Effects of Time and Chemical Curing Temperature on the Properties of Liquefied Wood-Based Precursors and Carbon Fibers

Junbo Shang,[a] Jian Lin,[a] Guangjie Zhao,[a,*] Jianhui Zhang,[b] Zimu Su,[a] and Sicen Guo [a]

Liquefied wood-based precursors and carbon fibers were prepared by various chemical curing processes to investigate the effects of curing time and temperature on the thermostability and tensile strength of carbon fibers. The primary fibers can be converted into high-performance precursors by directly heating at a targeted curing temperature. With the temperature and duration increasing, the number of methylene bonds in the precursors increased, resulting in the enhancement of cross-linkages among molecular chains and the improvement of the thermostability of the precursors. Carbon fibers prepared from the precursors (95 °C and curing time 3 h) exhibited the minimum value in the average interlayer spacing (d_{002}); however, they displayed the highest tensile strength, at almost 800 MPa, which can be classified as fibers of general grade.

Keywords: Chemical curing; Precursor; Carbon fibers; Tensile strength

Contact information: a: MOE Key Laboratory of Wooden Material Science and Application, College of Materials and Science Technology, Beijing Forestry University, 100083, Beijing, P.R. China; b: Planning and Design Institute of Forest Products Industry, SFA, Beijing, 100010, China;
* Corresponding author: zhaows@bjfu.edu.cn

INTRODUCTION

As a fibrous carbon material, the carbon content of carbon fibers is greater than 92% (Frank *et al*. 2012). Because of their excellent tensile strength, modulus of elasticity, heat resistance, abrasion resistance, and corrosion resistance, carbon fibers have been applied in many industries, such as aerospace, automobile, wind energy, and sports equipment (Huang 2009; Foston *et al.* 2013). In recent years, greater than 90% of raw materials with carbon fibers have been derived from polyacrylonitrile (PAN) and pitch. Although the international crude oil prices are falling, fossil resources are expected to be exhausted within years. In addition, the deterioration of the environment resulting from the reliance on fossil resources is excessive. Finding new raw materials to replace fossil resources for preparing carbon fibers has been put on the agenda.

Wooden biomass is a type of renewable, sustainable biomass that has been certified as one of the raw materials for preparing wooden carbon materials. As a widely planted economic forest in China, Chinese fir is used to prepare carbon fibers in order to enlarge its utilization fields, not only for traditional industries, such as for buildings, furniture, *etc*. (Ma *et al*. 2010). Recent preparation processes for carbon fibers or activated carbon fibers from liquefied wood in phenol include wood liquefaction, melting spinning, chemical curing, and carbonization or activation. The tensile strength of the wood-based carbon fibers almost qualifies for the general level of pitch-based carbon fibers (Ma *et al*. 2011; Li *et al*. 2013; Lin *et al*. 2013). Instead of thermal stabilization treatment with air or oxygen in the process of preparing PAN carbon fibers, chemical curing is used, which requires a

mixed solution of hydrochloric acid and formaldehyde to stabilize the primary fibers. The curing process begins by immersing the primary fibers in the mixed solution, then heating to 95 °C at a rate of 10 °C/ h and incubating for 4 h at 95 °C (Ma *et al.* 2007b). During the chemical curing process, the formaldehyde molecules in solution, *i.e.*, carbocations, begin to react and form into methylene in the benzene rings of the primary fibers, resulting in a three-dimensional network structure built between molecular chains. Then, the thermal-fusible primary fibers are transformed into thermal-setting precursors to prevent the precursors from melting during carbonization (Lin *et al.* 2012).

Chemical curing can take greater than 10 h for completion, which accounts for half of the preparation time from wood liquefaction to carbonization. Over long heating and incubation periods, this would lead to low yields and high production cost and energy consumption, and these factors impose important restrictions to the application of this technology. The work presented here was conducted to investigate the preparation technology of direct chemical curing and the effects of curing time and temperature on the thermal stability, microstructure of precursors, X-ray diffraction, and tensile strength of the carbon fibers.

EXPERIMENTAL

Materials

Chinese fir (*Cunninghamia lanceolata*) was obtained from the Fujian province, China. The chemicals, *i.e.*, phosphoric acid, phenol, hexamethylenetetramine (HMTA), acetone, hydrochloric acid, and formaldehyde were supplied by the Beijing Lanyi chemical products Corp., China.

Methods

A mixture of 25 g dried Chinese fir powder (20 to 80 mesh) and 100 g phenol was put into a bottle flask, and then 8 g phosphoric acid (8.0% based on the weight of phenol) was added. The flask was immersed in an oil bath, then heated rapidly from room temperature to 160 °C and incubated for 150 min. The flask was then cooled to room temperature with cool water, and acetone was added to the reaction products. The resultant mixture was filtered through a glass crucible filter (G2, pore diameter 30 to 50 μm) to separate the filtrate from the residue.

The resulting liquefied wood was mixed with HMTA (5.0 wt.% of liquefied wood) and transferred to a metal tube. The mixture was heated from room temperature to 120 °C within 40 min and maintained at 120 °C for 10 min to obtain the spinning solution. Under a nitrogen pressure, the melt-spinning process was conducted to prepare primary fibers through a spinneret 1 mm in diameter (Ma *et al.* 2007a).

The primary fibers from liquefied wood were immersed in a preheated mixed solution composed of hydrochloric acid (18.5 wt.%) and formaldehyde (18.5 wt.%). The curing temperatures were 65, 75, 85, and 95 °C, and each sample was incubated for 1, 1.5, 2, and 3 h, respectively. After the curing reaction, the precursors were obtained and washed with distilled water until no chemical residues existed. Then, the precursors were dried at 85 °C for 40 min.

Under the protection of a nitrogen atmosphere (100 mL/min), the precursors were carbonized in a carbonization furnace (Marshall 1370-20HTF, Thermcraft Inc., USA) at

1000 °C with a heating rate 10 °C/ min and then cooled to room temperature, followed by a 60-min thermal incubation to obtain carbon fibers from the liquefied wood in phenol.

Characterization

The weight loss behaviors and decomposition temperature (T_d) of the precursors were measured using thermogravimetric analysis (TGA 1/1600HT, METTLER-TOLEDO, Sweden) from room temperature to 800 °C, with the heating rate of 10 °C/ min in a high-purity nitrogen stream (30 mL/min).

The morphologies of the precursors were observed using scanning electronic microscopy (SEM; S-3400N, Hitachi, Japan) with gold-coated samples (E-1010, Hitachi, Japan) at a magnification factor of 1500 to 2000 and an accelerating voltage of 10 kV.

Fourier transform infrared (FTIR) spectroscopy of the precursors was performed using a FTIR spectrophotometer (TENSOR 27, Bruker Corp., Germany) and the KBr disk method.

The crystal structure of the carbon fibers in the range of 5° to 60° (2θ) was measured using X-ray diffraction spectrometry (XRD; D8 ADVANCE, Bruker Corp., Germany). The apparent crystallite thickness (L_c), the apparent layer-plane length parallel to the fiber axis (L_a), and the average interlayer spacing (d_{002}) were calculated using the Scherrer and Bragg formulas:

$$d_{002} = \lambda/(2 \sin\theta) \tag{1}$$

$$D = (K*\lambda)/(\beta*\cos\theta) \tag{2}$$

where θ is the Bragg angel of peaks (°), λ is the wave length of the X-ray used (0.154 nm), and β is the half height width of peaks (rad.). The factor K was 0.89 for L_c and 1.84 for L_a.

The tensile strength of the carbon fibers from liquefied wood were detected using a single fiber mechanical properties tester (JSF-10, Zhongchen, China). The data shown are the average value for at least 100 fibers of each group.

RESULTS AND DISCUSSION

Thermal Stability of the Precursors

The thermal weight loss of the precursors prepared at a curing temperature of 95 °C and curing times of 1, 1.5, 2, and 3 h is shown in Fig 1. The residual ratio curve of precursors exhibited three stages in the process of thermal decomposition (Zhang and Shen 2009). The first stage was from room temperature to 120 °C, in which water was removed from the precursors and the curve decreased linearly. The second stage was from 120 to 600 °C; the curve increased sharply at first, then reduced gradually, which indicated that small molecular substances escaped from the precursors while carbonizing. The last stage, from 600 to 800 °C, was the thermal decomposition and burning period of the precursors, which included the weight loss of the precursors and decomposition of small-molecular weight substances.

The thermal decomposition residual ratios were 48.8%, 51.1%, 52.0%, and 52.4% at 800 °C, indicating that as the curing time was extended, the degree of cross-linking of the internal molecular chain of precursors increased as well, enhancing thermal stability. Meanwhile, the increment of the residual ratio decreased from 2.3% per 0.5 h to 0.4% per h (gradually), indicating that the chemical curing rate slowed down and eventually ceased

as the curing time was extended. This was probably because the surface layer of the primary fibers was cured first and became denser as the reaction went on, hindering carbocations from entering the precursors to form cross-linking structures inside (Ma *et al*. 2008).
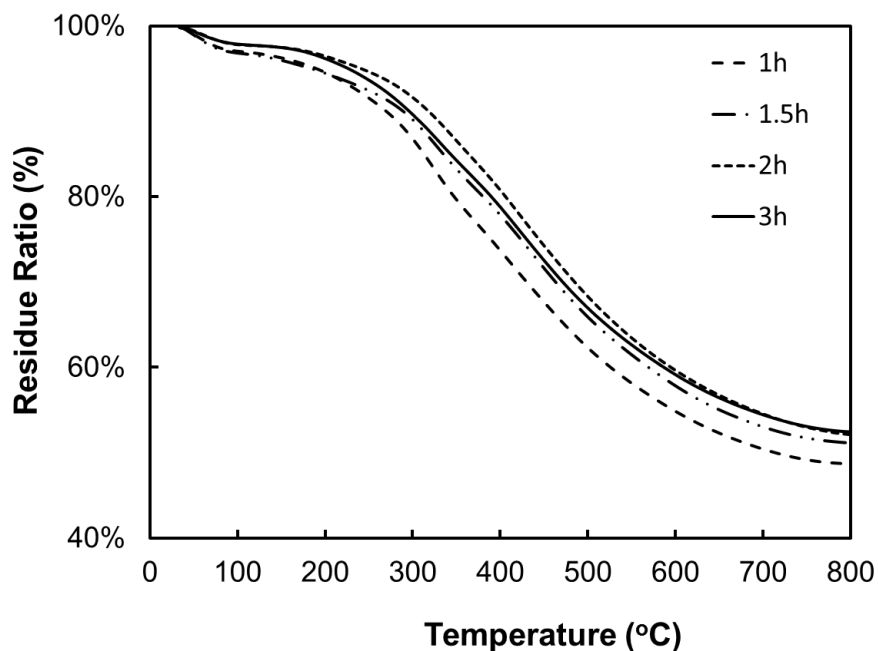

Fig. 1. Thermogravimetric curves of precursors prepared at 95 °C with various curing times
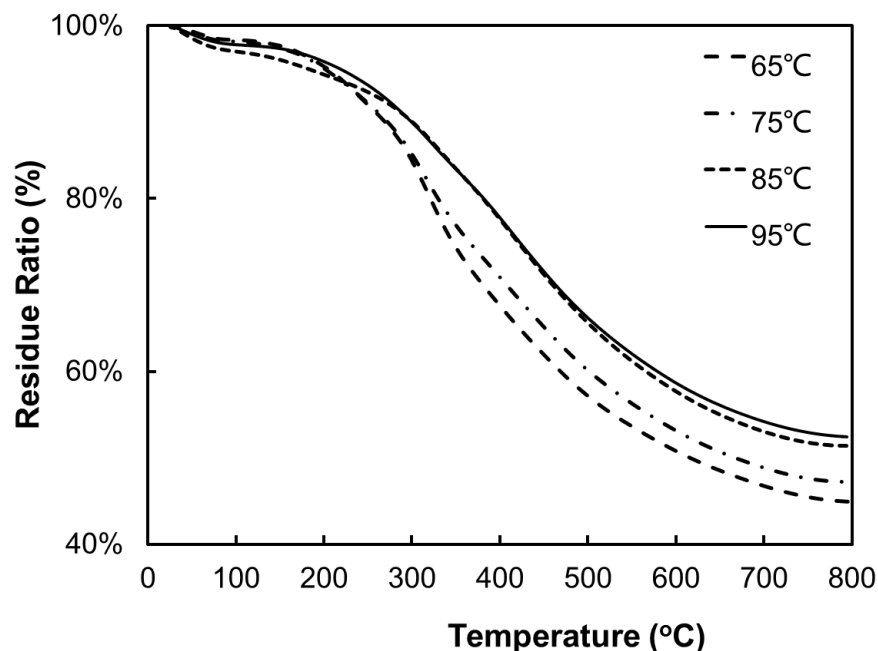

Fig. 2. Thermogravimetric curves of precursors prepared at various curing temperatures for 3 h

The thermal weight loss of precursors prepared for 3 h at curing temperatures of 65, 75, 85, and 95 °C are shown in Fig. 2. As the thermal treatment temperature was increased, especially above 200 °C, the pyrolysis loss ratio of the precursors cured at 65

and 75 °C increased more apparently than those at 85 and 95 °C. The final residue ratio of precursors cured at 65 (44.9%) and 75 °C (47.2%) were lower than those at 85 (51.4%) and 95 °C (52.4%), indicating that a higher curing temperature contributed to a stronger chemical curing degree and better thermal stability, mostly because the carbocation could move freely and enter the interior of the precursors before the surface layer became too dense to absorb the curing solutions.

Morphology of Precursors

Figure 3 shows the morphology of the precursors prepared at 65, 75, 85, and 95 °C for 3 h. There were no obvious sheath-core structures in the precursors prepared for 3 h; however, there were plenty of pores in the cross section of precursors prepared at curing temperatures of 65 and 75 °C. The pores were below the level of detection in the cross section of the precursors at temperatures of 85 and 95 °C. This was a result of the density of the internal structure. The morphologies of the precursors prepared at 95 °C for 1, 1.5, 2, and 3 h are shown in Fig. 4. When the curing time was 1.0 or 1.5 h, a considerable amount of pores was observed on the cross section of these fibers. When the time was extended to 2 h, fewer pores were observed on the fibers' surface. The 3-h treatment exhibited the least number of pores and defects on the cross section of the precursors. The results revealed that an extended curing time was conducive to reducing the amount of defects in the precursors. However, other than the various curing temperatures, extending the curing time produced a milder result during the reaction process.
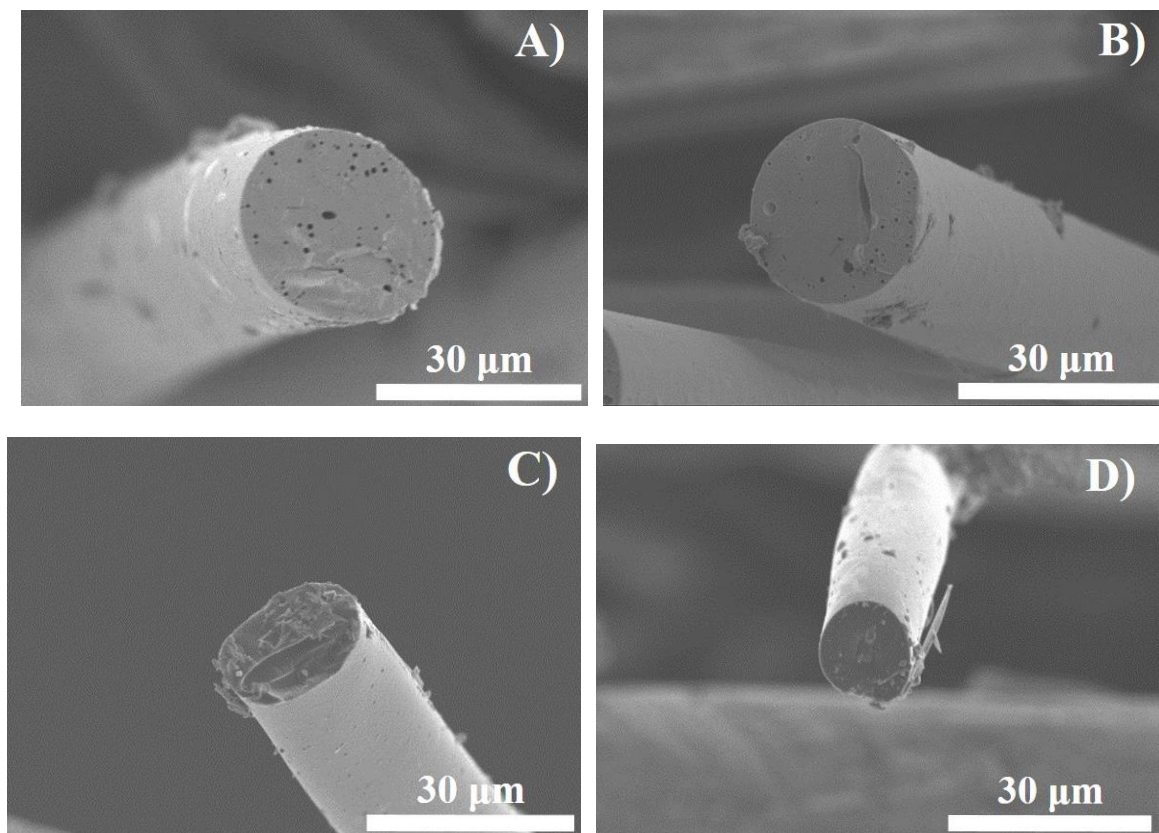

Fig. 3. SEM images of precursors prepared at various curing temperatures for 3 h: A) 65 °C; B) 75 °C; C) 85 °C; D) 95 °C
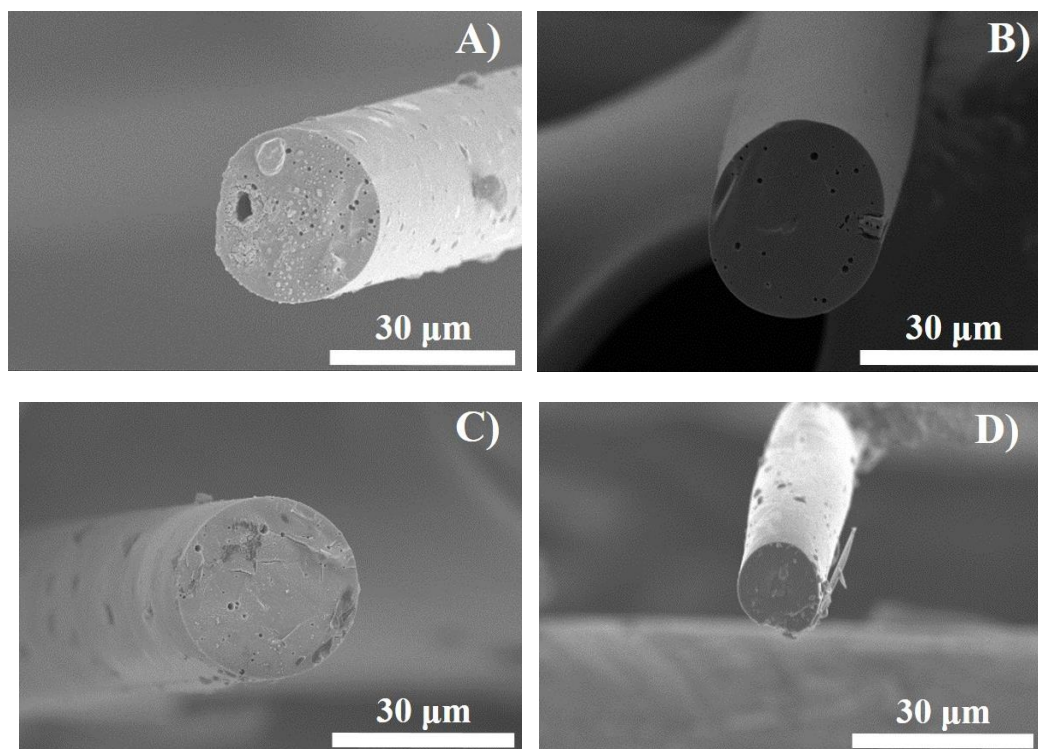
Fig. 4. SEM images of precursors cured at 95 °C for various times: A) 1 h; B) 1.5 h; C) 2 h; D) 3 h

FTIR Analysis of Precursors

During chemical curing, the reaction between carbocation and reactive carbon of the benzene rings in the primary fibers contributed to the generation of methylene groups within the benzene rings, the crosslinking of molecular chains, and the formation of three dimensional structures. Therefore, the crosslinking rate can be measured by the relative quantity of methylene groups (Ma *et al*. 2008). As shown in Fig. 5, the presence of a band centered at $v_{(C-H)} = 2930$ cm^{-1} showed the stretching vibration of methylene groups (Silverstein *et al*. 2005). The intensity of the absorption peak was enhanced as the curing temperature increased, which illustrated that at higher curing temperatures, more methylene groups and crosslinking appeared.

Under curing temperatures of 65, 75, 85, and 95 °C and a curing time of 3 h, the absorption peak intensity ratios of wavenumbers 2930 to 3440 cm^{-1} (stretching vibration of hydroxyl groups) and 1601 cm^{-1} (stretching vibration of C=C in aromatic rings) are shown in Table 1.

Table 1. FTIR Peak Intensity Ratios of Precursors for a 3-h Curing Time

Curing Temp.	Intensity Ratio of FTIR Peak	
	I_{2930}/I_{3341}	I_{2930}/I_{1608}
65 °C	1.061	1.000
75 °C	1.065	1.006
85 °C	1.071	1.010
95 °C	1.078	1.013

When the curing temperature was raised, the ratio of I_{2930}/I_{3341} and I_{2930}/I_{1608} increased. The relative quantity of methylene groups increased along with the curing temperature, indicating that the degree of cross-linking was enhanced.
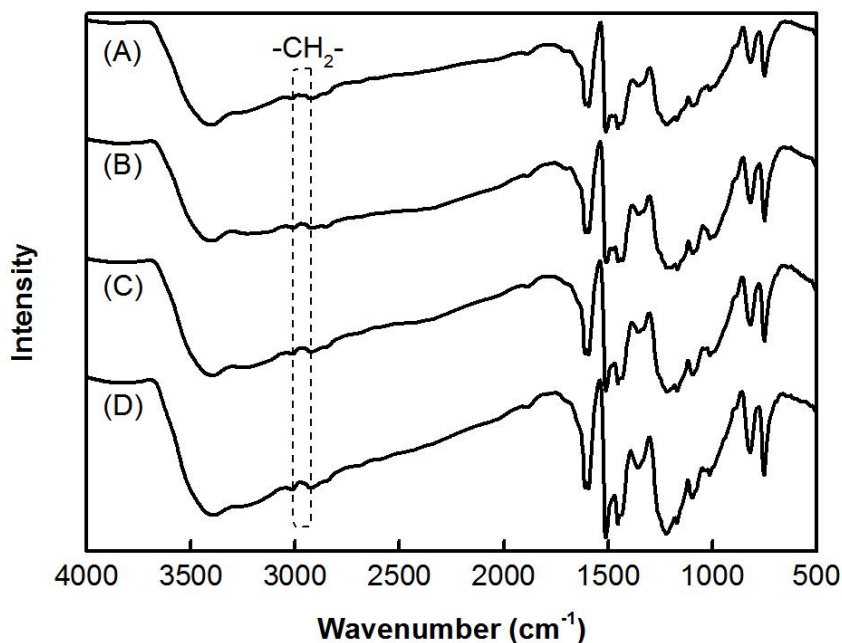

Fig. 5. FTIR spectra of precursors prepared at various curing temperatures for 3 h: A) 65 °C; B) 75 °C; C) 85 °C; D) 95 °C

As shown in Fig. 6, FTIR was conducted to investigate the impact of curing time on the relative quantity of methylene groups.
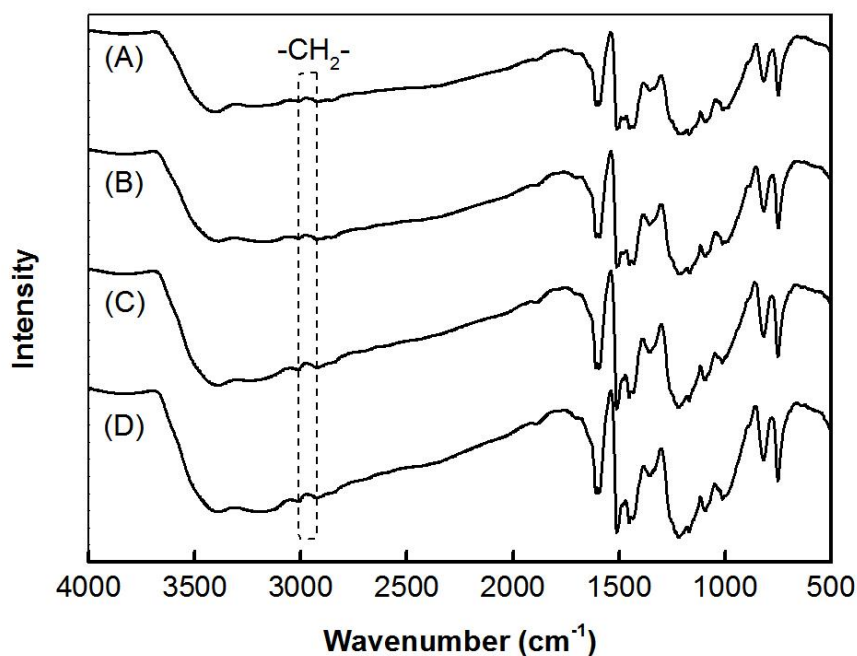

Fig. 6. FTIR spectra of precursors cured at 95 °C for various curing times: A) 1 h; B) 1.5 h; C) 2 h; D) 3 h

The presence of bands centered around $v_{(C-H)}$ = 2930 cm^{-1}, 3440 cm^{-1}, and $v_{(C-H)}$ = 1601 cm^{-1} can be attributed to the stretching vibrations of methylene groups, hydroxyl groups, and C=C in aromatic rings, respectively. Extending the curing time contributed to an increase in the intensity of absorption peaks and the relative quantity of methylene groups, demonstrating that the curing time had the same effect on the degree of cross-linking of precursors (Table 2).

Table 2. FTIR Peak Intensity Ratios of Precursors at 95 °C

Curing Time	Intensity Ratio of FTIR Peak	
	I_{2930}/I_{3341}	I_{2930}/I_{1608}
1.0 h	1.009	0.979
1.5 h	1.037	0.991
2.0 h	1.063	1.002
3.0 h	1.078	1.013

XRD Analysis of Carbon Fibers

The X-ray diffraction peaks for carbon fibers prepared using various chemical curing temperatures and curing times are illustrated in Figs. 7 and 8. All of the diffraction peaks showed possible unreacted, liquefied wood in the phenol in the precursors. The liquefied wood in phenol changed during carbonization, which widened the peaks (Ma *et al*. 2009).
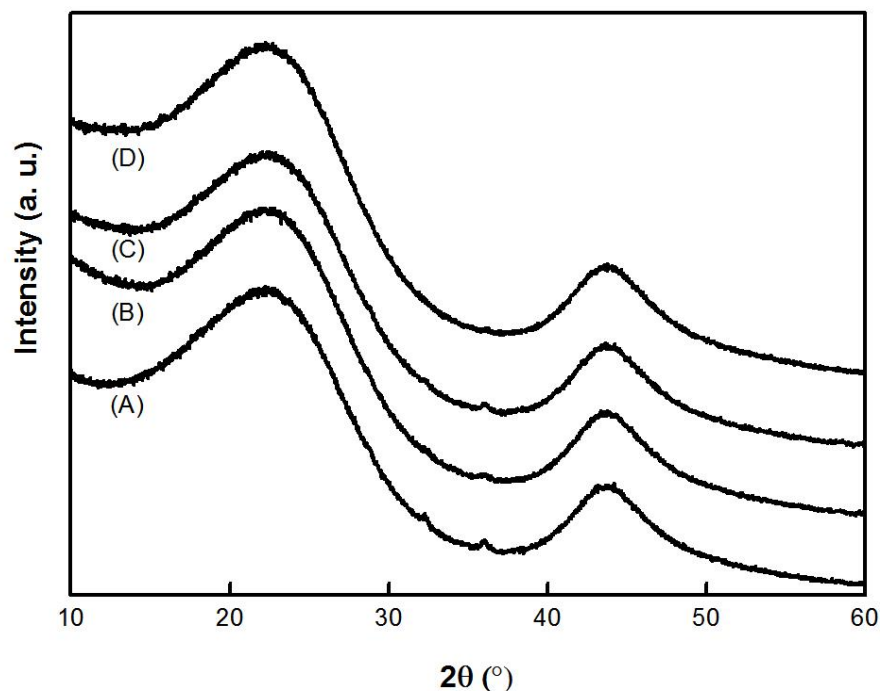

Fig. 7. X-ray diffraction peaks for carbon fibers cured at 95 °C for various curing times: A) 1 h; B) 1.5 h; C) 2 h; D) 3 h
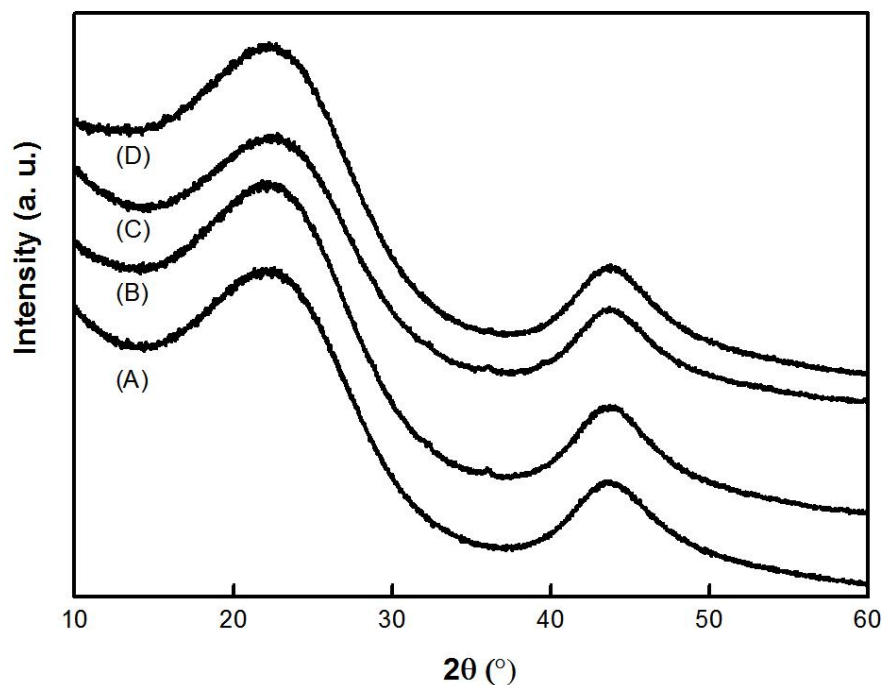
Fig. 8. X-ray diffraction peaks for carbon fibers prepared at various curing temperatures for 3 h: A) 65 °C; B) 75 °C; C) 85 °C; D) 95 °C

Table 3. Structure Parameters of X-Ray Diffraction for Carbon Fibers Prepared by Various Chemical Curing Processes

Temperature (°C)	Time (h)	2θ (002) (°)	d_{002} (nm)	L_c (nm)	2θ (100) (°)	L_a (nm)	L_c / d_{002}
65	3	22.99	0.3864	0.9326	43.40	3.5343	2.41
75	3	22.97	0.3867	0.9247	43.69	3.6801	2.39
85	3	22.99	0.3864	0.9623	43.74	3.7112	2.49
95	1	22.83	0.3891	0.9496	44.20	3.7740	2.44
95	1.5	23.06	0.3868	0.9489	43.73	3.7565	2.45
95	2	22.97	0.3867	0.9248	43.76	3.7520	2.39
95	3	23.71	0.3749	0.8782	43.73	3.7549	2.34

As it shown in Table 3, at 95 °C, the value of d_{002} decreased from 0.3891 to 0.3749 nm as the curing time was extended from 1 to 3 h. This was still greater than the d_{002} of graphite (0.3354 nm). However, the curing temperature hardly affected d_{002}. The value of L_c had the same trend with that of d_{002}, especially in terms of the curing temperature at 95 °C and the curing time of 3 h, which reached a minimum of 0.8782 nm. These results indicated that extending the curing time contributed to a reduction in both the L_c and d_{002}, and the microstructure of the carbon fibers became ordered during carbonization as a result. On the contrary, the L_a increased from 3.5343 to 3.7740 nm as the curing temperature was raised. The value of L_c/d_{002} was between 2.34 to 2.49, demonstrating that the number of graphene sheets reached two to three layers along the C axis of microcrystalline carbon

(Liu *et al*. 2009). Furthermore, the carbon fibers prepared from liquefied wood in phenol was a kind of material containing "turbostratic graphite structure" (Ma *et al*. 2009).

Tensile Strength Analysis of Carbon Fibers

The quality of the precursors has an effect on the mechanical properties of carbon fibers (He 2004). The tensile strength analysis of the carbon fibers prepared using different chemical curing technologies is illustrated in Fig. 9. The tensile strength of the carbon fibers showed a tendency toward improvement when the curing temperature was raised or the curing time was extend, especially at the curing temperature 85 and 95 °C, when the curing time was greater than 2 h. The greatest tensile strength (almost 800 MPa) was prepared at a curing temperature of 95 °C and a curing time 3 h, which was nearly twice that of the sample prepared at 65 °C, and was greater than the general pitch-based carbon fibers from Prauchner *et al*. (2005).
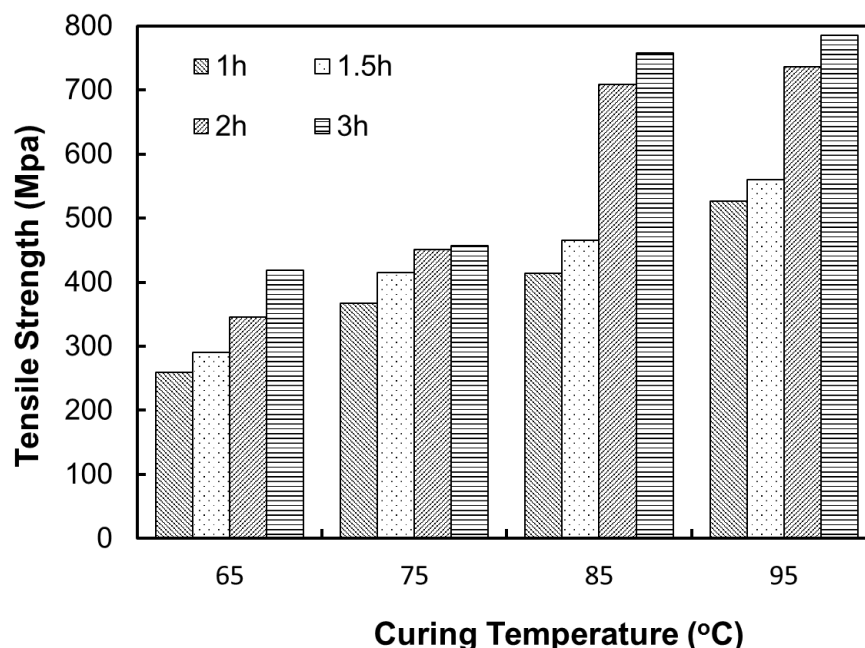

Fig. 9. Tensile strength of carbon fibers prepared with various chemical curing processes

Both the Griffith's micro-crack theory and Weibull's weakest link theory stress that one of the major factors that restricts the tensile strength of carbon fibers is the size and amount of the defects. The existence of defects contributes not only to the reduction of an efficient cross-section area for bearing loads, but also decreases the tensile strength as the stress highly concentrated at the tip of the cracks or pores under the condition of external forces. Furthermore, the random distribution of defects results in higher probability of large defects' occurrence, which is the weakest link connection (He 2004). Compared to the precursors prepared at curing temperatures of 85 and 95 °C, more pores were observed in the precursors prepared at the curing temperatures of 65 and 75 °C, which was retained in the next step of carbonization, leading to inferior tensile strength of the carbon fiber (He 2004; Lin *et al*. 2012). Furthermore, the degree of cross-linking between the carbocation and the benzene ring exhibited greater impacts on the quantity of the defects in precursors.

***bioresources*.com**

Therefore, the tensile strength of the carbon fibers increases with increasing curing temperature or longer curing time.

CONCLUSIONS

1. A direct chemical curing process was used for the preparation of the liquefied wood-based precursors and carbon fibers.

2. The quantity of the methylene groups increased as a result of the reaction between carbocations and benzene rings in the primary fibers. This indicated that the degree of molecular chains was enhanced and the precursors were more thermally stable.

3. Extending the curing time reduced the value of d_{002} to the minimum 0.3749 nm, and the tensile strength of carbon fibers prepared from the precursors was enhanced as the curing temperature and time were extended. When the curing temperature was 95 °C and the curing time was 3.0 h, the tensile strength of the carbon fibers prepared from the precursors was approximately 800 MPa, which was similar to general grade pitch-based carbon fibers.

ACKNOWLEDGMENTS

REFERENCES CITED

Foston, M., Nunnery, G. A., Meng, X. Z., Sun, Q. N., Baker, F. S., and Ragauskas, A. (2013). "NMR: A critical tool to study the production of carbon fiber from lignin," *Carbon* 52, 65-73. DOI: 10.1016/j.carbon.2012.09.006

Frank, E., Hermanutz, F., and Buchmeiser, M. R. (2012). "Carbon fibers: Precursors, manufacturing, and properties," *Macromol. Mater. Eng.* 297(6), 493-501. DOI: 10.1002/mame.201100406

He, F. (2004). *Carbon Fiber and Its Application Technology*, Chemical Industry Press, Beijing, China.

Huang, X. S. (2009). "Fabrication and properties of carbon fibers," *Materials* 2(4), 2369-2403. DOI: 10.3390/Ma2042369

Li, D. N., and Ma, X. J. (2013). "Preparation and characterization of activated carbon fibers from liquefied wood," *Cellulose* 20(4), 1649-1656. DOI: 10.1007/s10570-013-9981-8

Lin, J., Kubo, S., Yamada, T., Koda, K., and Uraki, Y. (2012). "Chemical thermostabilization for the preparation of carbon fibers from softwood lignin," *BioResources* 7(4), 5634-5645. DOI: 10.15376/biores.7.4.5634-5645

Lin, J., Shang, J.-B., and Zhao, G.-J. (2013). "The preparation and characterization of liquefied wood based primary fibers," *Carbohydr. Polym.* 91(1), 224-228. DOI: 10.1016/j.carbpol.2012.08.007

Liu, F. J., Wang, H. J., Fan, L. D., and Zhu, Z. P. (2009). "Analysis on the microstructure of MJ series carbon fibers," *New Chem. Mater.* 37(1), 41-43. DOI: 10.3969/j.issn.1006-3536.2009.01.017

Ma, X., and Zhao, G. (2007a). "Effect of spinning solution factors on properties of carbon fiber precursors prepared with liquefied wood," *Acta Mater. Compos. Sin.* 24(5), 119-124. DOI: 10.3321/j.issn:1000-3851.2007.05.022

Ma, X., and Zhao, G. (2007b). "Structure and performance of fibers prepared from liquefied wood in phenol," *Fiber. Polym.* 9(4), 405-409. DOI: 10.1007/s12221-008-0065-6

Ma, X., and Zhao, G. (2008). "Mechanical properties of carbon fiber precursors prepared from liquefied wood in phenol," *J. Beijing For. Univ.* 30(2), 133-137. DOI: 10.3321/j.issn:1000-1522.2008.02.023

Ma, X., and Zhao, G. (2009). "Effects of carbonized temperature on microstructure of carbon fiber precursors prepared from liquefied wood," *J. Beijing For. Univ.* 31(5), 112-116. DOI: 10.3321/j.issn:1000-1522.2009.05.020

Ma, X., and Zhao, G. (2010). "Preparation of carbon fibers from liquefied wood," *Wood Sci. Technol.* 44(1), 3-11. DOI: 10.1007/s00226-009-0264-3

Ma, X., and Zhao, G. (2011). "Variations in the microstructure of carbon fibers prepared from liquefied wood during carbonization," *J. Appl. Polym. Sci.* 121(6), 3525-3530. DOI: 10.1002/App.34142

Prauchner, M. J., Pasa, V. M. D., Otani, S., and Otani, C. (2005). "Biopitch-based general purpose carbon fibers: Processing and properties," *Carbon* 43(3), 591-597. DOI: 10.1016/j.carbon.2004.10.023

Silverstein, R. M., Webster, F. X., and Kiemle, D. J. (2005). *Spectrometric Identification of Organic Compounds* (7th ed.), Wiley, Hoboken, NJ.

Zhang, T., and Shen, Q. (2009). "Preparation and characterization of carbon fiber derived from lignin-phenol-formaldehyde resin," *Cellulose Sci. Technol.* 17(2), 6-11. DOI: 10.3969/j.issn.1004-8405.2009.02.002