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Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers

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ABSTRACT

Lignin, a highly aromatic biopolymer extracted as a coproduct of wood pulping, was investigated as a suitable precursor for carbon fibers. Lignin was chemically modified and blended with poly(lactic acid) (PLA) biopolymer before melt spinning into lignin fibers. The chemical modification of raw lignin involved butyration to form ester functional groups in place of polar hydroxyl (–OH) groups, which enhanced the miscibility of lignin with PLA. Fine fibers were extracted and spooled continuously from lignin/PLA blends with an overall lignin concentration of 75 wt.%. The influence of chemical modification and physical blending of lignin with PLA on the resulting fiber was studied by analyzing the microstructure of the fibers using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The influence of blend composition on the phase behavior was studied by differential scanning calorimetry (DSC). The effect of composition on the mechanical properties was studied by tensile tests of the lignin/PLA blend fibers. The thermal stability and carbon yield of the blended fibers with different concentrations of lignin were characterized by thermogravimetric analysis (TGA). The microstructure analysis of carbon fibers produced from lignin/PLA blends revealed composition dependent microporous structures inside the fine fibers.

1. Introduction

Carbon fiber based polymer composites have been recognized as advanced materials for structural applications. The unique reinforcing abilities of carbon fibers with their combination of high strength, low mass, and excellent fatigue resistance have made carbon fiber based composites exceptional compared to other fiber reinforced composites [1].However, the high cost of precursor materials for carbon fibers (which accounts for 51% of the cost of carbon fiber production) has limited the widespread applicability of carbon fibers [2–4].

Lignin is an aromatic biopolymer and has been investigated as a precursor for the production of carbon fibers because of its low cost and bio-renewable nature [5]. The molecular structure of lignin consists of repeating units of the phenylpropane: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [6], which makes it highly polar with a large number of hydroxyl (–OH) groups. The production of carbon fiber from low-cost renewable resources such as lignin has been hindered by difficulties in processing fine lignin fibers. Its complex, interconnected structure makes it difficult to spin and spool raw lignin into fibers without modifications.

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It is recognized that blending lignin with polymers is a convenient and inexpensive method to produce fibers with desired surface characteristics and mechanical properties. In previous studies, polyethylene terephthalate (PET), polypropylene (PP), and poly(ethylene oxide) (PEO) were successfully blended with lignin to produce fibers [7–9]. 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. A potential alternative to synthetic polymers is a biorenewable polymer acting as a plasticizer in the fiber spinning process. Polylactic acid (PLA) is a biopolymer derived from corn starch and sugarcane biomass [10,11]. Compared to traditional petroleum-based polymers used previously for plasticizing lignin, the crystallinity in bio-based PLA was observed to improve rheological properties of the melt. In addition, strain hardening, which favors processability of polymer melts, was observed in PLA when co-blended with an enantiomer [12]. Blending lignin with PLA not only offers the potential to make the carbon fiber production process greener and renewable, but also provides a low cost alternative precursor that allows for the processing of lignin fibers using conventional polymer processing techniques, such as melt spinning. However, the miscibility of lignin with a variety of plasticizing polymers is limited because of the presence of a large number of hydroxyl (–OH) groups. Adjusting the miscibility between lignin and PLA on the molecular level is essential to produce fine precursor fibers. Glasser et al. [13,14] have chemically modified lignin and found that esterification of lignin was more promising in enhancing its solubility in various organic solvents. The plasticization caused by esterification decreased the glass transition temperature (T_g) of lignin. Further, lignin was observed to be melt processable after esterification [15–17]. Wool et al. [18] have studied the effect of esterification of lignin by butyration to improve the solubility of lignin in styrene, a reactive diluent commonly used in polyester resins. In the present work, efforts were made to modify lignin by esterification to enhance its molecular level miscibility with PLA.

Porous or activated carbon fibers are also widely used for water purification and gas separation applications [19]. The specific absorption properties of porous carbon fibers have made them the material of choice for advanced applications such as electrochemical super-capacitors, hydrogen storage, and catalyst support [20]. Over the past decade, novel precursors and processing techniques have been developed to produce porous carbon materials [20,21]. Most of these research efforts were primarily focused on either enhancing the micro-porous surface area or controlling the porosity in the fibers. Ji et al. [22] studied the effect of blending PLA biopolymer as a pore generating phase with polyacrylonitrile (PAN) as a conventional carbon forming precursor to produce porous carbon fibers. The pore size, surface area, and volume were strongly influenced by the PAN/PLA blend composition. However, most of the studies were based on solution spinning processing techniques which require solvent extraction.

In the present work, softwood kraft lignin was modified and blended with PLA biopolymer to show that chemically modified lignin is compatible with PLA. Blends of the modified lignin and PLA were successfully melt-spun into fine fibers. The physical interaction between the blend components responsible for the development of miscibility at the molecular level in the fine fibers was investigated. The degree of phase compatibility was qualitatively studied by microscopic techniques and thermal analysis. The optimum blend composition necessary for producing continuous, fine fibers with high carbon yield after carbonization was investigated. Finally, the lignin-based precursor fibers were carbonized and the influence of PLA concentration on the porosity of the final carbon fibers was investigated systematically.

2. Experimental

2.1. Materials

Softwood kraft lignin (Indulin-AT) was provided by MeadWestvaco Corp., Richmond, VA. It was used as received and washed in dilute HCl solution (pH below 5) for 10 min to remove dissolved salts. The acid treated lignin was washed repeatedly with distilled water to neutralize the pH value. The washed lignin was vacuum-dried for several hours to remove the moisture content and then stored in dry air. Polylactide (PLA) was purchased from NatureWorks LLC, Minnetonka, MN. Butyric anhydride and 1-methylimidazole (1MIM) were purchased from Sigma–Aldrich and used as received. Deuterated dimethyl sulfoxide (DMSO-d6) used for NMR analysis was purchased from Cambridge Isotope Laboratories, Inc., Andover, MA. Potassium bromide (KBr) used for IR analysis was purchased from Fisher Scientific, Waltham, MA.

2.2. Blend preparation for fiber spinning

Lignin was butyrated prior to blending with PLA using the procedure described by Thielemans et al. [18]. Preparation and properties of butyrated lignin (B-lignin) is described in the supporting information. The degree of esterification of lignin was characterized. All the B-lignin/PLA blends were processed by melt mixing at 180 °C using a twin screw microcompounder from DACA Instruments, Santa Barbara, CA. The blends were processed by keeping the speed of the twin screws constant at 60 rpm. The residence time of the melt in the barrel was limited to 5 min to avoid thermal degradation. Fine fibers were extruded by a fiber spinning die attached to the end of the extruder. The extruded fiber was continuously spooled from the microcompounder with the help of an advanced DSM-Xplore micro fiber spinning device, DSM, Geleen, Netherlands. A constant stretching in the fibers was achieved by maintaining the speed of the winding drum constant.

2.3. Thermal and mechanical analysis

The influence of blend composition on the phase behavior was studied by differential scanning calorimetry (DSC). The glass transition (T_g) and melting (T_m) behavior of lignin/PLA blends was measured by DSC tests using a DSC-Q20 from TA Instruments. DSC scans were run from −50 to 200 °C at a heating rate of 20 °C/min under nitrogen atmosphere. The thermal stability and the carbon yield in all blend compositions were determined by thermogravimetric analysis (TGA)