradually, especially for PTPS6. It could be associated with the detachment of high-molecule PEG from the matrix and the limited interaction with starch; this favored the diffusion and accumulation of water through the percolating path of PEG.

Mechanical Properties

The effects of the PEGs and glycerol on the mechanical properties of PTPS were also studied. The impact strength and tensile properties of the specimens are illustrated in Figure 7. For PTPS1, because of the inherent brittleness and limited affinity between starch and PLA, its impact strength was only 5.1 kJ/m² [Figure 7(a)]. The impact strength of PTPS2 was increased to 10.9 kJ/m², and it was associated with the effective plasticization of PEG300 to PLA. Compared with PTPS2, the impact strengths

of PTPS3 and PTPS4 were increased by about 50 and 80%, respectively, although the plasticizing effect of PEG300 was better than those of PEG2000 and PEG4000; this could have been due to the limited affinity between the two phases in PTPS2. A similar improvement in EB was obtained as shown in Figure 7(b). The EB value of PTPS1 was the lowest, and the EB of PTPS2 was only 3.7%. As M_w of PEG increased to 2000 g/mol, the EB of PTPS3 increased by 200% compared with that of PTPS2. However, when M_w of PEG further increased, the impact strength and EB were markedly reduced; this might have corresponded to the decrease in the plasticizing effect and the miscibility of the PEGs.

As for Young's modulus, the addition of starch led to a decrease in the modulus of the blends; this could have been due to the lack of affinity between the two phases, and the intrinsic modulus of PLA was higher than that of starch. As expected, the Young's modulus of PTPS1 was higher than those of these PEG plasticized blends; this was mainly due to the stiffness of PLA without plasticization. For the PEG plasticized blends, the plasticization was improved when M_w decreased, as discussed previously. Therefore, the Young's modulus values of the blends increased accordingly with decreasing M_w of PEG. On the other hand, the starch particles were dispersed in the PLA matrix, and the interaction between the starch and PLA was limited. Consequently, the tensile strengths of the blends plasticized by PEGs had no significant differences and were much lower than that of neat PLA. The incorporation of a coupling agent to produce chemical bonds between PLA and starch might have been an effective approach for strengthening the blends.^{43,44}

CONCLUSIONS

In this study, the effects of PEGs with different molecular weights on the properties of PTPS blends were mainly investigated. Glycerol, as a well-known plasticizer for starch, was also used in PTPS and compared with the PEGs. We found that PEG300 and the glycerol of small-molecule plasticizers had more effective plasticization to PLA and starch, respectively. However, the obvious migration of small-molecule plasticizers and clear interface between TPS and PLA were detected. The PEGs of high-molecular-weight exhibited a limited plasticizing

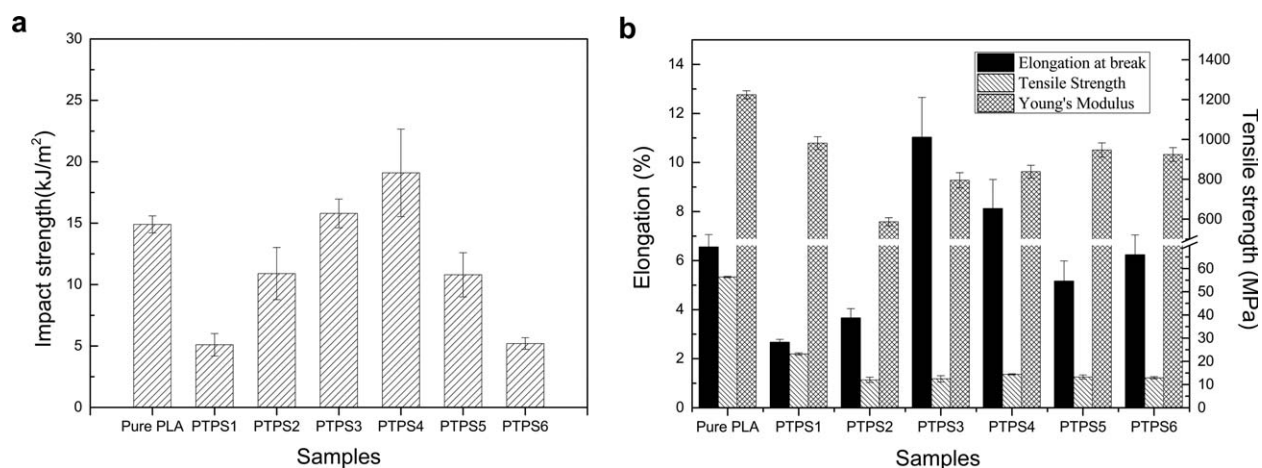


Figure 7. Mechanical properties of the ternary blends: (a) impact strength and (b) tensile properties.

effect and obvious phase separation. The results show that the moderate molecular weight PEGs, such as PEG2000 and PEG4000, facilitated the combination of efficient plasticization and reduced migration; this resulted in an obvious improvement in the impact strength, EB, and water-resistance properties. Therefore, we suggest that the proper molecular weight of plasticizers used in PTPS should be fully considered.

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