Influence of Oxygen Plasma Treatment on Interfacial Properties of Poly(*p*-phenylene benzobisoxazole) Fiber-reinforced Poly(phthalazinone ether sulfone ketone) Composite

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ABSTRACT: The influence of oxygen plasma treatment on both surface properties of poly(*p*-phenylene benzobisoxazole) (PBO) fibers and interfacial properties of PBO fiber reinforced poly(phthalazinone ether sulfone ketone) (PPESK) composite were investigated. Surface chemical composition, surface roughness, and surface morphologies of PBO fibers were analyzed by X-ray photoelectron spectroscopy (XPS), Atomic force microscopy (AFM), and scanning electron microscopy (SEM), respectively. Surface free energy of the fibers was characterized by dynamic contact angle analysis (DCAA). The interlaminar shear strength (ILSS) and water absorption of PBO fiber-reinforced PPESK composite were measured. Fracture mechanisms of the composite were examined by SEM. The results indicated that oxygen plasma treatment significantly improved the interfacial adhesion of PBO fiber-reinforced PPESK composite by introducing some polar or oxygen-containing groups to PBO fiber surfaces and by fiber surface roughening.
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Key words: fibers; composites; surfaces; interfaces; adhesion

INTRODUCTION

The rigid rod polymeric fiber poly(*p*-phenylene benzobisoxazole) (PBO) has been of great interest for researchers over the last decade. It is considered to be the super organic fiber because of exceptionally high specific strength and modulus, excellent thermal and oxidative stability, chemical resistance, cut and abrasion resistance, flame retardance, and long-term retention of these properties at elevated temperatures.[1–6] Although PBO fiber provides great potential applications as reinforcements for high performance composites in aeronautical and astronautical applications, the interfacial adhesion between PBO fiber and polymer matrix is poor because of the relatively smooth and chemically inactive fiber surface.[7–9] Therefore, surface modification of PBO fiber is of great importance in the field of composites application. Significant research efforts have been directed toward the modification of PBO fiber surfaces.[10–12] It was reported that plasma treatment is an effective method to modify the chemical and physical structures of PBO fiber surface without influencing the bulk properties of the fibers. However, the effects of oxygen plasma treatment on interfacial properties of PBO fiber-reinforced composite have been scarcely reported in the literature.

Traditional fiber-reinforced composites are based on reinforcing fibers combined with thermosetting resins as matrix materials. This despite distinct design and toughness limitation is inherent to the thermosetting resins.[13] Because of excellent thermal resistance property, high toughness and elongation, environmentally and economically advantages, thermoplastics have been widely used as matrix resin in fiber-reinforced composites. Poly(phthalazinone ether sulfone ketone) (PPESK) is a kind of novel thermoplastic that shows excellent thermal resistance property and good solubility. The glass transition temperature of PPESK is 284°C. It can be dissolved in usual solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and chloroform. Therefore, fiber-reinforced PPESK composite can be prepared by solution impregnating technique.[14]

This study is focused on the influence of oxygen plasma treatment on both surface properties of PBO fibers and interfacial properties of PBO fiber-reinforced PPESK composite. Special emphasis is

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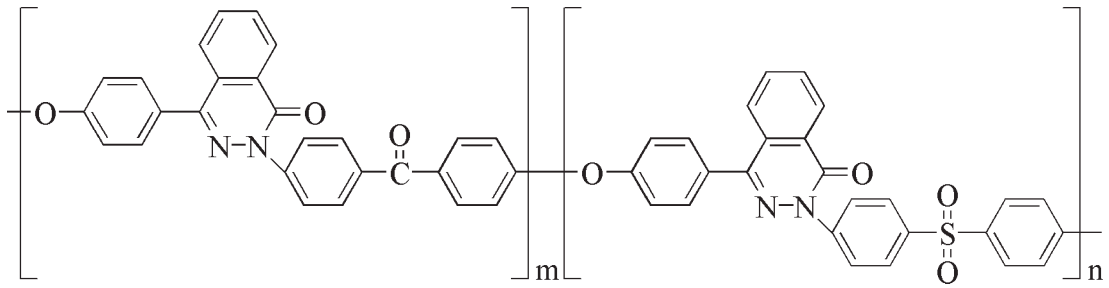

Figure 1 Chemical structure of PPESK resin.

put on characterization of improved interfacial adhesion between PBO fiber and PPESK matrix. Corresponding changes in surface chemical composition, surface roughness, and surface morphologies of PBO fibers were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and scanning electron microscopy (SEM), respectively. Surface free energy of the fibers was analyzed by dynamic contact angle analysis (DCAA). The interlaminar shear strength (ILSS) and water absorption of PBO fiber-reinforced PPESK composite were measured. Fracture mechanisms of the composite were examined by SEM.

EXPERIMENTAL

Materials

PBO fiber was received as high modulus (HM) yarn from Toyobo Co. Ltd., Japan. The fiber was washed subsequently with acetone and distilled water at room temperature. Each step took about 24 h to remove surface sizing or contaminants. The fiber samples were then dried at 100°C in a vacuum oven for 3 h prior to oxygen plasma treatment.

PPESK resin was supplied by Dalian Polymer New Material Co. Ltd., China. The characteristic viscosity is 0.53. Chemical structure of PPESK resin is shown in Figure 1.

Plasma treatment

The plasma treatment was conducted in an inductive coupling radio frequency (13.56 MHz) plasma reactor with a power source of 500 W. The treatment system includes a vacuum chamber, three mass flow controllers, a pressure gauge, a pumping system, and a radio source. Oxygen was fed into the vacuum chamber at a flow rate of about 30–50 SCCM. The operation pressure was set at 30 Pa. PBO fibers were rolled on a glass frame and treated by oxygen plasma for 5 and 10 min, under a power of 200 W.

Composite preparation

PPESK resin was dissolved in DMAc solvent forming a solution with concentration of about 13 wt %, continuous PBO fiber was then impregnated with the low viscosity PPESK/DMAc solution by wet winding process, after removing the solvent (120°C for 1 h in an oven, 175°C for 3 h in a vacuum oven), PBO fiber-reinforced PPESK composite was prepared by compression molding technique at 385°C.

XPS

Surface chemical composition of PBO fibers were analyzed by XPS (ESCALAB 250, Thermo). The XPS spectra were obtained using Al Ka ($h\nu = 1486.6$ eV) monochromated X-ray source with a voltage of 15 kV and a power of 250 W. The XPS measurements were performed at an operating vacuum better than 3.0×10^{-9} mbar. Spectra were acquired at a take-off angle of 90° relatively to the sample surface. The pass energy and energy step were 20 eV and 0.05 eV, respectively. Charge neutralization was used.

AFM

Surface roughness and surface morphologies of PBO fibers were characterized by AFM (PicoScan™ 2500, MI). Two or three PBO filaments were fastened to a steel sample mount. A tapping mode was used to scan the fiber surface. AFM images of PBO fibers were obtained with a scan area of 4 μm×4 μm. Surface roughness of PBO fibers were calculated from eqs. (1) and (2) by the instrument software:

$$R_q = \sqrt{\frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(z_{ij} - z_{av}\right)^2} \quad (1)$$

$$R_a = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left|z_{ij} - z_{cp}\right| \quad (2)$$

where R_q is root mean square (RMS) roughness, R_a is arithmetic mean roughness, N is the number of data points in the image, i and j are pixel locations

on the AFM image, z_{ij} is the height value at i and j locations, z_{av} is the average height value within the given area, and z_{cp} is the height value from the center plane.[15]

SEM

Surface morphologies of untreated and oxygen plasma-treated PBO fibers were examined by SEM (QUANTA 200, FEI). The fiber samples were adhered to a SEM mount with conductive adhesive. To examine fracture mechanisms of PBO fiber-reinforced PPESK composite and to investigate the effect of oxygen plasma treatment on interfacial adhesion between the fiber and matrix, surface morphologies of the fractured composite were still observed.

DCAA

Surface free energy of PBO fibers were measured by a dynamic contact angle analysis system (DCA-322, Thermo). Fiber surface free energy, which can be divided into two components: dispersive and polar, were derived from eqs. (3) and (4):

$$\gamma_l(1+\cos\theta) = 2\cdot\sqrt{\gamma_s^p\,\gamma_l^p} + 2\cdot\sqrt{\gamma_s^d\,\gamma_l^d} \tag{3}$$

$$\gamma_{\text{Total}} = \gamma_s^p + \gamma_s^d \tag{4}$$

where θ stands for the dynamic contact angle between fiber and the testing liquids, γ_l is surface tension of the testing liquid, γ_{Total} is total surface free energy of the fiber, γ_s^p and γ_s^d are the polar component and the dispersive component of the total surface free energy.[16]

The testing liquids used in the measurement were water (polar solvent) and diiodomethane (nonpolar solvent), their surface tension were 72.3 mN/m and 50.8 mN/m, respectively.

ILSS

Interfacial adhesion of PBO fiber-reinforced PPESK composite were evaluated by ILSS. The ILSS of the composites were measured using short beam shear tests according to ASTM D 2344. The tests were performed on a Shimadzu universal testing machine with a constant cross head speed of 2 mm/min and a span to thickness ratio of 5. Specimen dimensions were nominally $25 \times 6 \times 2$ mm^3. The tests were carried out at 20°C and 50% relative humidity. The ILSS was calculated from the following equation:

$$\tau = \frac{3P_b}{4\,b\cdot h} \tag{5}$$

where τ stands for the ILSS, P_b is the maximum load, b and h are the width and the thickness of the specimen. All of the ILSS results were taken as the average value of more than five successful measurements.

Water absorption

Water absorption behaviors of PBO fiber-reinforced PPESK composite were studied to evaluate the influence of oxygen plasma treatment on interfacial adhesion of the composite. The experiment was carried out according to the ASTM D-570 method. Percentage of water absorption can be calculated to the nearest 0.01% as follows:

$$\text{water absorption, }\% = \frac{m_w - m_c}{m_c}\times 100 \tag{6}$$

where m_w and m_c stand for the wet weight and the conditioned weight of the composite specimens, respectively.

RESULTS AND DISCUSSION

Surface chemical composition of PBO fibers

Surface chemical structure profoundly affects the surface free energy, which influences the wettability and the reactivity, and consequently, the interfacial properties of the fibers.[17] XPS analysis was used to characterize surface chemical composition of PBO fibers.

The surface chemical composition of untreated and oxygen plasma-treated PBO fibers is given in Table I. It was found that the carbon concentration declined sharply after oxygen plasma treatment. Oxygen concentration and the ratio of oxygen to carbon atoms increased from 17.5% and 0.22 to 29.1% and 0.44, respectively, after oxygen plasma treatment for 5 min. However, these two parameters kept increasing up to 31.8% and 0.50 after oxygen plasma treatment for 10 min.[18] It is likely that the oxygen plasma treatment introduced some polar or oxygen-containing groups to PBO fiber surface. However, the nitrogen concentration and the ratio of nitrogen to carbon atoms on PBO fiber surface experienced little change after oxygen plasma treatment. This

TABLE I
Surface Chemical Composition of PBO Fibers

Samples	Relative concentration of elements (%)				
	C	O	N	O/C	N/C
Untreated	78.6	17.5	3.7	0.22	0.05
Plasma treated for 5 min	66.5	29.1	4.4	0.44	0.07
Plasma treated for 10 min	64.1	31.8	4.1	0.50	0.06

TABLE II
Surface Roughness R_a and R_q of PBO Fibers

Samples	R_a (nm)	R_q (nm)
Untreated	164.8	595.9
Plasma treated for 5 min	177.0	717.5
Plasma treated for 10 min	182.1	596.2

may be explained that the oxygen plasma treatment could not introduce nitrogen element to the fiber surface.

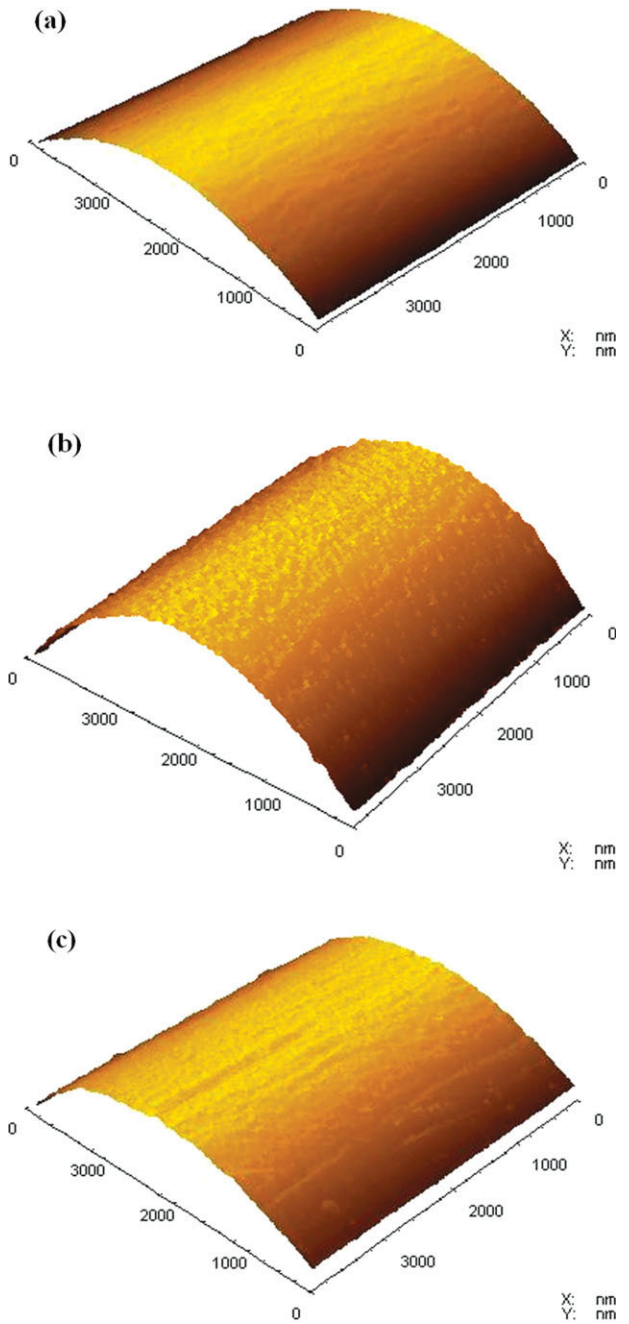

Figure 2 AFM images of PBO fibers (a) untreated, (b) plasma treated for 5 min, and (c) plasma treated for 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

Surface roughness and surface morphologies of PBO fibers

Surface roughness of PBO fibers was analyzed by AFM with the instrument software. The surface roughness R_a and R_q of untreated and oxygen plasma-treated PBO fibers are shown in Table II. For the untreated PBO fibers, the R_a and R_q were 164.8 nm and 595.9 nm, respectively.[18] However, after

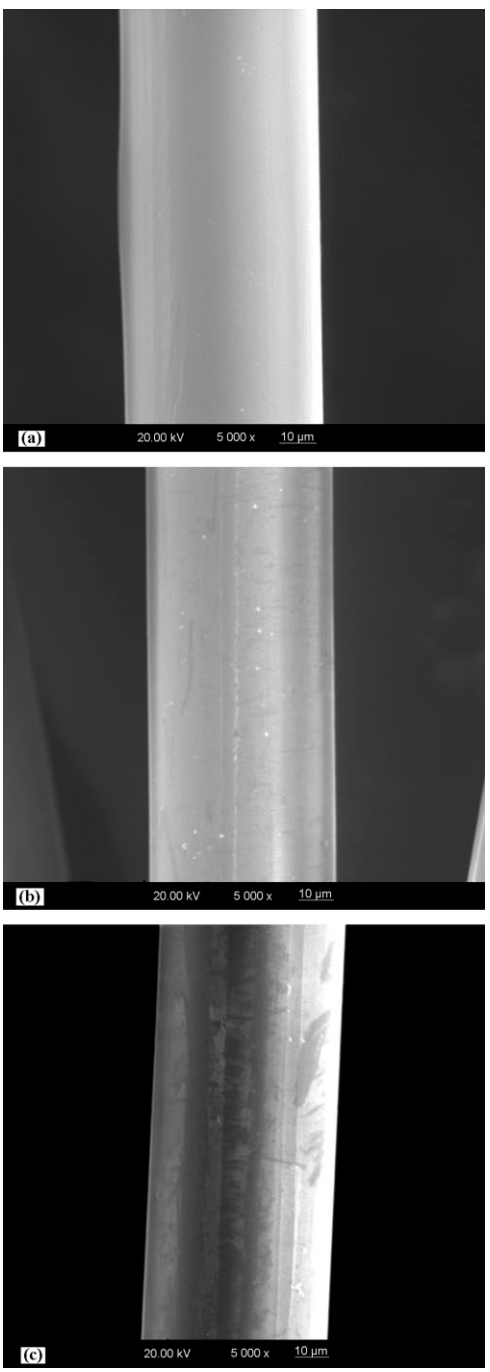

Figure 3 SEM images of PBO fibers (a) untreated, (b) plasma treated for 5 min, and (c) plasma treated for 10 min.

TABLE III
The Contact Angles (°) and Surface Free Energy (mN/m) of PBO Fibers

Samples	Water	Diiodomethane	γ^p	γ^d	γ_{Total}
Untreated	76.6 (2.5)	39.0 (1.7)	5.5	40.1	45.6
Plasma treated for 5 min	33.9 (1.6)	48.6 (0.9)	30.7	35.1	65.8
Plasma treated for 10 min	31.5 (1.2)	49.2 (1.8)	32.1	34.7	66.8

Standard deviations are in parentheses.

oxygen plasma treatment for 10 min, the R_a of PBO fibers increased to 182.1 nm, and it kept increasing with the duration of the plasma treatment. The R_q of PBO fibers experienced little change after oxygen plasma treatment for 10 min. It seemed that the surface roughness of PBO fibers was significantly increased by the oxygen plasma treatment.

Surface morphologies of untreated and oxygen plasma-treated PBO fibers are illustrated in Figures 2 and 3. It was found that the untreated PBO fiber had a smooth but streaked surface [Figs. 2(a) and 3(a)].[18] However, the fiber surfaces showed many notches [Fig. 2(b)] and spots [Fig. 3(b)] after oxygen plasma treatment for 5 min. While after oxygen plasma treatment for 10 min, many obvious streak flaws [Fig. 2(c)] and grooves [Fig. 3(c)] were presented on the fiber surfaces.[18] The results indicated that PBO fiber surfaces were notably roughened by the oxygen plasma treatment.

Surface wettability

Both surface free energy and contact angles were measured to evaluate the effect of oxygen plasma treatment on surface wettability of PBO fibers. Generally, the higher the surface free energy and the smaller the contact angles of water, the better the surface wettability of the fibers.[19]

The contact angles and surface free energy of untreated and oxygen plasma treated PBO fibers are shown in Table III. The contact angles of water, the polar component and the dispersive component of surface free energy on the untreated PBO fibers were 76.6°, 5.5 mN/m, and 40.1 mN/m, respectively, the total surface free energy were 45.6 mN/m.[18] However, after oxygen plasma treatment for 10 min, the contact angles of water on PBO fibers decreased to 31.5°, the polar component and the total surface free energy increased to 32.1 mN/m and 66.8 mN/m, while the dispersive component reduced to 34.7 mN/m. This may be explained that the oxygen plasma treatment introduced some polar or oxygen-containing groups and produced some new contact sites on PBO fiber surfaces because of chemical reactions and plasma etching. The newly formed polar groups and contact sites may increase chemical linkage and physical adsorption between fibers and the testing liquids, which appeared to result in an increase in surface free energy of the fibers. This outcome correlated well with the XPS and AFM results and certainly favored the wettability of the fibers in impregnation.

Interfacial adhesion

The interfacial adhesion between PBO fiber and PPESK resin was evaluated by ILSS and water absorption. The effects of oxygen plasma treatment on ILSS and water absorption of PBO fiber-reinforced PPESK composite are shown in Table IV. It was found that the ILSS and water absorption of the untreated composite were 32.7 MPa and 0.44%, respectively. However, after oxygen plasma treatment for 10 min, the ILSS of the composite increased to 42.6 MPa with an increment of about 30%, while the water absorption of the composite declined to 0.34%. In addition, the ILSS of the composite kept increasing and the water absorption of the composite kept degrading with the duration of the plasma treatment. These results suggest that oxygen plasma treatment significantly improved the interfacial adhesion of PBO fiber-reinforced PPESK composite by introducing some polar groups to PBO fiber surface and by fiber surface roughening, as already shown by XPS analysis (Table I) and SEM (Fig. 3) results. The improved interfacial adhesion between the fiber and matrix can effectively prevent water transporting into the composite.[20,21]

TABLE IV
The ILSS and Water Absorption of PBO Fiber Reinforced PPESK Composite

Samples	ILSS (MPa)	Water absorption (%)
Untreated	32.7 (0.7)	0.44
Plasma treated for 5 min	40.9 (1.8)	0.37
Plasma treated for 10 min	42.6 (3.2)	0.34

Standard deviations are in parentheses.

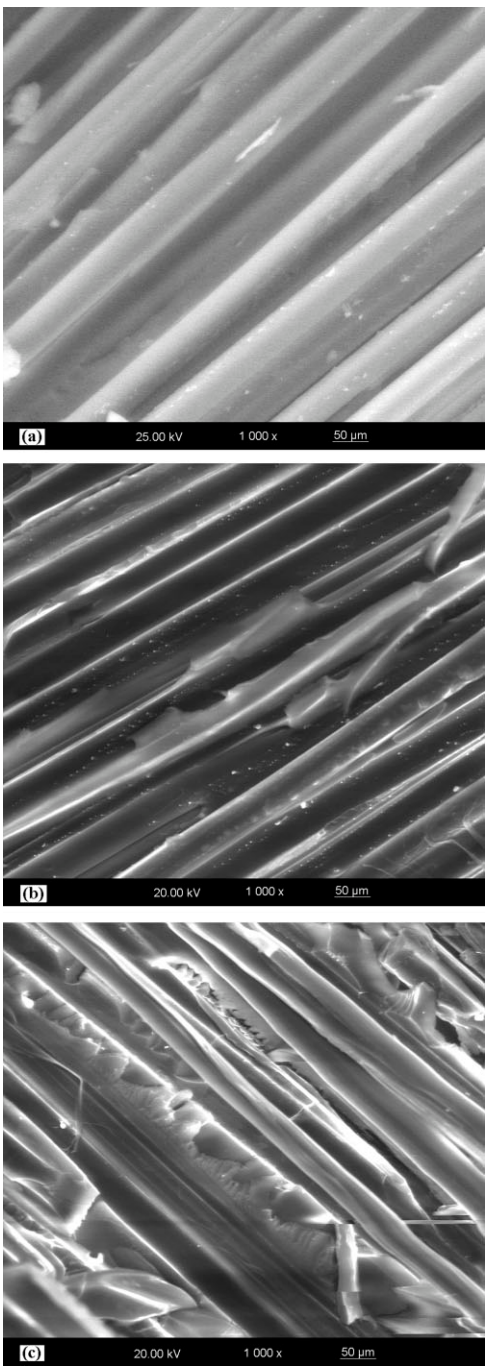

Figure 4 Fractured SEM images of PBO fiber-reinforced PPESK composite (a) untreated, (b) plasma treated for 5 min, and (c) plasma treated for 10 min.

Fracture mechanisms of the composite

The fracture mechanisms of PBO fiber-reinforced PPESK composite were investigated by SEM. Fractured SEM images of PBO fiber-reinforced PPESK composite are shown in Figure 4. It is obvious that in Figure 4(a), the fiber surfaces were smooth with little resin adhered to them, the failure location was the interface between PBO fiber and PPESK resin. However, as we can see in Figures 4(b) and (c), a large amount of matrices were tightly adhered to the fiber surfaces, the failure location shifted from the interface to matrix. The results showed that the interfacial adhesion of the untreated PBO fiber-reinforced PPESK composite was poor, the primary failure mode was interface failure; while the interfacial adhesion of the oxygen plasma-treated PBO fiber-reinforced PPESK composite was pretty good, the primary failure mode was matrix fracture. It suggests that the interfacial adhesion of PBO fiber-reinforced PPESK composite was largely improved by oxygen plasma treatment.

CONCLUSIONS

The influence of oxygen plasma treatment on both surface properties of PBO fibers and interfacial properties of PBO fiber-reinforced PPESK composite were investigated. XPS analysis suggested that oxygen plasma treatment introduced some polar or oxygen-containing groups to PBO fiber surfaces. AFM and SEM images of PBO fibers showed that the fiber surfaces were notably roughened by oxygen plasma treatment. DCAA results indicated that oxygen plasma treatment significantly enhanced surface free energy of PBO fibers. The ILSS and water absorption measurements of PBO fiber-reinforced PPESK composite indicated that the interfacial adhesion of the composite was largely improved by oxygen plasma treatment. The improved interfacial adhesion between the fiber and matrix can effectively prevent water transporting into the composite. Fractured SEM images of PBO fiber-reinforced PPESK composite showed that the interfacial adhesion of oxygen plasma-treated PBO fiber-reinforced PPESK composite was better than the untreated counterpart, the primary failure modes were matrix fracture, and interface failure, respectively.

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