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Melt rheology of polylactide/poly(butylene adipate-*co*-terephthalate) blends

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Abstract

Polylactide (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT) were melt blended using a twin-screw extruder. The phase morphology of PLA/PBAT blends was observed by scanning electronic microscopy (SEM). The linear and non-linear shear rheological behaviors of PLA/PBAT melts were investigated by an advanced rheology expended system (ARES). The results show that PLA/PBAT blend is a kind of immiscible, two-phase system where PBAT disperses evenly in PLA matrix. Linear viscoelastic limits of PLA/PBAT melts are smaller than that of neat PLA melt. At lower frequencies, storage moduli (G') of PLA/PBAT melts increase with PBAT content. PBAT content has no significant effect on loss moduli (G'') of PLA/PBAT melts, but the relaxation moduli of the melts increase with the introduction of PBAT. At the same time, the incorporation of PBAT results in a gradual increase of the melt viscosity and a decrease of flow activation energy. Besides PBAT causes a decrease of flow index n, which is in conformity with the more serious shear-thinning tendency of PLA/PBAT melts.

Keywords: Rheology; Polylactide; Poly(butylene adipate-*co*-terephthalate); Blends

1. Introduction

As a candidate of non-petroleum-based biodegradable polymeric materials, polylactide (PLA) has been a subject of great research challenge in materials science (Sinha Ray, Maiti, Okamoto, Yamada, & Ueda, 2002; Sinha Ray & Okamoto, 2003). PLA is a kind of linear aliphatic biodegradable thermoplastic polyester, produced from renewable resources with excellent properties comparable to many petroleum-based plastics (Jun, 2000; Martin & Averous, 2001). It has high mechanical properties, thermal plasticity, processing properties, and biocompatibility and has been proposed as a renewable and degradable plastic for uses in service ware, grocery, waste-composting bags, mulch films, controlled release matrices for fertilizers, pesticides, and herbicides (Fang & Hanna, 1999). However, some of other properties such as melt viscosity, impact strength, heat distortion temperature (HDT), gas barrier properties are frequently inadequate for various end-use applications (Ogata, Jimenez, Kawai, & Ogihara, 1997).

Properties of PLA can be modified by incorporation of organically modified layered silicate (Sinha Ray, Yamada, Okamoto, Ogami, & Ueda, 2003; Sinha Ray, Yamada, Okamoto, & Ueda, 2002), copolymerization (Hiljanen-Vainio, Karjalainen, & Seppala, 1996; Hiljanen-Vainio, Orava, & Seppala, 1997; Kylma & Seppala, 1997; Nakayama, Kavasaki, Arvanitoyannis, Iyoda, & Yamamoto, 1995; Stolt, Hiltunen, & Sodergard, 2001) and polymer blending techniques (Chen, Chueh, Tseng, Huang, & Lee, 2003; Peesan, Supaphol, & Rujiravanit, 2005; Sivalingam & Madras, 2004; Wang, Ma, Gross, & McCarthy, 1998). Poly(butylene adipate-co-terephthalate) (PBAT) is an aliphatic–aro-

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matic copolyester, which is fully biodegradable. It degrades within a few weeks with the aid of naturally occurring enzymes. The PBAT is a flexible plastic designed for film extrusion and extrusion coating. In the view of its high toughness and biodegradability, PBAT is considered as a good candidate for the toughening of PLA. PLA/PBAT blends were studied by Jiang, Wolcott, and Zhang (2006). The blends showed decreased tensile strength and modulus, however, elongation and toughness were dramatically increased. The failure mode changed from brittle fracture of the neat PLA to ductile fracture of the blends.

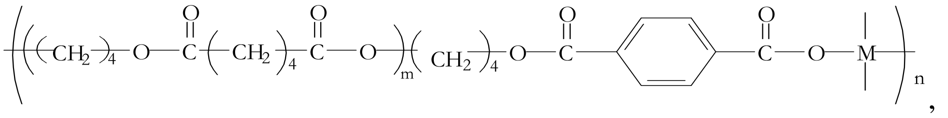
Generally, PLA is made into useful items using thermal processes, such as injection molding and extrusion (Fang & Hanna, 1999). Therefore, its rheological properties, especially its shear viscosity (η), have important effects on thermal processes, such as film blowing, paper coating, injection molding, sheet forming and fiber spinning (Aamer, Sardinha, Bhatia, & Tew, 2004; Fang & Hanna, 1999). And the study of rheological properties of any polymeric melts is crucial to gain fundamental understanding of the processability of the materials. Melt rheology of amorphous and semicrystalline PLA and PLA/layered silicate nanocomposites were reported (Fang & Hanna, 1999; Gu, Ren, & Dong, 2007; Lehermeier & Dorgan, 2001; Palade, Lehermeier, & Dorgan, 2001; Sinha Ray, Yamada, Okamoto, & Ueda, 2003). While relatively few studies on the rheology of PLA blends have appeared in the open literature. In the case of polymer blends, rheological behaviors are strongly influenced by their structures and interfacial characteristics. The studies of melt rheological properties are not only important to understand the knowledge of the processability of these materials, but also are helpful to find out the structure–property relationship in blends.

In this paper, the linear and non-linear shear rheological behaviors of PLA/PBAT melts were studied by an ARES rheometer. The objective of this paper is to map out the structure–rheological response of PLA/PBAT blends and provide academic information for the processability of the blends.

2. Experimental

2.1. Materials

PLA ($M_w = 180{,}000$, $M_w/M_n = 1.7$, L/D isomer ratio is ~96:4, $T_g = 58$ °C, $T_m = 155$ °C) was supplied by Institute of Nano- and Bio- Polymeric Materials, Tongji University (Shanghai, China). Poly(butylene adipate-*co*-terephthalate)



(PBAT, $T_g = -29$ °C, $T_m = 110$–115 °C, Ecoflex F BX 7011) was supplied by BASF.

Table 1
Compositions of PLA/PBAT blends

Samples	PLA100	PLA95	PLA90	PLA85	PLA80	PLA70
PLA (wt%)	100	95	90	85	80	70
PBAT (wt%)	0	5	10	15	20	30

2.2. Preparation of the blends

PLA/PBAT blends were prepared by melt mixing 70–95 wt% PLA and 5–30 wt% PBAT using a twin-screw extruder with a screw diameter of 27 mm and an L/D ratio of 42. Before extrusion, both PLA and PBAT pellets were dried under vacuum at 80 °C for 12 h. The extrusion temperature was independently controlled at eight zones along the extruder barrel and a strand die to achieve a temperature profile in the range of 155–175 °C. The screw speed was set at 100 rpm and feed rate was 30 g/min. In order to eliminate the degradation of PLA in the heating process, 0.5 wt% (weight ratio to PLA/PBAT) tris(nonylphenyl) phosphate (TNPP) was used as a stabilizer. TNPP acts as a chain extender reconnecting polymer chains that have been broken due to moisture and elevated temperature (Lehermeier & Dorgan, 2001; Palade et al., 2001). The compositions of the blends are shown in Table 1. Samples for rheological measurements were prepared by hot compression molding with ~3 MPa at 180 °C for 3 min into 1-mm-thick plates and then cut into 25-mm diameter parallel plates.

2.3. Structures of PLA/PBAT blends

The surface morphology of PLA/PBAT blends fractured at room temperature was observed by scanning electron microscopy (SEM) (Hitachi S-2360N). All specimens were gold coated prior to observation.

2.4. Melt rheology

Rheological behaviors of PLA/PBAT blends were investigated using a strain-controlled rheometer (ARES) with a torque transducer capable of measurements over the range of 2–2000 g cm. To determine the limits of linear viscoelastic properties of the melts, dynamic strain sweeps were performed with a 25-mm diameter plate. All measurements were performed at 180 °C and a frequency of 10 rad/s. The gap was set at a range of 0.8–1 mm.

Linear rheological measurements were performed by applying a time dependent strain of $\gamma(t) = \gamma_0 \sin(\omega t)$ and measuring the resultant shear stress $G(t) = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$, where $G'(\omega)$ and $G''(\omega)$ are the storage and loss modulous, respectively. The measurements were performed at a frequency range of 0.1–1000 rad/s. To obtain reasonable signal intensities even at evaluated temperature or low frequency and avoid non-linear response, the strain amplitude for dynamic measurements was fixed at 5%, and elastic moduli (G'), loss moduli (G''), and complex viscosities (η^*) were obtained. The temperatures were set in the range of 160–180 °C. The master curves were generated using the principle of time temperature superposition and shifted to a common reference temperature (T_{ref}) of 175 °C, which was chosen as the most representative of a typical processing temperature of PLA.

Steady-state shear measurements at a certain temperature were also conducted to investigate the non-linear rheology of the melts. The measurements were conducted at 170 °C using a 25-mm diameter cone with a cone angle of 0.1 rad. Shear rates ranging from 0.05 to 100 1/s were employed. The melt flow behavior of polylactide requires special attention because of the low thermal stability of PLA (Sarazin & Favis, 2003). For all the measurements, samples were dried in vacuum at 80 °C for 12 h to remove water prior to testing and equilibrated in the rheometer after loading at the desired temperature for 10 min to remove the thermal history.

2.5. Statistical data analysis

Minitab statistical software package (Minitab 14) was used for multiple linear regression.

3. Results and discussion

3.1. Structures of PLA/PBAT blends

To investigate the phase morphology of PLA/PBAT blends, fractured surfaces at room temperature of the blends were observed by SEM after being gold coated. As shown in Fig. 1, oval cavities and enclosed round PBAT particles are visible on the fractured surfaces. The blend is a kind of immiscible, two-phase system with PBAT dispersing evenly in PLA matrix because of the immiscibility between PLA and PBAT.

3.2. Linear viscoelastic properties

To determine the linear viscoelastic limits of PLA and PLA/PBAT melts, the dynamic strain sweep measurements were performed at 180 °C and a frequency of 10 rad/s. As shown in Fig. 2, storage moduli of the melts increase obviously with the incorporation of PBAT at lower strains. All the linear viscoelastic limits of PLA/PBAT melts are smaller than that of neat PLA. The curves of the blends are quite similar. The linear viscoelastic limits extend to a strain of about 50%. Therefore, the linear viscoelastic properties of PLA and PLA/PBAT melts were conducted at a strain of 5%.

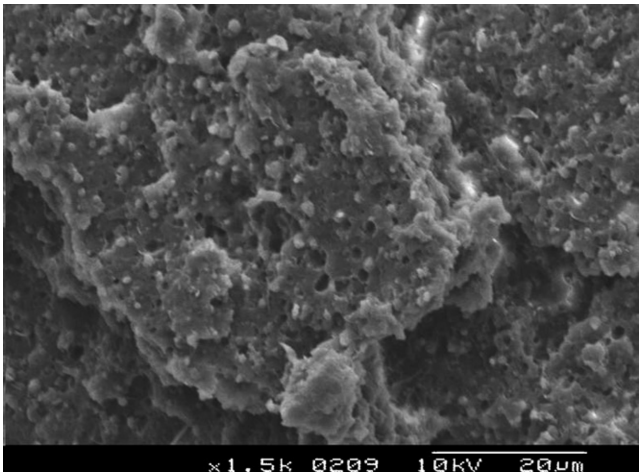


Fig. 1. Micrograph of fractured surface of PLA70.

Usually, a dynamic spectrum can be used to understand the structures and properties of polymers. It is well known that for thermo-rheologically simple materials, bilogarithmic plots of the isotherms of the storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and complex viscosity $|\eta^*|(\omega)$ can be superimposed by frequency shifts log (a_T) along the log (ω) axis, and modulus shifts given by log (b_T) such that (Utracki, 1990),

$$b_T G'(a_T\omega, T_{\text{ref}}) = b_T G'(\omega, T)$$

$$b_T G''(a_T\omega, T_{\text{ref}}) = b_T G''(\omega, T)$$

$$(b_T/a_T)|\eta^*|(a_T\omega, T_{\text{ref}}) = |\eta^*|(\omega, T)$$

where T_{ref} is the reference temperature. The linear viscoelastic master curves for the neat PLA and various PLA/PBAT melts are generated by the time–temperature super-

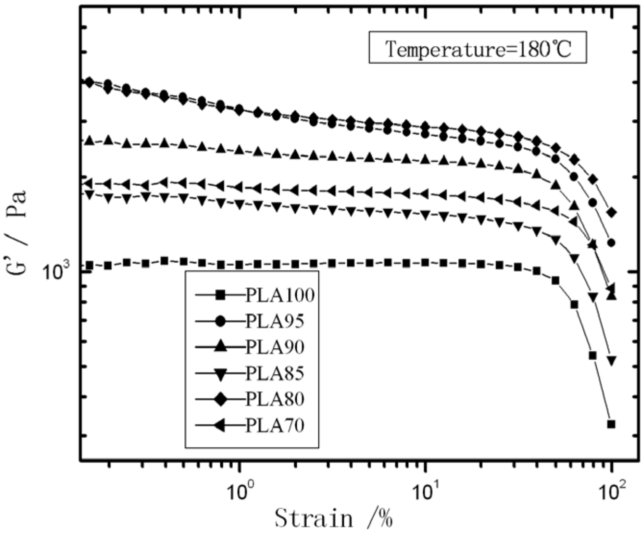


Fig. 2. Dynamic strain sweep tests of PLA and PLA/PBAT melts at 180 °C.

position principle and shifted to a common temperature (T_{ref}) of 175 °C with both frequency shift factor (a_T) and modulus shift factor (b_T).

As shown in Fig. 3a–c, PLA and PLA/PBAT melts show viscoelastic behaviors which are combination of irreversible viscous flow due to the polymer chain slippage and reversible elastic deformation due to molecular entanglement. At higher frequencies, samples experiencing a short thermal history produce a satisfactory overlapping of the curves. However, longer thermal exposures at lower frequencies produce significant departures from time temperature superposition due to degradation as reported by Palade et al. (2001). Besides the immiscible structures of PLA/PBAT melts might be another reason for the unsatisfactory overlapping of the curves, which was confirmed by Kapnistos' group when they investigated the rheology of polystyrene/poly(vinyl methyl ether) melts (Kapnistos et al., 1996). That is to say, the degradation during the course of testing and the immiscible structures have caused the materials to lose thermo-rheological simplicity.

As shown in Fig. 3a and b, the incorporation of PBAT has less effect on the storage moduli (G') and loss moduli (G'') of melts at higher frequencies. However, at low frequencies, G' increases with PBAT content. In the terminal region, the curves of PLA melt are expected to be expressed by power law of $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ which is similar to those of the narrow M_{w} distribution homopolymer melts as reported by Sinha Ray et al. (2003). The terminal zone slopes of PLA and PLA/PBAT melts from the master curves for $G'(\omega)$ and $G''(\omega)$ at lower frequencies ($\omega < 10$ rad/s) are calculated and presented in Table 2. All the correlation coefficients (r^2) are better than 0.98. And the standard deviation of residual S and p values for each calculation are less than 0.12 and 0.05, respectively. That is to say, $G'(\omega)$ and $G''(\omega)$ fit the power law well. The slopes of $G'(\omega)$ and $G''(\omega)$ in the terminal region of

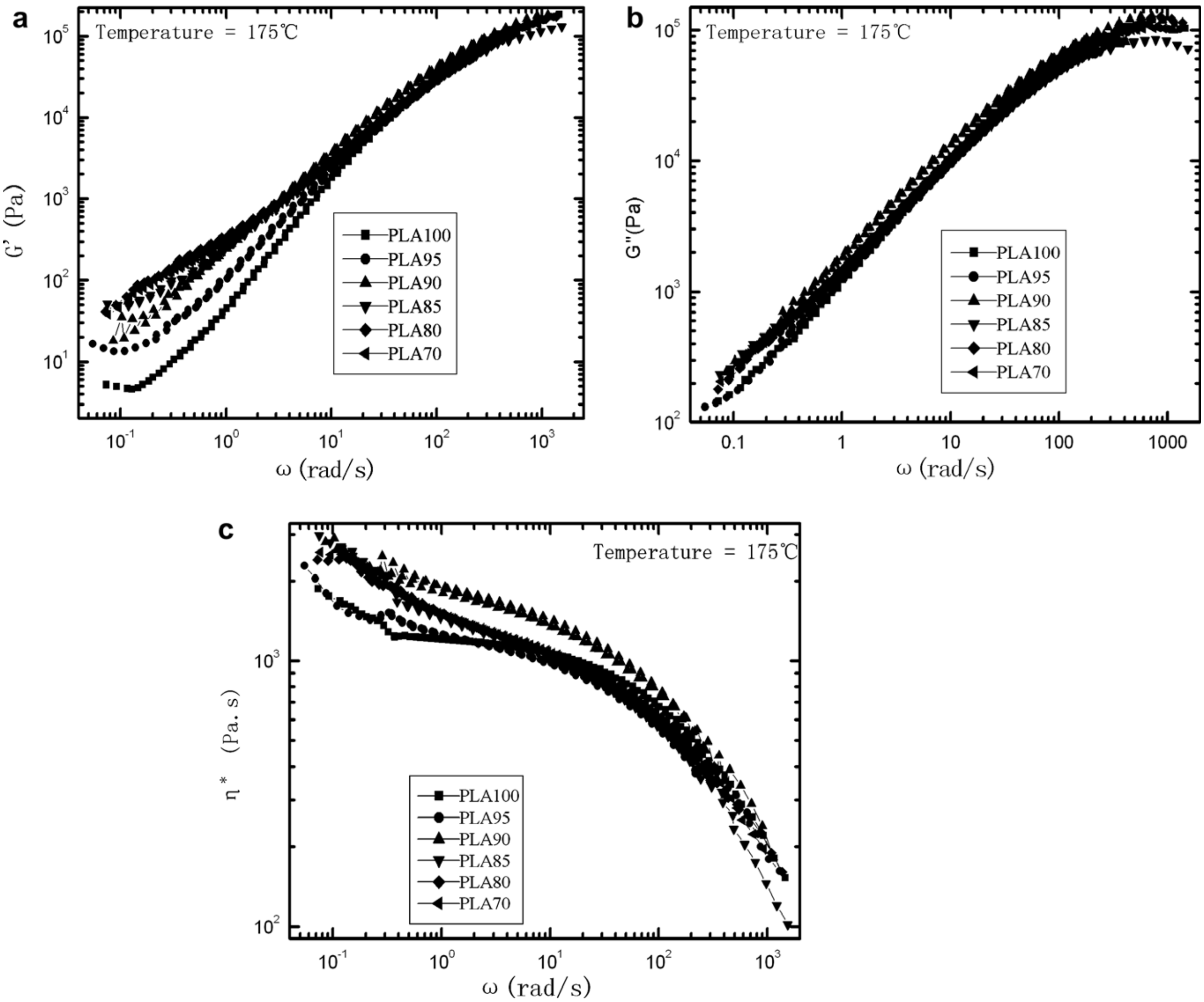


Fig. 3. Deduced frequency dependence of storage moduli G' (ω) (a), loss moduli G'' (ω) (b), and complex viscosity η^* (c) of PLA matrix and PLA/PBAT melts. $T_{\mathrm{ref}} = 175$ °C.

Table 2
Rheology characteristics of PLA and PLA/PBAT melts

Samples	PLA100	PLA95	PLA90	PLA85	PLA80	PLA70
Terminal region slope of $G'(\omega)$	1.62	1.32	1.18	1.04	0.96	0.86
Terminal region slope of $G''(\omega)$	0.93	0.87	0.85	0.83	0.84	0.85
Flow activation energy E_a (KJ/mol)	113.02	91.34	89.01	61.99	72.53	68.89
Flow index (n)	0.8555	0.8298	0.7374	0.7582	0.7260	0.7304

the master curves of neat PLA melt are 1.62 and 0.93, respectively. The values are in consistency with the results reported by Sinha Ray et al. (2003). On the other hand, the slopes of $G'(\omega)$ and $G''(\omega)$ for all PLA/PBAT melts are considerably lower. The lower slope values and higher absolute values of dynamic moduli indicate the formation of entanglement structures in PLA/PBAT melts. It is known that PBAT is a copolymer of butylenes, adipate and terephthalate. Its molecular chain is more flexible than that of PLA and is easier to entangle. The entanglement density is higher than that of PLA, leading to high reversible elastic deformation (G') of the melts. On the other hand, the relaxation of the structures with higher entanglement density is prevented partially. Therefore, the terminal slopes decrease with the incorporation of PBAT. Besides the immiscible structures of the blends as shown in Fig. 1 might be another reason for the deviation of the terminal slopes as reported by Kapnistos et al. (1996).

The master curves of dynamic complex viscosity η^* for PLA and PLA/PBAT melts are presented in Fig. 3c. When the frequency is lower than ~0.4 rad/s, the torque is too small, resulting in vibrating data detected because of the limit of the sensitivity of the torque transducer. Complex viscosities η^* of pure PLA melt displays a Newton liquid behavior at the frequency range of ~0.4–10 rad/s. In the other words, it is constant with the frequency increasing up to 10 rad/s where the shear-thinning behavior of η^* appears. Comparing to PLA melt, the complex viscosities of PLA/PBAT melts show stronger shear-thinning tendency at all frequencies and the tendency becomes stronger with the increasing of PBAT content.

3.3. Flow activation energy

The temperature dependence of the viscosity of polymer melts is one of the most important parameters in polymer flow. In a certain range of temperature, the dependence can be expressed in the Arrhenius form,

$$\eta_0 = A\ \exp(E_a/RT)$$

where η_0 is the zero shear viscosity, R is the gas constant, A is a constant, E_a is called the flow activation energy. The higher the E_a, the more temperature sensitive is the melt.

The flow activation energy values (E_a) of pure PLA and PLA/PBAT melts obtained from Arrhenius fit are presented in Table 2 (Ferry, 1980). Values of E_a are calculated by using η_0 data at temperatures of 160, 170 and 180 °C. For each calculation, the correlation coefficient (r^2) is better than 0.98. Standard deviation of residual (S) and p value are less than 0.1 and 0.05, respectively. The results obey Arrhenius model very well. It is clear that E_a tends to decrease with the introduction of PBAT. The results indicate that PLA/PBAT melts are easier to flow due to the introduction of the flexible PBAT molecular chains. On the other hand, the less temperature dependence of viscosity of PLA/PBAT melts makes it easier for the choosing of processing temperatures. PLA/PBAT blends have broader processing temperature window due to the less viscosity sensitivity to temperature.

3.4. Relaxation modulus

The stress relaxation data $G\ (t)$ (Fig. 4) were transformed by dynamic data using a method developed by Ninomiya and Ferry (Ferry, 1980). The slopes of $G\ (t)$ curves decrease with the introduction of PBAT, indicating that the relaxation time increases with the incorporation of PBAT. That is to say, the relaxation of PLA/PBAT melts is slower than that of neat PLA melt, resulting in higher G' of PLA/PBAT melts. The increasing of relaxation time of PLA/PBAT melts is due to the immiscible structure, which is conformity with the result obtained by Asthana and Jayaraman (1999) when they studied the rheology of polypropylene/Nylon-6 blend.

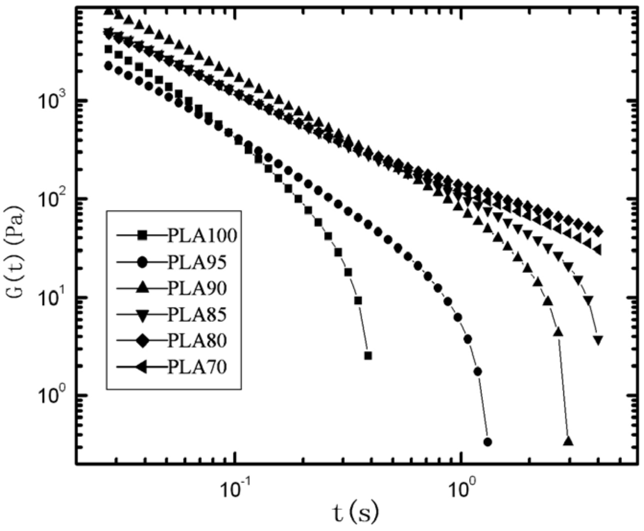


Fig. 4. Relaxation moduli from master curves of PLA and PLA/PBAT melts.

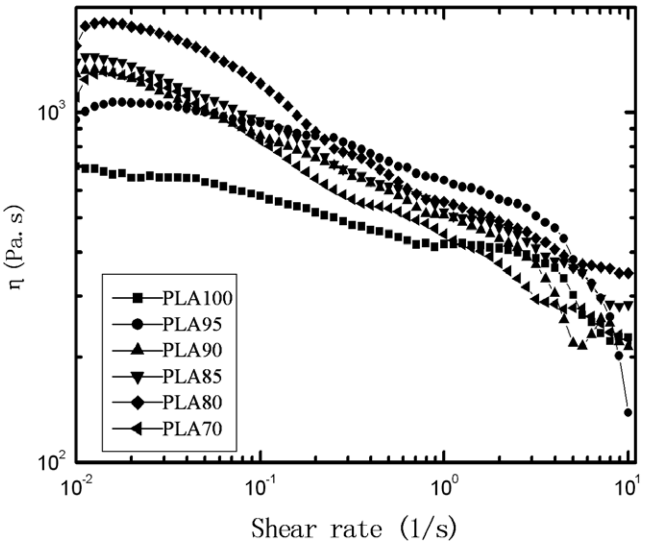


Fig. 5. Steady shear viscosity of PLA and PLA/PBAT melts at 170 °C.

3.5. Non-linear viscoelastic properties

The steady shear rheological behaviors of neat PLA and PLA/PBAT melts are shown in Fig. 5. PLA and PLA/PBAT melts behave as typical non-Newtonian fluids. At lower shear rates, the shear viscosities of PLA/PBAT melts are higher than those of pure PLA melt and increase considerably with PBAT content. On the other hand, the shear-thinning tendency of PLA/PBAT melts becomes stronger with the increasing of PBAT content so that the shear viscosities of PLA/PBAT melts are even lower than those of pure PLA melt at higher shear rates. The fluctuating of the data might be caused by the immiscible, two-phase structure.

Many models have been proposed for the viscosity function of non-Newtonian fluids, such as the power law (Skellard, 1967), Carreau model (Carreau, De Kee, & Chhabra, 1997), etc. The power law model is the most widely used model in practical applications.

To investigate the dependence of viscosity (η) versus strain rate ($\dot{\gamma}$), the power law model is employed to fit the non-Newtonian viscosity curves according to equation below,

$$\eta = m\dot{\gamma}^{n-1}$$

where n is the flow index and m is the consistency parameter. The slope of η versus $\dot{\gamma}$ on a log–log plot in the power law region is $n - 1$. When $n = 1$, the model reduces to that of a Newtonian fluid. When $n < 1$, the viscosity decreases with the increasing of strain rate and is referred to as shear-thinning fluid. When $n > 1$, the viscosity increases with the increasing of strain rate and is referred to as a dilatant fluid.

The power law equation fits the data well. All the equations have correlation coefficient (r^2) better than 0.99. All the p values are less than 0.0001. And all the standard deviations of residuals are less than 0.03. The calculated values of n for PLA and its blend melts are presented in Table 2. As shown in Table 2, the incorporation of PBAT leads to the decreasing of n. The result is in conformity with the more serious shear-thinning tendency of PLA/PBAT melts. Although the rheological data indicate higher viscosities of PLA/PBAT melts at 170 °C at lower frequencies, the introduction of PBAT was found to improve the processability because of the more serious shear-thinning tendency of PLA/PBAT melts.

4. Conclusions

PLA/PBAT blend is a kind of immiscible, two-phase system where PBAT disperses evenly in PLA matrix. The results reveal that linear viscoelastic limits of PLA/PBAT melts are smaller than that of neat PLA melt. At lower frequencies, storage moduli (G') of the blends increase with the increasing of PBAT content. But PBAT content has no significant effect on loss moduli (G'') of the blends at all frequencies. The complex viscosities of PLA/PBAT melts show stronger shear-thinning tendency at all frequencies. The slopes of $G'(\omega)$ and $G''(\omega)$ for all PLA/PBAT melts are considerably lower than those of neat PLA melt. The lower slope values and higher absolute values of dynamic moduli indicate the formation of entanglement structures in PLA/PBAT melts. The incorporation of PBAT results in a gradual increase of the viscosity and a decrease of flow activation energy. The relaxation moduli of the blends increase with the introduction of PBAT. The incorporation of PBAT results in a gradual increase of the steady viscosity of the blends. Besides the incorporation of PBAT leads to a decrease of flow index n. The result is in conformity with the more serious shear-thinning tendency of PLA/PBAT melts.

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