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Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends

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Abstract

Starch as an inexpensive and renewable source has been used as a filler for environmentally friendly plastics for about 2 decades. In order to improve the compatibility between hydrophilic starch granules and hydrophobic Poly(lactic acid) (PLA), glycerol, formamide, and water are used alone or combined as plasticizers for starch to enhance the dispersion and the interfacial affinity in thermoplastic starch (TPS)/PLA blend. And the properties of TPS/PLA blends are investigated through microscopy (SEM), rheological, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), tensile testing, and Dynamic mechanical thermal analysis (DMTA). In the presence of water and formamide, the plasticization of starch can be improved dramatically. At the same time, SEM can detect a homogeneous TPS/PLA blends. With increasing the dispersion between TPS and PLA, the blend becomes more thermal stability as shown in TGA. It also proves that PLA degrades in the presence of water during melt processing. In addition, FT-IR spectroscopy proves that formamide and water can improve the interaction between TPS and PLA. The tensile testing and DMTA suggest that the compatibility between TPS and PLA is improved in this paper.

Keywords: Depolymerization; Extrusion; Poly(lactic acid); Thermoplastic; Starch

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1. Introduction

Poly(lactic acid) (PLA) belongs to the family of aliphatic polyesters which is a thermoplastic, high-strength, high-modulus polymer. Generally, commercial PLA grades are copolymers of poly(L-lactic acid) (PLLA), and poly(L,D-lactic acid) (PDLLA). The ratio of L- to D,L-enantiomers are known to affect the properties of PLA (Garlotta, 2001). PLA as a biodegradable polymer has been studied in many fields in the past few decades. Recently, PLA has been considered as a major alternative to petroleum-based plastics for disposable items, such as trash bags and food utensils (Auras, Harte, & Selke, 2004). But PLA is more expensive than conventional petroleum polymers for disposable or short-term applications (Auras et al., 2004; Garlotta, 2001; Zhang & Sun, 2004). Starch as an inexpensive material and renewable source is completely biocompatible and biodegradable. Its small granular structure makes it as good particulate filler in many polymer blend systems (Ma, Yu, & Zhao, 2006; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Zhang & Sun, 2004). Many efforts have been made to develop PLA/starch blends to reduce total raw materials cost and enhance its degradability (Rodriguez-Gonzalez et al., 2003; Zhang & Sun, 2004). The major problem of this blend system is the poor interfacial interaction between hydrophilic starch granules and hydrophobic PLA.

In order to increase the compatibility between PLA and starch, reactive compatibilizers or coupling agent, such as maleic anhydride (MA) (Zhang & Sun, 2004), acrylic acid (AA) (Wu, 2005) and methylenediphenyl diisocyanate (MDI) (Wang, Sun, & Seib, 2002) have been used to enhance the interfacial interactions in PLA/starch blends.

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However, these poisonous compatibilizers are harmful to the health. Except some compatibilizers can be used to improve the compatibility between PLA and starch, gelatinization of starch is also a good method to enhance the interfacial affinity (David, Marshall, & Peter, 1995; Kim & Kim, 2000; Martin & Ave′rous, 2001). In the presence of water and other plasticizers (glycrol, sorbitol, urea, formamide (Ma, Yu, and Ma, 2005) and so on) the strong intermolecular and intramolecular hydrogen bonds in starch can be overcame. So thermoplastic material can be achieved under high temperatures and shear, which is usually called thermoplastic starch (TPS) (Shogren, 1992). TPS can not only improve the compatibility in starch/polymer blend, but also increase starch content (Rodriguez-Gonzalez et al., 2003).

However, PLA as a hydrophobic synthetic biopolymer can be depolymerized in the presence of water at elevated temperatures, which results in poor mechanical properties (Garlotta, 2001). At the same time, water is recognized as a much more efficient plasticizer than glycerol and starch chain mobility greatly dependent on the water content of the premix (Forssell, Mikkilä, Moates, & Parker, 1998; Hulleman, Janssen, & Feil, 1998; Lourdin, Coignard, Bizot, & Colonna, 1997). Therefore it is difficult to achieve a completely plasticized thermoplastic blend after excluding water. However, formamide with small volume and high polarity is a much more effective plasticizer than glycerol which can form stable hydrogen bonds with starch and improve the plasticization of starch (Ma et al., 2005). Moreover, formamide can improve the fluidity of TPS during extrusion processing. So in this paper, in order to achieve high dispersive and compatible TPS/PLA blends, one-step extrusion is used to prepare TPS/PLA blends. Glycerol, formamide and water are used as the plasticizers alone or combined for starch in TPS/PLA blends. The thermal plasticization of dry starch and its blending extrusion with PLA are accomplished simultaneously by one-step extrusion in a single-screw extruder.

2. Experimental

2.1. Materials

PLA was purchased from Natureworks LLC (United States). The weight-average molecular weight was about 160,000 ~ 220,000 Da. The concentration of the D-(−)-isomer was 12.0 ± 1.0%. Cornstarch (12% moisture) obtained from Langfang Starch Company (Langfang, Heibei, China). Glycerol and formamide (analytical reagent) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Samples preparation

Cornstarch was dried in an oven at 135 °C for 2 h. Glycerol, formamide, and water were used as plasticizers. The plasticizers were firstly mixed, and then blended (3000 rpm, 2 min) with dry starch by using of High Speed Mixer GH-100Y (Beijing, China). The mixtures were stored airtight until homogeneous systems were obtained. Then the former blended with the same weight PLA by using of High Speed Mixer. The sample codes and components were listed in Table 1. Thermoplastic dry starch was called DTPS to make difference with TPS in the paper. DTPS/PLA and TPS/PLA blends were prepared as following: The mixtures were fed in to the single-screw Plastic extruder SJ-25(s) (Screw Ratio $L/D = 25{:}1$, Beijing, China). The screw speed was 10 rpm. The temperature profile along the extruder barrel was 130, 140, 150, and 130 °C (from feed zone to die). The die was metal plate of 10 mm thick with eight holes of 3 mm diameter. The samples were stored airtight immediately. When the samples reached room time temperature (about 20 °C), the extruded strips were pressed into sheets with Flat Sulfuration Machine (Tianjin, China) and cut into tensile bars with certain size and stored in desiccator under room temperature immediately. The properties test would go on after one week.

2.3. Scanning electron microscopy (SEM)

The fracture surfaces of extruded strips were performed with Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, OR, USA), operating at an acceleration voltage of 20 kV. The samples were cooled in liquid nitrogen, and then broken. The fracture surfaces were vacuum coated with gold for SEM.

2.4. Rheology

The capillary viscometer used to determine the viscosity of the blends was XYL-IIcapillary rheometer (Jilin University Instrument Factory, Jilin, China). 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 radius of capillary was 1 mm and L/D was 40. 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 (10–15 min), and was then forced through the capillary by the plunger at pre-selected velocities. The load on the plunger and plunger speed provide the total pressure drop through the barrel and capillary and the volume flow rate. Shear rate (γ in s^{-1}) and shear stress (τ in Pa) were calculated by standard methods. In order to understand the processing properties and fluidity of TPS/PLA and DTPS/PLA blends, the rheology experiments were carried at 130, 140, and 150 °C, which covered the processing temperature range.

The melting volumetric flow rate through the capillary was given

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

Table 1
The sample codes and components

Sample	Formamide (wt%)	Glycerol (wt%)	Water (wt%)	Dry starch (wt%)	PLA (wt%)
TPS1/PLA	—	30	10	100	140
TPS2/PLA	10	20	10	100	140
TPS3/PLA	15	15	10	100	140
TPS4/PLA	20	10	10	100	140
TPS5/PLA	30	—	10	100	140
DTPS1/PLA	—	40	—	100	140
DTPS2/PLA	10	30	—	100	140
DTPS3/PLA	20	20	—	100	140
DTPS4/PLA	30	10	—	100	140
DTPS5/PLA	40	—	—	100	140

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

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

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

where ΔP = pressure at the capillary entrance, L = capillary length, R = capillary radius.

According to Onteniente Jean-Paul et al. (Onteniente, Abbès, & Safa, 2000), thermoplastic materials exhibited power-law behavior:

$$\tau = K\gamma^n \tag{3}$$

The apparent viscosity (η in Pa s) was defined by Eq. (3):

$$\eta = \tau/\gamma \tag{4}$$

where τ = shear stress, γ = shear rate at the capillary wall, K (Pa s^n) = consistency of the materials depending on the temperature, the structure and the formulation of the polymer.

Substituting Eq. (3) for τ in the relationship (2) between τ and γ yielded:

$$\eta = K\gamma^{n-1} \tag{5}$$

$$\lg\eta = \lg K - (1-n)\lg\gamma \tag{6}$$

If $y = \lg\eta$ and $x = \lg\gamma$, then the linear fit equation:

$$y = \lg K - (1-n)x \tag{7}$$

According to Arrehnius equation:

$$\eta = A e^{\Delta E_\eta/RT} \tag{8}$$

$$\lg\eta = \lg A + \Delta E_\eta/(RT\ln 10) \tag{9}$$

where ΔE_η = the vicious flow activation energy, A = the consistency related to structure and formulation, R = Gas constant 8.314 J mol^{-1} K^{-1}.

2.5. Thermogravimetric analysis (TGA)

The thermal properties of the blends were measured with a ZTY-ZP type thermal analyzer (Beijing University Instrument Factory, Beijing, China). The sample weight varied from 10 to 15 mg. Samples were heated from the room temperature to 600 °C at a heating rate of 15 °C min^{-1}. Derivatives of TGA thermograms were obtained using Origin 7.0 analysis software (RockWare Inc., Golden, CO).

2.6. Fourier transform Infrared (FT-IR) spectroscopy

The Fourier Transform Infrared (FT-IR) Spectroscopy was measured with BIO-RAD FTS3000 IR Spectrum Scanner (Hercules, USA). The extruded blend strips were pressured to slices with the thickness of around 0.2 mm in the Flat Sulfuration Machine.

2.7. Mechanical properties of blends

Samples were cut from the extruded strips and prepared with the Flat Sulfuration Machine. Tensile testing was done on the Testometric AX M350-10KN Materials Testing Machine (The Testometric Company Ltd, Rochdale, UK) at a crosshead speed of 10 mm/min was used for tensile testing (ISO 1184-1983 standard). Results from 5–8 specimens were averaged.

2.8. Dynamic mechanical thermal analysis (DMTA)

The DMTA using a Mark Netzsch DMA242 analyzer (Bavaria, Germany) was performed on hot-pressed thick specimens (40 mm × 7 mm × 2 mm, prepared by Flat Sulfuration Machine, 5 MPa, 100 °C), in a single cantilever bending mode at a frequency of 3.33 Hz and a strain $2N$, corresponding to a maximum displacement amplitude of 30 μm. The analyzer compared the stress and strain signals and resolved the strain into the in-phase (storage) and out-of-phase (loss) components, from which storage or elastic (E') and loss (E'') moduli as well as the $\tan\delta = E''/E'$ were obtained as functions of temperature. The range of temperature was from −120 to 120 °C. The standard heating rate was 3.0 °C min^{-1}. For polymeric materials, a drop in storage modulus and a peak in $\tan\delta$ were used as indicators of a glass transition.

3. Results and discussion

3.1. Blends morphology

The morphology structure of polymer blends was a very important characteristic to understand many properties of polymer blends (Willemse, de Boer, van Dam, & Gotsis, 1998), especially the mechanical properties. The SEM micrographs of PLA, DTPS/PLA, and TPS/PLA blends were shown in Fig. 1, respectively. Compared with the smooth fracture structure of pure PLA (Fig. 1a), the blends of DTPS1/PLA and TPS1/PLA (Fig. 1b, e) had a typical two-phase polymer blend structure. Especially in DTPS1/PLA, the sample surface was rugged. At the same time, many starch granules were obviously not plasticized and some of them were removed from the sample surface and left some cavities in the fracture surface, which could be ascribed to the high interfacial tension between hydrophilic polymer and hydrophobic one. On the other hand, glycerol was less effective plasticizer than water and the permeation effect for dry starch chain was poor (Forssell et al., 1998) which limited the mobility and orientation of polysaccharide during processing.

When 10%wt water was used to substitute the same weight glycerol, no visible starch granules could be detected on the fracture surface of TPS1/PLA (Fig. 1e). But the dispersion between TPS1 and PLA was deteriorated and the interface was very clear between TPS1 and PLA. With increasing formamide content (Fig. 1c, d, f, g), not only the plasticization of starch, but also the dispersion between two phases dramatically increased. As shown in Fig. 1d and g, homogeneous blends could be achieved when glycerol was replaced by formamide, because formamide could easily penetrate into starch granules and accelerate the fluidity of starch chain during extrusion processing. This would be proved in rheology study.

3.2. Thermogravimetric analysis (TGA)

TGA had been performed for PLA, DTPS/PLA, and TPS/PLA blends, the weight loss was due to the volatilization of the plasticizers and the degradation of products had been monitored as a function of temperature, as shown in Fig. 2. $T_{5\%}$, the temperature corresponding to 5% weight loss, was obtained from Fig. 2 and listed in Table 2. Compared with pure PLA, the thermal stability of DTPS/PLA and TPS/PLA blends decreased dramatically. When glycerol was replaced by formamide, $T_{5\%}$ of DTPS/PLA and TPS/PLA blends were shifted to low temperature because of the lower boiling point of formamide.

Derivative thermogravimetry (DTG) curves associated with the $T_{\max}$ values of PLA and starch in relative blends were shown in Fig. 3 and listed in Table 2. Here $T_{\max}$ was the temperature at the maximum rate of weight loss, that was, the decomposition temperature. For the PLA in DTPS/PLA blends, the $T_{\max}$ was about 5 °C lower than that of pure PLA, indicating that PLA slightly degraded during extrusion processing. But the $T_{\max}$ of PLA in

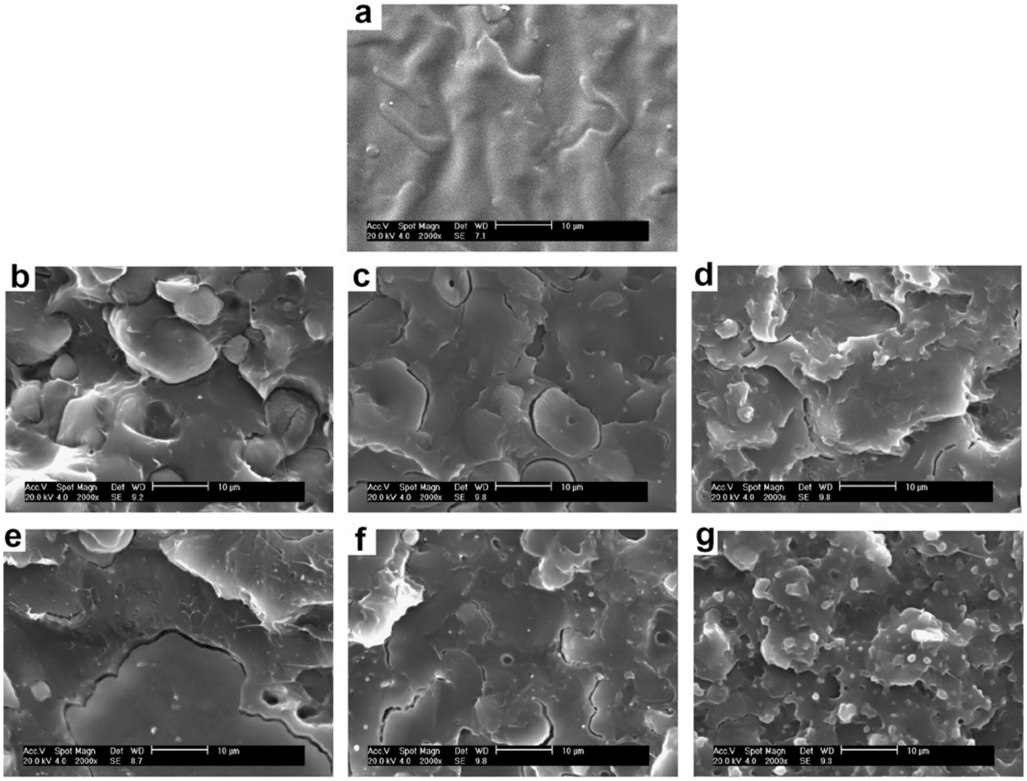

Fig. 1. The SEM photographs of pure PLA, DTPS/PLA, and TPS/PLA blends. (a) PLA; (b) DTPS1/PLA; (c) DTPS3/PLA; (d) DTPS5/PLA; (e) TPS1/PLA; (f) TPS3/PLA; (g) TPS5/PLA.

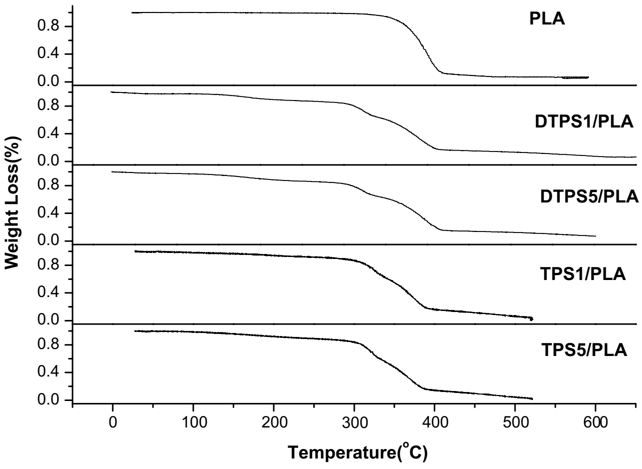

Fig. 2. Thermogravimetric curves of PLA, DTPS/PLA, and TPS/PLA blends.

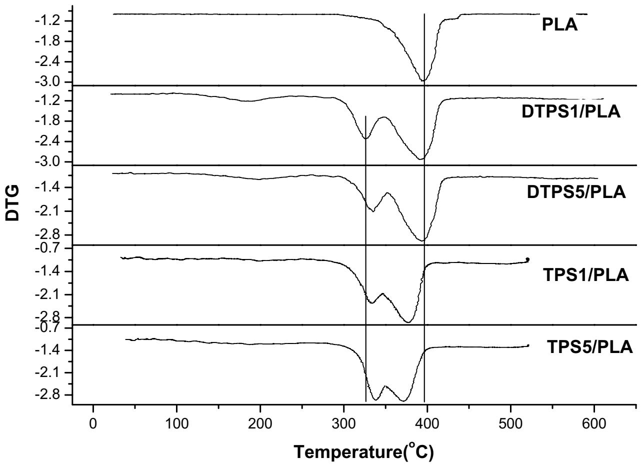

Fig. 3. DTG curves of PLA, DTPS/PLA, and TPS/PLA blends.

TPS/PLA blends was about 13 °C lower than that of pure PLA, which could be ascribed to the depolymerization of PLA in the presence of water under high temperature and shear. At the same time, $T_{\max}$ of starch in relative DTPS5/PLA and TPS5/PLA blends was about 3–4 °C higher than that in DTPS1/PLA and TPS1/PLA blends, respectively. This improvement could be ascribed to the increasing interaction between starch and PLA in the presence of formamide.

The activation energy of decomposition, E_t, of the polymer could be calculated from the TGA curves by the integral method proposed by Horowitz et al. (Horowitz & Metzger, 1963) with Eq. (10):

$$\ln[\ln(1-\alpha)^{-1}] = E_t\theta/RT_{\max}^2 \qquad (10)$$

Where α was the decomposed fraction, T was temperature, θ was $T - T_{\max}$, and R was the gas constant. From the plots of $\ln[\ln(1-\alpha)^{-1}]$ versus θ, which were shown in Figs. 4 and 5, respectively, E_t could be determined from the slope of the straight line of the plots. As demonstrated in Table 2, the E_t values of starch in DTPS/PLA and TPS/PLA blends increased as glycerol was replaced by formamide. So it might be certain that the increasing dispersion and compatibility between starch and PLA could increase the thermal stability of the blends. E_t of starch in DTPS5/PLA was 59.4 kJ/mol, whereas E_t of starch in TPS5/PLA was about 64.5 kJ/mol, which was a little higher than that of DTPS5/PLA. So in the presence of water, the thermal stability of starch was improved, but E_t of PLA in TPS5/PLA blend dramatically decreased.

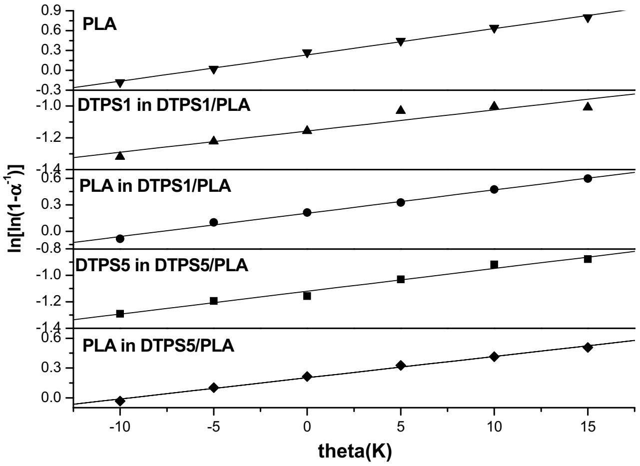

Fig. 4. Plots of $\ln[\ln(1-\alpha)^{-1})]$ versus of θ for the determination of E_t in DTPS/PLA blends. The straight line is the linear fit of the data points.

3.3. Rheology

As shown in Fig. 6, the $\eta \sim \gamma$ curves were plotted using a double logarithmic. With increasing shear stress, the viscosity of each blend decreased. Such flow behavior was called shear thinning. In addition, the effect of different plasticizers content and the temperature on the

Table 2
Thermogravimetric parameters of PLA, DTPS/PLA, and TPS/PLA blends

Samples	$T_{5\%}$ (°C)	Starch, $T_{\max}$ (°C)	PLA $T_{\max}$ (°C)	Starch		PLA	
				Slope	E_t (kJ/mol)	Slope	E_t (kJ/mol)
PLA	335	—	397	—	—	41.1×10^{-3}	156.6
DTPS1/PLA	167	324	392	10.4×10^{-3}	38.8	36.6×10^{-3}	134.6
DTPS5/PLA	165	337	392	19.2×10^{-3}	59.4	35.9×10^{-3}	132.0
TPS1/PLA	161	335	386	20.4×10^{-3}	62.6	17.5×10^{-3}	63.3
TPS5/PLA	156	339	384	20.7×10^{-3}	64.5	14.2×10^{-3}	51.9

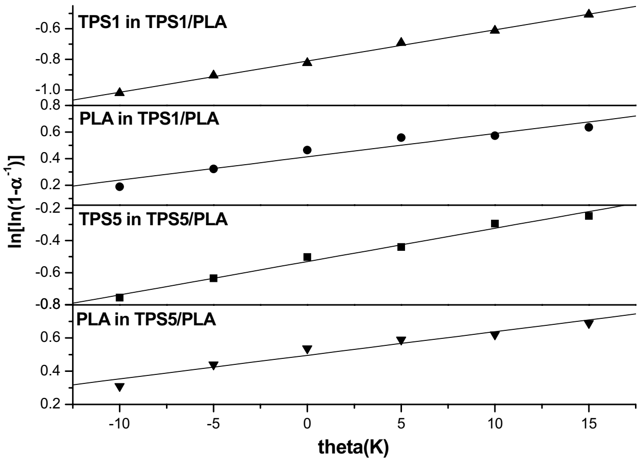

Fig. 5. Plots of ln[ln(1-α)$^{-1}$)] versus of θ for the determination of E_t in TPS/PLA blends. The straight line is the linear fit of the data points.

rheological behavior of PLA, DTPS/PLA, and TPS/PLA blends was much. According to the parameters of listed linear fit equations in Table 3, the blends were prone to flow along with the increasing temperature, and the apparent viscosity η of DTPS/PLA and TPS/PLA blends was decreasing with increasing formamide content at the same temperature.

As shown in Table 3, the flow index n, K, and viscous flow activation energy ΔE_η of PLA, DTPS/PLA, and TPS/PLA blends at 130, 140, and 150 °C, respectively. According to Eq. (7), the slope of linear fit equation was $n-1$ and the intercept was $\lg K$. As shown in Table 3, the flow index n of DTPS1/PLA decreased compared to that of pure PLA, which could be ascribed to the high viscosity of DTPS1 and the poor dispersion between DTPS1 and PLA. Moreover most residual starch granules (Fig. 1b) deteriorated starch chain orientation and fluidity. When glycerol was replaced by formamide, the flow index n of DTPS5/PLA and TPS5/PLA increased, respectively. This might be ascribed to the smaller size and high polarity of formamide was propitious to penetrate into starch chains and avoid the polysaccharide chain entanglement under high temperature and shear. At the same time, the increasing plasticized starch also was propitious to increase the fluidity of the blend. So, high dispersive and compatible blend could be achieved with the decreasing viscosity of starch. In addition, the flow index n of TPS/PLA blend was a little higher than the relative DTPS/PLA blend, because the depolymerization of PLA in TPS/PLA blends which had been proved in TGA study.

According to Eq. (9), $\lg\eta$ $(x=0)$ $\sim 1/T$ curves were linearized, and then ΔE_η $/(R\ln 10)$ was the slope. The viscous flow activation energy ΔE_η represented the effect of the temperature on the behavior of blends. The more ΔE_η was, the more sensitivity of the blend was to the temperature. According to the values of ΔE_η $(x=0)$ in Table 3, DTPS5/PLA was less sensitive to processing temperature.

3.4. Fourier transform infrared (FT-IR) spectroscopy

The interaction of polymer blends could be identified with FT-IR spectra. If two polymers formed completely immiscible blends, there were no appreciable changes in the FT-IR spectra of the blends with respect to the co-addition of each component (Zhang, Zhang, Zhou, & Shen, 2003). However, if two polymers were compatible, a distinct interaction (a hydrogen bonding or dipolar interaction) existed between the chains of one polymer and those of the other, causing FT-IR spectra for the blends to change (e.g., band shifts and broadening) (Peng, Wang, & Dong, 2005) [20]. As a result, FT-IR could identify segment interactions and provide information about the phase behavior of polymer blends.

Fig. 7 showed the FT-IR spectra of PLA, DTPS/PLA, and TPS/PLA blends in specific stretching regions, respectively. The peak band wave numbers related to hydrogen bonding of PLA, DTPS/PLA, and TPS/PLA blends were listed in Table 4. PLA had a strong carbonyl stretching absorption at about 1749 cm^{-1} (Fig. 7). With addition DTPS or TPS, this peak shifted to a lower wavenumber. At the same time, $-$C$-$O$-$ in $-$CH$-$O$-$ (1182 cm^{-1}) and $-$C$-$O$-$ in $-$O$-$C$=$O (1127 cm^{-1}, 1082 cm^{-1}, 1044 cm^{-1}) of PLA in both DTPS/PLA and TPS/PLA blends also shifted to low wavenumber. It suggested that these function groups took part in the interaction between PLA and DTPS. When glycerol was replaced by formamide, the carbonyl stretching absorption and other several character peaks of PLA in blends shifted to lower wavenumber. This might indicate that the interaction between these two immiscible polymers improved with increasing the dispersion between PLA and starch.

3.5. Mechanical properties

The mechanical properties (tensile strength, elongation at break) of DTPS/PLA and TPS/PLA blends, as well as pure PLA, were shown in Fig. 8. Both the pure component and the blends exhibited a typical brittle characteristic. Compared with the mechanical properties of pure PLA, that of DTPS1/PLA blend decreased dramatically, especially the tensile strength, which could be ascribed to the poor interfacial adhesion between two phases. When glycerol was substituted by formamide, the tensile strength of DTPS5/PLA was about 31 MPa, which was similar to that of pure PLA. At the same time, the elongation at break of DTPS5/PLA blend increased to about 4%. These improvements could be ascribed to the increasing dispersion and compatibility between PLA and DTPS5. But the high glass transition temperature (T_g) of PLA resulted to the poor elongation at break of the blends. The mechanical properties of PLA would be perfect after blending with plasticizers, such as triacetine, tributyl citrate, acetyl tributyl citrate and so on. And this work would be continued. In addition, it could be found in Fig. 8, water had a significant negative effect

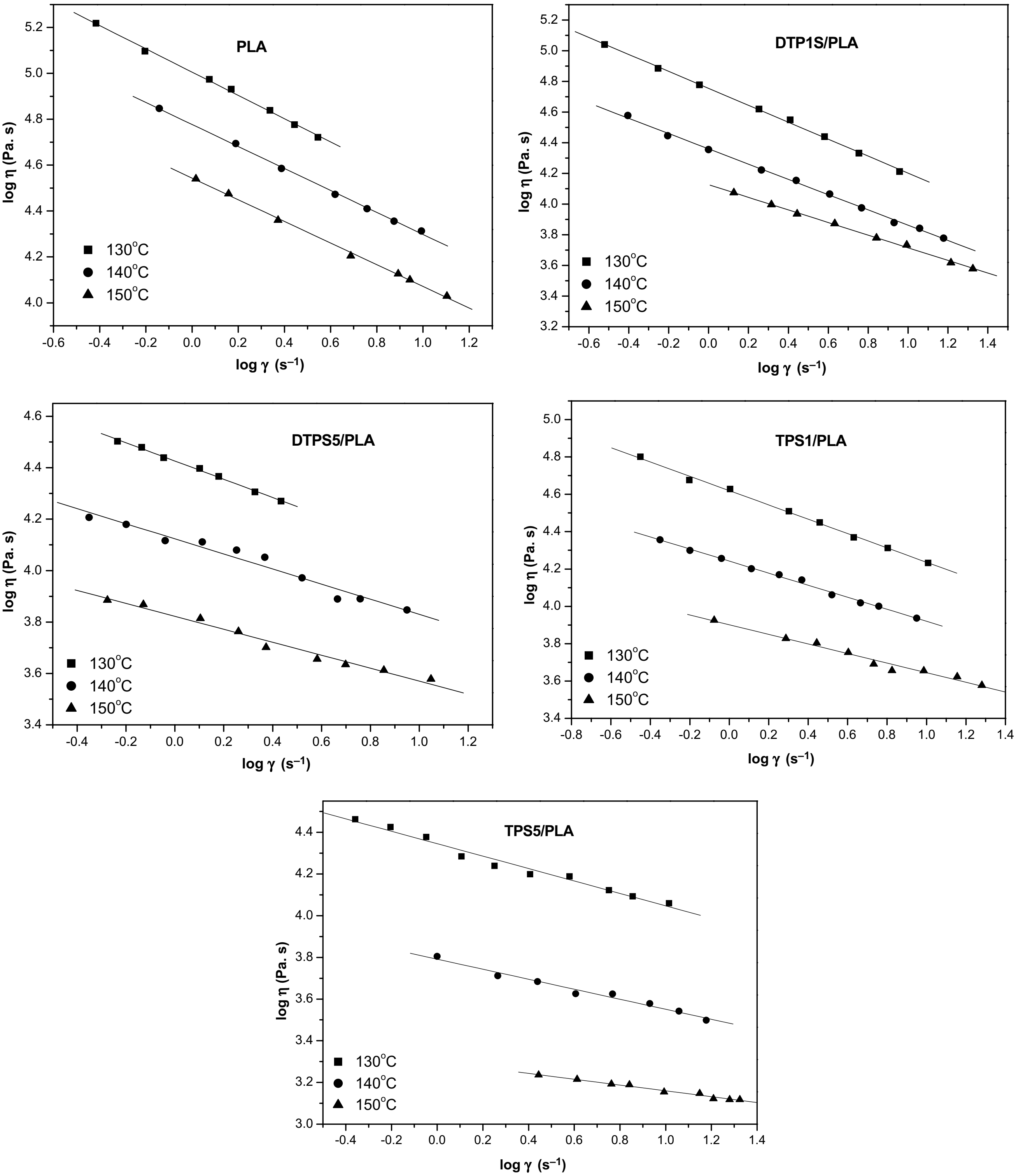

Fig. 6. The rheology curves of PLA, DTPS/PLA, and TPS/PLA blends at 130, 140, and 150 °C.

on the tensile strength of TPS/PLA blends. The tensile strength of the blends was reduced by about 44.4%, as the water content was about 10%wt in starch. Even though glycerol was substituted by formamide, the tensile strength of TPS/PLA blend was poor, which could be ascribed to the depolymerization of PLA during extrusion processing.

3.6. Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal data, which was, the storage moduli (E') and the loss factor ($\tan\delta$) for PLA, DTPS/PLA and TPS/PLA blends were shown in Fig. 9 and 10, respectively. E' was an important parameter of rigid materials. The E' of PLA, TPS/PLA and DTPS/

Table 3
The flow index n, consistency K and vicious flow activation energy ΔE_η ($X = 0$) of PLA, DTPS/PLA, and TPS/PLA blends at 130, 140, and 150 °C

Samples		PLA	DTPS1/PLA	DTPS5/PLA	TPS1/PLA	TPS5/PLA
130 °C	n	0.49	0.43	0.65	0.62	0.70
	K (Pa s^n)	1.02×10^5	5.69×10^4	2.67×10^4	4.17×10^4	2.24×10^4
140 °C	n	0.52	0.50	0.70	0.68	0.76
	K (Pa s^n)	5.89×10^4	2.34×10^4	1.33×10^4	1.75×10^4	6.17×10^3
150 °C	n	0.55	0.52	0.75	0.70	0.81
	K (Pa s^n)	3.47×10^4	1.34×10^4	6.64×10^3	7.98×10^3	1.26×10^3
ΔE_η ($x = 0$)	(KJ/mol)	75.40	100.25	78.57	117.18	203.15

PLA blends could be ranged in the order DTPS1/PLA > TPS1/PLA > DTPS5/PLA > TPS5/PLA > PLA. This might be ascribed to the plasticization of starch. It had been certain that water and formamide could increase the plasticization of starch and the dispersion between two phases from previous properties. Most remnant rigid starch granules embed in an entangled matrix content amylose and amylopectin network in DTPS1, which might deteriorate the mobility and orientation of molecular chain by physical cross-links.

In mechanical and dielectric relaxation studies of amorphous polymers, the observation of two thermal transitions in a single phase material were usually assigned to primary α-relaxation process associated with the upper transition temperature (T_g^u) and a lower transition temperature (T_g^l) associated with relatively localized molecular motions (β-relaxation). Compared with the T_g^u of PLA, the correlated T_g^l at about 45.6 °C was very small (as shown in Fig. 10) which could be ascribe to the poor mobility of relatively localized molecular of PLA. After blending with DTPS1, no change was found on the T_g^u of PLA. So it suggested that glycerol plasticized dry starch did not influence the T_g^u of PLA. In the presence of formamide and water in this blend, the T_g^u of PLA shifted to low temperature. This might indicate that the interaction between these two immiscible polymers improved with increasing the dispersion between two phases. So a partial miscible blend could be achieved.

As shown in Fig. 10, the α-relaxation and β-relaxation of DTPS, TPS in DTPS/PLA, and TPS/PLA blends were

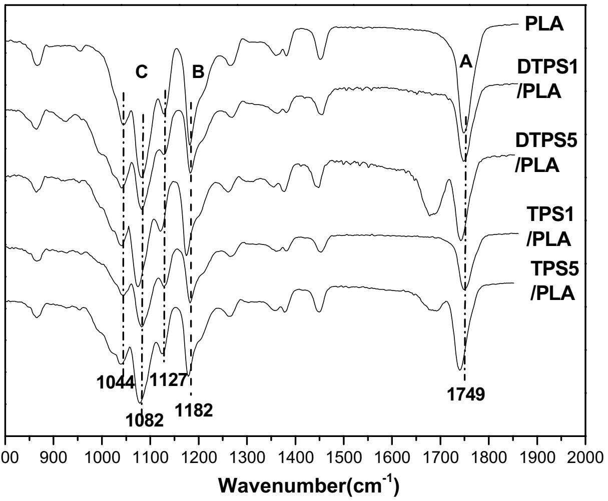

Fig. 7. FT-IR spectra of PLA, DTPS/PLA, and TPS/PLA blends.

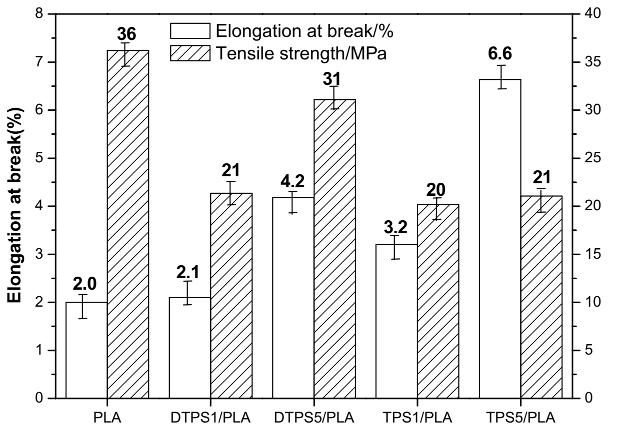

Fig. 8. The mechanical properties of PLA, DTPS/PLA, and TPS/PLA blends.

Table 4
The wavenumber related to the groups of hydrogen bonds in FT-IR spectrum and the change of the force constant Δf

Blends	The vibration wavenumber (cm^{-1})		
	—C═O (Carbonyl)	—C—O— in —CH—O—	—C—O— in —O—C═O
PLA	1749	1182	1127, 1082, 1044
DTPS1/PLA	1747	1181	1127, 1080, 1044
DTPS5/PLA	1741	1174	1121, 1074, 1040
TPS1/PLA	1745	1177	1125, 1078, 1042
TPS5/PLA	1740	1174	1120, 1073, 1040

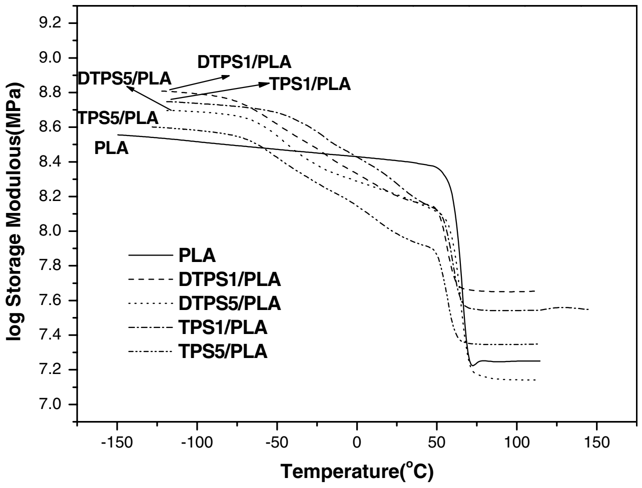

Fig. 9. Storage modulus vs temperature of PLA, DTPS/PLA, and TPS/PLA blends.

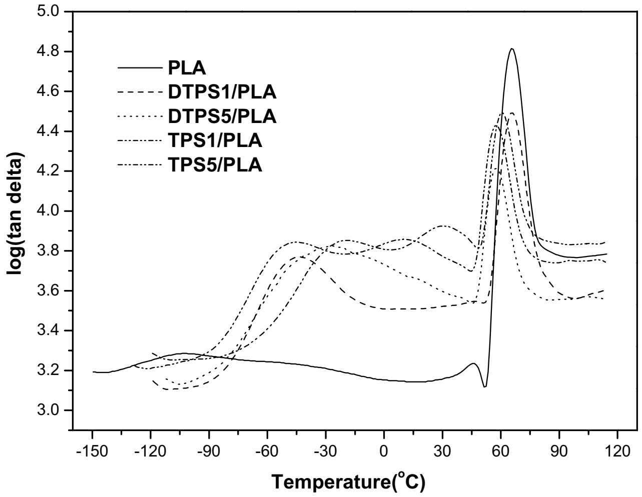

Fig. 10. Tanδ vs temperature of PLA, DTPS/PLA, and TPS/PLA blends.

Table 5
Temperatures of the α-relaxation β-relaxation of PLA, DTPS/PLA, and TPS/PLA blends

Sample	T_α (PLA) (°C)	T_α (starch) (°C)	T_β (starch) (°C)
PLA	65.7	—	—
DTPS1/PLA	65.7	—	−44.6
DTPS5/PLA	57.7	—	−27.5
TPS1/PLA	60.7	30.4	−19.6
TPS5/PLA	55.5	9.0	−46.8

studied and summarized in Table 5. The heat flow of TPS1 and TPS5 in relative blends exhibited two broad steps in Fig. 10, respectively. This two glass transitions were recognized to be a phase-separated in TPS materials (Forssell et al., 1998). The T_g^u was related to the glass transition in starch–water mixtures, and the T_g^l was due to glycerol mixed a small quantity of polymeric material. Compared with the two transition of TPS1, the relative one of TPS5 decreased about 21.4 and 27.2 °C, respectively. This evolution was ascribed to formamide could form stronger hydrogen bond with polysaccharide than glycerol (Ma et al., 2005). In addition, the T_g^u was not found in DTPS1 and DTPS5, because absented the interaction between water and polysaccharide (Forssell et al., 1998). But the T_g^l of DTPS5 also decreased about 17.1 °C. So it could be certain that formamide was a much more effective plasticizer for starch than glycerol after excluding water from the blend.

4. Conclusion

The properties test found that the dispersion and compatibility between glycerol plasticized starch and PLA was very poor. Moreover, it was difficult to achieve completely plasticized dry starch by glycerol during one step extruded DTPS1/PLA blends. When formamide and water was added into this blend, the plasticization of starch and fluidity of this blends improved dramatically. With increasing the dispersion of TPS/PLA blends, the interfacial tension decreased. So a homogeneous TPS/PLA blends could be achieved. At the same time, water was an effective plasticizer for starch, but it could depolymerize PLA during extrusion processing and deteriorate the properties of TPS/PLA blends. So it was only formamide propitious to improve the properties of DTPS/PLA blend. Finally, the mechanical properties of DTPS/PLA blends did not satisfy the practical application, especially the elongation at break. So the properties of PLA would be perfect after blending with the plasticizers, such as triacetine, tributyl citrate, acetyl tributyl citrate and so on.

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