Combination of lignin and L-lactide towards grafted copolymers from lignocellulosic butanol residue

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ABSTRACT

A series of BBL-*graft*-poly(L-lactide) copolymers were synthesized via ring-opening polymerization (ROP) of L-lactide (L-LA) with a biobutanol lignin (BBL) initiator and a triazabicyclodecene (TBD) catalyst under free-solvent at 135 °C. By manipulating the mass ratio of BBL/LLA, BBL-g-PLLA copolymers with tunable number–average molecular weight (M_n) (2544–7033 g mol^{-1}) were obtained. The chemical structure of PLLA chains was identifiable by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopies, in combination with UV–vis spectra to provide support for the existence of the BBL in the copolymer. This provided solid evidence for the successful synthesis of BBL-*g*-PLLA copolymer. The thermal properties and surface characterization of BBL-*g*-PLLA copolymers were different from those of linear PLLA. Furthermore, the BBL-*g*-PLLA copolymer film showed good absorption capacity in the UV region and high transparency in the visible light region, which was expected to find significant applications in UV-protective coating film.

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1. Introduction

As the second most abundant organic compound in nature after cellulose, lignin has received an increasing attention over the last decade because of the rapid consumption of petroleum and petro-chemicals [1]. Lignin shows a highly branched and irregular macromolecular structure, depending on the biomass species, growing conditions and extraction procedures [2–4]. Lignin is made up of three different types of phenylpropanoid monomers such as p-coumaryl, coniferyl and sinapyl alcohols and linked by aryl-ether, alkyl-ether, and carbon–carbon covalent bonds into a highly branched polymer network [5]. Currently, lignin is being utilized as a low-grade boiler fuel to provide heat from the combustion, or be disposed as waste [6]. Furthermore, hydrogen bonding and van der waals interactions led to aggregation of lignin, resulting in poor compatibility with other materials [7]. Butanol, an important industrial chemical, is considered as a superior liquid fuel with a potential to substitute for fossil fuel [8]. It is noted that lignocellulosic biomass can be used to produce butanol from biorefinery processes based on corn and wheat straw [9], which brings a large amount of lignocellulosic butanol residue, called biobutanol lignin

(BBL). There is no doubt that the development of a way to convert BBL to the higher-valued products could help to boost the economic viability of the biobutanol industries. Consequently, the conversion of BBL to higher-valued materials is an active area of research [9–13].

Due to the hydroxyl groups, lignin is most often functionalized by esterification [14,15]. Although this method could improve the compatibility between lignin and blended polymeric materials, it has limited impact on changing lignin toward desirable properties [16]. Graft polymerization is an attractive approach to modify the lignin, resulting in lignin graft copolymers used for a much wider range of applications [17]. In order to obtain the lignin graft copolymers, there are two general strategies: the so-called "grafting from" approach, where polymer chains are built on the lignin cores, and the "grafting onto" approach, where polymer strands are synthesized firstly and subsequently grafted to the lignin cores [18]. Among the graft polymerization methods, the "grafting from" technology is the most usually used procedure which can produce high graft density of copolymer compared to the "grafting onto" route [19]. Currently, using the "grafting from" route to produce lignin graft copolymers mainly includes two types of polymerization reactions. The first one is the ring opening polymerization (ROP), which uses surface hydroxyl groups of lignin as the initiator, while the second one is that firstly requires the creation of lignin "macro"-radical, and then initiates the polymerization of other vinylic monomers [20].

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Presently, there is a great interest in biomaterials from renewable resources due to low-cost, biodegradability and biocompatibility [21]. Increasing attention has been paid to obtain biomaterials from lactones and lactides. Currently, PLA is the most commonly biodegradable polymers and produce from Lactic acid (LA). However, there are some undesirable attributes of PLA such as its high cost, brittleness, poor UV light barrier properties and poor thermal stability, which have limited replace for commercial polymeric materials [22]. Overcoming aforementioned disadvantages, the grafting copolymerization of BBL with L-lactide is a promising approach, which can decrease the cost and improve thermal resistance and UV absorption capacity of PLLA [12,22].

Ring-opening polymerization (ROP) is considered to be an effective "graft from" polymerization technique for the preparation of lignin graft PLLA copolymers. The multiple hydroxyl groups at the surface of lignin could be act as available reactive sites for ROP [23,24]. Preparation of polyesters from lactones via ROP is the most conventional synthesis route at present. It is carried out in melt or in solution by different polymerization mechanisms (e.g., anionic, cationic, coordination-insertion), which depend on the used catalyst. Little metal residues will be in the final products when using metal-based catalysts, resulting in restricting the application in packaging [25]. Herein, the syntheses of BBL-*g*-PLLA copolymers in this study were performed using triazabicyclodecene (TBD) as the organic catalyst. Furthermore, TBD has been proven to be an effective catalyst for ROP of LLA in some literatures [22,25,26].

Recently, we have successfully prepared some different lignin graft copolymers using BBL as raw materials [10–13]. It was worth noting that BBL possessed high chemical activity [9], in comparison with kraft lignin or lignosulfonate studied in the literatures. This was because the biochemical reaction process of biomass was performed under moderate reaction condition, and some chemical groups (e.g., phenolic hydroxyl and alcoholic hydroxyl) were well preserved [27], In this paper, as a novel type of lignin, BBL was modified by LLA through "grafting from" ROP to combine the properties of BBL and PLLA, which could be viewed as a continuation of the abovementioned work, and BBL-*graft*-PLLA copolymer was synthesized via a practical route (Scheme 1), that is, "Grafting from" ROP was carried out to prepare a series of BBL-*graft*-PLLA copolymers using TBD as catalyst under solvent-free conditions. The graft copolymer was fully characterized by FT-IR, NMR, UV–vis, GPC, TGA, DSC, XPS, and FE-SEM. Furthermore, the UV absorption capability of the BBL-*g*-PLLA coating film was also explored in this study. The long term of this work is to fully utilize lignocellulosic butanol residue as the raw material to produce the biopolymer which can be used as UV-absorbent film.

2. Experimental section

2.1. Materials

Lignocellulosic butanol residue used in this work was supplied by songyuan bairui bio-polyos Co., Ltd., from Jilin province (China) and used before purified as described in previous report [11]. The physical and chemical characteristics of this biobutanol lignin (BBL) had been reported in our earlier work (details for Table 1) [10]. The L-lactide (L-LA) (optical purities, 99.5%) was purchased from Changchun SinoBiomaterials Co., Ltd., and used as received. 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene (TBD, 98%) was obtained from Sigma–Aldrich and used as received. Acetic acid, dichloromethane and anhydrous methanol were of analytical reagent grade and used without further purification.

2.2. Typical polymerization procedure (Table 2, BBL-PLLA-5%)

As shown in Scheme 1, the synthesis procedure of BBL-*g*-PLLA copolymer was described as follows [22]. The suitable amount of

Table 1
Chemical composition and structural properties of biobutanol lignin (BBL).

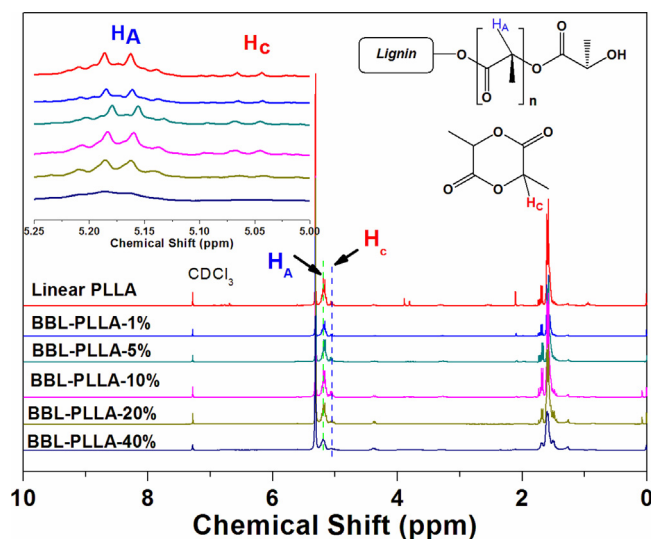| BBL			
	C [wt.%]		62.7
	H [wt.%]		5.47
	O [wt.%]		31.96
	N [wt.%]		0.75
	S [wt.%]		0.12
	C_9 formula		$C_9H_{8.160}O_{2.996}N_{0.094}$
			$S_{0.006}(OCH_3)_{0.594}$
^{1}H NMR analysis	Phenolic-OH [moL g^{-1}]		2.95
	Aliphatic-OH [moL g^{-1}]		2.67
	Methoxyl [moL g^{-1}]		3.24
GPC analysis	M_w [g moL^{-1}]		876
	M_n [g moL^{-1}]		543
	PDI		1.61

Fig. 1. ^{1}H NMR spectra for calculation of the conversion of LLA.

BBL (0.5 g, 5 wt.%), LLA (9.5 g, 95 wt.%) and TBD (1.5 g, 1.5 wt.%) were mixed in a polymerization reactor under magnetic stirring and heated in an oil bath to 135 °C for 4 h in a nitrogen atmosphere. After the polymerization reaction finished, the reactor medium was finally cooled to room temperature. The resulting black product was dissolved in a mixture solution of dichloromethane and acetic acid. When the residue dissolved, the sample was withdrawn from the flash with degassed syringes to determine the LLA conversion by ^{1}H NMR analysis in CDCl$_3$. The conversion of LLA was calculated using the following Formula (1), according to the integration of the L-lactide methide signal (H_c, 5.03 ppm) against the integration of PLA methide signal (H_a, 5.16 ppm) in ^{1}H NMR spectra of samples (Fig. 1).

$$C(\%) = \frac{H_a}{H_a + H_c} \times 100\% \qquad (1)$$

Finally, the remainder of the crude reaction mixture was precipitated with methanol to obtain a solid precipitate, and collected by centrifugation. The produced BBL-PLLA-5% copolymer was isolated and dried in vacuum at 50 °C for 12 h. The syntheses of the rest of BBL-*g*-PLLA copolymers were similar to the procedure described above. To better understand the changes suffered by BBL as a result of the chemical reaction, a blank sample was prepared (linear PLLA). The linear PLLA polymer was obtained under the same reaction conditions, but instead using TBD (75 mg, 0.539 mmol) together with 2-methoxy-4-propylphenol (232 mg, 1.396 mmol) as initiator for the polymerization of LLA (5 g, 34.7 mmol). The linear PLLA sample