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Effect of silane coating surface treatment on friction and wear properties of carbon fiber/PI composites

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PAN-based carbon fiber was surface-modified with silane coating, and a composite material was prepared using a PI resin as a matrix. The structure and surface properties of carbon fibers were studied by means of X-ray photoelectron spectroscopy (XPS) and SEM. The tensile strength of the composite was measured by a tensile tester, and the friction properties of the composite were measured by a micro-nano mechanics comprehensive test system. The results show that treatment with silane coating can improve the surface roughness and chemical activity of carbon fiber, improve the interface between carbon fiber and PI resin matrix, and improve the tensile strength and wear rate of the composite.

Keywords: *mechanical, PI, CF, friction, SEM*

1. Introduction

Carbon fiber has high temperature resistance, friction resistance, electrical conductivity, thermal conductivity and corrosion resistance [1]. Carbon fiber-reinforced composite materials have been widely used as friction materials because of their low friction coefficient and self-lubricity compared with steel [2]. The composite material can be divided into a matrix phase, a reinforcing phase, and an interface phase, wherein the interface plays a very important role in the performance of the composite material [3]. It is not only the bond between the reinforcing phase and the matrix in the composite material, but also the medium of stress transmission [4]. The untreated carbon fiber surface is inert and has poor adhesion to the resin and the two-phase interface, which affects the friction properties of the material [5]. During the friction process, the carbon fiber is easily peeled off from the resin matrix [6], so that the friction coefficient fluctuates greatly and the friction stability is greatly reduced [7]. Therefore, improving the interfacial bonding strength of fiber composite materials is the key to preparing friction composite materials with excellent performance [8]. Surface treatment of carbon fiber, increasing its specific surface area, and increasing surface active functional groups are the key to improving its interface with resin [9]. There are many methods for modifying the surface of carbon fibers to improve the properties of composite materials, such as chemical methods [10], electrochemical methods [11], plasma treatment [12], and so on. Compared with other methods, the experimental equipment required for concentrated nitric acid oxidation is simple and can be operated under normal conditions [13]. After oxidation, it can be treated with a coupling agent [14], which can effectively increase the surface activity of carbon fibers and achieve chemical bonding with the resin matrix [15].

Due to the chemical inertness and low surface energy of carbon fiber, the adhesion between carbon fiber and a matrix polymer is poor [16], introducing polar groups on its surface to significantly increase the polarity of carbon fiber [17], which

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makes it bond well with polymer [18] and increases its mechanical properties [19]. In this paper, the surface of carbon fiber was treated with silane coating. The morphology and active group changes of carbon fiber after surface treatment were analyzed by SEM and XPS. The carbon fiber PI resin composite samples were prepared by using different surface treated carbon fibers, and the brittle section and the wear scar morphology of the samples were observed by SEM. The samples were subjected to friction testing using a comprehensive micro-nano mechanics testing system to analyze the friction properties of the samples.

2. Experimental

2.1. Materials and composite preparation

Our materials included PAN-based carbon fiber: average diameter of 7 μm, length of 75 μm, tensile strength of 2,500 MPa, modulus of elasticity of 200 GPa, density of 1,760 kg/m^3, provided by Shanghai Xinxing Carbon Factory; Polyimide: GCPITM, Changzhou produced by Guangcheng Plastic Co., Ltd., a thermoplastic polyimide, a yellow powdery solid, whose properties are shown in Table 1. Silane coupling agent KH-550 purchased from Shanghai Yehao Chemical Co., Ltd was used as the silane coating.

PI was placed in a 500 ml four-necked flask equipped with a stirrer and a condenser, and heated to 80° – 100°C in a WC/09-05 constant temperature water bath, followed by a 37% formaldehyde solution and catalyst [20]. Finally, a silane coating was added, PAN-based carbon fiber was soaked in a silane coating for 24 h to remove the sizing agent and impurities, and it was ultrasonically washed with distilled water for 0.5 h and finally dried at 100°C. The carbon fiber was immersed in silane coating with concentration of 1, 2, and 3wt%, respectively, washed with distilled water until neutral, and dried. Then, it was taken out and placed in an oven at 110°C to dry to cure the silane. The prepared carbon fiber was separately distributed in PI with constant temperature magnetic stirrer HOI-3, Shanghai Mei Yingpu Instrument Manufacturing Co., Ltd. And then the mixture was placed in a vacuum oven at 40°C for 12 h, and then placed in a grinding tool at 170°C, 5 MPa, for 20 min to obtain a composite with 15vol% carbon fiber.

2.1.1. Performance test

We used a JSM-5,600 scanning electron microscope (JEOL Company, Japan), with an accelerating voltage of 25 KV, and the carbon fiber surface, the brittle section of the composite material, and the wear surface morphology were observed. XPS analysis of the carbon fiber surface was performed using an ESCALAB 250 type Kα X-ray spectrometer (Thermo Scientific, MA, USA) equipped with Al. The X-ray device is a monochromator Al Kα (200 W), and C1s (B. E = 285.0 eV) is used as the standard. First, we performed a broad-spectrum scan and then performed the C peak, O peak, N peak, and Si peak respectively. High-precision narrow-spectrum scanning was implemented to determine the content of chemical elements on the surface of carbon fiber. The tensile properties of the materials were tested using a Model 3,365 (Shenzhen Sans, China) tensile tester. The crosshead speed of the testing machine is 5 mm/min until the sample is broken. The friction properties of the composites were tested using a micro-nano mechanics integrated test system (UNMT-1) with a load pressure of 10 N and the sliding velocity at 10 m/min. The test duration was two hours. The friction and wear properties of CF/PI composites are measured by UMT-2MT friction testing machine (produced by CETR, USA). Figure 1 is a schematic diagram of the friction pair contact of the testing machine. The sample is fixed on the chassis and reciprocates linearly with the chassis. The stroke length is 5 mm. The size of the sample is 30 mm × 20 mm × 5 mm; the mating part is a GCr15 steel ball with a diameter of 3 mm, and its chemical composition is listed in Table 2. The surface hardness of the steel ball is 61 HRC, and the surface roughness Ra = 0.1 um.

$$\text{Wear rate} = V/(FL),$$

where V is the wear volume, S is the wear cross-sectional area, H is the wear scar length, K is the wear rate, F is the applied load, and L is the sliding distance.

Table 1. Main properties of PI (GCTP^{TM}).

Density (kg/m^3)	1350	Impact strength (kJ/m^2)	25
Tensile Strength (MPa)	95	Thermal expansion coefficient (°C^{-1})	4.8×10^{-5}
Elongation at break (%)	7	Tg (°C)	260
Flexural strength (MPa)	150	Thermal decomposition temperature (°C)	240

For the tensile properties and the friction and wear properties, five samples were tested for each composite, and the effective average was used. The statistical deviation is 5%.

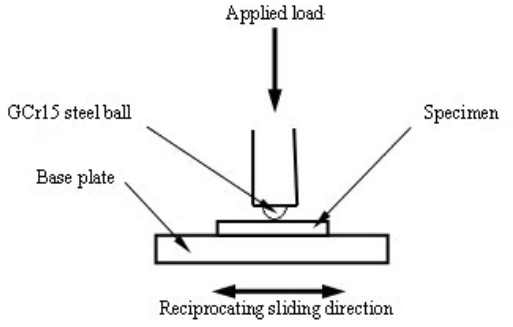


Fig. 1. The schematic diagram of the friction pair.

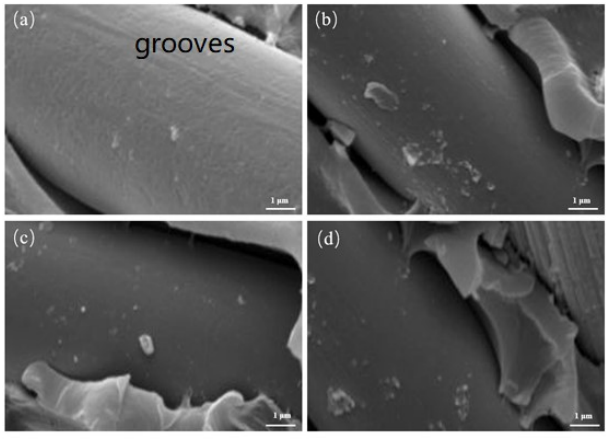


Fig. 2. Scanning electron micrograph of CF (a: untreated, b: 1wt% silane coating, c: 2wt% silane coating, and d: 3wt% silane coating).

3. Results and Discussion

3.1. Carbon fiber surface

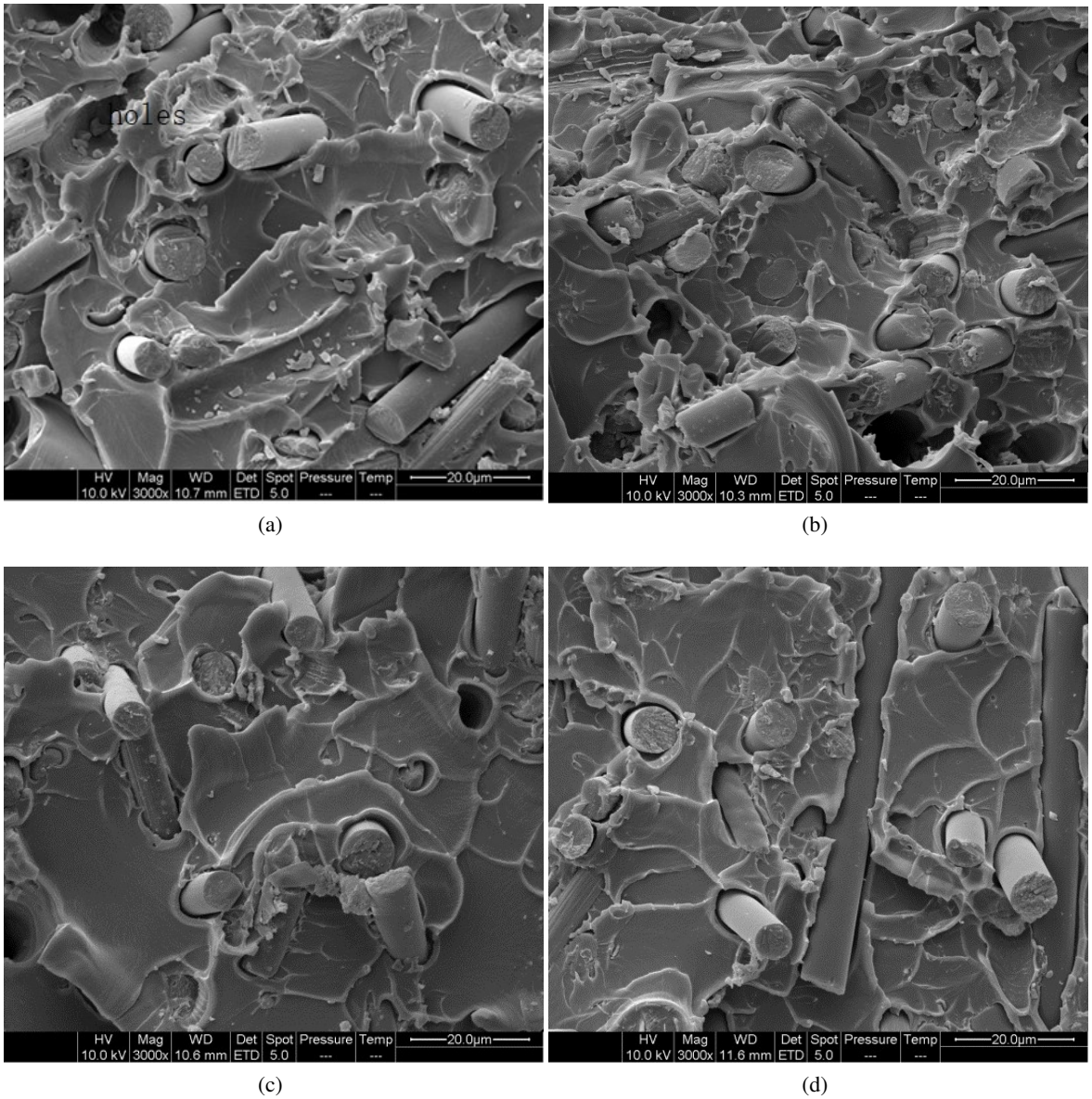
Carbon fiber surface morphology analysis in Figure 2 is a scanning electron micrograph of CF. As shown in Figure 2a, the untreated carbon fiber has a smooth surface and fewer grooves, which are produced during the preparation process. As the coating content increases, the coupling agent adheres well to the surface of the carbon fiber, as shown in Figure 2b and c, the coating content can effectively encapsulate the carbon fiber. After the 3wt% silane coating, no obvious grooves appear on the surface of the carbon fiber, as shown in Figure 2d.

3.2. XPS analysis

It can be seen from Table 3 that after surface treatment with different concentrations of coating, the content of O and N on the surface of the carbon fiber has been greatly increased. The oxygen concentration and nitrogen concentration on the carbon fiber surface change with the change of coating concentration. When the coating concentration is 0.3%, the oxygen concentration and nitrogen concentration on the carbon fiber surface both reach the maximum. This shows that the coating concentration has a great influence on the content of carbon fiber surface active functional groups. When the coating concentration is 0.3%, the fiber surface active functional group content is the highest. When the content of the coating is low, there are few organic active groups adsorbed by the coating of the surface of the carbon fiber, and the surface activity of the carbon fiber is not greatly improved. The coating is not enough to form effective chemical bonds with the C, O, and N elements on the surface of the carbon fiber. When the carbon fiber is combined with polyimide, the interface

Table 2. Chemical composition of GCr15 steel (wt %).

C	Si	Mn	Cr	P	S	Fe
0.95–1.05	0.15–0.35	0.2–0.4	1.30–1.65	$\leqslant$ 0.027	$\leqslant$ 0.02	Remainder



(a) (b)

(c) (d)

Fig. 3. Cross-sectional scanning electron micrographs of CF/PI (a: untreated, b: 1wt% silane coating, c: 2wt% silane coating, and d: 3wt% silane coating).

bonding area is a small amount of chemical bonding. Although the interface bonding of the composite material is improved to a certain extent, the effect is not ideal. The carbon fiber and PI resin are in direct contact with the interface, which becomes the weak point of the composite material, and interface failure occurs first under the action of external force, affecting the performance of the

composite material. When the coating content is appropriate, an effective adhesion interface layer can be formed on the surface of the carbon fiber. There is a strong chemical bond between the carbon fiber and the resin matrix, which effectively improves the interfacial bonding performance between the carbon fiber and the resin matrix. Under the action of external force, the chemical bond works together to transfer the applied load, thereby improving the mechanical properties of the composite material. The weak van der Waals force becomes a weak link for damage under the action of external force. As a result, the carbon fiber and the PI resin matrix cannot form an effective interface bond. The concentration of the coating also has a great influence on the interface strength and toughness of the composite material. When the coating content is moderate, a strong and tough interface layer can be formed. From a microscopic point of view, when the coordination number of the coating is fully utilized, the interface layer is strong. In other words, it is necessary not only for the coating to form sufficient chemical bonds on the surface of the carbon fiber, but also for the complete coordination of the chemical reaction between the coating and the PI molecules so that the mechanical properties of the composite material can reach the best level. In summary, the nature of the interface zone greatly affects the macroscopic mechanical properties of CF/PI composites.

3.3. Sectional morphology of the material

In Figure 3 a–d is a cross-sectional scanning electron micrograph of CF/PI. Figure 3a shows that there are fewer resins adhering to the carbon fibers, more holes, and longer fiber pull-out. This indicates that during the fracture process, the matrix cracks extend along the interface direction, and the effect of the matrix transfer load is insufficient; most of the damage occurs at the interface. Figures 3b–d show that the carbon fiber has more resin-attached substrates, less fiber pull-out, relatively fewer holes, and a smoother cross-section. This indicates that the matrix crack propagates along the interface during the fracture process and the carbon fiber and the matrix fracture together. At this time, the matrix can transmit the load to the carbon fiber better, and the failure mode is mainly the combined action of the resin matrix and the carbon fiber in the transverse direction. Therefore, it can be inferred that the interface between the carbon fiber and the PI resin matrix is improved after the carbon fiber is treated by the silane coating.

3.4. Tensile strength

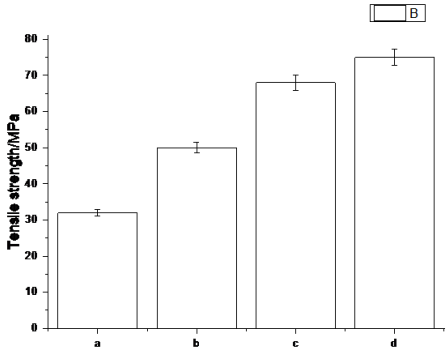


Fig. 4. The tensile strength of the composites (a: untreated, b: 1wt% silane coating, c: 2wt% silane coating, and d: 3wt% silane coating).

Figure 4 shows the tensile strength of several composites. It can be seen that the composites prepared by carbon fiber have lower tensile strength. After the carbon fiber is treated by silane coating, the carbon fiber and the PI resin matrix are chemically bonded, and the interfacial bonding force is increased so that the tensile strength of the composite material is obviously improved.

3.5. Friction performance

Figure 5 shows an SEM photograph of the composite after wear. Figure 5a shows that the surface topography of the CF/PI composite and the surface of the material are flat. Figures 5b–d show the wear scar morphology of the 1wt%, 2wt%, and 3wt% silane coating CF/PI composites, respectively. As shown in Figure 5b, the composite is severely worn, the fibers are peeled off from the matrix, and the friction surface produces a large amount of fiber debris. As shown in Figure 5d,

Table 3. Surface elementary composition of carbon fibers.

Surface treatment	Elementary composition / %				Atom ratio / %	
	C	O	N	Si2p	O/C	N/C
Untreated	82.3	10.2	7.5	–	12.4	8.9
0.1% coating	77.7	13.1	8.4	0.8	16.9	10.7
0.2% coating	75.3	14.4	9.1	1.2	19.1	12.1
0.3% coating	76.9	13.2	8.47	1.42	17.2	11.0

the composite wear surface is smoother, the carbon fiber is wrapped by the resin matrix, and only a few fibers are peeled and broken. In summary, after the carbon fiber is treated by silane coating, the composite material is ground. The carbon fiber peeling is improved during the damage process.

The average coefficient of friction of the composite is shown in Figure 6a. During the friction of the composite material, the carbon fibers are peeled off from the substrate and scattered on the wear surface, acting as a lubricant. The friction surface of the composite material with poor interface combined has more carbon fibers, resulting in less friction coefficient. When the interface is better combined, the carbon fiber is wrapped by PI resin, which is not easy to fall off during the friction process. The friction surface has more PI resin, while the pure PI resin has a larger friction coefficient than carbon fiber [9], so the composite material has a large friction coefficient.

It can be seen from Figure 6b that the composite material prepared by the carbon fiber treatment only has a large wear rate, the composite material prepared by the silane coating has a good interface, and the carbon fiber peeling off and the wear rate are reduced during the friction process. The wear resistance of the material is improved by 38.7%.

It can be seen from Figure 7a that the transfer film of the untreated CF/PI composite has uneven thickness, broken and loose discontinuities in the middle. This is mainly because the untreated CF agglomerated heavily on the surface of the substrate and had poor interfacial adhesion with the substrate, which failed to effectively inhibit the large-scale transfer of the PI. Under the action of shear stress and frictional heat, a transfer film with a rough and damaged surface formed. From Figure 7b it can be seen that the transfer film of silane coating CF/PI composite is significantly better than the untreated CF/PI composite and the surface flatness and smoothness of the transfer film are much improved, which indicates that the silane coating treatment effectively inhibited the large-scale exfoliation and transfer of PI.

4. Conclusion

As the silane coating increases, the groove on the surface of the carbon fiber is continuously deepened, and the reactive functional groups are continuously increased. The oxygen content on the surface of the carbon fiber increases after the 3wt% silane coating compared with the untreated carbon fiber. It can adhere to the surface of carbon fiber better, improving the interface between carbon fiber and PI resin.

The surface modification of carbon fiber with silane coating is an effective way to improve the interfacial adhesion of composite materials. The composites prepared have increased tensile strength, large friction coefficient, and low wear rate.

The transfer film of silane coating CF/PI composite is significantly better than the untreated CF/PI composite, and the surface flatness and smoothness of the transfer film are much improved, which indicates that the silane coating treatment effectively inhibits the large-scale exfoliation and transfer of PI.

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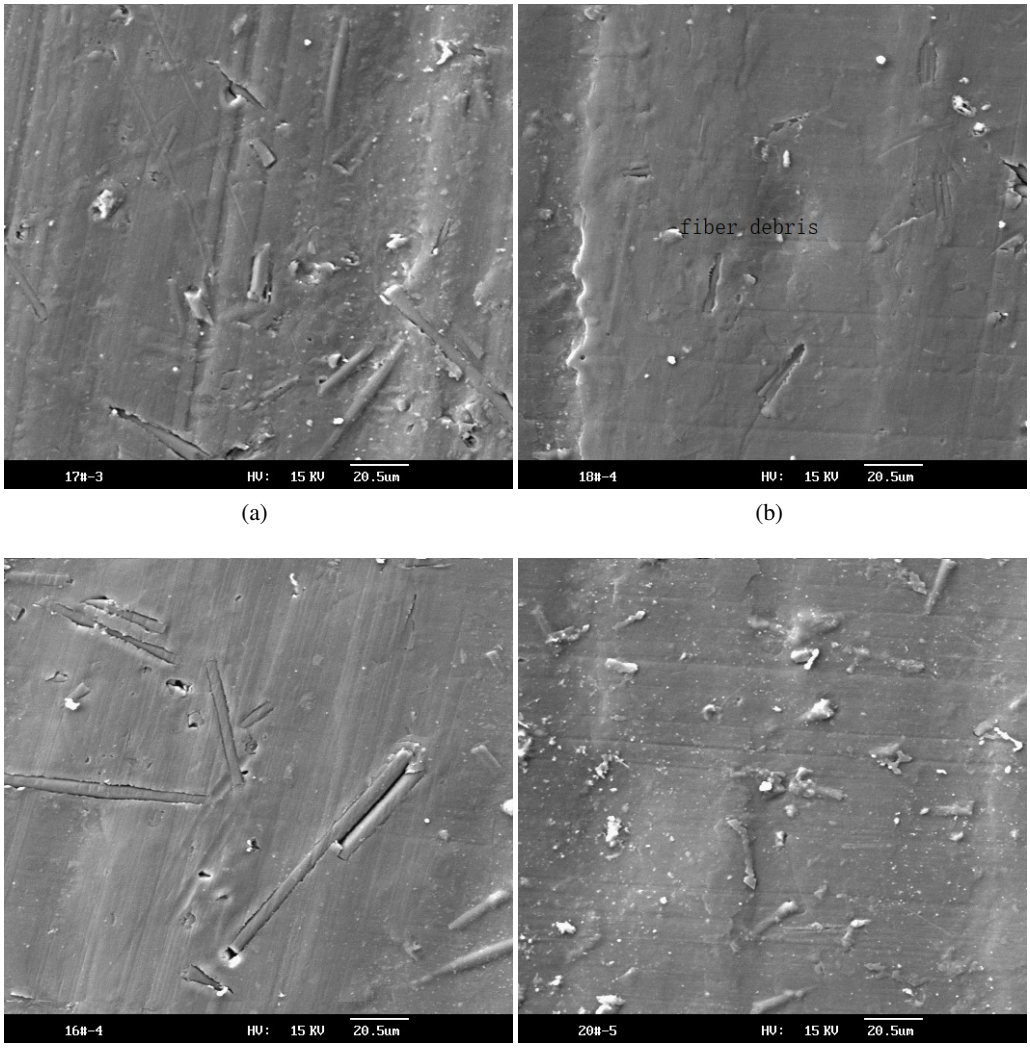

(a) (b)

(c) (d)

Fig. 5. SEM photographs of the composite after wear (a: untreated, b: 1wt% silane coating, c: 2wt% silane coating, and d: 3wt% silane coating).

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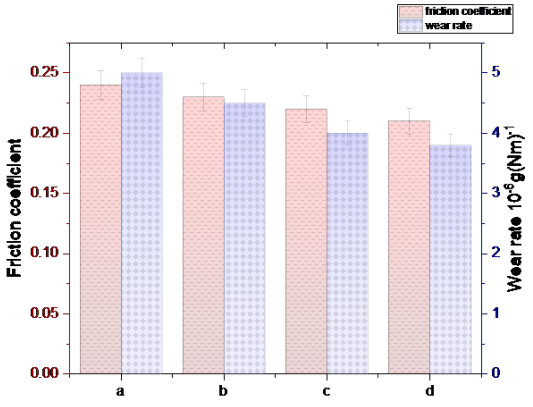
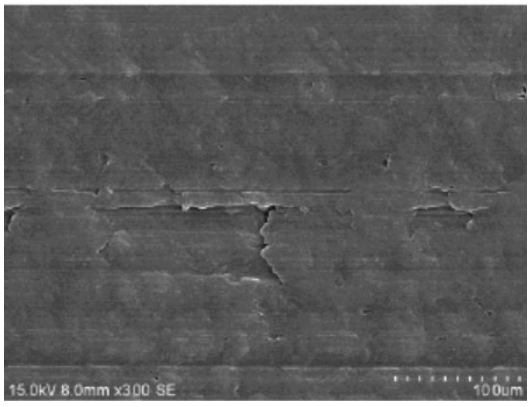
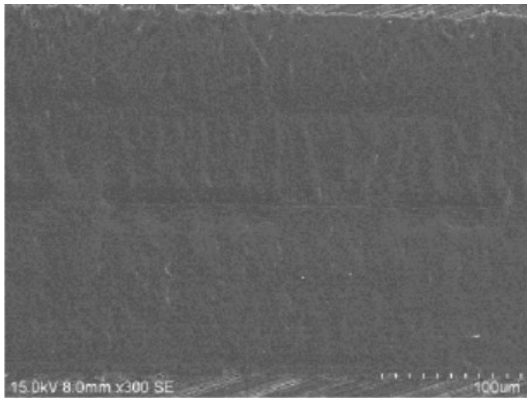


Fig. 6. The coefficient of friction and wear rate of the composite (a: untreated, b: 1wt% silane coating, c: 2wt% silane coating, and d: 3wt% silane coating).



(a)



(b)

Fig. 7. SEM micrographs of transfer film on the coupling surface (a: untreated and b: 3wt% silane coating).

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