

Article

Carbon Fibers from UV-Assisted Stabilization of Lignin-Based Precursors

Meng Zhang, Jing Jin and Amod A. Ogale *

Chemical Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634, USA; E-Mails: mzhang2@g.clemson.edu (M.Z.); jingj@g.clemson.edu (J.J.)

* Author to whom correspondence should be addressed; E-Mail: ogale@clemson.edu; Tel.: +1-864-656-5483.

Academic Editor: Jonathan Phillips

Received: 28 May 2015 / Accepted: 16 June 2015 / Published: 18 June 2015

Abstract: Production of high strength carbon fibers from bio-derived precursors is of topical interest. Recently, we reported on dry-spinning of a partially acetylated softwood kraft lignin to produce carbon fibers with superior properties, but the thermo-oxidative stabilization step required a long time due to a slow heating rate needed to prevent the fibers from being heated too rapidly and sticking to each other. Here we report a rapid strategy of dual UV-thermo-oxidative stabilization (crosslinking) of dry-spun lignin fibers that significantly reduces the stabilization time. The fibers undergo reaction close to the surface such that they can be subsequently thermally stabilized at a rapid heating rate without fibers fusing together, which reduces the total stabilization time significantly from 40 to 4 h. Consequently, the glass transition temperature of UV irradiated fibers was about 15 °C higher than that of fibers without UV treatment. Stabilized fibers were successfully carbonized at 1000 °C and resulting carbon fibers displayed a tensile strength of 900 ± 100 MPa, which is amongst the highest reported for carbon fibers derived from softwood lignin-based precursors. These results establish that UV irradiation is a rapid step that can effectively shorten the total stabilization time for production of lignin-derived carbon fibers.

Keywords: carbon fiber; softwood lignin; UV irradiation

1. Introduction

The vast majority of commercial carbon fibers are currently produced from polyacrylonitrile (PAN) precursor fibers that are obtained by a wet-spinning process [1–3]. Unfortunately, during subsequent thermo-oxidative crosslinking (also referred to as “stabilization”) and carbonization steps, toxic by-products (*viz.* hydrogen cyanide) are generated, and the wet-spinning process involves the use of hazardous solvents [1–3]. The environmental concerns and related costs associated with this process can be overcome by using alternative bio-based precursors. Amongst naturally occurring biomass, lignin is regarded as a potential carbon fiber precursor due to its low cost and high aromatic content.

Different types of lignin precursors have been explored to produce carbon fibers, and most of these studies involved melt-spinning of a fusible lignin, which possessed a low enough softening temperature [4–10]. On the other hand, the normally low glass transition temperatures (T_g) of such lignin precursors required a slow heating rate to achieve crosslinking without fibers becoming tacky. According to Braun’s analysis for continuous heating transformation [4], heating rate during thermal stabilization needs to be below 0.06 °C/min to maintain the operating temperature below T_g of the reacting hardwood kraft lignin. Also, it was reported that a slower heating rate led to higher T_g [4].

Kadla *et al.* [5] showed that hardwood kraft lignin fibers could be thermally stabilized at a heating rate of 2 °C/min. Sudo and Shimizu [6] converted a steam exploded lignin into carbon fiber using a heating rate between 1 and 2 °C/min. Uraki *et al.* [7] prepared carbon fiber using lignin from aqueous acetic acid pulping of hardwood with a stabilization heating rate of 0.5 °C/min. Eckert and Abdullah described carbon fibers produced from melt-spinning of a thermally-stable acetylated softwood kraft lignin, but no tensile properties were reported for the carbon fibers thus produced [8]. Organosolv lignin was found to be sensitive to the heating rate during thermal stabilization. A heating rate below 0.2 °C/min for Alcell lignin fibers was needed to prevent the fibers from fusing together [5]. Also, in a study reported by Baker *et al.*, an organic purified lignin even required a heating rate as low as 0.01 °C/min to crosslink [9]. Organosolv lignin is readily processed compared with other lignin precursors due to its low T_g and stable melt viscosity imparted by substituents, but it lacks the ability to crosslink rapidly. For these lignin-based carbon fibers, tensile strength was reported to be no more than 660 MPa.

A DOE presentation reported on melt-spun precursor fibers obtained from a modified technical lignin, with carbon fiber strength of 1.07 GPa [10]. However, further development efforts appear to be restricted by the unavailability of precursors (lignin grades not specified) that meet stringent melt spinning requirements [11]. Recently, we have reported on an alternative route, namely dry-spinning, using an acetylated version of commercially available softwood lignin where stable melt viscosity was not necessary for processing. The resulting carbon fibers displayed a tensile strength of 1.04 GPa [12], which is amongst the highest reported for lignin-based carbon fibers. However, the thermal stabilization step required about 40 h, a relatively long duration. Norberg *et al.* reported a fast oxidative-stabilization using 15 °C/min with fibers melt-spun from a selected type of softwood kraft lignin, but the diameter of resulting precursor and carbonized fibers were too thick, and no tensile properties were reported [13].

In other prior studies, we have investigated UV-assisted stabilization of PAN precursor fibers to accelerate the stabilization process using photo-sensitive precursors [14–17]. However, the role of UV irradiation for stabilization of lignin precursor fibers has not been systematically addressed. Many studies have focused on reducing photo-yellowing effect caused by light-induced deterioration of wood

surfaces [18–21], but none have taken advantage of UV irradiation to increase kinetics of stabilization for the production of lignin-based carbon fiber. Therefore, the primary objective of the present study was to investigate the effect of UV radiation on accelerating the stabilization of a partially acetylated softwood kraft lignin precursor to produce carbon fibers.

2. Experimental Section

2.1. Carbon Fiber Preparation

Lignin fibers were produced by dry-spinning of an acetylated softwood kraft lignin (Indulin AT™, Mead-Westvaco, Charleston, SC, USA). Softwood kraft lignin (SKL) was reacted with acetic anhydride (0.66 mL/g) at 90 °C to obtain acetylated SKL (Ace-SKL). Our objective was to increase the thermo-oxidative stabilization speed, thus hydroxyl groups were needed in the precursor fibers. We have recently reported that when acetic anhydride amount decreased from 15 to 0.66 mL per gram of lignin, the weight gain of modified lignin (due to acetylation) reduced from 18% to 5%, respectively, and the hydroxyl peak intensity in FTIR spectra increased three-fold [12,22]. Thus, we accomplished partial acetylation using a low acetic anhydride-to-lignin ratio (0.66 mL acetic anhydride per gram of lignin), in contrast to prior literature studies where a high degree of acetylation was done to achieve melt stability [8].

For dry-spinning, the above Ace-SKL was dissolved in acetone at a solid content around 75%. The viscous solution was transferred into a spinning barrel equipped with a 12-hole die (capillary diameter of 75 µm), and fiber spinning was performed at a constant throughput in a custom-designed batch spinning unit (AJA Inc., Greenville, SC, USA). The fiber tows were pre-stretched about 8× to obtain thin lignin-based precursor fibers with a diameter of about 15 µm.

The fiber tows were mounted in a fixture for UV irradiation. One side of the tow was fixed, whereas the free end was loaded to apply tension during UV treatment. The fiber tows were put into a UV chamber and irradiated with a Nordson 4.5 kW UV curing lamp having a mercury bulb radiation source. Cooling air was blown into the chamber during the irradiation procedure to maintain the chamber temperature below 50 °C.

The UV-treated fiber tows were removed from the UV irradiation fixture and thermo-oxidatively stabilized up to 250 °C under tension. After stabilization, fibers were carbonized under tension using a customized graphite rack in a HP 50 high temperature furnace (GT Advanced Technologies, Merrimack, NH, USA) at 1000 °C.

2.2. Characterization

For the FT-IR study, freshly prepared Ace-SKL powder was dissolved in acetone to prepare a 0.03 g/mL solution. 500 mg pure KBr were pressed into a 13-mm diameter pellet using a hydraulic press. Two drops of the Ace-SKL solution were applied on the surface of KBr pellet using a pipette and the Ace-SKL coated pellets were put into vacuum oven at 50 °C for 2 h to fully evaporate the acetone. FT-IR spectroscopy was performed in the transmission mode with a Thermo Nicolet Nexus 870 spectrophotometer (Thermo Scientific, Waltham, MA, USA).

Differential scanning calorimetry (DSC) was performed using a Pyris 1 DSC (Perkin Elmer Instruments, Waltham, MA, USA). The samples consisted of UV irradiated Ace-SKL fibers and “control” fibers that

were purposely blocked from UV radiation. The fibers were ground into powder and the sample pans containing grounded fiber were heated from room temperature to 250 °C under N₂ at a heating rate of 30 °C/min and cooled to room temperature at the same rate. For each sample, the second heating run was used to calculate T_g using the half ΔC_p method.

Gel permeation chromatography (GPC) was conducted for Ace-SKL fibers using a Waters Alliance GPCV 2000 model equipped with a Styragel HT4 column (Waters, Milford, MA, USA) and Polargel (Agilent, Santa Clara, CA, USA) column. Fibers were ground into powder and dissolved in dimethylformamide solution containing 0.05 M lithium bromide at a concentration of 1 mg/mL.

For tensile testing of carbon fibers, a Phoenix tensile testing device was used following the ASTM test method D-3379-75 [23]. The modulus and strain-to-failure values are reported without any system compliance correction. The load cell of the MTS apparatus has a maximum capacity of 500 g, and the cross head speed was set to 0.5 mm/min. Individual fibers were mounted on paper tabs for tensile tests, and nominally 25 samples per group of fibers were tested using a gage length of 10 mm. The fiber diameters were calculated via single slit laser diffraction method and further verified from SEM micrographs.

3. Results and Discussion

3.1. FTIR

The Ace-SKL coated KBr pellets were irradiated in the UV chamber for 3, 10, 15, 20, and 25 min total exposure time. Also, an Ace-SKL coated “control” pellet was wrapped in aluminum foil to block the UV but kept in the UV chamber for the same exposure time. The FTIR spectra for various samples are displayed in Figure 1. For the UV irradiated pellets, the spectra were normalized with the intensity of 1369 cm⁻¹ band attributed to C–H stretch in –CH₃ group [24,25], which is expected to remain fairly unchanged due to the relatively stable –CH₃ group.

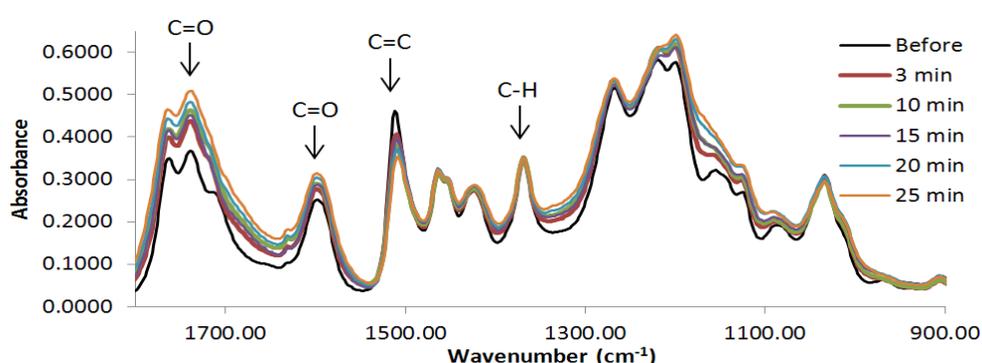


Figure 1. FTIR spectra of acetylated softwood kraft lignin (Ace-SKL) after different durations of UV treatment.

There was no measurable change in the FTIR spectrum of the control pellet. For UV irradiated samples, absorbance of 1740 cm⁻¹ and 1599 cm⁻¹ band increased significantly indicating the formation of new carbonyl groups [24,25]. The 1512 cm⁻¹ peak, attributed to the aromatic skeletal vibration [24,25], decreased during UV treatment, which indicates the degradation of aromatic rings. Relative intensities of I_{1740}/I_{1369} and I_{1512}/I_{1369} are plot in Figure 2 against the irritation time. Within the first 3 min, I_{1740}/I_{1369}

increased from 1.04 to 1.25, whereas the I_{1512}/I_{1369} decreased from 1.31 to 1.16. Then the change of relative intensities slowed down for larger reactions times of up to 25 min.

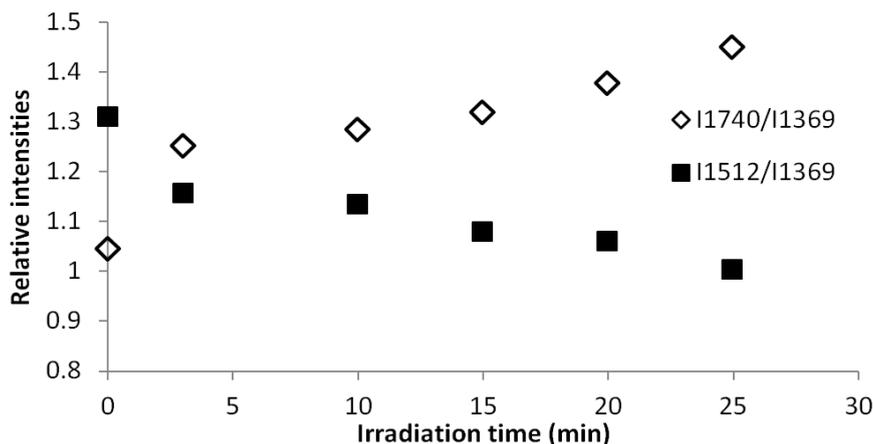


Figure 2. Relative intensity change of 1740 cm^{-1} and 1512 cm^{-1} peaks as a ratio of 1369 cm^{-1} peak after UV treatment for different durations.

It has been established in prior literature studies that esterification is an effective way to prevent the photo-yellowing of paper due to the reduced formation of phenoxy radicals [24,25]. In those studies, the sensitivity of lignin to UV was dramatically reduced when hydroxyl groups were completely substituted by ester groups. However, our study is aimed towards increasing thermo-oxidative stabilization speed, thus hydroxyl groups were needed in the precursor fibers. Therefore, as noted earlier, acetylation was performed using a low acetic anhydride to lignin ratio (0.66 mL acetic anhydride per gram of lignin) [12,22]. Thus, the acetylation in this study was a partial esterification where acetyl substituents enhanced solubility of the resulting precursor in acetone that allowed for subsequent dry-spinning, and yet preserved a fraction of hydroxyl groups for subsequent stabilization. As shown in the FTIR spectra, the Ace-SKL retained sensitivity to UV and the positive effect of UV to stabilization was proven in the following studies.

3.2. DSC

A 15-min UV treated fiber tow and a control fiber tow with UV blocked were both put into oxidation oven for thermo-oxidative stabilization and subjected to a $1.2\text{ }^{\circ}\text{C}/\text{min}$ heating rate. A portion of such fibers were taken out of the oven at 100, 130, 160, 190, and 220 $^{\circ}\text{C}$, for DSC testing. Control fibers removed at 160 $^{\circ}\text{C}$ and higher temperatures were almost completely fused together, as displayed in the SEM image of Figure 3. As illustrated in a later section, the UV irradiated fibers retained fiber shape without became tacky during the entire heat treatment.

The DSC thermograms are displayed in Figure 4. The results for fibers heat treated to 250 $^{\circ}\text{C}$ are not shown because the highly crosslinked samples did not give a clear T_g transition from DSC. After UV treatment, the UV treated fibers had a higher T_g of 134 $^{\circ}\text{C}$ as compared with 118 $^{\circ}\text{C}$ for control fibers. T_g for both group of fibers increased gradually as the thermo-oxidative crosslinking increased. After 160 $^{\circ}\text{C}$, T_g increased faster as shown in Figure 5 due to the higher reaction rate at elevated temperatures.

Although the T_g increase followed the same trend for control fibers, it was far below the oven temperature after reaching 160 °C, which caused fusing of the fibers.

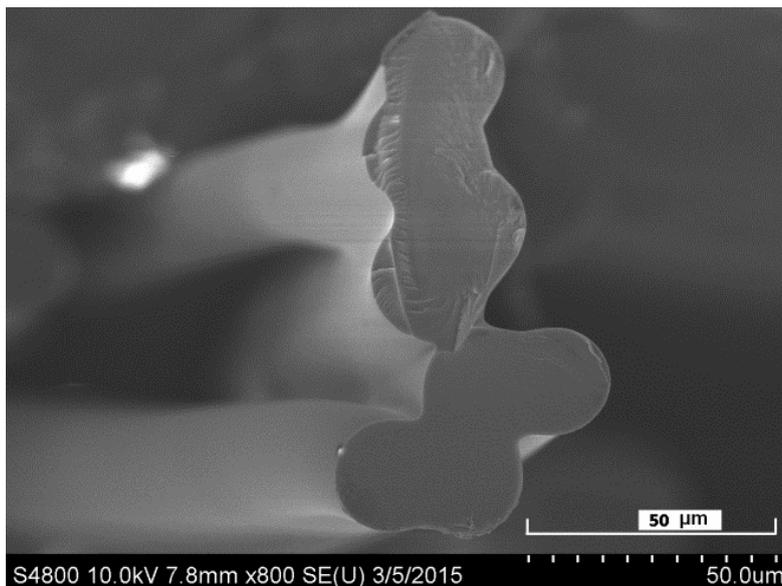


Figure 3. SEM image of Ace-SKL control fibers (without prior UV treatment) heated rapidly at 1.2 °C/min that led to multiple fibers fusing together.

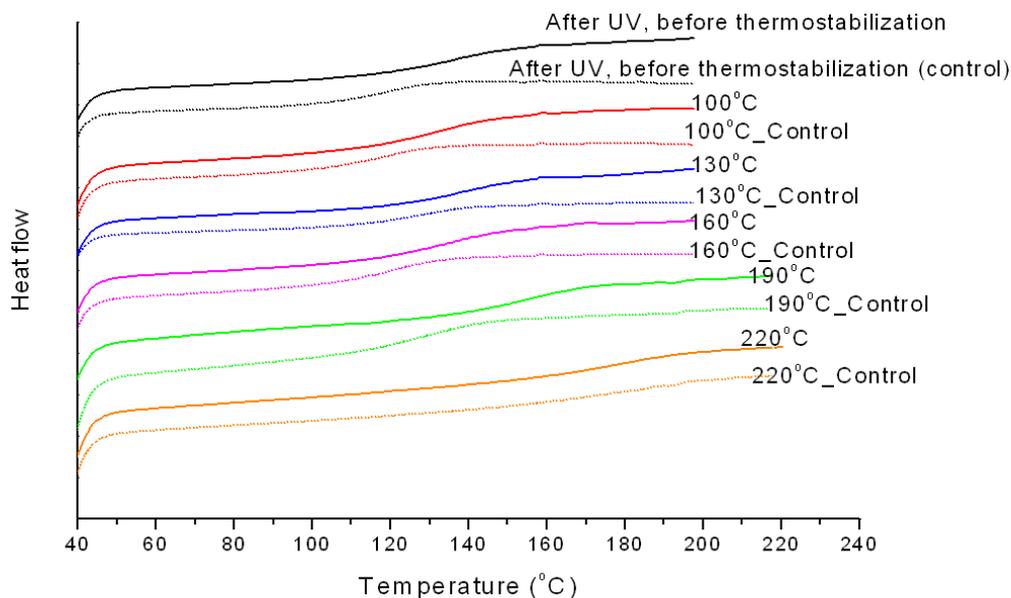


Figure 4. Differential scanning calorimetry (DSC) thermograms of various lignin-based precursor fibers thermally treated up to different temperatures. Solid curves: thermograms of fibers after UV irradiation; dashed curves: thermograms of control fibers without UV exposure.

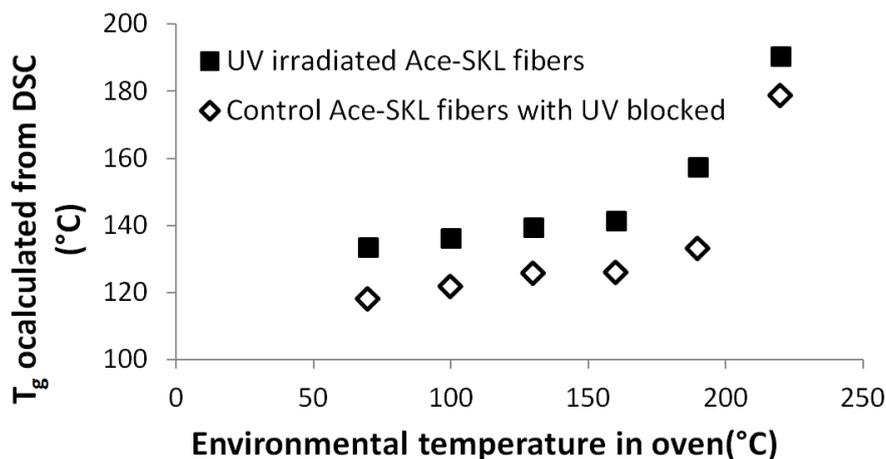


Figure 5. T_g shift of UV treated and control fibers as a function of thermal stabilization temperature.

3.3. GPC

Ace-SKL fibers UV-treated for 3 and 15 min, and a control group of fibers were studied using GPC. The chromatograms, displayed in Figure 6, enabled computation of the number average molecular weights (M_n) of 7790, 8756, and 10636 for control (no UV), 3-min, and 15-min UV-treated samples, respectively. The corresponding weight-average molecular weight (M_w) values were 63209, 72797, and 87163, confirming that the molecular weight of Ace-SKL fibers after UV treatment was higher than that for the control fibers.

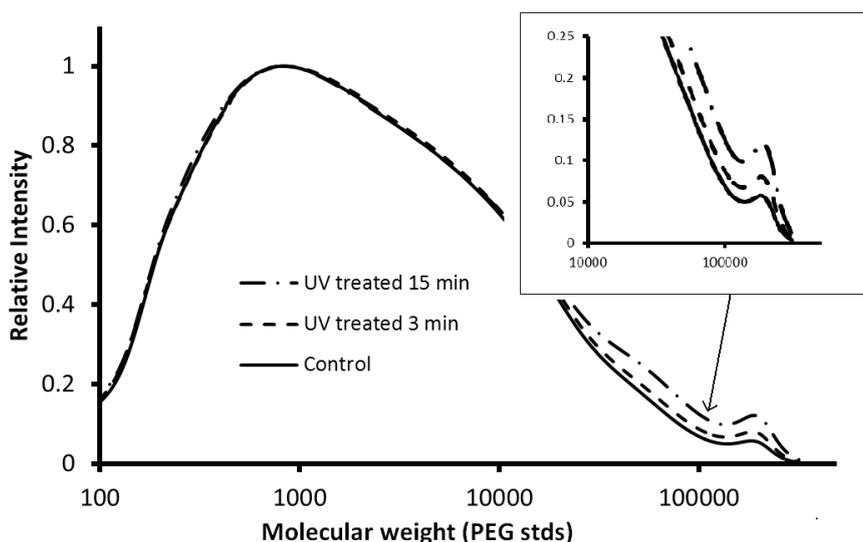


Figure 6. Gel permeation chromatography (GPC) chromatograms of Ace-SKL fiber samples with different UV treatment time.

Although the difference was small, the resulting molecular weights were obtained from the whole fibers including UV-affected surface and inner fiber cores. Broadened peaks for fibers with 15 min UV treatment clearly indicate the presence of a small portion of larger molecular weight fraction. This result matches with that from previous studies which indicated that long term of UV irradiation can result in

decomposition of lignin, but at the beginning of light treatment a higher molecular weight fraction can form due to secondary reactions [26,27].

3.4. UV/Thermal Dual Stabilization

As shown in Figure 7, the fiber diameter of stretched as-spun lignin fibers was less than 15 μm . The crenulations on the surface of these fibers were caused by evaporation of acetone during dry-spinning.

SEM images of UV irradiated fibers are shown in Figure 8. Compared with fibers before UV treatment, the UV treated fibers displayed a smoother surface and the crenulations were somewhat flattened. The results also demonstrate that surface of those fibers underwent exothermic reactions, and the heat led to some degree of softening on the fiber surface. Tension was applied during UV irradiation to preserve molecular orientation, as the absence of tension or inadequate tension results in shrinkage of the fiber after UV treatment.

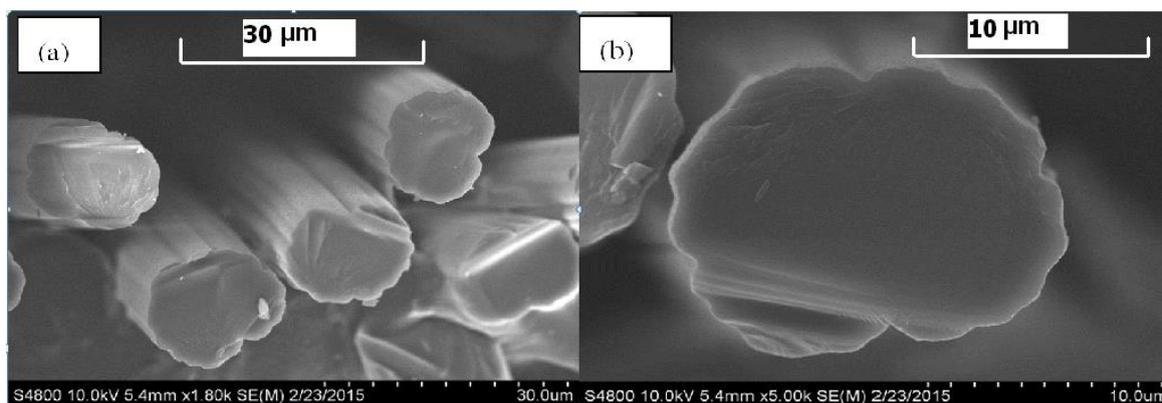


Figure 7. SEM micrographs of stretched as-spun Ace-SKL fibers at (a) low and (b) high magnification levels.

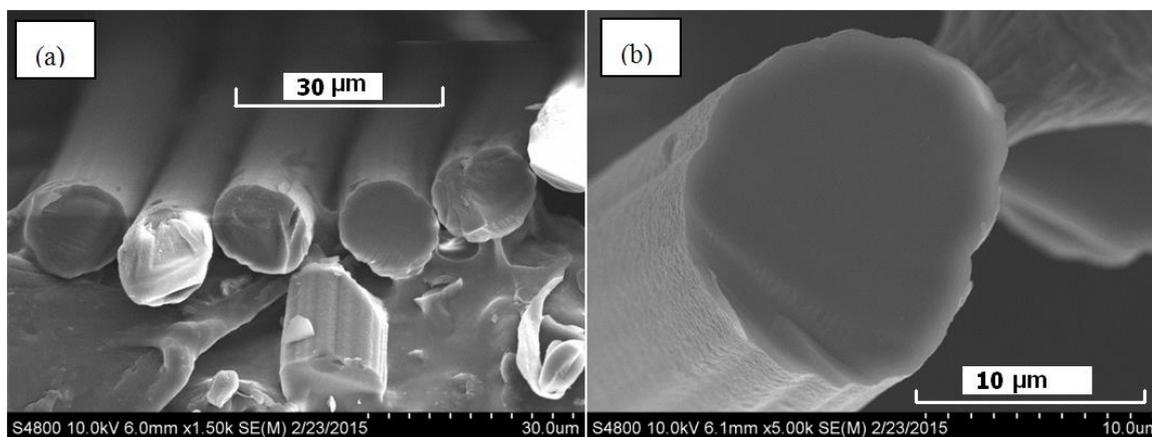


Figure 8. SEM images of UV-treated Ace-SKL fibers at (a) low and (b) high magnification levels.

Tension was also applied during thermal oxidative stabilization. In our previous study [12,22], Ace-SKL fibers required a slow heating ramp of 0.2 $^{\circ}\text{C}/\text{min}$ with several dwelling times to prevent fiber from being tacky. In contrast, UV-treated fibers in the present study could be thermally stabilized with a fast heating

rate of 1.2 °C/min without any dwell time. It is emphasized that at this fast heating rate of 1.2 °C/min, the control fibers that had not been UV irradiated completely lost the fiber shape when oven temperature reached 160 °C and multiple fibers fused together, as was shown earlier in Figure 3. The SEM image of stabilized fibers obtained using only thermo-oxidative stabilization (*i.e.*, no UV pretreatment), but a slow heating rate that took 40 h, are shown next in Figure 9a. Fibers stabilized by a UV/thermal dual mechanism at a fast heating rate of 1.2 °C/min are shown in Figure 9b. The flattened crenulations due to UV treatment are also displayed by the dual stabilized fibers.

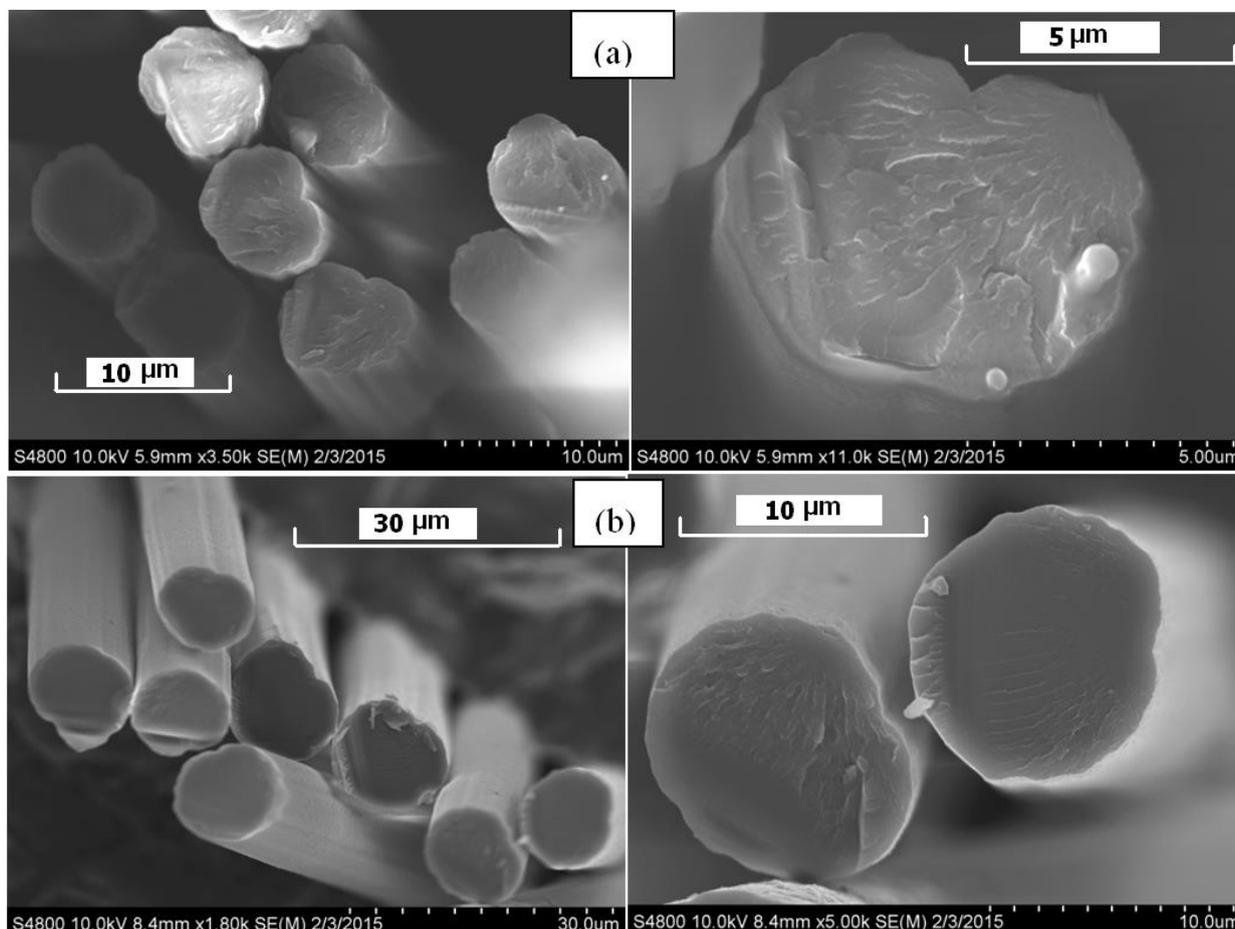


Figure 9. SEM images of stabilized Ace-SKL fibers (a) fibers without any prior UV treatment stabilized at a slow rate of 0.2 °C/min; (b) fibers with 15-min prior UV treatment stabilized at a fast rate of 1.2 °C/min.

The stabilized fibers obtained after UV treatment could be successfully carbonized. Figure 10a displays carbon fibers obtained after thermal/UV dual stabilization involving 15 min UV irradiation followed by a fast stabilization rate (1.2 °C/min) involving only 4 h. These carbon fibers prepared from dual stabilization method retained the crenulated shape of as-spun fibers. For comparison purpose, carbonized fibers obtained after a slow thermal oxidative stabilization (0.2 °C/min) over 40 h total are displayed in the micrograph of Figure 10b, which has many similarities to that in Figure 10a. Thus, the microstructural features of carbon fibers produced from UV/rapid oxidative stabilization are similar to those generated after single-step slow oxidative stabilization. When compared to circular fibers with the same cross-section area, rapidly stabilized fibers in Figure 10a have about 15% larger surface area, which

is slightly smaller than 21% larger area for carbon fibers obtained from slow stabilization, shown in Figure 10b. When such (lignin-based) carbon fibers will be embedded in an epoxy matrix to prepare a composite, the larger surface area will afford a larger interfacial bonding area and will lead to better fiber-matrix bonding.

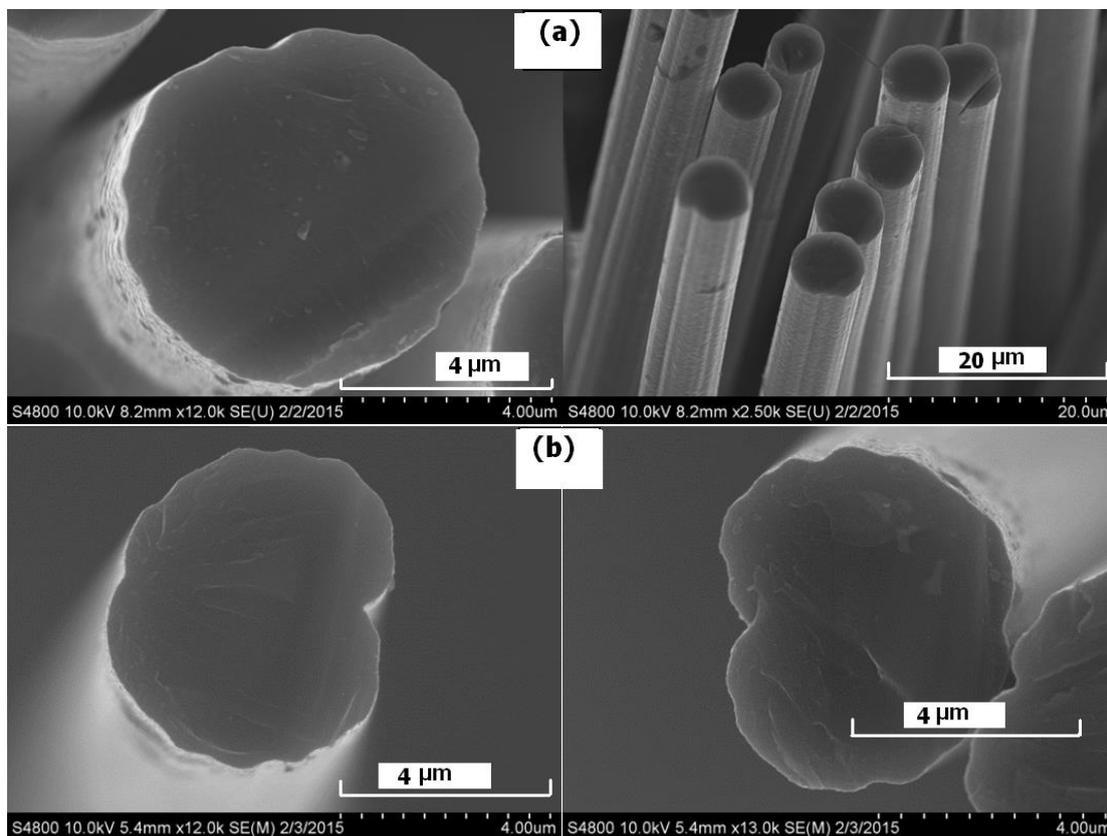


Figure 10. Carbonized Ace-SKL fibers from (a) UV/thermal dual stabilization (b) slow thermal stabilization.

The carbon fibers obtained from thermal/UV dual stabilization displayed a tensile strength, modulus and strain-to-failure values of 900 ± 100 MPa, 34 ± 2 GPa, and $2.6 \pm 0.2\%$, respectively. The corresponding values for carbon fibers obtained after a single-step slow stabilization process were 1040 ± 100 MPa, 52 ± 2 GPa, and $2.0 \pm 0.2\%$, as reported in our prior study [12]. Carbon fibers produced after the rapid stabilization process display about 10%–20% reduction in tensile strength and modulus, but about 20% increase in strain-to-failure. The heat generated from exothermic reactions during UV treatment likely led to some molecular relaxation within the oriented structure of the fibers, and result in the slight decrease in stiffness and strength. In future studies using a continuous process, such limitations can be overcome by increased draw-down throughout the entire process. It is noted, however, that the tensile strength reported here is still amongst the highest ones reported for lignin-derived carbon fibers obtained from rapid stabilization (*i.e.*, heating rate exceeding 1 °C/min) of precursors derived from commercially available softwood kraft lignin. As discussed earlier, some prior literature studies have reported high heating rates of 1 – 2 °C/min for hardwood kraft and steam exploded lignins, but those have resulted in lower tensile strengths of 422 and 660 MPa, respectively [5,6].

4. Conclusions

An acetylated softwood kraft lignin was dry-spun into fibers, and UV irradiated to induce crosslinking. The reactions induced with only 0.25 h (15 min) of irradiation effectively shortened the subsequent oxidative-stabilization time from 40 to 4 h, which is amongst the fastest stabilization processes reported for lignin-based carbon fibers. The increased extent of crosslinking reactions was confirmed using FTIR and GPC analysis, and it manifested into increased glass transition temperature. Stabilized fibers were successfully carbonized at 1000 °C, and resulting carbon fibers displayed a tensile strength 900 ± 100 MPa, which is amongst the highest reported for carbon fibers derived from softwood lignin-based precursors. These results illustrate that UV irradiation is a rapid route for shortening the stabilization time, which is often the rate-limiting step, for production of lignin-derived carbon fibers.

Acknowledgments

The authors gratefully acknowledge financial support from SERDP WP-1758 (ARL project monitor: John LaScala).

Author Contributions

Meng Zhang prepared the carbon fibers and conducted the characterization experiments. Jing Jin provided tensile test results and performed UV-treatment experiments. Amod A. Ogale provided overall instruction and supervision.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Edie, D.D.; Diefendorf, R.J. *Carbon-Carbon Materials and Composites*; Noyes Publications: Park Ridge, NJ, USA, 1993; pp. 20–33.
2. Fitzer, E.; Manocha, L.M. *Carbon Reinforcements and Carbon/Carbon Composites*; Springer: Berlin, Germany, 1998; pp. 17–28.
3. Peebles, L.H. *Carbon Fibers, Formation, Structure and Properties*; CRC Press: Boca Raton, FL, USA, 1995; pp. 7–24.
4. Braun, J.; Holtman, K.; Kadla, J. Lignin-based carbon fibers: Oxidative thermostabilization of kraft lignin. *Carbon* **2005**, *43*, 385–394.
5. Kadla, J.; Kubo, S.; Venditti, R.; Gilbert, R.; Compere, A.; Griffith, W. Lignin-based carbon fibers for composite fiber applications. *Carbon* **2002**, *40*, 2913–2920.
6. Sudo, K.; Shimizu, K. A new carbon fiber from lignin. *J. Appl. Polym. Sci.* **1992**, *44*, 127–134.
7. Uraki, Y.; Kubo, S.; Nigo, N.; Sano, Y.; Sasaya, T. Preparation of carbon fibers from organosolv lignin obtained by aqueous acetic acid pulping. *Holzforchung* **1995**, *49*, 343–350.

8. Eckert, R.C.; Abdullah, Z. Carbon Fibers from Kraft Softwood Lignin. U.S. Patent 7678358, 16 March 2010.
9. Baker, D.A.; Gallego, N.C.; Baker, F.S. On the characterization and spinning of an organic-purified lignin toward the manufacture of low-cost carbon fiber. *J. Appl. Polym. Sci.* **2012**, *124*, 227–234.
10. Warren, C.D.; Naskar, A.K. Lower cost carbon fiber precursors. Presentation at 2012 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Arlington, VA, USA, 16 May 2012. Available online: http://www1.eere.energy.gov/vehiclesandfuels/pdfs/merit_review_2012/lightweight_materials/lm004_warren_2012_o.pdf (accessed on 1 May 2015).
11. Baker, D.A.; Rials, T.G. Recent advances in low-cost carbon fiber manufacture from lignin. *J. Appl. Polym. Sci.* **2013**, *130*, 713–728.
12. Zhang, M.; Ogale, A.A. Carbon fibers from dry-spinning of acetylated softwood kraft lignin. *Carbon* **2014**, *69*, 626–629.
13. Norberg, I.; Nordström, Y.; Drougge, R.; Gellerstedt, G.; Sjöholm, E. A new method for stabilizing softwood kraft lignin fibers for carbon fiber production. *J. Appl. Polym. Sci.* **2012**, *128*, 3824–3830.
14. Paiva, M.; Kotasthane, P.; Edie, D.; Ogale, A.A. UV stabilization route for melt-processible PAN-based carbon fibers. *Carbon* **2003**, *41*, 1399–1409.
15. Naskar, A.K.; Walker, R.A.; Proulx, S.; Edie, D.D.; Ogale, A.A. UV assisted stabilization routes for carbon fiber precursors produced from melt-processible polyacrylonitrile terpolymer. *Carbon* **2005**, *43*, 1065–1072.
16. Morales, M.S.; Ogale, A.A. UV-induced crosslinking and cyclization of solution-cast polyacrylonitrile copolymer. *J. Appl. Polym. Sci.* **2013**, *128*, 2081–2088.
17. Morales, M.S.; Ogale, A.A. Carbon fibers derived from UV-assisted stabilization of wet-spun polyacrylonitrile fibers. *J. Appl. Polym. Sci.* **2014**, *131*, doi:10.1002/app.40623.
18. Plackett, D.; Dunningham, E.; Singh, A. Weathering of chemically modified wood. *Holz als Roh Werkstoff.* **1992**, *50*, 135–140.
19. Heitner, C. Light-induced yellowing of wood-containing papers: An evolution of the mechanism. In *Photochemistry of Lignocellulosic Materials*; Heitner, C., Scaiano, J.C., Eds.; American Chemical Society: Washington, DC, USA, 1993; Volume 531, pp. 2–25.
20. Feist, W.C.; Rowell, R.M.; Ellis, W.D. Moisture sorption and accelerated weathering of acetylated and methacrylated aspen. *Wood Fiber Sci.* **1991**, *23*, 128–136.
21. Chang, H.; Su, Y.; Chang, S. Studies on photostability of butyrylated, milled wood lignin using spectroscopic analyses. *Polym. Degrad. Stab.* **2006**, *91*, 816–822.
22. Zhang, M.; Ogale, A.A. Carbon Fibers Derived from Acetylated Softwood Kraft Lignin. In *Polymer Precursor-Derived Carbon*; ACS Symposium Series; Naskar, A.K., Hoffman, W.P., Eds.; American Chemical Society: Washington, DC, USA, 2014; Volume 1173, pp. 137–152.
23. Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single-Filament Materials (Withdrawn 1998); ASTM D3379-75(1989)e1; ASTM International: West Conshohocken, PA, USA, 1975

24. Faix, O. Classification of lignins from different botanical origins by FT-IR spectroscopy. *Holzforschung* **1991**, *45*, 21–28.
25. Paulsson, M.; Simonson, R. Acetylation of lignin and photostabilization of lignin-rich mechanical wood pulp and paper. In *Chemical Modification, Properties, and Usage of Lignin*; Hu, T.Q., Ed.; Springer: New York, NY, USA, 2002; pp. 221–245.
26. Koch, H.; Hübner, K.; Fischer, K. The influence of light on the molecular mass of lignin. *J. Wood Chem. Technol.* **1994**, *14*, 339–349.
27. Fischer, K.; Beyer, M. Comparison of light-induced and heat-induced yellowing of pulp. *Lenzing. Ber.* **2000**, *79*, 25–31.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).