

## Tribological Properties of PBO Fabric Composites Modified by Poly (vinyl alcohol)

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**ABSTRACT:** Friction and wear behaviors of poly (vinyl alcohol) (PVA) modified PBO fabric composites were evaluated in a pin-on-disc friction and wear tester, and the relationship between the properties and the structure change resulting from PVA modification were intensively investigated using thermogravimetric analysis (TG) and scanning electronic microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The results indicated that the PVA thin film formed on the fabric surface by chemical cross-linking reaction could improve the antiwear property of the PBO fabric composites efficiently. In argon-300°C condition, the antiwear property of the PBO fabric composites was improved by 35%, which was due to the improvement of the bonding strength between the fabric and resin and the dispersion of the shear stress induced by the shear creep and plastic deformation of the PVA film in friction. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1313–1320, 2013

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### INTRODUCTION

Fabric composites are highly attractive because they are lightweight, tougher, extremely tolerant to impact force and more flexible than conventional polymers and metals.<sup>1,2</sup> Besides, their properties and forms can be tailored to meet the needs of specific applications such as bulletproof composite materials and advanced bearing liner materials. Poly (1, 4-phenylene-*cis*-benzobisoxazole) (PBO), aromatic heterocyclic rigid-rod polymeric fibers, have a wide application in military and business fields due to their excellent mechanical property, flame resistance, thermal stability, and good resistance to creep, chemicals, and abrasion.<sup>3,4</sup> Especially, PBO fibers alone or blended with other fibers are used to fabricate particular composites with adhesive in the form of fabric.<sup>5</sup> It is essential and significant to study the mechanical and tribological properties of the fabric composites.

However, the interfacial bond between the PBO fiber and adhesive is poor because the PBO fiber surface is chemically inert and relatively clean, induced by its high crystallinity and the lack of polar functional groups in the polymer repeat unit.<sup>6,7</sup> Therefore, the modification of PBO fiber surface is of great importance in the field of composites, as the mechanical and tribological properties of the composites are dependent on the quality of the fiber/matrix interface.

Coating, surface polymerization, catalytic polymerization of monomers, and plasma polymerization are the most frequently used surface modification methods. Of these, the dip-coating is a facile and effective physical modification method of fiber materials. Dip-coating<sup>8–10</sup> can form a thin polymer film with certain combination strength on the surface of fibers or fabrics. After modification, the intrinsic strength of fibers as well as the physical and chemical properties of the coated polymer film can be maintained. Also, dip-coating modification may change the properties and molecular structure of the fabric surface, and then change the tribological properties of the fabric composites. Poly(vinyl alcohol) (PVA) is a non-toxic and low-cost linear poly-hydroxyl polymer, which has better filming properties, chemical stability, coating properties, tear resistance, and wear resistance.<sup>11,12</sup> It has been used as ideal coating modifiers to improve the properties of cellulosic fabric,<sup>13</sup> polypropylene non-woven fabric,<sup>14,15</sup> nanofibrous scaffold,<sup>16</sup> and hybrid fiber,<sup>17</sup> and the satisfactory coating effect was achieved. In addition, the moderate thermal treatment of PVA may generate carbon with the maximum yield of amorphous carbon.<sup>18</sup> Thus, PVA can be used as potential and promising coating modifiers to improve the tribological and interfacial bonding properties of high-performance fiber (PBO). However, no relevant research was reported about this to the best of our knowledge.

Based on above background, we choose PVA as the modifier to modify PBO fabric by a dip-coating method, and concentrate on the experimental determination and interpretation of tribological properties of PBO fabric composites modified with PVA. This research work also extends high-level applications of PBO fabric composites in dry-sliding bearing liner materials and bulletproof composite materials.

## EXPERIMENTAL

### Materials

The PBO fabric (plain woven fabric with the area density of 98 g/m<sup>2</sup>) used in this study was purchased from Du Pont which was woven from PBO fiber with the fineness of 278 dtex. The phenolic-resin adhesive was provided by Shanghai Xing-guang Chemical Plant, China. PVA with hydrolyzing degree of 99% and average molecular weight of 70 kDa was obtained from SCRC chemical Limited Company (Shanghai, China). Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 86%) was purchased from Tianjin Chemical Plant, China.

### Specimen Preparation

The aqueous solution of PVA was prepared by dissolving 4 g of PVA in 40 mL of distilled water at 90°C, followed by cooled to room temperature. Then, 6 mL of H<sub>3</sub>PO<sub>4</sub> was dropwise added to the PVA solution under continuous mechanical stirring until a homogeneous solution was formed. PBO fabric was fully immersed in the solution, and then dried in the cold air. The dried PBO fabric was placed in a tubular furnace and thermally treated at 150°C for 180 min, following at 300°C or 500°C for 60 min under air or argon atmosphere, respectively. Finally, the fabric was successively washed with distilled water, 0.5 mol/L NaOH solution, 0.5 mol/L HCl solution, and distilled water, and dried under vacuum. The carbonized PVA-modified PBO fabric was impregnated in the adhesive and dried. The relative mass fraction of the PBO fabric was about 65 ± 5%. The impregnated fabric was bonded on the surface of AISI-1045 steel (surface roughness  $R_a = 0.45 \mu\text{m}$ ) with the adhesive to fabricate fabric composites and then cured at 180°C for 2 h under the pressure of 0.15 MPa. For comparison, the unmodified PBO fabric composites (denoted as PFC) were prepared in the same way.

### Friction and Wear Test

The friction and wear behaviors of the PBO fabric composites were investigated using a Xuanwu-III pin-on-disk friction and wear tester (Figure 1). The pin-on-disk tester consisted of loading a stationary pin sliding against a rotating disk which was affixed with the PBO fabric composites. The flat-ended AISI-1045 pin (diameter 2 mm) was fixed to the load arm with a chuck. The distance between the centre of the pin and axis is 12.5 mm. The pin stayed over the disc with two degrees of freedom: a vertical one, which allowed normal load application by direct contact with the disc, and a horizontal one, for friction measurement.

Prior to the tests, the pin was polished with 350, 700, and 900 grade water-proof abrasive papers to a surface roughness  $R_a = 0.15 \mu\text{m}$ , and then cleaned with acetone. The sliding was performed at room temperature, with a speed of 0.26 m/s, a

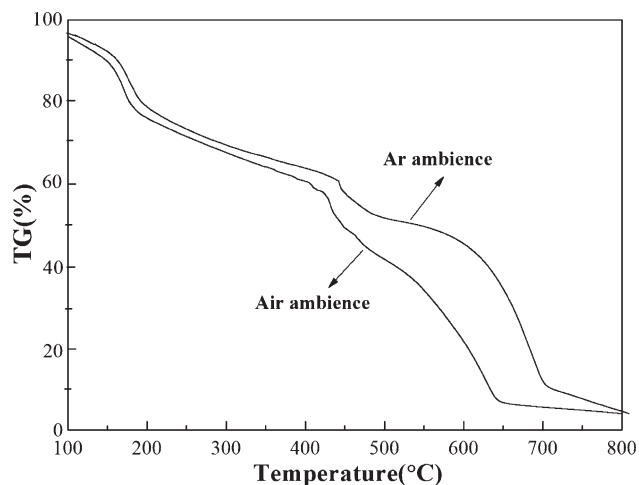


Figure 1. TGA curves of crosslinked PVA in different ambience.

load between 156.8~219.52 N and over a period of 2 h under dry sliding conditions. At the end of each test, the wear volume loss ( $V$ ) of the composites was calculated by measuring the depth of the wear scar using a micrometer with 0.001 mm resolution. The wear performance was expressed in terms of wear rate [ $w, \text{m}^3 \cdot (\text{N} \cdot \text{m})^{-1}$ ], eq. (1):

$$w = V/p \cdot L \quad (1)$$

where  $V$  is the wear volume loss in m<sup>3</sup>;  $P$  the load in Newton (N);  $L$  the sliding distance in meter (m). The friction coefficient was measured from the frictional torque gained by a load cell sensor, which obtained directly from the computer running the friction-measure software. Each experiment was carried out three times and the averages were used.

### Bonding Strength Test

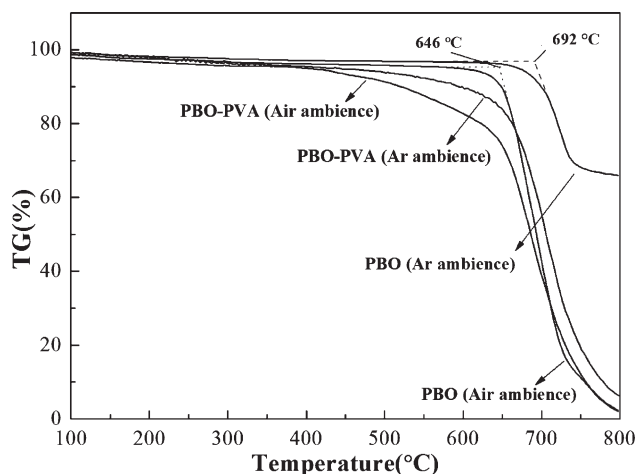
The bonding strength of the PBO fabric composites was determined using a DY35 universal materials test machine at a constant speed of 50 mm/min. Typically, PBO fabric was fully immersed in the PVA solution, and then dried in air. The immersion process was repeated for different times. For each time, the PVA modified fabric was labeled as PVA- $x$  ( $x$  denotes the immersion times, and is equal to 1, 2, 3, 4, 5). Before carrying out the bond property testing, the impregnated PBO fabric was cut into test pieces about 20 mm in length and 13 mm in width. Then the test piece was affixed between two 1Cr18Ni9Ti stainless steel plates with the adhesive and then cured at 180°C for 2 h under the pressure of 0.15 MPa. The bonding strength  $\tau$  (MPa) can be calculated using eq. (2).

$$\tau = F/L \cdot B \quad (2)$$

where  $F$  is the maximal pull force in Newton (N);  $B$  is the width in meter (m);  $L$  the length in meter (m). Each experiment was carried out six times and the averages were used.

### Analysis of PBO Fibers and Composites

Thermogravimetric (TG) analysis was carried out on a NETZSCA STA449C apparatus under air or nitrogen



**Figure 2.** TGA curves of pure and PVA impregnated PBO fibers in different ambience.

atmosphere at a flow rate of  $20 \text{ cm}^3 \cdot \text{min}^{-1}$ . The heating rate was  $10^\circ\text{C} \cdot \text{min}^{-1}$ , ranging from room temperature to  $800^\circ\text{C}$ . The surface morphology and EDS analysis of PVA-modified fabric were observed by JSM-5600LV scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer. The worn surfaces of the composites and the counterpart pin were also analyzed using SEM.

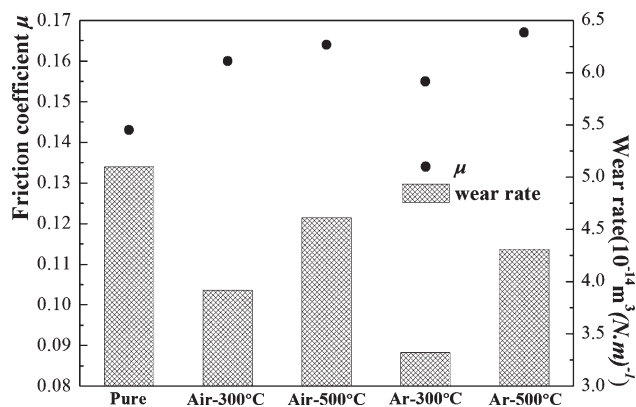
## RESULTS AND DISCUSSION

### TG Analysis

PVA polymer has outstanding chemical and thermal stabilities due to its strictly linear structure and hydrogen bonds among polymer chains. After heating treatment in the presence of  $\text{H}_3\text{PO}_4$ , the crosslinking reaction occurred and formed a network constitution with C, O, and P elements, and the mechanical strength and thermal stability of PVA will be further improved.<sup>19</sup> Further heating results in the decomposition of crosslinked PVA, and the pyrolysis rate is not identical in different atmosphere. Figure 1 shows TGA curves of crosslinked PVA in air and argon atmospheres. Two major weight losses were observed for crosslinked PVA. In the temperature range  $100\text{--}200^\circ\text{C}$ , crosslinked PVA will decompose partially and lose some small molecules, but still a network polymer. The crosslinked PVA will be decomposed and carbonized at high temperature. Two major weight losses appear at  $157$  and  $415^\circ\text{C}$  in air condition and at  $164$  and  $445^\circ\text{C}$  in argon condition. Crosslinked PVA has better thermal stability in argon than that in air. At  $300^\circ\text{C}$ , crosslinked PVA has a weight loss of  $26\%$  in air and  $24\%$  in

**Table I.** Bonding Strength of Unmodified and PVA-Modified PBO Fabric Composites

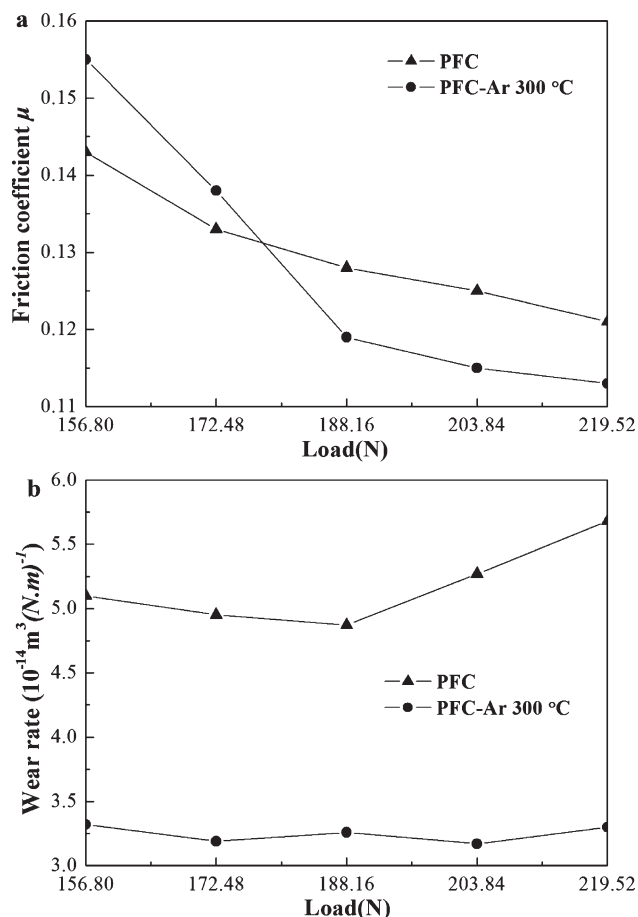
Samples	Unmodified					
	PBO	PVA-1	PVA-2	PVA-3	PVA-4	PVA-5
Bonding strength (MPa)	7.49	7.60	10.4	10.3	9.2	9.2



**Figure 3.** Comparison of friction and wear rate of composites with different modification ( $156.8 \text{ N}$ ,  $0.26 \text{ m/s}$ ).

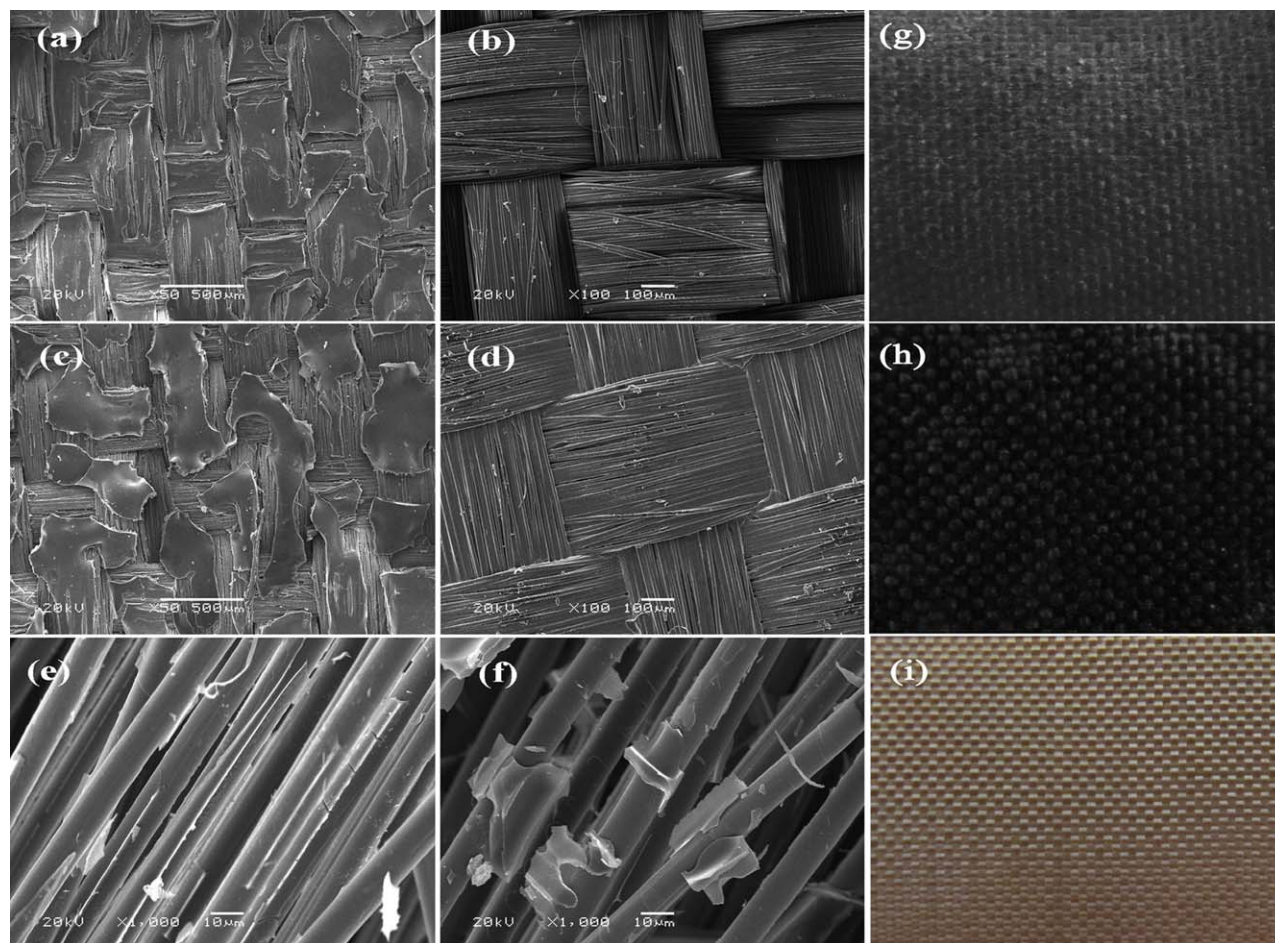
argon, whereas the weight loss reached  $47\%$  in air and  $38\%$  in argon at  $500^\circ\text{C}$ . In the whole temperature range, the weight loss of crosslinked PVA in air is greater than that in argon.

PVA-modified PBO fabric is prepared by immersing the fabric in a mixture of PVA and phosphoric acid, following by a heat treatment process. This results in crosslinking reaction and filming on the fabric surface. However, phosphoric acid will decrease the mechanical strength and thermal stability of the



**Figure 4.** Variation of friction coefficient (a) and wear rate (b) with load for two composites.





**Figure 5.** SEM images of fabric surfaces of (a) Air-300°C, (b) Air-500°C, (c) Ar-300°C  $\times$  50, (d) Ar-500°C  $\times$  100, (e) Ar-300°C  $\times$  1000, (f) Ar-500°C  $\times$  1000; and the digital photos of (g) Air-500°C, (h) Ar-500°C, and (i) unmodified PBO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

PBO fiber in the modified process because of its corrosive. Figure 2 shows TGA results of the unmodified and PVA-modified PBO fiber in air and argon. For the unmodified PBO fiber, the decomposition temperature is 646 and 692°C, and the residual mass fraction is 2 and 67% at 800°C in air and argon, respectively. The unmodified PBO fiber does not decompose below 600°C in air or argon, and the fiber strength does not decrease either. For PVA-modified PBO fiber, the pyrolysis rate, and residual mass fraction are different in different atmosphere. The weight loss is 6% at 300°C and 10% at 500°C, and the residual mass fraction is 2% at 800°C in air. Under argon, the weight loss is 5% at 300°C and 7% at 500°C, and the residual mass fraction is 5% at 800°C. After the modification of PVA, the pyrolysis rate of PBO fiber increases, especially at high temperature, while the mechanical strength of the fiber is decreased.

#### Mechanical Properties

Table I lists the bonding strength of the unmodified and PVA-modified PBO fabric composites. When the immersion process was repeated for two or three times, the bonding strength of the modified PBO fabric composite was enhanced by 38 ~ 39% in contrast to the unmodified one. This can be ascribed to the

enhancement of the fabric surface energy. Because the better bonding strength is the important premise of developing the tribological properties of composite, the PVA-2 sample with the best bonding strength was chosen to evaluate the tribological behavior of the composites.

#### Tribological Properties

The friction coefficient and wear rate of the PBO fabric composites modified under different conditions are shown in Figure 3. As can be seen, the friction coefficients of the modified fabric composites are higher than that of unmodified PBO fabric composites. The friction coefficient of pure PBO fiber is very low because that the fiber surface is quite smooth. After the fabric surface was covered by PVA film (300°C) or carbon powder (500°C), the fabric surface roughness was increased, and which caused the increase of friction coefficient of the composites. However, the PVA modification clearly improved the antiwear ability of the composites. When the modification temperature is 300°C, the PVA film formed on the fabric surface, resulting in improvement of the bonding strength between the fiber and resin and filling the interspaces in fabric structure and optimizing the overall structure of the composites, thereby reducing the wear rate of the composites. When the temperature was

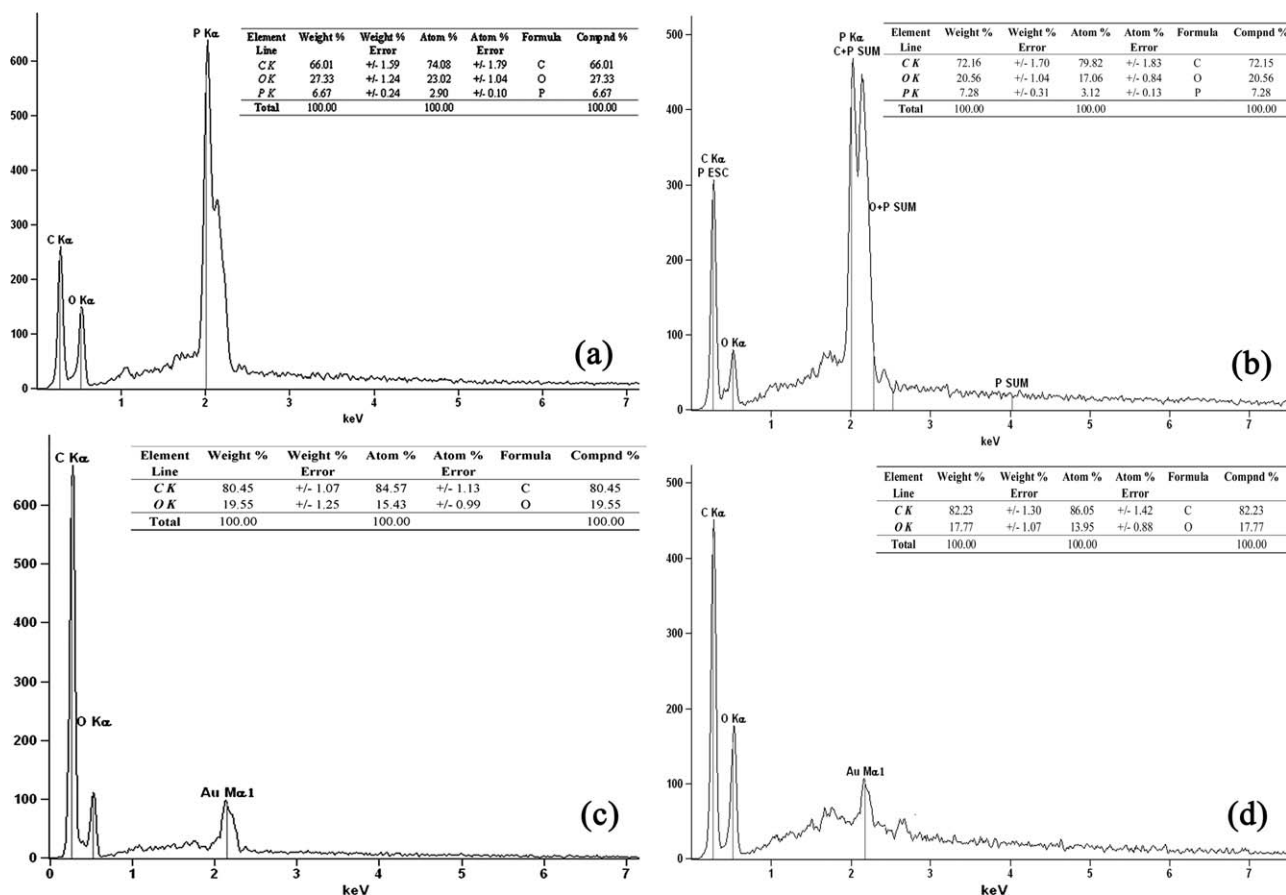


Figure 6. Element analysis of fabric surfaces of (a) Air-300°C, (b) Ar-300°C, (c) Air-500°C, and (d) Ar-500°C.

enhanced to 500°C, the residual carbon powder on the fabric surface plays a lubrication role and thus reduces the wear rate of the composites. At the same temperature, the PVA film or residual carbon powder on the fabric surface for the modified sample in air is less than that in argon, and the strength of fiber is decreased, so the wear rate of the composites modified in air is higher. As expected, the PVA modified PBO fabric composites at 300°C in argon show the best antiwear performance.

Friction coefficient and wear rate of the unmodified and PVA-modified PBO fabric composites at 300°C in argon as a function of the load were shown in Figure 4. The friction coefficients of two composites decrease with increasing load. The friction surface temperature risen with increasing load, which results in the softening of the composites surface, and thus reduces the friction coefficient. For the PVA modified composites, the softening degree becomes obvious with increasing the friction surface temperature due to the presence of the PVA film, which reduces the friction coefficient largely. Under different loads, the wear rate of the PVA modified composites is steady and obviously lower than that unmodified, and almost keeps constant with increasing load. This indicates that the modification of PBO fabric composites with PVA is favorable to improve the antiwear property.

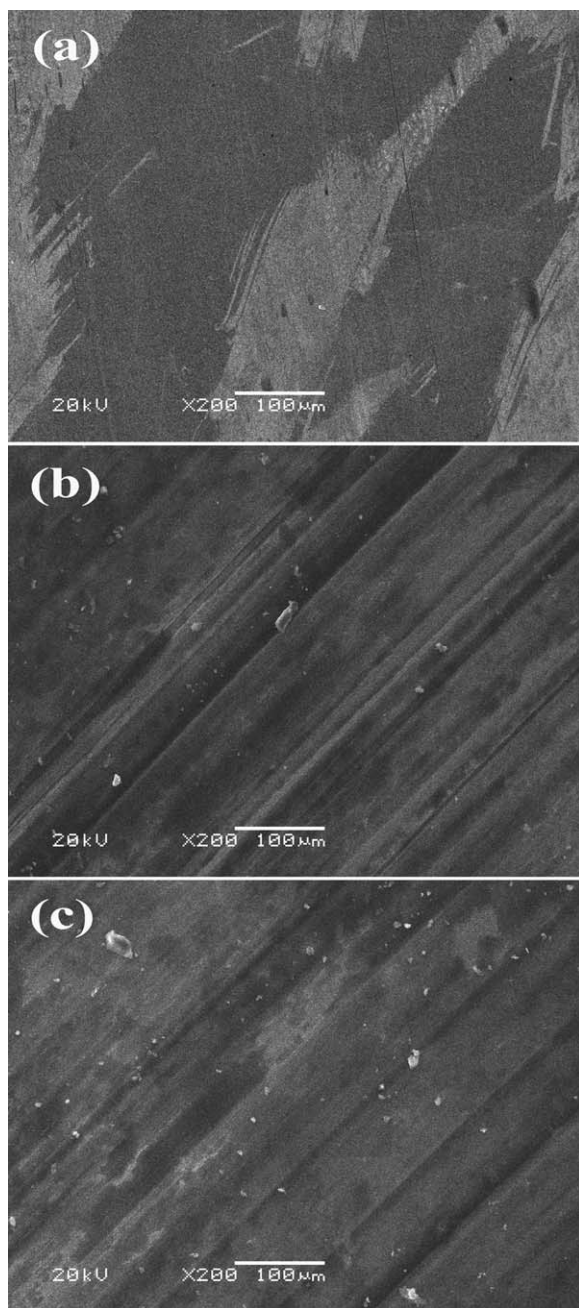
### SEM Analysis

Figure 5 shows the micrographs of the PBO fabric surface modified in different conditions. As can be seen, the

discontinuous PVA film was observed on the surface of the fabrics modified at 300°C in air [Figure 5(a)] or argon [Figure 5(c)], indicating that the crosslinking reaction occurs during the heating treatment process. Whereas the thickness of the film formed in argon [Figure 5(c)] are slightly larger than that formed in air [Figure 5(a)]. In air-500°C condition, there is a little residual carbon powder on the fabric surface instead of flaky PVA film, and the fiber bundles can be clearly observed [Figure 5(b)]. In argon-500°C condition [Figure 5(d)], there may have much residual carbon powder on the fabric surface. For proving the existence of carbon powder, the digital photos of the PBO fabric modified at 500°C in air and Ar atmospheres were taken and shown in Figure 5(g,h). It is obvious that the surface of yellow PBO [Figure 5(i)] becomes black after heating treatment, which implied the existence of carbon. Whereas, the EDS results of the modified PBO fabric surfaces was shown in Figure 6 (as discussed below), which also confirmed that the content of carbon in the PBO fabric modified at 500°C in Ar is higher than that in air. It can be seen from enlarged micrographs [Figure 5(e, f)] that the residual crosslinked polymer was clearly reduced after treated at 500°C due to the carbonization process.

In Figure 6, in both air-300°C and Ar-300°C conditions [Figure 6(a, b)], there are mainly C, O, and P elements on the fabric surface. In the presence of H<sub>3</sub>PO<sub>4</sub>, crosslinking and dehydration





**Figure 7.** SEM images of counterpart surfaces of (a) pure, (b) Air-300°C, (c) Ar-300°C (156.8 N, 0.26 m/s).

reaction of PVA leads to form a network polymer containing P–O–C structure.<sup>20</sup> The crosslinked polymer coated on the fabric surface enhanced significantly the surface energy of fabric. This results in the improvement of the bonding strength between the fiber and the resin. In air-500°C and Ar-500°C conditions [Figure 6(c, d)], the crosslinked PVA could be decomposed and carbonized.<sup>19</sup> The P–O bonds were broken and the –OH of PVA was dehydrated,<sup>19,20</sup> and the P elements were eliminated by the heat treatment and subsequent washing process. Thus the P elements fail to be detected in the fabric modified at Air-500°C and Ar-500°C, and the content of C element increases from 66% to 80%. By comparing the carbon content of the fabrics

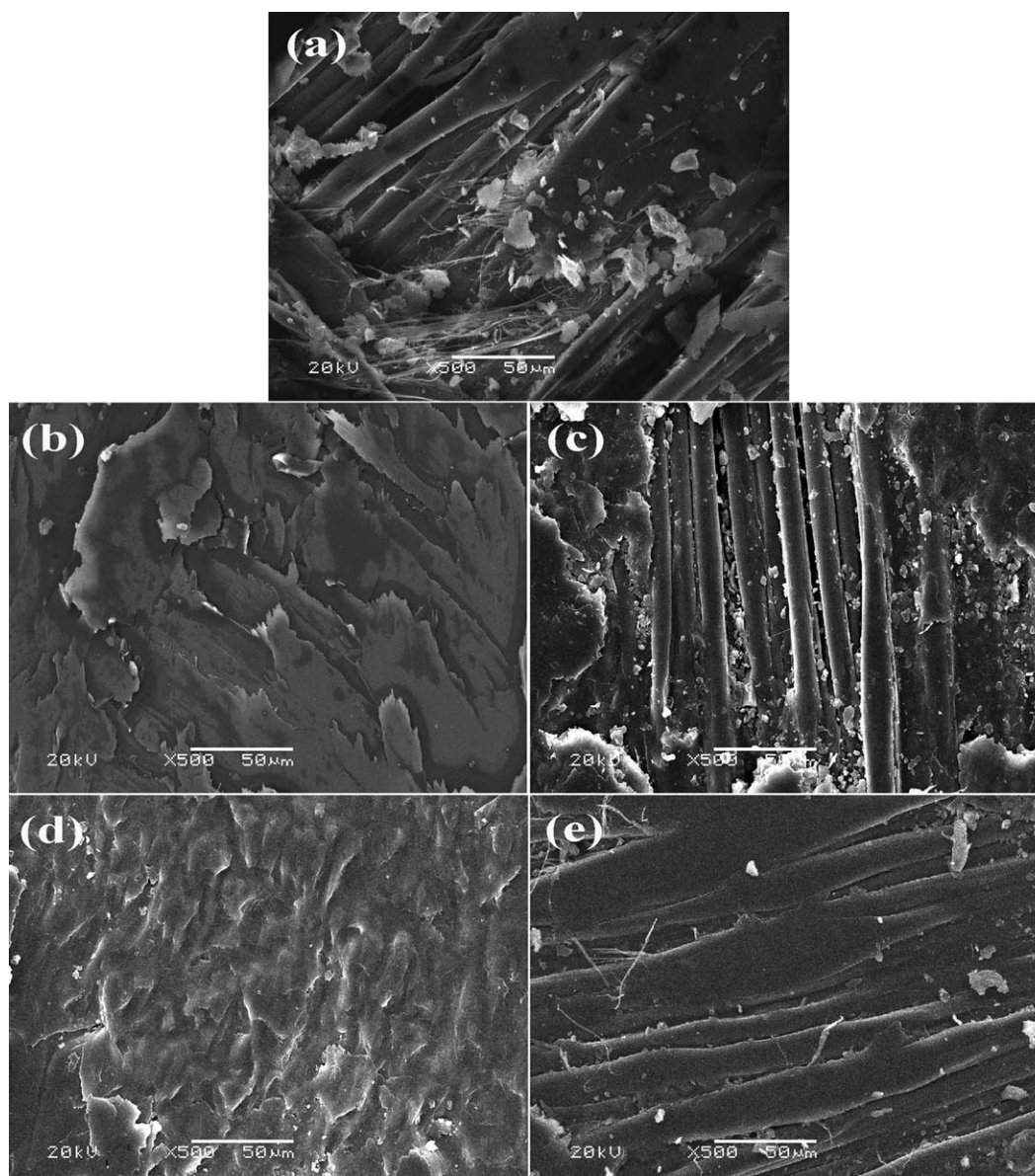
modified in Air-500°C and Ar-500°C conditions, it can be concluded that the argon atmosphere is favorable to the attachment of carbon powder on the fabric surface.

Figure 7 shows the micrographs of the counterpart surface of three different PBO composites after friction at 156.8 N and 0.26 m/s to illustrate their antiwear mechanisms. In Figure 7(a), the counterpart surface of the unmodified composites appears some scratches and there is no effective transfer film on the surface, which is corresponding to the high wear rate. The main wear mechanisms are abrasive wear. For the composites modified at 300°C in air, the transfer film appears to be coherent but relatively thicker [Figure 7(b)], and there are also visible scratches on the transfer film. The existence of the transfer film plays a protective role in the abrasion of the composites. The main wear mechanism is abrasive wear. For the composites modified at 300°C in argon, the transfer film appears to be compact and coherent [Figure 7(c)]. The depth and width of the scratches on the transfer film are very small. The formation of the transfer film can improve the antiwear ability of the PVA-modified composites effectively. The various characteristics of the transfer films on the counterpart surfaces also account for the difference in the friction and wear behaviors of three different composites.

Figure 8 shows the SEM morphologies of the worn surfaces of five PBO fabric composites after friction at 156.8 N. It can be seen that the worn surface of the unmodified composites after sliding is covered with bare fibers, and most fibers occur deformation and fibrillation [Figure 8(a)], which corresponding to severe damage. In air-300°C condition, the worn surface is intact comparatively [Figure 8(b)]. The deformation under the shear stress and the adherence under the compressive stress occur on the contact surface of the composites. In air-500°C condition, the adhesive resin has lost the restriction and protection capacity to the fibers [Figure 8(c)], and the wear resistance of the composites is decreased. In argon-300°C condition, there are large-scale plastic deformation and a few spalling traces owing to adhesive force [Figure 8(d)]. The PVA film formed on the fabric surface is viscoelastic, which will appear plastic deformation and compaction phenomenon under compressive stress. The PVA film not only improves the bonding strength between the fabric and resin, but also disperses the shear stress effectively in friction, so the antiwear capability of the composites was improved significantly. In argon-500°C condition, the composites after sliding is characterized by a large number of deformed fibers [Figure 8(e)], and the fibrillation occurs. The bonding resin is not scaled off, and the antiwear capabilities of the composites were improved in a certain degree.

## CONCLUSIONS

1. In argon-300°C condition, the PVA thin film formed on the fabric surface by chemical crosslinking reaction can improve the antiwear properties of the composites efficiently. There are three main reasons. First, the C, O and P elements introduced on the fabric surface can enhance the surface energy of fabric, resulting in the improvement of the bonding strength between fiber and resin, while retaining the



**Figure 8.** SEM images of worn surfaces of (a) pure, (b) Air-300°C, (c) Air-500°C, (d) Ar-300°C, (e) Ar-500°C (156.8 N, 0.26 m/s).

intrinsic structure and chemical stability of the fabric; Second, the crosslinked PVA fills in the interspaces of the fabric and improves the whole fabric structure; Finally, the PVA film appears shear creep and plastic deformation in friction, which can disperse the shear stress effectively.

- When the modified temperature risen to 500°C, the network polymer disappears and the carbon powder is residual due to the decomposition and carbonization of the crosslinked PVA. Although the residual carbon powder plays lubrication role, the antiwear performance of the composites is not enhanced significantly as expected because the fiber strength was decreased in the modification,

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