

Surface Modification of PBO Fibers by Argon Plasma and Argon Plasma Combined with Coupling Agents

Dandan Liu, Jian Hu, Yaoming Zhao, Xuesong Zhou, Ping Ning, Yi Wang

South China University of Technology, Guangzhou 510640, China

Received 15 September 2005; accepted 17 January 2006

DOI 10.1002/app.24287

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The methods of argon plasma and argon plasma combined with coupling agents were employed to modify the poly[1,4-phenylene-*cis*-benzobisoxazole] (PBO) fiber surface. The interfacial shearing strength (IFSS) of PBO fibers/epoxy resin was measured by the single fiber pull-out test. The surface chemical structure and surface composition of PBO fibers were determined by FTIR and X-ray photoelectron spectroscopy respectively. The morphology of the fiber surface was investigated by scanning electron microscopy and the specific surface area of the fibers was calculated by B.E.T. equation. Furthermore, the wettability of PBO fibers was confirmed by the droplet profile analysis method. The results showed that the elemental composition

ratio of the fiber surface changed after the modification. The IFSS increased by 42 and 78% when the fibers were treated by argon plasma and argon plasma combined with the coupling agents, respectively. Meanwhile, the specific surface areas of the treated fibers were improved. In addition, compared with the modification of argon plasma, the modification of argon plasma combined with the coupling agents inhibited the attenuation phenomena of the IFSS and the wettability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1428–1435, 2006

Key words: PBO fiber; argon plasma; interfacial shearing strength; coupling agent; epoxy resin; surface modification

INTRODUCTION

Poly(1,4-phenylene-*cis*-benzobisoxazole) (PBO), aromatic heterocyclic rigid-rod polymeric fibers, have a potential application as reinforcement fibers in advanced composites because they exhibit excellent mechanical properties, high flame resistance, high thermal stability, and good resistance to creep, chemicals, and abrasion.^{1–5} Some of the excellent physical properties of as-spun (AS) and high-modulus (HM) PBO fibers are summarized in Table I. However, the poor interfacial adhesion of PBO fibers/resins confines their applications because of the surface inertness and the relative surface smoothness of the fibers. The adhesion between the fiber and the resin in the composite system is a primary factor for the stress transfer from resin to fiber. Therefore, the surface modification to enhance the adhesion between the fiber and the resin is very important for the composite application.

Several surface modification techniques, including chemical modification,^{6–8} copolymerization modification,⁷ coupling agent modification,^{9,10} corona modification,^{11–13} thermal treatment,¹¹ radiation modification,^{14,15} ion sputtering,¹⁶ and plasma modification,¹⁷ have been developed to improve the interfacial shearing strength (IFSS) of PBO fibers/resin. The ultimate

goal of these modifications is to change the surface chemistry composition and microstructure of the material, and to modulate wettability, surface roughness, surface free energy, and the number of the polar groups on the surface. In the PBO fiber, the plasma modification method has been one of the methods newly studied as a surface modification that offers several advantages over other modifications. The major advantages of the plasma modification over other techniques include the selection modification of only the outer atomic layers of the substrate, the selection of the desired functional group, the minimization of thermal degradation, the cleaning process, and the rapid treatment time.^{18–20}

In this study, to improve the IFSS, the PBO fiber surface was modified by argon plasma and argon plasma combined with coupling agents. The single fiber pull-out test was used to measure the IFSS of PBO fibers/resin. X-ray photoelectron spectroscopy and scanning electron microscopy were used to study the surface element composition and the morphology of the fibers, respectively. The mechanical properties and the wettability of the fibers were also investigated.

EXPERIMENTAL

Materials

The fibers used in this study were the poly(1,4-phenylene-*cis*-benzobisoxazole) (PBO) fibers, Zylon AS, supplied by Toyobo, Japan. EPOS 828 epoxy resins

Correspondence to: Y. M. Zhao (psymzhao@scut.edu.cn).

TABLE I
Physical Properties of AS and HM Type PBO Fibers

Property	PBO-AS	PBO-HM
Density (g/cm ³)	1.54	1.56
Tensile strength (GPa)	5.8	5.8
Tensile modulus (GPa)	180	280
Elongation to break (%)	3.5	2.5
Moisture regain (%)	2.0	0.6
Decomposition temperature (°C)	650	650
Limiting oxygen index (%)	68	68

From Zylon (PBO fiber) Technical Information (2001), Toyobo Co.

were supplied by Shell, UK, and the curing agent was a low molecular polyamide (PA-650), which was supplied by Xiangtan chemical, China. Siloxane coupling agents were supplied by Duguesa, Germany. The trademarks were A-1100, A-187, A-174, and A-172, respectively.

Fiber surface treatments

PBO fibers were first immersed in ethanol at room temperature (25 ± 2)°C for 12 h, then washed repeatedly with distilled water at room temperature (25 ± 2)°C. The washed fibers were finally dried in a vacuum oven at 100°C for 12 h. The dried fibers were modified by two different surface modifications. The first one was to treat the dried fibers in HD-1B plasma instrument by argon plasma at the set pressure, power, and time; the other was to immerse the dried fibers in a solution of coupling-agent/toluene for 2 h at room temperature (25 ± 2)°C, then dry in a vacuum oven at 80°C for 1 h. At the end, the fibers in HD-1B plasma instrument were treated by argon plasma at the set pneumatic pressure, power, and time.

Specimen preparation and IFSS measurement

To determine the effects of the modification on the adhesion of PBO fibers to the epoxy resin, the single fiber pull-out test was performed and the mean IFSS was calculated.^{7,21–23} It is assumed that there is a linear relationship between the pullout force and the embedded length of the fiber and the force evenly distributes along the direction of the fiber axis. The EPOS 828 epoxy resin and PA-650 were mixed in 1 : 1 weight ratio in ethanol solvent. The small resin droplets were injected on each fiber with a syringe. They were pre-cured at 40°C for 24 h, then postcured for 1 h at 60°C. The embedded length of the fibers was controlled around 1 mm for all samples in this experiment. Specimens were tested at room temperature (25 ± 2)°C on the testing machine (YG001A, China) at a cross-head speed of 2 mm/min. The mean IFSS was calculated using the relation $IFSS = F/(\pi dL)$, where F is the

pull-out force, and d and L are the fiber diameter and the embedded fiber length respectively. Assuming round fibers, the average diameter from SEM micrographs for PBO fiber was $11 \pm 1.05 \mu\text{m}$. No significant difference in diameter was observed for the fiber with plasma surface modifications. The embedded length of the fibers was measured by an optical microscope attached with a calibrated eyepiece. Each obtained IFSS value was the average of more than 40 successful measurements.

Measurement of the single fiber tensile strength

Specimens were tested at room temperature (25 ± 2)°C on the testing machine (YG001A, China) at a cross-head speed of 2 mm/min. The mean single fiber tensile strength (SFTS) was calculated using the relation $SFTS = 4F/(\pi d^2)$, where F and d are the maximal load of the breaking and the fiber diameter respectively. Each obtained SFTS value was the average of more than 40 successful measurements.

Wettability

Contact angle has become an important method as the measure of wettability between water and monofilaments. Wettability of PBO fibers was characterized by the video based optical contact angle measuring device (OCA 15, Dataphysics, Germany) through the droplet profile analysis method.²⁴ Each value was the average of more than 20 specimens.

Morphology of the fibers

Scanning electron microscopy (SEM) is a very useful method to investigate the surface morphology of the fibers. The surface morphology of PBO fibers was investigated by SEM (LEO 1530VP, Germany). The specimens were coated with a thin conducting layer of gold to minimize charge and the microscope was operated under 10 or 15 kV. SEM photomicrographs of single filaments were also used to determine the fiber diameter. The fiber diameter was the average of more than 10 measurements from SEM micrographs.

Chemical structure of the fibers

The chemical structure of the fibers was characterized with an FTIR spectrometer (BRUKER Vctor33, Germany) at room temperature (25 ± 2)°C. The samples were prepared as KBr pellets, and the spectrum range was 4000–400 cm^{-1} .

Specific surface area

Nitrogen adsorption isotherms were determined with the apparatus VOVA-1000 (Ver. 3.70, Quantachrome,

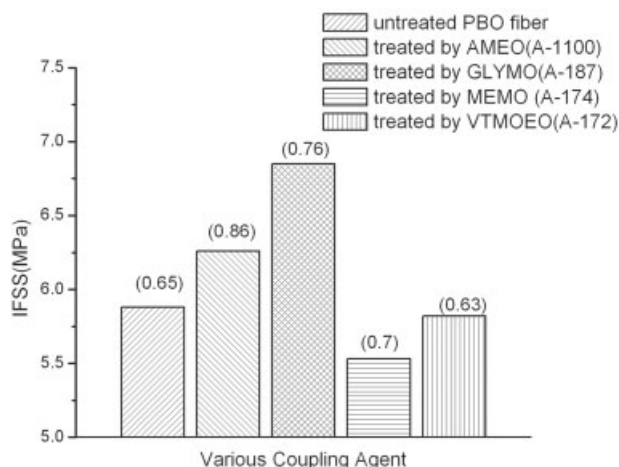


Figure 1 Effect of various coupling agents on the interfacial shear strength (IFSS) of PBO fiber-epoxy system (standard deviations are in parentheses).

America) through nitrogen adsorption at 77.4 K. The specific surface area was determined from the nitrogen adsorption isotherms, using the equation of B.E.T.

Elemental composition of the fibers' surface

The surface elemental compositions of the fiber samples were determined by X-ray photoelectron spectroscopy (XPS) using Physical Electronics ESCA PHI-5400. The vacuum chamber was pumped to 10^{-9} Torr. The sampling depth was less than 5 nm.

RESULTS AND DISCUSSION

Effect of the treatment conditions on the IFSS of PBO fibers/epoxy resin

Figure 1 shows the effect of the various coupling agents on the IFSS of PBO fibers/epoxy resin. The untreated samples exhibited an IFSS of 5.88 MPa and the samples treated by A-187 showed the highest IFSS, 6.85 MPa. A-187 has glycidyl groups, which can join the curing reaction of the epoxy resin and form a firm interfacial layer, and so it can improve the IFSS more when compared with other coupling agents. In the following experiments, coupling agent A-187 was chosen. Figure 2 shows the effect of the treatment time of argon plasma on the IFSS. The IFSS experienced a tendency to first increase and then decrease with increasing time. This phenomenon was based on the roughness, the number of the active polar groups, and free radical introduced on the fiber surface by argon plasma. The number of the active polar groups and free radical increased with increasing time. In a short time argon plasma acted only on the fiber surface. The increased roughness led to an increase in friction between the fiber and the resin. But when the treated

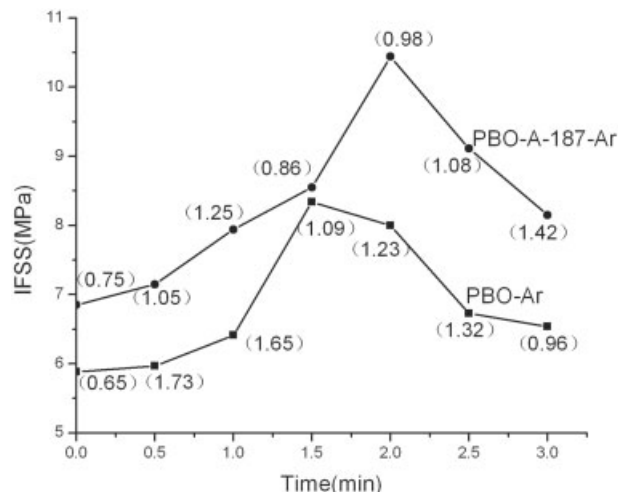


Figure 2 Effect of the treatment time of argon plasma on the IFSS of PBO fiber-epoxy system (standard deviations are in parentheses).

time was too long, the etching effects acted not only on the fiber surface but also on the core of the fiber, and produced the fragment that formed the weak interfacial layer. When the action of the weak interfacial layer became dominating, the IFSS started to reduce. At the set pressure and power, the IFSS of PBO fibers treated by argon plasma reach the highest of 8.34 MPa when the treatment time was 1.5 min, and the highest IFSS of the fibers treated by the argon plasma combined with the coupling agents was 10.44 MPa when the treatment time was 2 min. The optimal treatment time was protracted to 2 min because the fibers had a protective layer of the coupling agents.

Figure 3 shows the effect of the pressure of argon plasma on the IFSS. When the pressure was increased, the number of the polar groups introduced on the

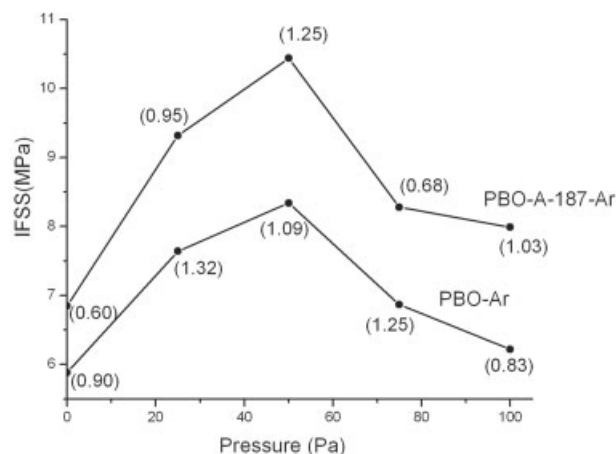


Figure 3 Effect of the pressure of argon plasma on the IFSS of PBO fiber-epoxy system (standard deviations are in parentheses).

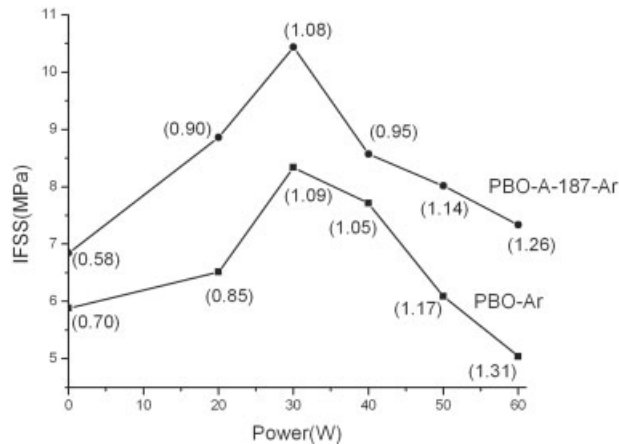


Figure 4 Effect of the power of argon plasma on the IFSS of PBO fiber-epoxy system (standard deviations are in parentheses).

fiber surface also increased. But when the pressure was increased too much (e.g. 100 Pa at low power), the number of the particles increased, which resulted in a decrease in the average energy of every particle and the mean free paths of the electron would be short. So it was difficult for the electron to accumulate the energy needed for the ionization between the intervals of the collision, and the number of the ionization active particles decreased. So there was a reasonable treated pressure. When the pressure was 50 Pa, the IFSS was maximal, as shown in Figure 3.

Figure 4 shows the effect of the power of argon plasma on the IFSS. When the treating power was increased, the voltage between the two pole boards increased, the ionization and the movement of the gas enhanced, and the etching action of plasma increased as well. When the power was less than 30 W, the IFSS increased with increasing power. Greater power (exceeding 30 W) did not improve the IFSS further. The etching effect of the plasma not only increased the roughness of the fiber surface but also destroyed the fiber core layer and produced the fragment that formed the weak interfacial layer. When the power was 30 W, the IFSS was maximal, as shown in Figure 4.

Figure 5 shows the effect of the concentration of the coupling agents on the IFSS. The IFSS was maximal when the concentration of A-187 was 2 wt %. It could be inferred that excess or insufficient coupling agents was not good for the IFSS.

The IFSS of PBO fibers treated by argon plasma and argon plasma combined with coupling agents were 8.34 and 10.44 MPa respectively (Figs. 2–5). The increase ratio of the IFSS was 42 and 78%, respectively, when compared with that of the untreated samples (5.88 MPa).

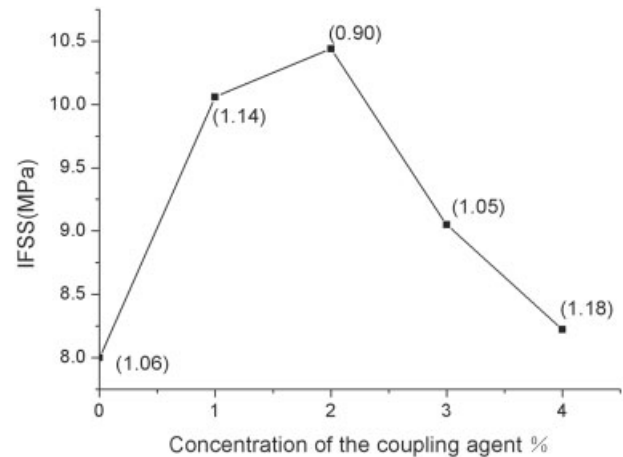


Figure 5 Effect of the concentration of the coupling agent (A-187) on the IFSS of PBO fiber-epoxy system (standard deviations are in parentheses).

Effect of the treatment conditions on the SFTS

The effect of the treatment conditions, such as the treatment time, pressure, and power of argon plasma, as well as the concentration of A-187, on the SFTS of PBO fibers are reported in Figures 6–9. The SFTS monotonically decreased with the increasing treatment time and power, as shown in Figures 6 and 7. PBO fibers exhibited a decrease in SFTS with increasing pressure from 25 to 75 Pa, and pressure greater than 75 Pa did not further decrease the SFTS, as shown in Figure 8. Figures 6–8 show that the coupling agents prevent the decrease of SFTS of the PBO fibers. At low concentrations (such as 1, 2%), the protective action of the couple agents was obvious, as shown in Figure 9. When the concentration of the coupling agents was 1

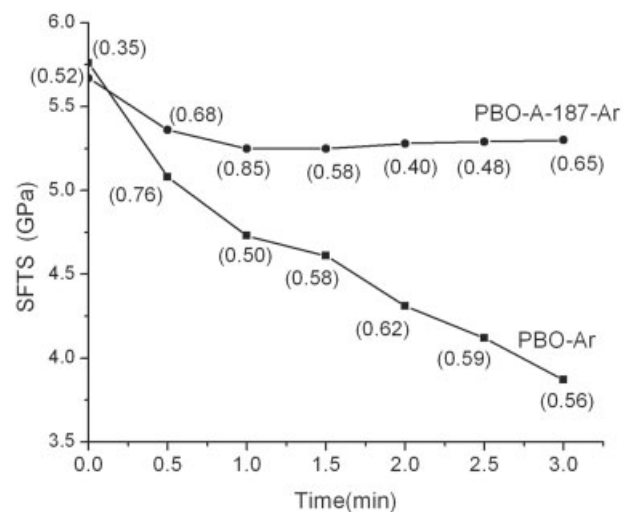


Figure 6 Effect of the treatment time of argon plasma on the single fiber tensile strength (SFTS) of PBO fiber (standard deviations are in parentheses).

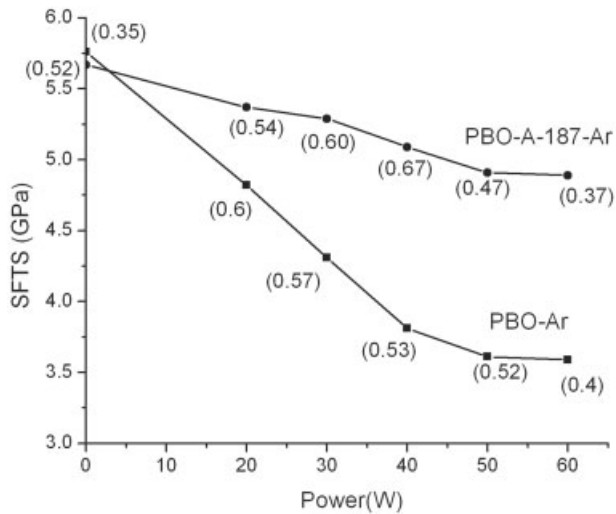


Figure 7 Effect of the power of argon plasma on the SFTS of PBO fiber (standard deviations are in parentheses).

and 2%, the SFTS were 5.15 and 5.28 GPa respectively, which were higher than those of the fibers treated by argon plasma (4.31 GPa). But the SFTS, at higher concentrations, increased slowly. It can be deduced that the coupling agents have a protective action on the SFTS of the fibers.

Wettability

Through the droplet profile analysis method, the contact angle of the fibers to water was measured. The contact angle of the untreated fibers to water was more than 90° , whereas that of the fibers treated by argon plasma and argon plasma combined with coupling agents were 55.5° and 54.5° , respectively. After the modification, the wettability of the fibers was improved. These improvements of the wettability would

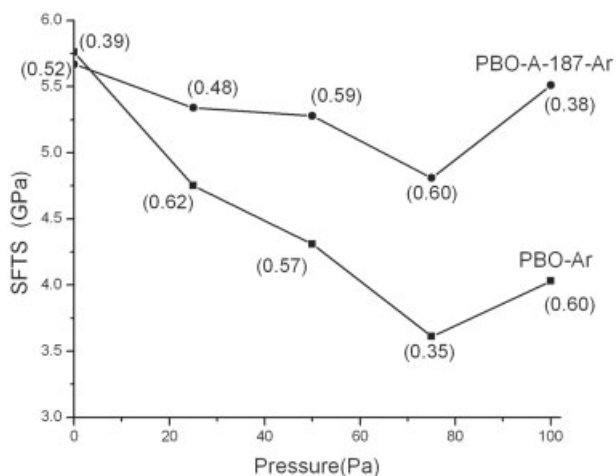


Figure 8 Effect of the pressure of argon plasma on the SFTS of PBO fiber (standard deviations are in parentheses).

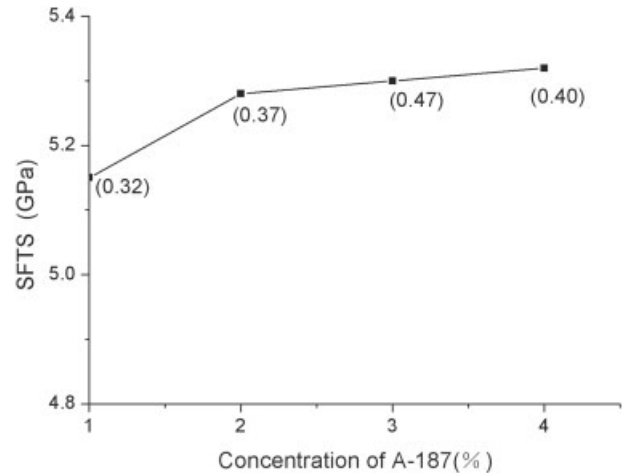


Figure 9 Effect of the concentration of the coupling agent (A-187) on the SFTS of PBO fiber (standard deviations are in parentheses).

be another decisive factor to enhance the IFSS of PBO fibers/epoxy resin.

Attenuation phenomena

To investigate the attenuation phenomena of the treated fibers, the attenuation of the wettability and the IFSS of the fibers were studied. Figure 10 shows the attenuation of the wettability of the fibers. The contact angle of the fibers treated by argon plasma increased significantly with increasing time, whereas that of the fibers treated by argon plasma combined with coupling agent changed a little with increasing time, as shown in Figure 10. Similarly, Figure 11 shows the attenuation of the IFSS of the fibers. The IFSS of the fibers treated by argon plasma decreased

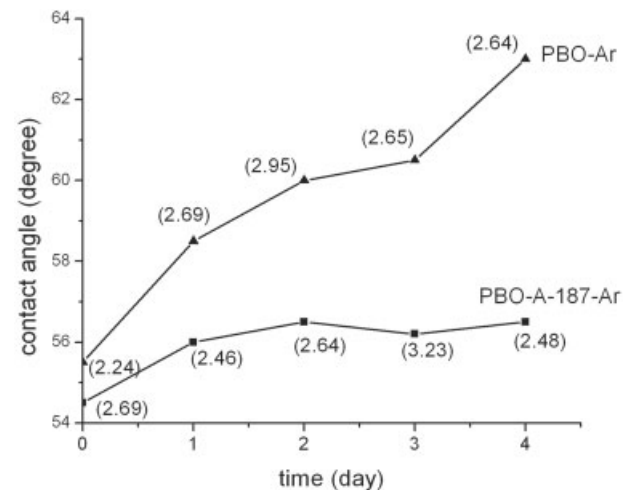


Figure 10 The attenuation of the contact angle between PBO fiber and water (standard deviations are in parentheses).

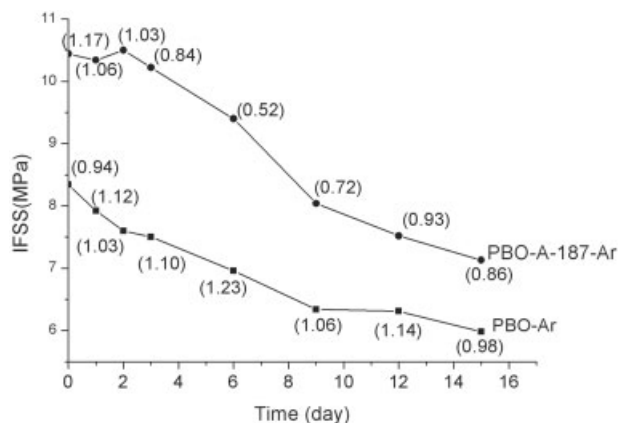


Figure 11 The attenuation of the IFSS of PBO fiber–epoxy system (standard deviations are in parentheses).

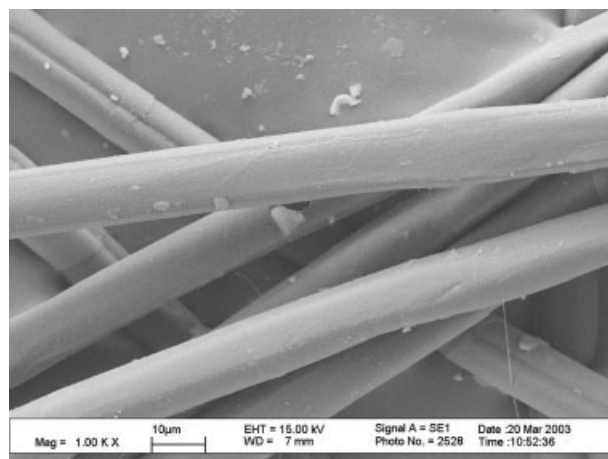
prominently with increasing time, but the attenuation of the fibers treated by argon plasma combined with coupling agents was inhibited by the pretreatment with the coupling agents. From the results of the attenuation phenomena, it can be deduced that the polarity and free radical content of the fibers also affected the results of the IFSS and the wettability, in addition to the surface roughness of the fibers.

SEM of PBO fibers

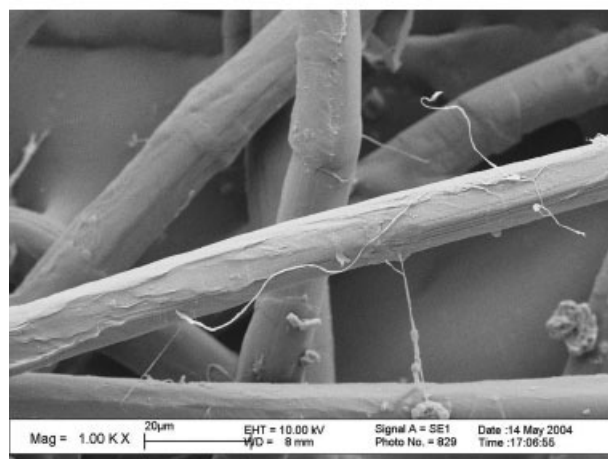
SEM micrographs of the fiber surface are showed in Figure 12(a–c). The surface of the untreated PBO fibers was smooth; after modification, the fiber surface became rough. The fiber surface treated by argon plasma was etched and the microfilament structure was exposed, as shown in Figure 12(b). Figure 12(c) shows that the coupling agent formed a protective layer on the fiber surface and the etching of the argon plasma was palliated. The coupling agents still existed, though the fibers were washed by acetone for 72 h. There was a chemical bond between the fibers and the coupling agents; in addition, the coupling agent A-187 had a glycidyl group, and so the IFSS of PBO fibers/epoxy resin was improved further.

FTIR spectra of PBO fibers

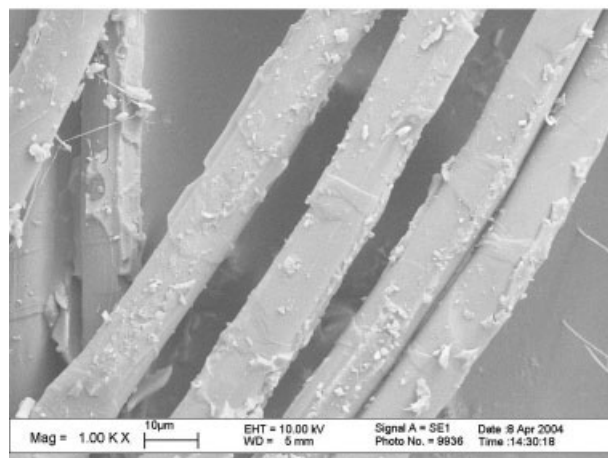
Figure 13 shows FTIR spectra of the untreated and treated fibers. A new peak appeared in the range of $3300\text{--}3500\text{ cm}^{-1}$ for the treated sample. It is well known that the position of the band for free hydroxyl groups is normally observed around 3500 cm^{-1} .²⁵ Two assumptions can be used to explain for this new peak. The first one is the presence of strong hydroxyl groups due to water molecules adsorbed by the fibers. The second is the hydroxyl group caused by argon plasma treatment. The presence of strong hydroxyl groups made the polarity of the fiber increase, and so



(a)



(b)



(c)

Figure 12 SEM micrographs of the samples for argon plasma treatment process: (a) the untreated PBO fiber, (b) PBO-Ar (PBO fiber treated by 30 W, 50 Pa for 1.5 min of argon plasma), and (c) PBO-A-187-Ar (PBO fiber treated by A-187, and then by 30 W, 50 Pa for 2 min of argon plasma).

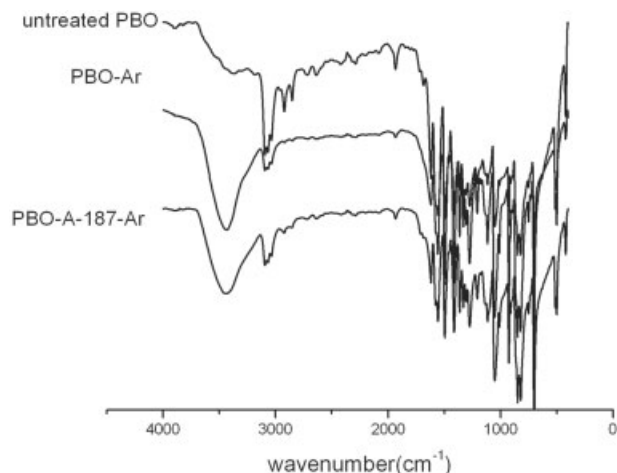


Figure 13 FTIR of the untreated PBO fiber, PBO-Ar (PBO fiber treated by 30 W, 50 Pa for 1.5 min of argon plasma), and PBO-A-187-Ar (PBO fiber treated by A-187, and then 30 W, 50 Pa for 2 min of argon plasma).

the adhesion between the fiber and the resin was improved. The IFSS was also improved.

Specific surface area

Table II presents the results of the specific surface area of the untreated and treated fibers. It showed a big increase due to the modification of argon plasma and argon plasma combined with the coupling agents. The specific surface area of PBO treated by argon plasma increased more than that of PBO treated by argon plasma combined the coupling agents. The phenomena were attributed to the skin-core structure of PBO fiber. There is a void-free region in the surface of the fiber and a void region in the core of the fiber. The thickness of the skin layer was $\approx 0.2 \mu\text{m}$. The skin of PBO treated by argon plasma was damaged much and revealed the core, which had many voids through which nitrogen could more easily penetrate. According to the B.E.T equation, the value of the specific surface area was large if much nitrogen was absorbed. So the specific surface area of PBO treated by argon plasma was larger than that of PBO treated by argon plasma with coupling agents. The etching action of argon plasma on the fiber surface may be inhibited by the layer of the coupling agents, as seen in the SEM micrographs, and so the specific surface area of PBO

TABLE II
The Specific Surface Area of PBO Fibers

Sample	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
PBO	0.73
PBO-Ar	1.34
PBO-A-187-Ar	1.09

TABLE III
XPS Analysis of the Surface Elemental Composition of PBO Fibers

Sample	C	O	N	Si	O/C	N/C
PBO theory value	73.7	14.0	12.3		0.190	0.167
PBO actual value	76.6	14.1	9.3		0.184	0.121
PBO-Ar	78.2	16.1	5.7		0.205	0.073
PBO-A-187-Ar	61.8	28.4	3.0	6.8	0.460	0.049

fiber treated by argon plasma combined coupling agents was smaller than that of PBO fiber treated by argon plasma. The results can also be used to explain that the SFTS of PBO treated by argon plasma decreased more when compared with that of the PBO treated by argon plasma combined with coupling agents.

X-ray photoelectron spectroscopy

The surface elemental compositions of the samples were determined by XPS. Though hydrogen did exist, it was too light to be detected. The results of XPS measurement of the samples are shown in Table III.

The theoretical composition of PBO fibers, according to the structure formula, are 2 oxygen atoms, 2 nitrogen atoms, and 14 carbon atoms per repeat unit of PBO fiber. From the results of XPS, it can be confirmed that the surface composition of the fibers was different from that of the bulk composition. At the surface, the carbon content of the untreated fibers was higher than that of the theoretical value. After modification, the surface content of carbon markedly decreased and the surface content of oxygen increased; the surface oxygen-to-carbon (O/C) ratios increased and the surface nitrogen-to-carbon (N/C) ratios decreased. This might result from argon plasma and argon plasma combined with coupling agents introducing the polar groups onto the fiber surface, and more polar groups were introduced to the surface of PBO treated by argon plasma combined with coupling agents. From the results of XPS, it can be stated that the introduction of the polar groups on the fiber surface was the most decisive contribution to improve the adhesion between the fiber and the resin, which can explain why the specific surface area of PBO treated by argon plasma combined with coupling agents was smaller than that of PBO treated by argon plasma: because more polar groups were introduced to the surface of the fiber treated by argon plasma combined with coupling agents; hence, the IFSS of the fiber treated by argon plasma combined with coupling agents was larger.

CONCLUSIONS

PBO fiber surfaces were modified by argon plasma and argon plasma combined with coupling agents.

When the treatment time was 1.5 min, power was 30 W, and pressure was 50 Pa under argon atmosphere, the IFSS increased from 5.88 to 8.34 MPa, an increase by 42% when compared with that of the untreated samples. However, when the fibers were pretreated by the solution of the coupling agent A-187 with 2% concentration and then treated by argon plasma at 30 W under 50 Pa for 2 min, the IFSS increased from 5.88 to 10.44 MPa, an increase by 78% when compared with that of the untreated samples. The surface oxygen contents, oxygen-to-carbon (O/C) ratios, and the specific area of the treated PBO were increased. Through the modification of argon plasma combined with coupling agents, the IFSS and the wettability of PBO fibers was improved more, and the attenuation phenomena were inhibited by the pretreatment of the coupling agent A-187. It has been suggested that argon plasma combined with coupling agents is an effective process for PBO fiber while its excellent tensile mechanical strength can be retained.

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