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Highly toughened polylactide/epoxidized poly(styrene-*b*-butadiene-*b*-styrene) blends with excellent tensile performance

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ABSTRACT

Polylactide (PLA) has inherent shortcomings which limit its widespread application: brittleness, low elongation and low melt strength. In this paper, these problems were addressed through melt blending of PLA with an epoxidized thermoplastic elastomer, epoxidized poly(styrene-*b*-butadiene-*b*-styrene) (ESBS). ESBS with different epoxidation degree were prepared by an in-situ peroxy-formic acid method. The T_g of ESBS increased while the flexibility decreased with increasing epoxidation degree. The impact strength improved from 29.9 J/m for pure PLA to 891.0 J/m for the blend with 30 wt% ESBS35.8%, meanwhile, the elongation at break increased from 3.5% to 253.8%. In-situ compatibilization of these immiscible blends was achieved via melt blending of PLA with ESBS that led to the formation of graft copolymer architecture at the interface. The compatibility between PLA matrix and ESBS phase increased gradually while the notched impact strength increased firstly and then decreased with increasing epoxidation degree of ESBS. The morphology of PLA/ESBS blends played an important role in notched impact strength and could be controlled by adjusting the epoxidation degree of ESBS. Rheological tests showed a drastic enhancement of melt viscosities for PLA/ESBS blends in oscillatory experiments. Therefore, the mechanical properties could be easily tailored by the epoxidation degree of ESBS.

1. Introduction

Polylactide (PLA) has been attracting the most attention among the commercially available bio-based and biodegradable thermoplastic polymers [1–4]. Advances in polymerization technology have reduced the production cost significantly and PLA has been considered to be economically competitive with petroleum-based plastics. PLA has high modulus and tensile strength but also exhibits very inherent brittleness, low elongation and low melt strength, which have restricted its wide applications [5,6]. In recent years, PLA toughening has become the focus of numerous investigations. Many strategies have been reported in literatures to improve the toughness of PLA, including copolymerization, plasticization, addition of rigid fillers, and blending with a variety of flexible polymers [7–11]. Among those strategies, melt blending with flexible polymers as modifiers is a much more convenient and economical method. Until now, numerous types of modifiers, especially, a variety of biodegradable and bio-based flexible polymers have been used for toughening PLA [12–16]. However, the impact properties have been improved slightly, still much lower than the engineering plastics. It is necessary for researchers to continue pursuing environment-friendly materials to solve the brittleness problem of PLA. However, blending PLA with

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nonbio-based or nonbiodegradable but readily available petroleum-based polymers to modify the properties of PLA has gained more and more consideration in recent years. Various commercial available nonbio-based or nonbiodegradable polymers, such as natural rubber (NR) [17], polybutadiene (PB) [18], acrylonitrile–butadiene–styrene copolymer (ABS) [19], acrylic impact modifiers, thermoplastic polyester elastomers, and polycarbonate (PC) have been reported to be used in toughening PLA [4]. Although it is not an ideal solution, it provides a viable and economic method to meet the requirement of consumers.

As we known, the mechanical properties of polymer blends, especially for impact toughness, are greatly governed by the morphological parameters [20]. Generally, optimum particle size range and narrow particle size distribution are essential to achieve an effective toughening for rubber-toughened polymers [18]. Usually, most of modifiers tend to be immiscible with PLA due to the difference of polarity. Therefore, to improve the compatibility between the modifier and the matrix, a third component is usually added as a compatibilizer. The compatibilizer can be premade or in-situ generated during blending. For example, Ho et al. [21] prepared a series of POE-*g*-PLA (Poly(ethylene-co-octene), POE) copolymers as premade compatibilizers and applied in PLA/POE toughening system. Anderson et al. [22,23] melt-blended PLA with linear low density PE (LLDPE) at a fixed PLA/LLDPE ratio (80/20, w/w) with PLA-*b*-PE diblock copolymers as a compatibilizer. Wannapa and coauthors [24,25] development of a synthetic method to produce novel bio-based diblock copolymer (PLA-NR) and triblock copolymer (PLA-NR-PLA) that consisted of poly(lactic acid) and natural rubber, which acted as toughening agents for PLA and also acted as compatibilizers for the PLA/NR blend. The compatibilization effect was observed in the morphology of the blend as a reduction in the rubber particle diameter. Addition of premade block copolymers into the binary blends resulted in improved interfacial adhesion and finer dispersion of modifier in PLA matrix. With the addition of a small amount of premade block copolymer, the impact strength has increased drastically. However, compared to in-situ reactive compatibilization, the addition of a specially tailored copolymer is usually expensive and less technological [26]. In-situ compatibilization has been used to control and stabilize polymer blend phase morphology more recently [1,10,18,27–29]. Usually, the reactive compatibilization is principally based on the reactions between end functional groups (such as: —OH or —COOH) of PLA and other active functional groups (such as: epoxide groups) [30,31]. As a result, improved interfacial adhesion and hence fine dispersion are achieved. For instance, to enhance the compatibility between PLA and ABS, Li and Shimizu [19] introduced styrene/acrylonitrile/GMA copolymer (SAN-GMA) as a reactive compatibilizer during melt blending. Fourier transform infrared (FTIR) analysis revealed that the epoxy group of SAN-GMA reacted with PLA end groups under the mixing conditions. It was also found that reactive compatibilization led to a remarkable decrease in the size of dispersed ABS domains. The compatibilized PLA/ABS blends exhibited improved impact strength and elongation at break with reductions in tensile modulus and tensile strength.

Most of the above modifiers in toughening PLA, when being used in combination with a compatibilizer or alone, proved to be fairly effective in enhancing impact toughness and ductility of PLA. However, the preparation process of the compatibility agent and the modification of the toughening agent are still relatively complicated, and there is little study for the influence of the compatibility agent on other properties of the blends. Moreover, relatively high component of flexible polymers was added, resulting in a sharp drop in tensile properties. Therefore, it is necessary to find a simple and efficient reactive toughening system.

In our recently published paper, we reported a facile method to prepare an epoxidized rubber of epoxidized polybutadiene (EPB), which was used as a modifier in toughening PLA [18]. It was found that epoxy groups showed a significant effect in enhancing compatibility between rubber phase and PLA matrix, giving rise to a remarkable decrease in the particle diameter of rubber phase. But, the tensile strength had an obvious drop after the addition of EPB, and the improvement of elongation was limited. Moreover, the high complex viscosities (η^*) of PLA/EPB blends would make the following processing more difficult. As we known, thermoplastic elastomer like poly(styrene-*b*-butadiene-*b*-styrene) (SBS) has better processing performance and more excellent tensile properties than the classical butadiene-based rubbers. It has been used as an important toughening agent for many engineering plastics. The use of SBS for impact modification of polypropylene (PP) [32–34], polypropylene-ethylene copolymer [35] and poly(butylene terephthalate) (PBT) [36,37] has been reported by a number of researchers with varied success. We considered that SBS was also a good candidate for toughening PLA with excellent tensile properties. Although it was mentioned that SBS and hydrogenated poly(styrene-*b*-butadiene-*b*-styrene) (SEBS) could improve the toughness of PLA in recent researches [38,39], in the case of SBS block copolymer both blocks tended to be immiscible with PLA matrix, leading to microphase separated blends. Therefore, in order to promote the compatibility between SBS and PLA, it is necessary to chemically modify SBS. In this research, epoxidized poly(styrene-*b*-butadiene-*b*-styrene) (ESBS) was prepared and used as toughener to improve the impact toughness and ductility of PLA.

ESBS with different epoxidation degree were firstly prepared and then melted blending with PLA. We studied the effects of epoxidation degree and the content of ESBS on the toughness of PLA/ESBS blends. The in-situ reactive compatibilization, the morphology and the rheological properties were also studied in detail.

2. Experimental section

2.1. Materials

All polymers used in this study were commercial grade. Polylactide (PLA) resin of 4032D was purchased from Natureworks (USA). SBS of LG501 was purchased from Jinling Corporation (China), and the M_w and M_w/M_n were 12.0×10^4 g/mol