

Effect on Tensile Strength of Wood-based Carbon Fiber Impregnated by Boron

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Wood-based carbon fiber derived from liquefied wood has the disadvantages of low mechanical strength and unstable performance. To improve its mechanical properties, wood-based carbon fiber precursors were impregnated with 5 wt.% and 8 wt.% boric acid solutions for 1 h and then carbonized at 900 °C for 1 h. The effect of boron content on fiber tensile strength and microstructure was investigated through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The tensile strength of wood-based carbon fibers impregnated with 5 wt.% boric acid reached 0.468 GPa, an increase of 44.89% compared with the untreated samples. In addition, the amount of graphitoidal crystal and the degree of graphitization increased with the boric impregnation. Furthermore, boron in the form of a boron-carbon solid solution in the graphene layer of carbon fibers effectively improved the tensile strength of wood-based carbon fibers.

Keywords: Carbon materials; Fiber technology; Microstructure; Crystal structure; Tensile strength

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INTRODUCTION

Wood liquefaction is a technique used to prepare carbon fibers (CFs), which show strong properties in terms of biodegradability. CFs prepared in a laboratory from liquefied wood have a tensile strength of up to 320 MPa (Zhang and Zhang 2013). The tensile strengths of the lignin-based and rayon-based CFs are approximately 350 MPa to 550 MPa (Zhang *et al.* 2014). The best lignin-based CFs produced to date have an average strength of 1.07 GPa and moduli of 82.7 GPa (Baker and Rials 2013). The mechanical properties of wood-based CFs are weak compared with other biomass-based fibers and commercial CFs (polyacrylonitrile (PAN) CFs or pitch-based CFs), which severely limits the use of wood-based CF in industrial areas. In general, graphitizable carbons show good planar alignment and stacking of the graphene layers, but non-graphitizable carbons have a turbostratic structure on the graphene layers (Ma and Zhao 2008). A wood phenol liquefaction product is categorized as a type of non-graphitizable carbon that is difficult to transform into a graphite crystallite structure for wood-based CFs, which are mainly composed of an amorphous carbon.

Among the inorganic additives tested, boron and its compounds are effective catalysts of carbon graphitization. Boron, as a unique catalyst, can substitute the positions of carbon atoms in a graphite-like structure and accelerate the graphitization process by preventing the formation of separate distinct carbon components. There have been several previous reports on the catalytic graphitization effect of boron on CFs (Tubnbull *et al.* 1966; Churikov *et al.* 2010; Wang *et al.* 2013). Wen *et al.* (2011) found that the tensile strength

and modulus of elasticity of PAN-based CFs with a 7 wt.% boric acid modification reached maximums of 2.46 GPa and 404 GPa, with respective increases of 26% and 16%. Thus, with their excellent mechanical properties, CFs have gained a lot of interest. Recent studies are focusing on the environmentally safe and sustainable preparation of CFs from biomass materials. Compared with fossil materials, such as polyacrylonitrile or acrylamide, biomass-based CF has a greater number of wide raw material sources. In the present study, CFs were prepared by wood liquefaction. To improve the mechanical properties of wood-based CFs, the precursor fibers were impregnated with a boric acid solution, and the impregnated precursor fibers were then carbonized to prepare wood-based CFs. The effects of boron on the mechanical properties of wood-based CFs and the relationship between the microstructure and tensile strength were investigated.

EXPERIMENTAL

Preparation of Wood-based Carbon Fibers

Oven-dried fir (*Cunninghamia lanceolata*) from Fujian, China, was ground and screened to the size of 60 to 80 mesh. The wood powder was mixed with phenol and phosphoric acid at a mass ratio of 1:6:0.48, and the mixture was heated in an oil bath at 160 °C for 2.5 h with continuous stirring. Hexamethylenetetramine (HMTA, 5%, based on the weight of the liquefied solution) was added as a synthetic agent to prepare the spinning solution. The mixture was then heated from room temperature to 170 °C over a period of 40 min. The spun filaments were prepared by melt spinning at 120 °C. The resultant fibers were cured by soaking in a solution containing hydrochloric acid and formaldehyde (30:37 v/v) at 90 °C for 2 h at a heating rate of 15 °C/h. The precursor carbon fibers (PCFs) were available after being washed with distilled water and dried at 80 °C for 4 h. The precursor fibers were immersed in the 5 wt.% and 8 wt.% boric acid solution for 1 h under a vacuum and dried at 80 °C until a constant weight was reached. The PCFs impregnated by boric acid were labeled as 5% PCF and 8% PCF. The precursor fibers treated with boron were carbonized in a N₂ flow, from room temperature to 900 °C with a heating rate of 4°/min, and held at 900 °C for 1 h. Lastly, the wood-based boron-doped carbon fibers were prepared and labeled as 5% CF and 8% CF. All chemicals used in the study were purchased from Beijing Chemical Works, Beijing, China.

Performance Test of Wood-based Carbon Fibers

The mechanical properties of the CFs were measured using an electrical tensile strength apparatus (JSF10, Zhongchen Company, Shanghai, China) with a crosshead speed of 0.6 mm/min. The tensile specimens were prepared by fixing the filament on a paper holder with an instant cyanoacrylate adhesive, as reported elsewhere (Naitoa *et al.* 2008). At least 15 samples were tested for each fiber specimen. X-ray diffraction analysis (XRD; XRD-6000, Shimadzu Company, Kyoto, Japan) with CuK α radiation (0.154 nm) measured the changes in crystal structure during the catalytic graphitization of wood-based CFs. The X-ray scan range (2θ) was from 5° to 40° at the speed of 2°/min, with a scanning step of 0.2°. Raman spectroscopy was used to examine the degree of graphitization of the CFs, with scanning from 1150 cm⁻¹ to 1800 cm⁻¹ with a 524 nm laser. An XPS analysis was performed (Escalab 250Xi, ThermoScientific, Waltham, MA, USA) with a monochromated AlK α X-ray source ($h\nu = 1486.6$ eV) at 10 mA and 13 kV. The survey scans were collected from the binding energy ranging from 0 eV to 1350 eV. A nonlinear

least squares curve-fitting program (XPSPEAK software version 4.1) was employed for the XPS spectral deconvolution.

RESULTS AND DISCUSSION

Mechanical Properties

The tensile strengths of PCF, CF, 5% CF, and 8% CF were 0.139 GPa, 0.323 GPa, 0.468 GPa, and 0.349 GPa, respectively (Fig. 1). The improvement in tensile strength was more obvious for 5% CF than for 8% CF. The boric acid was thermally decomposed to boron oxide. However, only limited amounts of boron oxide permeated into the fiber and filled its voids, whereas most boron oxide was attached to the fiber surface (Wang *et al.* 2014). It can be seen from Fig. 1 that fiber tensile strength decreased as boron concentration increased from 5% to 8%. This may be mainly caused by the surface flaws etched by decomposition of boron oxide. Excessive boron doping accelerated the generation of defects while appropriate boron content benefited the occupation in substitutional positions (Wen *et al.* 2012). Thus, the appropriate boron concentration improved the tensile strength of carbon fibers.

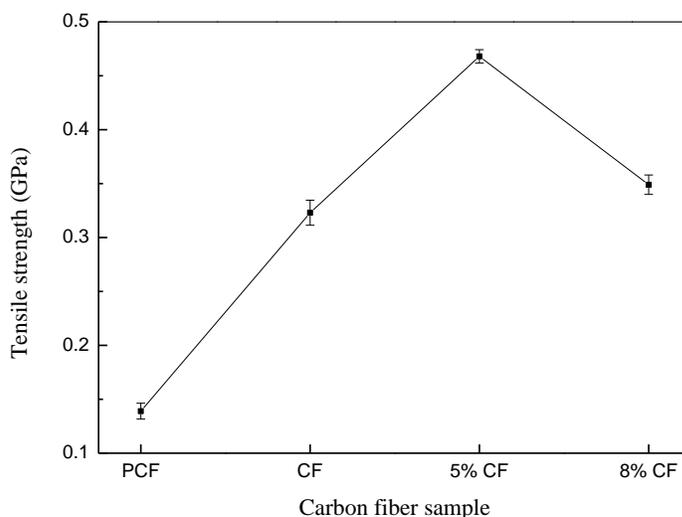


Fig. 1. Tensile strength of PCF, CF, and CFs impregnated by boron

X-ray Diffraction (XRD) Analysis

The XRD patterns of PCFs and CFs with different boron impregnation conditions are shown in Fig. 2. There was an obvious diffraction peak at the 2θ value of 20° , which was assigned to the disordered graphitic 002 plane, thus suggesting that the CFs prepared from liquefied wood consisted of graphite-like micro-crystallites (Deng *et al.* 2013). Compared with PCFs, the (002) crystal plane diffraction peaks of the CFs gradually approached the (002) plane peak of graphitoidal carbon, which illustrated that the amount of non-crystal carbon atoms was reduced. There were two clear diffraction peaks located at 15° and 27.6° for the PCFs, which were in good agreement with the diffraction peaks of the boric acid. Thus, boric acid impregnation had a remarkable effect on the PCFs. However, there were no diffraction peaks of the boron and its compounds in the XRD

patterns for CFs. There are two possible explanations for the lack of peaks. Boron may have completely evaporated or escaped from the CFs during the heating process. The other explanation may be that boron and its compounds did not exist outside of the graphite lattice, such that they entered the graphite layers or formed a substitutional or interstitial solid solution between the layers.

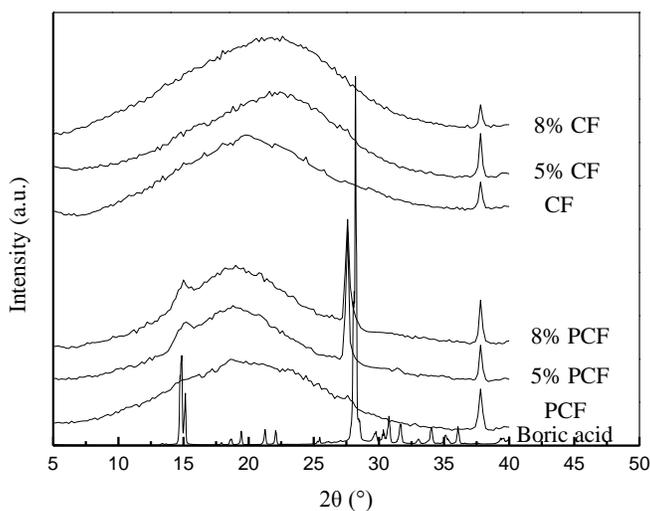


Fig. 2. X-ray diffraction (XRD) patterns of PCF, PCFs impregnated by boric acid, CF and CFs impregnated by boric acid

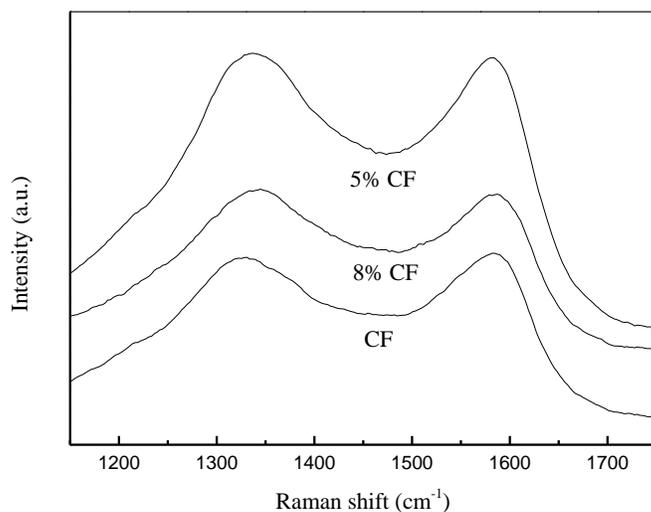


Fig. 3. Raman spectra of CF and CFs impregnated by boric acid

Table 1. Raman Spectra of CF and CFs Impregnated by Boric Acid

Sample	I_D	I_G	I_D/I_G
CF	88.16	88.72	0.99
5% CF	137.87	137.25	1.00
8%CF	80.56	79.33	1.01

I_D , intensity of D band; I_G , intensity of G band

Raman Spectroscopy Analysis

Raman spectroscopy is used to analyze the degree of graphitization and is an effective tool for observing the microstructures of carbon materials (Larouche and Stansfield 2010). Carbon materials mainly show two strong Raman bands: a G band of graphite at about 1580 cm^{-1} and a D band at about 1360 cm^{-1} . Both bands are related to the relative motion of sp^2 bonded carbon atoms (Xu *et al.* 2010). As shown in Fig. 3, the Raman spectra of the CFs exhibited noticeable changes after impregnation by boric acid, especially for the sample of 5% CF. The peak was sharper, and its intensity was increased. The D band corresponds to the defect lattice vibration mode, while the G band corresponds to an ideal graphitic lattice vibration mode. The intensity ratio ($R = I_D/I_G$) of the D band to the G band ranged from 1.01 to 0.99 (Table 1), and this result is also an important indicator of the degree of graphitization (Lewandowska *et al.* 2015). The integrated intensity ratio R showed little difference among the various CFs. However, the intensity of the G and D peaks of the sample 5% CF were noticeably higher than the others. These results imply that the 5% CF had the highest degree of graphitization; thus, the internal structure transformed from two-dimensional carbon layers to an ordered hexagonal graphitoid crystal structure. Based on the above results, strong mechanical properties of carbon fibers were obtained by treatment with 5 wt.% boric acid.

X-ray Photoelectron Spectroscopy (XPS) Analysis

To examine carbon fibers for the presence and valence state of boron, other elements, and surface functional groups, wood-based CFs were analyzed by XPS (Fig. 4). It was apparent that the C signal was larger than that of O. The element B is faintly visible in the spectra of the carbon fiber samples. The atomic concentrations on the surface of the CFs are summarized in Table 2. The variation in boron content indicated that part of the boron evaporated during carbonization. Besides, the boron content increased as boric acid concentration increased from 5% to 8%. This result confirmed that boron did not evaporate completely and that it could have formed a substitution or interstitial solid solution during graphitization. The characteristic peak of boron appeared in the XPS spectra, while it disappeared in the XRD patterns, suggesting that boron added to the PCFs could have entered either into or between layers of graphite. These results showed that stable boron-carbon bridging, namely a boron-carbon solid solution, formed in the graphene layer under high temperature conditions.

Because the C1s spectra of all samples were very similar, only the 5% CF sample is presented in Fig. 5. The C1s region exhibited an asymmetric tailing, which is partially due to the intrinsic asymmetry of the graphite peak or oxygen surface complexes. The C1s peak of 5% CF was subdivided into four components corresponding to the graphite (284.7 eV), C-O (285.5 eV), C=O (286.5 eV), and -COOH (288.3 eV), with the relative percentages of 62.6%, 18.53%, 12.07%, and 6.8%, respectively. The C-B peak was not observed, which confirmed the above results that boron exists in CFs as a solid solution in a graphite lattice. This information will help to resolve defects produced during the spinning and carbonization process. The substitutional boron would arrange the crystal lattice by replacing carbon atom and participate in the construction of hexagonal carbon lamellar during heat treatment (Shirasaki *et al.* 2000; Wen *et al.* 2012), so that the structural defects in carbon fibers were removed. As a result, the tensile strength of carbon fibers was improved. The wood-based CFs immersed in the boric acid solution showed a noticeable immersed effect.

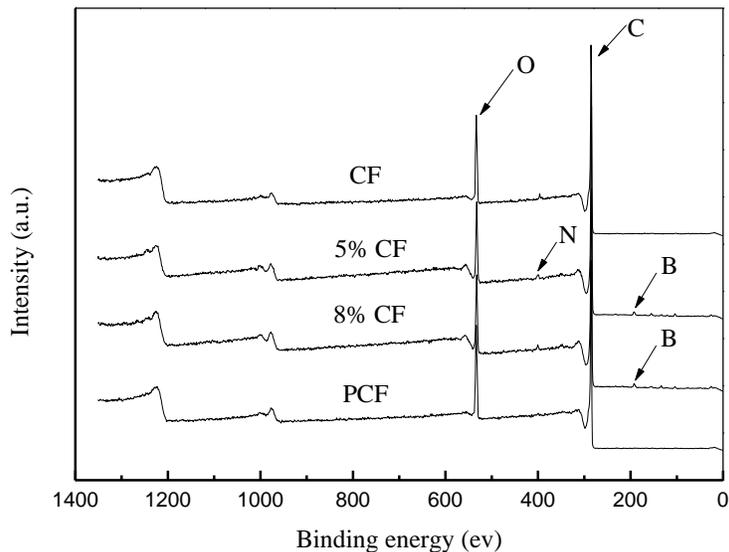


Fig. 4. X-ray photoelectron spectroscopy (XPS) spectra of PCF, CF and CFs impregnated by boric acid

Table 2. Surface Element Content of PCF, CF and CFs Impregnated by Boric Acid, as Determined by XPS

Sample	C (%)	O (%)	N (%)	B (%)
PCF	67.85	26.15	2.41	0
CF	86.30	12.8	0.87	0
5% CF	78.89	15.09	1.38	4.61
8% CF	77.93	15.55	1.49	5.03

C, carbon; O, oxygen; N, nitrogen; B, boron

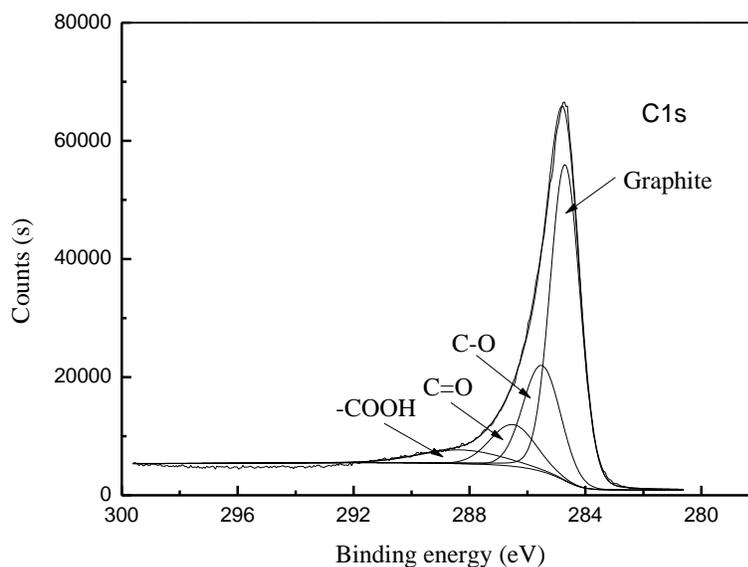


Fig. 5. X-ray photoelectron spectroscopy (XPS) spectra of the C1s region of carbon fiber (5% CF)

CONCLUSIONS

1. To improve the tensile strength of wood-based CFs, carbon fibers derived from wood liquefaction were impregnated with boric acid. The appropriate concentration somewhat improved the tensile strength of the precursors and wood-based CFs.
2. The tensile strength of the fibers increased with the boron concentration, with the maximum of 0.468 GPa at 5 wt.% boric acid indicating that 5% CF had the highest degree of graphitization.
3. The amount of graphitoidal crystal and the degree of carbonization of CFs were increased by boron impregnation.
4. Boron exists in the form of a boron-carbon solid solution in the graphene layer of CFs. The wood-based CFs impregnated with boric acid had improved mechanical properties.
5. The substitutional boron can arrange the crystal lattice by replacing carbon atom and participated in the construction of hexagonal carbon lamellar during heat treatment. The relationship between heat treatment temperature and the effect of boron on the mechanical properties of carbon fibers needs to be investigated.

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