



Low cost carbon fibers from bio-renewable Lignin/Poly(lactic acid) (PLA) blends



Shichao Wang, Yan Li, Hengxue Xiang, Zhe Zhou, Tienkiang Chang, Meifang Zhu*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, 201620, China

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ABSTRACT

We report that cylindrically shaped Lignin/PLA based carbon fibers having tensile strength between 258.6 and 159.2 MPa and tensile modulus ranging from 1.7 to 11.6 GPa can be prepared by melt spinning of Lignin/PLA blends followed by the thermal stabilization and carbonization of Lignin/PLA fibers. The introduction of PLA increased the spinnability of Lignin/PLA blends by employing the good spinnability of PLA, to produce continuously spooled Lignin/PLA fibers. The hydrogen-bonding interaction between lignin and PLA phases, demonstrated by DSC and FTIR, increased the tensile modulus of the blend-based carbon fibers relative to that from lignin. However, the tensile strength of Lignin/PLA based carbon fibers was decreased mainly due to the presence of voids that were caused by the volatilization of PLA in the thermal stabilization and carbonization processes.

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1. Introduction

Carbon fibers are defined as fibers with a carbon content of at least 92% made from polymeric precursors or carbon allotrope building blocks [1]. High tensile strength and modulus, low density, excellent creep and chemical resistance make carbon fibers attractive in aerospace, military and other high technology fields. Currently, carbon fibers are mainly manufactured from petroleum-based poly(acrylonitrile) (PAN) feedstock by solution spinning [2]. With the increasing concerns for the shortage of petroleum resources and the environmental pollution, non-petroleum based precursors combined with environmental friendly spinning methods are preferred for the production of carbon fibers. In addition, the high cost of carbon fibers restricted their further application in general fields, especially in that of light-weight vehicles [3]. Therefore, it is crucial to develop low cost carbon fibers from bio-renewable precursors.

Among bio-renewable materials, lignin is an ideal candidate for the manufacture of carbon fibers due to its high carbon content. As the nature's dominant polymer and the by-product of pulping, lignin is found in most terrestrial plants in the approximate range of

15%–40% dry weight [4,5]. Low cost, bio-renewable and melt processable make it even more attractive. According to the difference of structures, lignin can be grouped into three types: hardwood lignin, softwood lignin and grass lignin. The structure of these three types differs in the monolignols from which the corresponding lignin is built (Fig.S1) [1]. Hardwood lignin is composed of syringyl (S) and guaiacyl (G) units and softwood lignin has predominantly G units, while grass lignin is constructed with S, G and *p*-hydroxyphenyl (H) units. Both hardwood and softwood lignin are used to prepare carbon fibers by melt spinning method [6,7]. However, continuously spooled lignin fibers are hard to obtain without the pretreatment of lignin. The purity of lignin is a critical factor for achieving continuously spooled fibers. Baker et al. [2] extracted the hardwood lignin with organic solvents and obtained fine lignin filaments by melt spinning. The glass transition temperature (T_g) of lignin decreased from 130.2 °C to 88.0 °C after purification, resulting in the adhesion of fibers during the thermal stabilization process. Different from the organic extraction, the purification of lignin using ceramic membrane can also effectively remove the impurities but with just a slight decrease of the T_g of lignin [8]. Nordstrom et al. [9,10] blended kraft lignin with kraft lignin permeate and prepared the lignin based carbon fibers successfully. Unfortunately, the mechanical properties of hardwood lignin based carbon fibers were not mentioned in their study. In addition to purification, chemical modification is also a crucial step. The melt ability of lignin can be improved by acetylation and esterification to

* Corresponding author.

E-mail address: zhumf@dhu.edu.cn (M. Zhu).

a certain extent, but their cost is relatively high [11,12]. An inexpensive and convenient method to improve the spinnability of lignin is the blending of other polymer. Synthetic polymers were thermally blended with lignin to manufacture lignin based carbon fibers by Kubo et al. [13,14], both poly(ethylene terephthalate) (PET)/lignin and polypropylene (PP)/lignin blends were easily spun into fibers. Additionally, poly(ethylene oxide) (PEO) was also studied to facilitate the lignin spinnability [15,16]. However, developing a precursor utilizing a petroleum-based polymer may pose future problems considering limited oil reserves, which ultimately results in high price volatility for the precursor [17]. In this case, bio-renewable polymers play an irreplaceable role in acting as the plasticizer during the melt spinning process of lignin. Thunga et al. [17] prepared lignin based carbon fibers from a blend of butyrate softwood lignin and PLA, a biopolymer derived from corn, potato and other biomass materials [18,19]. Continuously spooled butyrate lignin (B-Lignin) and B-lignin/PLA fibers were obtained. The spinnability and tensile strength of B-lignin/PLA fibers were both improved with the addition of PLA. However, the post-carbonized fibers with 90 and 100 wt.% of B-lignin deformed from their initially cylindrical shapes to profiles with a flat surface because of the softening of the fibers. Besides, the high content of PLA in B-lignin/PLA blends produced many voids in the fibers after carbonization, making it difficult to determine the mechanical properties of B-lignin/PLA based carbon fibers.

In the present work, the lignin structure before and after purification using ceramic membrane was characterized. Continuously spooled lignin fibers and cylindrically shaped lignin based carbon fibers were manufactured by blending lignin with PLA. The thermal properties of Lignin/PLA blends, the interaction between lignin and PLA phases, the morphology and mechanical properties of lignin and Lignin/PLA blends based carbon fibers were investigated to give a comprehensive approach on the manufacture of low cost carbon fibers from a bio-renewable precursor.

2. Material and methods

2.1. Materials

Hardwood kraft lignin was kindly provided by Suzano Papel e Celulose S.A. Corp., Brazil. The chemical properties of purified lignin are shown in Table S1. PLA with a weight-average molecular weight (M_w) of 1.77×10^5 and a polydispersity index (PDI) of 1.3 was supplied by Nantong Jiuding Biological Engineering Co., Ltd, Jiangsu, China. Deuterated dimethyl sulfoxide (DMSO- d_6) used for ^{13}C NMR analysis was purchased from Sigma–Aldrich. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and were all used as received without further purification.

2.2. Purification of lignin

Lignin was dissolved in sodium hydroxide solution ($\text{pH} = 12$) and fractionated through ceramic membrane with the molecular mass cut-off value of 15 KDa (as given by the manufacturer: Laungy Membrane Filtration Technology, Shanghai, China). Next, sulfuric acid was added to precipitate lignin from the permeate by adjusting the pH of the solution to 2. The precipitated lignin was filtered and washed with deionized water repeatedly to neutralize the pH value. The neutralized lignin was dried at 80°C for 12 h and heat-treated at 200°C for 1 h under vacuum to remove moisture and volatiles.

2.3. Preparation of Lignin/PLA fibers

Lignin powders and PLA pellets were mixed together in a Haake Rheocord 90 batch mixer at 220°C for 5 min with the roller speed of 50 rpm. The contents of PLA were 0, 5, 10, 15 and 20 wt.% of the total weight, respectively. All the Lignin/PLA blends were fed into a twin screw micro-compounder equipped with a take-up device and processed at temperatures of 220°C – 240°C depending on the content of PLA. The winding rate was 100 m/min and Lignin/PLA fibers were collected on cylinders.

2.4. Thermal stabilization and carbonization of Lignin/PLA fibers

Lignin/PLA fibers were thermally stabilized and carbonized in an oven. The thermal stabilization process was carried out in an air environment. Lignin/PLA fibers were heated from 60°C to 280°C at a rate of $0.25^\circ\text{C}/\text{min}$ and held for 1 h before carbonization. The thermally stabilized fibers were subsequently carbonized in a nitrogen atmosphere. The temperature was increased to 1000°C at a rate of $3^\circ\text{C}/\text{min}$ before cooling to room temperature.

2.5. Structure and properties characterization

Nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25°C in DMSO- d_6 .

Differential scanning calorimetry (DSC) analysis was conducted according to the procedure described by Cui et al. [20] using a TA instruments Q20. Samples were heated from 30°C to 105°C at a rate of $5^\circ\text{C}/\text{min}$ and then kept isothermally for 40 min prior to being quenched to 30°C . Next, the DSC thermograms were recorded by increasing the temperature to 250°C at a rate of $10^\circ\text{C}/\text{min}$.

Fourier transform infrared spectroscopy (FTIR) was carried out using a Nicolet 8700 Fourier transform infrared spectrometer. All the samples were analyzed using KBr pellet technique and scanned in the range of 4000 to 400 cm^{-1} .

The morphology of Lignin/PLA fibers, before and after carbonization, was characterized using scanning electron microscopy (SEM) (JSM-5600LV, Japan).

The mechanical properties of Lignin/PLA based carbon fibers were measured using a fiber tensile tester (XQ-1A, manufactured by Shanghai Lipu Applied Science Institute). The tensile speed was $5\text{ mm}/\text{min}$ with a gauge length of 10 mm. Each fiber diameter result was an average of 5 measurements along the fiber. Tensile strength and modulus values were reported as the average of 10 fibers per sample.

3. Results and discussion

3.1. Chemical structure of lignin before and after purification

The structure of lignin that we used for production of carbon fibers were characterized by a set of multiple nuclei NMR spectra, especially the 2-D HMBC spectrum which reveals the strong coupling between Hs and adjacent Cs among the linkages and the phenyl groups, and was therefore used as the main evidence for the assignment of lignin structure. The ^{13}C NMR spectra of the samples prior to and after filtration through ceramic membrane are shown in Fig. 1(a) and (b), respectively. It can be found that only the signals at 97.3 (artifacts), 65.8–67.1 (C6 in cellulose) and 23.4–33.3 ppm (lipids (CH_2) and protein (sc)) were removed after filtration while other resonances remain the same before and after filtration [21–23]. This means that cellulose, carbohydrates and other impurities which are not conducive to melt spinning can be effectively removed by purification. Detailed analysis of the NMR spectra, especially the 2-D HMBC spectrum, reveals that the purified lignin

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