



Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: <http://www.elsevier.com/locate/compscitech>

Strong and biocompatible lignin /poly (3-hydroxybutyrate) composite nanofibers

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ARTICLE INFO

Article history:

Received 14 November 2017

Received in revised form

24 January 2018

Accepted 29 January 2018

Available online 5 February 2018

Keywords:

Sustainability

Ring-opening polymerization

PHB

Electrospinning

Mechanical reinforcement

ABSTRACT

Poly(3-hydroxybutyrate) (PHB) is an attractive biopolymer potential for various applications, but its brittle nature is a big handicap. In this study, we proposed lignin copolymers as mechanical reinforcement agents for PHB. A series of lignin copolymers (random and block) were synthesized via the solvent free ring-opening polymerization (ROP) of β -butyrolactone and/or ϵ -caprolactone onto lignin core. The lignin copolymers were characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). Next, these lignin copolymers were incorporated into PHB nanofibers as reinforcement fillers, in order to improve their mechanical properties. It is found that the lignin block copolymer with poly(ϵ -caprolactone) (PCL) segment followed by PHB segment (LPC + H) displayed the best mechanical improvement. Tensile strength of PHB nanofibers enhanced from 1.81 MPa to 3.13 MPa, and elongation at break increased from 15% to 55%. In the reinforced system, lignin plays as a rigid core, PCL acts a rubbery layer and PHB segment forms strong bonding with fiber matrix. Moreover, PHB/lignin nanofibers were demonstrated with superior biodegradability and biocompatibility, indicating that the new nanofibrous system holds great potential for biomedical applications.

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1. Introduction

There has been an increasing reliance on fossil fuels for energy generation to produce huge amount of consumers' products and to sustain our daily activities [1]. However, petrochemical-based polymer products are non-biodegradable and they causes waste management issues. An alternative to fossil fuel would be lignin, which is a biodegradable polymer and the second most abundant material on earth [2,3]. Although it is considered a byproduct in the paper or pulp industry, it exhibits advanced properties, such as good stiffness, anti-microbial activity, anti-oxidant properties and ultra-violet (UV) radiation protection [4]. Therefore, extensive

studies have been done to explore the possibilities of lignin-based functional materials for different applications.

Lignin constitutes a large portion of the cell walls of vascular plants, providing rigidity and strength for growth. Based on this function, lignin is believed to be able to reinforce the mechanical properties of polymeric composites as structural fillers [5]. Several studies has been conducted on lignin-based composites which involves the blending of lignin with thermoplastics, such as polypropylene, polyethylene, and polystyrene [6–10]. Despite these attractive properties of lignin, it can only be blended in small amounts due to its immiscibility in most thermoplastics. Synthesis of lignin copolymers is considered as an effective approach to improve the compatibility of lignin and polymer matrix.

Poly(3-hydroxybutyrate) (PHB) is a stereo-regular, biodegradable and biocompatible natural polymer, synthesized by various kinds of bacteria [11,12]. Being an isotactic polymer, PHB has high crystallinity, relatively high melting point and good hydrolytic stability. These properties make PHB attractive to be used for

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biomedical applications, such as drug carrier or tissue-engineering scaffolds [13–20]. However, its main drawback is the brittle nature. So far, several methods have been done to improve the ductility of PHB, such as blending with plasticizers, modification and copolymerization. Doherty's group prepared the lignin/PHB composites via extrusion and they found that the addition of lignin improved the viscosity and storage modulus of PHB [21,22].

In this study, we synthesized a series of lignin copolymers (random and block) via the solvent free ring-opening polymerization (ROP) of β -butyrolactone and/or ϵ -caprolactone onto alkali lignin. Such lignin copolymers were blending with PHB. Different from other studies of using solid and bulk composites, lignin/PHB porous nanofibrous materials were engineered via electrospinning. Electrospun nanofibers present many advantages, such as low density, high surface area and high permeability, and potentially can be used in various high-valued applications, including biomedical materials [23–25]. Our aim is to investigate the influence of lignin copolymers (and their structures) on the material properties (mainly mechanical and viscoelastic properties) of the composite nanofibers. Moreover, the potential of lignin/PHB nanofibers for biomedical applications was evaluated by *in vitro* biocompatibility tests.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich Chemicals and used as received except where noted. Alkali lignin (average molecular weight = 5 kDa) was dried at 105 °C overnight before use. β -butyrolactone and ϵ -caprolactone was purified by distillation under reduced pressure before use. Natural PHB was purified by dissolving in chloroform followed by filtration and subsequent precipitation in hexane before use. The absolute M_n and M_w of the purified PHB, characterized by multi-angle laser light scattering (MALLS) (Wyatt miniDAWN[®], using $dn/dc = 0.144$) [26], were 6.0×10^4 and $7.1 \times 10^4 \text{ g mol}^{-1}$ respectively. The apparent M_n and M_w of the purified PHB, characterized by GPC (Tosoh SEC RI detector) with PMMA calibration standards, were 2.5×10^5 and

$7.6 \times 10^5 \text{ g mol}^{-1}$ respectively.

2.2. Synthesis of lignin copolymers

The synthetic routes of the respective lignin copolymers by solvent free ring-opening polymerization of β -butyrolactone and ϵ -caprolactone are illustrated in Fig. 1. The weight ratio of lignin: monomers in all four copolymers was 2: 8. For the synthesis of lignin-PHB (LPB), 2 g of lignin was reacted with 8 g of β -butyrolactone in a two-necked 150 mL round-bottom flask. Tin (II) 2-ethylhexanoate (0.5 wt% of monomer as catalyst) was added and the mixture was stirred for 8 h at 130 °C and 350 rpm. After that, the mixture was cooled down and chloroform (100 mL) was added to dissolve the synthesized lignin copolymer (the unreacted lignin would not be dissolved). The unreacted lignin was removed by centrifuge and the supernatant was precipitated in ether twice. The lignin copolymer was dried overnight in the vacuum oven at 50 °C. For random lignin-PHB-PCL (LPHC), lignin (2 g) was reacted with 4 g of β -butyrolactone and 4 g of ϵ -caprolactone for 8 h with the catalyst, followed by precipitation and drying. For block lignin copolymers (LPH + C and LPC + H), 2 g of lignin was reacted with either 4 g of β -butyrolactone or caprolactone for the first 4 h. After that, unreacted monomers were removed through precipitation. The reaction was then continued by reacting 4 g of the other monomer for the next 4 h, followed by purification and drying. The yield of the copolymers were ~60%.

2.3. Characterization of lignin copolymers

The synthesized copolymers were dissolved in deuterated chloroform (CDCl_3). After dissolving, they were characterized by ^1H nuclear magnetic resonance (NMR, Bruker 400 MHz). The molecular weight and poly-dispersity index (PDI) of the polymer samples were analyzed by gel permeation chromatography (GPC). GPC analysis was carried out with a Viscotek GPC max module equipped with two phenogel columns (103 and 105 Å) (size: $300 \times 7.80 \text{ mm}$) in series and a Viscotek TDA 305 triple detector. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min at a column temperature of 40 °C. Monodisperse poly(methyl methacrylate)

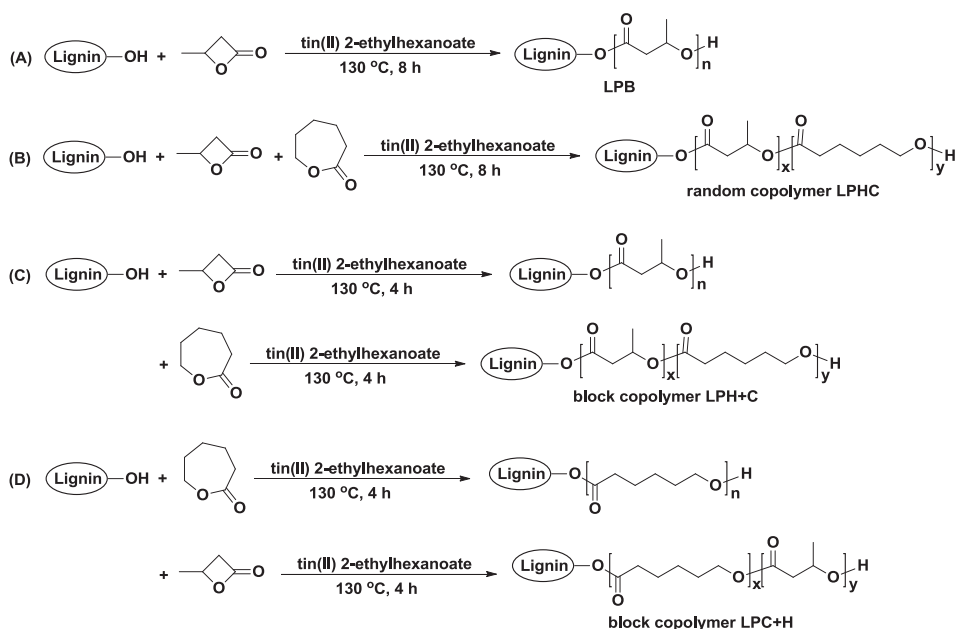


Fig. 1. The synthetic routes of lignin copolymers (A) LPB, (B) random copolymer LPHC, (C) block copolymer LPH + C and (D) block copolymer LPC + H.

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