MICROSTRUCTURE OF CARBON FIBERS DERIVED FROM

SOFTWOOD LIGNIN PRECURSORS

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Introduction

Lignin is an abundant biopolymer that possesses aromaticity and has drawn attention as an alternative precursor for producing low-cost carbon fibers [1, 2]. Most prior studies on lignin-based carbon fibers have focused on the fiber forming step. Although different types of lignin precursors have been developed to produce carbon fibers [1-6], the highest tensile strength reported was only 1.05 GPa [1,2]. In our recent study [7], the dry-spinning of a fractionated solvated lignin precursor (FSLP) and carbonization was discussed. A processable spinning window was established, the precursor fibers were stabilized under tension, and carbonized at 1000°C. The tensile strength and modulus of resulting carbon fibers was measured at 1.4 and 98 GPa, respectively, amongst the highest reported to date for carbon fibers derived from lignin precursors. The goal of the current work was to investigate the microstructure of such fractionated lignin-based fibers carbonized at higher temperatures ranging up to 2100°C.

Materials and Methods

The carbon fibers used in this study were produced from fractionated softwood kraft lignin precursor using an Aqueous Lignin Purification with Hot Acids (ALPHA) process developed by Thies and co-workers [8]. Lignin fibers were spun from the lignin fractions via dry spinning method developed by Zhang and Ogale [3], and then subjected to oxidative stabilization at 250°C for 1 h. Next, the stabilized fibers were carbonized to 1000°C. Portions of the fibers carbonized at 1000°C were further heated to higher temperatures ranging up to 2100°C.

Raman spectra of carbon fibers were obtained using a 785 µm laser in a Raman microscope system (Renishaw, West Dundee, IL). Carbon fibers were mounted on a glass slide and fixed with scotch tapes at both ends. Raman spectra using an objective lens of 50× magnification at 25 mW laser power with exposure time of 10 s. WiRE 3.4 software was used to analyze the spectra with Gaussian-Lorentzian curve fitting.

Results and Discussion

To evaluate the effect of carbonization temperature on crystalline structure of FSLP-based carbon fibers, only one type of carbon fiber: the highest MW FSLP-based carbon fibers were carbonized at different temperatures for further testing. Figure 1 displays the Raman spectra of the highest-MW FSLP derived carbon fibers prepared in the temperature range between 1000 and 2100 °C. The fibers carbonized at 1000°C and 1100°C present two broad, overlapping bands at ~1310 cm^{-1} (D band) and ~1585 cm^{-1} (G band), indicating a less well-organized carbon structure. The G' band is not pronounced in the spectra for these two types of carbon fibers. As the carbonization temperature increases to 1300°C and 1600°C, both D band and G band become narrower and their

intensities increase. Also, G' band starts to show at 2610 cm^{-1}, which is narrower and starts to slightly shift to higher frequency with increasing temperature. The spectrum for carbon fibers at 2100 °C shows well-resolved D and G bands. The G band increases in intensity with increasing temperature, whereas for the D band, the intensity decreases due to the structural ordering of carbon with increasing carbonization temperature.

The width of D and G bands was used to estimate the degree of graphitic crystallinity. The full-width at half-maximum (FWHM) of D and G bands are listed in Table 1. The FWHM of D band decreases by a factor of about 4 over the carbonization temperature range, indicating an increase of order within carbon layers at higher carbonization temperatures. For the G band, the trend is the same, i.e., the FWHM of G band decreases from 96 to 40 cm^{-1}. The ratio of integrated area of the D and G bands, I_D/I_G can be used to estimate the in-plane crystalline size, La, via the equation proposed by Tuinstra and Koenig [9] (Eq 1).

$$L_a = (2.4 \times 10^{-10} nm^{-3}) \times \lambda^4 \times \left(\frac{I_D}{I_G}\right)^{-1} \tag{1}$$

where λ is the wavelength of the laser, which is 785 nm in this study. The I_D/I_G ratio became smaller with increasing carbonization temperature, which is consistent with that observed for PAN based carbon fibers [10]. The average L_a values for these lignin-derived carbon fibers are listed in Table 1. The average crystalline size L_a at 1000°C is 24.9 nm, which is consistent with the values of 2.3-55 nm reported in prior literature studies [11,12]. The average L_a increases to 46.2 nm at 2100°C. The crystalline size L_a increases with increasing temperature, indicating that the ordered content grows by conversion of the disordered structures. Although there is a significant improvement in the structural arrangement and ordering within the highest MW lignin based carbon fiber as the heat-treatment temperature increases, the carbon fibers still possess relatively low graphitic crystallinity compared to that found in mesophase-pitch based carbon fibers, where I_D/I_G ratio is 0.8, and L_a is ~120 nm [13]. The lower graphitic content is a consequence of the nonhomogeneous chemical structure of lignin that cannot form extended 3-dimensional graphitic crystallite.
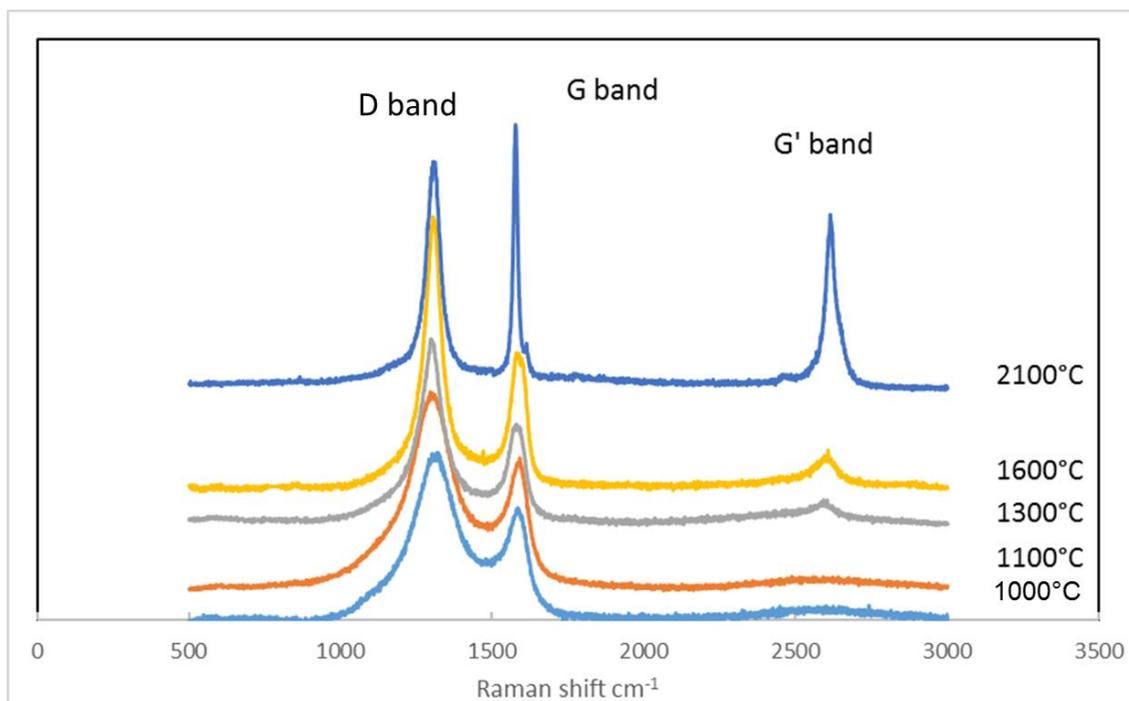
Figure 1. Raman spectra of highest-MW FSLP derived carbon fibers heat-treated at different temperatures between 1000°C to 2100°C.

Table 1. Raman spectroscopy results of highest MW FSLP-based carbon fibers.

Carbonization temperature (°C)	D FWHM (cm^{-1})	G FWHM (cm^{-1})	I_D/I_G	L_a (nm)
1000	203±16	96±1	3.61±0.52	24.9±3.1
1100	183±15	87±7	3.41±0.25	26.1±2.0
1300	158±38	83±5	3.24±0.16	27.5±1.3
1600	88±9	64±4	2.65±0.09	33.6±1.1
2100	59±2	40±7	1.92±0.07	46.2±1.6

Conclusions

High-purity lignin fractions were dry-spun into thin lignin fibers and converted to carbon fibers with the highest reported tensile strength and modulus of 1.4 and 98 GPa, respectively. Raman spectroscopy was conducted on carbon fibers derived from a lignin sample with a number-average molecular weight (M_n) of about 7 kDa. An area ratio of G-to-D peaks (I_G/I_D) of 0.18 was measured, which indicates a low level of graphitic development. However, the ratio increased to 0.23 for carbon fibers produced from lignin with a larger M_n of about 14 kDa, and further to 0.28 for carbon fibers derived from lignin with the highest M_n of about 28 kDa. At low carbonization temperatures in the range 1000-1600°C, the lignin-based carbon fibers display very low degree of graphitic crystallinity. Carbonization temperatures above 2000°C improved the layer plane ordering and reduced spacing within carbon fibers. However, the lignin-based carbon fibers did not show a true 3-D graphitic structure even at a carbonization temperature above 2000°C.

Acknowledgment

References

1. Baker, D. A.; Rials, T. G. Recent advances in low-cost carbon fiber manufacture from lignin. *J Appl Polym Sci* **2013***, 130*, 713-728.
2. Ogale, A. A.; Zhang, M.; Jin, J. Recent advances in carbon fibers derived from biobased precursors. *J Appl Polym Sci* **2016**.
3. Zhang, M.; Ogale, A. A. Carbon fibers from dry-spinning of acetylated softwood kraft lignin. *Carbon* **2014***, 69*, 626-629.
4. Nordström, Y.; Norberg, I.; Sjöholm, E.; Drougge, R. A new softening agent for melt spinning of softwood kraft lignin. *J Appl Polym Sci* **2013***, 129*, 1274-1279.
5. Hosseinaei, O.; Harper, D. P.; Bozell, J. J.; Rials, T. G. Improving Processing and Performance of Pure Lignin Carbon Fibers through Hardwood and Herbaceous Lignin Blends. *International journal of molecular sciences* **2017***, 18*, 1410.
6. Baker, F.; Gallego, N.; Baker, D. Low cost carbon fiber from renewable resources. *EERE, US Dept of Energy Project ID# lm_03_baker* **2010**.
7. Jing Jin, Junhuan Ding, Adam Klett, M. C. Thies*, and A. A. Ogale*, "Carbon Fibers Derived From Fractionated–Solvated Lignin Precursors for Enhanced Mechanical Performance", ACS Sus Chem Eng, 2018**,** DOI:10.1021/acssuschemeng.8b02697
8. Klett, A. S.; Payne, A. M.; Thies, M. C. Continuous-Flow Process for the Purification and Fractionation of Alkali and Organosolv Lignins. *ACS Sustainable Chemistry & Engineering* **2016***, 4*, 6689-6694.
9. Tuinstra, F.; Koenig, J. L. Raman spectrum of graphite. *J. Chem. Phys.* **1970***, 53*, 1126-1130
10. Ko, T. Raman spectrum of modified PAN-based carbon fibers during graphitization. *J Appl Polym Sci* **1996***, 59*, 577-580
11. Rodríguez, J. J.; Cordero, T.; Rodríguez-Mirasol, J. In *Carbon Materials from Lignin and Their Applications;* Production of Biofuels and Chemicals from Lignin; Springer: 2016; pp 217-262.
12. Snowdon, M. R.; Mohanty, A. K.; Misra, M. A study of carbonized lignin as an alternative to carbon black. *ACS Sustainable Chemistry & Engineering* **2014***, 2*, 1257-1263.
13. Alway-Cooper, R. M.; Anderson, D. P.; Ogale, A. A. Carbon black modification of mesophase pitch-based carbon fibers. *Carbon* **2013***, 59*, 40-48.