Influence of High Temperature and Pressure Ammonia Solution Treatment on Interfacial Behavior of Carbon Fiber/Epoxy Resin Composites

L. H. Meng, Z. W. Chen, X. L. Song, Y. X. Liang, Y. D. Huang, Z. X. Jiang

Department of Polymer Materials and Engineering, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT: The method of high temperature and pressure ammonia solution treatment to improve the interfacial performances of carbon fiber/epoxy composites is discussed in this study. Besides, the influence of high temperature and pressure ammonia solution treatment on carbon fiber and its reinforced epoxy composite interface performance were studied. The untreated and treated carbon fibers were characterized by monofilament tensile test, X-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM). The interfacial adhesion of the untreated and treated carbon fibers reinforced epoxy resin composites were also evaluated by interface shear strength (IFSS) test, interlaminar shear strength (ILSS) test, and fracture morphology analysis. It was found that the interfacial adhesion of composites increased greatly after high temperature and pressure ammonia solution treatment. The improvement of interfacial adhesion was attributed to the increase of polar functional groups and surface roughness of carbon fibers surface after treatment. J Appl Polym Sci 113: 3436–3441, 2009

Key words: high temperature and pressure ammonia solution; carbon fiber; interface; adhesion

INTRODUCTION

The addition of carbon fiber (CF) reinforcement is always used to improve the stiffness, strength, and high temperature performance of polymeric materials. The mechanical properties of the resulting CF reinforced composite materials not only depend on the properties of each primary component but also on the performance of the fiber/matrix interface. A suitable interface generally leads to better composite properties; hence, many effective interfacial modifications for CF has been investigated.[1,2] The common method for CF is oxidation treatment, which includes liquid oxidation, gas oxidation, electrochemical oxidation, etc. The polar function groups are introduced to CF surface after oxidation treatment; hence, the wettability of CF and resin is improved, and the adhesion between fiber and resin is also enhanced. In addition, some methods are also used for CF modification, such as vapor deposition,[3–5] ultrasonic deposition,[6] and couple agent,[7,8] which improve interfacial adhesion in CF reinforced composites through forming coating layer.

Recently, γ-ray,[9,10] electron beam,[11] laser,[12] plasma,[13–17] and the Ar^+ irradiation[18] are all studied for CF modification. These treatments improve interfacial adhesion of CF and polymer matrix by the introduction of active point. Especially, some researchers have focused on other treatment for CF, such as supercritical fluid treatment. However, the method of supercritical fluid treatment does not have been deep investigated now.

Therefore, in this study, the effect of high temperature and pressure ammonia solution (HTPAS) treatment on CFs was investigated. Through the effect of erosion and oxidations of ammonia solution, the active function groups are introduced on the surfaces of CFs, and the mechanical property of CF/epoxy resin composite increases.

EXPERIMENTAL

Materials

All experiments were achieved on the CFs supplied by Jilin Chemical Industrial Company of China as strand formed with about 3000 single fibers each having 7.0-μm diameter. The CFs were refluxed by acetone and petroleum ester, respectively, for 24 h before use.

Correspondence to: L. H. Meng (menglinh@hit.edu.cn).
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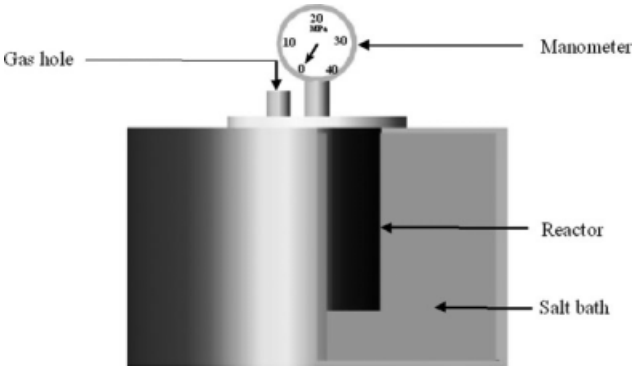

Figure 1 Schematic diagram of equipment of HTPAS treatment.

E-51 type epoxy resin, which was condensate product of bisphenol A and epichlorohydrin, was used with hardener phthalic anhydride and benzyl dimethylamine as the matrix material. The ratio of epoxy to hardener used was 100 : 70 : 1 by weight, as recommended by the manufacturer.

High temperature and pressure ammonia solution treatment

The apparatus used for the HTPAS treatment of the CFs is schematically illustrated in Figure 1. The CFs were twisted on a frame made by glass and put into the reaction vessel. Then, 22 mL ammonia (25 wt %) was put into the vessel (90 mL). After that, the vessel was heated in a salt bath of sodium nitrate and potassium nitrate mixture. The HTPAS treatment time is defined as the time between the moment of pressure reaching the critical point 9.82 MPa and cooling the reaction vessel in water.

After the HTPAS treatment, the fibers were washed with distilled water and dipped in water for 24 h for complete removal of the residual ammonia. After that, the fibers were dried at 120°C for 24 h in a vacuum of 1×10^5 Pa before use.

Analysis methods

XPS measurements were performed using a Thermo ESCALAB 250 photoelectron energy spectrometer. The spectra were collected using an Al Ka X-ray source (1486.6 eV). To compensate for the surface charging, all the binding energies of the core level spectra were referenced to the C1s hydrocarbon peak at 284.3 eV. The pass energy for the analyzer was 20 eV with the emission angle of 90° and a power of 200 W.

A Solver P47 atomic force microscopy (NT-MDT Co., Zelenograd Research Institute of Physical Problems, Moscow, Russia) was used to observe the morphology of CF surfaces before and after treatment. All images were obtained in a noncontact mode with a silicon cantilever (nominal spring constant of 3 N/m, minimum tip radius of 10 nm) and observed area was 4×4 μm^2. The AFM images were displayed with different shades of gray (dark gray indicating lower parts and light gray higher parts of the surface).

The fractographic image of CF/epoxy resin composite was examined using scanning electron microscopy (JEOL JSM-5410). The fiber samples were coated with a thin gold layer (−20 nm) by sputtering before the SEM study at 20 kV.

Determination of the tensile strengths of single carbon fiber

Single tensile strengths were measured according to ASTM standard D3379. The CF was fixed on a paper frame straightly. Epon 834 mixed with 15 wt.% of TEPA was used as the bonding agent for this task. The testing length for single fiber was 20 mm. The testing speed for the fiber was 10 mm/min, with a WD-1 material testing machine.

The tensile strength value of a single CF was obtained by averaging the results of at least 30 test specimens. The single filament tensile test was conducted to determine if and when he HTPAS treatment would become detrimental to the fiber strength.

Determination of the interfacial shear strengths of microcomposites

One of the most common and popular techniques to measure the interfacial bond strength between reinforcing fibers and polymer matrices is the pull-out method.[19] A microbond test was performed to evaluate the IFSS between CF and matrix by pulling out a fiber from cured epoxy resin droplet. The composite specimens were prepared by dipping epoxy resin droplets on a CF monofilament with the embedded length of 60–80 μm using a fine-point applicator. The specimens were cured thrice at 90°C for 2 h, 120°C for 2 h, and finally 150°C for 4 h. After this curing process, the single filament pull-out test was carried out on an interfacial microbond evaluation instrument, which was made by Tohei Sangyo, Japan. The pull-out test was performed at a crosshead displacement rate of 0.5 μm/s. The value of IFSS was calculated according to the equation

$$\mathrm{ILSS} = \frac{F_{\max}}{\pi d l} \tag{1}$$

where F is the maximum load, d is the radius of the fiber, and l is the embedded length of the fiber in the epoxy resin.

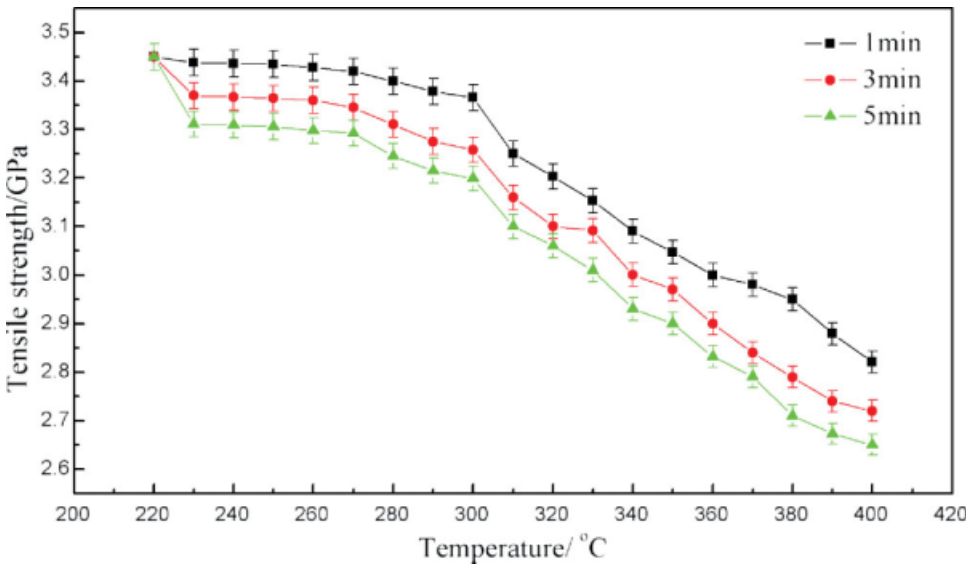

Figure 2 The monofilament tensile strength of CFs. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com.]

Determination of interlaminar shear strengths of composites

Interlaminar shear strength (ILSS) testing was conducted using the three-point bending method described in ASTM standard D2344. These measurements were made on CFs composite samples prepared according to the following procedure.

The unidirectional long CFs reinforced epoxy composites were made with both untreated and HTPAS-treated CFs. Curing was performed in a compression moulding machine by the method of compression moulding, and the content of the resin in composites was controlled at about 35%. The curing processing was shown as follows: 90°C for 1 h, 100°C for 2 h, 120°C for 2 h, and 150°C for 3 h. After the curing process, the mould was cooled to room temperature with the pressure maintained. All composite samples were about 60 ± 1 mm in width and 2 ± 0.1 mm in thickness.

The composites were converted into test samples by cutting into small blocks: three-point bending test samples were 10 mm × 20 mm × 3 mm. Three-point bending tests were conducted using a Wd-1 material testing machine to determine the ILSS. The ILSS was calculated according to the following equation:

$$\mathrm{ILSS} = \frac{3P}{4bt} \tag{2}$$

where P is the maximum force the sample could tolerate during the test, b is the sample width, and t is the sample thickness. The two sample support points were separated by a distance equal to five times the sample thickness.

RESULTS AND DISCUSSION

The effect of HTPAS treatment on tensile strength of monofilament carbon fiber

The tensile changes of monofilament CF tensile strength treated by HTPAS are shown in Figure 2. It can be seen from Figure 2 that the tensile strength of CF decreases with the treated temperature. The tensile strength of CF also decreases with the treated time when the treated temperature is the same.

The monofilament tensile strength of CF decreases slowly below 300°C, but rapidly above 300°C. The monofilament tensile strength of CFs treated at 400°C for 1, 3, and 5 min decrease from initial value 3.45 to 2.82 GPa, 2.72 and 2.65GPa, respectively. This indicates that the HTPAS treatment has some etching and erosion effect on the CFs, which leads to loss of the monofilament tensile strength. Furthermore, the effect of etching and erosion effect becomes more severe by the increase of temperature, so the loss of monofilament tensile strength becomes much greater.

The effect of HTPAS treatment on IFSS of microcomposites

The pull-out test method allows the use of microsize specimens. Figure 3 provides IFSS results of epoxy resin microcomposites reinforced with untreated and treated CFs.

From Figure 3, it can be clearly seen that no matter what the treatment time is 1 or 3 or 5min, the trend of microcomposites interfacial adhesion force is increased first, then reach a maximum value and

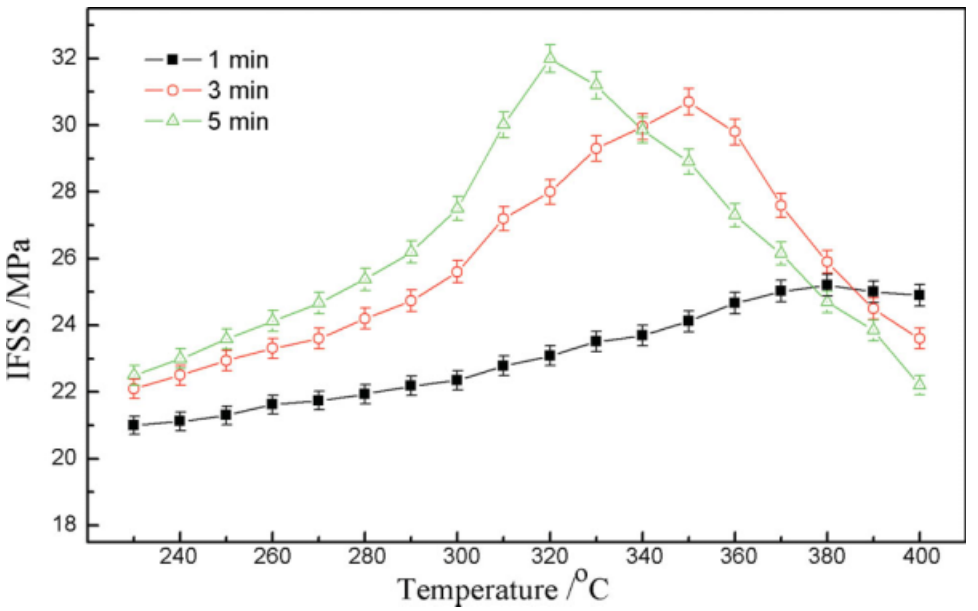

Figure 3 The IFSS of CF-epoxy resin microcomposites. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com.]

finally decrease as increasing HTPAS treatment temperature. And the maximum IFSS of microcomposites are 25.20 MPa at 380°C for 1 min, 30.70 MPa at 350°C for 3 min, 31.99 MPa at 320°C for 5 min, the rate of accretion are 31.25, 59.89, and 66.61% from untreated fiber/epoxy microcomposites 19.20 Mpa, respectively. So, it indicates that HTPAS treatment indeed can improve the interfacial adhesion force of CF/epoxy resin composites. At the HTPAS treatment time 3 min, the maximum IFSS arrives at lower temperature(compared to 1 min) and more efficient (compared to 5 min). So CFs treated by HTPAS for 3 min is deemed to optimum.

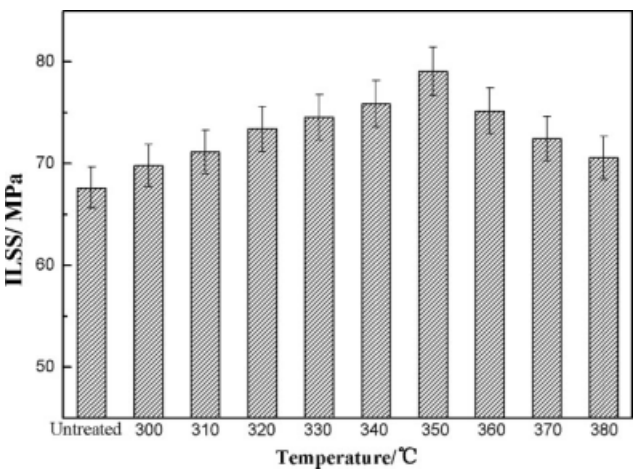

Figure 4 The ILSS of carbon fiber-epoxy composites.

The effect of HTPAS treatment on ILSS of composites

To study the effect of HTPAS treatment on the ILSS of practical composites, the CFs treated by HTPAS from 300 to 380°C for 3 min were investigated.

Figure 4 shows the ILSS of CF/epoxy resin composites. As shown, the ILSS of treated fibers/epoxy composites are all higher than the untreated fiber/epoxy composites. In the range of treated time of 300~380°C, the ILSS of composites increases first and then decreases with the treated temperature increase. With the treated time increase from 300 to 350°C, the reaction activity of CF surfaces raise, and so the interfacial adhesion of composites increases first. While treated temperature increases from 350 to 380°C, the monofilament tensile strength decreases, which contribute to the fall of ILSS of composites. In addition, when treated temperature is 350°C, the balance of increase of reaction activity

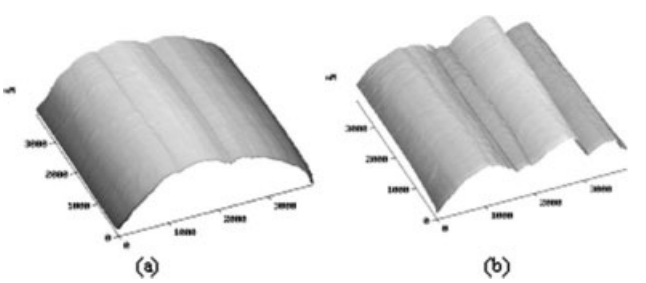

Figure 5 Three-dimensional AFM micrographs of carbon fiber surface.

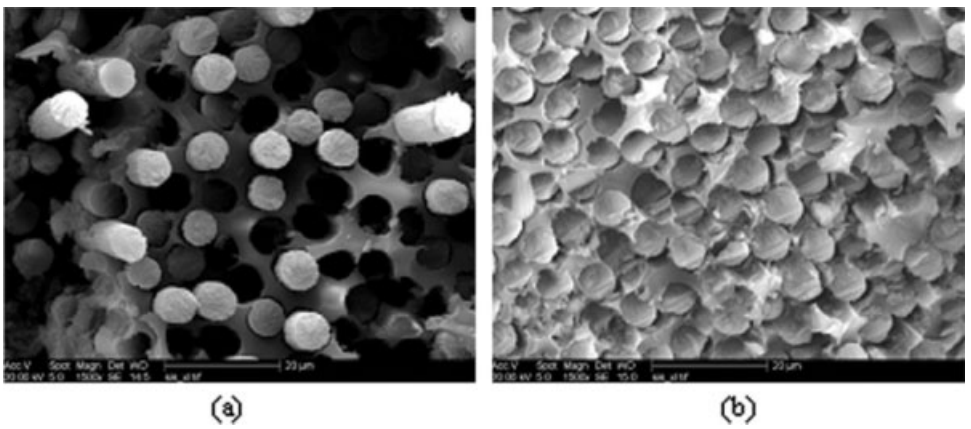

Figure 6 Representative images of the breakage region of samples after ILSS test.

and decrease of monofilament tensile strength is formed; thus, the ILSS of treated CFs composite reached the highest value 79.07 MPa, 16.93% higher than the untreated CF/epoxy composite. Thus, the following research will be focused on the CFs treated by HTPAS treatment with 350°C for 3 min.

AFM analysis

Surface topographies of the CF before and after HTPAS treatment at 350°C for 3 min are characterized by AFM. Resultant AFM images of 4 μm × 4 μm are shown in Figure 5. Similar to other PAN-based CF,[20] all the fiber surfaces have clear ridges and striations running along the axis of the fiber [Fig. 5(a)]. Furthermore, it can be seen from Figure 5(b) that the longitudinal ridges and the striations of treated CFs are more obvious than untreated CFs. This presents that original features of the surface topography are changed after HTPAS treatment. The surface topography and roughness of untreated CFs and treated CFs change significantly because of the etching effect of HTPAS treatment.

Fractographic analysis by SEM

The fractographic image of untreated CFs reinforced epoxy resin composite and CFs treated by HTPAS at 350°C for 3 min reinforced epoxy resin composite is shown in Figure 6.

For the untreated CFs reinforced epoxy resin composite [Fig. 6(a)], bundles of fibers were pulled out, and nearly no resin attached on the surface of fibers. This indicates that the interfacial adhesion between fibers and resin is so weak that, when the untreated composite is loaded, the interface of composite break away, and could not transfer the stress. Thus, the ILSS of untreated CFs reinforced epoxy resin composite is low. Whereas, for CFs treated by HTPAS at 350°C for 3 min reinforced epoxy resin composite [Fig. 6(b)], nearly no fiber is pulled out, the epoxy resin tightly adhere to fibers, and the fibers and resin are fracture simultaneity. This indicates that the interfacial adhesion of composite is greatly improved too.

Element analysis of carbon fiber surface

The elements composition of the surface of the untreated and treated (350°C for 3 min) CFs are investigated by X-ray photoelectron spectroscopy (XPS), and the relative content of elements is shown in Table I.

XPS analysis of the CFs treated by HTPAS at 350°C for 3 min showed an increase in the oxygen and nitrogen concentrations (194.4% and 435.4%) and a decrease in the carbon concentration. The concentration of polar elements "O" and "N" increases increasing the reaction activity pointes of fiber surface, which is advantageous in the enhancement interfacial adhesion force of CF/epoxy composites. To extensively characterize the changes of polar element, the C1s peak region are deconvoluted into six functional components (Figs. 7 and 8): (1) B.E. (binding energy) of C—C is about 284.30; (2) B.E. (binding energy) of C—N is about 285.70; (3) B.E. (binding energy) of C—O—C with B.E. is about 287.50; (4) B.E. (binding energy) of C=O is about 287.50; (5) B.E. (binding energy) of COO is about 289.00; (6) B.E. (binding energy) of CO_3^{2-} is about 290.80.

These data are summarized in Table II. From this result, it can be analyzed that the relative concentration of C=O, COOH, COOR increases, due to the oxidation effect of the HTPAS treatment. In addition,

TABLE I
The Relative Content of Elements of the Untreated and Treated Carbon Fiber

	The concentration of elements (%)		
Carbon fiber	C	O	N
Untreated fiber	96.13	3.39	0.48
Treated fiber	91.32	6.59	2.09

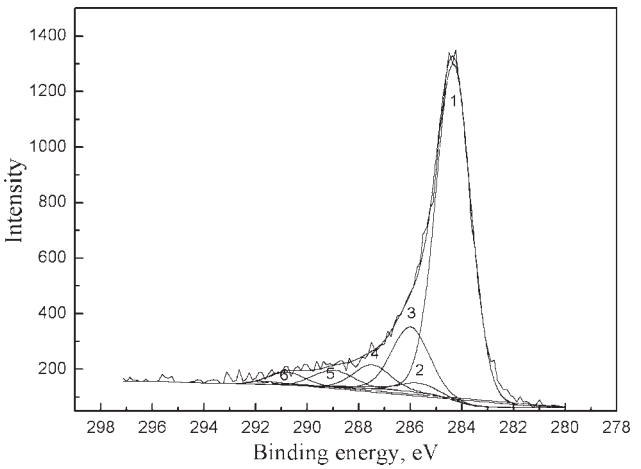

Figure 7 Deconvolutation C1s peak of untreated carbon fiber.

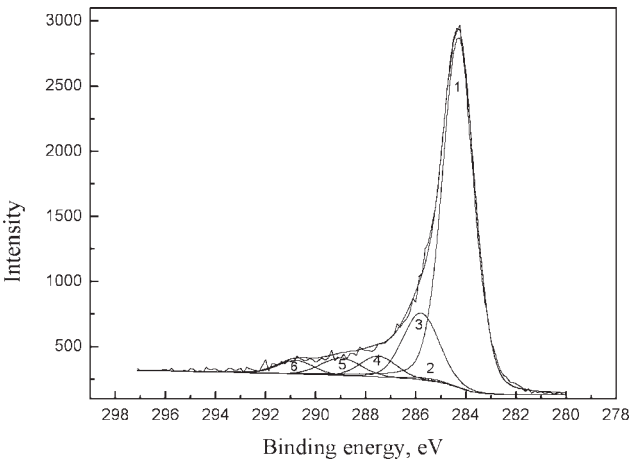

Figure 8 Deconvolutation C1s peak of carbon fiber treated by HTPAS at 350°C for 3 min.

TABLE II
Functional Components of C1s Peak of the Untreated and Treated Carbon Fiber

		C 1s peak					
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
Untreated fiber	Binding energy (eV)	284.30	285.70	285.90	287.50	289.00	290.80
	Relative content (%)	72.40	0.50	14.98	4.69	4.37	3.06
Treated fiber	Binding energy (eV)	284.34	285.70	286.00	287.50	289.00	290.80
	Relative content (%)	70.89	2.12	14.47	5.36	5.22	1.94
Chemical bond		C—C	C—NH_2 CN NCO	C—OH C—O—C	C=O	COOH COOR	CO_3^{2-} $\pi \rightarrow \pi^*$

after the HTPAS treatment, the relative content of N increases synchronously. Thus, it can be concluded that the content of polar function groups on the surface of CFs are significantly increased after HTPAS treatment, which lead to the improvement of the mechanical property of CF/epoxy composites.

CONCLUSIONS

A new method based on HTPAS treatment technique was proposed to improve the interfacial bond strength of CF/epoxy composites in this article. SEM, AFM, and XPS analysis the surface of untreated and treated CFs demonstrated that the HTPAS treatment has the physical etching and chemic dual effect on the surface of CF. Although the tensile strengths of single CF decreased, the LFSS and ILSS of treated CF/epoxy composites increased by correctly controlling the treatment time and temperature. CF treated by HTPAS at 350°C for 3 min reinforce epoxy resin composite got the best interfacial adhesion.

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