

# Influence of the Coupling Agent on the Mechanical Properties of SiC<sub>f</sub>/Poly(phenylene benzobisoxazole) Composites

# Li Wang, Fa Luo, Wancheng Zhou, Dongmei Zhu

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

Correspondence to: L. Wang (E-mail: wanglisdu@126.com)

**ABSTRACT**: Poly(phenylene benzobisoxazole) (PBO) was first used as matrix to fabricate the two-dimensional SiC<sub>f</sub>/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<sub>f</sub>/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. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39805.

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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;<sup>1–5</sup> 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.<sup>10,11</sup>

Because of the aforementioned advantages, SiC<sub>f</sub>/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<sub>f</sub>/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,<sup>15</sup> copolymerization modification,<sup>16-18</sup> 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;<sup>21-24</sup> 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

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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/cm<sup>3</sup>. A silane coupling agent of  $\gamma$ -(2,3-epoxypropoxy) propytrimethoxysiliane (KH560) was provided by Nanjing Shuguang Chemical Group Co, Ltd. (China). PBO was synthesized in our laboratory, and the density of PBO was 1.54 g/cm<sup>3</sup>.

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.<sup>25</sup> 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<sub>f</sub>/ 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 ( $\sigma$ ) was calculated by eq. (1):

$$\sigma = \frac{3PL}{2bh^2} \tag{1}$$

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<sup>-1</sup> were assigned to the stretching vibrations of the C=N and C-O of oxazole rings. The bands at 1573 and 1490 cm<sup>-1</sup> resulted from the stretching vibrations of C=C of benzene. The band at 1415 cm<sup>-1</sup> resulted from the C-C stretching of the phenyl ring. The bands at 875 and 855 cm<sup>-1</sup> were from the out-of-plane C-H vibrations of aromatic ring. The pattern exhibited a new peak corresponding to hydroxyl groups<sup>26</sup> in the range 3400-3500 cm<sup>-1</sup> 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

	Surface elemental composition (%)				Atomic ratio (%)	
PBO sample	С	0	Ν	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.<sup>23</sup>

#### 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.]

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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 6. Flexural stress-strain curves of the composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

# Effects of the Amount of Coupling Agent on the Flexural Strength of the Composites

Figure 6 shows the flexural stress-strain curves of composites with different concentrations of coupling agent. All of the composites exhibited good toughened fracture behavior. The flexural strength of the pure PBO bulk was about 15 MPa, and that of the pure SiCf/PBO composite was the same as that of the pure PBO bulk. The reason was that SiC fiber could not suffer the load because of the poor adhesion between the PBO matrix and the SiC fiber. The flexural strength of composites at first increased with increasing content of coupling agent but decreased with excessive addition of the coupling agent. When the mass fraction of the coupling agent was 7%, the flexural strength of the composites reached the highest of 89 MPa, which is enhanced by 493.3% comparing with untreated composite, because of the increase of surface poplar functional groups from KH560. The flexural strength of the composite was closely dependent on the porosity, the microstructure of the composite, and the interfacial bonding strength between the fiber and the matrix. Therefore, the sample numbers and porosity of the samples are listed in Table II. All of the samples showed a large porosity of more than 10%. The

Table II. Components and Properties of the Samples

Sample number	KH560 content (%)	Porosity (%)
SO	0	20
S1	2	17.5
S2	5	13.8
S3	7	10.7
S4	10	18.1
S5	15	18.9
S00	Pure PBO bulk	15.2

porosity of sample S0 reached the highest value of 20%, and the minimum porosity was 10.7% when the PBO matrix was treated by 7 wt % KH560. The reason for the large porosity in the composite was that poly(phosphoric acid) was washed out during the cold bath, so the void was generated in the composite.

The interface played an important role in the mechanical properties of the composites. The load could be effectively transferred from the PBO matrix to the SiC fibers through good interfacial bonding. For the composites without coupling agent, the adhesion of the PBO and SiC fiber was weak, as shown in Figure 5(a), and interfacial debonding began to occur when the load was put on the composite. This resulted in a low flexural strength in the composites. Although the adhesion of the PBO and SiC fiber began to increase after the PBO was treated with KH560, when the coupling agent concentration was low, the interpenetrating web formed by the coupling agent and PBO was thin, so there was no effective adhesion in the interface of SiCf/PBO because of the small quantity of effective bonds formed. When the coupling agent concentration was too high, the interpenetrating web was thick; this prevented the PBO matrix from permeating. When the coupling agent concentration was appropriate, the thickness of the interpenetrating web was moderate; this not only formed effective bonds but also helped the PBO matrix permeate into the SiC woven layer easily. As a result, the flexural strength of the composites was obtained with an appropriate KH560 content.

By comparison of the flexural strength of the untreated and treated PBO matrix composite, we confirmed that the coupling agent treatment was an effective approach for enhancing the interfacial properties of PBO.

# Coupling Mechanism Analysis

KH560 can be described as Y—Si—X3, where X is alkoxyl group  $(-OCH_3)$  and Y is a short hydrocarbon chain with an epoxy group; the chemical structure of the coupling agent (KH560) is shown as follows:

The coupling mechanisms mainly include chemical bonding, physical absorption theory, and hydrogen theory. On the basis of the model of Arkles and the analysis by FTIR spectroscopy and XPS, we deduced the possible mechanisms among the PBO, SiC fiber, and coupling agent, as shown in Figure 7. When KH560 was added to PBO, on the one hand, the hydroxyl group was introduced to the surface of PBO; this resulted in the improvement of wettability. On the other hand, PBO was linked to the coupling agent by intermolecular interaction; this was accompanied by physical adsorption, adhesion, friction, and sediment at one side. At the same time, it formed hydroxyl on the surface of the SiC fiber by adsorbing water; KH560 reacted with free protons on the SiC surface and formed firm chemical bonds at the other end. Thus, the interfacial layer between the SiC and PBO matrix was generated. This interfacial layer was





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 O=C-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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#### REFERENCES

- Tamargo-Martinez, K.; Villar-Rodil, S.; Paredes, J. I. Chem. Mater. 2003, 15, 4052.
- So, Y. H.; Froelicher, S. W.; Kaliszewski, B.; DeCaire, R. Macromolecules 1999, 32, 6565.

- 3. Kitagawa, T.; Yabuki, K.; Young, R. J. Polymer 2001, 42, 2101.
- 4. Robert, A.; Bubeck, M. U.S. Pat. (1994).
- 5. Wolfe, J. F.; Arnold, F. E. Macromolecules 1981, 14, 909.
- 6. Wu, G. M.; Shyng, Y. T. J. Polym. Res. 2005, 12, 93.
- Wang, J. L.; Liang, G. Z.; Zhao, W.; Zhang, Z. P. Surf. Coat. Technol. 2007, 201, 4800.
- 8. Wu, G. M.; Shyng, Y. T. Compos. A 2004, 35, 1291.
- 9. Larsson, F.; Svensson, L. Compos. A 2002, 33, 221.
- 10. Guo, S. Q.; Kagawa, Y. J. Eur. Ceram. Soc. 2002, 22, 2349.
- 11. Ding, D. H.; Zhou, W. C.; Zhang, B.; Luo, F.; Zhu, D. M. J. Mater. Sci. 2011, 46, 2709.
- 12. Wu, G. M.; Shyng, Y.; Kung, S. F.; Wu, C. F. Vacuum 2009, 83, 5271.
- Liu, D.; Chen, P.; Chen, M. X.; Liu, Z. Surf. Coat. Technol. 2012, 206, 3534.
- 14. Park, J. M.; Kim, D. S.; Kim, S. R. J. Colloid Interface Sci. 2003, 264, 431.
- 15. Wu, G. M.; Shyng, Y. T. J. Polym. Res. 2005, 12, 93.
- 16. Zhang, T.; Jin, J. H.; Yang, S. L.; Li, G. Jiang, J.M. J. Macromol. Sci. Part B: Phys. 2009, 48, 1114.
- 17. Yalvac, S.; Jakubowski, J. J.; So, Y. H.; Sen, A. *Polymer* **1996**, 20, 4657.
- Zhang, T.; Hu, D. Y.; Jin, J. H.; Yang, S. L.; Li G.; Jiang, J. M. Eur. Polym. J. 2009, 45, 302.
- Zhang, C. H.; Huang, Y. D.; Wang, S. W.; Sun, B. H. Mater. Sci. Technol. 2007, 15, 305.
- 20. Wang, B.; Jin, Z. H.; Qiu, Z. M. J. Xi'an Jiaotong Univ. 2002, 36, 975.



- 21. Zhang, C. H.; Yuan, W. J.; Wang, S. R.; Liang, X. F. J. Appl. Polym. Sci. 2011, 121, 3455.
- 22. Qian, J.; Wu, J. L.; Liu, X. Y.; Zhuang, Q. X.; Han, Z. W. J. Appl. Polym. Sci. 2013, 2990.
- 23. Song, B.; Meng, L. H.; Huang, Y. D. Appl. Surf. Sci. 2012, 258, 10154.
- 24. Li, Y. W.; Zhao, F.; Song, Y. J.; Li, J.; Hu, Z.; Huang, Y. D. Appl. Surf. Sci. 2013, 266, 306.
- 25. Zhang, C. Y.; Shi, Z. X.; Zhu, Z. K. Chem. J. Chin. Univ. 2004, 25, 556.
- 26. Liu, D. D.; Hu, J.; Zhou, X. S.; Ning, P.; Wang, Y. J. Appl. Polym. Sci. 2006, 102, 1428.

