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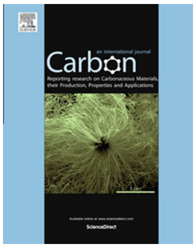

Shell–core structured carbon fibers via melt spinning of petroleum- and wood-processing waste blends

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ABSTRACT

In the last decades, carbon fibers with light weight and high strength have experienced the largely increased uses in various industrial applications. However, their expected uses in the automotive industry and building are largely limited because of their high production cost. Herein, we have demonstrated an effective method of making low cost carbon fibers via the melt spinning of petroleum-processing residue (pyrolyzed fuel oil, PFO)/lignin blends. Careful selection of tetrahydrofuran as the solvent to dissolve both PFO and lignin was made to optimize the miscible blend. The melt spinnable blend with a softening point of 260–280 °C exhibited good spinning ability at 280 °C. The plasticizing function of PFO allowed the highly cross linked lignin-based pitch to have high fluidity in the melt spinning process. Based on detailed TEM observations, the thermally treated fiber prepared at 2800 °C exhibited a shell–core structure, consisting of a highly crystalline surface from PFO and an amorphous disordered core from lignin. Such a crystalline surface structure gave rise to a high modulus value (up to 100 GPa) to the prepared carbon fibers.

1. Introduction

The micro-sized continuous carbon fibers, containing at least 92% carbon atoms have attracted a lot of attention from both the academic and the industrial sectors as one of the most important energy saving materials [1,2]. Some of their unique features, such as light weight, superior mechanical strength and high electrical and thermal conductivities have made them suitable for applications in various industrial products, including the commercial airplanes [3]. However, their promising uses in the automotive industry and building are largely limited because of their high production cost [4,5], where polymer precursors, *e.g.*, polyacrylonitrile (PAN) shares 50% of the total production cost of the commercialized carbon fibers. To realize the practical use of the carbon fiber reinforced plastics in the automotive industry, carbon fibers should have a tensile strength above 1.72 GPa, a tensile modulus above 172 GPa, elongation above 1% and their price should be lower than \$11/kg [6].

Thus, low-cost alternative precursors, *e.g.*, pitch, textile PAN, polyolefin, and lignin have been extensively and intensively examined to achieve such targets, low cost and general grade carbon fibers. Petroleum-, coal tar- and synthetic

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pitches have been investigated to produce general performance carbon fibers because of their inherent advantages, such as low raw materials and high carbon yield [7–11]. However, the high processing cost to prepare the melt-spinnable pitch from coal tar and petroleum residue still needs to be reduced. Textile PAN-based carbon fibers although showed good mechanical properties, large variations in their properties were highly undesirable [12]. Recent studies proved that polyethylene-derived carbon fiber showed a high performance/cost ratio, but their long (or slow) air-stabilization time should be addressed [13].

Alternatively, a huge effort has been focused on the fabrication of carbon fibers from lignin, since lignin is easily generated as a by-product from conventional paper pulp production, as well as from the ethanol bio-refineries [14,15]. Interestingly, lignin based carbon fiber has a long history. The lignin-based carbon fiber was commercialized by Nippon Chemical Co. in 1970s, but the poor mechanical property of the fiber did not make their business successful [16,17]. Sudo et al. reported the possibility of making carbon fibers via the melt spinning of the hydrogenated, phenolated and acetylated lignin [18,19]. Lignin obtained through solvent extraction using acetic acid and ethanol was also used as precursors for making carbon fibers [20]. Furthermore, various synthetic polymers, such as polyethylene oxide, poly (ethylene terephthalate) and polypropylene were examined as modifiers to produce melt-spinnable lignin-based carbon fibers [21,22]. Pyrolytic lignin isolated from a commercial bio-oil had also been examined as a precursor for making carbon fibers [23]. Up to now, there has been a distinctive research trend to improve the melt-spinnability of lignin, reduce the air-stabilization time and at the same time keep the lignin's intrinsic cost low. Thus, preparation of high purity lignin with a high spinning ability has become crucial for the synthesis of high performance lignin-based carbon fibers.

The purpose of this work is to explore the possibility of making lignin-based melt spinnable pitch for the production of low cost and general grade carbon fibers using petroleum-process reside as modifier. In the current study, tetrahydrofuran was judiciously selected as the solvent to obtain a homogeneous melt of the spinnable lignin-based dope through a complete removal of salts, volatile matter and heavily cross-linked high molecular weight portion, whereas pyrolyzed fuel oil (PFO) was used as plasticizer to improve the spinning ability of the lignin-based dope. To this end, we examined the spinning ability of the lignin based dope as a function of blend ratio and then measured the physical properties and micro texture of the carbon fibers. The carbon fiber consisted of PFO-derived highly crystalline shell and lignin-derived disordered core.

2. Experimental

2.1. Starting materials

The PFO (GS Caltex, Korea) was used as received. The hardwood lignin (PC 1369, Induline, MeadWestvaco Co, USA) was desalted five times using 1 N hydrochloric solution. The desalted lignin was then washed with distilled water for several times until pH = 7 and finally it was vacuum-dried to get powder-type lignin.

2.2. Preparation of miscible lignin/PFO blends

The desalted lignin and PFO were mixed at different ratios, viz. 9:1, 8:2, 7:3 and 6:4 to form several blends of lignin and PFO. The blends were dissolved separately in THF to obtain an 8% (w/w) solution. Any insoluble part in the solutions were then removed through centrifugation at 3000 rpm followed by thermal treatment of the solutions for 4 h at 230 °C, which removed all volatiles and THF and formed the melt spin able dope.

2.3. Melt spinning, air-stabilization and thermal treatment

The prepared dope was melt-spun into fibers at 260–280 °C through a round-shaped single-hole spinneret (0.5 × 0.5 mm) (L/D = 1) under 5 kgf/cm^2 pressure of nitrogen. The winding rate varied from 70 to 100 m/min. The melt-spun fibers were oxidatively stabilized by increasing the temperature from 200 to 280 °C, at a heating rate of 1 °C/min. To avoid any thermal fusion during the above heating process, the fibers were further left undisturbed in a stream of continuous air flow (5–20 ml/min) for an hour. Finally, the air stabilized fibers were again thermally treated sequentially at 800 and 2800 °C in argon to obtain the desired carbon fibers.

2.4. Characterizations

The softening point of the blend pitches were measured using Metller FP90 (Metller-Toledo, Switzerland). The changes in functional groups were monitored using FT-IR (Nicolet 520p, USA) and NMR (Varian XL-400, USA). Thermal analysis (Thermogravimetric analysis and differential scanning calorimeter) was carried out under nitrogen to measure the thermal stability and behaviors. The glass transition temperature of the samples (T_g) were measured as onset temperature of the step change in heat capacity in the DSC curves. Macroscopic morphology of the carbon fiber (*e.g.*, surface property and diameter) was observed using a SEM (Hitachi, S-4700, Japan), whereas their microtexture was evaluated using a TEM (Tecnai F20, FEI, USA). The mechanical strength of the individual carbon fibers was measured according to the ASTM standard (D 3379-75) with an Intron model 4411 using a 0.5 N load cell and a gauge length of 25 mm. X-ray diffraction patterns were recorded using a Rigaku diffractometer at 40 kV and 200 mA in the range from 10° to 90°. The diffraction scans were corrected for intrinsic instrumental and strain broadening effect. Then, the in-plane crystallite size (L_a) was determined from the (110) peaks using the Scherrer equation whereas the stacking height (L_c) was estimated from the (002) peaks [24,25]. Raman spectra (Renishaw, UK) were taken using a 633 laser line. All peaks were curve-fitted using a Lorentzian distribution function. R value (I_D/I_G) was obtained by dividing the integrated intensity of the D band by the integrated intensity of the G band.