Evaluation of Tribological Performance of Surface-Treated Carbon Fiber-Reinforced Thermoplastic Polyimide Composite

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ABSTRACT: The effect of surface treatment [rare earth solution (RES) and air oxidation] of carbon fibers (CFs) on the mechanical and tribological properties of carbon fiber-reinforced polyimide (CF/PI) composites was comparatively investigated. Experimental results revealed that surface treatment can effectively improve the interfacial adhesion between carbon fiber and PI matrix. Thus, the flexural strength and wear resistance were significantly improved. The RES surface treatment is superior to air oxidation treatment in promoting interfacial adhesion between carbon fiber and PI matrix. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1147–1153, 2008

Key words: fibers; polyimide; composites; adhesion; matrix

INTRODUCTION

Fiber-reinforced polymers (FRP) are able to provide a beneficial balance between the traditional properties of a polymer (low part weight and ease of processability) and selective properties of metals (high strength, modulus, and toughness). FRP allow tailoring of unique combinations of such properties to meet a variety of requirements. Polyimide and its composites attract extensive concern by tribological scientists worldwide because of their high mechanical strength, high wear resistance, good thermal stability, high stability under vacuum, good antiradiation, and good solvent resistance.[1,2] Carbon fiber reinforcement dominates in high-performance applications due to its outstanding mechanical properties combined with low weight. The performance of these composites depends largely on the quality of the matrix-reinforcement interface, which determines the way loads can be transferred from the polymer to the fiber. However, the interfacial adhesion of carbon fiber-reinforced polyimide (CF/PI) composite is poor because carbon fiber has chemically inert and smooth surface, and the oxygen-containing functional groups are very few. Therefore, to improve the properties of carbon fiber composites, surface treatment for carbon fibers (CFs) is absolutely necessary. A lot of approaches such as electrochemical oxidation, plasma treatment, and liquid phase oxidation of carbon fiber have been pursued to improve interfacial adhesion strength of carbon fiber-reinforced composites.[3]

Air oxidation of carbon fiber is a simple and economic method to improve the adhesion between carbon fiber and matrix resin, accordingly to improve the mechanical properties of carbon fiber composites.[4,5] Rare earth solution (RES) surface treatment has been successfully applied to improve the adhesion of glass fiber and PTFE and aramid fiber and epoxy, respectively.[6–8] In the present study, RES and air oxidation methods were applied in the carbon fiber surface treatment, and their effects on the mechanical and tribological properties of PI composites were investigated. The goal of this research is to develop new materials that combine the best properties of PI and CFs. The study of the friction and wear characteristics of PI will help provide an important scientific basis for further improving their properties.

EXPERIMENTAL

Sample preparation

Materials

In the present study, GCTP^{TM} thermoplastic PI powder provided by Nanjing University of Technology was used as the matrix. The reinforcements were polyacrylonitrile-based unmodified and unsized high strength CFs (supplied by Shanghai Sxcarbon Technology, China) with the following specified properties: tensile

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strength, 2500 MPa; elastic modulus, 200 GPa; density, 1760 kg/m^3; diameter, 7 μm; length 75 μm.

Carbon fiber modification

Two types of surface treatment methods were used in the carbon fiber treatment: RES modification and air oxidation modification. Oxidation of the CFs was carried out in an oxidizing furnace, under programmed heating and with an isothermal hold at 450°C for 10 s, and then cooled in the oxidizing furnace to room temperature. The selected oxidation condition has been proved to be the most effective one for this kind of carbon fiber.[9] Before the RES surface treatment of CFs, RES with the concentration varying from 0.1 to 0.5 wt % were prepared. Equivalent CFs were immersed into the RES with different concentration according to the mass ratio of 2 : 1, respectively, for 10 min and mixed uniformly. Then the CFs were dried for 4 h at 120°C. Rare earth compound $LaCl_3$ purchased from Shanghai Yuelong New Materials. was used as main component of RES applied in surface modification. Ethylenediamine tetraacetic acid (EDTA), ammonium chloride, and nitric acid were commercially obtained without further purification. For the preparation of the rare earth solution, $LaCl_3$, EDTA, ammonium chloride, and hydrogen nitrate were added to ethanol. The final pH of solution was 5.

Preparation process

The hot-molding technique was employed to prepare the composite specimens, which is the most common technique for the sintering of pure PI without any sintering aids. In this process, the filler CFs and the PI were churned together in a mixer. Mixing was done for a few minutes at the addition of each component for about 20 min. Sintering powder (20 vol % CFs and 80 vol % PI) was placed inside a stainless mold with its inner walls coated with a BN slurry to avoid any interaction between the powder and steel and also to facilitate the demolding process. The compounds were put into the QLB-D170 × 170 vulcanizing machine at the temperature 280°C for 1 h with the constant pressure 12 MPa, and then heated from 280 to 340°C with the heating rate of 60°C/h in 1 h. When the temperature reached 340°C, the temperature remained constant for 1 h. Afterward, the compounds were cooled from 340°C to 200°C with the cooling rate of 120°C/h in 70 min. During the whole process, the pressure was constant. The compounded materials were then cooled to room temperature to get the composites. The sintering cycle can be visualized as shown in Figure 1.

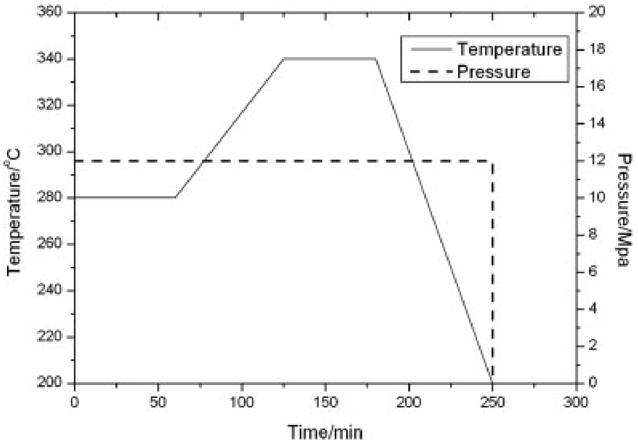

Figure 1 The change of temperature and pressure with time.

Testing procedure

The CF/PI composite plates were cut into narrow-waisted dumbbell-shaped specimens in accordance with the Chinese standard GB/T9341-2000. The three-point bending test was carried out on a computer-controlled Universal Testing Machine (made in China) at room temperature. The load was applied centrally at 90° to the long axis of the specimen at a crosshead speed of 0.01 mm/min keeping the distance between the supports at 40 mm. This crosshead speed was chosen to allow the maximum amount of time for slow crack growth to take place within the specimen. The tensile testing was carried out in accordance with the Chinese standard GB/T1040-1992 at room temperature, and the beam rate was at 5 mm/min.

For a more accurate determination of the material parameters and consideration of the possible scatter in the experimental data, the measurements were made at five magnitudes of a constant load for five specimens. The obtained quantities were then averaged.

The surface elementary composition of carbon fiber was determined by a PHI-5702 X-ray photoelectron spectroscopy (XPS). During the XPS analysis, a 250-W Al Ka line (hv = 148616 eV) was used, the pass energy was 29.350 eV, and the binding energy of C1s (284.6 eV) was used as a reference.

Friction and wear tests were done using a ball-on-block reciprocating UMT-2MT tribometer (The contact schematic diagram of the frictional pair is shown in Fig. 2) at room temperature with a relative humidity of 45–55%. The specimen disks, cut from the above-sintered composites, were 30 mm in length, 20 mm in width, and 5 mm in thickness. The disks were polished using a fine grade SiC emery paper and cleaned ultrasonically with acetone and dried before testing. The counterpart was a GCr15 steel ball of hardness HRC61 and surface roughness Ra about 0.05 μm with a diameter of 3 mm. The reciprocating friction stroke was 5 mm, and tests were conducted at a normal spring-driven load. The test duration was 2 h, and the friction coefficient was the

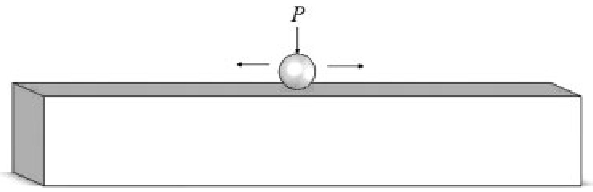

Figure 2 Contact schematic diagram for the frictional pair.

average value of the whole process. During the tests, the friction coefficient was continuously measured using a load cell. The cross-section of the wear scars was measured using a surface profilometer (Model 2206, Harbin Measuring & Cutting Tool Group, China). The wear volume of the specimen was calculated using the equation $V = Sl$, where V is the wear volume in m^3, S is the area of cross-section, l is the length of the stroke. Specific wear rate of the composite was calculated using the equation of $K = V/LF$, where V is the wear volume (m^3), L is the sliding distance (m), F is the applied load (N). Five tests were conducted under each test condition, and the average values of measured friction coefficient and specific wear rate were used for further analysis. The worn surfaces of CF/PI composites were investigated with scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Flexural properties

Figure 3 represents the flexural strength and flexural modulus of RES-treated CF/PI composite as a function of RES concentration. The RES concentration varies from 0.1 to 0.5 wt %. It is seen that the flexural strength and flexural modulus increase with the increase in the RES concentration, reaching the maximum value of 177.2 MPa and 5.8 GPa, respectively, at 0.3 wt % RES concentration. Above the maximum value, the flexural properties decrease gradually with the increase in the RES concentration. Rare earth elements have the chemical activity, which depends on their special electron structure (- - - $4f^{0–14}$). The rare earth compounds are capable of coordinating and ionic combination reacting with some functional groups of polymers (such as sulfonic group (—SO_2—) and carbonyl (C=O) on the PI), organic functional groups (such as hydroxyl (C—OH), carbonyl (C=O) and carboxyl (COOH) groups on the carbon fiber), and carbon atom.[10] According to the chemical bonding theory, it is suggested that rare earth elements are adsorbed onto both the carbon fiber surface and the PI matrix through chemical bonding, which increases the concentration of reactive functional groups due to the chemical activity of rare earth elements.[11] These reactive functional groups can improve the compatibility between carbon fiber and PI matrix and form a chemical combination between the carbon fiber and PI matrix. So, the interfacial adhesion between CFs and PI matrix is increased. However, excess rare earth elements may cause the decrease of the flexural properties of CF/PI with the formation of rare earth salt crystals on carbon fiber surface,[8] which affects the effective bond between the fiber and the matrix due to the existence of weak van der Waals force. On the other hand, when the rare earth elements are too scarce, there is no effective adhesion effect between the carbon fiber and PI matrix.

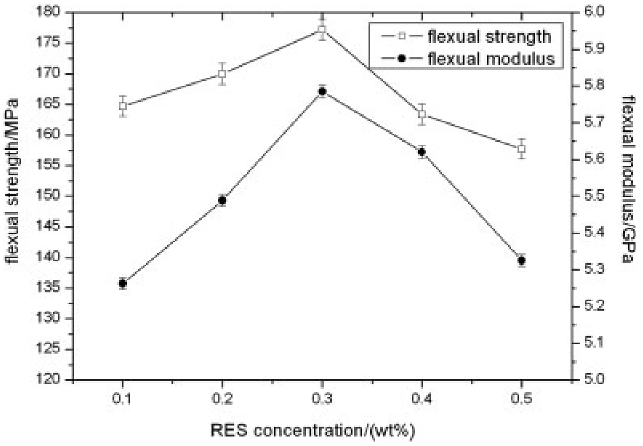

Figure 3 The effect of RES concentration on flexural properties.

According to earlier flexural experimental results, the concentration of RES was fixed at 0.3 wt %, while a comparison between RES treatment and air oxidation treatment was made as shown in Figure 4. It is seen from Figure 4 that the flexural strengths of RES-treated and that of air-oxidized CF/PI composite are improved by factors of 18.7% and 13.6%, respectively, when compared with the untreated

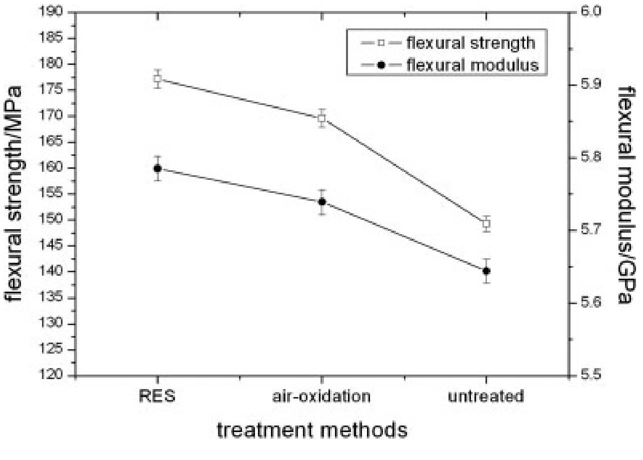

Figure 4 The influence of modification methods on flexural properties.

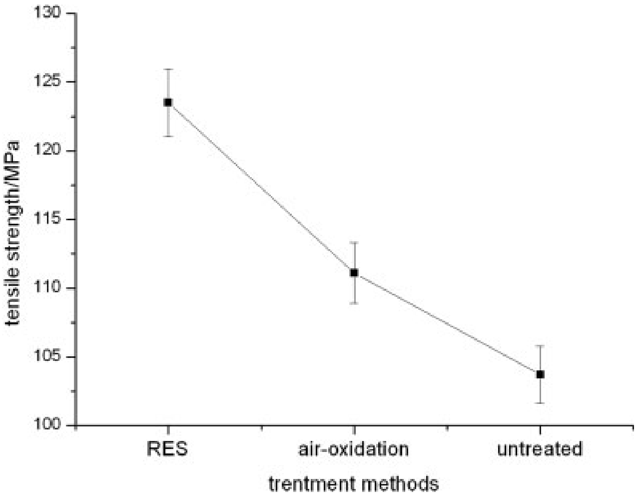

Figure 5 The influence of modification methods on tensile strength.

ones. Obviously, the flexural strength of CF/PI composite treated by RES is superior to that treated by air oxidation method. These enhancements in flexural strength of CF/PI are due to effective load transfer through strong interfacial bonding between carbon fiber and PI matrix, in which the interface acts as a successful compatibilizer, which could help more strain energy absorption before fracture. And the flexural modulus of the CF/PI composite modified by RES method reaches the highest value.

Because the fiber types and fiber contents are identical in these specimens, the differences between the flexural properties shown in Figure 4 must reflect the effects of the different treatment methods. The air oxidation treatment method mainly increases the surface functional groups of CFs and the roughness to improve the adhesion ability of the interface, which will do damage to carbon fiber for the scaling of carbon fiber surface. And the generation of voids and defects at the interfaces will affect the load transfer between the fiber and matrix and finally affect the flexural properties of the composites. Whereas RES-treated method will not do damage to CFs. The existence of strong interfacial bonding between the CFs and matrix is capable of transferring the stress load and preventing the sliding of CFs during flexure. RES is the most effective modification method in promoting the interfacial adhesion between the carbon fiber and PI.

Tensile strength

A comparison of tensile strengths was made in Figure 5. It is seen from Figure 5 that the tensile strengths of RES and air oxidation-treated CF/PI composites have been improved about 18.2% and 4.1%, respectively, when compared with that of untreated composite.

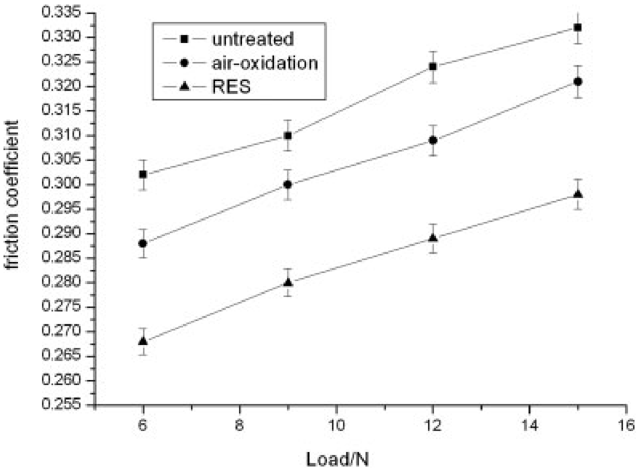

Figure 6 Variations of friction coefficient with load for the PI composites.

Friction and wear properties

Figure 6 shows the variation of the friction coefficient of the CF/PI composites with load. It is seen from Figure 6 that friction coefficient of all PI composites increases as the load increases from 6 to 15 N under the same reciprocating sliding frequency 8 Hz. This can be explained by the friction-induced thermal and mechanical effects, which may increase the actual contact area between the frictional pair as the load increased. Changes of the friction coefficient of CF/PI composites with reciprocating sliding frequency are shown in Figure 7. The friction coefficient decreases as the reciprocating sliding frequency increases from 1 to 12 Hz under the same load 12 N. This was attributed to the increased softening and plastic deformation of the polymer matrix, which was caused by the increased reciprocating sliding frequency. The RES-treated CF/PI composite exhibits the lowest friction coefficient, and the untreated PI

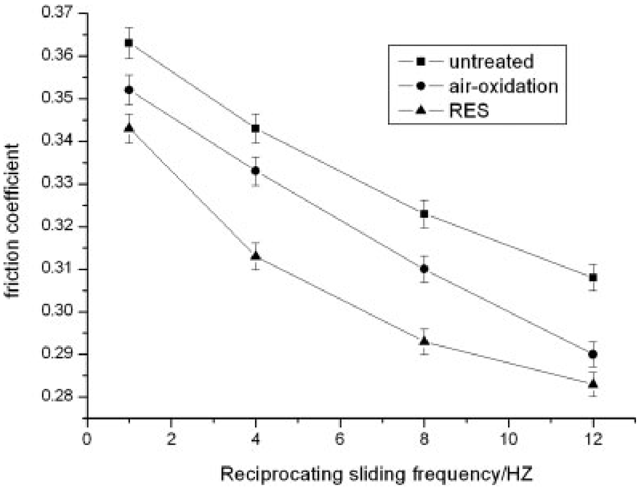

Figure 7 Variations of friction coefficient with reciprocating sliding frequency for the PI composites.

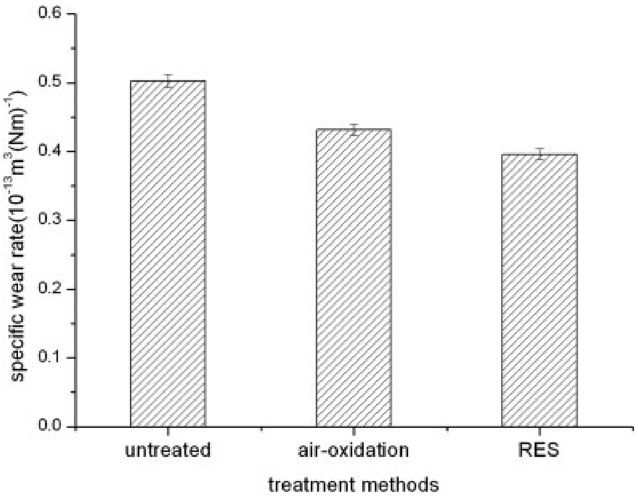

Figure 8 Specific wear rate of PI composites under a load of 12 N and a reciprocating sliding frequency of 8 Hz.

composite exhibits the highest friction coefficient both under the same reciprocating sliding frequency (Fig. 6) and at the same load (Fig. 7). The modification of the CFs strengthens the combination of the interface between the fibers and the PI matrix and increases the elastic modulus of the PI composites. This will be the reason why the friction coefficient of the modified carbon fiber-reinforced PI composites is reduced.

Figure 8 gives the specific wear rate of three CF/PI composites under the load of 12 N and reciprocates the sliding frequency of 8 Hz. It is seen that the untreated composite has the highest specific wear rate, while the RES-treated composite has the lowest. The specific wear rate itself depends on the properties of the filler, matrix, and filler/matrix bond strength. In addition, the relative hardness of the filler to that of the counterface, content, shape, size, distribution and orientation of filler, and the abrasiveness of filler against the matrix are important parameters. In this system, the difference of specific wear rate mainly comes from the bond strength between the reinforcement and the matrix. It can be seen from Figure 8 that the modification of the CFs can improve the wear resistance of the PI composites, reflecting the effectiveness of the modification of the CFs on increasing the combining strength of the interface between the CFs and PI matrix. The above-mentioned experimental results reveal that RES treatment greatly improves the friction-reducing and wear-resistance properties of PI composite under dry sliding condition.

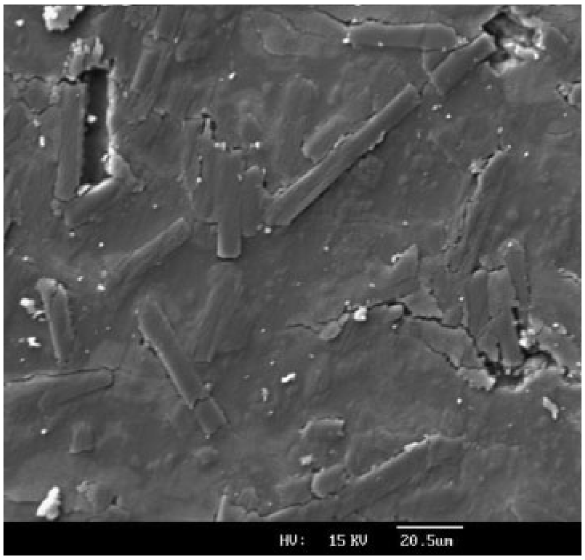

Figure 9 SEM photographs of the worn surfaces of untreated PI composites.

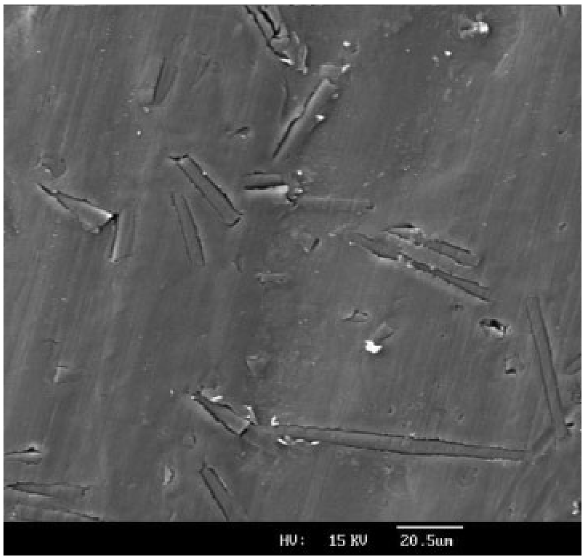

Figure 10 SEM photographs of the worn surfaces of air-oxidated PI composites.

The normal load and reciprocating sliding frequency were fixed at 12 N and 8 Hz, respectively. SEM images of the worn surfaces of PI composites filled with differently surface-treated CFs are shown in Figures 9–11. For the PI composite filled with untreated CFs, there are many cracks located near the CFs, as shown in Figure 9. Deep pores exist between CFs and PI matrix, which indicates that there is a very poor interfacial adhesion between the fiber and the PI matrix. So, the untreated fibers are more prone to be peeled off due to the weak interface bonding. The fillers are easily detached from the matrix under a load of 12 N leaving cavities whose boundaries are the same shape as the filler fibers remove. Many cavities within the matrix material structure lead to many stress concentrations in the matrix resulting in higher local stresses, microcracking, and, in a consequence, a high-specific wear rate. Furthermore, the detachment of fillers causes the adjacent matrix to be poorly supported and

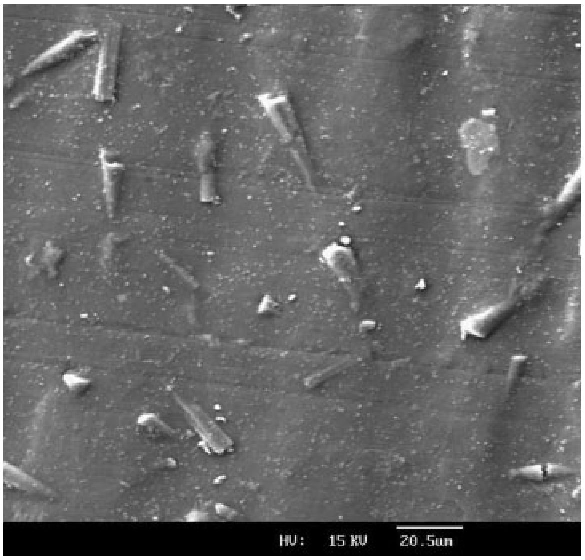

Figure 11 SEM photographs of the worn surfaces of RES-treated PI composites.

hence is subjected to greater stress and thus more susceptible to fracture. Therefore, the load-carrying capability of the composite is reduced resulting in a decrease in wear resistance property.

On the worn surfaces of the PI composites containing the modified fibers, the damage became weaker, indicating the effective action of the surface modification of CFs upon the improvement of the wear resistance of the PI composites, as shown in Figures 10 and 11. For the air-oxidated CF/PI composite, the worn surface is smoother than the untreated one, as shown in Figure 10. There are also pores between CFs and PI. This indicates that the interfacial adhesion between CFs and PI is not strong enough, even though CFs are air oxidated. Poor interaction leads to high abrasion wear due to the ease of fiber cracking or pull out. The reinforcing fibers are apt to be pulled out if the resultant force of applied load and friction force exceeds the interface bonding strength during wear. Microcracks are observed at the surface either at the fiber-matrix boundary or at the weak spots in the matrix and eventually lead to the delamination of the matrix material. Poor adhesion of the filler to the matrix gave rise to the initiation of these cracks and hence increased the wear rate.[12] Probably, a crack follows the fiber/matrix interface and passes between the fibers at their closest distance. The crack propagates under the original surface matrix layer and causes the fragments of the matrix to be broken off, leaving the fibers bare. The driving force for the crack comes from the friction forces being applied on the matrix surface. Where the fibers are close to each other, the matrix between the fibers are often fragmented and broken off when the crack propagates along the fiber surface. Additionally, the cavity shown in the PI matrix is the result of a filler carbon fiber detaching from the matrix due to loss of matrix around it and poor adhesion between the filler and matrix.

TABLE I
Surface Elementary Composition of Carbon Fibers

	Elementary composition (%)			Atom ratio (%)
Surface treatment	C	O	La3d	O/C
Untreated	90.87	9.13	–	10.05
Air oxidation	86.72	13.28	–	15.31
RES-treated	72.63	25.02	2.35	34.45

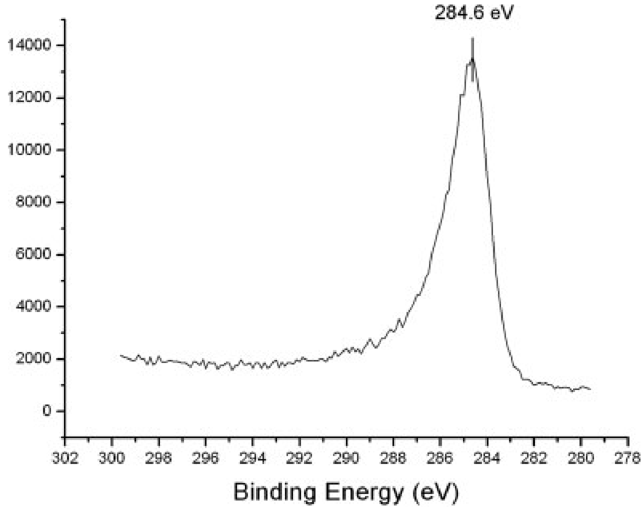

Figure 12 XPS C1s peak of untreated carbon fibers.

For the composite filled with RES-treated CFs, as shown in Figure 11, the worn surface is quite smooth and no cracks are visible. CF and PI are compactly bonded, and no pores exist between the fiber and the matrix. This indicates that the filler CFs

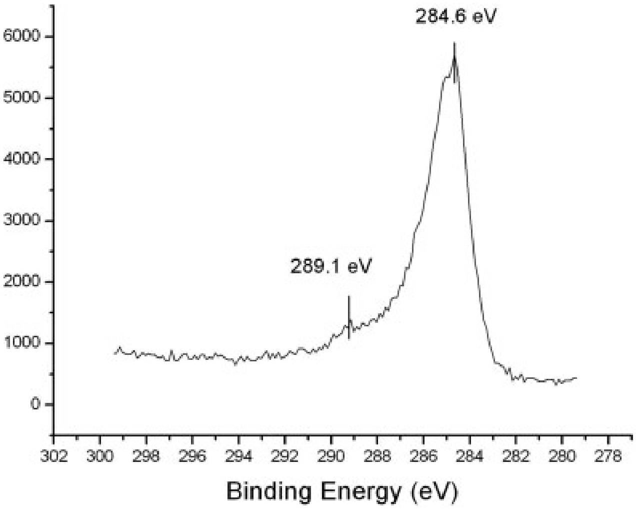

Figure 13 XPS C1s peak of air-oxidated carbon fibers.

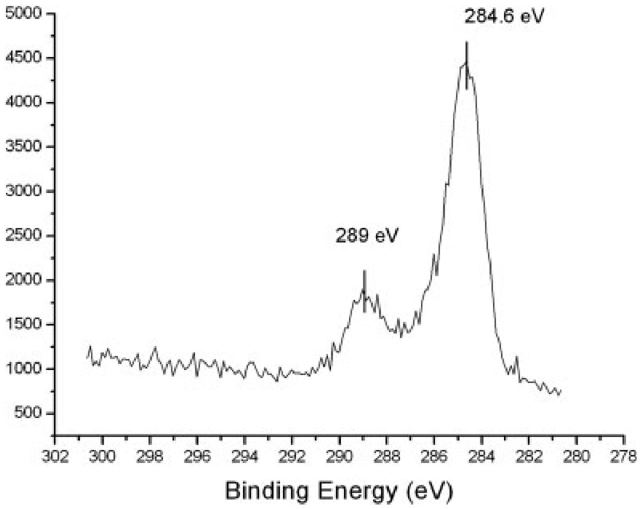

Figure 14 XPS C1s peak of RES-treated carbon fibers.

in RES-treated CF/PI have good bonding to the matrix and support the load from the counterbody effectively. The CFs are not easy to be detached from the PI matrix in friction process due to the improvement of the interfacial adhesion between the CFs and PI matrix after RES treatment. Thus, the load is effectively supported by CFs and the large-scale transfer and rubbed off of PI will be restrained. Accordingly, the wear of the PI composite filled with RES-treated CFs was reduced.

XPS analysis of the carbon fiber surfaces

Table I shows the surface elementary composition and O 1s/C 1s atomic ratios of CFs obtained from XPS. The untreated fibers (Fig. 12) display a smallest O 1s/C 1s ratio (10.05%) while RES-treated samples show highest O 1s/C 1s ratios (34.45%). XPS spectra of the C 1s region (Fig. 13) shows that here is a small bunch at the binging energy of 289.1 eV on the C 1s peak of air-oxidated carbon fiber, which indicates that a small quantity of carboxyl groups are introduced onto the carbon fiber surface after air oxidation.[13] On the C 1s spectra of RES-treated composite (Fig. 14), the peak of carboxyl groups is much higher and more obvious than that of air-oxidated composite, which means a largely increase in the amount of carboxyl groups after RES treatment. This result is consistent with the data shown in Table I, in which the O 1s/C 1s atomic ratio increased after RES treatment.

XPS studies show that RES treatment increases the amount of carboxyl groups on carbon fiber surface, which is helpful to increase the interfacial adhesion between carbon fiber and PI, accordingly the tribological properties of CF/PI composite is improved.

CONCLUSIONS

1. The mechanical strength of RES-treated CF/PI composite is improved effectively when compared with that treated by air oxidation.
2. The friction coefficient and specific wear rate of CF/PI composite can be decreased after surface treatment of CFs. Whereas RES-treated composite has the lowest friction coefficient and specific wear rate under given applied load and reciprocating sliding frequency.
3. RES surface treatment effectively improves the interfacial adhesion between CFs and PI. The strong interfacial adhesion of the composite makes CFs not easy to detach from the PI matrix and prevents the rubbing off of PI, accordingly improves the friction and wear properties of the composite.

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