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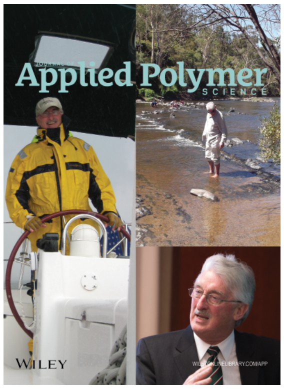
Special Issue: Sustainable Polymers and Polymer Science Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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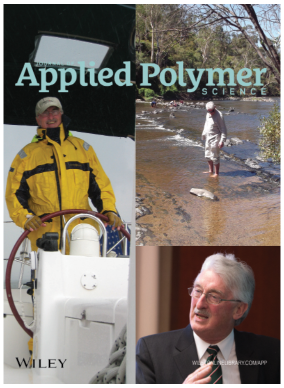

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Effect of temperature and concentration of acetylated-lignin solutions on dry-spinning of carbon fiber precursors

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ABSTRACT: Carbon fibers derived from biomass such as lignin have received increasing attention due to the sustainability of the precursor. In this study, partially acetylated softwood Kraft lignin (Ace-SKL) was investigated for the purpose of dry-spinning into carbon fiber precursors. The viscosity of solutions prepared from different concentrations of acetylated-lignin and acetone were investigated at high shear rates encountered during fiber spinning. Ace-SKL solutions displayed a significant shear-thinning behavior at all temperatures studied with power-law exponents ranging from 0.33 to 0.82, confirming the macromolecular nature of the Ace-SKL lignin/acetone solutions. As expected, elevated temperatures led to lower viscosities and facilitated extrusion at moderate pressures. Dry-spinning was performed over a range of concentrations and temperatures. Fibers obtained from room temperature dry-spinning displayed a relatively smooth surface but the pressure drop was excessive. Lignin fibers from elevated temperatures spinning displayed more crenulated surface pattern, and more crenulations achieved for fibers spun at higher temperatures. Presence of some doubly-convex and sharp crevices was found on fibers produced from solutions containing lower concentrations (1.85 and 2.00 g lignin/mL solvent). In contrast, no crevices were found on the fibers obtained from the concentrated solution (2.15 g/mL), likely due to the reduced extent of solvent out-diffusion. It was observed that the sharp crevices found in the lignin fibers spun at lower concentrations led to carbon fibers with occlusion type defects, thence reduced strength. In summary, this study elucidates the importance of precursor composition and processing conditions on microstructure and properties of resulting precursor and carbon fibers. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43663.

KEYWORDS: cellulose and other wood products; fibers; structure-property relations

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INTRODUCTION

Carbon fibers are the primary reinforcements in high performance composites because they possess excellent strength and stiffness, low density, and outstanding electrical and thermal conductivity. In addition, carbon fibers are chemically stable and fire-retardant.[1–3] Currently, the dominant carbon fiber precursor material is polyacrylonitrile (PAN). The high cost of carbon fibers manufactured from PAN precursor has limited their application. At the same time, development of environmentally friendly processes is gaining importance. Amongst these, conversion of low-cost biomass such as lignin into carbon fibers has received increasing attention.

Several review papers have covered the topic of lignin-based sustainable precursors for producing carbon fibers.[4–7] Due to the complexity and irregularity of lignin molecular structure, significant efforts are being devoted to improve the processibility of this raw material. Much of the previous research dealing with lignin-derived carbon fibers has focused on melt-spinnable lignin precursors. Sudo and Shimizu[8] modified a steam-exploded birch lignin by hydrogenolysis and solvent extraction. A fusible lignin fraction was obtained with a stable melt viscosity of under 400 Pa s. Kubo and coworkers[9] extracted a hardwood lignin using acetic acid. The low molecular weight fraction of this organosolv hardwood lignin was fusible and could be melt spun without any modification.[10] They also studied the processibility of a softwood lignin but could not easily convert it into a fusible precursor. They concluded that softwood Kraft lignin (SKL) is not a suitable raw material for thermoforming,[11] but hardwood Kraft lignin and Alcell organosolv lignin are fusible without any chemical modification.[12]

To increase spinnability, poly(ethylene oxide) (PEO) has been added as a plasticizer,[12] which helps reduce the spinning temperature. However, even with the addition of PEO, softwood Kraft lignin did not soften. Instead, it charred due to the larger extent of cross-linked structure in softwood lignin, in contrast to hardwood lignin.[12] Therefore, some studies have reported on mixing hardwood lignin into softwood lignin before extrusion to improve the flow characteristics.[13–15] In another study,

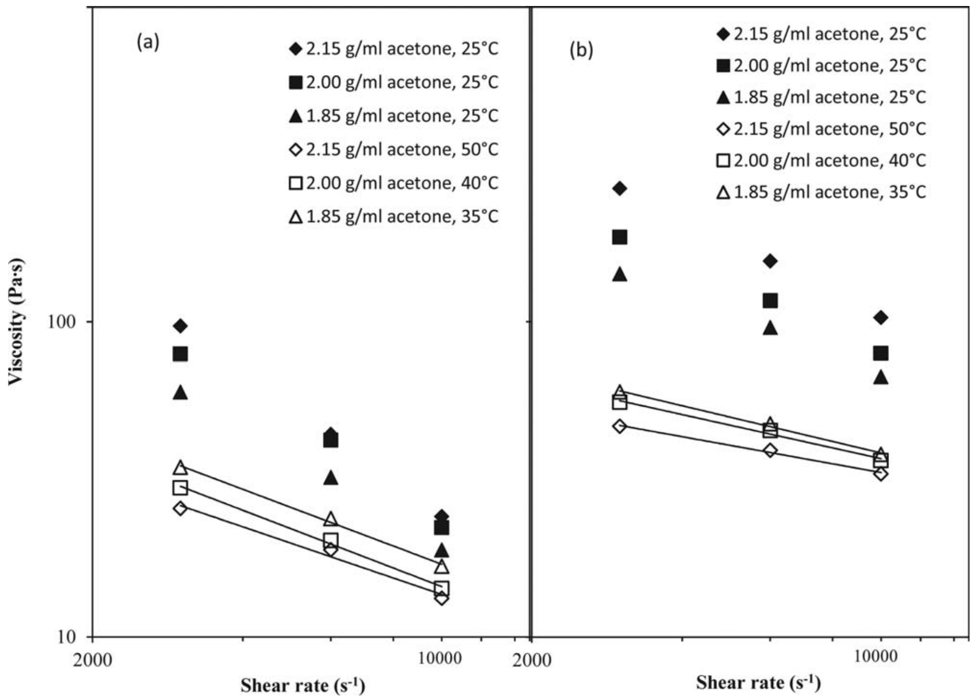

Figure 1. Shear viscosity of Ace-SKL solutions over a range of shear rates. (a) Viscosity obtained after Bagley correction using capillaries with L/D = 5, 15, and 20; (b) Viscosity obtained from capillaries with L/D = 5, without Bagley correction.

organoclay (organically modified montmorillonite) was introduced into a lignin as a reinforcement.[16] The strength of resulting carbon fibers from these studies was no higher than 660 MPa.[8] Baker and coworker employed thermal pretreatment to improve the melt flow properties of a lignin and the best carbon fibers they produced had strength of 1,070 MPa.[7]

Several recent studies have made attempts to introduce acrylonitrile (AN) or polyacrylonitrile (PAN) into lignin using wet spinning to develop carbon fibers. Maradur *et al.*[17] prepared a copolymer using a hardwood lignin and AN. The lignin-PAN copolymer was dissolved in dimethyl sulfoxide (DMSO) and converted into fibers through wet-spinning using a coagulation bath containing water. Xia *et al.*[18] conducted wet-spinning using lignosulfonate/PAN mixture and lignosulfonate-AN copolymer, respectively. Macrovoids were found in the as-spun fibers derived from lignosulfonate/PAN mixture, acting as defect in the resulting carbon fibers. However, the as-spun fibers obtained from lignosulfonate-AN copolymer were solid without voids. The resulting carbon fibers from this copolymer displayed a strength of 540 MPa. Similarly, lignosulfonate/PAN blend solution was prepared for wet spinning.[19] The lignin content used in this study ranged from 15% to 47%. Voids were still observed in the as-spun fibers. Liu *et al.*[20] produced carbon fibers from PAN/lignin and PAN/lignin/CNT precursor blends using gel-spinning technique. The low temperature spinning led to circular fibers with relatively smooth surface. A tensile strength of 1.72 ± 0.2 GPa was reported for the resulting carbon fibers. The stabilization kinetics of such blend as-spun fibers was discussed in a recent publication.[21] However, it is noted that the use of lignin-PAN blends still retains some of the environmental issues associated with PAN precursors.

In another recent study, we have reported on dry-spinning of acetylated softwood lignin solution where stable melt viscosity was not necessary.[22,23] The softwood Kraft lignin was partially acetylated to preserve a fraction of hydroxyl groups, which was favorable for the following thermal stabilization. In this process, only acetone was used as a solvent and spinning was conducted at ambient temperature. Lignin fibers solidified in the air while acetone evaporated rapidly. There are several advantages of this process. First, the thermal stability of precursor lignin was not a concern. Second, acetone is a benign solvent that can be recovered and recycled, and is used in scalable industrial processes such as cellulose acetate fibers.[24] Third, the resulting carbon fibers developed a crenulated surface, which presents a larger surface area that can enhance the fiber/matrix bonding when such fibers are converted into composites. The carbon fibers produced from such crenulated precursors displayed a tensile strength of 1,040 ± 100 MPa, which is amongst the highest reported for dry-spun lignin-based carbon fibers.[22,23] Also, in a recent study, we have reported on a novel UV-thermal process for rapid stabilization of dry-spun acetylated lignin fibers.[25] This dual mechanism led to a significant reduction of about 90% in the stabilization time (from 40 down to 4 h) and still produced carbon fibers that displayed a tensile strength of 900 MPa and modulus of 34 GPa.

The results reported above on lignin-derived carbon fibers are from lab-scale studies, which need to be scaled up for potentially manufacturing carbon fibers from such biomass-derived precursors. However, the flow characteristics and mass-transfer issues associated with acetylated-lignin/acetone solutions have not been systematically reported in the literature, although they play an important role during fiber spinning

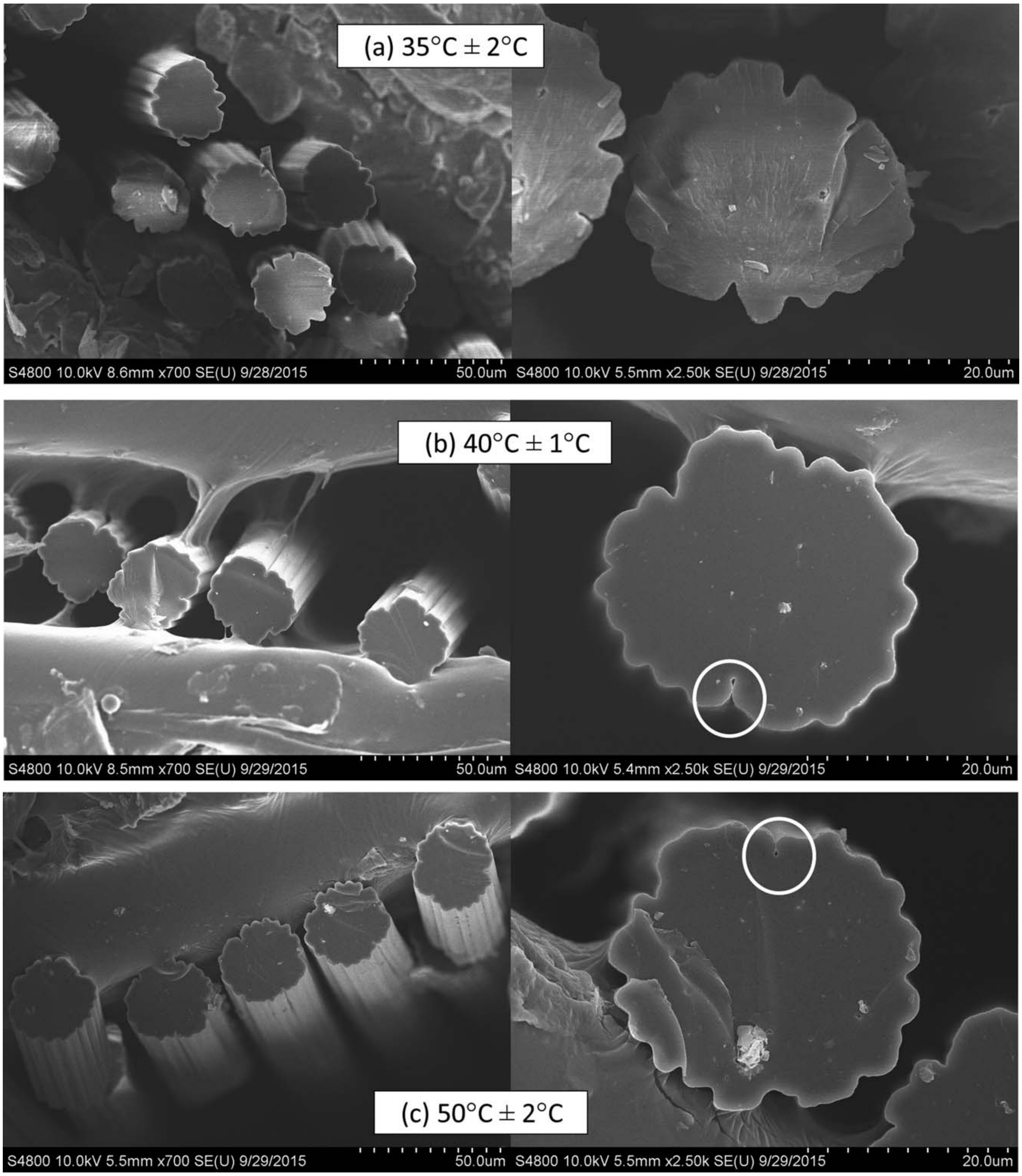

Figure 2. SEM images of Ace-SKL lignin fibers from a 1.85 g/mL solution, at various spinning temperatures.

(including evaporation of solvent) to form solid filaments. Therefore, the goal of this study was to investigate modified lignin-acetone solutions to establish a range of suitable combinations of solution concentrations and spinning temperatures that can facilitate scale-up studies. The specific objectives were to conduct dry-spinning under various conditions to obtain different precursor fiber morphologies and then to determine their effect on the microstructure and properties of resulting carbon fibers.

EXPERIMENTAL

Materials

Softwood Kraft lignin, Indulin^{AT} (SKL), was obtained from MeadWestvaco, Charleston, SC. This grade of lignin was specifically

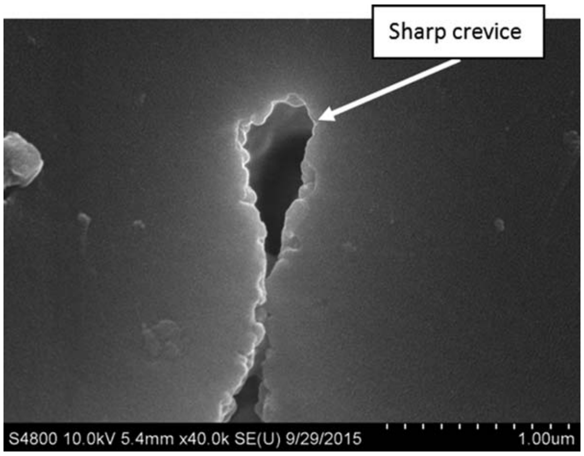

Figure 3. Magnified SEM image of a sharp crevice on the surface of as-spun lignin fiber obtained from 1.85 g/mL solution.

chosen for current fiber spinning studies because it is commercially available and amenable to process scale-up. Purification was performed by repeatedly washing of the SKL with acetified DI water (pH = 2) until ash content was below 0.15%. Purified SKL was mixed with acetic anhydride and reacted at 85–90 °C for 15 min. Details of purification and acetylation are described in our recent study.[22,23] The partially acetylated SKL (Ace-SKL) was capable of crosslinking during thermal oxidation.

Ace-SKL solution was prepared by mixing 50 g of Ace-SKL dry powder with 100 mL acetone. The mixture was manually stirred, and solvent evaporated until solution was concentrated to above 1.7 g solids/mL acetone. In addition, the concentrated solutions were put into ultrasonic tank to achieve homogeneity. To measure the precise concentration of various solutions, the solution was weighed precisely, vacuum dried at 95 °C for 2 h, and re-weighed.

Processing and Characterization

The viscosity of Ace-SKL solutions at various concentrations and temperatures was measured using an ACER 2000 capillary rheometer (Rheometric Scientific). High shear measurements were conducted at shear rates ranging from 3000 to 10,000/s. Capillaries of 1 mm diameter and three L/D ratios (5, 15, and 25) were used.

Dry-spinning was performed using a batch unit custom-designed by AJA (Greenville, SC). The viscous solution was transferred into a spinning barrel fitted with a 4-hole die, with each hole having a diameter of 75 µm and a length of 225 µm. The spinning barrel had a diameter of 12.5 mm. In this lab-scale process, the solvent was vented, but in a commercial process, the solvent can be condensed and recycled.

The Ace-SKL/acetone solutions can be drawn into filaments when the concentration exceeds 1.7 g solids/mL acetone. Thus, Ace-SKL/acetone solutions were prepared at three concentrations: 1.85, 2.00, and 2.15 g solids/mL acetone. These solutions were dry-spun at temperatures ranging from ambient (25 °C) to 52 °C. During spinning, the draw-down ratios (DDR) were controlled between 5.7–6.9 at a nominal roll speed of 130 m/min. Stabilization and carbonization of the Ace-SKL as-spun fibers was performed under tension as established in our recent studies.[22,23]

Tensile testing of carbon fibers was performed using a Phoenix tensile testing device. The load cell 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 25 samples per group of carbon fibers were tested using a gage length of 25 mm. The fiber diameters were obtained through single slit laser diffraction method.

Scanning electron microscopy (SEM, Hitachi S4800) was used to analyze the cross-section shape and dimension. The perimeter and area of single fibers were measured using Quartz PCI software and "Free-hand shape measuring tool". For each group of as-spun fibers, 10 fiber samples were measured to obtain the average cross-sectional area and perimeter, as well as other fiber-shape features.

RESULTS AND DISCUSSION

Viscosity and Flow Characteristics

In typical commercial fiber spinning equipment, pressure drop across spinnerets must be limited to about 14 MPa (2000 psi). In preliminary experiments, it was found that the pressure drop across the spinneret was excessive even at the lowest concentration (1.85 g/mL) when the experiment was conducted at ambient temperature (25 °C). Therefore, flow characteristics were needed at elevated temperatures to decrease the viscosity and resulting pressure drop.

Figure 1(a) displays the viscosity of the three solutions at ambient and elevated temperatures. For these results, entrance pressure drop was subtracted using Bagley correction method.[26] Results show clearly that Ace-SKL/acetone solutions are shear-thinning at all temperatures and concentrations investigated. As expected, viscosity increased as Ace-SKL concentration increased (ambient temperature = solid symbols). In addition, viscosity of all three solutions could be reduced to a suitable level by increasing the temperature (open symbols). The extent of temperature increase was higher for the most concentrated solution.

The viscosity curves were fitted to a power-law model. It should be noted that for a Newtonian fluid the power law exponent (n) equals 1, whereas for polymeric solutions $n < 1$. For the Ace-SKL solutions, the power-law exponent was found to range from 0.33 to 0.82, which confirms the macromolecular nature of the Ace-SKL lignin precursor.

The power-law parameters were also used to predict pressure drops (ΔP) expected in the spinnerets using the following equation for a power-law fluid[27]:

$$Q=\left(\frac{\pi R^3}{1/n+3}\right)\left(\frac{R\Delta P}{2mL}\right)^{1/n} \tag{1}$$

where Q is the flow rate, R is the capillary diameter, L is the capillary length, and m and n are the power law parameters. Calculations were performed using power-law parameters obtained for the three combinations: 1.85 g/mL at 35 °C, 2.00 g/mL at 40 °C, and 2.15 g/mL at 50 °C. For the three

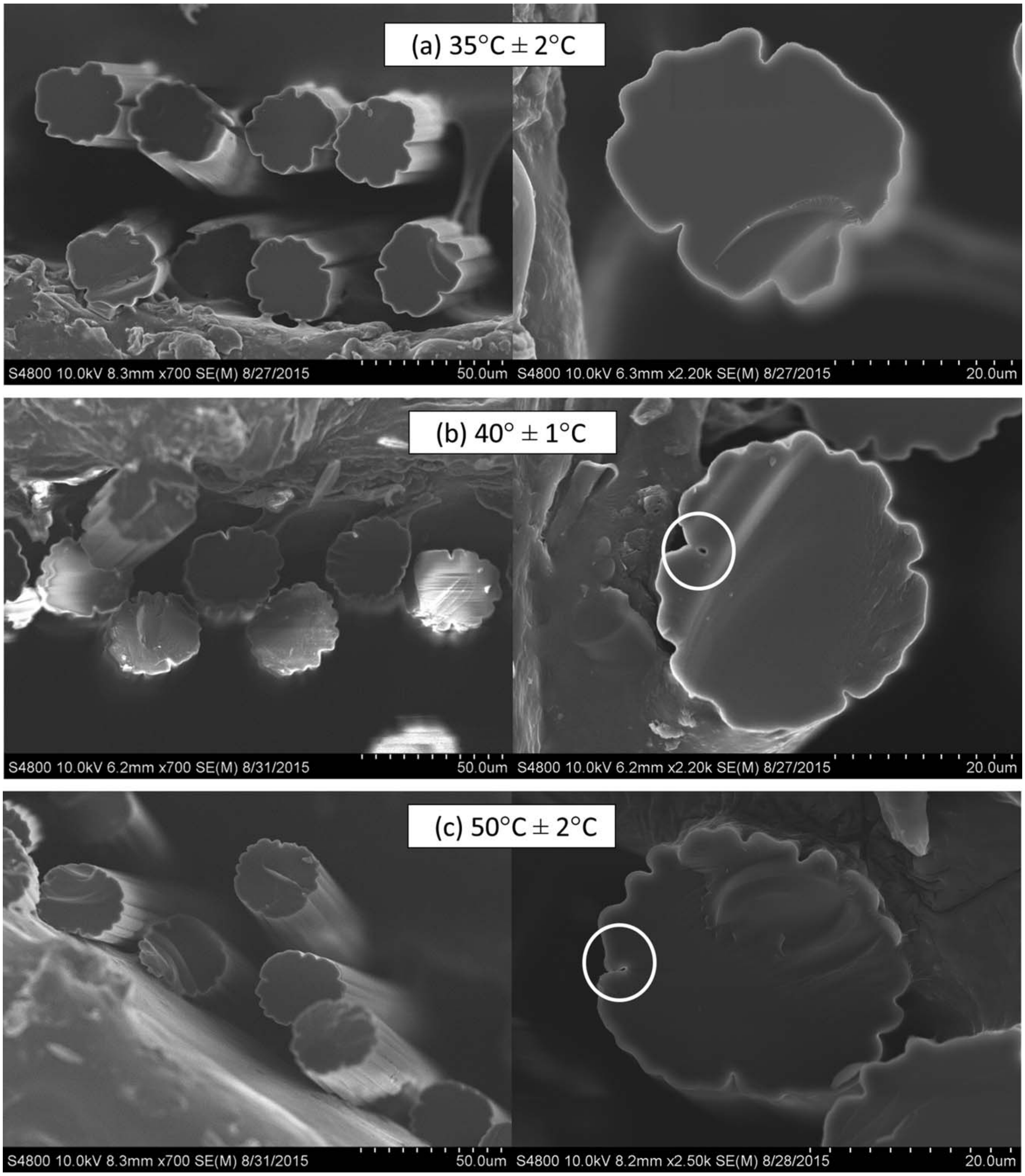

Figure 4. SEM images of Ace-SKL lignin fibers from a 2.00 g/mL solution, at various spinning temperatures.

concentrations, (1.85, 2.0, and 2.15 g/mL), the predicted ΔP were 4.1 MPa (590 psi), 3.4 MPa (490 psi), and 3.4 MPa (500 psi). However, these predicted ΔP values do not include end-effects. Therefore, viscosity results from the short aspect ratio (length/diameter) $L/D = 5$ capillary, presented in Figure 1(b), were also used. The predicted values were 12.0 MPa (1740 psi), 11.8 MPa (1710 psi), and 11.5 MPa (1670 psi), which are fairly consistent with the measured values of 10.1 MPa (1460 psi), 10.0 MPa (1450 psi), and 8.4 MPa (1220 psi).

Fiber Formation by Dry-Spinning

Figure 2 displays SEM images of lignin fibers obtained by dry-spinning of a 1.85 g/mL solution. Continuous filaments could be drawn consistently at a roll-speed of 130 m/min and

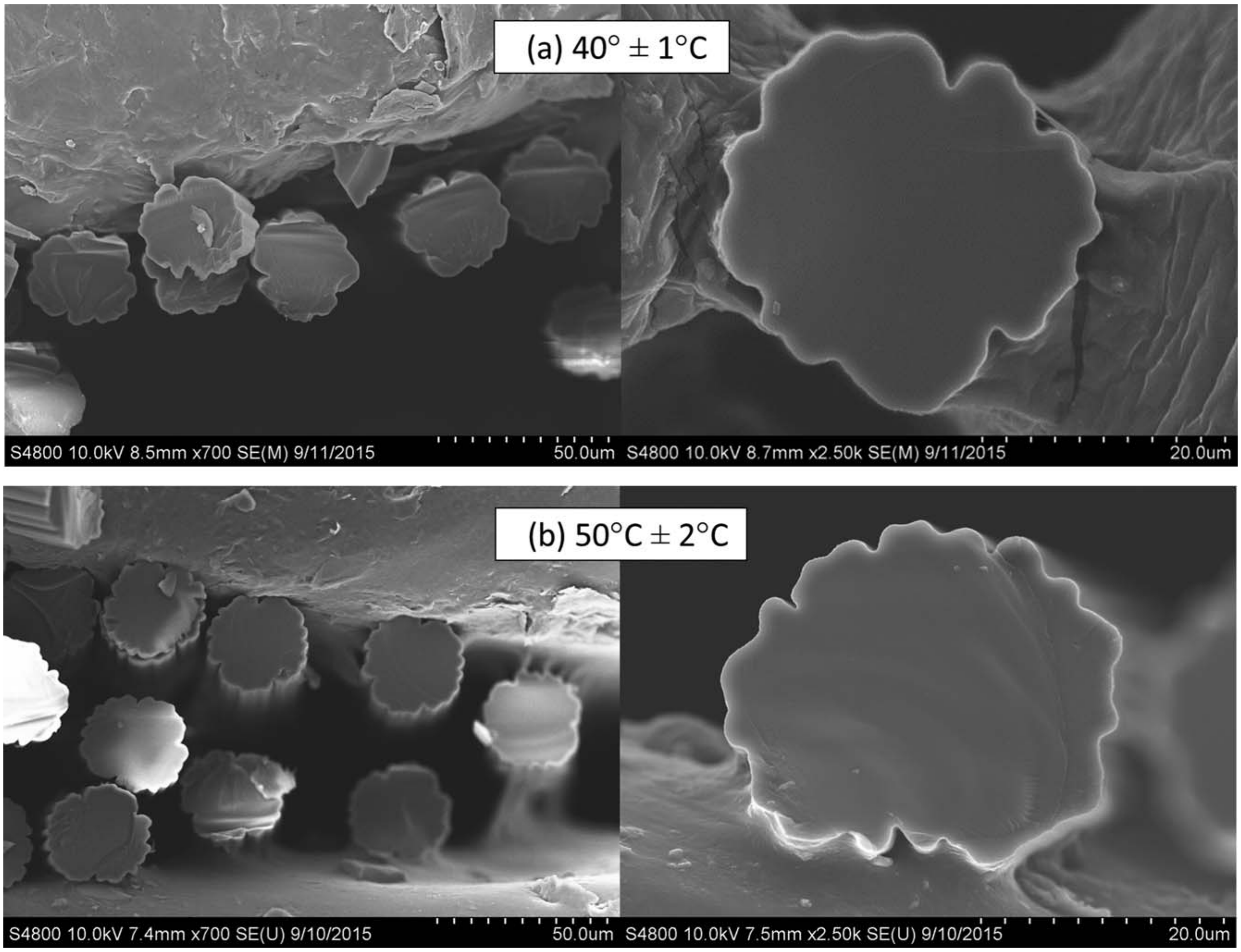

Figure 5. Ace-SKL lignin fibers from dry-spinning of 2.15 g/mL solution at various spinning temperatures.

spinning temperatures of approximately 30 °C from this lowest concentration solution. It is noted that the as-spun fiber diameters were quite fine, about 30 to 40 μm. Another interesting feature of the dry-spun lignin-based precursor fibers is their crenulated shape. When used in polymeric composites, the crenulated shape can enhance the interfacial bonding between carbon fibers and resin by providing increased contact area, and is a desirable feature. Therefore, these characteristics were studied further.

As displayed in Figure 2 (also at a concentration of 1.85 g/mL), as the spinning temperature increases, fibers developed more crenulations. In addition, some crenulations became doubly convex crevices, such as that identified by the encircled region in the SEM images displayed in Figure 2. An SEM micrograph of a crevice at higher magnification is shown in Figure 3. Such sharp crevices are not desired as these would be difficult to infuse with polymeric resins and result in inadequate fiber-surface wetting if such carbon fibers were

Table I. Fiber Surface Characteristics of Ace-SKL As-Spun Fibers at Various Concentrations and Appropriate Processing Temperatures

	Temperature	35 °C ± 2 °C	40 °C ± 1 °C	50 °C ± 2 °C
1.85 g/mL	C_N (Average number of crenulations per fiber)	15.1 ± 0.4	19.1 ± 1.2	24.6 ± 0.8
	SR (%) (Enhancement of lateral surface area)	135.1% ± 1.2%	134.2% ± 1.9%	132.4% ± 0.9%
2.00 g/mL	C_N (Average number of crenulations per fiber)	11.8 ± 0.6	16.1 ± 0.4	19.4 ± 0.5
	SR (%) (Enhancement of lateral surface area)	131.2% ± 1.2%	133.5% ± 1.4%	136.4% ± 1.1%
2.15 g/mL	C_N (Average number of crenulations per fiber)	Too viscous	13.6 ± 0.4	17.3 ± 0.1
	SR (%) (Enhancement of lateral surface area)	Too viscous	127.1% ± 1.5%	136.5% ± 1.7%

C_N is the average number of crenulations on each fiber, and SR is the ratio of the enhanced surface area of the crenulated fibers compared with circular fibers possessing equal cross-sectional area.

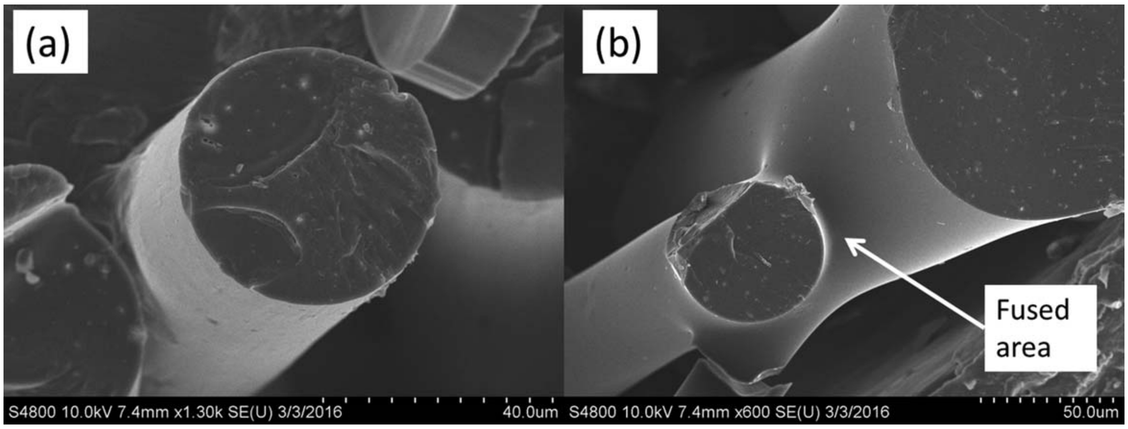

Figure 6. Lignin fibers obtained from melt-spinning of fractionated Ace-SKL: (a) as-spun fibers and (b) fused fibers obtained after stabilization.

converted into composites. Therefore, other dry-spinning conditions were investigated next.

Figure 4 displays the SEM images from a more concentrated solution, 2.00 g/mL. Higher spinning temperature was required to achieve lower viscosity and better processability. Stable filament winding could be achieved for spinning temperatures of about 35 °C and higher. Again, the crevices started to show up when spinning temperature was above 40 °C. The sharp notches on the surface of some fibers fused together at the outer edge, leaving a hollow space/void.

The highest concentration solution used in this study was 2.15 g/mL, and Figure 5 displays SEM micrographs of fibers obtained from this solution. Fibers could be continuously spun when solution temperature approached 40 °C. Due to a lower fraction of solvent in this concentrated solution, a smaller volume reduction resulted in fibers during the drying step. Consequently, the collapse of fiber surface during diffusion was not as significant as for the more dilute concentrations. Thus, fibers produced from this concentrated solution did not possess sharp crevices at any of the spinning temperatures. Clearly, 2.15 g lignin/mL solvent is a suitable concentration for the given Ace-SKL to produce fibers with the desired morphology. These results establish the importance of precursor solution concentration in determining the shape and features of the resulting lignin fibers.

A quantitative analysis of fiber microstructure is listed in Table I. The average number of crenulations on each fiber (C_N) is reported because the exact number varies from fiber to fiber. Another measure of the surface undulation is the ratio of the enhanced lateral surface area of the crenulated fibers compared with circular fibers possessing equal cross-sectional area, which is reported in Table I as SR. This represents the enhancement of fiber-matrix surface area due to crenulations for a given volume fraction of the reinforcing fibers in a composite material. For all concentrations, current results confirm that fibers spun at a higher temperature had a larger number of crenulations, which facilitates rapid out-diffusion of solvent. As discussed previously, higher spinning temperatures also helped reduce the solution viscosity and resulting pressure drop within spinnerets.

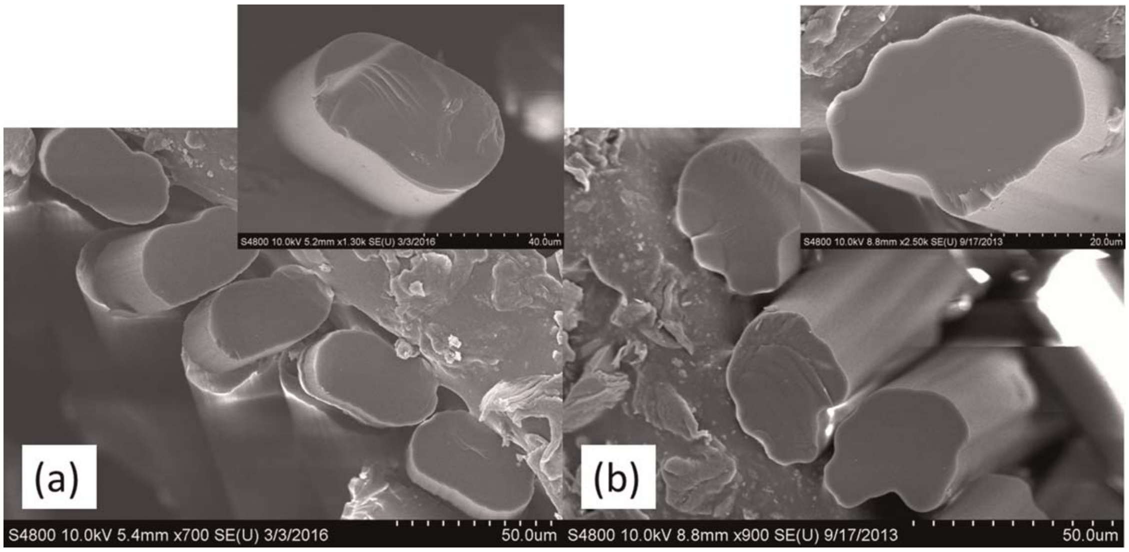

Figure 7. As-spun fibers from dry-spinning of Ace-SKL/acetone solutions at room temperature at two different concentrations: (a) 2.15 g/mL and (b) 2.00 g/mL.

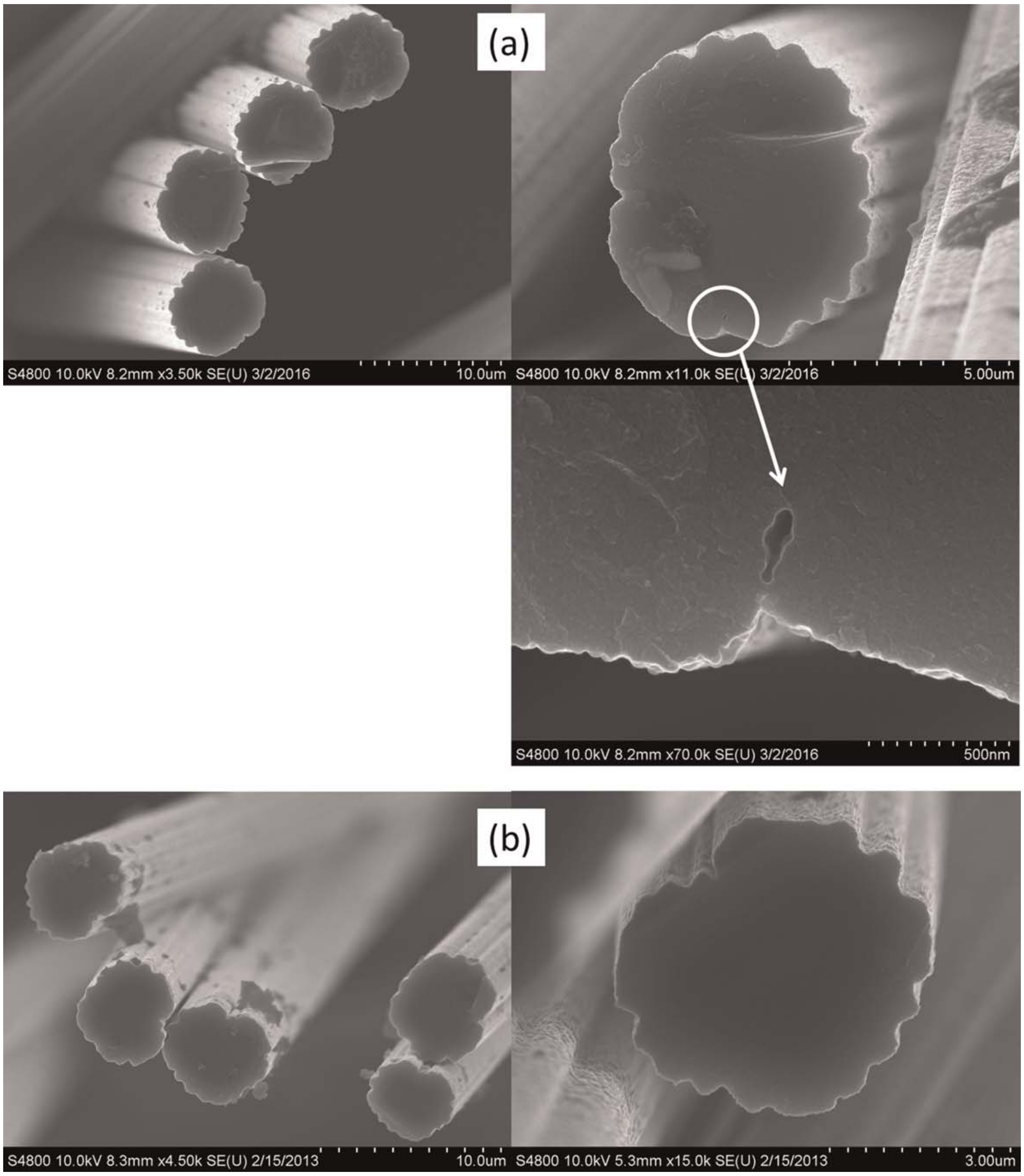

Figure 8. SEM micrographs (at various magnifications) of carbon fibers heat treated at 1000 °C and obtained from dry-spinning at 50 °C of lignin–acetone solutions at two concentrations: (a) 2.00 g/mL and (b) 2.15 g/mL.

Dry-spinning is a complex process that includes three simultaneous phenomena: non-Newtonian fluid flow (fiber extrusion and draw-down), heat-transfer (fiber cooling), and mass transfer (solvent evaporation). So, exact mathematical modeling is beyond the scope of this work, but the development of crenulations can be explained semi-quantitatively as follows.

During evaporation of acetone through the circular (nominal) fiber, the radial mass flux n_{Ar} scales with the concentration gradient:

$$n_{Ar} \sim D_{AB}\frac{\partial \omega_A}{\partial r} \tag{2}$$

where D_{AB} is the mass diffusivity of acetone in the solution and ω_A is the weight fraction of acetone. As the solvent diffuses out, the volume of the fiber decreases and so does its surface area, which for a circular cross-section would lead to a decrease in overall evaporation rate (mass/time). However, to facilitate the overall mass-transfer rate, the fiber cross-section changes from smooth (circular) to crenulated, which increases the specific area. As demonstrated in Table I, crenulated fibers possess about 35% more external specific surface area compared with circular fibers with the same cross-sectional area (SR).

As-spun fibers obtained from various concentrations have been carbonized, and the crenulated cross-sectional shape was preserved in the carbon fibers thus obtained. For carbon fibers, it is known that smooth circular cross-section leads to better strength than

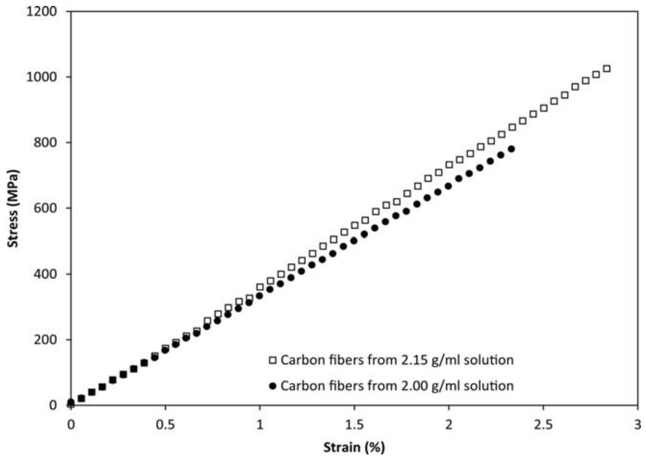

Figure 9. Representative stress–strain curves of single carbon fibers, obtained from two different precursor solution concentrations (2.00 and 2.15 g/mL), displaying an almost linear/elastic response to failure.

the ones containing sharp crevices such as that observed in the mesophase pitch (MP) based carbon fibers CFs that possess a "pac-man" split.[28] For dry-spun Ace-SKL precursor fibers, it is not possible to obtain circular fibers because the finite rate of out-diffusion of solvent (at any temperature or solvent concentration) still produces a wavy surface. However, from a fractionated grade of highly acetylated lignin (15 mL acetic anhydride per gram of lignin), we have produced fairly circular lignin fibers by melt-spinning, as displayed in Figure 6(a). The high degree of acetylation prevents lignin molecules from reacting and leads to a stable melt viscosity suited for stable melt-spinning. However, it is exactly this high chemical stability, coupled with a low softening temperature, which prevents subsequent cross-linking (stabilization) of precursor fibers. The result is an agglomerate of partially melted and fused lignin fibers stuck to each other, as displayed in Figure 6(b), that cannot produce individual carbon fibers.

Next, in an attempt to produce fibers with smooth surface and shapes close to circular from dry-spinning, a 2.15 g/mL solution was dry-spun at room temperature for slower diffusion of acetone. The spinning was extremely difficult and the process had to stop due to plugging of spinneret hole as the pressure drop approached the high alarm value of 24 MPa (3500 psi). The limited fibers that were collected are illustrated in Figure 7(a). Although the as-spun fibers displayed a ribbon-like shape and smooth surface, the extrudate could not be drawn-down to fine fiber diameters below about 30 μm that are highly desired for producing high strength carbon fibers. To enable dry-spinning at room temperature (25 °C), a solution at a lower lignin concentration of 2.00 g/mL was prepared. The spinning was still difficult due to a high pressure drop of 2700 psi within the spinneret. The as-spun fibers, shown in Figure 7(b), displayed a relatively smooth lateral surface but noncircular cross-section.

The lignin precursor fibers produced from 2.15 g/mL were post-stretched to reduce the diameter down to about 12 μm and oxidatively cross-linked (also referred to as "stabilization"), as reported in our recent study.[14] In this study, lignin precursor fibers produced from a lower concentration of 2.0 g/mL were also post-stretched and thermo-oxidatively stabilized to investigate the effect of the sharp crevices observed in as-spun lignin fibers. These lignin-based precursor fibers were heat treated to 1000 °C to obtain carbon fibers, and their SEM micrographs are displayed in Figures 8(a) and (b). It is evident that the carbon fibers retained the cross-sectional pattern from their as-spun state. In Figure 8(a), for fibers derived from 2.00 g/mL solution, it is evident that occlusions were formed within the carbon fibers from sharp notches present on the precursor fiber surface. In contrast, the smoother crenulations observed in lignin fibers obtained from the more concentrated solution (2.15 g/mL) resulted in carbon fibers with smoother crenulations and no occlusions.

Stress-strain curves of two representative single carbon fibers derived from the 2.00 and 2.15 g/mL precursor solutions are displayed in Figure 9. Both types of carbon fibers display an almost linear/elastic response to failure, with similar slopes (moduli) but different stress values at failure (strengths). Carbon fibers derived from the concentrated solution (2.15 g/mL), possessing smooth crenulations, strength of 1060 MPa. These fibers displayed a tensile modulus of about 35 GPa without system compliance correction or 50 GPa.[22,23] The strength value is amongst highest reported for carbon fibers derived solely from lignin biomass. In the current study, tensile tests were conducted for carbon fibers derived from lignin fibers obtained from lower concentration of 2.00 g/mL solution. These carbon fibers displayed a similar modulus of about 35 ± 1 GPa (without compliance correction), but their strength was only about 790 ± 80 MPa. The similar moduli are consistent with numerous prior observations that carbon fiber modulus is not affected by defects but usually controlled by the extent of carbonization, which in turn is governed by the carbonization temperature for a given type of precursor.[1–3] However, carbon fiber strength is a strong function defects, and the lowered tensile strength observed for current carbon fibers with occlusion-type defects can be attributed to precursor fibers containing sharp crevices.

CONCLUSIONS

Shear viscosity of Ace-SKL solutions displayed a significant shear-thinning behavior at all temperatures studied. The viscosity results could be modeled with power-law exponents ranging from 0.33 to 0.82, confirming the macromolecular nature of the Ace-SKL lignin/acetone solutions. As expected, elevated temperatures lead to lower viscosities and facilitate extrusion at pressures under 10 MPa (about 1500 psi). As-spun fibers produced from dilute solutions (1.85 and 2.00 g/mL) at temperature between 35–50 °C developed sharp crevices on the fiber surface. These are undesirable for subsequent processing of resulting carbon fibers into composites by resin-infusion. For the most concentrated solution investigated in this study, 2.15 g/mL, the resulting fibers contained no sharp crevice. All fibers produced by the dry-spinning process led to crenulated fiber surface, with the highest spinning temperature leading to most crenulations. Room temperature spinning was also attempted for the purpose of obtaining fibers with circular cross-section, but resulted in excessive pressure drop during dry-spinning that is not suited for scaled-up processes. In addition, these precursor solution compositions (2.00 g/mL solution) led to the formation of carbon fibers with occlusions and resulted in reduced tensile strength as compared with that with smooth crenulations (from 2.15 g/mL solution). It is noted that smooth crenulations result in about 35% larger surface as compared with equivalent circular fibers, indicating the potential of such biomass-derived fibers in providing larger fiber/matrix bonding area when used in composites. In summary, this study establishes the important effects of precursor composition and processing conditions on microstructure and properties of resulting precursor and carbon fibers.

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