POPLAR LIGNIN-DERIVED CARBON FIBERS: CAN THEY DEVELOP GRAPHITIC MICROTEXTURE?

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Abstract

High strength carbon fibers (CFs) are used in various parts of automobile to improve fuel efficiency or range of the electric vehicle. Currently, all such CFs are produced from synthetic polyacrylonitrile precursor that not only leads to toxic byproducts during production but also use solvents that are not environment friendly. Thus, carbon fibers produced from bio-renewable precursors are of growing industrial interest. this study reports on the microstructure of CFs derived from hybrid poplar (HP) lignin as it is one of the fast-growing hardwood trees. Precursor lignin fibers were dry-spun using fractionated HP lignin solutions in ethanol-water solvent, crosslinked by thermo-oxidative stabilization and carbonized primarily at 1000ºC. CFs possessing a nominal circular cross-section and diameters of less than 10 µm were produced that displayed an average tensile strength of about 800 MPa and modulus of 60 GPa [1]. These tensile properties are among the highest reported for HP lignin-derived CF, but not comparable to properties of PAN-derived CFs. So microstructural analysis was conducted and Raman spectroscopy revealed a D peak at 1310 cm^{-1}, a G peak at 1580 cm^{-1}, and a low I(G)/I(D) ratio of 0.22, which is comparable with softwood kraft lignin-derived CFs [2]. Wide-angle x-ray diffraction measurements showed d002 peak at about 21º, which is much lower than that observed for PAN-based CFs (> 25º). SEM micrographs revealed the presence of small defects within the CF cross-section and lateral surface that explain the lower strengths. Interestingly, transmission electron microscopy (TEM) revealed the generation of graphite-like layers in a limited grade of CFs obtained at 1500ºC, but not those at 1000ºC. Inter-layer spacing was estimated at about 0.4 nm and suggests that higher carbonization temperatures need to be systematically investigated to potentially enhance tensile properties.

Background

Tighter fuel economy standards due to environmental pollution concerns, and the need for long-range electrical vehicles, incentivize the use of carbon fiber-reinforced composite materials in automotive parts. Weight savings of 100 kg for a vehicle roughly translates into 100 km increase in driving range for an electric car or 0.3 L gasoline saving per 100 km driving. It has been estimated that weight reduction using carbon fiber-reinforced composites (40-65%) is significantly higher than glass fiber-reinforced composites currently used in the transportation industry (20-35%). The reason is that carbon fibers possess the highest specific tensile strength and tensile modulus because of a low density of about 1.8 g/cm^3.

Production of carbon fibers, however, is a complex process. The reason is that carbon does not melt, so its fibers (CFs) must be produced starting with organic precursor fibers. About 90% of commercial CFs are produced using poly-acrylonitrile (PAN). Unfortunately, the process used to convert PAN into CFs uses non-ecofriendly solvents and produces toxic by-products like hydrogen cyanide [3]. Currently, only 10-20% of the carbon fibers produced are consumed in the transportation industry because of their high cost. Although about half of the CF cost comes from the complex process, the other half comes from the cost of the precursor [3]. Hence, low-cost

precursors, such as lignin, have gained renewed commercial interest.

Lignin is a renewable and abundantly available biopolymer that is commonly recovered from waste streams of the pulp and paper industry. Preliminary estimates have shown that lignin-based CFs would cost close to $5/lb vs. $8/lb for PAN-based CF [4,5]. Lignin sourced from hybrid poplar (HP) is a lucrative option given that it is one of the fastest-growing hardwood trees and has about 25 dry wt% lignin [6]. With growing energy demand and concerns about the harmful effects of carbon dioxide emissions, biofuels provide renewable alternative energy sources [6]. Our group recently reported average tensile strength of HP-lignin carbon fibers to be 800±180 MPa [1]. Although this is the highest ever reported strength for HP-lignin CF, it is much lower when compared with commercially available CFs. As pointed out in prior literature studies for PAN- and pitch-based CFs, graphitic microstructure plays an important role in influencing strength and modulus of CFs [7,8]. It has been reported that softwood kraft lignin-based CFs lead to graphitic development [9], but there is no significant discussion in the literature about graphitic microtexture in HP-based based CFs. Therefore, the objective of the study was to assess the microstructure of carbon fibers derived from HP-lignin.

Experimental

Fractionated HP lignin using ALPHA process by Tindall et al. [10] was used for this study. Using ethanol/water as solvent, lignin was dry-spun into precursor fibers and stabilized at 270ºC. Stabilized fibers were then carbonized primarily at 1000ºC, with a limited quantity carbonized at 1500ºC.

Individual filaments were scanned under Renishaw inVia Raman microscope with laser wavelength of 785 nm and laser power of 25 mW. Laser was focused on fiber surface using 50x objective lens, and the data was analyzed using WiRE Raman Software version 3.4.

Carbon fiber bundles were analyzed by wide angle x-ray diffraction in Bruker D Venture diffractometer with a copper Incoatec Microfocus source with source wavelength of 0.15406 nm operated at 50 kV and 1 mA. CF bundles were impregnated with an amorphous sizing solution and diffraction pattern was captured by Photon 100 CMOS detector after exposure of 90 seconds.

To analyze the cross-sectional microstructure and longitudinal surface of the carbon fibers, scanning electron microscopy (SEM) was conducted on samples using high resolution FESEM scopes (SU6000/SU5000/Regulus8230, Hitachi). High resolution transmission electron microscopy was conducted using Hitachi HR 9500 TEM operating at 300 kV. CF tow was embedded in an acrylic resin and microtomed to 70 nm slices and placed on 300 mesh copper grids. Image analysis was done using ImageJ software.

Results and discussion

We have recently reported average tensile strength of these carbon fibers to be 800±180 MPa [1]. These strength values are lower than 1.4 GPa reported in one of our earlier studies for softwood lignin derived CFs [2] . This suggests that a microstructural investigation of HP-derived CFs is needed to assess defects and microstructural characteristics present in the currents CFs and thus determine what changes may be warranted in future studies. Figure 1 displays SEM micrographs of CFs carbonized at 1000 and 1500ºC. Fibers were mostly circular in cross-section,

but some noncircularity was evident due to the dry-spinning process employed to produce the precursor fibers. Although no gross holes or voids were seen, presence of some defects was evident in fiber cross-section as well as the lateral surface. Overall, the texture was similar to that seen for turbo-stratic carbon (as in PAN-based CFs) and not the the highly ordered and layered graphitic structure seen in mesophase pitch-based CFs [11] .

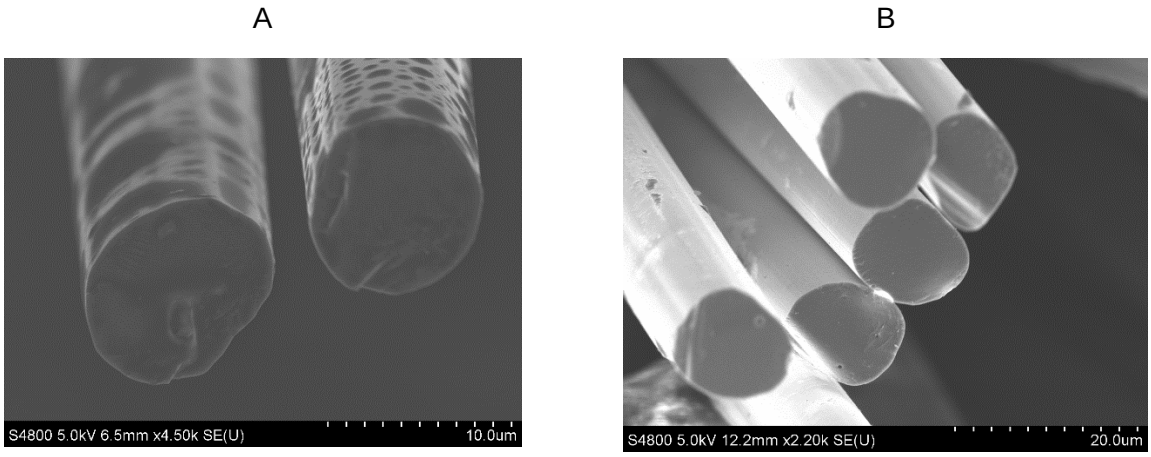


Figure 1 SEM micrographs of Carbon fibers carbonized at: (a) 1000ºC and *(b)* 1500ºC

Next, as displayed in Figure 2, Raman spectroscopy of carbon fibers showed D peak at 1310 cm^{-1} and G peak at 1580 cm^{-1} . I(G)/I(D) area ratios were 0.23 and 0.24 for CF treated at 1000ºC and 1500ºC, respectively. These values are similar to previously reported values for softwood kraft lignin [9], showing that there is dominantly disordered structure. $La_{||}$ values calculated using I(D)/I(G) ratios, as discussed by Cancado et al. [12], is about 21 nm for fibers carbonized at both 1000ºC and 1500ºC. In contrast, $La_{||}$ measured for K1100 CF was much higher at 150 nm, which is close to that reported in literature studies [2].

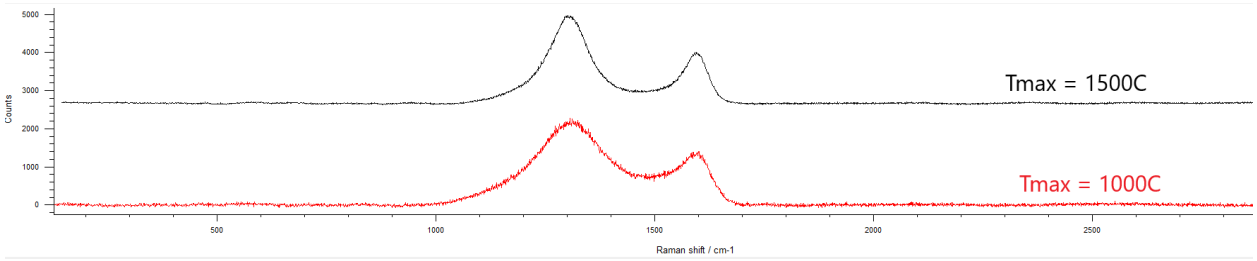


Figure 2 Raman spectra of carbon fibers carbonized at 1000°C and 1500°C.

Wide-angle x-ray diffractograms are displayed in Figure 3. Two-theta peaks associated with (002) layer planes for CF treated at 1000ºC and 1500ºC both appeared at approximately 21.5 degrees. Carbon layer spacing, d_{002}, as calculated from Bragg's law, was about 0.413 nm.

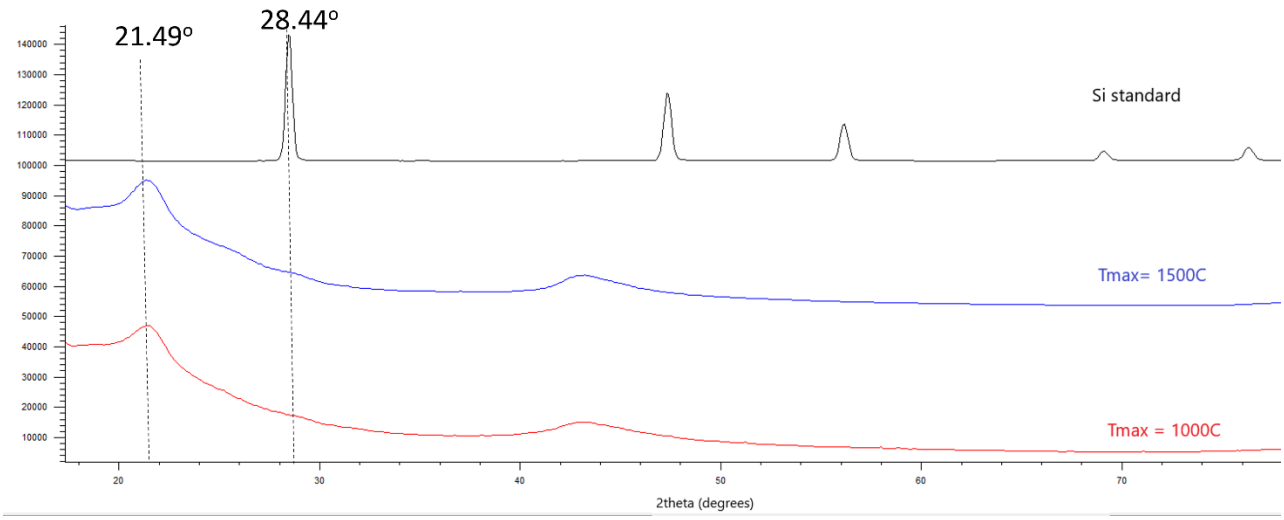
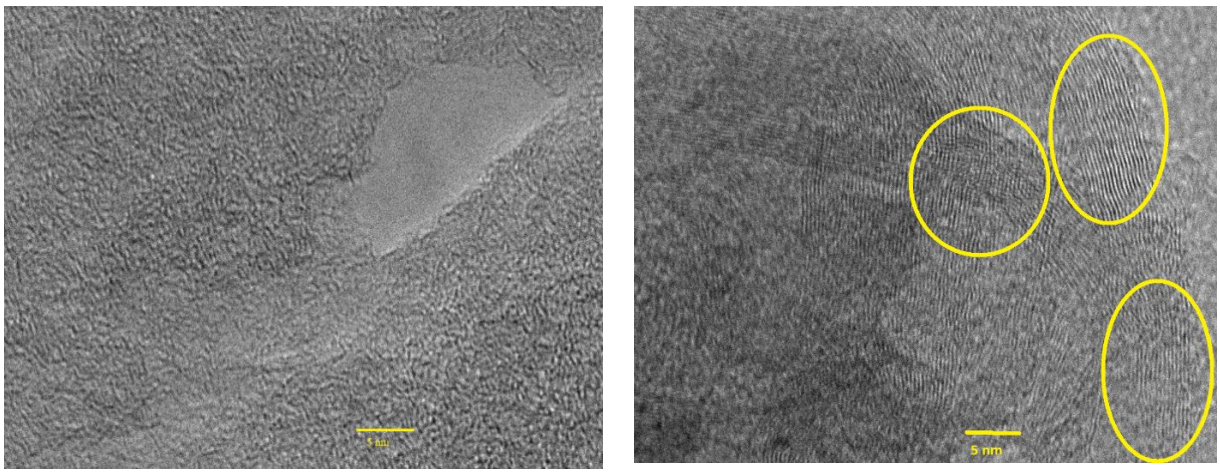


Figure 3: Two-theta profiles from WAXD of carbon fibers treated at 1000ºC and 1500ºC; spectrum for NIST-grade silicon standard was used for calibration.

TEM

Figure 4 displays transmission electron micrographs of CFs carbonized at two different temperatures, 1000 and 1500ºC. An examination of the micrographs reveals that there is not a significant development of graphitic microtexture for fibers carbonized at 1000ºC. However, for a higher heat treatment temperature of 1500ºC, graphitic development is significantly higher as noted from the ordered carbon layer formation identified by circles in figure 3. For CF treated at 1500ºC, average d_{002} spacing measured from TEM image is about 0.392 nm, , which is consistent with the measurements from WAXD analysis for CFs treated at 1500ºC. The stacking layer thickness, L_c, was measured at about 6 nm for the limited graphitic domains highlighted on TEM micrographs.



A B

Figure 4 TEM images of CF treated at a) 1000ºC and b) 1500ºC.

Conclusions

HP lignin precursor fibers were dry-spun and carbonized at primarily 1000ºC, with a limited sample treated to 1500ºC. Microstructure analysis of bulk CFs carbonized at 1000ºC and 1500ºC using Raman and WAXD did not show a significant difference in graphitic microtexture. TEM analysis, however, showed significantly higher ordered carbon layer formation with stacking layer (Lc) about 6 nm and d002 spacing of 0.39 nm for CFs carbonized at 1500ºC. WAXD and Raman are bulk measurement methods whereas TEM detects localized regions of the CF microtexture. Ongoing studies are investigating the effect of graphitic microstructure on CF properties like tensile properties and electrical resistivity.

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