

Influence of the Coupling Agent on the Mechanical Properties of SiC_f/Poly(phenylene benzobisoxazole) Composites

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ABSTRACT: Poly(phenylene benzobisoxazole) (PBO) was first used as matrix to fabricate the two-dimensional SiC_f/PBO composites by a lamination method. Different amounts of coupling agent were introduced to improve the bonding between silicon carbide (SiC) fibers and the PBO matrix during the fabrication of the SiC_f/PBO composites. The surface structure and composition of the as-received PBO and PBO treated with the coupling agent were analyzed, and the morphology and flexural strength of the composites were characterized. The Fourier transform infrared analysis indicated that the hydroxyl groups from the coupling agent were successfully introduced to PBO. The flexural strength of the composites increased at first with increasing content of the coupling agent but decreased with excessive addition of the coupling agent. The flexural strength of the composites was improved from 15 to 89 MPa. The test results suggested that the interaction between the SiC fiber and the treated PBO with the coupling agent was intensified.

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INTRODUCTION

Polymer matrix composites have been the focus of much research attention because of their favorable properties, including a light mass and high strength–weight ratio. Poly(phenylene benzobisoxazole) (PBO) fibers exhibit excellent physical and mechanical properties and a superior tensile strength (5.8 GPa) and modulus (280 GPa) compared to other organic fibers because of their unique extended, rigid rodlike configuration. The chemical structure of PBO is shown in Figure 1. Consequently, PBO-based materials exhibit a good toughness, good chemical and flame resistance, and outstanding thermal stability;^{1–5} their decomposition temperature can reach 650°C. The latter property of PBO makes it a material of choice for high-temperature applications. At the same time, PBO can be synthesized in poly(phosphoric acid) with a high viscosity, can flow at a suitable temperature, and is easy to form. So it has superiority as a matrix compared with other resin matrices. Because of its excellent properties, PBO has been widely applied in aerospace, military industries, and sporting goods industries.^{6–9}

Silicon carbide (SiC) fibers have been used as reinforcements in high-temperature composites because of their excellent thermal resistance, high tensile strength, and high oxidation resistance.^{10,11}

Because of the aforementioned advantages, SiC_f/PBO composites have a lot of attractive potential in comparison with other composites. This composite has both the high thermal resistance of ceramic and the high fracture toughness and low density of polymer materials; therefore, the composite can be used in high-temperature and high-strength applications, such as in lightweight armor and military apparatus. However, data are rare on the preparation of SiC_f/PBO composites. Almost all researchers have focused on PBO fiber-reinforced composites. However, the poor interfacial adhesion between the PBO fiber and matrix because of the relatively smooth and chemically inactive PBO fibers prevents many of their applications. So, a great effort has been made to research surface modification techniques of PBO, including plasma modification,^{12–14} chemical modification,¹⁵ copolymerization modification,^{16–18} γ -ray irradiation modification,¹⁹ coupling agent modification,²⁰ and modification by a combination of several techniques. In recent research, carbon nanotubes, nano-TiO₂, polyhedral oligomeric silsesquioxanes, and graphene oxide have also been used to modify PBO fibers;^{21–24} this demonstrated that the grafting of these materials could increase the interfacial properties of the PBO-fiber-reinforced composites.

In this study, a different kind of composite was prepared. PBO was used as a matrix to prepare SiC_f/PBO composites, SiC fibers were used as the enforcement phase, and we aimed to

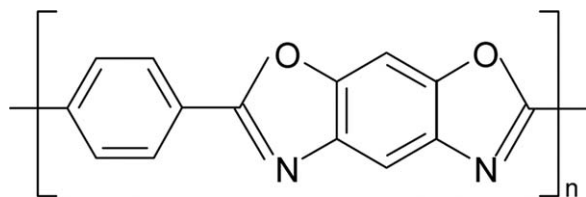


Figure 1. Structure of PBO.

investigate the effect of a coupling agent of the PBO matrix on the flexural strength of the composites. The chemical structures of the untreated and treated PBO were characterized by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) was used to study the fracture surface morphologies of the composites. The flexural strength of the composites was also investigated.

EXPERIMENTAL

Materials and Sample Preparation

SiC fiber fabric was provided by the National University of Defense Technology (China). The volume fraction of the fabric was 40%, and the density of the SiC fiber was 2.54 g/cm³. A silane coupling agent of γ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH560) was provided by Nanjing Shuang Chemical Group Co, Ltd. (China). PBO was synthesized in our laboratory, and the density of PBO was 1.54 g/cm³.

SiC-fiber-woven fabrics were placed in a vacuum furnace for desizing. Then, the SiC fiber woven fabrics were soaked in acetone at room temperature for 30 min and dried at 60°C. PBO was synthesized according to the process of Zhang et al.²⁵ The coupling agent was added to PBO at a set content with stirring after PBO was synthesized, and then the treated PBO was brushed to the surface of the SiC fiber woven fabrics. The layers of the SiC-fiber-woven fabrics brushed with PBO were overlaid in the die and hot-pressed under 5 MPa at 120°C for 30 min. When the temperature was cooled to room temperature, the composite was taken out, cured through a cold bath, and then dried at 120°C.

Characterization

Chemical Structure of PBO (FTIR Spectroscopy). The chemical structures of PBO before and after treatment with the coupling agent were characterized by an FTIR spectrometer at room temperature with a thin film.

XPS. The surface chemical components of PBO were examined by XPS (K-Alpha, Thermo-Fisher). The surface chemical elemental composition was calculated from the area of relevant spectral peaks.

Mechanical property testing. The flexural strength of the SiC/PBO composites was measured on a CSS-4200 instrument with a three-point, short-beam bending test method at a crosshead speed of 0.5 mm/min, and the gauge length was set as 30 mm. The specimens for testing were 40 mm in length, 4 mm in width, and 3 mm in thickness. Five specimens were tested to

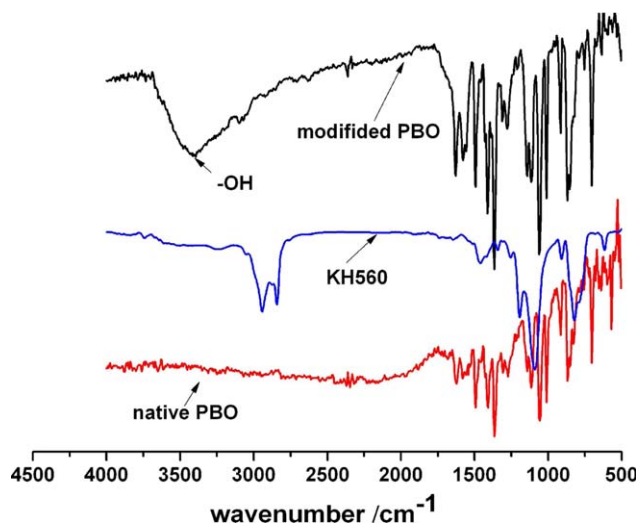


Figure 2. FTIR spectra of KH560, PBO, and treated PBO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtain the average strength. The flexural strength (σ) was calculated by eq. (1):

$$\sigma = \frac{3PL}{2bh^2} \quad (1)$$

where P is the load on the force–displacement curve, L is the gauge length, b is the specimen width, and h is the specimen thickness. The open porosity of the composite was measured with the Archimedes method with distilled water as a medium.

Morphology of the Composite (SEM). The surface morphologies of the composites were characterized by a JSM-6360LV scanning electron microscope. The samples were coated with gold sputtering for 1 min before observation.

RESULTS AND DISCUSSION

FTIR Spectroscopy

Figure 2 shows the spectra of the as-received PBO, KH560, and PBO treated with KH560. The bands at 1620 and 1052 cm⁻¹ were assigned to the stretching vibrations of the C=N and C=O of oxazole rings. The bands at 1573 and 1490 cm⁻¹ resulted from the stretching vibrations of C=C of benzene. The band at 1415 cm⁻¹ resulted from the C–C stretching of the phenyl ring. The bands at 875 and 855 cm⁻¹ were from the out-of-plane C–H vibrations of aromatic ring. The pattern exhibited a new peak corresponding to hydroxyl groups²⁶ in the range 3400–3500 cm⁻¹ for the treated sample, whereas it was absent in the pure PBO and pure KH560. This proved that the hydroxyl groups were successfully introduced to PBO. The presence of hydroxyl groups helped to improve the polarity and wettability between the matrix and the fibers; this resulted in an improvement in the bond properties between the SiC fiber fabric and the PBO matrix. In other words, the interfacial adhesion of the composite was improved through the coupling agent treatment.

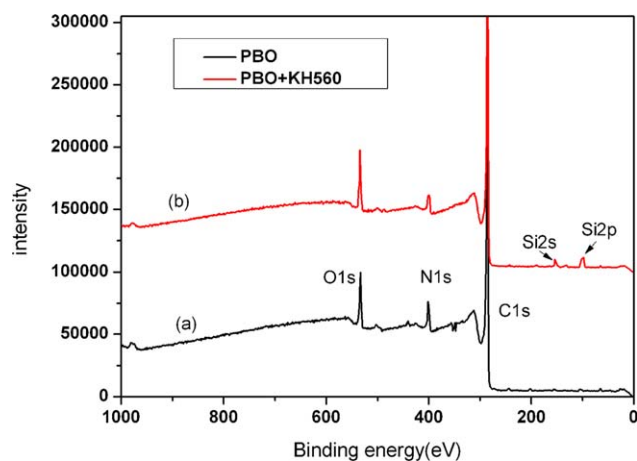


Figure 3. Wide-scan XPS of (a) untreated PBO and (b) treated PBO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XPS Analysis

The wide-scan XPS spectra of PBO before and after treatment with KH560 are shown in Figure 3. The oxygen, nitrogen, and carbon elements were detected on the untreated PBO surface. Although it was obvious that there was silicon present on the surface of the PBO treated with KH560. Meanwhile, the absorption peak related to nitrogen decreased, and that related to oxygen increased sharply. The changes in the PBO surface composition are shown in Table I. According to Table I, the contents of carbon, nitrogen, and oxygen of untreated PBO

Table I. Surface Elemental Compositions of PBO by XPS

PBO sample	Surface elemental composition (%)				Atomic ratio (%)	
	C	O	N	Si	O/C	N/C
Untreated	75.42	18.76	5.81	—	24.87	7.7
Treated	71.47	20.9	3.68	3.93	29.24	10.32

were 75.42, 5.81, and 18.76%, respectively. The O/C and N/C atomic ratios were 24.87 and 7.7%, respectively. Compared with those of the untreated PBO, the contents of carbon and nitrogen of the treated PBO decreased to 71.47 and 3.68%, respectively, whereas the content of oxygen increased to 20.9%, and the silicon content increased from 0 to 3.93%. The untreated PBO displayed an O/C ratio value of 24.87%, whereas the 7 wt % KH560-treated PBO displayed an O/C ratio value of 29.24%. The obvious increase in the oxygen content was attributed to the —OH emerging from the coupling agent treatment; this was consistent with the FTIR test.

Figure 4 shows the spectra of the native and treated PBO deconvoluted into multiple subpeaks of C1s with Gaussian-Lorentzian fit. The peaks with binding energies of about 284.4, 285.5, 286.5, and 288.3 eV were attributed to C—C, C—N, C—O, and N=C—O groups, respectively. After treatment, the C—N peak of the PBO disappeared; however, a new characteristic peak appeared at a higher binding energy of 289.3 eV; this was assigned to the O=C—O group.

From the XPS results, we inferred that the treatment with KH560 increased the amount of polar groups (e.g., OH) on the PBO surface; this helped to improve the wettability of PBO. As a result, the adhesion between the PBO and SiC fibers was improved.²³

SEM Analysis of the Composites

The effects of KH560 on the interfacial adhesion between the SiC fibers, and the PBO was more apparent in the fracture surface examination of each composite. Figure 5 shows the typical SEM images of the fracture surface. It was demonstrated that the interfacial adhesion between the SiC fiber and PBO matrix was significantly improved by the KH560 treatment. There was little PBO resin adhering to the SiC fibers when the PBO was not treated by KH560; as shown in Figure 5(a), the SiC fibers were smooth. With increasing amount of KH560, the PBO adhering to the SiC fibers increased, as shown in Figure 5(b–d). The reason was that the coupling agent treatment increased the wettability between the matrix and the fibers; this was beneficial for the matrix in the penetration of the SiC fiber fabric. When the PBO was treated by

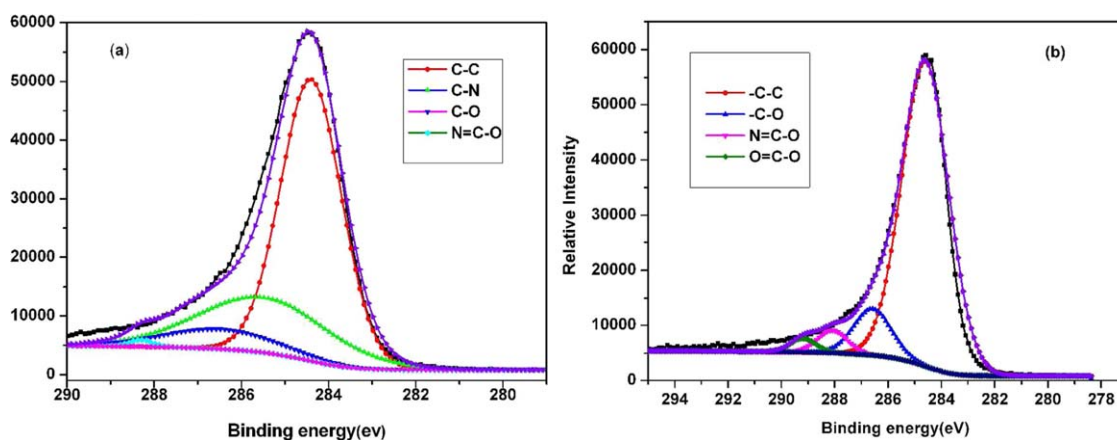


Figure 4. C1s spectra of (a) untreated PBO and (b) treated PBO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

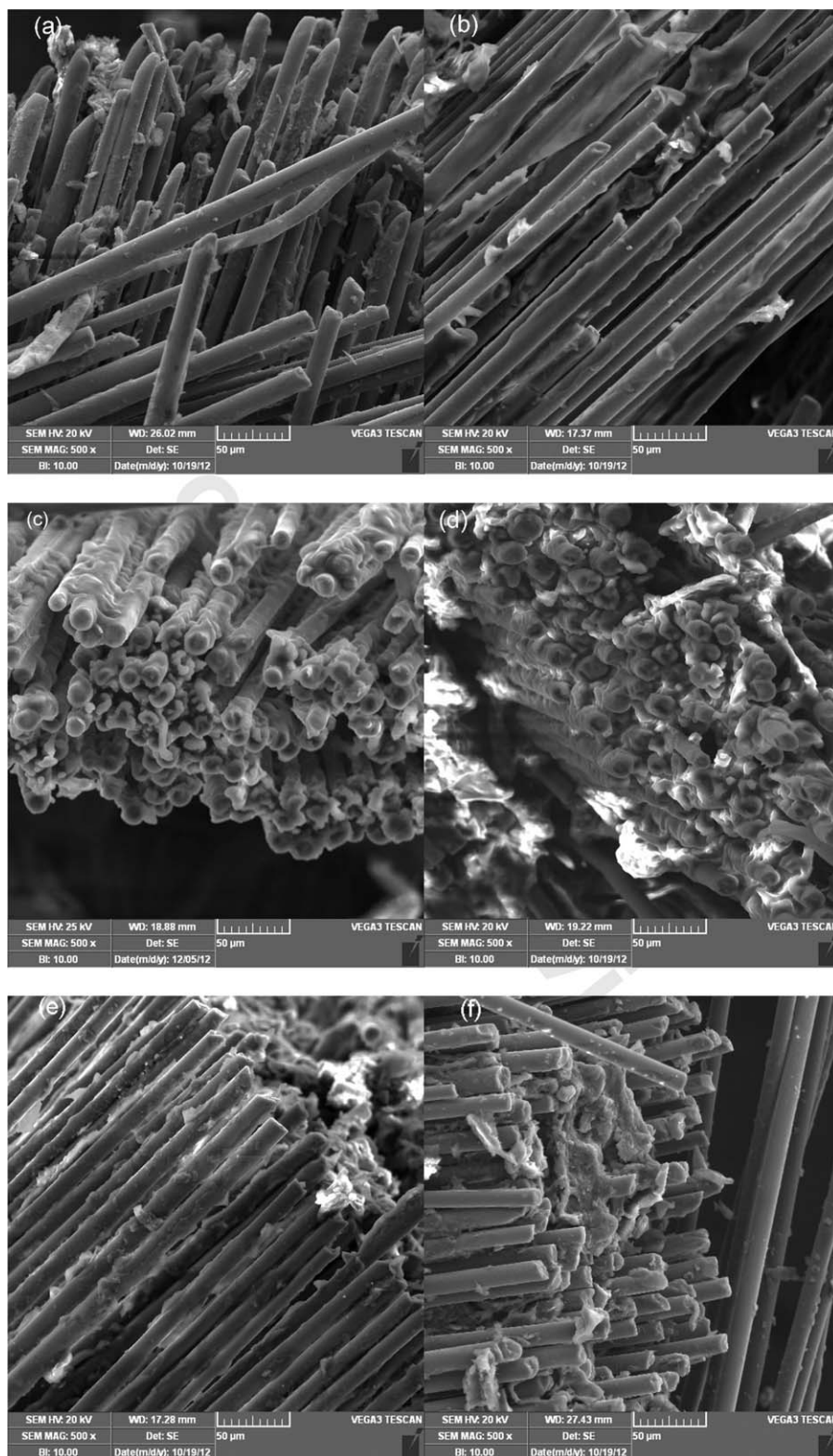


Figure 5. SEM images of the composites: (a) untreated, (b) 2% KH560-treated, (c) 5% KH560-treated, (d) 7% KH560-treated, (e) 10% KH560-treated, and (f) 15% KH560-treated PBO.

7% KH560, as shown in Figure 5(d), we observed that the SiC fibers were well coated with the matrix. However, when the PBO was treated with excess KH560, the PBO adhering to the

SiC fibers was decreased, as shown in Figure 5(e,f). Therefore, the highest flexural strength was obtained in the composite with 7% KH560.

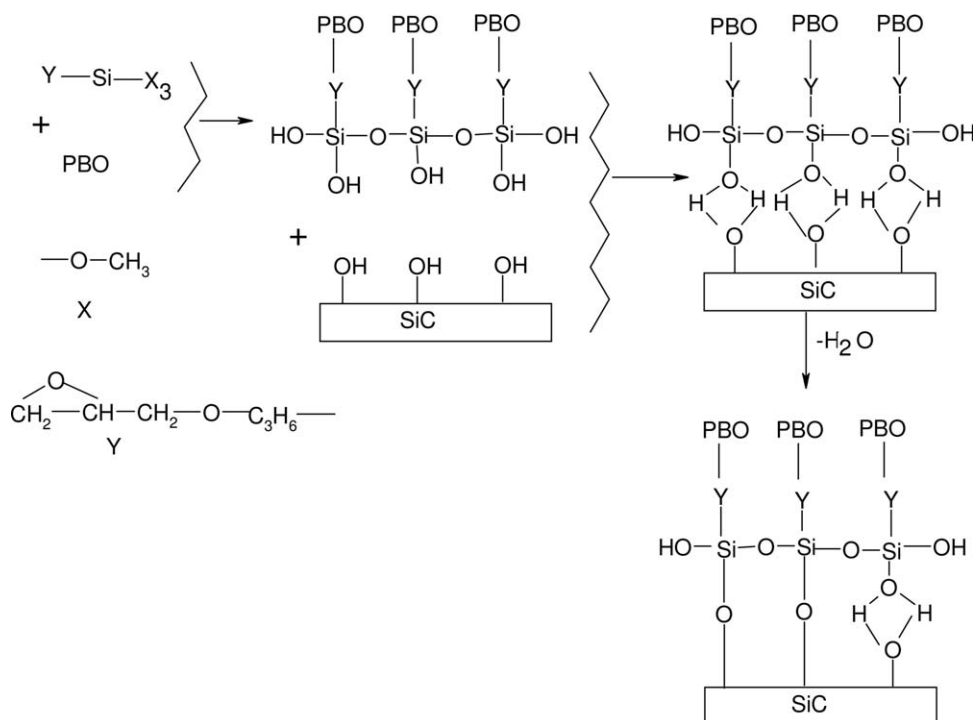


Figure 7. Possible reaction between PBO, KH560, and SiC.

beneficial to improve the adhesion between the PBO matrix and the SiC fiber; as a result, the flexural strength of the composite could be improved.

CONCLUSIONS

The SiCf/PBO composites were fabricated by a hot press. The influence of the coupling agent on the flexural strength of the composites was investigated. The flexural strength of the composites increased from 15 MPa to a maximum of 89 MPa with the 7 wt % coupling agent treatment and then declined when the amount of coupling agent was increased.

The oxygen-to-carbon (O/C) ratio was increased from 24.87 to 29.24%, and a new group of $\text{O}=\text{C}-\text{O}$ was formed after treatment. We verified that the poplar hydroxyl groups were successfully introduced into the PBO.

SEM images of the composites illustrated that more PBO adhered to the SiC fiber after the PBO was treated by KH560 than when the PBO matrix was untreated; this indicated that the interface was indeed enhanced by the coupling agent.

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