Study on Preparation and Structural Properties of High Toughness Polylactic Acid

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Abstract. Different mass ratio of polylactic acid (PLA)/maleic anhydride grafted styrene-ethylene-butadiene-styrene (SEBS-g-MAH) were prepared by melt blending and characterized by means of ATR-FTIR, SEM and mechanical properties tests. The results of investigation demonstrate: when the thermoplastic elastomer SEBS-g-MAH was added into the PLA, the two phases have certain compatibility. When adding suitable amount of SEBS-g-MAH, the toughness of the blend was remarkably improved.

1. Introduction

Because of polylactic acid production process without pollution, and the product can be biodegradable. Therefore, it can achieve the cycle in nature, which the most mature industry, the largest output and the most widely used (medicine, food, packaging, automotive, agriculture and forestry, electronic appliances, roads Transportation, etc.) bio-based plastic [1]. However, PLA crystallization rate is slow, qualitatively hard and brittle, poor toughness, at room temperature is a brittle thermoplastic material [2], limiting its application in the production and life.

The high performance of PLA has been a hot issue in the research direction of modified polylactic acid by adjusting the copolymer structure which consists of soft body and hard segment structure [3]. The thermoplastic elastomer has both plastic workability and elasticity of rubber. Preparation of styrene-ethylene-butadiene-styrene copolymer (SEBS) has a mature technology and the products can be recycled [4]. It has a soft segment and hard segment structure, on the one hand the hard segment micro-distribution plays a role of physical cross-linking point in the polymer, which can improve the rigidity of the polymer. On the other hand, the soft segment structure has good compatibility with nonpolar polymer, which can effectively improve the toughness of the polymer. In addition, in order to improve the blend interface binding force, we choose the larger SEBS-g-MAH and PLA to blend, and the compatibility and mechanical properties of blend material were studied.
2. Experiment

2.1. Materials
PLA, 4032D, was purchased from Nature works LLC, UBA. It is a semi-crystalline material containing 2% D-lactide units. SEBS-g-MAH, FG1901, was purchased from Kraton, USA. Its graft ratio was 1.7%.

2.2. Preparation of PLA/SEBS-g-MAH blends
Before blending, both PLA and SEBS-g-MAH pellets were dried under vacuum at 80 °C for 12 hours to remove moisture. The dried PLA and SEBS-g-MAH pellets were mixed in a mass ratio of 100/0, 95/5, 90/10, 85/15, 80/20. Then these samples were blended by a twin-screw extruder (TSE-40A, Nanjing Ruiya Polymer Processing Equipment Co, China). The extrusion temperature was in the range from 170 to 190 °C, and the screw rotation speed was 170 r/min. The PLA/SEBS-g-MAH samples obtained from the extruder were cut into the pellets at room temperature and dried in a vacuum oven at 80 °C for 12h.

The PLA/SEBS-g-MAH samples intended for the mechanical properties tests were prepared using an injection molding machine (CJ80m3V, Zhengde, China) at a temperature between 170 and 190 °C.

2.3. Characterization

2.3.1. Fourier transformation infrared spectroscopy (FTIR). Infrared spectra of neat PLA and PLA/SEBS-g-MAH blend were obtained with an FTIR Nicolet 6700 in attenuated total reflectance (ATR) mode with a diamond crystal collecting 32 scans. Each spectrum was obtained within the range of 4000-650 cm\(^{-1}\) with a wavelength resolution of 4 cm\(^{-1}\).

2.3.2. Scanning electron microscopy (SEM). The samples were immersed in liquid nitrogen for 1 hour and cryogenically fractured. The cross section was sputter coated with 10–15 nm Au/Pd. For the imaging, an instrument ZEISS SUPRA 40VP Scanning Electron Microscope (SEM) was used. The actual imaging was done in high vacuum mode with a high-efficiency In-lens detector.

2.3.3. Mechanical properties. Tensile and bending properties were studied according to the GB/T1040.2-2006 standard using a material testing machine (WdW-10C, Shanghai Hualong Instrument Company, China). For the tensile tests, a crosshead rate of 50 mm /min was used. Bending properties were studied according to the GB/T1040.2-2006 standard using a material testing machine (WdW-10C, Shanghai Hualong Instrument Company, China), the bending rate was selected to 2 mm /min. Notch impact tests were performed according to the GB/T1043.1-2008 standard using an impact tester (XJUD-5.5, Xiamen Chongda Instrument Company, China). The notch depth was 2 mm and the angular radius of the notch was 0.25 mm. All mechanical tests were performed at room temperature, and the presented values represent the average values from at least five different samples.

3. Results and discussion

3.1. ATR-FTIR spectrum analyses
It can be seen from figure 1 (a), that the strong absorption peaks appearing at 1747 cm\(^{-1}\) and 1080 cm\(^{-1}\) are the stretching vibration peaks of C=O and secondary-OH of the ester groups of PLA, and the absorption peak at 1183 cm\(^{-1}\) is the C-O stretching vibration peak of PLA. In Fig.1 (b), an absorption peak stronger than the appears show in Fig.1 (a) at 1747 cm\(^{-1}\). It’s probably due to the fact that in the high-temperature melt blending process, the carboxyl groups of five-membered cyclic structure in maleic anhydride grafts are reacted with the terminal hydroxyl groups of PLA, which increase the stretching vibration of C=O in blends.
3.2. SEM analyses

It showed that the brittle cross section of PLA/SEBS-g-MAH blends shows "sea-island" structure, and the continuous phase is PLA-based, and the dispersed phase is granular SEBS-g-MAH (Figure 2.). Figure 2 (a). Showed that the two-phase interface between the dispersion phase and the matrix is blurred and less holes, indicating that the two phases have some compatibility. With the increase of SEBS-g-MAH content, the pore size between the two phases becomes larger and larger, the particle size of the dispersed phase becomes larger and the interface between the two phases becomes more and more obvious, indicating that the bonding strength of the two phases is weak and the compatibility is deteriorated. According to SEM analysis, it probably because the two-phase reaction increases the force between the two phases. On the other hand, this may be that the soft segment structure of SEBS-g-MAH molecular chain can form continuous structure with PLA molecular chain, but with the increase of SEBS-g-MAH content, the increase of hard segment content hinders the activity of SEBS-g-MAH molecular chain, which inhibits the interaction between the soft segment of SEBS-g-MAH molecular chain and PLA. Resulting in weakening the binding force between the two phases, and the hole becomes larger and more, thus forming an interspersed structure.
3.3. Mechanical properties analysis
In the blending system, with the increasing of SEBS-g-MAH content, the notched impact strength and elongation at break of the blend showed a tendency to rise first and then decrease, and the tensile strength decreased gradually (Figure 3.). When the content of SEBS-g-MAH was 15%, the notched impact strength and elongation at break of blending materials are maximum, which was 78% and 137% higher than that of pure PLA. By FTIR and SEM analysis, it can be seen that the reaction between the two phases to enhance the interfacial interaction, so the toughness of blend is improved.

![Graphs showing mechanical properties](image)

**Figure 3.** Notch impact strength (a), tensile strength and elongation at break (b) of PLA and PLA/SEBS-g-MAH resin as a function of SEBS-g-MAH content

4. Conclusion
The PLA/SEBS-g-MAH blends were prepared by melt blending. ATR-FTIR spectra showed that the reaction between the polar groups of SEBS-g-MAH and the matrix materials. SEM analysis showed that there is a certain compatibility between the dispersion phase and the matrix. Mechanical properties analysis showed that when adding suitable amount of SEBS-g-MAH, blending material notched impact strength and elongation at break are maximum, strength degradation is lesser, comprehensive performance to achieve the best. Because of the addition of SEBS-g-MAH provides a soft segment and hard segment structure for PLA. Among them the soft segment structure has good compatibility with nonpolar polymer, which can effectively improve the toughness of the polymer.

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