On the Characterization and Spinning of an Organic-Purified Lignin Toward the Manufacture of Low-Cost Carbon Fiber

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ABSTRACT: A Kraft hardwood lignin (HWL) and an organic-purified hardwood lignin (HWL-OP) were evaluated as potential precursors for the production of low-cost carbon fibers. It was found that the unpurified HWL exhibited poor spinnability while the HWL-OP exhibited excellent spinnability characteristics. Fibers of various diameters were obtained from the HWL-OP. Thermo-stabilization studies showed that oxidative stabilization can only be used to convert HWL-OP-based fibers into carbon fibers if extremely low heating rates are applied. Carbonized lignin-based fibers had tensile strength of 0.51 GPa and tensile modulus of 28.6 GPa. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 227–234, 2012

Key words: biofibers; crosslinking; fibers; mechanical properties; stabilization

INTRODUCTION

At present, the majority of carbon fiber is manufactured from polyacrylonitrile (PAN) starting materials while a small amount, $\sim$ 5%, is derived from pitches, notably mesophase. However, due to the high cost of these petroleum-based precursors and their associated processing costs, carbon fiber remains a specialty product and as such has been largely limited to use in aerospace, high-end sporting goods, and advanced industrial applications.

Currently, as part of the US Department of Energy (DOE) Automotive Lightweight Materials Program, Oak Ridge National Laboratory (ORNL) is conducting research directed at examining the potential of lignin as a precursor material for the manufacture of low-cost carbon fiber. Carbon fiber-reinforced composites could substantially reduce the weight of passenger vehicles, increase vehicle fuel economy, and result in lower greenhouse gas emissions. To place

the potential increase in fuel economy into perspective, body-in-white modeling indicates that over 60% of the steel in a vehicle could be replaced with carbon fiber-reinforced composite materials, without impacting vehicle crash worthiness, and every 10% reduction in weight of the vehicle translates into an increase of fuel economy of 6–8%.[1] However, PAN-based carbon fiber is too expensive for large scale automotive use, which necessitates a large reduction in cost of appropriate strength fiber ($\geq$172 GPa tensile modulus and $\geq$1.72 GPa tensile strength) from about \$20/lb to about \$5/lb. The cost of PAN precursor material currently accounts for about 50% of the cost of manufacturing carbon fibers, and therefore emphasis in the ORNL research work described in this article has been placed on the development of processes utilizing lignin, a low cost and renewable resource material, as a precursor for low-cost carbon fiber production.

Several groups have investigated the possibility of producing carbon fibers from various lignins.[2–6] Such work has included the synthesis of fibers from unpurified Kraft lignins[7] (i.e., lignin obtained as a byproduct of paper manufacture), processed or purified lignins,[8–11] chemically modified lignins,[8,9,12] plasticized lignins,[13] and biolignins[7,14] (i.e., isolated as a by product from the production of ethanol fuel from lignocellulosic materials). However, previous studies were carried out on a small scale, producing small quantities of single filament lignin fibers that were subsequently stabilized and carbonized. The fibers obtained were typically of greater than 30 μm in diameter,[15,7] exhibited many flaws visible by scanning electron microscopy, and had relatively

poor mechanical properties, e.g., tensile strength $\leq$0.66 GPa and moduli $\leq$45 GPa.[7,8]

ORNL is evaluating several diverse sources of lignin as potential feedstock for low-cost carbon fiber manufacture. In this article, we describe the efforts directed at the characterization and evaluation of a Kraft lignin material derived from the Kraft pulping of hardwood (predominantly red and white oaks) for the production of paper.

EXPERIMENTAL

Materials

The hardwood lignins used for this study were supplied by MeadWestvaco Corp., Charleston, SC. The first lignin, designated as "HWL," was isolated in powder form from the black liquor obtained during the Kraft pulping process. The second lignin, "HWL-OP," was a modified version of the first lignin and was obtained by a proprietary purification process, which involved extraction of the lignin with organic solvents to eliminate contaminants present in the original HWL material and to enhance its melt spinnability.

Characterization of lignin precursor

The potential of each lignin as a precursor for carbon fiber production was ascertained by examination of the purity, melt properties, rheological properties, and thermal properties of the lignins. Before any characterization and/or processing, lignin samples were dried under vacuum at 80°C for at least 48 h to minimize moisture content.

The softening, melt, and decomposition behavior of the HWL and HWL-OP lignins were characterized optically using a Fisher-Johns melting point apparatus. A small amount of dried lignin sample was placed between two microscope cover slips and placed on the heating platform of the instrument. An initial test with a fast heating rate was run to determine the temperature range for the softening point. Subsequent tests were done using a slower heating rate ($\sim$ 1–3°C/min) within $\sim$ 20°C of the expected transition temperature previously determined. Temperature values were recorded when the onset of softening, localized melting, appreciable melting, and full melting, respectively, were observed.

The glass transition temperature (T_g) of the lignins was measured by differential scanning calorimetry (DSC) using a TA Instruments Q200 apparatus. Dried lignin samples (2 $\pm$ 0.1 mg) were placed in a standard aluminum pan with lid and heated under nitrogen (UHP, 50 mL/min) to 80°C and held for 30 min to expel any remaining moisture in the sample. The sample was then cooled and equilibrated at 0°C. A second DSC trace was then obtained on heating the sample to 300°C at 5°C/min under nitrogen (UHP, 50 mL/min).

Ash content and carbon yield of the two lignins were measured by thermogravimetic analyses on a TA Instruments Q5000IR apparatus. Approximately 7.5 mg of lignin was mounted in a platinum pan and heated to 1000°C at a rate of 5°C/min under nitrogen (UHP, 50 mL/min), to give the carbon yield. The sample was then held isothermally for 30 min under an oxidative atmosphere (Zero air, 50 mL/min) to burn off the carbon and measure the inorganic ash residue.

Isothermal rheological characterization of the two lignins was carried out using a Rheometrics' Advanced Rheometric Expansion System (ARES) to evaluate viscosity changes as a function of time at constant temperature. Tests were conducted on each lignin sample at several temperatures around their softening points. Transient viscosity values were recorded isothermally and at a constant shear rate of 0.1 s^{-1} for durations of up to 2 h.

Melt spinning of lignin precursor and fiber characterization

The melt spinnability of the HWL and HWL-OP lignins was initially evaluated using a single filament Dynisco Laboratory Mixing Extruder (LME) with winding unit. Multifilament spinning trials were conducted using a pilot scale melt spinning unit, custom built by Alex James and Associates (Greenville, SC). The unit consists of a hopper, single-screw extruder with four heating zones, a Koch static mixer, a spin head housing a Zenith metering pump, and a spinneret assembly.

Before fiber melt spinning, dried lignin was pelletized using the pilot-scale melt spinning unit adapted with a 2-hole strand die, each hole being 3 mm in diameter. Pellets were then melt spun into fibers using the pilot-scale melt spinning unit adapted with a 12-hole spinneret, each hole being of 150 μm in diameter. Once suitable melt spinning conditions were established, the take-up (winding) speed was varied to change the drawdown ratio and therefore obtain fibers of various diameters, including the target diameter of 10 μm for carbon fiber production.

The lignin fiber samples were examined for flaws in their morphology using a Philips XL30FEG scanning electron microscope (SEM) and an optical microscope. Fiber diameter measurements were obtained from both SEM and optical images. A minimum of 10 diameter measurements were obtained for each fiber sample from which the average diameter and standard deviations were calculated.

Heat treatment of lignin fiber and characterization of carbonized fibers

Heat treatment studies to determine appropriate oxidative-stabilization conditions for lignin fibers

TABLE I
Softening and Melt Characteristic of Lignins Using Fisher-Johns Apparatus

	Melt description (°C)			
Lignin	Initial softening	Localized melting	Appreciable melting	Melting point (°C)
HWL	172	184	192	202
HWL-OP	108	112	120	128

were conducted using a Lindberg Blue M 4L Box Furnace, modified for increased air flow and distribution, using an air flow rate of 20 L/min. Carbonization studies to temperatures up to 1000°C were carried out on a Lindberg Blue M 2.54-cm diameter tube furnace with a nitrogen flow rate of 1 L/min after purging at 10 L/min for 15 min.

When possible, the tensile properties of carbonized fibers were measured by single-filament testing, according to ASTM standard D3379-75 procedure, using an Instron tensile testing machine model 3342 with $5N$ load cell. The diameter of the fibers was determined using SEM imaging.

RESULTS AND DISCUSSION

Characterization of lignin precursor

Results from the characterization of the softening, melt, and decomposition behaviors of both HWL and HWL-OP using the Fisher-Johns melting point apparatus are summarized in Table I. The HWL initially softened at 172°C exhibiting a change in hue from light to dark brown, whereas localized melting was observed at 184°C which was characterized by the formation of tiny droplets of liquid around solid particles. At 192°C, about half of the material had melted, and at 202°C, the sample was apparently fully melted, although a small amount of residual solid material could be observed, indicating that both melting and crosslinking (stabilization) of the lignin occurred simultaneously and/or that infusible components, such as three-dimensional lignin structures, cellulosic materials, or inorganic salts were present. The melt was dark reddish–brown in appearance and with continued heating to higher temperature, began to solidify indicating that crosslinking occurred. The HWL-OP initially softened at 108°C, showed localized melting at 112°C, appreciable melting at 120°C, and was fully melted at 128°C. The melt was of a clear brownish–red appearance and, in contrast to the HWL lignin, did not appear to crosslink under more prolonged heating at temperatures up to 200°C, indicating good thermal stability of the melt.

Results from TGA analysis in an inert atmosphere (N_2) showed that, after adjusting for moisture con-

tent, HWL gave a carbon yield of 38.5% at 1000°C and had an inorganic material (ash) content of 2.7 wt %. HWL-OP gave a carbon yield of 34.4% and, in marked contrast to HWL, did not contain any inorganic materials. The inorganic material contents of the two lignin materials were as expected since HWL is essentially lignin as isolated from the "black liquor" in the Kraft pulping process; the HWL-OP lignin was the HWL material purified in such manner to specifically eliminate the inorganic salts. The lower carbon content of the HWL-OP material was most likely due to a decrease in the molecular weight of the lignin as a result of the purification process, which also led to a lower melting temperature. DSC results (Fig. 1) showed that HWL exhibited a glass transition temperature (T_g), of 130.2°C, whereas the HWL-OP had a T_g of 88.0°C. It is apparent that there are significant differences in melt behavior between the lignins; these could be explained by the differences in their molecular masses, the relative degree of branching, 3D networking, and possibly differences in the distribution of chemical functionalities.

Isothermal rheological test results for both HWL and HWL-OP are shown in Figure 2. The data shows that HWL exhibited an unstable behavior, having a continuously increasing viscosity over time at constant temperature, indicating that degradation of the material occurs over relatively short periods of time, well below the residence time incurred during melt spinning (typically in the range of 30–60 min depending on throughput rate). This instability in viscosity is undesirable as it indicates that stable spinning conditions cannot be obtained. Lowering the temperature to reduce the rate of crosslinking or degradation is also impractical because the viscosity
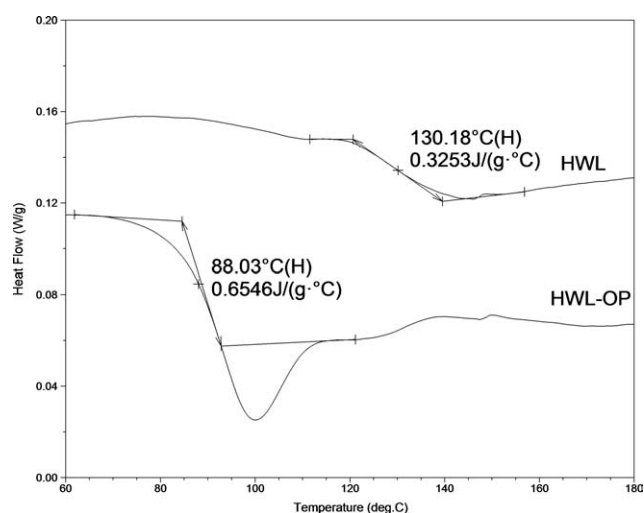

Figure 1 DSC traces for HWL and HWL-OP lignins under nitrogen. T_g values were calculated using the half-height (H) method.
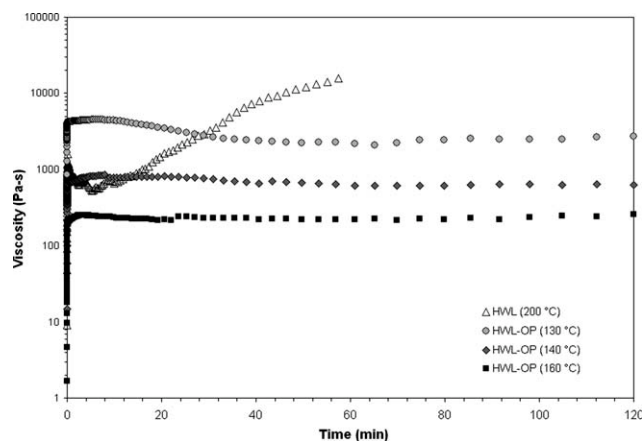
Figure 2 Transient viscosity of HWL and HWL-OP lignins at selected temperatures.

of the lignin melt would increase far beyond the useful range (100–1000 Pa s). In marked contrast, HWL-OP exhibited excellent viscosity-time stability over a relatively wide temperature range, with viscosity values between 200 and 1000 Pa s. The HWL-OP lignin material maintained a stable viscosity at each of the temperatures tested for at least 2 h; i.e., well above the residence time during melt spinning. This

Figure 4 SEM images of lignin fibers produced from HWL-OP lignin.

behavior is highly desirable, and, in general, indicates that the material could be readily melt spinnable.

Lignin melt spinning and fiber characterization

As indicated by the rheological data, initial melt spinning trials using the single filament LME unit showed that HWL exhibited very poor spinnability. Although the LME unit requires very short residence times for pelletization, the residence time during fiber spinning is much longer; the HWL foamed and subsequently crosslinked after being fed into the unit, making it impossible to obtain any fibers from this lignin material. On the other hand, HWL-OP was melt spun with very positive results and several single-filament spools were collected using the LME unit.

Spinning trials of the HWL-OP lignin were quickly moved from the LME to the pilot scale multifilament unit. Once appropriate process conditions were established in the extruder, metering pump, and spinneret, fibers were continuously spun over several hours without interruption (other than to change take-up spools) and without the need for the addition of alloying or plasticizing agents. Several spools of fiber were obtained at take-up speeds between

Figure 3 Spools of fibers produced from HWL-OP lignin utilizing the pilot scale unit with 12-hole spinneret. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
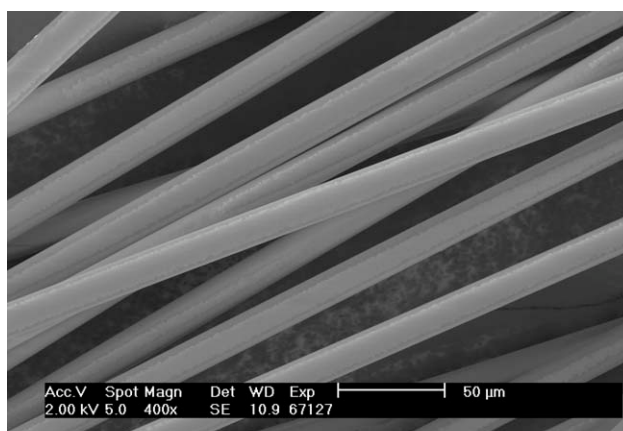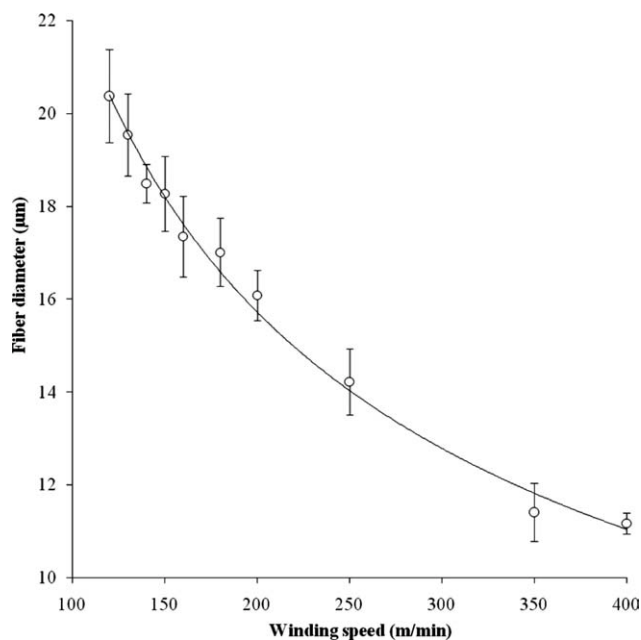
Figure 5 Lignin filament diameter as a function of winding speed for fibers produced from HWL-OP lignin. Data points are measurements from SEM imaging; line represents best fit of data; errors bars represent the standard deviation.

Figure 7 Glass transition temperature T_g (solid line) and heat capacity C_p (dashed line) for oxidized HWL-OP lignin fibers as a function of heating rate applied during oxidation.

120 m/min and 400 m/min. A photograph of some of these spools is shown in Figure 3.

SEM imaging of the lignin fibers produced from the HWL-OP lignin (Fig. 4) revealed that the filaments exhibited very uniform diameters, smooth outer surface, and a cross section structure that was totally devoid of air entrapment, impurity particles, or other observable defects. Diameter measurements were recorded from SEM imaging of samples obtained at various take-up speeds (Fig. 5). It was noteworthy that fibers as small as 11 μm in diameter were obtained. This represented a significant milestone in the demonstration of continuous
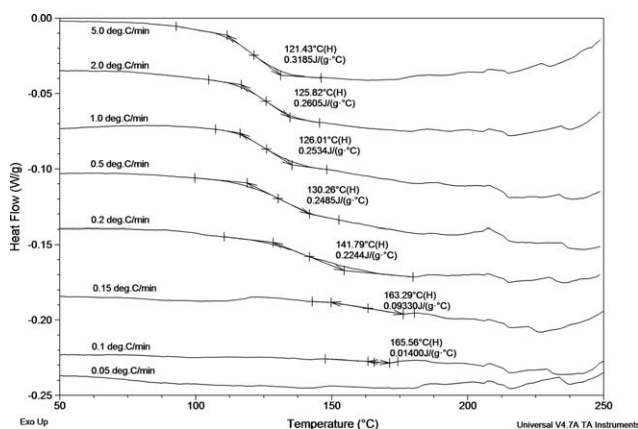

Figure 6 DSC traces of HWL-OP fiber showing the change in T_g due to heat treatment at various heating rates under oxidative conditions.
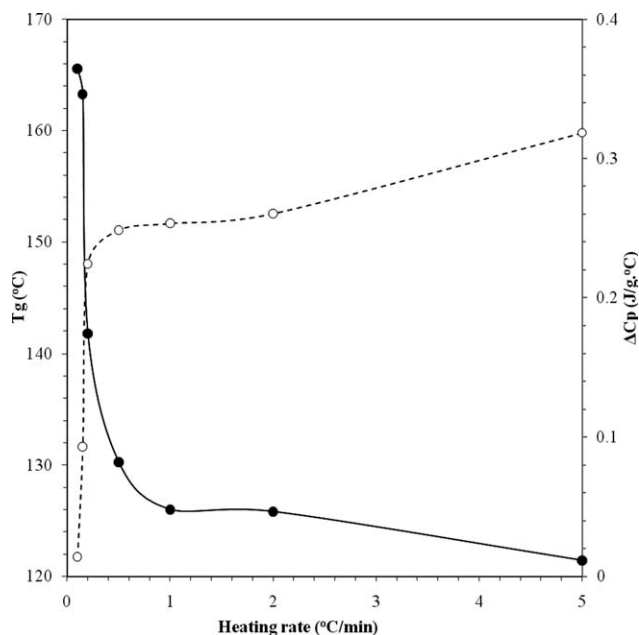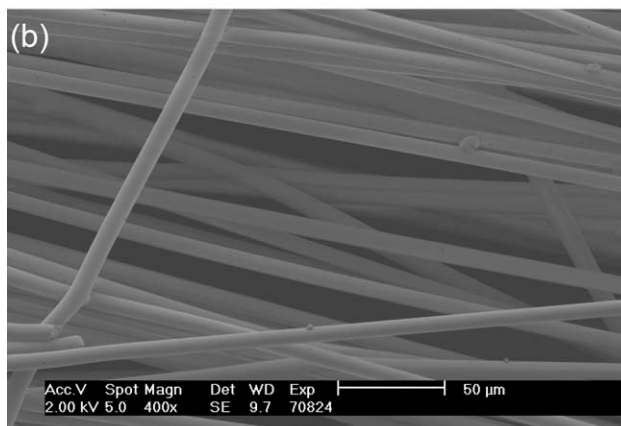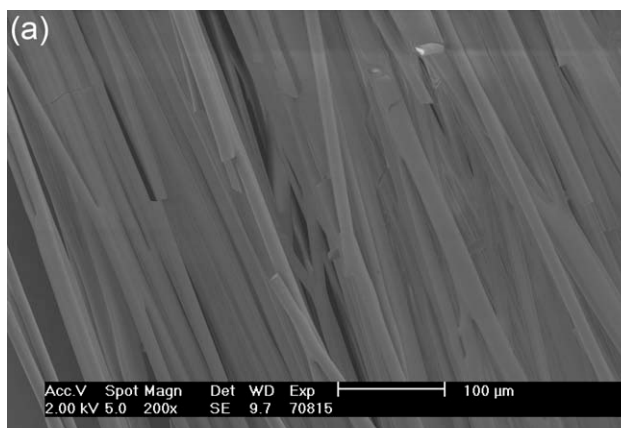

Figure 8 SEM micrographs of HWL-OP fiber oxidized at a heating rate of (a) 0.05°C/min and (b) 0.025°C/min, showing varying degree of axial fusing of fibers.
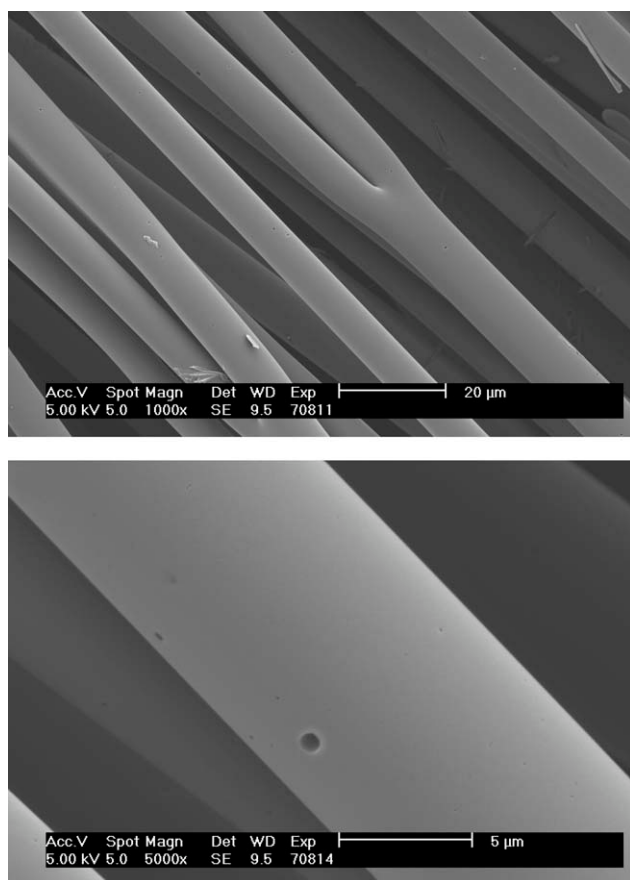
Figure 9 SEM micrographs of HWL-OP fiber carbonized to 1000°C at 2°C/min after stabilization at a heating rate of 0.05°C/min to 250°C.

melt spinning of lignin to produce lignin tow and was in marked contrast to previous studies[6,7,11,13] which have produced only semicontinuous fiber with a smallest diameter of 30 μm.

Thermostabilization studies

Carbonization by thermal treatment of the lignin fiber for conversion into carbon fiber is only possible if proper stabilization, which renders the material infusible, is achieved. Conventional oxidative stabilization of fiber typically involves bringing about a series of chemical reactions which give rise to preferential crosslinking through an oxidative mechanism; this requires elevated temperatures and precise control of the heating rate. Without this prior stabilization, the fibers will melt and fuse together during carbonization.

Although HWL-OP lignin showed excellent spinability and good fibers were obtained, the low melt temperature of the lignin presented a challenge for achieving proper stabilization. Fiber integrity depends on the ability to induce crosslinking in the lignin, so that the T_g of the material is maintained above the oxidation temperature, during thermal ramping.

To determine if oxidative stabilization ("oxidation") conditions were appropriate and a shift of T_g was achieved, thermal treatment studies on HWL-OP fibers of small diameters (in the range of 10–12 μm) were carried out using DSC. HWL-OP fibers were subjected to oxidative thermal pretreatment to 250°C, at heating rates as low as 0.01°C/min under air. The T_g of the resulting oxidized fibers was then determined from their subsequent DSC traces. The results (Fig. 6) showed that progressively slower rates of thermal oxidation increased the T_g of the fiber while reducing its heat capacity (Fig. 7). At oxidation rates lower than 0.05°C/min, T_g essentially disappeared, indicating that fully stabilized, infusible fibers, ought to be obtained at those rates. In agreement with the DSC results, thermal treatment of the HWL-OP fibers resulted in various degrees of fusibility, which was directly related to the thermal ramping rate; namely, fibers treated by heating at rates greater than 0.2°C/min melted during the heat treatment; fibers treated at rates of 0.15 and 0.10°C/min fused extensively and fiber form was significantly degraded; finally, fibers treated at rates of 0.05, 0.025, and 0.01°C/min maintained fiber form
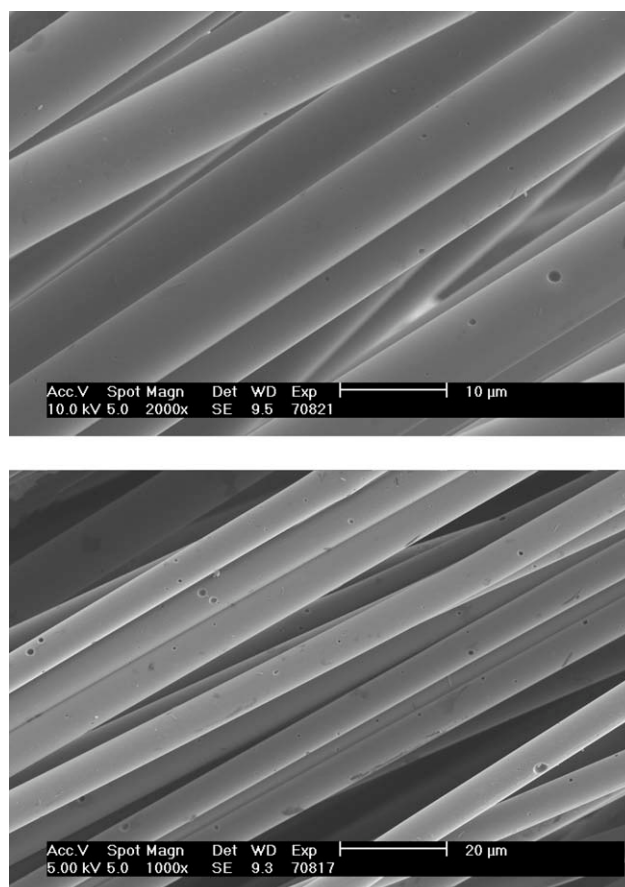

Figure 10 SEM micrographs of HWL-OP fiber carbonized to 1000°C at 2°C/min after stabilization at a heating rate of 0.025°C/min to 250°C.
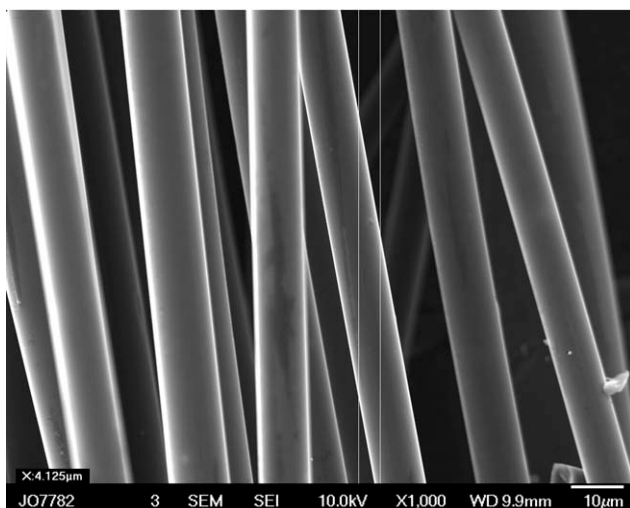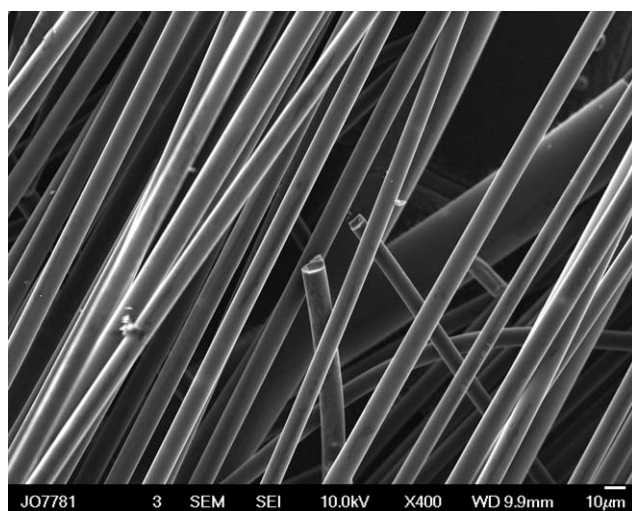
Figure 11 SEM micrographs of HWL-OP fiber carbonized to 1000°C at 2°C/min after stabilization at a heating rate of 0.01°C/min to 250°C.

but exhibited varying degrees of fusing along the fiber axis (Fig. 8).

Carbonization

Fibers that were oxidized at heating rates of 0.05, 0.025, and 0.01°C/min to 250°C and exhibited only light fusing were selected for further heat treatment (i.e., carbonization) to 1000°C in nitrogen at a heating rate of 2°C/min. SEM analysis of the carbonized samples showed that fibers oxidized at 0.05°C/min continue to retain fiber form but fused with characteristic "Y" joints. Furthermore, at higher magnifications evidence of volatiles escaping during the heat treatment procedures was observed, so that a few small holes could be observed on the fiber surface (Fig. 9).

Fibers that were stabilized at 0.025°C/min showed no extensive fusing upon carbonization; however, the fibers were not easily separable because partial
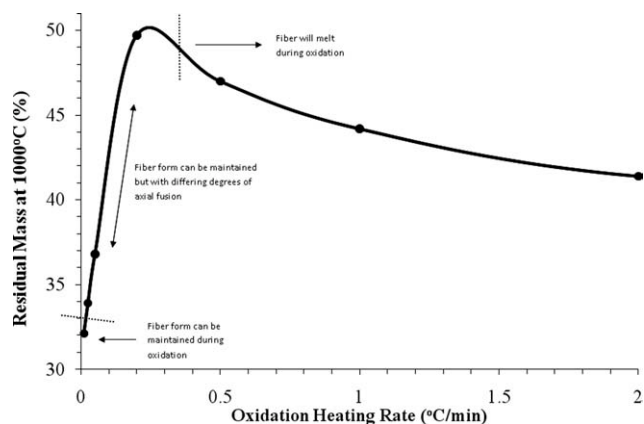

Figure 12 Residual mass of HWL-OP lignin as a function of heating rate during oxidation in air at 200°C and further thermal treatment to 1000°C in nitrogen.

fusing did occur along the fiber axis, indicating that the fibers were not fully stabilized (Fig. 10). These fibers were damaged during separation, and testing of mechanical properties was therefore not possible.

The fibers stabilized at the slowest rate of 0.01°C/min were separable upon carbonization with only little resistance, indicating a very small amount of axial fusing, and that a higher degree of stabilization was achieved at this very slow, but impractical, heating rate. The carbonized fibers (Fig. 11) had a mean diameter of 9.9 ± 0.8 μm, based on 20 measurements. Mechanical properties of the fibers were measured by single filament testing and the results showed that the fibers had a tensile strength of 0.52 ± 0.182 GPa (74.7 ± 26.4 ksi) and a tensile modulus of 28.6 ± 3.2 GPa (4.16 ± 0.46 Mpsi). These properties, although lower than some of the mechanical properties reported by previous works[7,8] and lower than the current target properties of 1.72 GPa tensile strength and 172 GPa tensile modulus, represent a significant step toward the continuous production of carbon fibers by melt spinning of lignin precursor.

The effect of varying the heating rate during the oxidation studies on the potential residual mass after further treatment (carbonization) to 1000°C in nitrogen was evaluated via TGA analysis of the powder HWL-OP lignin. Figure 12 shows that the residual mass of carbonized lignin powder increased as the oxidation heating rate increased until it reaches a maximum at a heating rate of 0.2°C/min. Unfortunately, due to the low melting temperature of the lignin, the fibers cannot maintain their form at or above this heating rate.

CONCLUSIONS

We have demonstrated that it is possible to significantly increase the spinnability characteristics of

a hardwood Kraft lignin, HWL, via an organic purification process. The purification process dissolves the bulk of the lignin away from contaminants (mineral and carbohydrate), and lower molecular weight lignin fractions are preferentially solubilized over higher molecular weight fractions. Thus, the organic-purified lignin, HWL-OP, contained a large proportion of low-molecular-weight fractions that were plasticizing agents for the lignin as a whole, which imparted the excellent melt spinnability characteristics.

Stabilization and carbonization studies on lignin fibers of small diameter ($\sim$ 11 μm) showed that fibers from HWL-OP could be oxidative stabilized only at very slow heating rates ($<0.05°C/min$). Gradually increasing heating rates led to various levels of fusing between the fibers, including melting of the fibers, and therefore loss of fiber form. DSC studies showed that decreasing heating rates increased the T_g and decreased its magnitude progressively so that crosslinking of the HWL-OP fibers could precede softening during heat treatment. Thus a stabilized fiber could be obtained.

Carbonization of fibers was only possible on those fibers oxidized at a maximum heating rate of $0.05°C/min$. However, mechanical properties of the carbonized fibers were poor. Efforts continue toward evaluation of alternative stabilization techniques to decrease the processing time. Additionally, mixing the lignin with other polymers is being evaluated as a means to improving the mechanical properties.

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