Improvement of Interfacial Adhesion Between PBO Fibers and Cyanate Ester Matrix

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ABSTRACT: Poly(p-phenylene benzobisoxazole) (PBO) fibers were activated by the horseradish peroxidases (HRP) and then treated by 3-Glycidoxypropyltrimethoxysilane (KH-560) to improve the wettability and the interfacial adhesion between PBO fibers and cyanate ester matrix. The chemical compositions of PBO fibers were characterized and analyzed by FTIR and XPS. Surface morphologies of PBO fibers were examined by SEM. The wettability of PBO fibers was evaluated by the dynamic contact angle analysis test. The mechanical properties were evaluated by tensile strength and interfacial shear strength, respectively. The results demonstrated that hydroxyl groups and epoxy groups were introduced onto the surface of PBO fibers during the treatments. These treatments can effectively improve the wettability and adhesion of PBO fibers. The surface free energy of PBO fibers was increased from 31.1 mN/m to 55.2 mN/m, and the interfacial adhesion between PBO fiber and cyanate ester resin was improved to 10.77 MPa. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40204.

INTRODUCTION

In recent decades, poly(p-phenylene benzobisoxazole) (PBO) fibers have been widely applied in many fields such as aerospace, military, and general industry, owing to their excellent properties, such as high modulus and strength, salient chemical and fire resistance, light weight and excellent toughness, etc.[1,2] Moreover, their low dielectric constant makes them an ideal reinforcing material in advanced wave-transparent composites.[3–6] However, the interfacial adhesion between PBO fibers and polymer matrix is very poor because of the smooth and chemical inactive surface of PBO fibers. Therefore, many efforts have been devoted to improve the surface wettability of PBO fibers and enhance the interfacial adhesion between PBO fibers and resin matrix.[7–11] Various techniques including plasma treatment,[9] acid treatment,[12] and coupling agent treatment[13] were employed to make the surface of fibers rough or introduce polar functional groups onto the surface of fibers. For example, Wang et al.[11] and Zhang et al.[14] studied the effects of plasma treatment on surface properties of PBO fiber. After treatment, polar groups were introduced onto the surface of fibers, the wettability and adhesion of fibers were enhanced and surface morphology of PBO fibers became more complicated. These results proved that the plasma treatment is an effective method to enhance the interfacial adhesion between PBO fibers and epoxy resin.[15]

But the apparatus of plasmas treatment was expensive, and acid treatment seriously etched the surface of PBO fibers. Coupling agent treatment has less etch on the surface of PBO fibers and this method is simple and facile. Moreover, treating PBO fiber with horseradish peroxidases (HRP) can effectively introduce hydroxyl groups,[16] which can be beneficial to the reaction of coupling agent. Therefore, in this article the treatment of PBO fiber was designed with two steps. The PBO fiber was firstly activated by HRP and then treated by coupling agent of 3-Glycidoxypropyltrimethoxysilane (KH-560).

Cyanate ester (CE) is one of high performance thermosetting resins for advanced composites, which has good properties such as low dielectric constant (2.8–3.2), dielectric loss (0.002–0.008), high heat resistance (Tg, 240–260 °C), low moisture absorption (<1.5%), small thermal expansion coefficient, excellent mechanical properties, and bonding properties.[17–19] Attributed to these excellent properties, CE has been widely applied in aerospace and defense industries, especially as an ideal potential wave-transparent material.

With the development of science and technology, the wave-transparent materials require not only low dielectric constant and dielectric loss over a wide frequency range but also high mechanical properties. So, it is necessary to improve the interfacial shear strength of fiber-resin systems which were used as wave-transparent materials. In this work, CE and PBO fibers
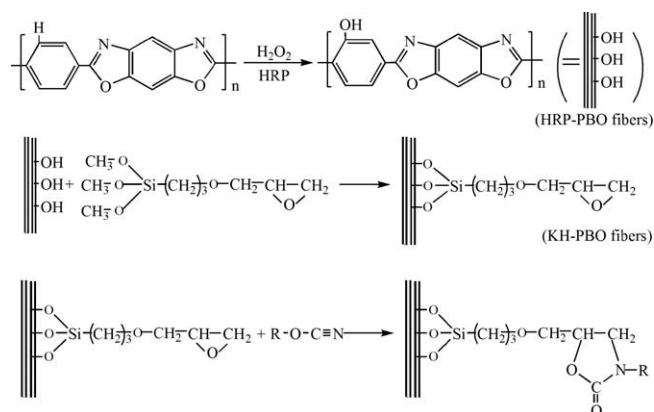
Figure 1. The schematic of treatment of PBO fibers and reaction between fiber and CE.

were chosen as the resin matrix and reinforce, respectively. The effects of different contents of KH-560 on the interfacial shear strength of the PBO fibers–CE system were investigated, and the mechanisms of the improved adhesion were discussed. This work will pave the way for the further research of advanced wave-transparent composites.

MATERIALS AND METHODS

Materials

PBO fibers were purchased from Toyobo Co. (Japan). Horseradish peroxidases (HRP) were supplied by Shanghai Crystal Pure Industrial Co. (Shanghai, China). Hydrogen peroxide and glycerol were bought from Xi'an Chemical Reagent Plant (Shaanxi, China). 3-Glycidoxypropyltrimethoxysilane (KH-560) was purchased from Jingzhou Fine Chemical Plant (Hubei, China). Acetone was bought from Tianjin Fuyu Fine Chemical Plant (Tianjin, China). 1,4-Dioxane was purchased from Tianjin Fuchen Chemical Reagent Plant (Tianjin, China). Phosphate buffer was supplied by Sinopharm Chemical Regent Co. (Shanghai, China). Bisphenol A type cyanate ester was supplied by Wuqiao Resin Factory (Jiangsu, China). All of the chemical reagents in this article were used as received without any further treatments.

Surface Modification of PBO Fibers

PBO Fibers Activated by Horseradish Peroxidases. PBO fibers were washed by acetone and distilled water for three times, respectively. And the fibers were then dried in a vacuum oven at 60°C for 12 h. The HRP activation of the fibers was carried out as follows.[16] The predetermined amount of dried PBO fiber immersed in the 20.0 mg HRP of phosphate buffer in 500 ml flask, and 100 ml 1,4-dioxane (pH = 7.0) was added into the flask, and stirred at 35°C in the presence of N_2 for 30 min. The different volumes of hydrogen peroxide (3.0 wt % aqueous solution), 4 ml, 3 ml, and 3 ml, were added dropwise into the mixture every 30 min. Then, the mixture was maintained at 40°C for 2 h. Finally, the fibers were pulled out, washed in acetone and distilled water for three times, and dried in a vacuum oven at 60°C for 12 h to obtain HRP-activated PBO fibers (HRP-PBO fibers, as shown in Figure 1).

PBO Fibers Modified by KH-560. The predetermined HRP-PBO fibers were immersed into different contents of KH-560

solutions (1.0 vol %, 2.0 vol %, 3.0 vol %, and 4.0 vol %) at 45°C for 24 h. Finally, the fibers were pulled out, washed, and dried as above HRP-PBO fibers to get KH-560-modified PBO fibers (KH-PBO fibers, as shown in Figure 1).

Characterization

Infrared Spectroscopy (FTIR). FTIR technique was employed to characterize the changes of chemical bonds on the surface of PBO fibers with a WQF-310 Fourier transform infrared spectrophotometer (the Second machine factory of Beijing, China).

Scanning Electron Microscopy (SEM). The surface morphology of PBO fibers was measured by SEM (Hitachi S-4800, Japan) with accelerating voltages of 10 kV. The fibers samples were adhered to an SEM mount with conductive adhesive and coated with a thin gold layer by sputter prior to capture a clear image of the treated surface.

Single Fiber Tensile Test and Pull-Out Test. Single fiber tensile strength was measured with WDW-20 model Electronic Universal Tester (Shanghai Hualon Test Instruments Co., China). The load cell, the gauge length, and the strain rate were 5 N, 50 mm, and 5 mm/min, respectively. The diameter of the fiber is about 12 μm. At least 30 samples were required for every group specimen.

Single fiber pull-out test was performed to evaluate the interfacial shear strength between fibers and resin matrix. Here, bisphenol A type cyanate ester was chosen as the resin. Small resin droplets were injected onto each fiber with a syringe and embedded the fibers. Then, the samples were cured at 180°C for 2 h and at 200°C for 2 h, then slowly cooled down to room temperature. After curing, single-filament pull-out tests were performed with a self-made apparatus which is shown in Figure 2.[20] The interfacial shear strength (IFSS) between PBO fibers and cyanate ester resin was calculated from the following equation[20]:
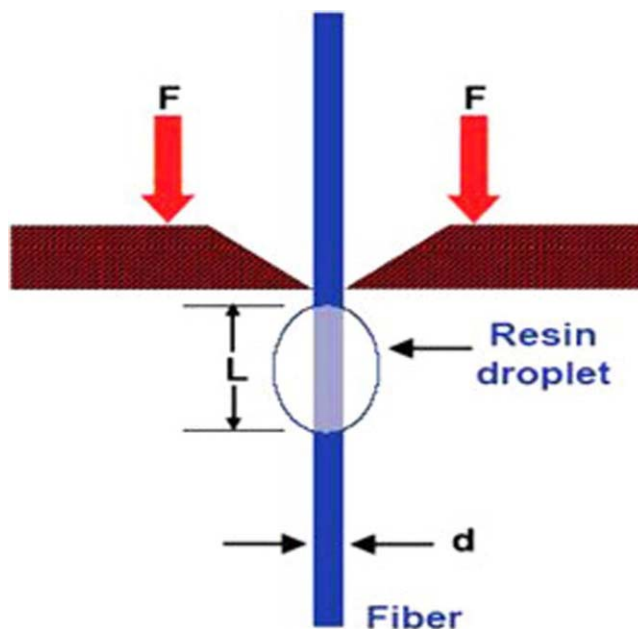

Figure 2. The schematic of single fiber pull-out test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
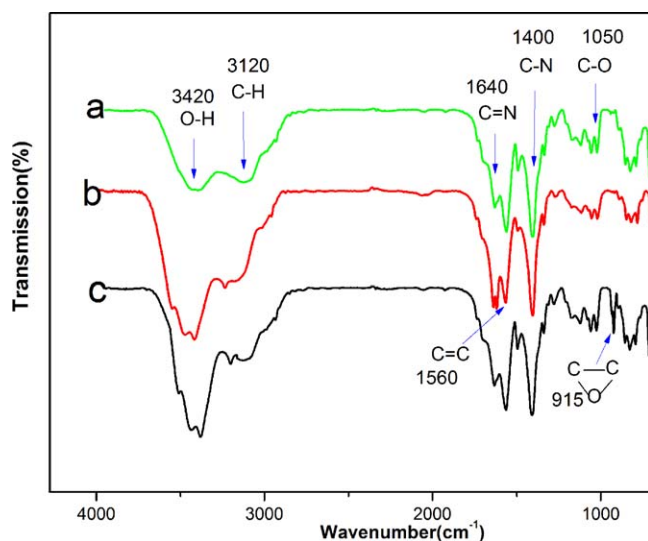
Figure 3. FTIR spectra of the PBO fibers: (a) original PBO fibers; (b) HRP-PBO fibers; (c) KH-PBO fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\tau = F/\pi DL \qquad (1)$$

where τ is the IFSS, F is the pull-out force; D and L are the fiber diameter and the embedded fiber length, respectively. At least 30 samples for each type were tested and the tested value was the average value of specimens.

Dynamic Contact Angle Analysis Test (DCAT). The dynamic contact angles and corresponding surface free energy of PBO fibers were studied by a dynamic contact angle analysis system (JY-82, China). The surface free energy of all samples was calculated from the following equations [eqs. (2) and (3)].[21]

$$\gamma_l(1 + \cos\theta) = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \qquad (2)$$

$$\gamma_{\text{total}} = \gamma_s^d + \gamma_s^p \qquad (3)$$

where θ is the dynamic contact angle, γ_l is the surface tension of the test liquid, γ_{total} is the total surface free energy of fiber,

and γ_s^p, γ_s^d are the polar and dispersive components of total surface free energy, respectively. In the present study, the deionized water and glycerol were chosen as the testing liquids and the surface tensions are 72.8 mN/m and 63.7 mN/m, respectively.

X-Ray Photoelectron Spectroscopy Analysis (XPS). XPS experiments were carried out on a PHI-5000C ESCA system (RBD Enterprises, USA) to analyze the elements (including C, N, O, and Si) on the surface of PBO fibers. The XPS was obtained using Al Kα (radioactive source 1486.6 photons) at a voltage of 15 kV and a power of 250 W. The pressure of vacuum chamber was better than 3.0×10^{-9} mbar.

RESULTS AND DISCUSSION

FTIR Spectra of the Fibers

Figure 3 shows the FTIR spectra of original PBO, HRP-PBO, and KH-PBO fibers. In original PBO fibers spectrum [Figure 3(a)], a strong and broad absorption peak at 3420 cm^{-1} was observed, which was due to the O–H stretching vibration. This O–H may be produced by incomplete ring-closure reaction in the synthesis of PBO fiber. The peak at 3120 cm^{-1} was attributed to the C–H stretching vibration of benzene. The other characteristic absorption peaks at 1640 cm^{-1} (C=N), 1560 cm^{-1} (skeletal vibrations from phenyl group), and 1050 cm^{-1} (C–O) accorded well with the structure of PBO fiber. The absorption at 1400 cm^{-1} may be attributed to C–N stretching vibration. Comparing Figure 3(a) with Figure 3(b), it can be seen that there was no obvious difference except that the absorption of the –OH (3400 cm^{-1}) in Figure 3(b) increased in intensity, which indicated that there was more hydroxyl groups introduced onto the PBO fibers surface. Furthermore, it also can be seen from Figure 3(c) that a new absorption band appeared at 915 cm^{-1}, which may be attributed to stretching vibration of epoxy group. This result proved that KH-560 has been grafted on the fibers surface.

SEM Analysis of the Fibers

Figure 4 shows the SEM micrographs of original PBO, HRP-PBO, and KH-PBO fibers. As can be seen from Figure 4, surface morphologies of the fibers became more complicated after being treated by HRP and KH-560. The surface of original PBO fibers
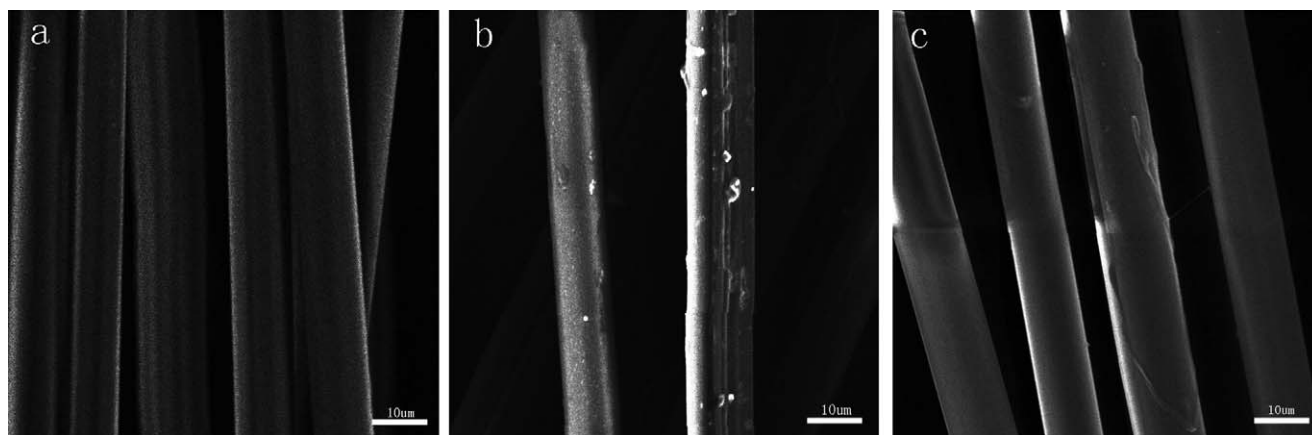

Figure 4. SEM analysis of the fibers: (a) original PBO fibers; (b) HRP-PBO fibers; (c) KH-PBO fibers.
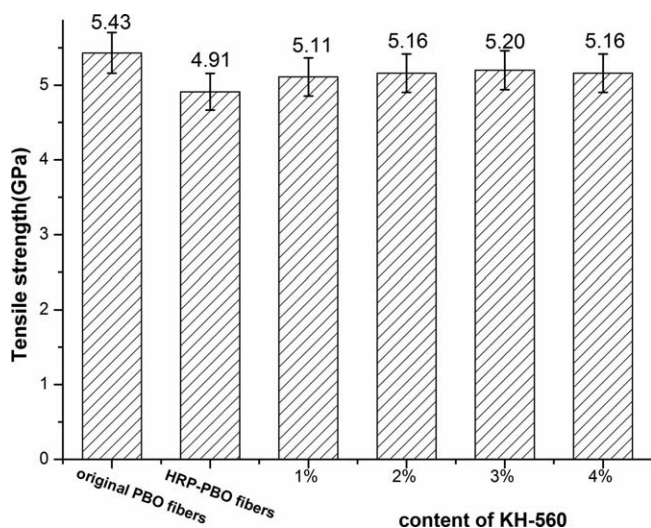
Figure 5. Tensile strength of different PBO fibers.

was smooth [Figure 4(a)], while the surface of HRP-PBO fiber became rough [Figure 4(b)], and the surface of KH-PBO fibers [Figure 4(c)] was smoother than that of HRP-PBO fibers but rougher than that of original PBO fibers. Moreover, during the experiment it was found that the HRP-PBO fibers were a little softer than the original PBO fibers. But after being treated by KH-560, PBO fibers became hard, suggesting the repair function of KH-560 to the corrosion of HRP.

Tensile Strength and Pull-out Strength of Single Fibers
Figure 5 depicts the tensile strengths of different PBO fibers. In Figure 5, the tensile strength of HRP-PBO fibers was 4.91 GPa which was a little less than that of the original PBO fibers. While the tensile strengths of KH-PBO fibers were higher than that of HRP-PBO fibers, which indicated KH-560 had the repair function agreed with the results of SEM.

Figure 6 shows the interfacial shear strengths of different PBO fibers. It can be seen from Figure 6 that the interfacial shear strength of HRP-PBO fibers was improved by 13.6%. Further-
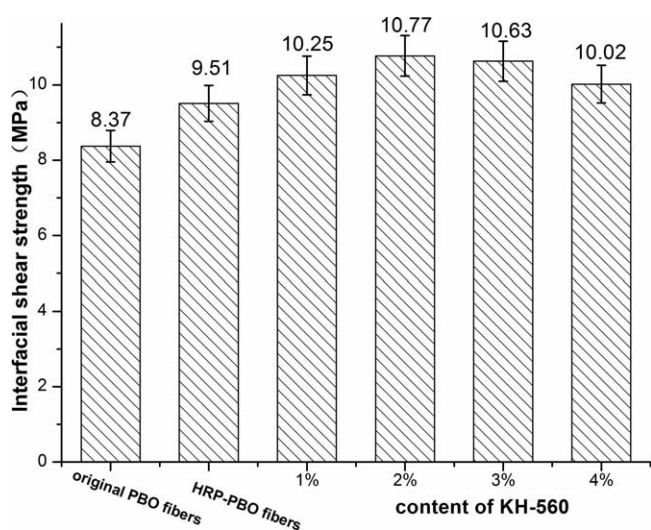

Figure 6. Interfacial shear strength of different PBO fibers.

Table I. Contact Angle (°) and the Surface Free Energy (mN/m) of PBO Fibers (20 °C)

Sample	Contact angle		The surface free energy		
	Water	Glycerol	γ_s^d	γ_s^p	γ_{total}
Original PBO fibers	85	90	1.5	29.6	31.1
KH-PBO fibers	50	52	7.4	47.8	55.2

The content of KH-560 which was used to treat PBO fibers was 2.0 vol %.

more, the interfacial shear strength of KH-PBO fibers was increased with the increasing content of KH-560. Especially, when the content of KH-560 was 2.0 vol %, the interfacial shear strength of KH-PBO fibers was much higher than that of HRP-PBO fibers and reached the maximum value of 10.77 MPa. However, when the content was more than 2.0 vol %, the interfacial shear strength of KH-PBO fibers was decreased. This phenomenon could be attributed to the special interface layer formed between fiber and CE resin. When the content of KH-560 was little (≤2.0 vol %), it may contribute to forming the monomolecular layer of KH-560 on the surface of PBO fiber, and the epoxy group of KH-560 in the interface layer could react with the CE resin resulting in chemical bonds connection between PBO fiber and CE resin,[22] as shown in Figure 1. However, when the content of KH-560 was excessive (>2.0 vol %), the excessive KH-560 absorbed on the surface of fibers depending on intermolecular forces which are weaker than chemical bonds, resulting in the decrease of the interfacial shear strength between PBO fiber and CE resin.[23,24]

Contact Angle and Surface Free Energy
Table I presents the contact angle and surface free energy of original PBO fibers and KH-PBO fibers. It can be seen from Table I, the original PBO fibers had a large contact angle of 85° in water, 90° in glycerol and a low surface free energy of 31.1 mN/m, while the contact angles of KH-PBO fibers in water and in glycerol decreased to 50° and 52°, respectively, suggesting that the wettability of PBO fibers was greatly improved after the treatment. Additionally, the surface free energy of KH-PBO fibers was 55.2 mN/m which was increased by 77.5% in contrast with original PBO fibers (31.1 mN/m). The improvement of the surface free energy was mainly attributed to the significant increase of the polar component,[23] because there were many

Table II. The Surface Elements of Different PBO Fiber Samples

Sample	Surface elemental composition (%)				Atomic ratio (%)	
	C	O	N	Si	O/C	N/C
Original PBO fibers	63.98	29.65	6.37	0	46.34	9.96
HRP-PBO fibers	61.66	30.52	7.82	0	49.50	12.68
KH-PBO fibers	55.54	30.52	7.60	6.34	54.95	13.68

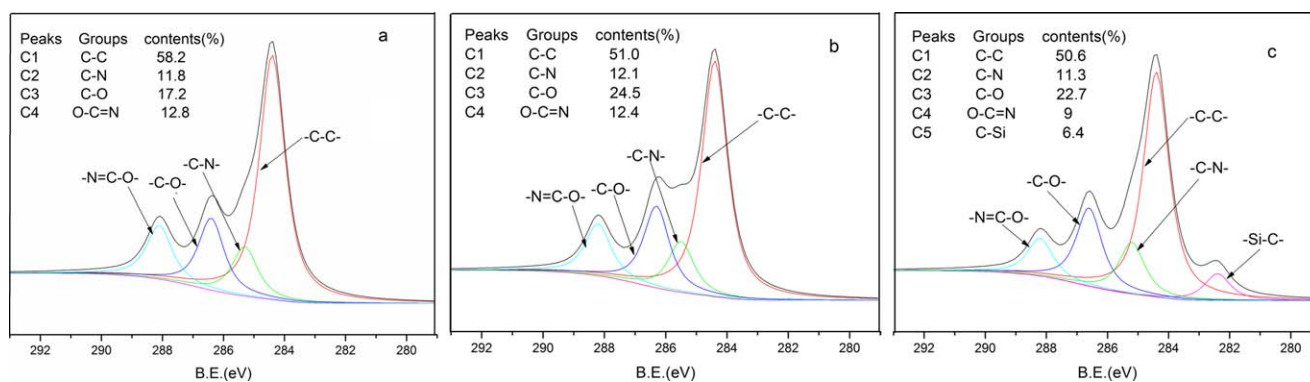The content of KH-560 which was used to treat PBO fibers was 2.0 vol %.

Figure 7. XPS spectra of PBO fibers: (a) original PBO fibers; (b) HRP-PBO fibers; (c) KH-PBO fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

epoxy groups and hydroxyl groups introduced onto the PBO fibers surface. The increase of wettability and the introduction of polar groups can be beneficial to increase the adhesion between PBO fiber and CE resin, which was in very good agreement with the results of pull-out strength of single fiber.

XPS Analysis

Table II lists the surface elemental compositions of original PBO, HRP-PBO, and KH-PBO fibers. It can be seen from Table II that the original PBO fibers surface contained small amounts of oxygen atom and high concentration of carbon atom, which was in accordance with its molecular structure.[25] After HRP activated and KH-560 treated, the atomic ratios of oxygen-to-carbon atoms (O/C) of PBO fibers increased from original 46.34% to HRP-PBO fibers' 49.50% and to KH-PBO fibers' 54.95%, respectively, which revealed HRP has introduced hydroxyl groups on the PBO fibers' surface and KH-560 was grafted onto PBO fibers' surface. It can also be seen that the Si elements have appeared on the surface of KH-PBO fibers and its concentration was 6.34%, which further indicated that KH-560 was grafted onto the PBO fiber surface.

The detailed high-resolution C1s spectrum of the original PBO fibers, HRP-PBO fibers, and KH-PBO fibers are shown in Figure 7. The C1s spectra were decomposed into four fitting peaks: C1 at 284.5 eV (C–C), C2 at 285.3 eV (C–N), C3 at 286.4 eV (C–O) and C4 at 288.3 eV (O–C=N), respectively.[26] Moreover, it obvious changes were found in the C1 and C3 peaks. The C–C content and C–O content of original PBO fibers were 58.2% and 17.2% [Figure 7(a)], while in HRP-PBO fibers the C–C content was decreased to 51.0% and C–O content was increased to 24.5% [Figure 7(b)], suggesting –OH was introduced onto PBO fiber surface. And a new peak of C5 in the KH-PBO fibers [Figure 7(c)] was generated at a position of lower binding energy of 282.4 eV, which may be assigned to C-Si.[27] The results indicated that HRP and KH-560 have successfully treated PBO fibers and made many active functional groups appear on the surface of the PBO fibers.

CONCLUSIONS

Horseradish peroxidases and KH-560 were used successively to treat PBO fibers. And when the content of KH-560 was 2.0 vol %,

the KH-PBO fibers exhibited excellent mechanical properties. The interfacial shear strength of PBO fibers with CE resin was increased from 8.37 MPa to 10.77 MPa. DCAT results showed that contact angle of PBO fiber in water was decreased from 85° to 50° and the surface free energy of PBO fiber was increased from 31.1 mN/m to 55.2 mN/m, which suggested the wettability of the PBO fibers was improved evidently. It may be concluded that PBO fibers treated with horseradish peroxidases and KH-560 successively could effectively improve the wettability and adhesion of PBO fibers.

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