

Employing a novel bioelastomer to toughen polylactide

Hailan Kang^a, Bo Qiao^a, Runguo Wang^a, Zhao Wang^a, Liquan Zhang^{a,b,*}, Jun Ma^{c,**}, Phil Coates^d

^aState Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China

^bKey Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

^cSchool of Advanced Manufacturing and Mechanical Engineering, University of South Australia, SA5095, Australia

^dSchool of Engineering, Design & Technology, Bradford University, BD7 1DP, UK

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ABSTRACT

Biodegradable, biocompatible polylactide (PLA) synthesized from renewable resources has attracted extensive interests over the past decades and holds great potential to replace many petroleum-derived plastics. With no loss of biodegradability and biocompatibility, we highly toughened PLA using a novel bioelastomer (BE)—synthesized from biomass diols and diacids. Although PLA and BE are immiscible, BE particles of $\sim 1 \mu\text{m}$ in diameter are uniformly dispersed in the matrix, and this indicates some compatibility between PLA and BE. BE significantly increased the cold crystallization ability of PLA, which was valuable for practical processing and performance. SEM micrographs of fracture surface showed a brittle-to-ductile transition owing to addition of BE. At 11.5 vol%, notched Izod impact strength improved from 2.4 to 10.3 kJ/m², 330% increment; the increase is superior to previous toughening effect by using petroleum-based tougheners.

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1. Introduction

Biobased polymers from renewable resources have received considerable interests from academia and industry in recent years, due to environmental concerns for ever-declining petroleum resources [1–3]. The use of biobased polymers is currently a major alternative to conventional petroleum-based polymers, and will provide a solution to the environment problem of plastic wastes [4]. Polylactide (PLA) is a polymer produced from renewable resources such as corn on a commercial scale [5]; it is a thermoplastic aliphatic polyester and has been proven viable in replacing petroleum-based plastics in some applications [6]. However, PLA is inherently brittle, which severely limits its application in industries. Toughening PLA has thus attracted great interests.

Low-molecular weight plasticizers toughened PLA moderately but this was obtained at the cost of losing stiffness [7–11]. Inorganic fillers such as clay improved toughness little, although enhancing stiffness obviously [12–14]. The most practical and economic used methods for toughening PLA is to adopt flexible polymers or elastomers. Poly (ϵ -caprolactone) (PCL) was the

earliest polymer used for toughening PLA [15–21]. Since PCL and PLA are not compatible, compatibilizers such as PLLA-PCL-PLLA triblock copolymer have been developed [18]; it produced an improvement in notched Charpy impact strength from 1.1 to 3.7 kJ/m² at 30 wt% PCL. Compatible PLA/PCL blends were prepared through reactive processing induced by catalysts [19] or cross-linkers [20,21]. Jiang et al. [22] improved Izod impact strength by 170% via mixing PLA with 20 wt% poly (butylene adipate-co-terephthalate) (PBAT). Li et al. [23] prepared PLA/poly(ether) urethane (PU) blends with improved impact strength from 64 kJ/m² to 315 kJ/m². Zhang et al. [24] used polyamide elastomer (PAE) to toughen PLA, resulting in a increase in elongation at break from 5.1% to 194.6% at 10 wt% PAE. PLA was blended with four synthetic rubbers, including ethylene–propylene copolymer (EPM), ethylene–acrylic rubber (AEM), acrylonitrile–butadiene rubber (NBR), and isoprene rubber (IR), but toughening was only achieved by PLA/NBR blend with a 1.8 times higher value of Izod impact strength in comparison with PLA [25]. Even though these polymers toughened PLA effectively, unfortunately these polymers are either nonrenewable or nondegradable. A recent trend for toughening PLA is to adopt degradable, renewable polymers, including starch [26,27], poly (butylene succinate) (PBS) [28,29], poly (hydroxyalkanoates) [30,31], polymerized soybean oil [32] and polyamide11 (PA11) [33]; these are fabricated from renewable resources, and upon disposal are able to degrade completely in the environment within dozens of years. Shibata et al. [29] toughened

* Corresponding author. State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China.

** Corresponding author.

E-mail addresses: ZhangLQ@mail.buct.edu.cn (L. Zhang), Jun.Ma@unisa.edu.au (J. Ma).

PLLA by poly (butylene succinate-co-L-lactate) (PBSL) and poly (butylene succinate) (PBS); at 10 wt%, these two tougheners achieved 160% and 120% higher elongation at break, respectively. Robertson et al. [32] achieved 400% and 600% increase in elongation at break and tensile toughness by using polymerized soybean oil, respectively. However, most tougheners derived from renewable resources are less effective than those derived from petroleum resources in improving the PLA toughness. On the other hand, most studies used the improved elongation at break rather than the notched impact strength to gauge the toughening effects, while the impact testing is far more useful in practice. Therefore, the challenge is to develop biocompatible, highly toughened PLA blends which retain both completely renewable origins and ultimate degradability if necessary [34].

Considering the fact that elastomers have commonly been adopted as a second phase polymer for toughening many kinds of brittle polymer materials, such as epoxy [35,36], polypropylene [37], poly(methyl methacrylate) [38], and so on, it becomes very interesting and important to look for or design/synthesize the new bio-based and biocompatible elastomers to toughen PLA. Recently we have developed novel bioelastomers from polymerizing commercial bio-based monomers—sebacic acid, itaconic acid, succinic acid, propanediol and butanediol—all of which are derived from renewable resources [39]. While possessing complete biocompatibility, these elastomers exhibit satisfactory elasticity and good mechanical strength. It is noteworthy that the repeat units of these bioelastomers are based on ester groups, implying some compatibility with other ester bond-based polymers such as PLA [7,28]. Thus, a hypothesis made in this study is that our bioelastomers have great potential for toughening PLA.

In this work, we will significantly toughen PLA by compounding with our synthetic bioelastomer. The morphology, thermal behaviors, rheological properties and mechanical properties of the blends will be extensively investigated.

2. Experimental section

2.1. Raw materials

Itaconic acid (IA) (purity 99.0%), succinic acid (SA) (purity 99.0%), 1, 3-propanediol (PDO) (purity 99.0%) and 1, 4-butanediol (BDO) (purity 99.0%) were purchased from Alfa Aesar. Sebacic acid (SeA) (purity 99.0%) was obtained from Guangfu Fine Chemical Institute of Tianjin. Tetrabutyl orthotitanate (TBOT), hydroquinone and phosphorous acid were supplied by Fluka, Beijing Yili Fine Chemical Co. Ltd, and Sinopharm Chemical Reagent Co. Ltd, respectively. Polylactide (PLA, 5051x) was provided by Natureworks USA. It exhibits a weight-average molecular weight of $\sim 159,000$ g/mol, a polydispersity index of 1.67 (GPC analysis), and a glass transition temperature and melting point of 60 °C and 152 °C (DSC analysis), respectively. The liquid silicone rubber (SiR) was commercial products and the number-average molecular weight is 20,000 g/mol. The PLA and BE chemical structures are shown in Fig. 1.

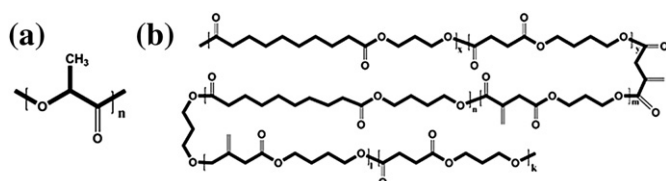


Fig. 1. Chemical structures of (a): Polylactide (PLA) and (b): Bioelastomer (BE).

2.2. Synthesis of BE

Our bioelastomer (BE) was synthesized according to our recent work [39]. In brief, we charged PDO (12.54 g, 0.165 mol), BDO (14.85 g, 0.165 mol), SA (15.04 g, 0.1275 mol), IA (5.85 g, 0.045 mol), SeA (25.76 g, 0.1275 mol), and inhibitors hydroquinone (0.0296 g) and phosphorous acid (0.0074 g) into a 100-ml three-neck flask. The mixture was purged with nitrogen and then heated at 180 °C for 2 h; the water formed during the reaction was distilled off. In the second phase, after adding TBOT (0.05 wt% relative to the quantity of all reactants) as the catalyst, the mixture was heated to 220 °C under reduced pressure (<300 Pa) for 3–4 h until the Weissenberg effect was found. The resulting product BE exhibits a weight-average molecular weight of $\sim 181,000$ g/mol, a polydispersity index of 3.7 (GPC analysis) and a glass transition temperature of -56 °C (DSC analysis).

2.3. Sample preparation

PLA and BE were dried in a vacuum oven at 60 °C for 24 h prior to use. Blends were prepared by melt-mixing BE at different weight ratios (0, 5, 10, 15, and 20 wt%) with PLA for 10 min using a Haake Remix (Remix 600p, Thermal Electron Co., USA) at 170 °C with a rotary speed of 80 rpm. All the samples were finally hot-pressed under 10 MPa at 190 °C for 5 min to produce 1-mm thick sheets. The density of PLA and BE were 1.24 g/cm³ and 1.06 g/cm³; thus, we were able to convert wt% to vol%.

2.4. Characterization

The average molecular weight and polydispersity index were determined by gel permeation chromatographic (GPC) measurements on a Waters Breeze instrument equipped with three water columns (Steorage HT3 HT5 HT6E) using tetrahydrofuran as the eluent (1 ml/min) and a Waters 2410 refractive index detector. Polystyrene standard was used for calibration.

Dynamic mechanical thermal analysis was carried out with a V Dynamic Mechanical Thermal Analyzer (Rheometric Scientific Co.) with a tension mode at 1 Hz and 3 °C/min from -100 to 150 °C. Differential scanning calorimetry measurements were performed with a Mettler-Toledo DSC instrument under nitrogen. All samples were heated to 200 °C at 50 °C/min and kept isothermal for 5 min to remove previous thermal history. Then they were cooled to -100 °C at 10 °C/min, and reheated up to 200 °C at 10 °C/min to determine glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and melting temperature (T_m). Isothermal crystallization behaviors of PLA/BE blends were also evaluated using DSC by premelting samples at 200 °C for 5 min, followed by rapid cooling to -100 °C and heating to 125 °C at 50 °C/min. Then the samples were kept at 125 °C for 30 min to allow cold crystallization from the quiescent melt. The exothermic curves of heat flow as a function of time were recorded. X-ray diffraction (XRD) measurements were carried out on a D/Max2500 VB2+/PC X-ray diffractometer (Rigaku, Japa) with a Cu target radiation for a 2θ range of $5-50^\circ$ at an angular resolution of 0.05° . The XRD samples were treated with the following procedures: (i) all samples were heated to 200 °C and kept for 5 min; (ii) then they were cooled to room temperature at 10 °C/min. The heating/cooling process was *in situ* conducted during the testing.

The morphology of the blends was determined by scanning electron microscopy (S4700, Hitachi Co., Japan) at 5 kV. After immersing in liquid nitrogen for 10 min, notched samples were fractured by a vice, and then surface-coated with a thin gold layer. The number-average particle diameter (D_n) was determined by Nano Measurer 1.2 and 100 particles were analyzed per sample. The

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