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# Improvement of Mechanical Properties of Softwood Lignin-Based Carbon Fibers

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**Abstract:** PEG-lignin fibers obtained by a solvolysis pulping of Japanese cedar with polyethylene glycol (PEG) 400 were successfully converted into defect-free, infusible fibers as a precursor for carbon fibers (CFs) by chemical curing followed by oxidative thermostabilization. The curing was performed by immersing PEG-lignin fibers in an aqueous mixed solution of hexamethylenetetramine (60 g/L) and hydrochloric acid (3 M) at 85 °C for 1 h, resulting in the formation of cross-linkages between lignin molecules

through methylene groups. These cured fibers were completely thermostabilized by heating up to 250 °C at a heating rate of 2 °C/min under an air atmosphere. Finally, the thermostabilized fibers were carbonized to yield CFs, which showed about 1.5 times the tensile strength of our CFs with many defects prepared previously.

**Keywords:** Softwood lignin, Chemical curing, Hexamethylenetetramine, Carbon fibers, Mechanical properties

## **INTRODUCTION**

Carbon fibers (CFs) can be used in a variety of industries including aerospace, civil engineering and automotive applications due to their high performance.<sup>[1]</sup> Several types of lignin have been used as a feedstock for such CF production.<sup>[2-9]</sup> In general, the principal processing steps for preparing CFs typically cover spinning, stabilization, carbonization, and sometimes graphitization. In general, oxidative thermostabilization to convert fusible fibers into infusible ones is performed with increasing temperature at a considerably slow heating rate under an oxidizing atmosphere. The heating rate affects the production time and cost of CFs. In the case of lignin, this conversion is based on the formation of cross-linkages among lignin molecules by introduction of oxygen through a series of elimination, rearrangement, and oxidative reactions of free radicals derived from homolysis of  $\beta$ -O-4 ether bonds in lignin.<sup>[10]</sup> Besides, softwood lignin possesses more cross-linked structure such as  $\beta$ -5 and 5-5 bonds than hardwood lignin, probably leading

to faster stabilization.<sup>[9]</sup>

We have developed fusible softwood lignin (PEG-lignin) by a solvolysis pulping of Japanese cedar with PEG400, and it was easily fabricated by melt-spinning. We evidenced that the fusibility of the PEG-lignin was caused by PEG moiety introduced by the pulping process.<sup>[8]</sup> To prepare thermostabilized fibers as precursory fibers for CF production from PEG-lignin fibers, an oxidative thermostabilization was firstly attempted. As a result, this attempt was found unsuccessful even at a relatively low heating rate of 0.1 °C/min, because the obtained fibers melted and adhered to each other. Next, we developed an alternative thermostabilization process, namely, “chemical thermostabilization,” to obtain infusible fibers. This process was achieved by removing some of PEG moiety from PEG-lignin. However, the chemically thermostabilized fibers had some defects such as splits and flabby structures by the release of PEG moiety during this process. The defects also remained in the corresponding CFs, which was a disadvantage for preparing CFs with high mechanical properties.<sup>[8]</sup> If defect-free thermostabilized fibers can be prepared, the mechanical strength would be improved.

A curing reaction is considered as one of the effective techniques to generate a large amount of cross-linkages. As a common cross-linking reagent, hexamethylenetetramine (HMTA) is generally used for curing to prepare thermosetting products,<sup>[11]</sup> such as phenolic resin. When HMTA is applied to softwood lignin, HMTA can crosslink aromatic carbons at unsubstituted position of aromatic ring through methylene bridge, because softwood lignin consists of more than 95 % of guaiacyl units.<sup>[12]</sup>

Accordingly, we investigated how chemical cross-linking of PEG-lignin powder

and PEG-lignin fibers works by HMTA treatment. By a combination of this curing reaction and oxidative oxidation, we have succeeded in obtaining defect-free, infusible fibers with a smooth surface. In this paper, the mechanical properties of CFs prepared from the infusible fibers are also discussed.

## **EXPERIMENTAL**

### **Materials**

PEG-lignin powder was isolated from cedar wood chips, and then spun to the corresponding fibers as previously reported.<sup>[8]</sup> Other all chemicals used in this study were of analytical grade and used as received.

### **Chemical Curing of PEG-lignin**

Chemical curing was performed with HMTA in the form of lignin powder and lignin fibers. PEG-lignin powder was manually mixed with HMTA powder (1-5 wt% on PEG-lignin) by using a mortar and a pestle, and then subjected to melt-spinning.

PEG-lignin fibers were immersed in HMTA aqueous solution at concentrations of 5 to 60 g/L, containing 0 to 3 M HCl. The mixture systems were then heated at the temperature of 60, 80, and 100 °C for 1 h, respectively. The resultant fibers were washed twice with distilled water, and then roughly dried *in vacuo* at 40 °C for 2 h.

The cured PEG-lignin fibers were subjected to the oxidative thermostabilization. This treatment was performed on heating from room temperature to 250 °C at heating rates of 0.5 to 2 °C/min under an air atmosphere in an electronic muffle furnace (KDF S90/S90G, Denken Co. Ltd., Kyoto, Japan), and then the temperature was maintained at 250 °C for 1 h.

### **Carbonization**

The thermostabilized fibers were carbonized in the same electronic muffle furnace from room temperature to 1000 °C at a heating rate of 3 °C /min under a N<sub>2</sub> stream at a flow rate of 0.15 L/min, and then held at 1000 °C for 1 h to yield CFs.

### **Analyses**

PEG content was measured, according to the modified Morgan method.<sup>[8,13-14]</sup> Changes in other functional groups during the chemical curing were monitored on a Fourier-transform Infrared (FTIR) spectrometer (BIO-RAD FTS-50A FTIR, Hercules, CA, USA), using a diffuse reflectance method with KBr fine powder. Numbers of scan was 128, with a spectral resolution of 2 cm<sup>-1</sup>.

Thermomechanical analysis (TMA) was performed on a TMA-4000S System (MAC Science System 010, MAC Science, Yokohama, Japan) at temperatures ranging from 30 to 300 °C under a compression loading of 5 g under a N<sub>2</sub> stream at 0.15 L/min.

Fiber morphology was observed under an optical microscope (Violet laser color 3D profile microscope VK-9500, Keyence Japan, Osaka, Japan). The average diameter for at least 30 fibers was reported as the mean value  $\pm$  standard deviation. A scanning electronic microscope (SEM; JSM-6301F [FE-SEM], JOEL Ltd., Tokyo, Japan), using gold-sputtered samples at a magnification factor of 2500 - 8500 and at an accelerating voltage of 5 kV. Tensile strength of fibers was measured on a testing apparatus reported previously,<sup>[15]</sup> and calculated using the average diameter.

X-ray diffraction (XRD) of PEG-lignin based CFs and chemically cured CFs were carried out on a Rigaku RINT2000 X-ray diffractometer (Tokyo, Japan), after pulverization of CFs. Data were collected with a scan speed of 0.5 degree/min and a scan step of 0.02 degree at 40 kV and 200 mA in the 2 theta ( $\theta$ ) range from 5 to 60 degrees, using Cu-K $\alpha$  radiation.

## **RESULTS AND DISCUSSION**

### **Blends of PEG-lignin powder and HMTA**

PEG-lignin was isolated from cedar wood chips,<sup>[8]</sup> and milled into fine powder. After mixing this powder manually with varying amounts of HMTA, the blends were subjected to melt-spinning to obtain cross-linked fibers. However, no fiber was obtained even at the smallest addition (1 % on PEG-lignin) of HMTA. PEG-lignin seemed to have already converted to an infusible material by crosslinking reaction on the heating for melt-

spinning. This conversion was also confirmed by TMA measurement of the blends, by which the thermal properties of powdered lignin can be analyzed.<sup>[16]</sup> As shown in Fig. 1 (A), the TMA curve of PEG-lignin powder without HMTA showed two transition points at 79 °C and 141 °C, corresponding to its glass transition temperature ( $T_g$ ) and thermal-flow starting temperature ( $T_f$ ), respectively. By the addition of 1% HMTA to PEG-lignin (Fig. 1 (B)),  $T_g$  was shifted to 102 °C, and the blend still showed the second transition point ( $T_f$ ), indicating it exhibits thermal fusibility. In addition, this lignin blend expanded at the spinning temperature of about 170 °C, probably due to the thermal decomposition, as observed in softwood kraft lignin.<sup>[16]</sup> This result indicated that melt-spinning was practically impossible. Even with further increase in HMTA charge (Figs. 1 (C) and (D)),  $T_g$  was almost identical to that at 1 % charge of HMTA, but no  $T_f$  was observed in their TMA profiles. These results suggested that PEG-lignin was cross-linked easily by using HMTA to be converted to infusible material.

### **Chemical curing of PEG-fibers with HMTA**

To obtain infusible fibers, PEG-lignin fibers prepared by melt-spinning without HMTA addition were immersed in an aqueous HMTA solution at the concentrations ranging from 5 g/L to 60 g/L, and then heated at the temperature of 60, 80, and 100 °C for 1 h. The resulting fibers were observed to have almost the same morphology as the original fibers, except for the fibers treated at 100 °C. The fibrous morphology was changed at the treatment temperature of 100 °C, because the temperature was about 20 °C higher than the  $T_g$  of PEG-lignin fibers. The treated fibers were, in turn, subjected to oxidative

thermostabilization. Unfortunately, all the oxidatively thermostabilized fibers melted and adhered to each other at a heating rate of 0.5 °C/min, indicating that the curing reaction was insufficient. These results may be caused by the limited amount of cross-linkages among lignin molecules with formaldehyde released from HMTA.<sup>[17-18]</sup>

The decomposition of HMTA to generate formaldehyde and ammonia is strongly dependent on the pH in the reaction medium<sup>[19]</sup>; the lower the pH is, the more formaldehyde is generated. Therefore, the chemical curing of PEG-lignin fibers with several amounts of HMTA was attempted in aqueous HCl solutions at various concentrations of 0.1 to 3 M, because defects would probably appear at much stronger acid concentration, just like chemically thermostabilized fibers reported previously.<sup>[8]</sup>

All the resultant fibers kept the fibrous shape and a smooth surface, as shown in Figs. 2 (A) and (B). They still showed  $T_g$ , but did not expand over 200 °C from the TMA profiles of these cured fibers (Fig. 3), where the first value and the second value in parentheses of the figure captions denote the concentration of HCl (M) and the amount of HMTA (g/L), respectively. These results implied that PEG-lignin fibers were converted to relatively thermally stable fibers through the curing reaction.

Fig. 4 illustrates the FTIR spectra of PEG-lignin fibers and chemically cured fibers. A relative peak intensity of all chemically cured fibers (Figs. 4 (B)-(E)) at 2937  $\text{cm}^{-1}$  was likely to become stronger than that of the original PEG-lignin fibers (Fig. 4 (A)). The ratio of intensity at 2937  $\text{cm}^{-1}$  to that at 3341  $\text{cm}^{-1}$  (O-H stretching vibration) or that at 1600  $\text{cm}^{-1}$  (C=C ring stretching vibration) clearly showed the increase in the relative intensity at 2937  $\text{cm}^{-1}$  (Table 1). This result indicates that increasing number of

methylene group was generated by the curing with HMTA under stronger acidic conditions and it acted as methylene bridge for cross-linking.<sup>[20, 21]</sup>

Table 1 also showed that PEG content in the cured fibers was slightly but gradually decreased, with an increase in the concentration of the acid used for curing. This result may be caused either by the release of PEG by HCl treatment, or by the introduction of methylene group, or both. Accordingly, the cured fibers treated with 3 M of HCl and 60 g/L of HMTA showed the highest  $T_g$  among the treated fibers, probably due to the densest cross-linking and the lowest flexibility.

### **Oxidative thermostabilization of chemically cured fibers**

The existence of  $T_g$  and the observed changes in volume in TMA curves of chemically cured fibers (Fig. 3) implied that the fibers were not completely infusible. To prevent the fusion of individual fibers upon further carbonization, the oxidative thermostabilization were further attempted. Generally, heating rate is considered to be one of the most significant factors affecting the thermal stability of fibers during oxidative thermostabilization,<sup>[22]</sup> and the production cost for CFs. In our previous work,<sup>[8]</sup> PEG-lignin fibers was able to be converted to infusible fibers at low heating rate of 0.1 °C/min (2-days treatment), but fusion and adhesion of fibers occurred during the process.

The authors sought out for the highest heating rate to cure fibers without losing the fibrous morphology, by increasing heating rate at an interval of 0.5 °C/min. Results are shown in the last column in Table 1. As seen in the table, the highest heating rate was increased with an increase in the concentrations of HCl and HMTA in the curing process.

Accordingly, the PEG-lignin fibers thermostabilized by the curing with 3 M of HCl and 60 g/L of HMTA (3, 60) followed by oxidative thermostabilization under an air atmosphere, showed the highest heating rate of the 2 °C/min. As expected, the resultant fibers had smooth surface without any defect [Fig. 2 (C) and (D)]. In addition, TMA profiles also indicated that all the fibers prepared by the curing reaction, followed by oxidative thermostabilization, were converted to completely infusible fibers without showing  $T_g$  (OT-Fs in Fig. 3).

### **Carbonization**

The thermostabilized fibers were, in turn, carbonized by heating the fibers from room temperature to 1000 °C at a heating rate of 3 °C/min under a stream of nitrogen, and then the temperature was maintained at 1000 °C for 1 h. As shown in Figs. 2 (E) and (F), no obvious defect such as split and flabby structures appeared on the surface of CFs. Table 2 shows the mechanical properties of the CFs from both the chemically cured fibers prepared in this study and the chemically thermostabilized fibers reported previously.<sup>[8]</sup> All the CFs prepared in this study showed much stronger tensile strength and modulus than the previously prepared CFs. Especially, CFs derived from the chemically cured fibers (3, 60) showed 1.5 times greater tensile strength than that of the previous CFs, and its value is almost comparable to that of CFs prepared from hardwood kraft lignin blended with 25 % polyethylene terephthalate (PET), which was considered as the strongest lignin-based CFs among the CFs reported so far.<sup>[23]</sup>

The XRD profiles of CFs derived from chemically cured fibers (3, 60) and chemically thermostabilized fibers with Cu-K $\alpha$  irradiation are shown in Fig. 5. Although a weak broad peak was observed at around  $2\theta=44^\circ$  that nearly corresponds to the diffraction of turbostratic carbon,<sup>[24]</sup> there was no clear peak at about  $22^\circ$  in both diffractograms. This result suggests there is no graphite structure developed during carbonization process. Consequently, the enhancement of the tensile strength for CFs prepared from the chemically cured fibers is not attributed to the development of graphite structure, but to the defect-free, smooth surface of the CFs.

## CONCLUSIONS

Hexamethylenetetramine (HMTA) was found to act as an effective cross-linker for the curing of PEG-lignin. HMTA in aqueous HCl solution accelerated the curing for PEG-lignin. PEG-lignin fibers were successfully converted to completely thermostabilized fibers without defect by the chemical curing with HMTA in aqueous HCl solution, followed by the oxidative thermostabilization under an air atmosphere. The oxidative thermostabilization of the fibers, cured chemically with a mixed solution of 3 M of HCl aq. and 60 g/L of HMTA, was carried out at a heating rate of  $2^\circ\text{C}/\text{min}$ . These results suggested that all thermostabilization process was completed for 3 h. The resultant defect-free CFs showed the highest tensile strength of about 700 MPa, which was comparable to the strongest lignin-based CFs previously reported.

## ACKNOWLEDGEMENT

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**Figure captions:**

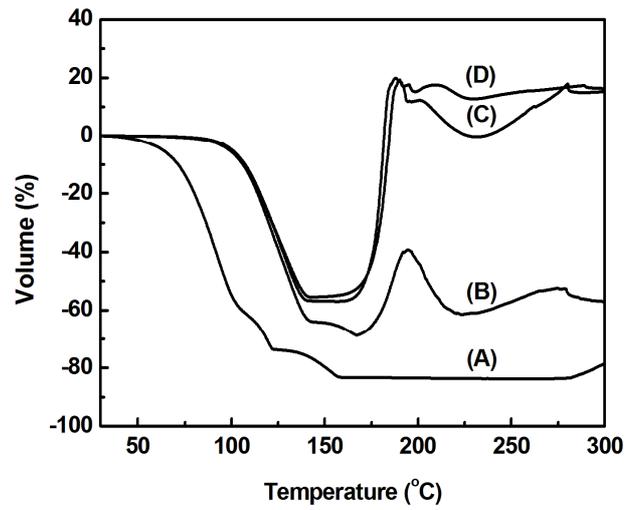
**Figure 1.** TMA curves of PEG-lignin powder blended with varying amounts of HMTA. (A), 0 %, (B), 1 %, (C), 2 %, (D), 5 %.

**Figure 2.** SEM images of chemically cured fibers with 3 M of HCl and 60 g/L of HMTA (3, 60) (A and B), their oxidatively thermostabilized fibers at the heating rate of 2 °C/min (C and D), and CFs from cured and oxidatively thermostabilized fibers (E and F).

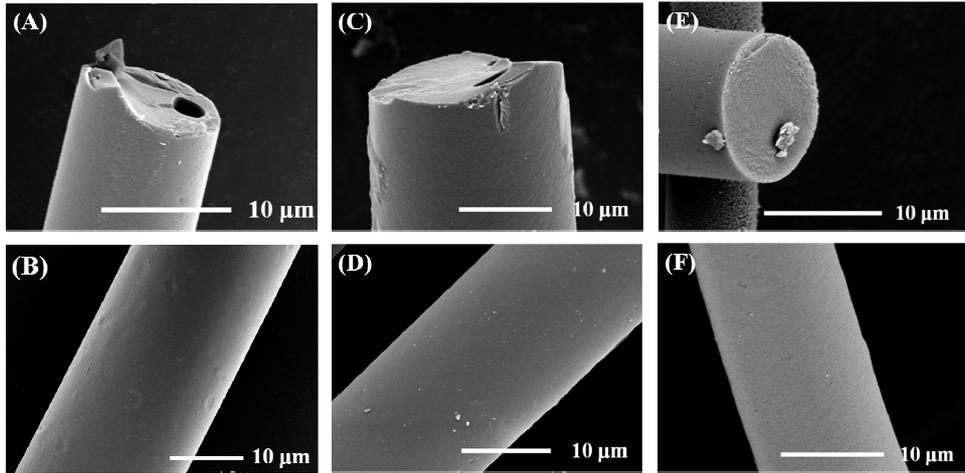
**Figure 3.** a) TMA profiles for PEG-lignin fibers and their thermostabilized fibers. (A), PEG-lignin fibers; (B), chemically cured fibers with (0.1, 20); (C), with (2, 40); (D), with (3, 40); (E), with (3, 60); (OT-Fs), oxidatively thermostabilized fibers derived from chemically cured fibers (B), (C), (D), and (E), respectively. b) Expanded TMA of OT-Fs derived from chemically cured fibers (B), (—); (C), (·····); (D), (- - -); and (E), (- · - · -), respectively.

**Figure 4.** FTIR spectra of PEG-lignin fibers (A) and chemically cured fibers treated under various conditions (B) (0.1, 20), (C) (2, 40), (D) (3, 40) and (E) (3, 60), respectively.

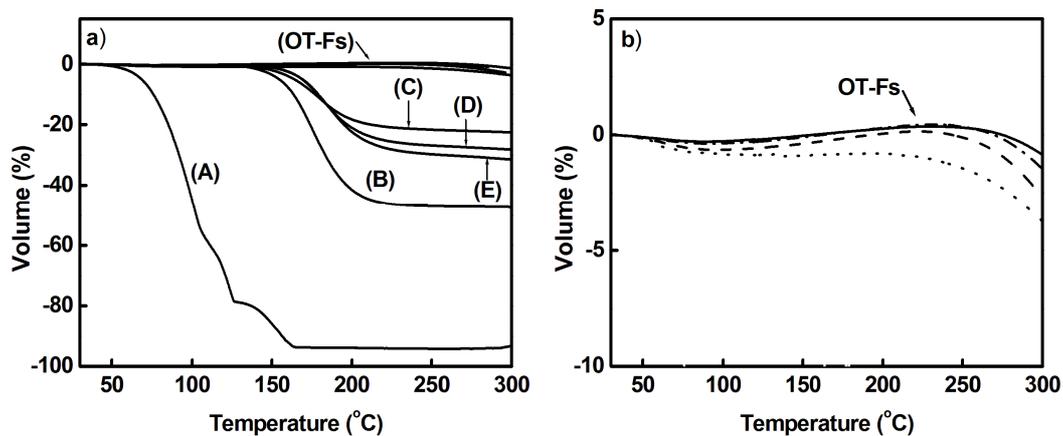
**Figure 5.** X-ray diffractions of PEG-lignin based carbon fibers (CFs) prepared from the cured and oxidatively thermostabilized fibers (A), and CFs from chemically thermostabilized fibers (B).



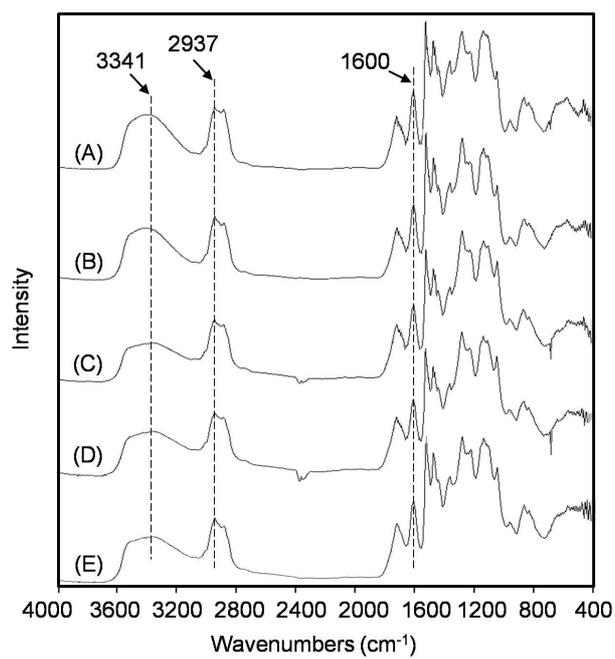
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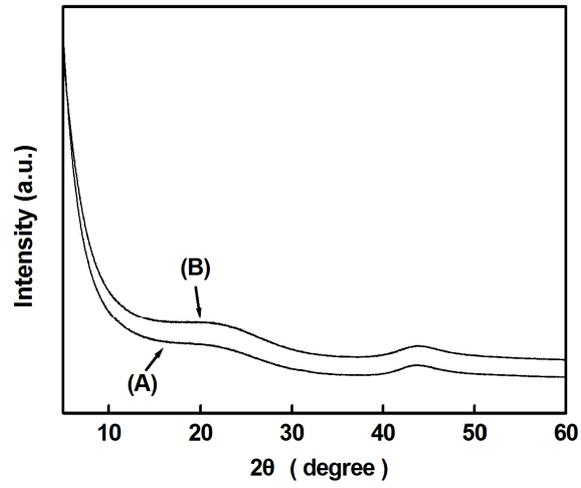
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**Figure 5.** X-ray diffractions of PEG-lignin based carbon fibers (CFs) prepared from the cured and oxidatively thermostabilized fibers (A), and CFs from chemically thermostabilized fibers (B).

**Table 1.** Glass transition temperature, FTIR peak intensity ratio and PEG content of PEG-lignin fibers and chemically cured fibers.

Samples <sup>1</sup>	$T_g$	FTIR peak intensity ratio		PEG content (%)	Heating rate <sup>2</sup> (°C/min)
	(°C)	( $I_{2937} / I_{3341}$ )	( $I_{2937} / I_{1600}$ )		
PEG-lignin fibers	79	1.12	0.789	40.56	< 0.1
CC-F (0.1, 20)	155	1.19	0.796	39.11	0.5
CC-F (2, 40)	158	1.51	0.824	37.50	1.5
CC-F (3, 40)	161	1.38	0.819	37.45	1.5
CC-F (3, 60)	165	1.41	0.850	37.23	2.0

<sup>1</sup> CC-F (0.1, 20), (2, 40), (3, 40), and (3, 60) denote chemically cured fibers treated with various concentrations of HCl and HMTA of (0.1 M, 20 g/L), (2 M, 40 g/L), (3 M, 40 g/L), and (3 M, 60 g/L), respectively.

<sup>2</sup> The highest heating rate at which fibers were cured without losing their fibrous morphology.

**Table 2.** Mechanical properties of lignin-based CFs and composite material.

Samples <sup>1</sup>	Diameter ( $\mu\text{m}$ )	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
CFs (0.1, 20)	$8.9 \pm 1.3$	$590 \pm 63$	$41.7 \pm 9.1$	$1.47 \pm 0.32$
CFs (2, 40)	$8.4 \pm 0.8$	$620 \pm 47$	$41.9 \pm 7.9$	$1.52 \pm 0.25$
CFs (3, 40)	$8.6 \pm 0.9$	$653 \pm 90$	$47.2 \pm 9.4$	$1.42 \pm 0.23$
CFs (3, 60)	$8.2 \pm 1.0$	$695 \pm 124$	$47.3 \pm 11.5$	$1.51 \pm 0.25$
PEG-lignin CFs	$10.4 \pm 1.3$	$457 \pm 188$	$26.2 \pm 13.3$	$2.11 \pm 1.07$
HWKL/PET (75/25)	$34.0 \pm 5.0$	703	94.0	1.06

<sup>1</sup> CFs (0.1, 20), (2, 40), (3, 40) and (3, 60) denote carbon fibers from chemically cured fibers (0.1, 20), (2, 40), (3, 40), and (3, 60), respectively. The mechanical properties of PEG-lignin CFs and HWKL/PET (75/25) are cited from literatures.<sup>[8,23]</sup>