

Improvement of Interfacial Shear Strengths of Polybenzobisoxazole Fiber/Epoxy Resin Composite by n-TiO₂ Coating

Jun Qian, Junling Wu, Xiaoyun Liu, Qixin Zhuang, Zhewen Han

Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Correspondence to: J. Qian (E-mail: qianjun@ecust.edu.cn)

ABSTRACT: Smooth polybenzobisoxazole (PBO) fiber has limited interfacial interaction with resin matrix. In this article, nano-TiO₂ coating on PBO fiber is applied to improve the interfacial adhesion between PBO fiber and epoxy resin. The test results suggest that the PBO fiber had good interaction with epoxy resin matrix after its treatment with n-TiO₂ sol. Nano TiO₂ particle embedded onto PBO fiber surface, acting as a chock, which made fiber implanted into the resin better. This greatly improved the shear strengths (IFSS) of PBO fiber/epoxy resin composite. It has been found that a 56% increase in interfacial IFSS has achieved without sacrificing mechanical properties of fiber. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: PBO fiber; IFSS; N-TiO₂ coating; composite

Received 31 January 2011; accepted 27 April 2012; published online

DOI: 10.1002/app.37970

INTRODUCTION

As a class of heterocyclic polymer, poly(*p*-phenylene benzobisoxazole) (PBO) has received great interest because of its high performance, excellent mechanical properties, good thermal stability, and environmental stability.^{1–4} Typically, PBO fibers have been used in high strength applications, such as in body armor and ropes.^{5–11} PBO fibers have also been widely used in the advanced composites. According to Bruswick's report on the winding performance, the tensile strength of a PBO fiber (5.5 GPa grade) is 31% higher than that of a T-40 carbon fiber (5.65 GPa grade).¹²

Due to the lack of polar functional group in the polymer repeating unit and smooth surface of PBO, the adhesion between PBO fiber and matrix is poor, which limits its applications as high-performance reinforcement for composite material. Therefore, it is worth trying surface modification on PBO fiber to improve adhesion between fiber and resin matrixes, and further enhance the overall mechanical properties of the composite. There are a number of reports about surface modification of PBO fiber, such as surface etching, coupling agent treatment, copolymer method, plasma treatment, corona treatment, and radiation treatment etc.^{13–15} Previous studies by Dow Chemical Company indicated that approximately a two-fold increase (from 19.4 to 33.2 MPa) in IFSS could be attained by using the oxygen plasma¹⁶ while a bit loss of strength of the

fiber and the incorporation of benzocyclobutene diketone (BCB) end-capped PBO into the PBO fiber exhibited an 33% increase in interfacial shear strength (IFSS).¹⁷ The disadvantage of copolymer method was that the spun fiber exhibited significantly lower mechanical properties than the PBO fiber.

Liu used silicone-coupling agents to coat PBO fiber. Since PBO fiber is often used in heat-resisting material field, the coupling agent should be highly heat-resistant. Huang also studied surface modification of PBO fiber by coating reactive monomers on the surface of PBO fiber and treating the surface of PBO fiber by the radiation of high energy ray. But radiation would cause deterioration of fiber.

The corona discharge consists of the ionization of the air molecules when an electric discharge of high voltage is applied between two close electrodes.¹⁸ Lei treated weave PBO fiber by corona, and tested the lamella of composite made of the basketwork of PBO fiber and epoxy resin. The strength and modulus of the composite were not obviously improved.

Plasma was excited by a radiofrequency generator with a continuously variable power in a reactor room with a stable mass flow. Chen¹⁹ got the conclusion that the oxygen plasma treatment introduced some polar groups to PBO fiber surface, which improved the surface roughness. Also, the surface morphologies of PBO fibers could be changed by plasma etching and oxidative reactions. However, aging effect of the plasma treated PBO

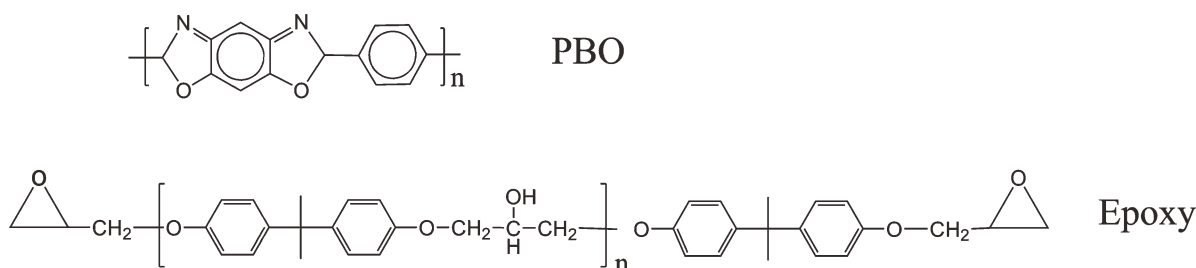


Figure 1. The chemical formula of the PBO and epoxy resin.

fibers showed that the fiber surface wettability degraded greatly in the several hours after the plasma treatment. And, its the high expense and complex process is not suitable for continuous-treatment in industry. In this study, we report a new method to improve IFSS between the PBO fiber and epoxy resin by using nano TiO_2 ($n\text{-TiO}_2$) coated PBO fiber. The most advantages of this method are its simple and convenience in continuous-treatment in industry.

Figure 1 showed chemical formula of the PBO fiber and epoxy resin. Meanwhile, the effects of treatment temperature, heat treatment time, and soaking time on the IFSS of PBO fiber were investigated.

MATERIALS AND METHODS

Preparation of $n\text{-TiO}_2$ Sol

Reagents, including anhydrous alcohol, tetrabutyl titanate, triethanolamine, triethylene tetramine, ethyl silicate, and epoxy resin, were purchased from Shanghai linfeng chemical reagent company.

Tetrabutyl titanate and triethanolamine were first put into a four-necked flask and mixed at 60°C for 30 min. Then anhydrous alcohol was added and reacted for 4 h. At the same time, the mixed solution of anhydrous alcohol and deionized water was slowly dropped. After adjusting pH value to 8–9, a colorless transparent $n\text{-TiO}_2$ sol was obtained (the weight percentage of $n\text{-TiO}_2$ in sol was 0.7 wt %).

Coating $n\text{-TiO}_2$ on PBO Fiber Surface

Since the commercial PBO fiber surfaces had a protection coating, it is necessary to pretreat and clean this coating before coating with $n\text{-TiO}_2$. Pretreatment process was done as follows: PBO fibers were first extracted with deionized water for 24 h, and then dipped in acetone for 12 h to remove impurity on the fiber surface. Then, the fibers were dried at 110°C for 24 h.

The PBO fibers were soaked into $n\text{-TiO}_2$ sol with different concentration treatment for different time. The fibers were taken out and dried at room temperature for 24 h. Subsequently, the fibers were heat-treated at 400°C under N_2 atmosphere.

Characterization of PBO Fiber/Epoxy Resin Composite

To determine parameters of interfacial interaction between fibers and matrices, quite a large number of various micromechanical tests have been developed, and one kind of these tests is microbond pull-out test developed by Miller et al.⁵ The IFSS of PBO fiber/epoxy resin composite in this article was also measured by microbond pull-out test (Figure 2). The untreated and treated fibers were fixed at regularly separated distances in a article frame. Microdroplets of epoxy were formed on each fiber axis using a

sharp pin. The size of the microdroplet was measured individually using an optical microscope. It was controlled at about 0.6 mm. The mechanical tests were done at 25°C . The sample was cured at 25°C for 36 h, and then cured at 80°C in oven for 6 h.

Microbond pull-out tests were performed in the XQ-1 single filament tensile tester. The test rate was 1 mm/min. Number of effective data of each sample was not <20 .

IFSS (MPa) was calculated by formula²⁰:

$$\tau_{\text{IFSS}} = F_m / (\pi dl)$$

In which, F_m (N) is pull-out force, d (μm) is fiber diameter, l (m) is the length of fiber embedded in resin.

The tensile strength of fiber was tested in a XQ-1 single filament tensile tester. Holding length was 20 mm, extension rate was 10 mm/min, 30 points were collected in each group, and data were processed by statistical analysis.

Tensile strength of fiber (σ) (MPa) was calculated by formula:

$$\sigma = F / \pi r^2$$

In which, F (N) is the breaking pull of fiber, r (mm) is the semi-diameter of fiber.

The surface morphology of PBO fiber was observed by scanning electron microscope (SEM, JSM-6460) and TS-5136 mm SEM (Mode: SE Detector; Voltage: 20.0 KV; Working distance: 12–34 mm). Samples were sprayed with carbon before observing. The sizes of $n\text{-TiO}_2$ particle of were measured with Zetasizer 3000HS particle diameter instrument.

RESULTS AND DISCUSSIONS

Characterization of $n\text{-TiO}_2$ Particle

The $n\text{-TiO}_2$ sol was produced by sol-gel method in this study, and the size of hydrosol particles was measured. Figure 3

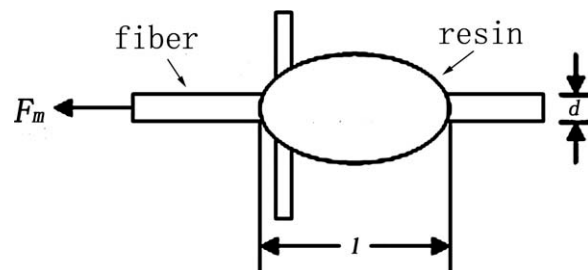


Figure 2. Scheme of microbond pull-out tests.

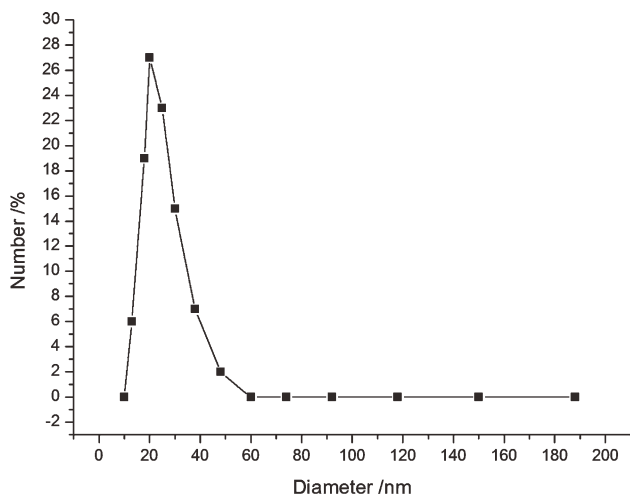


Figure 3. The distribution of size of particle of titanium hydrosol.

showed the relation between the sizes of n-TiO₂ hydrosol particles and statistical number. It was found that the average diameter of n-TiO₂ hydrosol particles is 29 nm with a narrow distribution. Since the diameter of PBO fiber is about 20 μm, the n-TiO₂ hydrosol particles could meet the requirement for coating on the fiber surfaces.

Effect of Treatment Conditions on IFSS of PBO Fiber/Resin Matrix

The IFSS of fiber/epoxy resin composite is 11.29 MPa for PBO fiber before treatment. The effect of treatment conditions on IFSS was discussed as follows. The results were from the average of the IFSS of 20 samples. Error bars were also shown in the figure.

Selection of Treatment Temperature. To investigate the optimal coating condition, the coating was done at 400°C. It is found that when the experimental time reaches 15 min, the layer of n-TiO₂ coating was perfect. If the time exceeds 15 min, the PBO fiber's performance became poor. So the optimal coating condition was selected to be at 400°C for 15 min. As shown in Figure 4, it was found that this treatment temperature had little influence on the strength of PBO fiber.

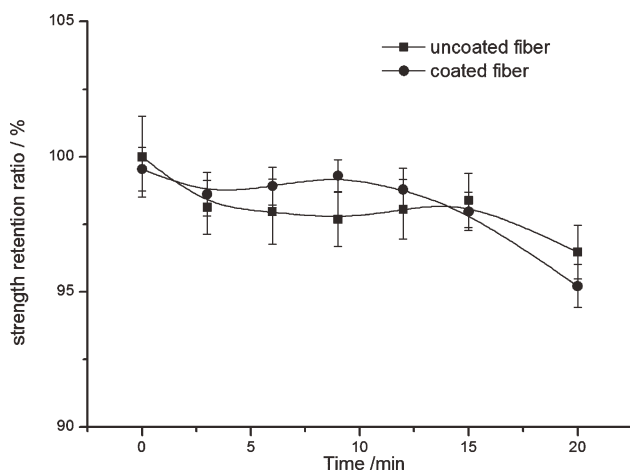


Figure 4. Effect of heat treatment time on strength of PBO fiber in 400°C.

As a heat-resistant high-performance fiber, PBO fiber could be subject to high treatment temperature. The optimal temperature for heat-treating PBO fiber is 350–400°C in which the chemical property of PBO fiber do not change.²¹

Effects of Heat Treatment Time on the IFSS of PBO Fiber. Figure 5 shows the relationship between IFSS of PBO fiber and heat-treating time. The IFSS of PBO fiber increased with the increase of treatment time when treatment time was <4 min, and decreased with the increase of treatment time when treatment time was over 4 min. The maximum IFSS of PBO fiber was 17.4 MPa when treatment time was 4 min (the 1 min 2min 3 min 4 min 5 min 10 min 15 min stand for soaking time? If so, describe in the figure).

Since the strength of PBO fiber did not change under the heat-treatment temperature of 350–400°C, it was reasonable to believe that the changes of IFSS of PBO fibers under different treatment time were attributed to the change of roughness of the fiber's surface.

Figure 6 shows surface morphology of PBO fiber treated for different time. When the treatment time was 1 min, a small portion of n-TiO₂ started to deposit onto the surface of the fiber. When treatment time reached 8 min, the big TiO₂-particle flaked away from the fiber surface, and led to the decrease of IFSS. The optimized treating condition was at 400°C for 4 min.

Effect of Soaking Time on IFSS of PBO Fiber. As shown in Figure 7, when soaking time was <3 min, the IFSS of PBO fiber increased with the increase of soaking time. However, when the soaking time was >3 min, the IFSS of PBO fiber decreased with the increase of soaking time. It is possible that more n-TiO₂ particles were coated onto the fiber surfaces with the increase of soaking time when the soaking time was <3 min. If the fiber was treated >3 min, n-TiO₂ particle started to flake away from the fiber surface, and the decrease the IFSS of PBO fiber. According to Figure 7, the best soaking time of PBO fiber was 3 min. The results indicated that the soaking time had directly influence on the bulk and amount of n-TiO₂ particle on the fiber surfaces.

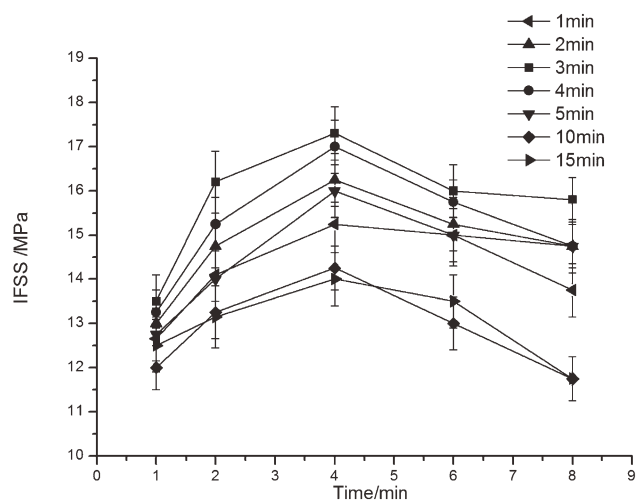


Figure 5. Effect of the heat treatment time on IFSS of PBO fiber/epoxy resin.

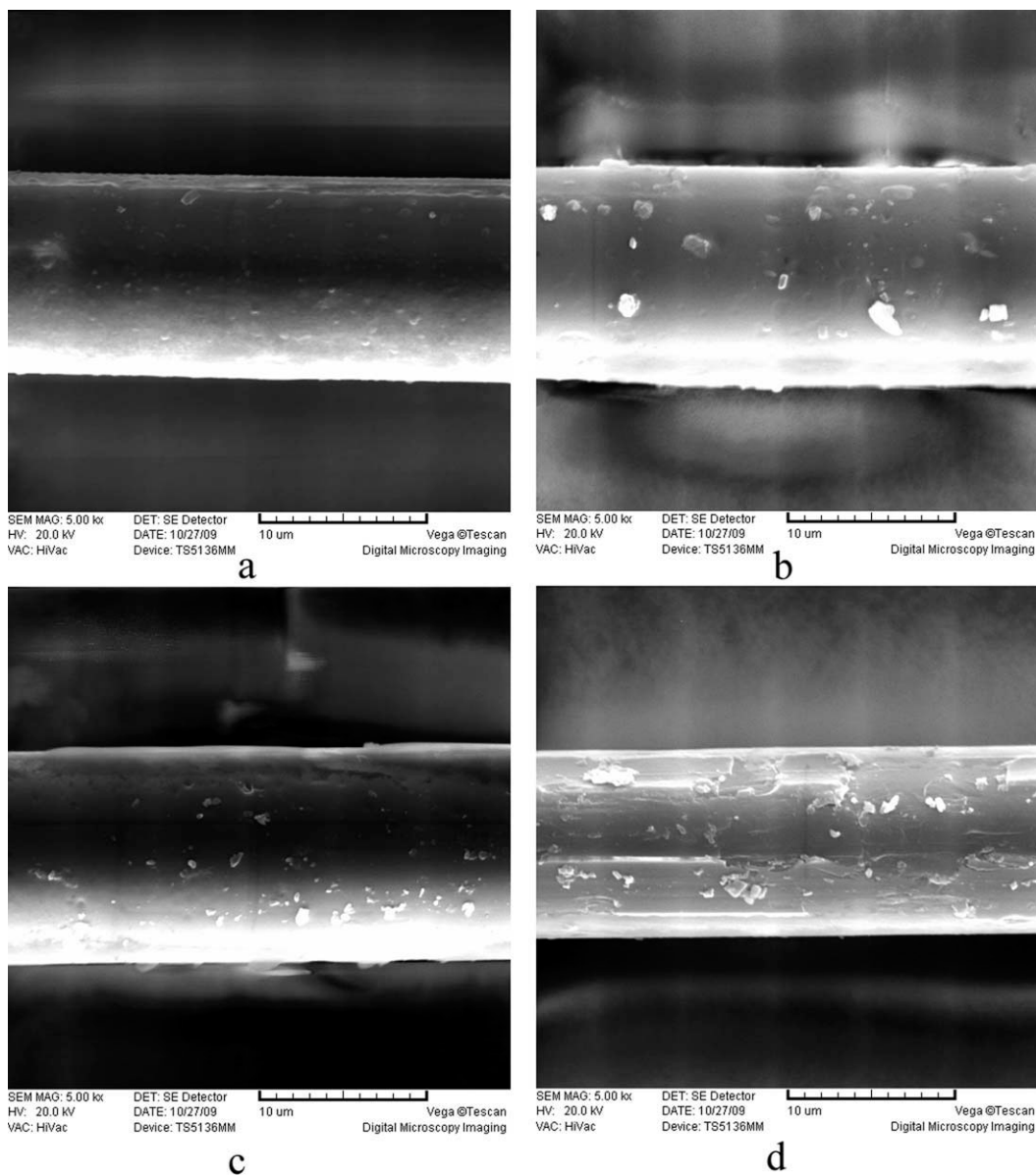


Figure 6. SEM of PBO fiber treated for different time (a: 1 min; b: 2 min; c: 4 min; d: 8 min).

Figure 8 shows the morphology of PBO fiber surface coating with $n\text{-TiO}_2$ particle. The untreated PBO fiber possesses smooth surface, while the fibers treated for 2–15 min show rough surfaces. Figure 8 also shows that the $n\text{-TiO}_2$ particles on fiber surface were few after treated for 2 min, and the number of $n\text{-TiO}_2$ particle on fiber surface increased with the increase of treatment time till 7 min. However, the number of $n\text{-TiO}_2$ particle on fiber surface decreased when treatment time was over 10 min. The possible reason was that too thick $n\text{-TiO}_2$ particle layers on fiber surface might be easy to fall off. According to Figure 8, it was reasonable to conclude that the best treatment time was 3 min.

IFSS and SEM Analysis of PBO Fiber/Epoxy Resin Composite
Based on above experimental results, the optimized treatment condition was soaking PBO fiber into $n\text{-TiO}_2$ sol for 3 min, and

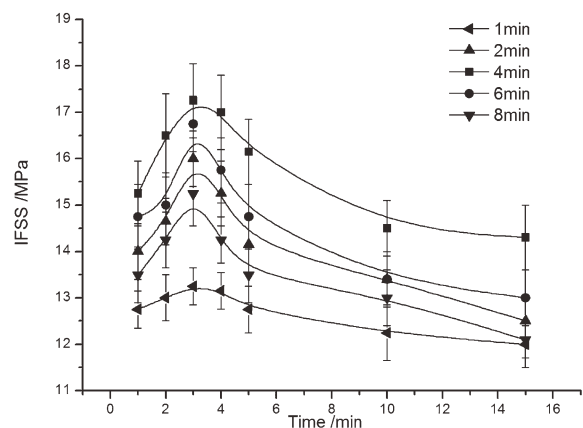


Figure 7. Effect of the sol-treatment time on IFSS of PBO fiber/epoxy resin.

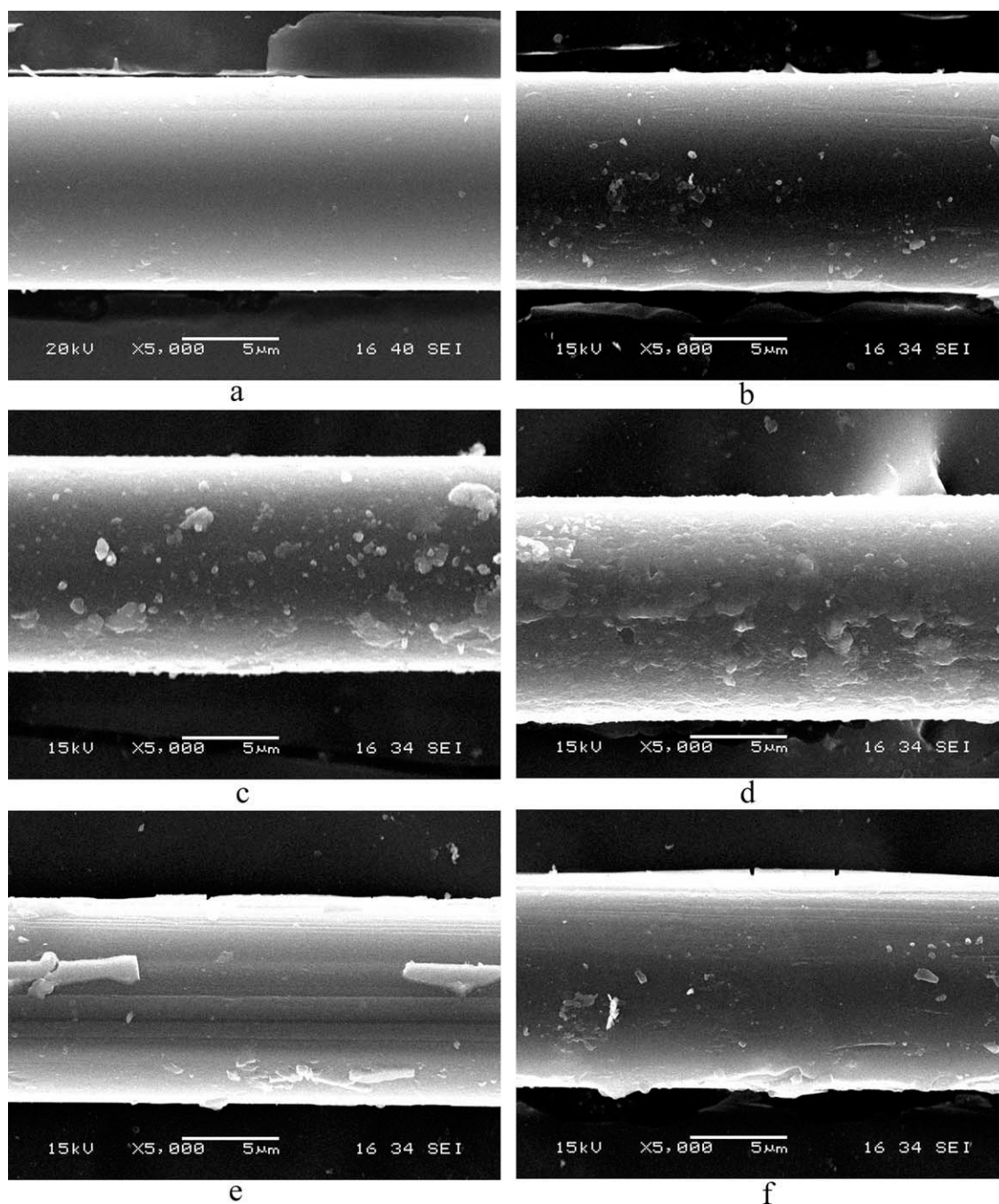


Figure 8. SEM of PBO fiber soaked for different time (a: original fiber; b: 2 min; c: 3 min; d: 5 min; e: 10 min; f: 15 min).

then treating at 400°C for 4 min. Under this condition, the IFSS of PBO fiber/epoxy matrix composite would increase by about 56% comparing with that of untreated fiber/epoxy matrix composite.

To further study the effects of n-TiO₂ treatment on PBO fiber, surface morphology of fiber/resin composite after pull-out test was investigated by SEM. As shown in Figure 9, the PBO fiber surface after pull-out test was very rough, and there were some granular resin matrix left on the fiber surface. From the holes of resin matrix after pull-out test, tearing can be clearly observed. This sug-

gests treated PBO fiber had a good interaction with epoxy resin matrix. Nano-particles on PBO fiber surface acted as a chock, which made fiber implanted into the resin better. This would greatly improve the IFSS of PBO fiber/epoxy resin composite.

CONCLUSION

In this study, nano-TiO₂ sol was produced by sol-gel method, and applied to modify PBO fiber surface. Effects of treating conditions, including heat-treatment time and soaking time, on the IFSS of PBO fiber/epoxy resin composite were studied. The

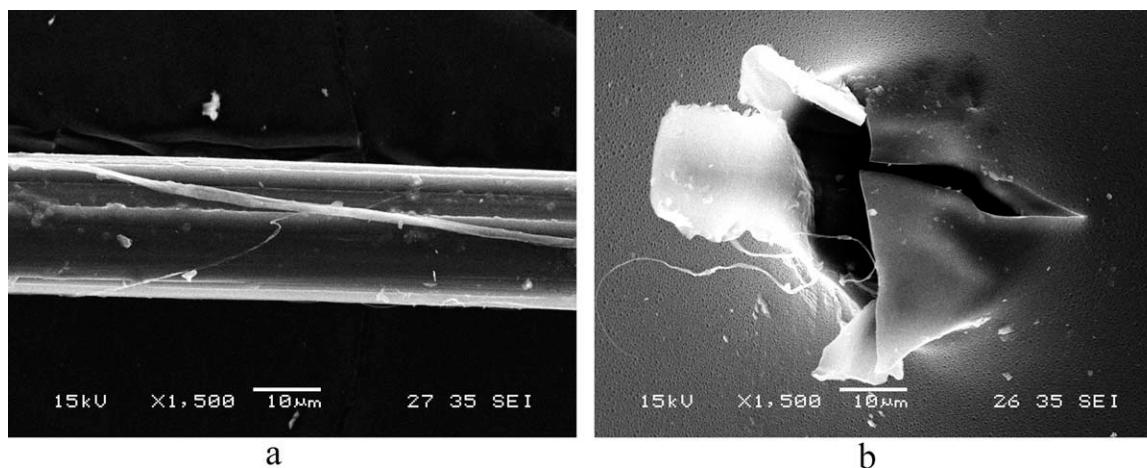


Figure 9. SEM of PBO fiber/epoxy resin after pull-out test (a: fiber; b: resin).

optimized treatment condition was soaking BPO fiber into nano-TiO₂ sol for 3 min and then heat-treating at 400°C for 4 min. Under above conditions, the IFSS of PBO fiber/epoxy resin was 17.4 MPa. There is a 56% increase comparing with 11.29 MPa for untreated fiber/epoxy resin.

It is found that the PBO fiber surface was very rough after pull-out test from PBO fiber/epoxy resin, composite and there were some granular resin matrix left on of fiber surface. The results suggest that the PBO fiber had much better interaction with epoxy resin matrix after treated with n-TiO₂ sol. Nano TiO₂ particle on PBO fiber surface acted as a chock, which made fiber implanted into the resin better. Another advantage of this method is its simplicity. By this method, IFSS could be improved while the strength of the fibers had been maintained. Moreover, this method can be used as a continuous-treatment procedure in the spinning line.

ACKNOWLEDGMENTS

The authors express their gratitude to the National Natural Science Foundation of China (NSFC) for their financial support. Contract grant numbers are 50703010 and 50973028.

REFERENCES

- Wolfe, J. E.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909.
- Song, B.; Fu, Q.; Ying, L. H.; Liu, X.; Zhuang, Q.; Han, Z. *J. Appl. Polym. Sci.* **2012**, *124*, 1050.
- Joseph, W. D.; Abed, J. C.; Mercier, R.; McGrath, J. E. *Polymer* **1994**, *35*, 5046.
- Fu, Q.; Zhang, H.; Song, B.; Liu, X.; Zhuang, Q.; Han, Z. *J. Appl. Polym. Sci.* **2011**, *121*, 1734.
- Im, J.; Percha, P. A.; Yeakle, D. S. *Mater. Res. Soc. Symp. Proc.* **1989**, *134*, 307.
- Xu, X. H.; Liu, X.; Zhuang, Q.; Han, Z. *J. Macromol. Sci., Part A Pure Appl. Chem.* **2010**, *47*, 977.
- Xu, X. H.; Zhang, H.; Liu, X.; Zhuang, Q.; Han, Z. *Eur. Polym. J.* **2010**, *46*, 528.
- Xu, X. H.; Liu, X.; Zhuang, Q.; Han, Z. *J. Appl. Polym. Sci.* **2010**, *116*, 455.
- Martin, D. C.; Thomas, E. L. *Macromolecules* **1991**, *24*, 2450.
- Soo-Jin, P.; Min-Kang, S.; Jae-Rock, L. *J. Colloid Interface Sci.* **2003**, *268*, 127.
- Chen, X. J.; Liu, X.; Qian, J.; Zhuang, Q.; Li, X. X.; Han, Z. *J. Appl. Polym. Sci.* **2008**, *110*, 1899.
- Ma, der, E.; Melcher, S. *J. Mater. Sci.* **2007**, *42*, 8047.
- Wu, G. M.; Chang, C. H. *Mater. Chem. Phys.* **2007**, *81*, 1159.
- Wu, G. M. *Mater. Chem. Phys.* **2004**, *85*, 81.
- Lei, S. Y.; Young, R. J. *Compos. Part A* **2001**, *32*, 499.
- Vedula, M.; Madison, N. L.; Tsang, F.; Jakubowski, J. J.; Kneibel, C. E.; Stanley, C. Improved Compressive Strength of Polymeric PBO Fiber. Air Force Weapons Laboratory Technical (AFWL) report. No. AFWL-TR-92-4030. **1992**, *6*.
- Yalvac, S.; Jakubowski, J. J.; So, Y. H.; Jakubowski, A. S.; et al. *Polymer* **1996**, *37*, 4657.
- María, D. R. S.; Pastor-Blas, M. M. *Int. J. Adhes. Adhes.* **2003**, *23*, 1.
- Cheng, P. *Appl. Surf. Sci.* **2008**, *255*, 3153.
- Miller, B.; Muri, P.; Rebenfeld, L. *Compos. Sci. Technol.* **1987**, *28*, 17.
- Song, B.; Ying, L.; Liu, X.; Zhuang, Q.; Han, Z. *Adv. Mater. Res.* **2012**, *391*, 864.