Variations in the Microstructure of Carbon Fibers Prepared from Liquefied Wood During Carbonization

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ABSTRACT: After spinning by adding hexamethylenetetramine and the curing treatment, carbon fibers from liquefied wood (LWCFs) were prepared by direct carbonization. Microstructure change of LWCFs during carbonization is studied by X-ray, Raman spectroscopy, and FTIR. Raman spectroscopy shows both the D peak at 1360 cm^{-1} and the G peak at 1595 cm^{-1} exist after 600°C, and a significant decrease is found in I_D/I_G during carbonization. X-ray diffraction shows the crystallite size ($L_{c(002)}$ and $L_{a(100)}$) of LWCFs firstly decreases before 800°C and then increases with heat treatment temperature (HTT) increasing, whereas the interlayer spacing (d_{002}) gradually decreases during carbonization. It is also found that the crystallite shape (L_a/L_c) and the degree of graphitization (G) all increase with increasing HTT. It is also found that structure of the precursor fibers from liquefied wood has been completely changed after carbonization. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3525–3530, 2011

Key words: carbon fiber; microstructure; crystallite size; liquefied wood

INTRODUCTION

Carbon fibers are now widely used as a kind of reinforcement material in the lightweight composite, because of its high strength, high elastic modulus, and low density.[1] However, its application is very limited with precursor cost increasing due to the shortage of fossil sources. To solve the problem, extensive work has been carried out to find new precursors for carbon fibers.

In the past decades, cellulose and lignin from wood have been used as the precursors for carbon fibers,[2–5] but wood utilization is still very low due to the difficult separation of wood components. Recently, wood is almost completely converted into useful liquid chemical raw by liquefaction technique[6–8] that greatly improves the utilization of wood. Moreover, many studies have been reported on preparing carbon fibers from liquefied wood (LWCFs) instead of fossil sources.[9–12]

It is well known that the graphitic crystallite or carbonization behavior of a carbon material has great influence on its properties. As the properties of carbon fibers directly depend on the structure, the control of structure, and the study on relationship between the structure and properties during carbonization have been extensively studied, for example, PAN-based carbon fibers.[13–16] However, the study of microstructure of LWCFs during carbonization has not appeared yet in the literature.

In this article, the evolution of microstructure of LWCFs during carbonization was examined by X-ray diffraction and Raman spectroscopy. In particular, the relationship between heat treatment temperature (HTT) and microstructure parameters, such as the crystallite and shape, as well as the degree of graphitization, was investigated.

EXPERIMENTAL

Materials

The raw material was Chinese Fir [*Cunninghamia lanceolata* (Lamb.)]. Debarked chips were ground, and the powder of 20–80 mesh size was dried in an oven at 105°C for 24 h before use. All other chemicals in the study were reagent grade, and they were used without further purification.

Preparation of spinning solution

Wood meals were mixed with phenol containing 8-wt % H_3PO_4 as a reaction catalyst. The ratio was wood/phenol = 1/6 by weight. The mixture was
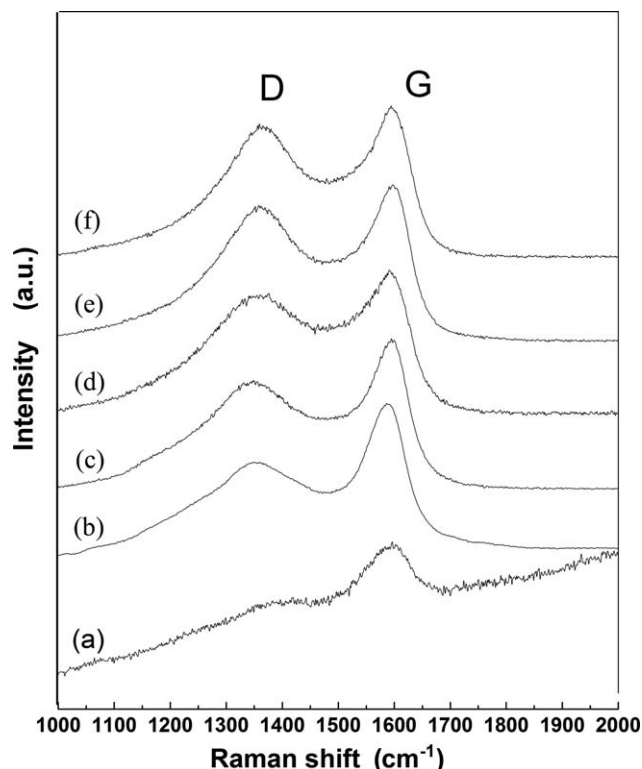
Figure 1 Raman spectra of LWCFs at various heat treatment temperatures: (a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C; (e) 900°C; (f) 1000°C.

liquefied by holding at 160°C for 2.5 h with stirring. Liquefied wood was obtained. Subsequently, hexamethylenetetramine as synthetic agent was added to liquefied wood by 5 wt % and hold for 5 min after heating to 120°C in 40 min to prepare spinning solution.

Preparation of carbon fibers

After the spinning solution was directly spinned, the spun filaments were cured by soaking in an acid solution HCHO and HCl as main components at 95°C for 4 h, washed with deionized water, and finally dried at 90°C for 2 h. The carbon fiber precursors from liquefied wood were prepared. The precursors were carbonized for 2 h by heating from a room temperature to 1000°C at a heating rate 4°C min^{-1} in

a stream of nitrogen. Tensile strength, modulus, and yield of these LWCFs were 1.22 ∼ 1.7 GPa, 114 ∼ 176 GPa, and 55.8%, respectively.

Raman spectroscopy

The Raman scattering measurements were performed in a Raman spectrometer (Nicolet, Almega XR) at room temperature under a nitrogen atmosphere, using a 473 nm line of an argon ion laser as the incident radiation. The Raman-scattered light was dispersed by an optical grid and detected by a CCD camera. The Raman spectrometer was operated in the continuous scanning mode with laser beam powers of 4 mW and exposure times of 20 s.

X-ray diffraction

A Rigaku d/max-rc X-ray diffractormeter with Ni-filtered CuKa radiation (wavelength = 0.15418 nm) was used to determine the structural parameters of fibers. The scanning rate is 4° min^{-1} with a scanning step of 0.02. The value of d_{002} was calculated using Bragg's law, and the crystallite size L_c and L_a were calculated from the Scherrer's formula:

$$L = \frac{k\lambda}{\beta \cos \theta} \qquad (1)$$

$$d_{002} = \frac{\lambda}{2 \sin \theta} \qquad (2)$$

where θ is the scattering angle, λ is the wavelength of the X-ray used, and β is the full width at half the maximum intensity (FWHM). The form factor K is 0.89 for L_c, and 1.84 for L_a, respectively.[17,18]

The degree of graphitization, G, can also be calculated from the below formula:

$$G = \frac{(0.3440 - d_{002})}{(0.3440 - 0.3554)} \qquad (3)$$

FTIR spectroscopy

Infrared spectra were recorded on Brukert Tensor27 spectrometer using the KBr disk technique to

TABLE I
Variation of Raman Spectra of Carbon Fibers After Gauss Curve Fitting

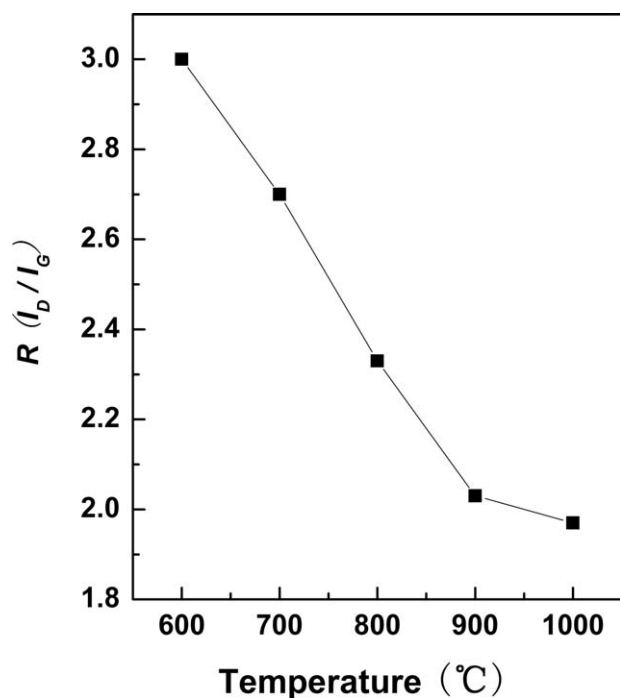| Temperature (°C)	D Peak			G Peak		
	I_D	FWHM (cm^{-1})	Position (cm^{-1})	I_G	FWHM (cm^{-1})	Position (cm^{-1})
600	75	288	1367	25	87	1594
700	73	302	1364	27	88	1595
800	70	265	1359	30	103	1595
900	67	234	1359	33	100	1594
1000	67	234	1359	34	99	1594

Figure 2 Variation of R ratio with carbonized temperature.

investigate the change of functional groups of the fibers under various temperatures. The fibers were pulverized (150–200 mesh) and mixed with KBr before being pressed into a disk. The concentration of the sample in KBr was 2.5%, and 0.2 g of KBr was used in the preparation of the reference and sample disks.

RESULTS AND DISCUSSION

Characterization with Raman spectroscopy

Raman spectroscopy has been shown to be a powerful method for characterizing the structural perfection in carbonaceous materials.[19,20] There are two peaks dominating the first-order spectrum of any carbon material, the G and D peaks. The position of the G line is between 1575 and 1600 cm^{-1}, corresponding to the "in-plane" displacement of the carbons strongly coupled in the hexagonal sheets. The D band can be found about 1355 or 1360 cm^{-1} and is a good indicator of disorder in the crystal structure.

Figure 1 shows the first-order spectra of LWCFs at various temperatures. The first Raman peak, D band, is initially observed when HTT reaches 600°C, suggesting that a disordered carbon sheet structure is formed at first. This will transform partly and increasingly into ordered portions of carbon, resulting in the second G peak at higher Raman shift. The higher HTT, the larger, and the more evident are the peaks. This indicated that more and more ordered carbon structure has been formed, which will further significantly affect and improve the resulting structure and mechanical properties of LWCFs.

Table I shows variation of Raman spectra of carbon fibers after Gaussian curve fitting. The relative intensity of D peak (I_D) decreases with increasing HTT from 600 to 1000°C, whereas the G peak (I_G) increases, indicating the amount of SP2 (graphite) clusters increases and the degree of graphitization of LWCFs gradually improves. It is also found from Table I that the FWHM of D peak decreases from
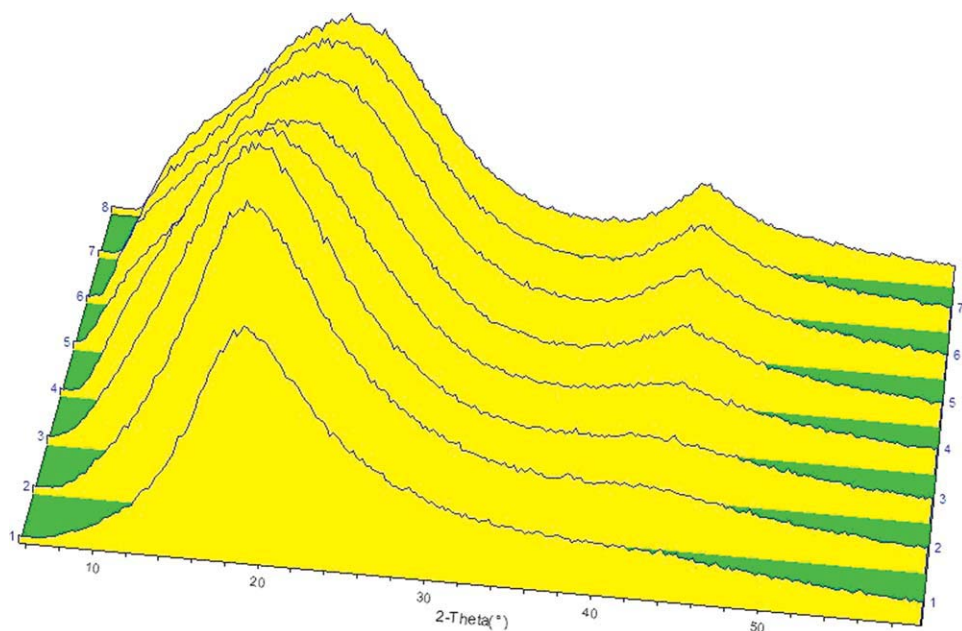

Figure 3 X-ray diffraction profiles of LWCFs at various heat treatment temperatures: (1) the precursor; (2) 400°C; (3) 500°C; (4) 600°C; (5) 700°C; (6) 800°C; (7) 900°C; (8) 1000°C.

TABLE II
X-ray Diffraction Structure Parameters

HTT (°C)	2θ (002) (°)	FWHM 002	$d_{(002)}$ (nm)	$L_{c(002)}$ (nm)	2θ (100) (°)	FWHM 100	$L_{a(100)}$ (nm)
400	18.2	10.01	0.4870	0.8034	43.6	7.08	2.4697
500	18.2	10.84	0.4869	0.7419	43.3	6.02	2.9016
600	18.4	12.19	0.4817	0.6599	43.6	5.88	2.9738
700	19.3	12.95	0.4594	0.6220	44.3	5.36	3.2703
800	19.8	13.04	0.4480	0.6182	44.5	5.41	3.2424
900	19.8	12.99	0.4479	0.6206	44.6	5.49	3.1963
1000	20.6	12.59	0.4306	0.6411	44.7	5.04	3.4829

288 cm^{-1} at 600°C to 234 cm^{-1} at 1000°C. In addition, the central position of D band closes to 1360 cm^{-1} with increasing HTT, and the position of G peak is observed around 1595 cm^{-1}. The results show that the internal structure of LWCFs has been changed with increasing HTT.

The rise of the I_D/I_G intensity ratio with annealing temperature is consistent with a model that predicts a growth in number and/or size of crystallites, because heating of a carbon sample will change its structure to match that of single-crystal graphite.[21] As indicated in the Figure 2, there is a large decrease in I_D/I_G during the HTT from 600 to 1000°C, indicating that the crystal structure of LWCFs becomes more ordered.

Characterization with X-ray diffraction

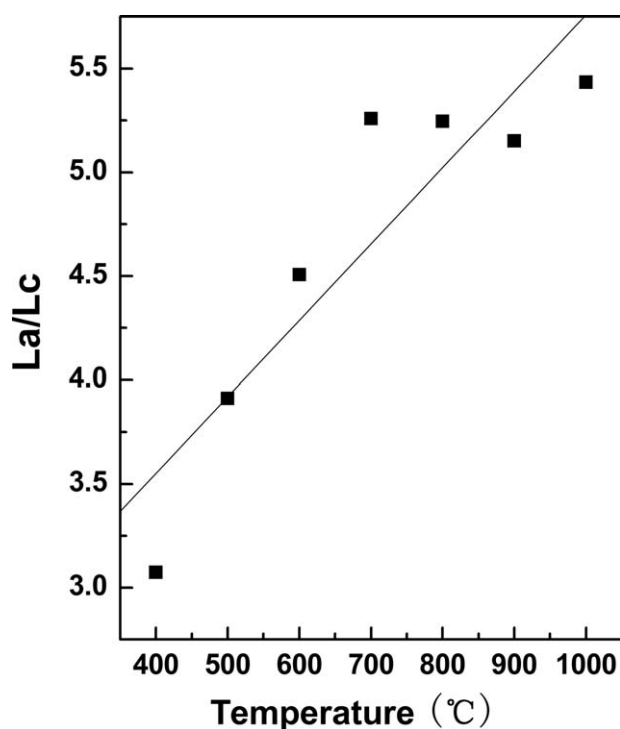Figure 3 shows the X-ray diffraction profiles of LWCFs at various temperatures. There is an evident difference between the precursors and LWCFs. It can be seen that the diffraction of 002 peak only exists in the precursors. With the increasing temperature, 002 peak in LWCFs becomes obviously wide. It is notable that 002 peak observed at 400°C in LWCFs belongs to unliquefied wood. While above 400°C, 100 peak around 44.3°in LWCFs begins to appear and gradually strengthens with temperature increasing. From the above results, it is clear that structure of the fibers has been completely changed during carbonization.

Table II shows the X-ray diffraction structure parameters of LWCFs at various temperatures. As shown from Table I, with the temperature increasing from 400 to 1000°C, 2θ of 002 and 100 peaks move to high angle. 002 Peak in LWCFs does not occur around 26°C, considering that the carbonization temperature is very low. Meanwhile, the average
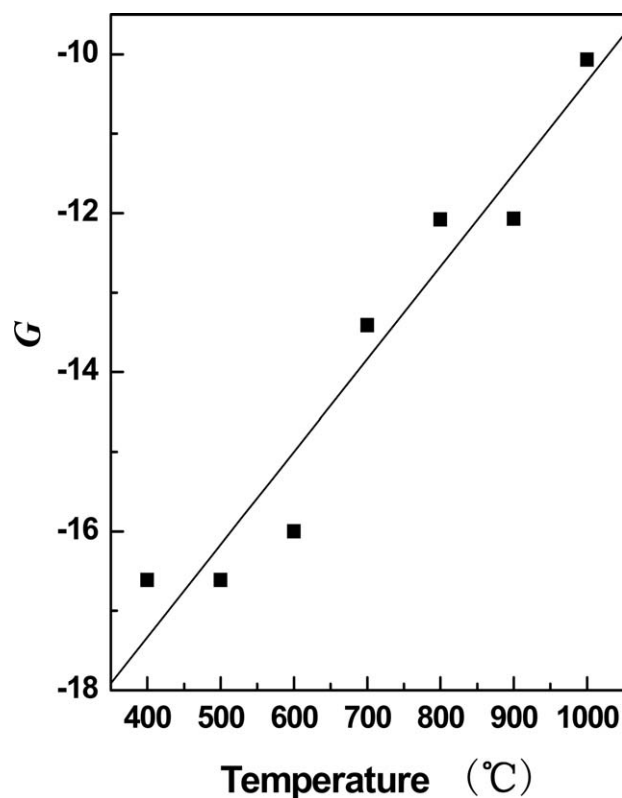

Figure 4 Effects of heat treatment temperature on the crystallite shape L_a/L_c.

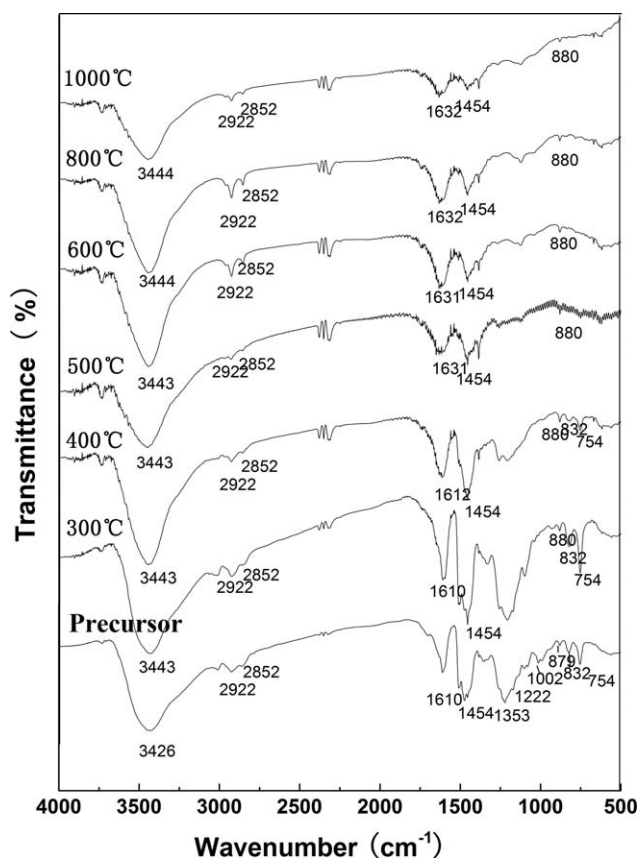Figure 5 Variation of G with carbonized temperature.

Figure 6 FTIR spectra of LWCFs at various heat treatment temperatures.

interlayer spacing, d_{002}, has an obvious decrease from 0.4870 nm at 400°C to 0.4306 nm at 1000°C. In addition, the apparent crystallite size ($L_{c(002)}$) and the apparent layer-plane length parallel to the fiber axis ($L_{a(100)}$) gradually increase after 800°C. The results indicate that the preferred orientation of layer plane of graphite along fiber axis and the degree of graphitization of LWCFs can be significantly improved with the increasing temperature. On the other hand, $L_{c(002)}$ and $L_{a(100)}$ decrease and then increase during carbonization, indicating that the microstructure evolution of LWCFs is more complex than other carbon fibers.

Crystallite shape was defined by Richards as the ratio of the crystallite diameter to the crystallite height.[22] Figure 4 shows effects of HTT on the crystallite shape L_a/L_c. The value of L_a/L_c increases from 3.07 to 5.43 with the temperature increasing from 400 to 1000°C, indicating the rate of growth in the apparent of layer-plane length parallel to the fiber axis is greater than that of the apparent crystallite thickness with increasing temperature. The results may be attributed to the formation of more fused benzene ring structure in LWCFs during carbonization.

Figure 5 shows variation of G with carbonization temperature. Although G is still negative values, the value of G increases from −16.6 to −10.1 with carbonization temperature increasing. It is further demonstrate that the degree of graphitization of LWCFs increases with the temperature increasing.

Characterization with FTIR spectra

Figure 6 shows FTIR spectra of LWCFs at various HTTs. During carbonization, the intensity of absorption peak at 3426 cm^{-1} assigned to O—H stretching band in the precursors, gradually weakens and shifts to 3444 cm^{-1} (at 1000°C).[23] The absorption peaks at 2922 and 2852 cm^{-1} (mainly methylene bridge) increase and then slowly reduce with temperature increasing. The bands at 1632 and 1454 cm^{-1} distinctly decrease due to the formation of many condensed rings. At 1000°C, the bands at 1353 cm^{-1} assigned to O—H, 1222 cm^{-1} attributed to C—O and 1002 cm^{-1} assigned to hydroxide methyl group have completely vanished.[24] In addition, the absorption peaks at 754 and 832 cm^{-1} basically disappear at 1000°C, whereas the weak absorption peak at 880 cm^{-1} is still visible. These results indicate that the network crosslinking structure of the fibers is broken due to the scission of methylene bridge of benzene ring and the formation of many condensed rings during carbonization.[25]

CONCLUSIONS

To obtain perfect properties of carbon fiber from liquefied wood, the evolution of microstructure of fibers during carbonization is studied. Experimental results show the D peak in LWCFs appears above 600°C and gradually closes to 1360 cm^{-1} with increasing HTT. Meanwhile, the G peak around 1595 cm^{-1} strengthens slightly with temperature increasing, and a significant decrease is found in I_D/I_G during carbonization.

The crystallite size ($L_{c(002)}$ and $L_{a(100)}$) of LWCFs firstly decreases before 800°C and then increases with temperature increasing, whereas the interlayer spacing (d_{002}) gradually decreases during carbonization. On the other hand, the crystallite shape (L_a/L_c) and the degree of graphitization (G) increase with the temperature increasing. These results indicate that the preferred orientation and the degree of graphitization of LWCFs are improved with HTT increasing during carbonization.

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