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Preparation and properties of biodegradable poly(lactic acid)/poly(butylene adipate-*co*-terephthalate) blend with glycidyl methacrylate as reactive processing agent

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Abstract Poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) were melt-blended in the presence of glycidyl methacrylate (GMA) by twin-screw extrusion. The physical properties, phase morphology, thermal properties, and melt rheological behavior of the blends were investigated by tensile tests, Charpy impact tests, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and advanced rheology expended system (ARES). With 2 or 5 wt% GMA, the tensile toughness of the PLA/PBAT blend was greatly increased without severe loss in tensile strength. The impact strength of the blend was also significantly improved at 1 wt% of GMA addition but ultimately trended to be saturated with increasing GMA. SEM micrographs revealed that better miscibility and more shear yielding mechanism were involved in the toughening of the blend. DSC results indicated that the blend is still a two-phase system in the presence of reaction agent and the addition of GMA was found to enhance the interfacial adhesion between PLA and PBAT. Rheological results revealed that the addition of T-GMA increased the storage moduli (G'), loss moduli (G'') and complex viscosity of the blends at nearly all frequencies. The decreased shear-thinning tendency of the blends in the presence of T-GMA also implied improved melt stability during processing.

Introduction

Development of consumer products from biodegradable and renewable materials is currently an area of great interest for researchers [1–5]. Poly(lactic acid) (PLA) is a kind of linear aliphatic polyester derived from biomass through bioconversion and polymerization. PLA is environmentally biodegradable and can eventually be converted to be carbon dioxide, water, and humus [6, 7]. The extrusion grade PLA has high modulus (over 3 GPa) and strength (over 50 MPa) comparable to that of many petroleum-based plastics, but its low glass transition temperature (about 60 °C) and low toughness limit its application, so that neat PLA is hard to be designed for film extrusion [8].

PBAT is an aliphatic-aromatic copolymer, which is prepared by melt polycondensation of 1,4-butanediol (BDO), dimethylterephthalate (DMT) and adipic acid with tetrabutylorthotitanate (TBOT) as the catalyst [9, 10]. A typical procedure was as follows: into a stainless reactor vessel under N2 atmosphere were introduced BDO, DMT, and TBOT. The reactants were heated to 160 °C, and methanol was distilled out. After 1 h, adipic acid was added to the reaction mixture and the temperature was raised to 180 °C and kept for 1 h. Water was distilled out. A vacuum was then slowly applied and the reaction temperature was raised to 270 °C. Excess BDO was distilled in this period. Afterwards, high vacuum (1–3 mbar) was applied. Total time for the vacuum phase was 2.5 h. Because of the excellent physical properties as well as

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still having biodegradability, a commercial P(BA-co-44mol%BT) with the trademark Ecoflex® was produced by BASF AG [10]. But the high cost of PBAT comparable to that of many general purpose plastics has led to the limitation of its application.

Various miscible and immiscible biodegradable polymer blends have been reported [11, 12]. So combining the high toughness of PBAT and the relatively low price of PLA can result in a novel blend [13, 14]. The two fully biodegradable polymers have been considered as a complementary blender for each other. It has been studied that the elongation and toughness of blends of PLA and PBAT increased dramatically with the increase of PBAT content (5–20 wt%) [15].

However, as a two-phase system, the incompatibility between PLA and PBAT especially at interfaces is still an unfavorable factor [16, 17]. Glycidyl methacrylate (GMA) may be useful for reactive processing of PLA/PBAT blend because carboxylic and hydroxyl groups that are hydrolyzed in PLA and PBAT under heat and high shear stress in extruding equipment may react with epoxy groups [18, 19]. Considered the control of reactivity and the facility in processing, a random terpolymer of ethylene, acrylic ester and GMA (abbreviated as T-GMA) was used for the reaction at the PLA/PBAT interface to enhance its physical properties. The molecular weight of T-GMA is 240,000 g/mol. The acrylic ester content is 24% and GMA content is 8% in T-GMA. Figure 1 shows the predict reaction of PLA, PBAT, and the reactive processing agent T-GMA.

Therefore, in this article, PLA was blended with PBAT in the presence of reactive agent T-GMA by two screw extrusion. Then, the mechanical properties, miscibility, phase morphology, thermal properties, and rheology of the polymer blend were investigated.

Materials

Pellets of PLA (Mw = 130,000 g/mol, Tongjieliang Biomaterials Co., Ltd., Shanghai, China), pellets of PBAT (Mw = 145,000 g/mol, Ecoflex®, BASF Corp.), and pellets of T-GMA (Mw = 240,000 g/mol, GMA content = 8%, LOTADER, ARKEMA Corp.) were used without further purification.

Characterization

Tensile strength

The tensile tests were conducted by using a CMT5105 electromechanical universal testing machine (Sans Group

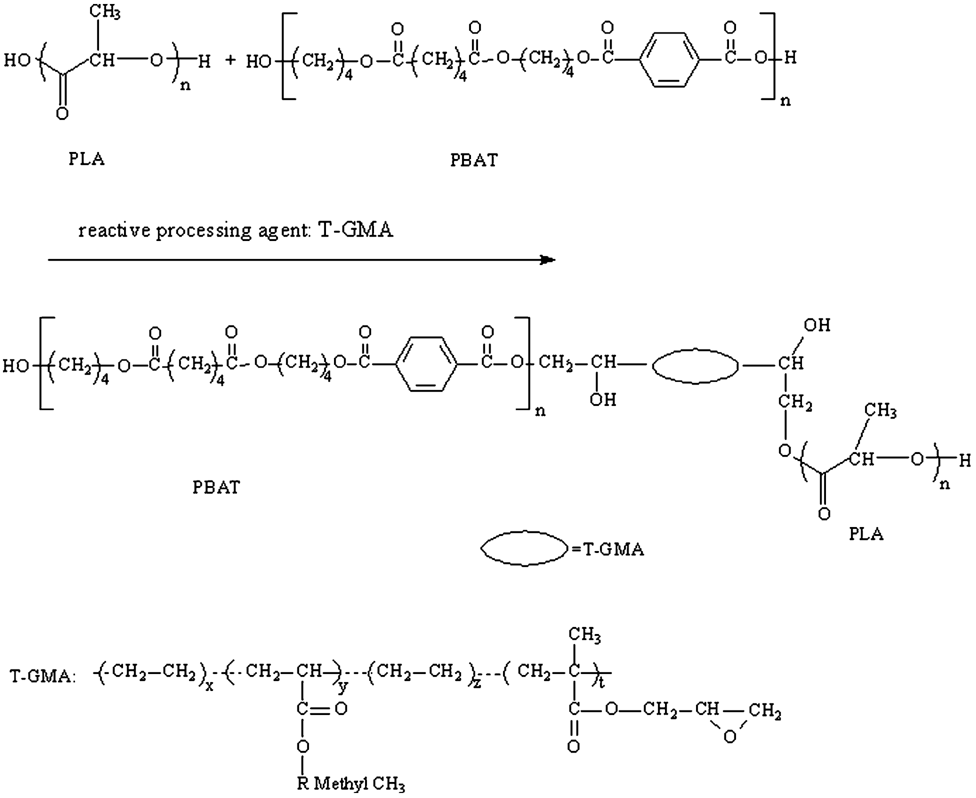

Fig. 1 Predicted reaction of PLA, PBAT, and T-GMA

Company) adapted to the standard ISO 527-1993. The crosshead speed was 20 mm/min.

Impact strength

Charpy impact tests were conducted by using a ZBC1400-2 impact tester (Sans Group Company) and a pendulum of 4 J adapted to the standard ISO 179-2003. Tests were done on notched specimens of 80 × 10 × 4 mm^3. Five replicates were tested for each sample to get an average value.

Scanning electron microscopy

The PLA/PEG blends and PLA/PCL blends were investigated by scanning electron microscopy (SEM, Hitachi S-2360N). Fracture-frozen cross sections of the impact test specimens of blends, taken either in a longitudinal or transverse way, were coated with gold and observed under SEM at an accelerating voltage of 20 kV.

Differential scanning calorimetry

Thermal analysis data were measured by differential scanning calorimetry (DSC, Q100, TA instruments, USA). All specimens were sliced from injection-molded material and all measurements were performed under nitrogen. In this study, DSC measurements were carried out by heating from −50 to 200 °C at a rate of 10 °C/min. DSC studies revealed the significant thermal properties of the samples, such as glass transition temperature (T_g), crystallizing point (T_c), crystallinity enthalpy change (ΔH_c), melting point (T_m), and melting enthalpy change (ΔH_m). T_g was taken as the midpoint of the inflection, and T_c and T_m were the peak temperatures of the crystallization exotherms and the melting endotherms. ΔH_c and ΔH_m were calculated by TA thermal analysis software.

Melt rheology

Rheological behaviors of PLA/PBAT blends were investigated using a strain-controlled rheometer (ARES). Samples were tested using a parallel-plate geometry ($d = 25$ mm) operated at 170 °C. A dynamic frequency sweep test was performed to determine the dynamic properties of blends. The strain and frequency range used during test was 5% and 0.1–200 rad/s, respectively.

Preparation of blends of PLA/PBAT with T-GMA as reactive processing agent

The blends were melt-blended using a co-rotating twin-screw extruder (LEISTRITZ Inc., Germany). The length–diameter ratio of screw is 41/1, and there are eleven heating zones, which can be controlled independently. The blend enters the extruder at zone 1 and exit at zone 11. The zone temperatures were set as shown in Table 1. The test specimens were prepared from the extruded blends by using an injection molding machine (JETMASTER JN55-E) with a nozzle at 170 °C. The temperature of the mold was 25 °C and the cycle time was approximately 50 s.

After exiting from zone 11, the blend strips were cooled through flume and then cut into pellets by dicing cutter.

Results and discussion

Mechanical properties of PLA/PBAT blend in the presence of T-GMA

PLA was blended with viscous PBAT with T-GMA as a reactive agent and the mechanical properties, rheological properties, and compatibility of the blends were investigated. Blends of PLA with 10, 20, 30, and 40 wt% of PBAT were prepared. T-GMA was added at 1.0–10.0 wt% to the PLA/PBAT blends.

Figure 2 shows stress–strain curves of PLA/PBAT (90/10 wt%) blend in the presence of T-GMA. As shown in Fig. 2, the ultimate strain was higher in the presence of T-GMA than in its absence. With the addition of T-GMA, the samples showed visible yield stress and necking. Further addition of T-GMA beyond the optimum amount had the opposite effect on tensile ultimate strain as embrittlement sets in. This result agreed with that of literature [20]. The ultimate strain of PLA/PCL blend composites with 0.1–0.2 wt% of DCP as a compatibilizer increases but then drops with the increase of DCP content because of cross-linking. On the other hand, the tensile strength did not monotonically decrease with increasing T-GMA (Fig. 3). This result did not agree with that of the literature [21]. The addition of LTI and LDI as reactive agents did not improve the tensile strength of PLA/PBS blend composites but gradually decreased it.

Figure 4 shows the effect of T-GMA on the impact strength at PBAT 10, 20, and 30 wt% in PLA. In the

Table 1 Zone temperatures used for blending

Zone	1	2	3	4	5	6	7	8	9	10	11
Temperature (°C)	160	165	175	180	185	185	185	180	180	180	175

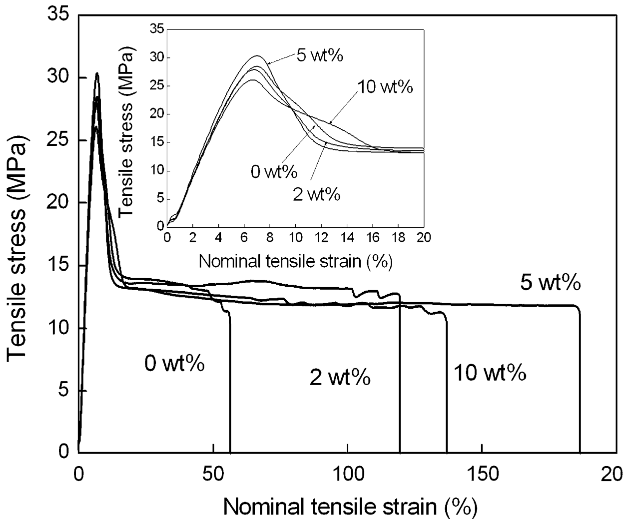

Fig. 2 Stress–strain curves of PLA/PBAT (90/10 wt%) blend in the presence of T-GMA. The inset gives details of stress–strain of the blends in the neighborhood of yield points

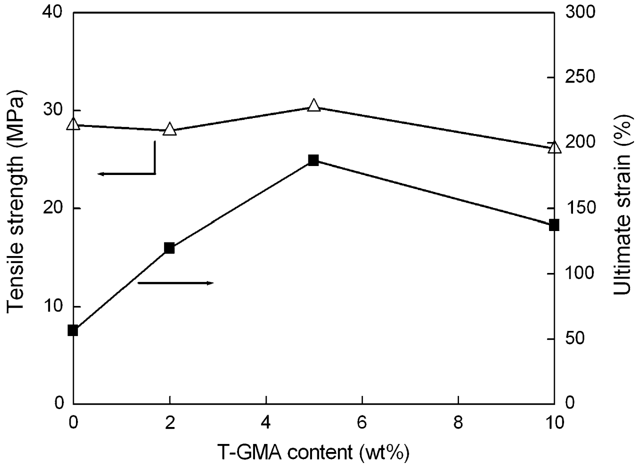

Fig. 3 Tensile strength and ultimate strain of PLA/PBAT (90/10 wt%) blends with different T-GMA content

absence of T-GMA, the impact strength increased with the increase of PBAT. This result agreed with that of the literature [15], that is, in the case of blending of PBAT as viscous biodegradable polymer to PLA, the impact strength of PLA clearly increased with the increase of PBAT content. At 10 wt% of PBAT content, the impact strength increased gradually with the increase of T-GMA and was saturated at 4 wt% of T-GMA. At 20 and 30 wt% of PBAT, the impact strength suddenly increased at 1 wt% of T-GMA and then trended to be saturated. However, with further addition of T-GMA beyond optimum amount range, the impact strength gradually decreased. These results indicate that reactions might occur between epoxy groups of T-GMA and carboxyl or hydroxyl groups at the terminals of the polymer so that the interfacial adhesion between

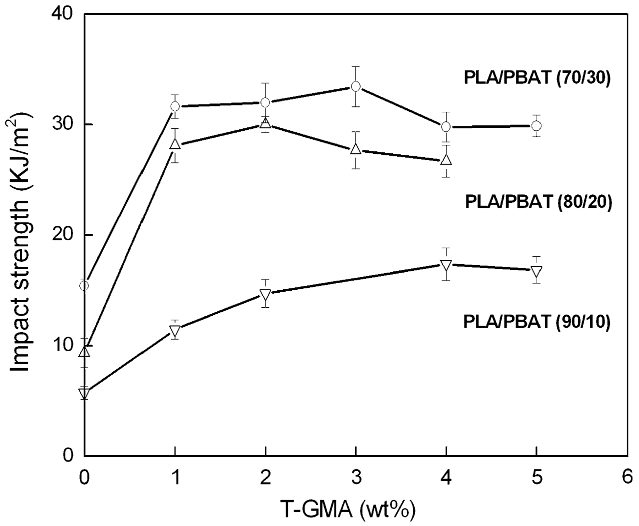

Fig. 4 Effect of T-GMA concentration in the PLA/PBAT blends (PLA/PBAT = 90/10, 80/20, 70/30 wt%) on impact strength

PLA and PBAT might increase the impact strength. Thus, excess epoxy groups easily led to crosslinking so that the impact strength was saturated and evenly decreased.

Morphology of PLA/PBAT blend in the presence of T-GMA by SEM

In order to investigate the reactive compatibility of PLA/PBAT blend, the fracture surface of impact tested specimens was observed by using SEM, operated at an acceleration voltage of 15 kV. The SEM image of the fracture of PLA/PBAT (70/30 wt%) blend with 0 and 5 wt% T-GMA is shown in Fig. 5a and b. Crazing, cavitation, shear banding, crack bridging, and shear yield have been identified as important energy dissipation processes involved in the impact fracture of toughened polymer systems [22–28]. In Fig. 5a, the blend showed a kind of immiscible, namely, two-phase structure with PBAT dispersing evenly in PLA matrix and the cavitation caused by debonding can be clearly identified. As a comparison in Fig. 5b, with the presence of T-GMA (5 wt%), the blend of PLA and PBAT showed better misciblility and more shear yielding when it was fractured.

Thermal analysis

DSC curves of PLA/PBAT (70/30 wt%) blend with different T-GMA contents are shown in Fig. 6. Each sample displayed a cold crystallization exotherm, a melt endotherm and two glass transitions (about −25 °C for PBAT and about 60 °C for PLA). This result implied that the PLA/PBAT blend was still a two-phase system despite the fact that mechanical properties of blend were efficiently

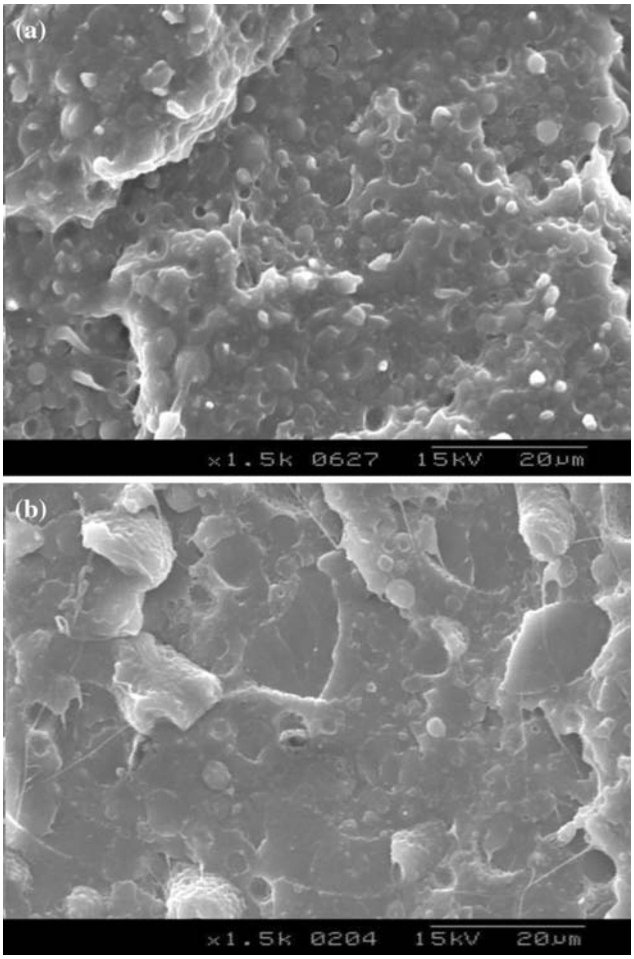

Fig. 5 SEM images of Charpy-fractured brittle surface of the blend. **a** PLA/PBAT(70/30 wt%) blend in the absence of T-GMA. **b** PLA/PBAT(70/30 wt%) blend in the presence of T-GMA (5 wt%)

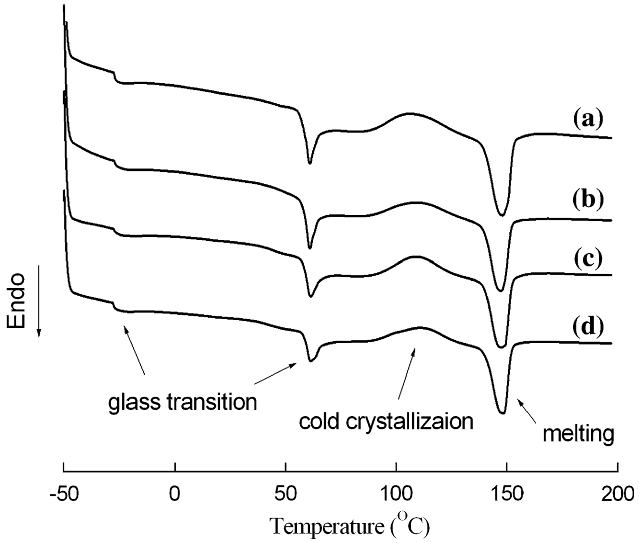

Fig. 6 DSC curves of PLA/PBAT (70/30 wt%) blend in the presence and absence of T-GMA. Heating rate = 10 °C/min. (a) Absence of T-GMA, (b) 2 wt% T-GMA, (c) 5 wt% T-GMA, and (d) 10 wt% T-GMA

Table 2 Thermal properties of PLA in blends at different T-GMA contents

T-GMA content (%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0	106.5	8.021	148.2	12.06
2	108.5	6.688	146.9	11.93
5	109.2	7.512	147.6	10.67
10	110.6	6.374	148.2	11.49

improved by addition of T-GMA. However, there are still something different in the presence and absence of T-GMA. Comparing curves of Fig. 6b–d with Fig. 6a, the incorporation of T-GMA increased cold crystallization temperature (T_c), T_gs of PLA phase and PBAT phase, respectively, but slightly decreased melting point (T_m, Table 2). Higher T_gs imply a hampered activity of polymer chains while higher T_cs and lower T_ms indicate a depressed crystalline ability of PLA. The lower enthalpy of crystallization and melting also indicate lower degree of crystallization. These results confirmed that the interfacial adhesion between PLA and PBAT was enhanced by reactions between T-GMA and polymers.

Rheological properties of PLA/PBAT blend composites in the presence of T-GMA

As the addition of T-GMA resulted in a finer phase structure (Fig. 5) and effectively increased the ultimate strain of PLA/PBAT blends, its addition also influenced the rheological properties of the blends.

G' and G'' of the blends with different T-GMA contents are listed in Figs. 7 and 8. It was reported that the incorporation of PBAT had less effect on the G' and G'' of blend melt at higher frequencies. However, as shown in Figs. 7

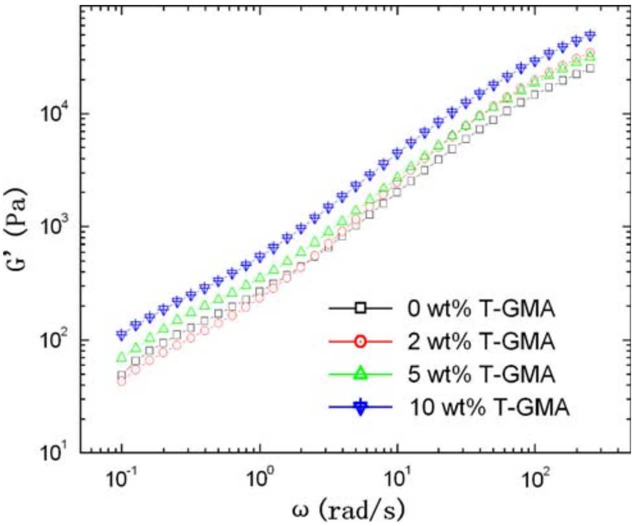

Fig. 7 Frequency dependence of storage moduli $G'(\omega)$ of PLA/PBAT (70/30 wt%) blends with different T-GMA contents

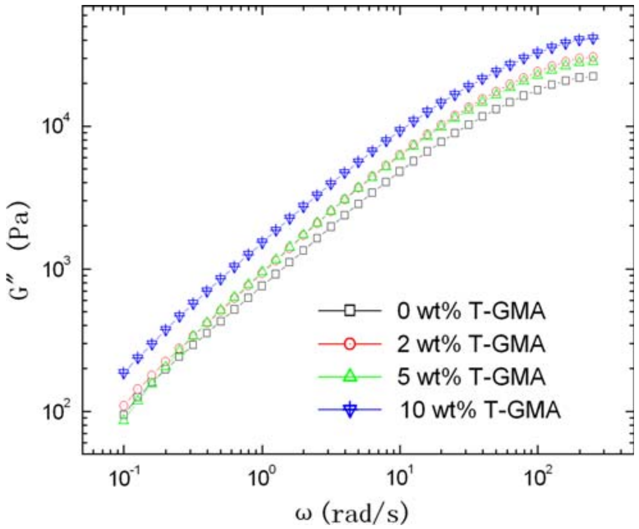

Fig. 8 Frequency dependence of loss moduli $G''(\omega)$ of PLA/PBAT (70/30 wt%) blends with different T-GMA contents

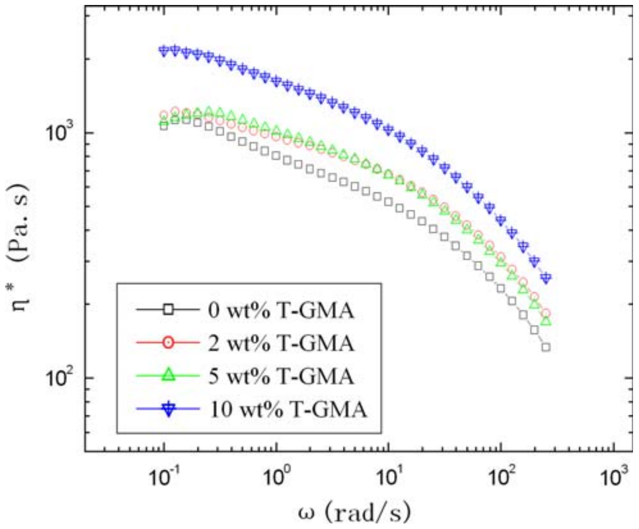

Fig. 9 Frequency dependence of complex viscosity η^* of PLA/PBAT (70/30 wt%) blends with different T-GMA contents

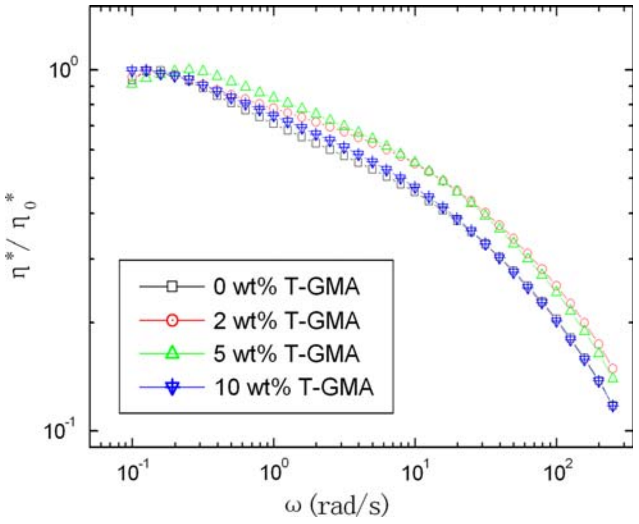

Fig. 10 Frequency dependence of relative complex viscosity ratio (η^*/η_0^*) of PLA/PBAT (70/30 wt%) blends with different T-GMA contents. η_0^* is obtained from Newtonian region

and 8, with the addition of T-GMA, the G' and G'' of PLA/PBAT blend melts were influenced at nearly all frequencies. The melt with 10 wt% of T-GMA content have higher G' and G'' at all frequencies, and the melt with 2 and 5 wt% of T-GMA content still show higher G' and G'' at higher frequencies. It indicated that the addition of T-GMA has exactly changed the rheological properties of PLA/PBAT blend. In addition, at lower frequencies, the incorporation of T-GMA increased G' values of blend melt (except 2 wt% content) but has less effect on G'' (except 10 wt% content). The higher absolute values of dynamic moduli indicate the formation of entanglement structures in PLA/PBAT melts. PBAT is a copolymer of butylenes, adipate, and terephthalate, and its molecular chain is more flexible than that of neat PLA and is easier to entangle. Now the higher reversible elastic deformation (G') of the melts with the addition of T-GMA obviously indicates a further increased entanglement density [29]. As a terpolymer, T-GMA has an observably high molecular weight, which is mainly attributed to the long chains of polyethylene. So the immiscibility of polyethylene in PLA/PBAT blend may increase G' and G'' value at higher T-GMA content. But at low content of T-GMA, the long linear chains of polyethylene may play a role of plasticizer. So the exception at 2 wt% content and 10 wt% content may be due to the high molecular weight size of T-GMA.

The curves of dynamic complex viscosity η^* for PLA/PBAT blend with different T-GMA contents are presented in Fig. 9. It is clear that the addition of T-GMA results in much higher η^* at nearly all frequencies. This change indicates that the reaction between T-GMA and the PLA/PBAT blend greatly increased the molecular interactions of the blend system, and the movement of molecular chains was hindered remarkably. Moreover, the observably high η^* at 10 wt% content may also be partly due to the high molecular weight of T-GMA. On the other hand, the incorporation of T-GMA has less effect on the expansion of Newtonian region. The relative complex viscosity ratio as a function of frequency is presented in Fig. 10 to investigate the shear-thinning degree of PLA/PBAT blend with different T-GMA contents [30]. All samples display a shear-thinning tendency at frequencies higher than ~0.2 rad/s but the tendency becomes weaker with the addition of T-GMA at the frequency range from ~0.2 to 10 rad/s. The increase of η^* may indicate a lower fluidity of melt but the decrease of shear-thinning tendency may indicate an improved melt stability during processing.

Conclusion

The blends of PLA/PBAT with GMA as reactive processing agent were prepared by two screw extrusion. GMA as a reaction agent has obvious effect on the properties of PLA/PBAT blends. With 2 or 5 wt% T-GMA, the tensile toughness of the PLA/PBAT blend was greatly increased without severe loss in tensile strength. The impact strength of the blend was also significantly improved at 1 wt% of T-GMA addition but ultimately trended to be saturated with increasing T-GMA. SEM micrographs revealed that better misciblility and more shear yielding mechanism were involved in the toughening of the blend. DSC results indicated that the blend is still a two-phase system in the presence of reaction agent and the addition of T-GMA was found to enhance the interfacial adhesion between PLA and PBAT. Rheological results revealed that the addition of T-GMA increased the storage moduli (G'), loss moduli (G''), and complex viscosity of the blends at nearly all frequencies. The decreased shear-thinning tendency of the blends in the presence of T-GMA also implied improved melt stability during processing.

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