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Tannic acid-induced crosslinking of epoxidized soybean oil for toughening poly(lactic acid) via dynamic vulcanization

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A B S T R A C T

Epoxidized soybean oil (ESO) was incorporated into poly(lactic acid) (PLA) to formulate fully biobased and highly tough ESO/PLA blends by using tannic acid (TA) as a green vulcanizing agent. The crosslinking degree of ESO molecules and the interfacial compatibility between the ESO phase and PLA matrix were thus improved. The properties of the TA-ESO phase and its interfacial adhesion with PLA matrix were tailored by changing the molar ratio of TA to ESO, which significantly influenced the crystallization behavior, mechanical properties, thermal stabilities, and morphologies of the TA-ESO/PLA blends. After the incorporation of 10 wt% TA-ESO (based on the final blend) with a –OH groups to epoxy rings molar ratio of 0.8 into PLA system, the elongation at break (242%) and tensile toughness (57.4 MJ/m^3) of the resulting PLA blend were 7 and 4 times higher than those of the blend with 10 wt% ESO, respectively. Compared to the 10 wt% ESO/PLA blend, the glass transition temperatures and thermal stabilities of the TA-ESO/PLA blends were slightly enhanced due to the increased crosslinking density of the TA-ESO phase; however, a slightly decreased crystallinity was observed for PLA after the addition of TA into ESO phase.

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1. Introduction

Biodegradable polymers originated from renewable feedstocks have been utilized instead of their nondegradable and petroleum-based counterparts due to the growing environmental awareness and shortage of oil resources. Poly(lactic acid) (PLA) is one of the most promising biobased and biodegradable polymers. Because of its compelling advantages including high strength, easy processability, and non-toxicity to human beings and environmental friendliness, PLA has great potential for applications in many areas [1–5]. However, some significant shortcomings of PLA, including inherent brittleness, high prices, and low glass transition temperature, have greatly inhibited its wider application.

Many strategies, such as plasticization, copolymerization, and polymer blending, have been developed to toughen PLA [6]. Polymer blending is a convenient and efficient method via directly incorporating ductile polymers into PLA system. Vegetable oils, which consist of glycerol esters with three flexible long-chain fatty acids, are cost-effective products characterized by high availability and superb environmental credentials [7]. These characteristics make vegetable oil derivatives very attractive to be used as plasticizers for PLA. Extensive research has been addressed to improve the toughness of PLA by blending PLA with epoxidized soybean oil (ESO) [8–10], epoxidized palm oil [11], maleinized linseed oil [12], maleinized and epoxidized cottonseed oils [13,14], and modified fatty acids [15], etc. However, they are immiscible with PLA and might leach or migrate to the surface of PLA products when in use; hence, sufficient toughening efficiency is not accessible for the blends. In addition, the introduction of these flexible polymers into PLA is usually accompanied with a significant compromise in mechanical strength and thermal stability. Therefore, a PLA star polymer with acrylated epoxidized soybean oil (AESO) core was synthesized and introduced into ESO/PLA blends to increase the compatibility between ESO and PLA, which resulted in a great

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enhancement in the tensile properties of the blends [16]. The tensile toughness of the blends from polymerized soybean oil and poly(L-lactide) was greatly improved after the use of poly(isoprene-*b*-L-lactide) block copolymer as a compatibilizer [17].

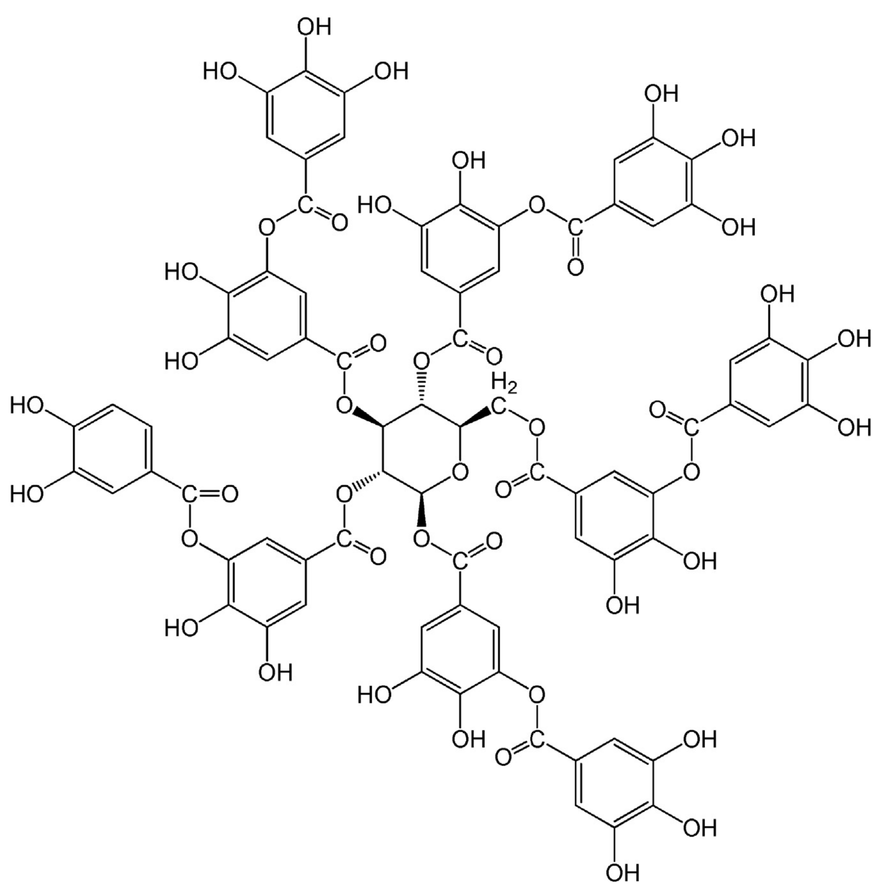
Dynamic vulcanization technique is effective in improving the interfacial compatibility of PLA-based blends and hence the toughening efficiency of the incorporated flexible components on the blends. Dynamic vulcanization for rubber phase and thermoplastic PLA is a melt-compounding process which results in a two-phase blend consisting of vulcanized rubber phase and thermoplastic PLA [18]. Much work has been done on toughening PLA blends by dynamic vulcanization with various elastomers such as thermoplastic polyurethane [19–21], biobased polyester [22,23], unsaturated low-molecular-weight poly(ethylene glycol)s [24], epoxy-containing elastomer [25], ethylene-*co*-vinyl acetate rubber [26,27], and natural rubber [18,28–30]. The most commonly used vulcanizing agents are free radical initiators such as Luperox 101 [19,23,24] and dicumyl peroxide [18,29–31]. As for using vegetable oils in toughening PLA, the dynamic vulcanization of PLA with castor oil by using diisocyanates as crosslinkers resulted in the formulation of a tough blend with superior toughness and mechanical strength [32,33]. However, the use of petroleum-based isocyanates as vulcanizing agents reduces the sustainability and biodegradability of the toughened PLA blends.

In order not to sacrifice the renewability of PLA products, fully biobased ESO/PLA blends with high toughness were fabricated via selecting a green monomer, i.e., tannic acid (TA), as a vulcanizing agent to crosslink ESO during dynamic vulcanization. TA is a specific form of tannin that is widely distributed in many species of plants. The chemical formula of commercial TA is often given as $C_{76}H_{52}O_{46}$, as shown in Scheme 1. The presence of abundant phenolic –OH groups makes it highly reactive towards some chemicals such as acids and epoxy. It is known that most traditional epoxy hardeners, such as amines, acids, and anhydrides, are petroleum-based and toxic. Therefore, TA was employed as a green curing agent in the absence of catalysts to cure epoxy resins including ESO [34,35]; however, the obtained TA-ESO thermoset showed inferior tensile strength, tensile modulus, and elongation at break. In this work, TA was selectively used to replace petroleum-based crosslinking agents to cure ESO during dynamic vulcanization with PLA, which would form a stable phase-separated structure while maintaining the mechanical strength, thermal resistance, and sustainability of the resulting PLA products. To the best of our knowledge, designing a completely biobased rubbery phase in the PLA system from rigid TA and flexible ESO via dynamic vulcanization technique has rarely been reported. The compositions and properties of the formed TA-ESO rubbery phase and its interfacial compatibility with PLA matrix were tailored via adjusting the stoichiometric ratio of TA to ESO. The toughening efficiency and mechanism of TA-ESO crosslinking on PLA were correlated with the tensile properties, dynamic mechanical properties, crystallization behavior, thermal stabilities and morphologies of the toughened PLA blends.

2. Experimental section

2.1. Materials

Poly(lactic acid) (PLA, Ingeo 3001D) was obtained from NatureWorks Japan (Tokyo, Japan). Epoxidized soybean oil (ESO)



Scheme 1. Chemical structure of tannic acid.

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