Chemical Interaction Between Carbon Fibers and Surface Sizing

Zhishuang Dai,[1,2] Baoyan Zhang,[2] Fenghui Shi,[2] Min Li,[1] Zuoguang Zhang,[1] Yizhuo Gu[1]

[1]*Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China*
[2]*Beijing Institute of Aeronautical Materials, Beijing 100095, China*

Received 12 April 2011; accepted 8 July 2011
DOI 10.1002/app.35226
Published online 26 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Functional groups on the surface of Polyacrylonitrile (PAN)-based carbon fibers and in fiber surface sizing are likely to react during the curing process of composites, and these reactions could affect the infiltration and adhesion between the carbon fibers and resin. T300B-3000-40B fibers and fiber surface sizing were heat-treated at different temperatures, and the structural changes of both the fiber surface sizing and extracted sizing after heat treatment were investigated by Fourier transform infrared spectroscopy. The results show that the concentration of epoxy groups in both the fiber surface sizing and extracted sizing decreased with increasing heat-treatment temperature and decreased to zero after treatment at 200°C. The concentration of epoxy groups in the extracted sizing was lower than that of the fiber surface sizing after treatment under the same conditions; this indicated that the rate of reaction between the carbon fibers and fiber surface sizing was higher than the reaction rate of the fiber surface sizing system. X-ray photoelectron spectroscopy analysis reveals that the content of C—O bonds and activated carbon atoms on the surface of the desized treated carbon fibers was the highest when the heat-treatment temperature was 150°C; this proved the reaction between the carbon fibers and the fiber surface sizing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2127–2132, 2012

Key words: coatings; fibers; FT-IR; surfaces

INTRODUCTION

Carbon-fiber-reinforced resin matrix composites have been widely used in the aerospace, architecture, and automobile industries during the past few decades because of their good engineering properties, including a high specific strength and modulus and lower density.[1–3] In carbon-fiber-reinforced resin matrix composites, the matrix determines the chemical and thermal resistance of the composite, and the carbon fiber provides strength and stiffness and dominates the mechanical properties of its composites.[4]

A coating method is provided because unsized carbon fibers are brittle and have low elongation, which would result in fluffiness and yarn breakage during impregnation with the matrix. *Sizing*, a thin coating applied to the surface of the carbon fiber, has been shown to improve the processability of the carbon fibers and/or alter the manner in which the load gets transferred from one failed fiber to another.[5–11] In addition, sizing can alter the surface free energy of the carbon fiber and, thus, alter the thermodynamic driving force for wetting.[12] Moreover, the sizing of carbon fibers has been reported to enhance the interfacial properties. A heat-resistant sizing agent composed of thermoplastic polyimide GCPI and thermosetting epoxy resin for PAN-based carbon fibers was investigated by Cao et al.;[13] their study indicated that the sized fiber possessed an improved wear resistance and a 97% improvement in interfacial shear strength compared to the unsized fiber. Paipetis and Galiotis[9] found that the sized M40B fiber/epoxy system had a higher interfacial shear strength than their unsized system. The interfacial failure of the sized M40B system consisted mainly of mixed-mode cracking, whereas clear fiber/matrix debonding was observed in the unsized one.

Sizing on carbon fibers has been reported to introduce a number of functional groups, such as C—OH, C=O, and COOH.[14] The interaction between such functional groups at different stages of the curing process could affect the mechanical properties of composites.[15] Therefore, the mechanical performance of carbon-fiber-reinforced composites depends not only on the properties of the reinforcing fiber and matrix but also on the fiber/sizing and sizing/matrix interfacial properties; therefore, investigation of the reaction and/or interaction between sizing and carbon fibers during heat treatment is important.

Correspondence to: B. Zhang (zhangbaoyan0916@yahoo.com).

© 2011 Wiley Periodicals, Inc.

To investigate the chemical interaction between carbon fibers and sizing on the surface during composite manufacture, heat treatment of the carbon fiber and sizing was carried out with reference to the curing process of carbon-fiber-reinforced Bismaleimide (BMI) and/or epoxy matrix composites. The chemical structure of the sizing was measured by Fourier transform infrared (FTIR) spectroscopy, and the surface chemical properties of desized untreated and treated carbon fibers were investigated via X-ray photoelectron spectroscopy (XPS). By comparing the chemical properties of the surface sizing and desized carbon fibers at different stages of treatment, we studied the chemical interaction between the carbon fibers and the sizing.

EXPERIMENTAL

Materials

Commercially available T300B-3000-40B (T300B for short) carbon fibers, with a diameter of about 6–7 μm and purchased from Toray (Tokyo, Japan), were used in this work. The sizing of the carbon fibers was obtained by acetone extraction at 75°C for 6 h, with a returning rate of 30 min, followed by drying at 60°C in a vacuum oven for 8 h. Epoxy E51 resin and the hardener 4,4′-diaminodiphenyl sulfone were provided by Wuxi Resin Factory (Wuxi, China) and Suzhou Yinsheng Chemical Co., Ltd. (Suzhou, China), respectively.

Heat treatment

The carbon fibers and sizing were heat-treated in a vacuum-drying chamber at 150, 180, and 200°C for certain times. The control processing cycles were as follows: heating from 25 to 150°C at 2°C/min, holding at 150°C for 2 h, heating from 150 to 180°C at 2°C/min, holding at 180°C for 2 h, heating from 180 to 200°Cat 2°C/min, and holding at 200°C for 4 h. The heat-treated specimen was removed to a desiccator when each step of the heat treatment was finished. Each step contained all of the previous steps. With the second step of heat treatment at 180°C taken as an example, the removed specimen underwent a process of heating at 150°C for 2 h and 180°C for 2 h. The sizing obtained by extraction from the heat-treated carbon fibers is called *extracted sizing*, and the sizing that experienced heat treatment is called *fiber surface sizing* in this article. The fiber samples that were obtained by desizing treatment of the heat-treated carbon fibers are called *desized treated carbon fibers*.

Characterizations

FTIR spectroscopy (Nicolet, Ltd., USA) was applied to study the structures of the fiber surface sizing and extracted sizing. The sizing was abraded with KBr at a weight ratio of 1 : 200–1 : 100 to guaranty moderate transmittance and pressed to prepare pellets. Spectra were obtained in an optical range of 400–4000 cm^{-1}.

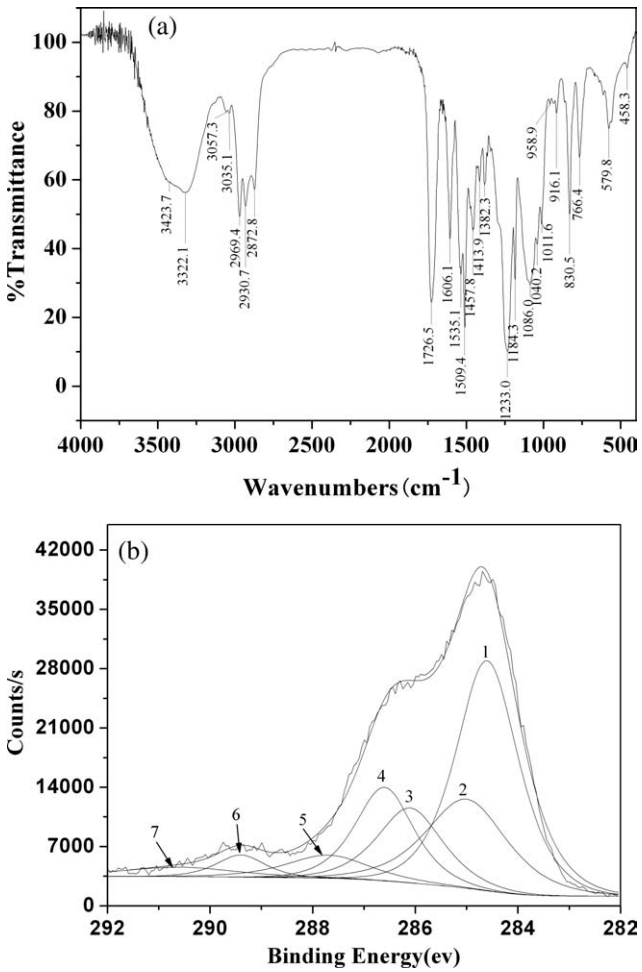


Figure 1 Surface chemical properties: (a) FTIR spectrum of sizing and (b) curve-fitted C1s of desized T300B.

XPS was used to evaluate the chemical compositions of the desized carbon fiber surface. A Physical Electronics ESCALAB 250 system (USA) provided by ThermoFisher Scientific with a concentric hemispherical analyzer and a monochromatic Al Kα X-ray source (1486.6 eV) was operated in an evacuated chamber at approximately 5.0×10^{-9} mbar. An electron takeoff angle of 45° with respect to the sample plane was used. A spot of 400 μm in diameter, with 150 eV of pass energy for survey scan and 30 eV for high-resolution scans (293.7–273.7 eV), was used in all of the measurements. The carbon fibers were fixed by a conductive adhesive to avoid warp. A seven-parameter curve fitting was conducted for the carbon C1s spectra with 284.6 eV taken as the reference peak.

RESULTS AND DISCUSSION

Surface chemical properties

The FTIR transmittance spectra of the T300B fiber surface sizing is shown in Figure 1(a). The band at

TABLE I
C1s Peaks of Desized T300B Carbon Fibers and Relative Peak Areas

	C1s peaks in different states Binding energy (BE) (eV; area, %)							
Sample	Peak 1 (284.6)	Peak 2 (285.0)	Peak 3 (286.1)	Peak 4 (286.6)	Peak 5 (287.7)	Peak 6 (289.4)	Peak 7 (290.6)	Activated carbon atoms (%)
T300B	39.88	20.08	13.52	15.10	5.32	3.00	3.09	40.03
Peak assignment	Reference	—C—C —C—H	—C—OH —C—O—C C—NH_2	*C—O—C=O Epoxy groups	—C=O C=N	—COOH —COOR	—COO^- π–π*	

3422 cm^{-1} was attributed to the vibrations of hydroxyl groups, the band at 3221 cm^{-1} was attributed to asymmetric stretching vibrations of —NH_2, the band at 2965–2872 cm^{-1} was attributed to the vibration of —CH_3 and —CH_2—, the band at 1725 cm^{-1} was attributed to the vibrations of C=O, the bands at 1183 and 1363 cm^{-1} were attributed to the bending vibrations and stretching vibrations of —O—, respectively, and the band at 916 cm^{-1} was attributed to epoxy groups. This information indicates that the sizing of the T300B carbon fibers was composed of bisphenol A epoxy, alkyl substances with long chains, and a small number of amino compounds.

XPS analysis of the desized untreated T300B, which is illustrated in Figure 1(b), indicated that there were mainly seven kinds of functional groups on the desized carbon fiber surface; these are listed in Table I. The reactive functional groups on the desized carbon fiber might have been epoxy groups, hydroxyl groups, and —COOH and —NH_2 groups.

The results indicate that the main reactions between the desized T300B fiber and the fiber surface sizing or in the fiber surface sizing system during the heat-treatment process might have been as shown in Schemes 1–3.

Effect of heat treatment on the extraction percentage of the sizing

As shown in Figure 2, the extraction percentage of the sizing decreased with increasing heat-treatment temperature, and the declining rate was the highest when the heat-treatment temperature increased from 150 to 180°C. The solubility of fiber surface sizing in acetone was investigated; this showed that the fiber surface sizing was completely soluble in acetone after treatment at 150 and 180°C and was partially soluble after treatment at 200°C. The results indicate that the decrease in the extraction percentage of the sizing when the heat treatment was lower than 180°C was due to covalent bonds, which could not be extracted down by acetone and were generated via the reaction between the fiber surface sizing and the carbon fibers. However, a substance insoluble in acetone was produced when the heat-treatment temperature was 200°C; this resulted in a further decline of the extraction percentage of the sizing. However, there were still some substances in the fiber surface sizing that did not take part in the crosslinking reaction, and the extraction percentage of sizing was still 0.216% after the fiber was heat-treated at 200°C.

Scheme 1 Reaction of amino and epoxy groups.

Effect of heat treatment on the structure of the sizing

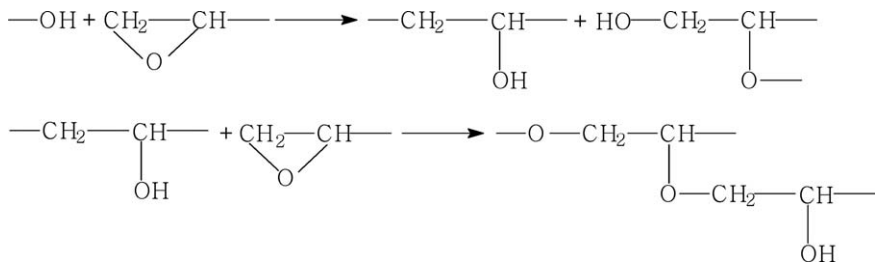
Figure 3 illustrates the infrared spectrogram of the fiber surface sizing [Fig. 3(a)] and extracted sizing [Fig. 3(b)] at different heat-treatment temperatures. The reactive functional groups in the fiber surface sizing included epoxy groups, hydroxyl groups, and —NH_2 groups, whose concentration during the heat-treatment process was studied. It was difficult to calculate the intensity of the peaks of hydroxyl and —NH_2 asymmetric stretching vibrations because some overlaps were present between the two groups. However, the absorption peaks at about 3300 to 3500 cm^{-1} in both the fiber surface sizing and extracted sizing moved to higher wave numbers with increasing heat-treatment temperature; this indicated that the concentration of —NH_2 in the sizing decreased because —NH_2 reacted with other groups (Scheme 1).

The peak at 830 cm^{-1}, which was assigned to the vibration of the benzene ring, was selected to be the reference peak; its intensity was heavy and did not change during the reaction. The concentration of functional groups could be calculated by eq. (1):

$$c_x = \frac{I_x}{I_{830}} \tag{1}$$

where c_x is the concentration of functional group x, I_x is the peak intensity of x, and I_{830} is the peak intensity at 830 cm^{-1}.

The change in the concentration of epoxy groups in both the fiber surface sizing and extracted sizing with increasing heat-treatment temperature is shown



Scheme 2 Reaction of hydroxyl and epoxy groups.

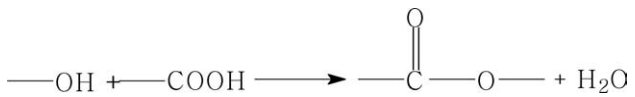
in Figure 4. The concentration of epoxy groups in both the fiber surface sizing and extracted sizing decreased with increasing heat-treatment temperature and was zero after heat treatment at 200°C because no peak at 915 cm^{-1} was found in the spectrum of the fiber surface sizing and extracted sizing. The concentration of epoxy groups in the extracted sizing was lower than that of the fiber surface sizing after treatment under the same conditions; this was because the rate of reaction between the carbon fibers and the fiber surface sizing (Scheme 2) was higher than the reaction rate of the fiber surface sizing system.

XPS analysis

The surface chemical properties of desized treated carbon fibers were studied by XPS technology. The C1s curve was fitted because the mainly variational groups were oxygenous functional groups. The curve-fitted C1s of the desized fiber of untreated sample is shown in Figure 1(b), and the curve-fitted C1s of the desized carbon fiber of the heat-treated samples at 150, 180, and 200°C is illustrated in Figure 5.

As shown in Table II, epoxy groups were found on the desized fibers of the untreated sample. This was because the carbon fibers were dried in the temperature range 120–150°C during the sizing process, and chemical bonds, which could not be wiped off by solvent, were generated because of the reaction between the epoxy groups in the fiber surface sizing and functional groups on the carbon fiber surface.

The content of peak 3 (—C—OH and C—O—C) on the desized fiber surface increased when the heat-treatment temperature rose to 180°C; this was due to the reaction between —C—OH (or $—NH_2$) and epoxy groups (including epoxy groups on the desized carbon fiber surface and in the fiber surface sizing). However, compared with the maximal value at 180°C, the content of peak 3 in the desized carbon fibers treated at 200°C decreased significantly. This was attributed to the esterification between —C—OH (286.1 eV) and —COOH (289.4 eV).



Scheme 3 Reaction of hydroxyl and carboxyl groups.

The epoxy group content of the desized carbon fibers after treatment at 150°C was higher than that of the desized untreated fibers; this illustrated that the epoxy groups in the fiber surface sizing reacted with the hydroxyl groups on the fiber surface, and the unreacted end of bisphenol A epoxy was left on the fiber surface and could not be extracted down by acetone. The content of epoxy groups in the desized carbon fibers further decreased after the carbon fibers were treated at 180°C because the residual epoxy groups reacted with other functional groups. As can be seen from the infrared spectrum analysis, no epoxy groups were found in either the fiber surface sizing or extracted sizing after treatment at 200°C; this illustrated that the functional group whose binding energy was about 286.6 eV and content was 14.43% on the desized carbon fiber surface was *C—O—C=O. The reaction between carbon fiber and fiber surface sizing during the composite manufacture was conducive to the enhancement of the carbon fiber/sizing interfacial adhesion and the improvement of the interfacial properties of composites.

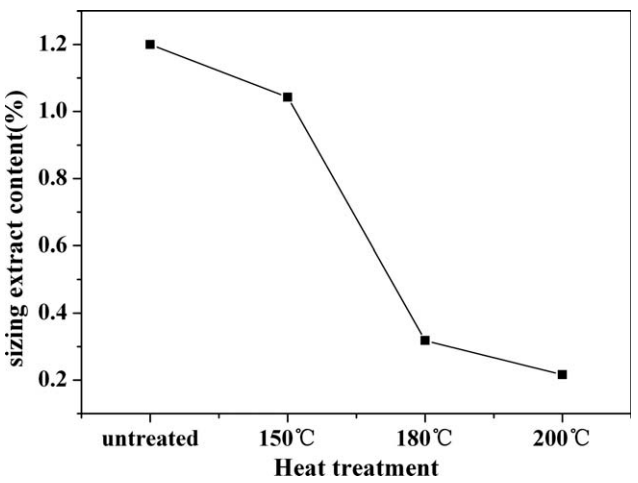


Figure 2 Change of the extraction percentage of sizing with increasing heat-treatment temperature.

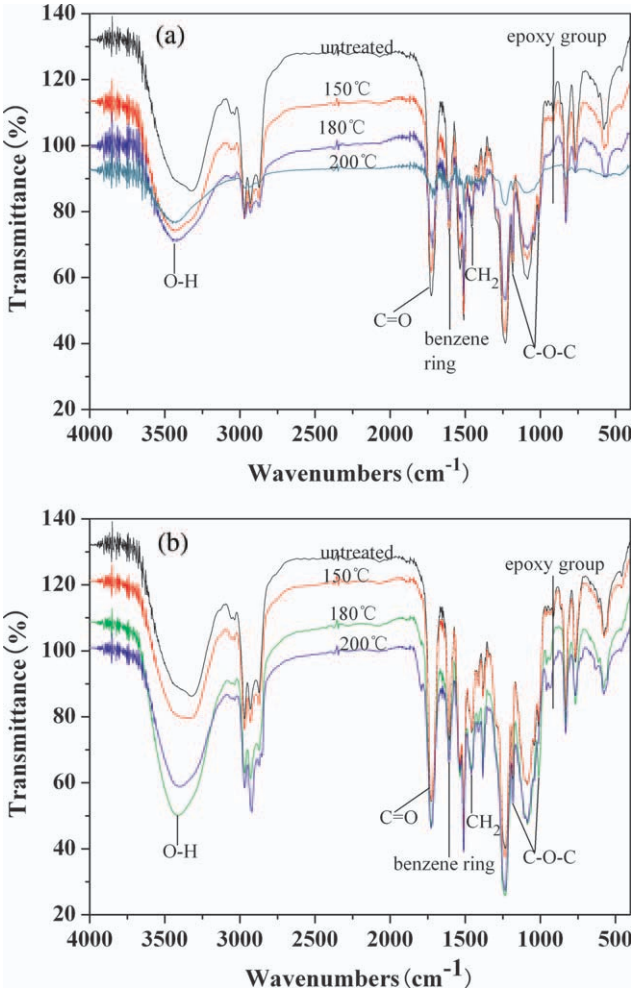


Figure 3 Chemical structures of T300B sizing under different heat-treatment temperatures: (a) fiber surface sizing and (b) extracted sizing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

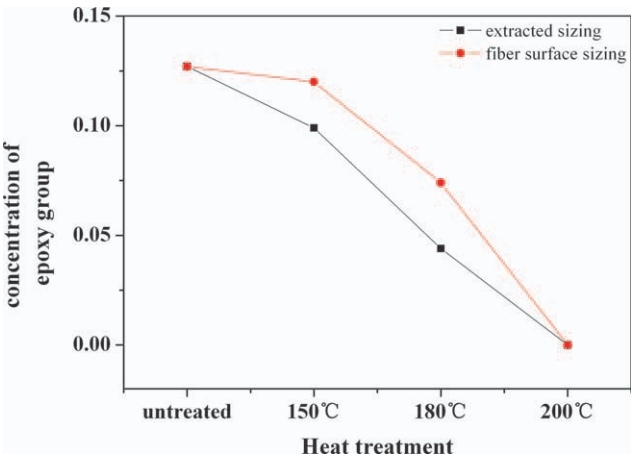


Figure 4 Change in the concentrations of epoxy group with increasing heat-treatment temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

A reaction of the functional groups between the carbon fiber surface and the fiber surface sizing and in the fiber surface sizing system occurred during heat treatment of the carbon fibers and fiber surface sizing. The main reactive functional groups were hydroxyl groups, amino groups, and epoxy groups. The concentration of epoxy groups in both the fiber

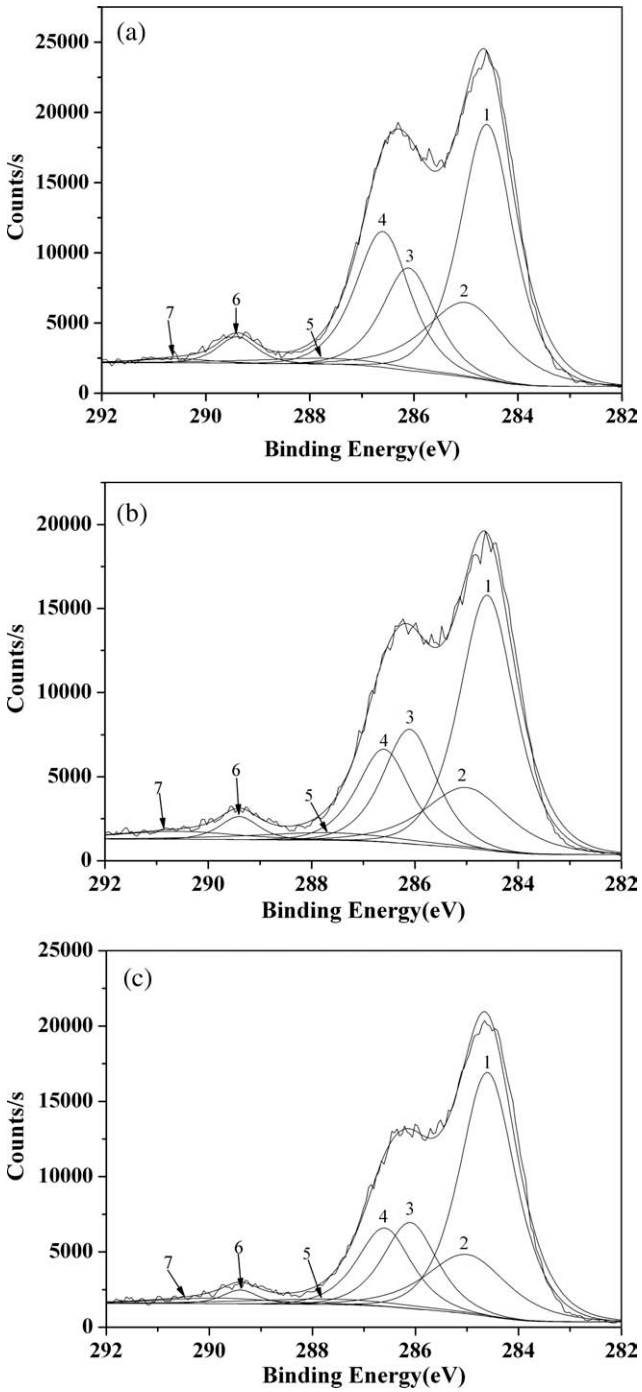


Figure 5 Curve-fitted C1s of desized T300B after heat treatment at different temperatures: (a) 150, (b) 180, and (c) 200°C.

TABLE II
C1s Peaks of the Desized T300B Carbon Fibers after Heat Treatment at Different Temperatures

	C1s peaks in different states BE (eV; area, %)							Activated carbon atoms (%)
Desized sample	Peak 1 (284.6)	Peak 2 (285.0)	Peak 3 (286.1)	Peak 4 (286.6)	Peak 5 (287.7)	Peak 6 (289.4)	Peak 7 (290.6)	
Untreated	39.88	20.08	13.52	15.10	5.32	3.00	3.09	40.03
150°C	39.73	17.40	15.59	21.20	2.33	2.94	0.80	42.87
180°C	42.78	15.20	18.33	14.74	3.34	2.68	2.88	42.02
200°C	46.70	16.44	15.73	14.43	2.90	1.64	2.15	36.86
Peak assignment	Reference	—C—C —C—H	—C—OH —C—O—C— C—NH_2	*C—O—C=O Epoxy groups	—C=O C=N	—COOH —COOR	$—COO^-$ π–π*	

surface sizing and extracted sizing decreased with increasing heat-treatment temperature and declined to zero after treatment at 200°C. The concentration of epoxy groups in the extracted sizing was lower than that of fiber surface sizing after treatment under the same conditions; this indicated that the rate of reaction between the carbon fibers and fiber surface sizing was higher than the reaction rate of the fiber surface sizing system. The contents of C—O bonds and activated carbon atoms on the surface of the desized carbon fibers were the highest when the heat-treatment temperature was 150°C; this illustrated the reaction between the carbon fibers and fiber surface sizing. An amino compound was found in the T300B fiber surface sizing, which could promote the generation of insoluble substances in acetone.

References

1. Rezaei, F.; Yunus, R.; Ibrahim, N. A. Mater Des 2009, 30, 260.
2. Seo, M. K.; Park, S. J. J Colloid Interface Sci 2009, 330, 237.
3. Xu, Z. W.; Chen, L.; Huang, Y. D.; Li, J. L.; Wu, X. Q.; Li, X. M.; Jiao, Y. A. Eur Polym 2008, 44, 494.
4. Dilsiz, N.; Wightman, J. P. Carbon 1999, 37, 1105.
5. Guan, R. B.; Yang, Y. G.; Zheng, J. T.; He, F. Fiber Compos 2002, 1, 23.
6. Drzal, L. T.; Rich, M. J.; Koening, F.; Lloyd, P. F. J Adhesion 1983, 16, 133.
7. Dilsiz, N.; Wightman, J. P. Carbon 1999, 37, 1105.
8. Drzal, L. T.; Sugiura, N.; Hook, D. Compos Interfaces 1997, 4, 337.
9. Paipetis, A.; Galiotis, C. Compos A 1996, 27, 755.
10. Chen, W. M.; Yu, Y. H.; Li, P.; Wang, C. Z.; Zhou, T. Y.; Yang, X. P. Compos Sci Technol 2007, 67, 2261.
11. Guo, H.; Huang, Y. D.; Liu, L.; Shi, X. H. Mater Des 2010, 31, 1186.
12. Zhang, R. L.; Huang, Y. D.; Liu, L.; Tang, Y. R.; Su, D.; Xu, L. W. Appl Surf Sci 2011, 257, 1840.
13. Cao, X.; Wen, Y. F.; Zhang, S. H.; Yang, Y. G. New Carbon Mater 2006, 4, 337.
14. Chen, W. M.; Yu, Y. H.; Li, P.; Wang, C. Z.; Zhou, T. Y.; Yang, X. P. Compos Sci Technol 2007, 67, 2261.
15. He, F.; Wang, M. Z. Carbon Fiber and Its Composites; Science Press: Beijing, 1995.