POLYMER TESTING

Material Properties

Tailoring toughness of fully biobased poly(lactic acid)/natural rubber blends through dynamic vulcanization

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A B S T R A C T

Direct blending of poly(lactic acid) (PLA) with elastic natural rubber (NR) could not generate highly toughened blend, due to immiscibility between PLA and NR. In this study, we improved the compatibility of PLA/NR blend by dicumyl peroxide (DCP) initiated dynamic vulcanization and systemically investigated the effect DCP content on the morphology and mechanical properties of the resulting fully biobased PLA/NR blends. Both the pristine PLA/NR and dynamically vulcanized PLA/NR blends showed phase-separated morphology with dispersive NR particles dispersed in the PLA matrix. The particle size of NR decreased, the interfacial adhesion between the components increased, and the toughness of the sample first increased and then decreased with increase in the DCP content. When the DCP content was 3 wt%, the blend showed the highest toughening efficiency with impact strength and elongation at break of 220.2 J/m and 42.1%, respectively, which were 305% and 859% higher than those of pristine PLA/NR blend with the values of 72.1 J/m and 4.9%, respectively. The tensile strength and Young's modulus of the dynamically vulcanized samples were comparable to those of the pristine PLA/NR blend.

1. Introduction

The demand for biodegradable polymers, especially those derived from biobased feedstocks, has been increasing rapidly in recent years, due to the increased environmental concerns and resources over consumption with respect to the fossil-based polymers [1,2]. Poly(lactic acid) (PLA), as a promising alternative to fossil-based polymers, has attracted ever-increasing attentions because of its inherent advantages such as biodegradability, renewability, biocompatibility, high mechanical strength, high melting temperature and easy processibility [3–6]. However, PLA was generally marked on "brittle material", as evidenced by the short break elongation and low impact strength, which limits its large-scale commercial applications [7–10]. Therefore, many attentions have been paid to improve the toughness of PLA for application expanding [11–16].

Physical blending with a flexible polymer represents an economic and practical way to toughen PLA [17–19]. Nevertheless, direct blending PLA with most of the flexible polymers usually leads to phase-separated blends with insufficient mechanical properties, due to the immiscibility between PLA and most of the flexible polymers [20–23]. Dynamic vulcanization, involving selective crosslinking of rubbery

phase during melt blending with a thermoplastic, represents an efficient way to toughen PLA [24–26]. The interfacial adhesion and phase morphology of the blends are easily tailored during dynamic vulcanization, which usually leads to highly toughened PLA blends, due to the increased interfacial compatibility and the formed fine morphology of the resulting blends. Super-tough PLA blends with impact strength of higher than 530 J/m are also available through dynamic vulcanization with some specific elastomers [26–28]. For examples, Liu et al. prepared a super-toughened PLA ternary blend with by dynamically vulcanized PLA with elastomeric ethylene-n-butyl acrylate-glycidyl methacrylate (EBA-GMA) and a zinc ionomer of ethylene-methacrylic acid (EMAA-Zn) copolymer [26]; Liu et al. reported a super-tough PLA blends by dynamic vulcanization with an unsaturated aliphatic polyester elastomer (UPE) [28]. Although super-tough PLA blends were fabricated in those references, the blending components are usually fossil-based elastomers or non-commercial synthetic aliphatic polyesters with high cost [26–28], which are not favorable from the viewpoint of practical application.

Natural rubber (NR), a biobased elastic polymer from rubber tree, can be used as a toughening component for PLA [29,30]. However, PLA and NR are immiscible, due to the large difference in molecular polarity

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[31]. Therefore, highly toughened PLA/NR blend is not obtainable by simple blending. Many attentions have been payed to improve the compatibility between PLA and NR. Huang et al. [32] compatibilized PLA/NR (95/5) blend with a free radical initiator, which induces interfacial compatibilization of the blend. Incorporation of some polar structures such as epoxy, carbonyl and poly(butyl acrylate) could also be used to compatibilize PLA/NR blend [33–35]. Although the compatibility was somewhat improved, the enhancement in toughness seemed still unsatisfied. Recently, Chen's group has reported a super-toughened PLA/NR blend prepared by free radical induced dynamic vulcanization [29,36]. When the content of NR was 35 wt%, the blend showed a super toughness with an impact strength of 58.3 kJ/m^{-2}. It is noted that when the content of NR was less than 35 wt%, the improvement in impact strength is very much less prominent. For the highly toughened PLA/NR blend, the tensile strength and Young's modulus would reduce considerably, due to the rather high content of NR [29]. The low mechanical strength and modulus could also impart negative effects to the application of the material. In fact, balanced toughness and strength are more important from the viewpoint of practical application.

In the previous study, we found that the content of free radical initiator played an important role in tailoring the morphology and toughness of PLA/UBE blend [28]. However, the effect of free radical initiator content on the morphology and mechanical properties of PLA/NR was hardly investigated. To fabricate fully biobased PLA/NR blends with balanced toughness and strength, we studied the effect of initiator content on the morphology and mechanical properties of dynamically vulcanized PLA/NR (80/20) blend in detail in this study.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA, 4032D) with molecular weight (M_w) of 1.76×10^5 g/mol was procured from NatureWorks and used without purification. Natural rubber (SMR CV60) was provided by Guangzhou rubber industry research institute (China). Dicumyl peroxide (DCP) and Irganox 1010 were purchased from Micxy Chemical Co., Ltd. (Chengdu, China). PLA was vacuum dried at 80°C over 12 h prior to melt processing. All other chemicals were used without further purification.

2.2. Sample preparation

Dynamic vulcanization of PLA and NR was performed in a Hapro torque rheometer (Harbin China) with two rollers at 180°C and 80 rpm for about 7 min. A series of PLA/NR blends with feed weight ratio of 80/20 and DCP content relative to the weight of NR varying from 0 to 1, 2, 3, 4 and 5 wt% were prepared through dynamic vulcanization. The specific procedures were as follows: PLA, NR and Irganox 1010 (0.2 wt %) were first melt mixed in the chamber for ~5 min, then DCP with predetermined amount was added into the mixing chamber to initiate the dynamic vulcanization for ~3 min until the melt torque levelled off. For convenience, the obtained PLA/NR blends were abbreviated as VPLR-x, x represent the contents of DCP. The sample without DCP was designated as PLA/NR. The specimens for mechanical property measurements were prepared by injection molding with a WZS10D MiniJet (Shanghai, China). The barrel and mould temperatures were 180 and 50 °C, respectively.

2.3. Characterization

DSC measurement was performed on a NETZSH instrument DSC-214. The samples with ~7 mg were first melted at 200 °C for 5 min to remove thermal history, and then quenched to −60 °C at a rate of 100 °C/min, and finally reheated to 200 °C at a rate of 10 °C/min after maintaining at −60 °C for 5 min. All the operations were carried out

under N$_2$ atmosphere. The last heating curve was recorded for analysis.

Rheological behavior was studied by a DHR-1 (TA Instruments) rotational rheometer with a parallel plate geometry (diameter: 25 mm) and a gap of 1 mm. Oscillatory frequency sweeps were performed from 0.01 to 100 Hz at 180°C with a strain of 1%.

The cryo-fractured and impact-fractured surfaces were observed by a JSM-6510LV (JEOL, Japan) scanning electron microscopy at an accelerating voltage of 20 kV. The surfaces were sputtered with a layer of gold before testing.

Dynamic mechanical properties were studied by a Q800 (TA Instruments) dynamic mechanical analyzer under a tensile mode. Experiment was carried out from −100 to 120 °C at a heating rate of 3 °C/min and an oscillation frequency of 1 Hz. Tensile properties were measured on a MTS E44 Universal Testing Machine at room temperature with a crosshead speed of 10 mm/min in general accordance with ISO 527. The gauge length between the two grips were 25 mm. The notched Izod impact strength was measured on a Sansi ZBC7000 (Shenzhen, China) impact tester at room temperature in general accordance with ISO 180. At least five measurements were performed for each sample and the averaged result was reported.

3. Results and discussion

3.1. Fabrication and characterizations of PLA/NR blends

To describe the dynamic vulcanization process, we recorded the curve of melt torque versus time for preparation of the samples. Fig. 1 shows the evolution of melt torque over time for PLA/NR and VPLRs with different contents of DCP. At the beginning, the melt torque for all the samples underwent a rapid growth, attributing to the melting of PLA pellets. When the sample melted completely, the melt torque decreased gradually with time due to the shear shining effect of polymer melt. When the DCP was added at ~5 min, the melt torque underwent a drastic growth, corresponding to the crosslinking of NR initiated by free radicals formed by thermal decomposition of DCP. After ~3 min, the increase of melt torque ceased, indicating the end of dynamic vulcanization. The final melt torque of PLA/NR did not undergo a growth step, since no crosslink occurred in the absence of DCP. Interestingly, the melt torque increased with the DCP content, which should be attributed to the enhanced crosslink of the sample with increasing free radicals.

3.2. Rheological behavior

Rheology is a powerful way to study the microstructure of polymer blends from the viscoelastic response of the materials [24]. Fig. 2 shows the storage modulus (G′) and complex viscosity (|η*|) as a function of frequency for PLA/NR and VPLRs. The G′ of PLA/NR exhibited a
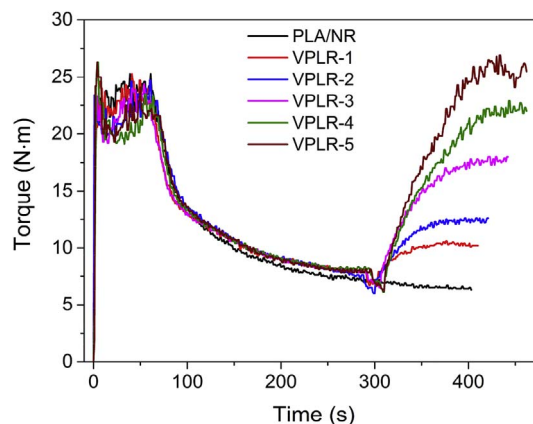

Fig. 1. Torque *versus* time for dynamic vulcanization of PLA/NR and VPLRs.