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## Material Properties

## Poly(lactic acid)/biobased polyurethane blends with balanced mechanical strength and toughness

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## ABSTRACT

The mechanical strength and modulus of poly(lactic acid) (PLA) are usually reduced significantly during toughening modification. Herein, we report a PLA blend with balanced strength and toughness via incorporation of a biobased polyurethane (COIPU) consisting of castor oil (CO) and isosorbide (IS) through dynamic vulcanization. The composition of COIPU played an important role in the morphology and the final mechanical properties of the PLA/COIPU blends. The compatibility between PLA and COIPU increased with increasing IS content, as shown by the gradually reduced particle size of the dispersed COIPU phase. The tensile strength and Young's modulus increased gradually while the elongation at break and notched Izod impact strength first increased and then decreased with increasing IS content. The blend with balanced mechanical strength and toughness may find extensive application where both toughness and high strength are required.

## 1. Introduction

Biodegradable polymers originating from renewable resources have attracted considerable attentions in recent years due to the resources crisis and environmental issues with respect to fossil-based polymers [1,2]. Among these emerging biodegradable polymers, poly(lactic acid) (PLA), has been considered as the most promising candidate to replace petroleum-based polymers because it combines several advantages such as excellently biodegradability, biocompatibility, fairly good mechanical strength and processibility [3–6]. Therefore, PLA has captured attention in various applications, including packaging [7], 3D printing [8] and biomedical application [9]. However, the further widespread application of PLA has been restricted by its inherent brittleness, as evidenced by the short elongation at break and low impact strength [10–12]. Therefore, toughening PLA has been extensively investigated [13–16].

Various approaches, such as plasticization [17], copolymerization [18] and melt blending [19], have been developed to toughen PLA, and melt blending was proved the most efficient and inexpensive method. However, directly blending PLA with most flexible polymers usually leads to poor performance due to the immiscibility between PLA and the blending partners [20–22]. It is well-known that the final properties of polymer blends depend essentially on the compatibility and

morphology of the blends. Dynamic vulcanization is reported as a powerful technique to regulate compatibility and phase morphology of phase-separated polymer blends, due to selective vulcanization of the rubber phase to fix the final morphology and properties of the desired blends [23–26]. Highly toughened or even super tough PLA blends have usually been prepared by dynamic vulcanization [27–30].

It is notable that the mechanical strength and modulus of PLA are usually sacrificed drastically after toughening, due to the high flexibility and low modulus of the rubbery polymer [31–33]. Previously, we reported toughened PLA blends with a castor oil based polyurethane (COP) prepared by dynamic vulcanization [16,24]. The elongation at break of the blends was increased to more than 300% by incorporation of 20 wt% COP, compared to 7.5% of neat PLA. However, the yield strength was drastically reduced to ~35 MPa from 65 MPa of neat PLA. In our recent study, we found the castor oil based polyurethane could be reinforced and toughened simultaneously by incorporation of isosorbide (IS) as a stiff chain extender, since the rigid isosorbide can increase the stiffness and decrease the crosslink density of the polyurethane simultaneously [34].

If such a biobased polyurethane was incorporated into PLA matrix, high performance PLA blend with balanced mechanical strength and toughness can be anticipated, due to the high strength and excellent toughness of the blending partner. Hence, in this work, we incorporate

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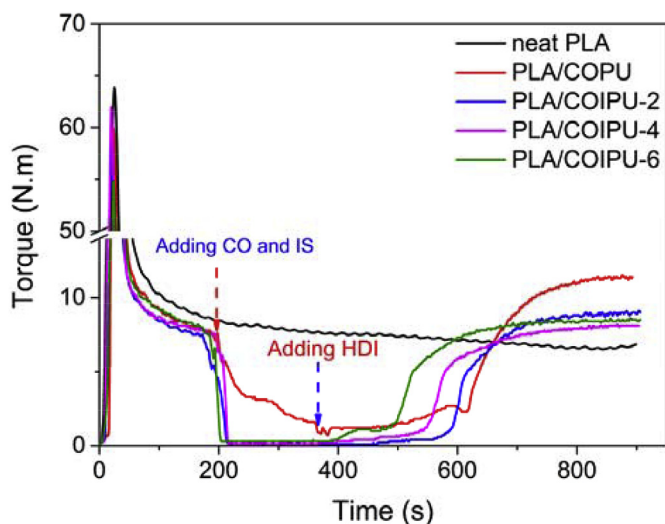


Fig. 1. Torque versus time of neat PLA and reactive blending of PLA and COIPU with various weight ratio of CO/IS.

a polyurethane consisting of castor oil and isosorbide into PLA matrix via dynamic vulcanization with the aim of achieving balanced mechanical strength and toughness, and investigate the effect of composition of the polyurethane on the morphology, compatibility, thermal behavior, mechanical properties and toughening mechanism of the blend in detail.

## 2. Experimental

### 2.1. Materials

Castor oil (CO, AR grade) was purchased from the Micxy Chemical Co., Ltd. (Chengdu, China). Isosorbide (IS, 98%) was procured from the Adamas Reagent Ltd. (Shanghai, China). Poly(lactic acid) (PLA 4032D) with average molar weight ( $M_w$ ) of  $1.76 \times 10^5$  g/mol was obtained from Natureworks and was dried at 80 °C for 8 h prior to use. Hexamethylene diisocyanate (HDI, 99%) was obtained from the Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). All chemicals were used without further purification.

### 2.2. Sample preparation

A series of blends consisting of 80 wt% PLA and 20 wt% COIPU with different compositions were prepared via dynamic vulcanization, which was performed in a XSS-300 torque rheometer (Shanghai Kechuang Co. Ltd) at 180 °C with a rotor speed of 80 rpm. The composition of COIPU was controlled by changing castor oil/isosorbide weight ratio from 10:0 to 8:2, 6:4 and 4:6. The molar ratio of -NCO from HDI to -OH of CO plus IS was fixed at 1:1 for all samples. The four samples were abbreviated to PLA/COPU, PLA/COIPU-2, PLA/COIPU-4 and PLA/COIPU-6, respectively. The detailed processing procedures were as follows: PLA was first melted in the rheometer for ~3 min, and then predetermined amounts of CO and IS were added chamber and mixed for another ~3 min to get uniform mixture. Finally, a certain amount of HDI was added into blends to perform dynamic vulcanization, which was terminated when the melt torque levelled off. For comparison, neat PLA was also processed by the same procedure. Standard tensile specimens (ISO 527) and Notched Izod impact (ISO 180) specimens were injection molded with a WZS10D MiniJet (Shanghai, China), with cylinder and mold temperatures of 180 and 50 °C, respectively.

### 2.3. Characterization

The morphology of the samples was observed by a JSM-6510LV (JEOL, Japan) scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. The surfaces were sputtered with a layer of platinum before testing.

Thermal transition and crystallization were studied by differential scanning calorimetry on a NETZSH instrument DSC-214. The samples (7 mg) were first melted at 200 °C for 5 min to remove thermal history. Then, they were cooled to -60 °C at a rate of 100 °C/min, and finally reheated to 200 °C at a rate of 10 °C/min after being held at -60 °C for 5 min. The final heating curves were recorded for analysis. All the operations were carried out under N<sub>2</sub> atmosphere with a flow rate of 50 mL/min.

Thermal stability was measured on a TGA Q600 (TA Instruments) from 25 to 600 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.

Dynamic mechanical properties were investigated by a DMA Q800 (TA Instruments) under tensile mode using a scan from -70 to 140 °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 notched Izod impact strength was measured on a Sansi ZBC7000 (Shenzhen, China) impact tester at room temperature in general accordance with ISO 180. Five measurements were performed for each sample and the average result was reported.

## 3. Results and discussion

### 3.1. Fabrication and characterizations of PLA/COIPU blends

The variation of melt torque with time was recorded during dynamic vulcanization, as shown in Fig. 1. At the beginning, the melt torque for all the samples first went up and then declined, corresponding to melting and shear thinning of PLA. When castor and isosorbide were added, the melt torque reduced dramatically, due to the low viscosity of the additives. The melt torque of PLA/COPU was relatively higher than those of PLA/COIPUs, possibly due to the plasticization effect of isosorbide. After adding HDI, the melt torque first increased and then levelled off, indicating the occurrence and termination of dynamic vulcanization, respectively. It was noted that the time required for the sample to reach maximum melt torque decreased with increasing isosorbide content, which may indicate that isosorbide is more reactive than castor oil during reaction with HDI. The final melt torque of PLA/COPU was higher than those of PLA/COIPUs, which can be attributed to the higher crosslink density of COPU due to the absence of bifunctional chain-extender.

Phase morphology plays an important role in the final physical properties of polymer blends. The cryo-fractured surfaces of PLA/COPU and PLA/COIPU were observed by SEM, as shown in Fig. 2. All the blends showed phase separated morphology with COPU or COIPU particles dispersed in PLA matrix. PLA/COPU exhibited poor morphology with large COPU particles distributed in PLA matrix non-uniformly (Fig. 2a). The size of some particles was as large as ~10 μm. The boundary between dispersed COPU and the surrounding PLA matrix can be distinguished. Those phenomena indicated the poor compatibility between PLA and COPU. In contrast to PLA/COPU, PLA/COIPU blends showed better phase morphology with COIPU particles of much smaller size distributed more uniformly in PLA matrix. It is interesting to find that the particle size of COIPU reduced gradually with increasing isosorbide content. Some COIPU particles with size around 2 μm could be found for PLA/COIPU-2 (Fig. 2b). The size of the COIPU particles in PLA/COIPU-4 and PLA/COIPU-6 were all around 1 μm, as shown in Fig. 2c and d. In addition, the phase boundaries between PLA and COIPU in PLA/COIPUs were much less clear than the boundaries between PLA and COPU in PLA/COPU. All the results indicated that

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