Impact of Thermal Oxidative Stabilization on the Performance of Lignin-Based Carbon Nanofiber Mats

Mijung Cho, † Frank K. Ko, ‡ and Scott Renneckar* †

†Advanced Renewable Materials Laboratory, Department of Wood Science and ‡Advanced Fibrous Materials Laboratory, Department of Materials Engineering, University of British Columbia, Vancouver, BC, Canada V6T1Z4

Supporting Information

ABSTRACT: Lignin is a renewable biopolymer considered as a potential precursor for low-cost carbon materials. Thermal oxidative stabilization (TOS) is an important processing step to maintain fiber geometry during carbonization, yet the impact of TOS on the properties of lignin-based carbon materials has not been clearly identified in the literature. Yield, change in fiber diameter/distribution, elemental composition, and mechanical properties were explored for both stabilized and carbonized lignin fibers. Vibrational spectroscopy and solid-state 13C nuclear magnetic resonance spectroscopy were used to analyze the changes in lignin molecular structure after exposure to various heating conditions during the TOS steps. Further, studies were focused on the effects of TOS conditions on the resulting carbon structure of fiber mats through Raman spectroscopy measurements and electrical conductivity analysis. Although TOS conditions influenced the properties of the oxidized lignin fiber mats, properties of the carbonized samples were invariant to the TOS procedures used in this study over most of the conditions. As a result, there was flexibility for the parameters (time and temperature) in the TOS process when conditioning softwood lignin materials for carbon fibers.

INTRODUCTION

Lignin is the second most abundant natural polymer after cellulose constituting about one fourth of the cell wall of plants. It is obtained as a byproduct in the pulp and paper industry as well as in developing second-generation bioethanol industry. Currently, recovery of softwood kraft lignin, on a semi-industrial scale, is done by three companies in North America producing more than 100 t/day. Pulping conditions and two patented recovery options impact the structure and the breakdown products; however, all the lignins isolated come from softwood resources. These lignins are generally viewed favorably for carbon fiber production with their ability to undergo thermal oxidative stabilization (TOS); the lignin is derived from the polymerization of mainly coniferyl alcohol and the resulting guaiacyl lignin has open positions on the aromatic rings for carbon−carbon bonds. This structure creates opportunity to undergo significant cross-linking during stabilization for the production of lignin-based fiber materials from softwood kraft lignin.

Only a small percentage, less than 2%, of the 50 million tons of lignin produced from the pulp and paper industry is utilized, with the remainder used as fuel in the chemical recovery furnaces. Current applications of industrial lignins include dispersants, emulsion stabilizers, concrete additives, surfactants, and binders. However, several decades of research has allowed improvements in properties of lignin-based materials by investigating the relationships between the heterogeneous structure and the molecular properties of different lignins, including processability and performance. Still, there has been little commercial progress in lignin materials based on its potential to serve as a feedstock for renewable materials. Yet, with its relatively high carbon content, it is seen as a great precursor for carbon fiber, which as been studied as far back as 1969.

The impetus to utilize lignin lies in the fact that it is a byproduct of a current industrial process and would potentially reduce the environment footprint of materials such as carbon fiber sourced from fossil resources. Carbon fibers have numerous potential applications, including not only structural applications such as aviation, aerospace, automotive, and wind power but also nonstructural applications such as thermal management, catalyst supports, electrodes for batteries (Li-ion batteries, fuel cells), and supercapacitors. Not only the abundance qualifies lignin for its application in carbon fiber, but also compared with other carbon fiber precursors, lignin is already oxidized and allows for stabilization at a rate that is faster than pitch. This shortened cross-linking stage and relatively high carbon yield reduces the manufacturing costs. Therefore, this low-cost, renewable, and abundant material has been highlighted to serve a potential role as a precursor for carbon fibers as a substitute for petroleum-based commercial precursors.

Traditionally, lignin-based carbon fibers have been produced in micron-sized fibers by melt spinning or dry spinning.
methods. These carbon fibers had heterogeneous cross sections with defects, with a lack of orientation between the crystalline planes resulting in lower mechanical properties than petroleum-derived carbon fibers. Recently, gel spinning has been investigated to enhance fiber properties. Another approach to address these issues involves forming nanoscale fibers by electrospinning, which is a simple method to produce fiber with reduced defects, high surface area, and potentially highly oriented molecules in the fibers. Electrospinning of various lignin solutions has been reported for carbon fiber production yielding fibers with the above characteristics.

One issue of carbonizing fibers, especially with nanoscale diameters is the loss of fiber geometry during heating. Hence, thermal oxidative stabilization (TOS) is critical for carbon fiber production unless there are nanoscale additives placed in the fiber. TOS helps reduce further thermal degradation and prevents the fusion of individual fibers prior to further heat treatment, i.e., carbonization, by inducing additional oxygen into the lignin structure. Essentially, this process results in thermoset fibers from thermoplastic fibers. Moreover, the TOS process is considered to be the most important step because it largely governs the final carbon structure of the fiber and hence its ultimate mechanical properties. There are just a few studies that show the effects of TOS process parameters on properties of lignin powder or ground samples from lignin-based fibers. Most of the TOS studies focused on micron-sized lignin fibers produced by extrusion with respect to stabilization time; these studies would have different impact compared to high surface area to volume nanoscale fibers. Although a study showed statistical analysis of the impact of carbonization process on properties of carbon nanofibers, there is a dearth of studies that report how the TOS process affects properties of the final carbonized lignin fibers. Whereas most of TOS studies focused on chemical structural changes of thermally stabilized fibers after various temperatures and final carbon structure of the subsequently carbonized micro-sized fibers, they did not show the effect on the mechanical properties of carbonized nanoscale fibers or fiber mats.

With the growing interest in carbonized electrospun lignin fiber materials, it is unclear if there is a dominant factor for TOS that controls the performance of the carbon fibers or fiber mats. Considering the high surface area of fibers, and their change in structure with high temperature treatment, this class of materials may behave differently due to the surface area to volume differences. In this study, the effect of TOS on the properties of carbonized nanofibers and nanofiber mats were explored including yield, change in diameter/distribution, elemental composition, internal structure, and mechanical performance as a function of stabilization temperature, rate, and time. The novelty of the research integrates the fundamental knowledge of lignin oxidative processing on the important properties of carbonized fiber related to both its mechanical and electrical performance.

### RESULTS AND DISCUSSION

#### Influence of TOS Parameters on Stabilized Lignin Nanofiber Mats

Among different design-of-experiments-based techniques, two-level factorial design experiments (2FD) are the most effective for the optimization of parameters in specific engineering applications. This analysis can help identify the effects and interactions of relatively few variables (2–4 variables) or to analyze the most significant parameter from many variables (over 5 variables). In the current study, a 2-level factorial design with 3 variables (2FD3, 23), which included final temperature, holding time, and heating rate, was used to determine the impact on yield after the thermal oxidative stabilization (TOS) process. Ranges for these experiments were chosen such that the final hold temperature was high enough to cause some degradation to the lignin but not too significant to cause serious weight loss based on thermogravimetric analysis (TGA) data, as shown previously. Holding time was chosen based on literature for TOS of softwood lignin, whereas heating rate was analyzed from previous lignin-based fiber studies. Based on this analysis, the most influential parameter on the yield after the TOS was found to be the final temperature (Table 1).

| experimental number | final temperature (°C), X1 | holding time (min), X2 | heating rate (°C/min), X3 | yield (%) |
|---------------------|----------------------------|------------------------|---------------------------|-----------|
| 1                   | 200                        | 30                     | 1                         | 88.9      |
| 2                   | 200                        | 60                     | 1                         | 91.2      |
| 3                   | 250                        | 30                     | 5                         | 80.0      |
| 4                   | 250                        | 60                     | 5                         | 76.0      |
| 5                   | 200                        | 30                     | 5                         | 93.5      |
| 6                   | 200                        | 60                     | 5                         | 90.0      |
| 7                   | 250                        | 30                     | 1                         | 81.4      |
| 8                   | 250                        | 60                     | 1                         | 78.0      |

*Single measurement, but other values were averaged from triplicates.

Experimental data showed that mass loss after the oxidative processing increased with increasing final temperature for both heating rates (Figure 1). Furthermore, holding time had a greater impact on mass loss than heating rate. These data were different from the literature for lignin materials (powder and micron-scale fibers), as Brodin et al. reported that holding time was the most influential factor on yield after the TOS process. Moreover, there was minimal influence on the interaction among the parameters on yield, as the dominant effect was the single parameter of the final holding temperature. Temperatures used in this study were similar to torrefaction temperatures in the literature, which were great enough to cause some decomposition with loss of water.
Figure 2. SEM images of lignin fibers after TOS process under different heating rates (1 and 5 °C/min), final temperatures of 200, 230, 250, 280, 300, and 350 °C, and 60 min holding time (scale bar = 10 μm).

Figure 3. (a) Average fiber diameter of as-spun and stabilized nanofibers with various final temperatures and heating rates and (b) yield after stabilization process by weighing at various final temperatures with 5 °C/min heating rate (p value < 0.05).
(dehydration) and carbonaceous gas (CO and CO2) release, along with compounds such as methanol and methane from loss of methoxy groups.28

As expected, higher temperatures caused mass loss during the TOS process, and this affected the morphology of the fibers. As seen in the scanning electron microscope (SEM) images in Figure 2, the TOS nanofibers after lower final temperatures at 200 and 230 °C had their original shapes compared to the control samples without the thermal treatment (Figure S1). Further, lignin nanofibers after TOS at higher temperature, above 250 °C, showed a curved-like shape along the fiber axis. This change was evident when the fibers were exposed to faster heating rates, 5 °C/min, compared to the slower rate of 1 °C/min. In a previous study based on the in situ thermal analysis of lignin-based nanofiber mats, the lower heating rate allowed sufficient time for cross-linking of the lignin prior to significant softening, whereas the higher heating rate allowed for greater mobility of the chains prior to thermally induced cross-linking.17

The average fiber diameter and yield also decreased as a function of increasing final temperature as shown in Figure 3a,b. Average diameters decreased at higher TOS temperatures when compared to the initial fiber diameter (Figure 3a). As shown in Figure 3b, yield after TOS process at various final temperatures decreased with increasing final temperature. Significant changes in yield, of around 37%, occurred between 300 and 350 °C when compared to other temperatures. Only 10% yield change occurred between 200 and 250 °C, followed by a sharp decline between 250 and 300 °C, equating to 23% of mass change (Figure 3b).

The fiber diameter decreased further for the samples that were stabilized at 1 °C/min compared to those stabilized at 5 °C/min heating rate, beyond 300 °C, as indicated in Figure 3a. This result suggested that a longer heating time, by increased total time for heat exposure, affected the diameter of fibers.

**Effects of TOS Temperatures on Chemical Composition and Structure of Stabilized Lignin Nanofibers.** Heating lignin in an oxygen-rich atmosphere impacts lignin’s chemical structure through the addition of additional oxygen into the compound. As a result, elemental analysis is an effective way to study the effect of TOS temperatures on changes in the lignin structure of stabilized lignin fibers. The elemental composition, i.e., carbon, hydrogen, oxygen, and nitrogen, for the lignin composite nanofiber mats stabilized at different temperatures is reported in Table 2. No nitrogen was detected except for the stabilized sample at 350 °C (0.48%). For the control sample, either residual protein in the lignin or residual solvent (N,N-dimethylformamide, DMF) would impact this value. At temperature above 250 °C, the oxygen content increased with increasing temperature of thermal stabilization. Braun et al. also reported the effect of stabilization parameters (temperature and heating rate) on the elemental composition of lignin.21 They reported that an increase in oxygen content occurred at treatment temperatures up to 250 °C, followed by a decrease in oxygen content beyond 250 °C. However, in the current case, the oxygen content increased even above 250 °C, but content of both carbon and hydrogen decreased with increasing temperature. This result suggested that TOS proceeded beyond 250 °C (as opposed to combustion).

Further, the effect of TOS temperature on the change in each element of stabilized lignin fiber mats (E) was shown as a ratio to the control mat (E0) (i.e., as-spun is referred as 1) in

**Table 2. Elemental Composition of Lignin Powder (MWL, SKL, and F,SKL), As-Spun Lignin Fiber Mat and Stabilized Lignin Fiber Mats after Various TOS Final Temperature**

| Sample      | Carbon | Hydrogen | Oxygen | Nitrogen |
|-------------|--------|----------|--------|----------|
| pine MWL    | 65.00  | 5.80     | 29.20  | 0.02     |
| SKL         | 65.50  | 5.60     | 25.20  | 0.40     |
| SKL         | 62.88  | 5.86     | 30.12  | 0       |
| F,SKL       | 65.12  | 5.79     | 29.09  | 0        |
| as-spun     | 62.45  | 5.82     | 31.73  | 0        |
| TS200       | 64.96  | 5.22     | 29.82  | 0        |
| TS230       | 63.98  | 4.68     | 31.34  | 0        |
| TS250       | 63.10  | 3.87     | 33.03  | 0        |
| TS280       | 60.87  | 3.03     | 36.10  | 0        |
| TS300       | 59.23  | 2.77     | 38.00  | 0        |
| TS350       | 58.57  | 2.10     | 38.85  | 0.48     |

*pine MWL measured by Hu et al.30 F,SKL, indulin AT measured by Hu et al.* Oxygen content calculated by subtracting the sum of the other composition fractions (C, H, and N). *Nonfractionated SKL in this work with sulfur content of 1.14%.

**Figure 4.** As the oxidation process proceeded at higher temperatures, the loss of carbon content was up to 7% and the hydrogen content decreased significantly by about 60%. The oxygen content increased by 20% up to 350 °C compared to the initial content of the as-spun lignin fibers. The data in Figure 4 indicated that even at lower temperature of 200 °C with hydrogen loss, reactive processes occurred with some C−H or O−H bond cleavage. Although elemental analysis cannot reveal products of the reaction, lignin is known throughout the literature to readily form free radicals, which for lignin leads to depolymerization but also leads to significant repolymerization of the lignin in a cross-linked structure.29

Because TOS causes lignin to undergo cross-linking reactions, lignin was no longer soluble for many characterization methods; hence, solid-state NMR (SS NMR) was used to determine chemical changes in stabilized lignin nanofibers as previously reported for lignin characterization of lignin melt-spin fiber27 and melt-blown spun fiber.32 As shown in Figure 5, 13C cross-polarization/magic-angle spinning (CP/MAS) SS NMR spectra showed a significant decrease in ~147 ppm region for various TOS treatments, which indicated an aryl−ether linkage cleavage, whereas the region for aliphatic side chain inter-unit carbon (61−83 ppm) almost disappeared under various TOS treatments. The relative intensity of a peak
at 55 ppm (−OCH₃) decreased significantly after 280 °C as major reaction occurred in TOS attributed to demethoxylation. After continued heating at higher temperatures, the signal completely disappeared after 350 °C treatment. The region from 160 to 170 ppm increased slightly after TOS at 250 °C and showed a broad band at 350 °C. This region was related to esters and anhydrides attributed to oxygenation, as found in the elemental analysis, and cross-linking. At 350 °C, the spectrum showed a broad resonance from 100 to 140 ppm, centered around 124 ppm. These results were similar to those of other reports, with the loss of significant peak signatures.

Similar to solid-state NMR, Fourier transform infrared (FTIR) spectroscopy can be used to characterize the functional groups of solid materials enhancing the analysis of the changes during TOS of lignin. As shown in Figures 6 and 7, the relative intensity of various FTIR spectra absorbance bands decreased with increasing TOS temperature. In detail, the intensity of the O−H stretching band (νO−H, ~3600 cm⁻¹) and C−H stretching bands (νC−H ~2800 cm⁻¹) decreased with increasing final TOS temperature. This result was interpreted because of significant loss of hydroxylated C₇, typically released as formaldehyde, and the formation of enol ethers and ketone products, along with loss of hydrogen that was reflected in the elemental analysis (Figure 4). Also, 1510−1500 cm⁻¹ decreased and nearly disappeared at 300 °C, which indicated the formation of anhydride linkages. As shown in Figure 7 for normalized peak intensity of each functional groups as a function of temperature, changes to the aromatic signal (~1500 cm⁻¹) began at 230 °C, whereas carbonyl signals (~1700 cm⁻¹) rapidly increased above 250 °C. In similar fashion, the guaiacyl ring-stretching modes (~1270 and 1210 cm⁻¹) stayed nearly constant up to 250 °C, which dramatically decreased at higher temperatures. These data corresponded with the loss of methoxy groups at these higher temperatures, as seen for the ¹³C NMR data (Figure 5).

**Thermal Properties of Stabilized Lignin Nanofiber Mats Treated under Various TOS Temperatures.** TGA analysis of the heat-treated lignin revealed that the derivative peak temperature and residue increased with increasing final temperature, as shown in Table 3. As the samples were heated...
to relatively higher TOS temperatures, the labile linkages off-gassed, which would suggest the remaining materials would have improved the thermal stability of the lignin fiber mat; this result was found by the increased value of the derivative peak temperature from 382 to 518 °C after thermal oxidative stabilization.

According to TGA results (Figure S2), the as-spun lignin-based fiber mats showed around 15% mass loss at 300 °C and then more significant mass loss was observed above 300 °C (derivative weight peak temperature in Table 3). Statistical analysis of the results did not reveal a significant difference for the residue (%) remaining at 1000 °C, with a p value above 0.05 (one-way analysis of variance (ANOVA)), which means that all values are in same range with the large variance. This result was further correlated with uniformity and stability of composite nanofibers after the carbonization process. Yield (% in Table 3 indicated the weight difference before and after the carbonization process for stabilized lignin fiber mats, which demonstrated varied responses with the TOS temperature. Hence, although the final temperature had a significant impact on yield after stabilization (Figure 3b), it did not impact the yield of the carbonized samples.

Carbonized lignin nanofibers at different TOS temperatures showed similar morphology, as shown by the SEM images in Figure 8. All samples consisted of uniform individualized nanofibers; some slightly curved fibers could also be observed. The carbonization process decreased the average fiber diameter compared to that of the as-spun fiber as shown in Figure 9. Further, there was scatter among the average values

| temperature (°C) | deriv. weight peak temp (°C) | residue at 1000 °C, % by TGA | yield % by weighing before and after carbonization |
|-----------------|-----------------------------|-----------------------------|--------------------------------------------------|
| as-spun         | 382 ± 1                     | 23 ± 10                     | N/A                                              |
| 200             | 369 ± 9                     | 36 ± 26                     | 38.4                                             |
| 230             | 421 ± 5                     | 34 ± 7                      | 44.4 ± 4.7                                       |
| 250             | 424 ± 2                     | 40 ± 14                     | 47.9 ± 1.3                                       |
| 280             | 428 ± 8                     | 47 ± 6                      | 49.1 ± 4.4                                       |
| 300             | 436 ± 3                     | 43 ± 9                      | 44.8                                             |
| 350             | 518 ± 12                    | 60 ± 13                     | 46.9                                             |

*Heating rate: 5 °C/min for TOS process. *p value < 0.05 (statistically different). *p value > 0.05 (statistically same).
that revealed different dimensions for stabilized fibers with different final temperatures during TOS. However, with the variance it was not clear if individual heating temperatures impacted the carbonized average fiber diameter. It was noteworthy to compare differences among stabilized and carbonized samples. As compared with values in Figure 9, the nanofibers stabilized at 200 °C showed the largest diameter change of about 28% before and after carbonization. Also, the TOS temperature at 200 °C gave the lowest yield after carbonization, and this was constant with the yield value for TGA results shown in Table 3. The smallest average change in the diameter of carbonized nanofibers was shown for the nanofibers stabilized at 250 °C; however, there was significant variance for all nanofibers.

As shown in Figure S3, the elemental analysis of carbonized lignin fiber mats revealed that TOS had minor impact on carbon content. Overall, a comparison of the elemental analysis in Table 2 of the stabilized fibers with that in Figure S3 shows that the carbon and nitrogen content in carbonized lignin nanofibers after carbonization increased from 58–65 to 83–88% and from 0% up to 0.4–0.7%, respectively. The increased nitrogen content was attributed to the nitrogen flow during the carbonization process. Also, oxygen and hydrogen content decreased from 30–39 to 10–15% and from 2–6 to 0.4–0.9%, respectively. Through the carbonization process, the carbon content was increased but was below 92%, as reported for carbon-based materials. The final carbonization temperature of 1000 °C was not high enough to completely deoxygenate the material under the current test conditions, but it was still in the carbonization temperature range; other recently published papers also carbonized at 900–1100 °C for electrospun lignin-based carbon nanofibers. Moreover, it was reported that the inert gas selection can impact the carbon content and the graphitization process, as argon has been used for polyacrylonitrile-based carbon fiber production.

Mechanical Properties of Stabilized and Carbonized Fiber Mats as a Function of TOS Temperature. The overall tensile properties of the random fiber, as-spun mat improved after heat treatment in the air atmosphere. The ultimate tensile strength (UTS) was increased from 7 MPa up to 29 MPa and modulus was increased from 741 to 1.6 GPa. In Figure 10a, the samples stabilized at 250 °C showed the highest value of UTS (29 MPa) and then decreased above 250 °C with increased standard deviation. Based on the FTIR and NMR data, significant chemical changes, like forming carbonyl groups, occurred to the lignin above 250 °C, impacting the strength of the material. Further, the modulus value showed improved values for different final temperatures after TOS and also showed the highest value at 250 °C.

For the tensile test of carbonized samples, the carbon nanofiber mats stabilized at 200 °C and 350 °C could not be further analyzed. Both samples stabilized at 200 and 350 °C were too brittle to prepare specimens for reproducible tensile tests. As shown in Figure 10b, lignin carbon nanofiber mats after stabilization at various temperatures showed little difference in tensile strength and modulus but statistically no difference in one-way ANOVA analysis (p value > 0.05). These samples had significant variance, especially at the highest TOS final temperature. This result indicated that carbon yield/ content maybe the most critical parameter when evaluating the effect of TOS final temperature, as it had minimal impact on the final properties of the carbonized samples heated between 230 and 300 °C. This observation provides a critical finding that there was flexibility in the TOS process when creating lignin-based carbon nanofibers from kraft lignin, as this processing step does not need to be closely controlled for carbon fiber production within a given range.

It would be worth while to investigate the relationship between mechanical properties and carbon structure of single-carbon nanofibers. One work showed significant difference between the tensile properties of fiber mats and single fibers from softwood kraft lignin source, similar to this work. Compared with lignin-based carbon fiber mat, single-carbon nanofiber showed 309 ± 39 MPa tensile strength and 34 ± 8 GPa tensile modulus. However, dealing with single nanofibers is challenging for characterization, along with isolating single-carbon nanofibers. Therefore, it is hard to achieve reasonable tensile properties with single nanofibers and atomic force microscopy or nanoindentation is required.

Raman Spectroscopy and Electrical Conductivity of Carbonized Lignin Nanofiber Mats as a Function of TOS Final Temperature. Raman spectra of the carbonized mats after various TOS conditions are shown in Figure 11. The intensity ratio (I_D/I_G) between D (disordered) band and G (graphitic) band changed as a function of TOS temperature. As shown in Figure 12a, the I_D/I_G ratio was significantly decreased after stabilization at 250 °C, indicating that the graphitic structure (G band) was more developed after this temperature than that of carbonized samples that were previously stabilized at 200 and 230 °C. Further, the I_D/I_G
ratio was similar for carbonized samples after thermal stabilization between 250 and 300 °C. Higher thermal stabilization temperatures led to a further decrease in the ratio, suggesting a higher degree of order for carbon mats stabilized at 350 °C. These results indicated that at higher TOS temperature, graphitic clusters developed in the carbonized lignin nanofibers. Moreover, the crystallite size \( (L_s) \) was calculated from the Raman spectra using the following eq 1

\[
L_s = \frac{C(\lambda)}{R}
\]

where \( R \) is \( I_D/I_G \), \( C \) is a function of laser wavelength \( (2.4 \times 10^{-10}) \times \lambda^4 \), and \( \lambda \) is the wavelength of the incident laser (here 785 nm)\textsuperscript{24}. As shown in Figure 12a, the higher temperature in TOS produced larger \( L_s \) of the carbonized lignin nanofibers, and the values were significantly increased after TOS at 250 °C. The calculated \( L_s \) values in this study were larger or similar to the previously reported data (25–45 nm) for lignin-based carbon fibers analyzed with the same laser wavelength\textsuperscript{24,42}. As shown in Figure 12b, the \( I_D/I_G \) ratio was inversely proportional to the crystallite size. This relationship agreed with reported works\textsuperscript{37,43}, although this difference in \( I_D/I_G \) values did not greatly impact the mechanical properties of the carbonized nanofiber mats for this range of \( I_D/I_G \) values.

Based on previous analysis, larger crystallites was expected to have higher electrical conductivity\textsuperscript{44}. A multimode device was used to measure the electrical resistance of thermally stabilized and subsequently carbonized mats as a function of thermal stabilization temperature. As shown in Figure 13, the carbonized mats had an electrical conductivity value of nearly 6 S/cm, with a relatively large variance for the measurements. The statistical analysis showed no difference among the mean values. This result demonstrated that the changes in carbon structure did not lead to a uniform conduction path, where most likely, there was still resistive amorphous carbon along the individual nanofibers. The values of conductivity were comparable to other studies with lignin-based carbon nanofiber mats. Carbon fiber mats from kraft lignin grafted with acrylonitrile showed 7.1 S/cm\textsuperscript{45} and carbon nanofibers from softwood kraft lignin had 2.3 S/cm\textsuperscript{46,47}.

### CONCLUSIONS

The thermal oxidative stabilization (TOS) processing conditions (especially the final stabilization temperature) impacted the properties of stabilized lignin-based fiber mats. Specifically, changes were observed extensively in chemical, structural, and mechanical properties of stabilized lignin-based nanofibers or nanofiber mats related to the addition of oxygen and the loss of hydrogen. Further, loss of methoxy groups occurred at temperatures above 280 °C during this stabilization process. However, additional heat treatment of the sample during carbonization caused the differences that arose in thermally stabilized lignin performance to become minimum. The properties of the carbonized lignin-based fiber materials were independent of this parameter under most of the TOS conditions. It is noted that there was a minor effect of TOS conditions on the structure of carbonized lignin nanofibers and/or nanofiber mats, and these differences did not correlate with changes in mechanical performance. Although surprisingly, this observation demonstrated that there was flexibility in the thermal oxidative stabilization process when creating lignin-based carbon nanofibers in the range from 230 to 300 °C.

### EXPERIMENTAL SECTION

**Materials.** Organic solvent fractionation of commercially available softwood kraft lignin (SKL, Indulin-AT, WestRock, Glen Allen, VA) was carried out by sequential extraction with organic solvents based on a published procedure\textsuperscript{17,48}. The 4th fractionated SKL (F4SKL) from methanol/methylene chloride (70:30, v/v) extraction was selected for producing lignin-based nanofibers. As indicated in the Supporting Information (Table S1), molecular weight analysis (Figure S4) and chemical characterization of the lignin (Figure S5) were carried out according to previously published methods\textsuperscript{33,49}. Nanocrystalline cellulose (NCC) was produced by authors as described in

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**Figure 11.** Raman spectra of lignin carbon nanofiber mats after various TOS temperatures in the range from 900 to 1800 cm\textsuperscript{-1}.

**Figure 12.** \( I_D/I_G \) ratio and crystallite size from Raman spectra of carbonized lignin nanofiber mats as functions of TOS temperature.

**Figure 13.** Electrical conductivity of carbonized lignin nanofiber mats as a function of TOS temperatures (\( p \) value > 0.05: statistically same).
the published procedure. Poly(ethylene oxide) (PEO) with average molecular weight of $1 \times 10^{6}$ g/mol was obtained from Sigma-Aldrich and used as received. N,N-Dimethylformamide (DMF), methanol, methylene chloride, and sulfuric acid of 98% were all ACS reagent grade and cellulose filter papers (Whatman No 1001-110) were also purchased from Fisher Scientific and used as received.

Electrospinning Process. As described earlier, F4SKL was used as the raw material for electrospinning. F4SKL/NCC suspension/PEO solutions in DMF were prepared at 80 °C for 3–4 h in the oil bath. NCC suspension in DMF was mixed at loadings of 1 wt % with respect to lignin solid weight as an additive to help control the molecular orientation of the lignin. The lignin solution concentration was kept constant at 27 wt %. Only 1 wt % PEO was added to the solution based on lignin solid weight to help form consistent fibers.

As described in the earlier studies, electrospinning was carried out in a vertical orientation using a 1 mL syringe pump (New Era Pump Systems, Inc, Wantagh, NY) operating at a flow rate of 0.01 mL/min supplied the polymer solution to the spinneret.

Thermal Oxidative Stabilization Process. Electrospun F4SKL/NCC/PEO composites nano fiber mats (1 wt % NCC loading) were stabilized at 1–5 °C/min to various final temperatures in a gas chromatography oven (Hewlett Packard 5890 Series II) and held isothermally for 30–60 min in air. After treatment, the yield after TOS was calculated gravimetrically. 2 Level Factorial Design with 3 variables (2FD3) was carried out in a vertical orientation using a 1 mL syringe pump connected to the positive clamp was cut prior to the test. The tests were conducted using a Kraftech KES-G1 tensile tester using 500 g of stabilized fiber mats and 100 g of load cell for carbonized fiber mats under 0.01 cm/s deformation rate and voltage constant of 10 V.

Characterization. One FTIR Spectrometer (PerkinElmer), equipped with Spectrum software, and 32 scans were collected with spectral resolution of 4 cm$^{-1}$. The spectra were normalized at 1600 cm$^{-1}$ for lignin-based fiber mats, and the relative intensity of absorption bands was measured. As reported in the previous research, the absorbance at 1600 cm$^{-1}$ showed a more accurate spectra collection.

Solid-state NMR measurements were carried out on a Bruker Advance-400 spectrometer operating at frequencies of 100.61 MHz for $^{13}$C and 400.09 MHz for $^1$H NMR in a Bruker double resonance MAS probe head at spinning speeds of 16 kHz for all experiments. $^{13}$C CP/MAS experiments utilized a 3 μs (90°) $^1$H pulse, 2 ms contact pulse, 4 s delay, and 2000 scans modified from earlier work.

Thermogravimetric analysis (TGA) was performed for the as-spun nanofiber mats, stabilized fiber mats using Q500 TA instruments (New Castle, DE). Two to three milligrams of nanofiber mats were heated to 600 °C for the as-spun fiber mats and to 1000 °C for stabilized fiber mats at a heating rate of 10 °C/min under nitrogen flow.

Mechanical tests were conducted for the stabilized and carbonized lignin nanofiber mats prepared at different final temperatures at the heating rate of 5 °C/min. Five sample strips of mats were prepared with 0.5 cm by 3 cm size and mounted on the tensile test frames. Prior to mounting, the samples were held in a paper C-clamp and the support of the clamp was cut prior to the test. The tests were conducted using a Katotech KES-G1 tensile tester using 500 g of stabilized fiber mats and 100 g of load cell for carbonized fiber mats under 0.01 cm/s deformation rate and voltage constant of 10 V.

Raman spectra of carbonized fiber mats were recorded on a RM1000 Raman Microscope system (Renishaw, Gloucestershire, U.K.) equipped with a 785 nm diode laser. A total of 2 scans per sample at 1% laser power were collected in the range of 800–2000 cm$^{-1}$ using an X50 microscope objective. Baseline correction of data points in the range was applied before curve fitting. The D-band was fitted with a Lorentzian line shape and the G band was fitted with a Breit–Wigner–Fano line shape using Origin 8.5 software. The ratio of two bands, $I_D/I_G$, was calculated as the ratio of the intensities (I, heights) of the D and G bands.

The DC resistance, $R$ (Ω), of carbon nanofibers mats was measured by a 2-point probe using a multimeter (Agilent U1272A). The samples were cut into approximately 1.5 cm length and 0.3–0.6 cm width and painted at each end with silver paint on clean glass slides. Conductivity was calculated based on the measurement $R$ in Ω and the dimensions of the samples using eq 2.

$$\frac{(S/cm)}{L} = \frac{(w \cdot t \cdot R)}{2}$$

where $L$ is the distance between the nonpainted part in cm, $w$ is the sample width in cm, and $t$ is the thickness of the sample in cm. The average values were calculated from the three measurements from each sample.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00278.
image of electrospun lignin-based fibers; TGA graph of lignin fiber mat; Elemental analysis of carbonized lignin fiber mats (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: scott.renneckar@ubc.ca.*

**ORCID**

Scott Renneckar: 0000-0002-7972-1091

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was partially funded by the NSERC LIGNOWORKS Biomaterials and Chemicals Strategic Research Network. Additionally, the work was supported by the Canadian Research Chairs program and the Paul and Edwina Heller Memorial Fund, along with the MRPF.

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