PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE POLYLACTIDE/ETHYLENE METHYL ACRYLATE COPOLYMER BLENDS

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Abstract

The poly(lactic acid)/ethylene methyl acrylate copolymer (PLA/EMA) blends were melt blended with by a twin-screw extruder. The phase morphologies, mechanical, and rheological properties of the PLA/EMA blends with three weight ratios were investigated. The results showed that the addition of EMA improves the toughness of PLA at the expense of the tensile strength to a certain degree. All the PLA/EMA blends display typical droplet-matrix morphology, and different characteristic linear viscoelastic properties in the low frequency region, which were investigated in terms of their complex viscosity, storage modulus, and Cole-Cole plots. The interfacial tension between the PLA and EMA is calculated using the Palierne model conducted on the 80/20 PLA/EMA blend, and the calculated result is 3.3 mN/m.

Introduction

Biobased and biodegradable poly(lactic acid) (PLA) has undergone the most investigation because PLA exhibits high strength and stiffness, and is thought as one of the most promising replacement materials for petroleum-based polymer. [1] However, the inherent brittleness of PLA largely impedes its wide applications in several fields [2]. In order to improve its toughness, PLA was blended with other flexible polymers or rubbers, such as poly(butylene succinate) (PBS),[3, 4] ethylene acrylic acid copolymer (EAA),[5] and thermoplastic polyurethane.[6, 7] EMA has excellent environmental stress cracking resistance at elevated temperature with superior mechanical properties, as well as excellent resistance to ageing, hydrocarbon oil and low temperature.[8, 9] Moreover, EMA exhibits well compatibility with polymer, and high flexibility and toughness. However, to the best of our knowledge, no work has been reported on polymer systems of EMA as a thermoplastic elastomer toughened PLA. This work aimed to, for the first time, toughen PLA through melt blending with EMA. Phase morphologies and dynamic rheological properties of the PLA/EMA blends were also investigated. Moreover, the interfacial tension between the PLA and EMA phases was calculated based on the morphological and rheological results of the PLA/EMA blends.

Experimental

Materials

The matrix polymer used in this work was a biodegradable PLA (grade 2003D, NatureWorks® LLC, USA). Its density, melt temperature, and melt flow index are of 0.94 g/cm³, 157°C, and 8.8 g/10 min (210°C, 2.16 kg), respectively. The EMA (grade 14MGC02, Arkema group, France) with a density of 0.94 g/cm³, a melt temperature of 87°C, and a melt flow index of 2.7 g/10 min (190°C, 2.16 kg) was used as the dispersed phase.

Sample Preparation

PLA and EMA were dried at 80°C and 50°C for 12 h in a vacuum oven, respectively. Melt blending of PLA/EMA at three ratios (90/10, 80/20 and 70/30, w/w) was conducted using a Brabender counter-rotating twin-screw extruder (Germany) with a screw diameter of 25 mm and a length/diameter ratio of 20:1. The profile temperatures were 140, 160, 180, 180, 180, 180, and 180°C. The feeding rate and screw speed were 2 kg/h and 60 rpm, respectively. For comparison, the pure PLA and EMA were also processed under the same conditions. The blend samples for scanning electron microscope (SEM) observation and dynamic rheological measurement were collected from the exit of the extruder and quenched in iced water as soon as possible to preserve blend morphology, followed by drying at 50°C for 12 h in a vacuum oven. The collected blend samples for SEM observation were in the form of disks with a...
diameter of 25 mm and a thickness of about 2 mm. In addition, the blend and pure PLA strands collected from the exit of the extruder were cut into granules, and then compression molded into the pieces with the thickness of 1 and 4 mm by using a Flat Sulfuration Machine (model QLB-25D/Q, China) at 10 MPa and 180°C for 6 min. The sheets were cooled to room temperature about 30°C, removed from the mold, and then cut into the test bars. The bars were conditioned at 50% relative humidity and 25°C for at least 48 h before tensile and impact testing.

Characterization

Tensile test was conducted on all the prepared blend and pure PLA samples using an Instron Universal Testing Machine (model 5566, USA). Crosshead speed and gauge length were 20 mm/min and 70 mm, respectively. Notched Izod impact tests for the prepared blends and pure PLA were measured using a Zwick Impact Tester (model 5117, Germany) with a pendulum hammer of 5.4 J. The elongation at break, tensile strength, and impact strength were determined as an average of at least five repeats.

Dynamic rheological properties of the prepared PLA/EMA blend, pure PLA and EMA samples were carried out using a Bohlin Rheometer (model Gemini 200, UK) equipped with a parallel-plate fixture (25 mm diameter) in an oscillatory mode. The complex viscosity (η*), storage modulus (G′), and loss modulus (G″) as a function of angular frequency (ω) ranging from 0.0628 to 628 rad/s were determined by frequency sweep at 180°C. A fixed strain of 1% was used to ensure that the measurements were carried out within the linear viscoelastic range of the samples investigated.

Phase morphologies of all the prepared blend samples were examined using a FEI SEM (model Quanta 200, Holland) at an accelerating voltage of 20 kV. Before observation, the blend samples were immersed in liquid nitrogen for about 15 min and fractured perpendicular to the flow direction; then, they were gold sputtered and their cryo-fractured surfaces were used to examine. The diameters of the dispersed droplets were measured using Image Pro image analysis software (Media Cybernetics Inc., Silver Spring, Maryland). The volume and number average radii (Rv, Rn) of the droplets were calculated by:

\[ R_v = \frac{\sum n_i R_i^3}{\sum n_i R_i^2} \]  
\[ R_n = \frac{\sum n_i R_i}{\sum n_i} \]

where \( R_i \) is the radius of each droplet, and \( n_i \) is the number of droplets with \( R_i \).

Results and Discussion

Mechanical properties

The stress-stain curves of the prepared pure PLA and PLA/EMA blends are shown in Figure 1. It is clear from Figure 1 that, pure PLA displays a distinct yield point, beyond which failure occurs immediately with the tensile load. It indicates that pure PLA is rigid and brittle. The addition of EMA changes the tensile behaviors of PLA. The continuous development of deformation appears after yield in all of the blends. The stress-stain curve shows an elastic stress plateau, and the blend samples eventually show failure at a large elongation. No distinct yield point is observed for the 70/30 PLA/EMA blend; this indicates that the 70/30 PLA/EMA blend presents the tensile behavior like as an elastomer. Moreover, the stress-whitening phenomena are observed for all blends during their tensile deformation. As shown in Figure 2, the pure PLA displays a low elongation at break (6.4%) and a high tensile strength (75.7 MPa). The elongation at break for the blends is rapidly increased with the addition of 10 wt% EMA, and attained a maximum of 27.0% (which is 4.1 times as large as that of PLA) with the addition of 20 wt% EMA. Further increase in the EMA content results in a slight decrease in the elongation at break for the blends. However, the tensile strength for the blends decreased gradually from to 49.6 to 20.4 MPa with increasing the EMA content from 10 to 30 wt%. As shown in Figure 3, the impact strength of the blends improved sharply to 7.0 KJ/m² (which is 4.2 times as large as those of PLA) with the addition of 10 wt% EMA, and then decreased slowly to 4.5 KJ/m² with increasing the EMA content to 30 wt%.

Aforementioned results suggested that the fracture behavior changes from brittle fracture of PLA to ductile fracture of the blends, and the addition of the EMA improves the toughness of PLA at the expense of the strength to a certain degree. The decrease in the strength of blends, on the one hand, resulted from the low tensile strength of EMA; on the other hand, maybe caused by the absence of strong interactions between the PLA matrix and the EMA droplets, and the interfacial interaction between two phases can be characterized by interfacial tension. In addition, the mechanical properties of blends are strongly related to their phase morphology. So, in the following, the phase morphologies and dynamic rheological properties of the prepared blends were investigated. Based on these results, the interfacial tension between the PLA and EMA phases was calculated.

Phase morphology
As shown in Figure 4, spherical droplets of EMA are dispersed homogeneously in PLA matrix on a micrometer scale with clear interfaces for PLA/EMA blends. It indicates that the PLA is incompatible with the EMA. The mean diameter of EMA droplets increases gradually with increasing EMA content.

**Dynamic rheological properties**

Figure 5 shows the \( \eta^* \) versus \( \omega \) curves for the pure PLA and EMA, and PLA/EMA blends with various weight ratios. It can be seen that, the value of the \( \eta^*(\omega) \) for pure EMA is higher than that for pure PLA, and the \( \eta^*(\omega) \) curves for the blends are located between those of the pure PLA and EMA in the high frequency region. It was worth to note that the values of the \( \eta^* \) for all the blends are higher than those of the pure PLA and EMA in the low frequency region. In addition, compared with the pure PLA and EMA, the 80/20 and 70/30 PLA/EMA blends began to exhibit the shear thinning behavior at lower frequencies. These behaviors may be owing to the relaxation of the deformed droplets, and were also reported in previous studies about the PLA/PBS [4] and PLA/EAA blends.[5] The relaxation of the deformed droplets also reflected on the other dynamic rheological functions, such as \( G'(\omega) \) curve and Cole-Cole plot (\( \eta^* = G'/\omega \) versus \( \eta^* = G''/\omega \) plot). In the following, these two types of dynamic rheological curves are investigated.

As shown in Figure 6, in the high frequency region, the values of the \( G'(\omega) \) for the blends and pure components are close to each other. In the low frequency region, the \( G'(\omega) \) curves for the 90/10 PLA/EMA blend is located between those of the pure PLA and EMA, and the values of \( G'(\omega) \) of the 80/20 and 70/30 PLA/EMA blends are higher than those of pure PLA and EMA; the values of the \( G' \) for the blends increase with the increase in the EMA content, which may be attributed to the aforementioned relaxation of the deformed droplets for the blend with droplet-matrix morphology.[10,11] Increasing EMA loading increases the deformation degree of the dispersed droplets,[12] which increases the elastic energy generated by their deformation and thus the value of the \( G' \) in the low frequency region.

Figure 7 displays the Cole-Cole plots of the prepared PLA/EMA blends and pure components. As can be seen, the 90/10 PLA/EMA blend as well as pure PLA and EMA only presents one circular arc on their Cole-Cole plots. Figure 7 also shows that there exist a circular arc and a tail in the low frequency region on the Cole-Cole plots for 80/20 and 70/30 PLA/EMA blends, respectively. These results indicate that the 90/10 PLA/EMA blend is partial miscible, while 80/20 and 70/30 PLA/EMA blends are immiscible.

**Interfacial tension of PLA and EMA**

Based on the Palierne modal [13, 14], Xu and Huang [4] suggested that the reciprocal of the frequency corresponding to the peak in the low frequency region on the \( \eta^*(\omega) \) plot for the binary immiscible blend is defined as its longest relaxation time, and the interfacial tension between the two phases of the blend is calculated using eq.

\[
\lambda_s = \frac{R_s \eta_{0,d} (19K + 16)[2K + 3 - 2\phi(K - 1)]}{4\alpha 10(K + 1) - 2\phi(5K + 2)}
\]

where \( K = \eta_{0,d}/\eta_{0,m} \) is the zero-shear viscosity ratio of the dispersed phase and matrix; \( \phi \) is the volume fraction of the dispersed phase; \( \alpha \) is the interfacial tension between the components of the blend.

Figure 8 shows the \( \eta^*(\omega) \) plots of the PLA/EMA blends with various weight ratios and pure PLA and EMA. It can be seen that, only the 80/20 PLA/EMA blend displays a peak in the low frequency region on its \( \eta^*(\omega) \) plot, on which a peak is also observed in the high region. The 90/10 PLA/EMA blend as well as pure PLA and EMA only presents one circular arc, and 70/30 PLA/EMA blend shows a tail and a circular arc in the low- and high- frequency regions on their \( \eta^*(\omega) \) plots, respectively. So in this work, the calculation of the interfacial tension between PLA and EMA was conducted on the 80/20 PLA/EMA blend. The longest relaxation time of the 80/20 PLA/EMA blend is obtained from its \( \eta^*(\omega) \) plot, which is 1.6 s.

In the calculation of the interfacial tension, \( R_{V_s} \), \( \eta_{0,d} \) and \( \eta_{0,m} \) should be used. The \( R_V \) and \( R_s \) of the EMA droplets in the 80/20 PLA/EMA blend calculated by eqs. (1) and (2) are 0.67 and 0.87, respectively. The \( R_{V_s}/R_s \) is calculated, which is equal to 1.3 and does not exceed a value of about 2.3 as mentioned above. The \( \eta_{0,d} \) and \( \eta_{0,m} \) are calculated by [15]:

\[
\eta_s = \lim_{\omega \to 0} \frac{G''}{\omega}
\]

The calculated value of the interfacial tension between the PLA and EMA is 3.3 mN/m.

**Conclusions**

PLA/EMA blends with three different weight ratios were prepared by a twin-screw extruder to improve toughness of PLA. The results showed that the elongation at break and impact strength for the blends increase followed by a decrease with increasing the EMA content. All the PLA/EMA blends display droplet-matrix morphology. The
The mean diameter of EMA droplets increases with increasing EMA content. The complex viscosity curves for the blends are located between those of the pure PLA and EMA in the high frequency region, and higher than those of the pure PLA and EMA in the low frequency region. The relaxation of the deformed droplets induces that the complex viscosity, storage modulus, and Cole-Cole plots present obvious shape features. Based on morphology and rheological results, the interfacial tension between the PLA and EMA phases was calculated, and the calculated result is 3.3 mN/m.

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References


Key words: Biodegradable, Blends, Mechanical properties, Rheology; Morphology.
Figure 3. Impact strength for pure PLA and PLA/EMA blends.

Figure 4. SEM micrographs of PLA/EMA blends with various weight ratios (w/w): (a) 90/10, (b) 80/20, and (c) 70/30.

Figure 5. Complex viscosity versus angle frequency for PLA/EMA blends and pure PLA and EMA.

Figure 6. Storage modulus versus angle frequency for PLA/EMA blends and pure PLA and EMA.

Figure 7. Cole-Cole plots for PLA/EMA blends and pure PLA and EMA.

Figure 8. \( \eta''(\omega) \) plots for PLA/EMA blends and pure PLA and EMA.