CARBON COMPOSITE FIBERS FROM BY-PRODUCTS OF LIGNIN/PETROLEUM RESIDUE OIL

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ABSTRACT

We have demonstrated an effective method of making low cost carbon fibers via the melt spinning of blends of lignin and petroleum-processing residue (pyrolyzed fuel oil, PFO). 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

Thus, low-cost alternative precursors, e.g., pitch, textile PAN, and lignin have been extensively and intensively examined to achieve such targets, low cost and general grade carbon fibers [1]. A large 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. 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. Sudo et al. reported the possibility of making carbon fibers via the melt spinning of the hydrogenated, phenolated and acetylated lignin [2]. Lignin obtained through solvent extraction using acetic acid and ethanol was also used as precursors for making carbon fibers [3]. 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 residue 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 [4].
2. Experimental

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. 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/cm² 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.

3. Results and discussion

To obtain carbon fibers, the air stabilized fibers are thermally treated at 800 and 2800 °C holding for 1 h in an argon atmosphere without using tension. In terms of macromorphology, there was no change in the fiber diameter after air stabilization (Fig. 1(c and d)). However, after the carbonization step the diameter of the fibers decreased from 30 to 22 μm (Fig. 1(e)), indicating a densification process through condensation reactions. Furthermore, on treatment of the fibers at 2800 °C, the diameter reduced to 15 μm (Fig. 1(f)).

In order to study such changes at the nano-scale, we carried out detailed TEM observations at different magnifications. A typical TEM image of the air stabilized fiber (Fig. 2(a and b)) indicated the amorphous structure. By contrast, when the fibers were thermally treated at 800 °C, blurred small sized curled fringes (Fig. 2(c and d)) appeared and the FFT diffraction pattern (the inset in Fig. 2(d)) supported a highly disordered carbon. Thus, to clearly visualize the structural evolution of lignin based carbon fibers, the carbonized fibers at 800 °C were further treated at 2800 °C using a graphite furnace, because high temperature thermal treatment is known to be effective to evaluate the microstructure of carbon materials. Interestingly, the detailed TEM observation on carbon fiber sample using microtome revealed that our fibers consist of heterogeneous nanotexture. In the core (Fig. 2(e)), the nanotexture is isotropic and disordered. More specifically, 10–15 stacked layers with a short range order (up to several nanometer ranges) are intermingled, in which nano sized pores were enclosed between the curled layers. By contrast, the region near the outer surface (Fig. 2(f)) had highly crystalline fringes along the fiber direction, in which the interlayer spacing was close to that of graphite. The evolution of such shell–core structure in our carbon fiber can be explained by the intrinsic properties of lignin and PFO constituent. In such a binary system, it is expected that PFO will be entrapped as island in lignin-based sea (Fig. 2(g)). During the fiber formation in the melt spinning process, a phase separation will occur by a high shear rate, thus the PFO constituent will be diffused into the outer surface region. No textural heterogeneity for carbon fibers at 800 °C was recognized due to limitations in the TEM instrument to prove such a subtle change in nanotexture. Thus, high temperature thermal treatment is a powerful tool to evaluate the nanotexture of carbon fibers.

Finally, we evaluated the crystallinity and mechanical strength of the carbon fibers, prepared both at 800 and 2800 °C. Fig. 3(a) shows the X-ray diffraction pattern of the carbon fibers. With increasing temperature, the intensified and sharpened (002) diffraction peak signifies an improved structural integrity; the interlayer spacing (d(002)) also changed from 0.37 to 0.34 nm, whereas the crystallite size (La) increased from 4.37 to 7.10 nm. Such kind of structural improvement was also supported by Raman studies (Fig. 3(b)). Two peaks at 1350 (defect-induced mode) and 1585 cm⁻¹ (E2g2 mode) were observed for the carbon fiber treated at 800 °C. On high temperature thermal treatment, the above two peaks became sharper, the R value (ID/IG, the integrated intensity of the D band divided by the integrated intensity of the G band) reduced and a new peak appeared around 1615
Fig. 3(c) shows typical stress–strain curves of the individual carbon fibers, prepared at 800 and 2800 °C. Noticeably, high temperature thermal treatment induced a large increase both in the tensile strength and the Young’s modulus (estimated by the slope), which can be easily explained by an increase in the crystallite size (based on XRD and Raman studies). Tensile properties of an individual carbon fiber were averaged from 20 fibers (Fig. 3(d)). We observed a large increase in tensile strength from 490 to 530 MPa and the Young’s modulus from 56 to 100 GPa. Moreover, we observed a large decrease in strain from 1.11% to 0.74%. A low strain value of our carbon fiber is ascribed to the crystalline outer surface, which originated from the PFO. We believe that there is large room to improve the physical properties of the carbon fibers by reducing the fiber diameter (below 7 μm) and the complete removal of volatile matters during the melt spinning process.

![Digital photographs showing (a) the continuously melt-spun carbon fibers on the surface of drum and (b) the detached carbon fibers from drum. SEM images of (c) melspun, (d) air-stabilized, (e and f) heat-treated carbon fibers at 800 and 2800 °C, at different magnifications](image1)

![TEM images of (a and b) air-stabilized and (c and d) heat-treated carbon fibers at 800 °C. There is no distinctive heterogeneity in the texture of carbon fiber at 800 °C. TEM images of heat treated fibers at 2800 °C showing that the region on the core (e) is isotropic and has disordered nanotexture (10–15 stacked layers with a short range order are intermingled, in which nano sized pores were enclosed between the curled layers), whereas the region near the outer surface (f) had highly crystalline fringes along the fiber direction. (g) The schematic explanation of such a shell–core structure. In a binary system, a lignin-based island will be entrapped as in sea PFO.](image2)
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Fig. 3 – (a) X-ray diffractions, (b) Raman spectra (using a 633 excitation laser line) and (c) typical stress–strain curves and (d) mechanical strength properties of carbon fibers prepared at 800 and 2800 °C.

4. Conclusion

We demonstrated an economic way of making carbon fibers by melt spinning petroleum-processing-residue modified lignin. To ensure a good melt spinnability of PFO/lignin blend, we found that THF was the most suitable solvent for making homogeneous mixing without any phase separation in solution state. It is believed that the effective removal of the low molecular weight volatiles and homogeneous mixture of the PFO/lignin in THF solvent improved largely the flow ability in the melt spinning process. Noticeably, our fiber consisted of two heterogeneous phases; disordered, the isotropic core structure consisted of intermingled 10–15 stacked layers with a short range order, enclosing nano-sized pores, whereas, the region near the outer surface had highly crystalline fringes along the fiber direction. General grade mechanical properties will allow our carbon fiber to be one of the promising candidates in automotive industry.

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