STRUCTURE AND PROPERTIES OF LIGNIN BASED CARBON NANOFIBERS

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ABSTRACT

Carbon nanofiber (CNF) made of inexpensive and bio-renewable raw materials can provide a pathway to lowering manufacturing cost of CNFs for structural composite applications. In this study, lignin nanofiber (LNF) mats were fabricated by electrospinning of a blend solution of polyacrylonitrile (PAN), lignin, and 1 weight percent (wt.%) of polyethylene oxide (PEO) in N, N-dimethylformamide (DMF). The LNFs were then subjected to heat treatment processes including thermostabilization at 240°C and subsequent carbonization at 1000°C. The effects of the PAN/lignin mass ratio and the heating rate on thermostabilization on the fiber morphology, fiber diameter, and mechanical properties of the CNF mats were systematically investigated. The scanning electron microscopy (SEM) images showed that as the lignin content in the precursor decreased, the diameter of the as-spun LNFs increased. However, the diameter, surface, and structure of the CNFs did not change significantly. The diameter of CNFs was about 700 nm. The strength of CNF mats increased as the proportion of lignin decreased, for slow heating rates (0.5–2 °C/min). However, with a faster heating rate (5°C/min), the strength of the CNF mats (with different PAN/lignin ratios) were identical. As the heating rate increased, the strength of the CNF mats increased greatly due to the fusing of the CNFs. The highest strength of the CNF mats was about 68.5 MPa. The diameter and surface features of the CNFs were found to be similar in all the samples (as a function of the heating rate). The strength of the PAN/lignin-based CNF mats was found to be much higher than that of pure PAN-based CNF mats at a fast heating rate (5°C/min). At slow heating rates of 0.5–2 °C/min, the mechanical properties of PAN/lignin-based CNF and PAN-based CNF mats were similar.

1 INTRODUCTION

Carbon nanofibers (CNFs) have high surface area and exhibit promising potential for a wide range of applications including composites, catalyst supports, biomedical materials, and energy fields [1–3]. CNFs can be fabricated through electrospinning [1,4] followed by stabilization and carbonization from carbon precursors, such as poly(acrylonitrile) (PAN) [1,5], phenolic resin [6], pitch [7] and polyimide [8]. Among various polymeric precursors, PAN is most widely used to produce the CNFs because of its supreme mechanical strength. However, PAN, as a petroleum derivate product, is unsustainable and relatively expensive, thus hampering the widespread use of PAN-based CNFs. In the recent years, substantial efforts have been made to develop low-cost CNFs by utilizing alternative raw materials, such as lignin [9] and cellulose [10].

Lignin, the second most abundant biopolymer behind cellulose, is the most important renewable source of aromatic structures. To date, there are a few reports on the production of electrospun lignin-based CNFs (LCNFs). The reported LCNFs show relatively low mechanical performance [11], resulting in their limited application. To integrate the cost merit of lignin and the superior mechanical properties of PAN, PAN/lignin blends have been considered [12, 13]. However, the details, regarding the effect of PAN content and heating rate during stabilization, were not discussed in these studies. Therefore, in this study, the effects of PAN/lignin ratio and stabilization heating rate on morphology, structure, mechanical and electrical properties of carbon fibers will be investigated.
2 EXPERIMENTAL

2.1 Materials
Polyacrylonitrile (PAN) and lignin were supplied by International Paper, WA, USA. Poly(ethylene oxide) (PEO, $M_w = 10^6$ g·mol$^{-1}$) and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich and Fisher Scientific (Ottawa, ON), and used without further purification.

2.2 Carbon Nanofiber Production Process
PAN/lignin/PEO solutions were prepared in DMF at a total concentration of 25 wt%, containing 1 wt% PEO and 99 wt% PAN/lignin blend. In order to investigate the effect of PAN/lignin blend on the properties of CNFs, a number of different PAN/lignin ratios (20/80, 65/35, and 50/50 wt%) were prepared and electrospun. The fiber mats were thermally stabilized, at different heating rates (0.5 - 5°C·min$^{-1}$), under air (in a Thermolyne-79400 tube furnace) from room temperature to 240°C, then they were isothermally held for an hour. The thermostabilized mats were subsequently carbonized under argon at a heating rate of 5°C·min$^{-1}$ up to 1000°C, and then held isothermally for an hour. Finally, the carbonized mats were cooled down to room temperature. In addition, for comparison, the CNF mats made of pure PAN were prepared in the same manner.

3 RESULTS AND DISCUSSION
As shown in Figure 1, all the as-spun nanofibers (NFs) have a uniform fibrous morphology. As is apparent from the SEMs, the surface of the 20/80 and 35/65 NFs is smooth, whereas the 50/50 NFs have grooves on the surface. In addition, the average diameter of the as-spun NFs increases with the increasing of the PAN ratio (Figure 1(d)) from 833±231 nm (for the 20/80 PAN/lignin) to 1636±297 nm (for the 50/50 PAN/lignin). This is mainly attributed to the viscosity of the solutions. It is well known that during electrospinning, when all other factors are equal, a higher viscosity results in as-spun NFs with larger diameter. The viscosity of lignin solution is much lower than that of PAN [11, 13], and as a result, the viscosity greatly increases with the increase of the PAN content.
Figure 1: SEM images of as-spun nanofibers with various PAN/lignin ratios: (a) 20/80, (b) 35/65, and (c) 50/50.

Figure 2 shows the CNFs after thermostabilization at different heating rates (0.5 - 5 °C/min) and carbonization. It was observed that with the heating rate increasing, more fibers are fused. In addition, the number of the fused fibers decreases as the proportion of PAN increases (Fig. 2: a-d; e-h; i-l), especially for the faster heating rates (2 - 5 °C/min).

Figure 2: SEM images of CNFs with various PAN/lignin ratios thermostabilized at different heating rates (0.5 - 5.0 °C·min⁻¹): (a-d) 20/80; (e-h) 35/65; and (i-l) 50/50. The red circles represent areas where fusion of the fibers has occurred.
In addition, the diameters of these CNFs are much smaller than that of the as-spun NFs (Fig.3). This is due to the thermal decomposition of PAN and lignin during the heat treatment. Interestingly, almost all of the CNFs have similar average diameters of about 700 nm.

![Figure 3: Diameters of the CNFs with various PAN/lignin ratios thermostabilized at different heating rates.](image)

Figure 3: Diameters of the CNFs with various PAN/lignin ratios thermostabilized at different heating rates.

Figure 4(a-c) shows the stress-strain curves of each NF mats with various PAN/lignin ratios thermostabilized at different heating rates. The strength of the PAN/lignin based CNF mats, as well as pure PAN based CNF mat, are demonstrated in Figure 4(d). The mechanical properties of the mats are summarized in Table 1. From table 1, the impact of the heating rate and the PAN/lignin ratio on the initial elastic modulus and elongation at break can be studied.

![Figure 4: Stress-strain curves of the CNFs mats with various PAN/lignin ratios thermostabilized at different heating rates: (a) 20/80, (b) 35/65, (c) 50/50, and (d) the strength of the CNF mats.](image)

Figure 4: Stress-strain curves of the CNFs mats with various PAN/lignin ratios thermostabilized at different heating rates: (a) 20/80, (b) 35/65, (c) 50/50, and (d) the strength of the CNF mats.
As displayed in Figure 4(d) and Table 1, the strength of CNF mats increases as the heating rate increases. This is as a result of the increased number of fused fibers, which improve the strength of the CNF mats. In addition, at medial heating rates (1.2 C/min), the strength of the CNF mats increases with the increased proportion of PAN; however, at a slower or faster heating rate (0.5 or 5.0 C/min), the CNFs with 35/65 ratio have slightly higher strengths. The highest strength of 68.47±4.19 MPa was obtained from the CNFs with PAN/lignin of 35/65 ratio which were thermostabilized at 5 C/min.

In addition, the strength of the PAN/lignin-based CNF mats was found to be much higher than that of pure PAN-based CNF mats at a fast heating rate (5°C/min). At slow heating rates of 0.5-2°C/min, the mechanical properties of PAN/lignin-based CNF and PAN-based CNF mats were similar. Accordingly, both the heating rate for stabilization and the PAN/lignin ratios show great effects on the mechanical properties of CNFs mats. Although in the current study the heating rate for carbonization was not varied, it is conceivable that this may also affect the mechanical properties of CNFs mats, and hence will be investigated.

<table>
<thead>
<tr>
<th>Samples – Stabilization heating rate (°C/min)</th>
<th>Initial elastic modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Elongation at break (%)</th>
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</thead>
<tbody>
<tr>
<td>20/80-0.5</td>
<td>5.2±0.7</td>
<td>35.2±5.0</td>
<td>0.75±0.02</td>
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<td>20/80-1.0</td>
<td>5.6±0.2</td>
<td>39.8±1.9</td>
<td>0.71±0.05</td>
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<tr>
<td>20/80-2.0</td>
<td>7.1±0.2</td>
<td>42.5±1.6</td>
<td>0.60±0.02</td>
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<tr>
<td>20/80-5.0</td>
<td>9.4±0.8</td>
<td>61.5±3.7</td>
<td>0.67±0.09</td>
</tr>
<tr>
<td>35/65-0.5</td>
<td>9.4±0.8</td>
<td>49.0±5.6</td>
<td>0.53±0.09</td>
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<tr>
<td>35/65-1.0</td>
<td>7.7±0.8</td>
<td>45.6±1.7</td>
<td>0.58±0.05</td>
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<tr>
<td>35/65-2.0</td>
<td>8.6±0.4</td>
<td>59.1±6.6</td>
<td>0.72±0.10</td>
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<tr>
<td>35/65-5.0</td>
<td>9.7±0.4</td>
<td>68.5±4.2</td>
<td>0.71±0.06</td>
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<tr>
<td>50/50-0.5</td>
<td>8.2±1.0</td>
<td>40.0±1.5</td>
<td>0.50±0.07</td>
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<tr>
<td>50/50-1.0</td>
<td>10.0±0.7</td>
<td>47.5±3.3</td>
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<tr>
<td>50/50-2.0</td>
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<td>0.62±0.05</td>
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<tr>
<td>50/50-5.0</td>
<td>8.9±0.3</td>
<td>66.0±2.3</td>
<td>0.74±0.03</td>
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</table>

Table 1: The mechanical properties (an average +/- the standard deviation) of the CNF mats with various PAN/lignin ratios at different heating rates.

Figure 5(a) shows the conductivity of the CNF mats for the various PAN/lignin ratios thermostabilized at different heating rates. It was observed that the conductivity increases as the heating rate increases, and it decreases with the increasing proportion of PAN. The 20/80 CNF mat (with heating rate of 5.0°C/min) has the highest conductivity (15.29±1.37 S/cm). Generally, the conductivity of CNF mats depends on the carbon structure of CNFs and the texture of mats. Raman spectroscopy was employed to compare the carbon structure of CNFs with different PAN/lignin ratios. As shown in Figure 5(b), the two major broad peaks centering at about 1330 and 1586 cm⁻¹ in the spectra are attributed to D-band and G-band, respectively [14]. The G-band is an in-plane stretching mode of sp² carbon bonds existing in the ideal graphitic lattice. The D-band originates from a hybridized vibrational mode related to graphene layer edges, indicating the number of defects in the graphitic structure. It is well known that the ratio of G-band to D-band depends on both the degree of graphitization and the alignment of graphitic planes [15]. From the spectra, it can be confirmed that the I_G/I_D value of CNFs are 0.941 (20/80), 0.947 (35/65), 0.923 (50/50), respectively. This implies that degree of graphitization and the alignment of graphitic planes are similar for the CNFs. Moreover, a comparison of the high-resolution XPS C 1s spectra showed no differences between the 20/80 CNF mats exposed to heating rates of 2.0 versus 5.0°C/min (data not shown). This suggests that there are no differences in the surface carbon structure, contrary to what was demonstrated by Jang et al [16], who showed differences in XPS spectra of CFs treated at different heating rates, but not significant differences in the Raman spectra. Overall, the results obtained in this work suggest that the differences
in conductivity as well as the mechanical properties observed may be linked to the texture of CNF mats. As presented in Figure 2, the degree of fusion among the CNFs increases as the heating rate or the proportion of lignin increases.

Figure 5: (a) Conductivities of the CNFs mats using various PAN/lignin ratios at different stabilized heating rates, and (b) Raman spectra of the CNFs mats for different PAN/lignin ratios, using a heating rate of 5.0°C/min.

4 CONCLUSIONS

CNFs were successfully prepared via electrospinning of PAN/lignin blend with 1 wt.% of PEO, followed by thermostabilization and carbonization. The diameters and surfaces of the CNFs remain constant at about 700 nm. The strength of CNF mats increases as the fraction of lignin decreases when a slow heating rate was applied (0.5-2 °C/min). At a faster heating rate (5 °C/min), the strength of the various CNF mats were comparable. As the heating rate increases, the strength of the CNF mats increases greatly reaching a highest strength of 68.47±4.19 MPa. It is of interest to note the strength of PAN/lignin-based CNF mats was much higher than that of PAN-based CNFs mat when the heating rate was 5 °C/min. At slow heating rates of 0.5-2.0 °C/min, the PAN/lignin-based CNF mats exhibited comparable mechanical properties to PAN-based CNF mats. The conductivity increases as the heating rate increases, while it decreases with increasing proportion of PAN. A highest conductivity of 15±1 S/cm was obtained for CNF mats made of 20/80 PAN/lignin with a heating rate of 5 °C/min.

This study demonstrated the feasibility of the fabrication of carbon nanofibers from PAN/lignin polymer blends. The heating rate for the thermostabilization process was found to play an important role in the strength of the CNF mats. It is anticipated the strength of the CNF mats can be further improved by optimization of fiber architecture, spinning conditions and carbonization conditions. Finally, the results presented here and future work could lead to sustainable production of CNFs, as lignin is a more ecologically-friendly product than PAN, and since faster heating rates translate into energy savings during production.

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