Tribological properties of PTFE composites filled with surface-treated carbon fiber

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Abstract Carbon fibers (CF) were surface treated with concentrated HNO_3, silane coupling agent, rare earth solution and rare earth sol, respectively. The friction and wear behavior of polytetrafluoroethylene (PTFE) filled with differently surface treated CF were studied. The worn surfaces of CF/PTFE composites were then examined with scanning electron microscope (SEM). It is found that the wear volume loss of the rare earth sol treated CF filled PTFE composites reaches the lowest value when the modifier concentration is 10 wt%. It is only about 65% of the wear volume loss of the PTFE filled with untreated CF. Among all the treatments to CF, rare earth sol treatment is the most effective and the lowest friction and wear volume loss of CF/PTFE composite is exhibited.

Introduction

Polytetrafluoroethylene (PTFE) is widely used for tribological applications due to its superior properties such as low friction coefficient, high temperature stability and high chemical resistance. Unfortunately, PTFE exhibits poor wear resistance and abrasion resistance, each leading to failure and leakage problems in the machine parts [1]. In order to improve the wear resistance of PTFE, various reinforcing fillers have been added [2–6].

Many researchers found that glass fiber (GF) and carbon fiber (CF) were effective fillers for distinct effect on the friction and wear behaviors of polymer composites [7–9]. The advantages of GF include the low cost, high tensile and impact strength as well as a high chemical resistance. On the other hand, its low modulus, the low fatigue resistance, its self-abrasiveness and its poor interaction with some matrix resins limit this type of fiber for some tribological applications [10]. CF not only shows a high strength and modulus, but also has an excellent heat stability and chemical inertness. Furthermore, CF is preferred as fillers in tribo-composites because it imparts reinforcement, conductivity and better friction and wear behavior [8]. However, these fillers have some disadvantages such as difficulty of uniform distribution, poor interfacial adhesion, etc. [11].

Surface treatment of carbon fiber (e.g. air-oxidation [12], ozone-oxidation [13], aqueous ammonia [14], electron beam [15] or plasma [16], etc.) is commonly used to improve the fiber-matrix adhesion, interfacial shear strength, etc. However, only several works are focused on the effect of the surface modification of filler on the friction and wear properties of the composites [17, 18].

It is reported that rare earths are superior to the silane coupling agent in promoting the interfacial adhesion and interfacial toughness between glass fibers and PTFE, and largely enhance the tensile properties and tribological properties of glass fiber-reinforced PTFE composites [17]. And sol–gel method is an effective way for the surface modification of fibers or particles. In the present work, rare earth sol, rare earth solution, HNO_3 and silane coupling agent are applied to treat CF, and their effects on the tribological properties of PTFE composites have been evaluated.

The purpose of this work is to study the tribological properties of the PTFE composites filled with modified CF under dry conditions. It is expected that this research can be helpful to the use of PTFE composites in practice.

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Experiment

Materials

In the experiments, the powder of PTFE with particle size of 20–100 μm was supplied by Dupont (7A-J, commercial product) and CF (polyacrylonitrile (PAN)-based, high strength) with the average diameter of 20 μm and average length about 150 μm was obtained from Liaoning Xinxing Carbon Co. Ltd. Amino silane coupling agent was bought from the Nanjing Shuguang Chemical General Company under the trade name of KH-550. The chemical formula of KH-550 is shown in Fig. 1. La_2O_3 was purchased from Shanghai Yuelong New Materials Co. Ltd. Nitric acid (HNO_3) and CH_2Cl_2 was obtained by Shanghai Chemical Reagent Co. Ltd. Doubly distilled water was used throughout the experiments.

Preparation of surface modifiers and modification of carbon fiber

Four types of surface modifiers were used: (1) concentrated HNO_3 (HNO_3 was used directly); (2) 1.0 wt.% alcoholic solution of KH-550 (KH-550 was added into alcohol as proportions); (3) solution of La_2O_3 (La_2O_3 particles were added into doubly distilled water as proportions); (4) La_2O_3 sol (adjusting the pH value of La_2O_3 solution to about 7.8 by 1 mol/L HNO_3 to form La_2O_3 sol). The concentration of La_2O_3 solution and La_2O_3 sol varied from 1 wt% to 20 wt%.

The commercially sized fiber was desized in CH_2Cl_2 during 7 days. Subsequently, it was washed repeatedly with water for 2 days. Finally, it was dried under vacuum at 70 °C for 24 h. After that, CF was dipped into the surface modifiers at room temperature for 2 h. Then it dried at 70 °C under vacuum for 48 h.

Preparation of CF/PTFE composites

The fraction of CF in the composites was 15 wt%. First, the PTFE and CF powders were mixed mechanically. Then the mixtures were molded into the slab specimens by compression molding at a pressure of 70 MPa at room temperature for 5 min, then released from the mold. After that, the PTFE composite block was sintered at 380 °C for 4 h. Then the composite block was cooled, at a rate of 40 °C/h, back to room temperature. Finally, the sintered block was cut to a shape that is shown in Fig. 2c with 26 mm in external diameter and 22 mm in inner diameter and 2.5–3 mm in shoulder height.

Friction and wear tests

The friction and wear tests were carried out on a ring-on-ring friction and wear tester. The contact schematic diagram of frictional pairs is shown in Fig. 2. The counter material is a steel ring made from 45 steel (0.42–0.45% C, 0.17–0.37% Si, 0.58–0.80% Mn, P < 0.040%, S < 0.040%) with a hardness of HRC 51. The steel ring is 36 mm in external diameter and 18 mm in inner diameter and 8 mm in thickness. Sliding was performed under dry friction condition and ambient conditions (temperature: 25 °C, humidity: 50 ± 5%) at sliding velocities of 1.4 m/s, normal load of 400 N. The test time was 60 min. The friction force was measured with a torque shaft, provided with strain gauges, and the coefficient of friction was calculated from the friction force. And the friction coefficient was the average value of the last 45 min. Before each test, the surfaces of specimen and counterpart ring were polished with 800 grit paper to a surface roughness of 0.2–0.4 μm and were cleaned with alcohol. At last the wear volume loss was calculated out from the difference of each specimen's weight.

In this work, three replicate friction and wear tests were carried out so as to minimize data scattering, and the average of the three replicate test results was reported.

SEM and EDS tests

The surface of the modified CF was investigated by a scanning electron microscope (SEM, QUANTA-200) coupled with an energy dispersive spectrometer (EDS). The worn surfaces and transfer films morphologies of the composites were also examined with the QUANTA-200 SEM.

Results and discussion

The effect of the concentration of La_2O_3 solution and La_2O_3 sol on friction and wear behaviors of CF/PTFE composites

The coefficient of friction and wear volume loss of CF/PTFE composites as the function of La_2O_3 solution and La_2O_3 sol concentration are shown in Figs. 3 and 4. As seen in Fig. 3, after the surface treatment of CF, the friction
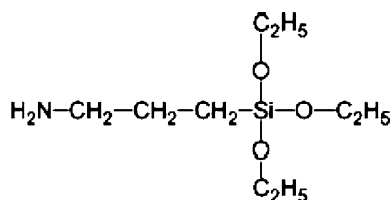
Fig. 1 The chemical formula of KH-550

Fig. 2 Configuration of the friction pairs: (**a**) Ring-on-ring contact, (**b**) counterpart ring, (**c**) sample ring

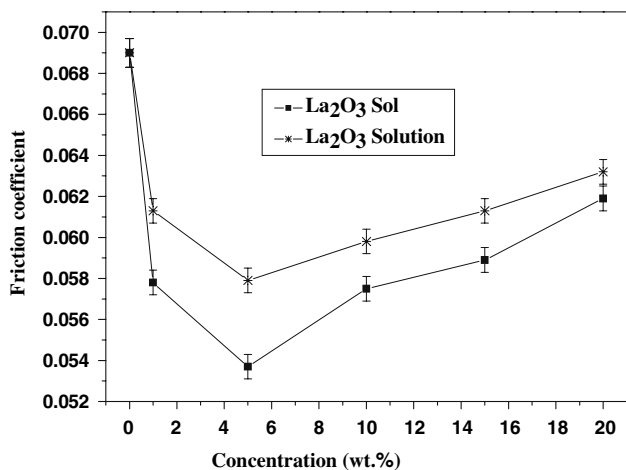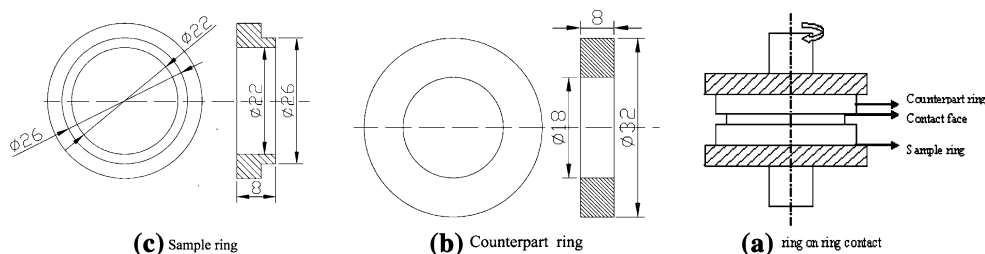(**c**) Sample ring   (**b**) Counterpart ring   (**a**) ring on ring contact

Fig. 3 Relationship between modifier concentration and the friction coefficient of CF/PTFE composites
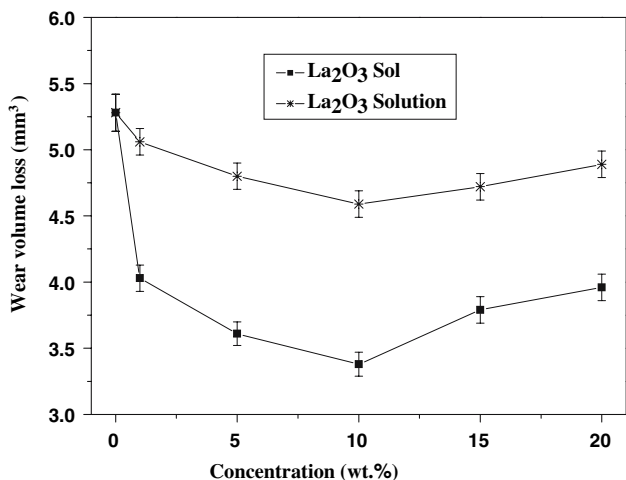

Fig. 4 Relationship between modifier concentration and the wear volume loss of CF/PTFE composites

coefficient of CF/PTFE composites is decreased. The friction coefficient of the two kinds CF/PTFE composites decreases with the modifier concentration at first, and reaches the minimum value at the modifier concentration of 5 wt%. After that it increases a little. And the friction coefficient for La_2O_3 sol treated CF filled PTFE composites

is lower than that of La_2O_3 solution treated CF filled PTFE within all modifier concentration.

The wear volume loss of the modified CF filled PTFE is very similar (Fig. 4). The wear volume loss of the two kinds of PTFE composites decreases with the modifier concentration initially up to 10 wt% then it increases afterwards. The volume loss of La_2O_3 sol treated CF filled PTFE composites is lower than that of the PTFE composite filled with untreated CF. And the wear volume loss of the 10 wt% La_2O_3 sol treated CF filled PTFE is only about 65% of that of the PTFE filled with untreated CF.

The effect of the modifier variety on friction and wear behaviors of CF/PTFE composites

The friction coefficient and the wear volume loss of five kinds of PTFE composites are indicated in Figs. 5 and 6. It should be pointed out here that the concentrations of La_2O_3 sol and La_2O_3 solution used in this section are both 10 wt%. It can be seen from Fig. 5 that the friction coefficient of the five kinds of PTFE composites is different from each other. The PTFE composite filled with La_2O_3 sol treated CF shows the lowest friction coefficient, while the composite filled with concentrated HNO_3 treated carbon
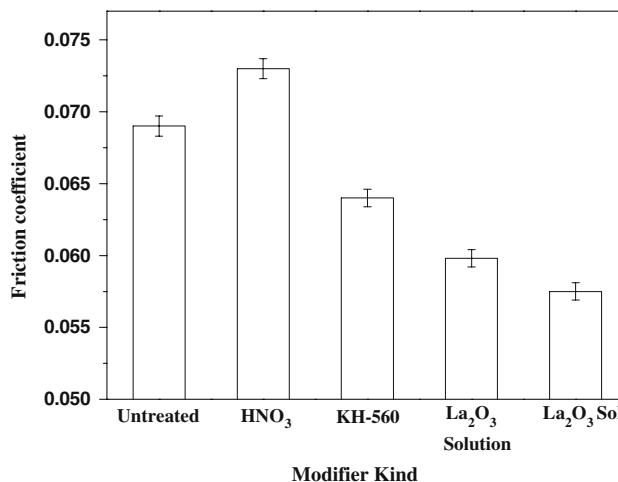

Fig. 5 The friction coefficient of PTFE composites filled with the CF treated by different modifiers
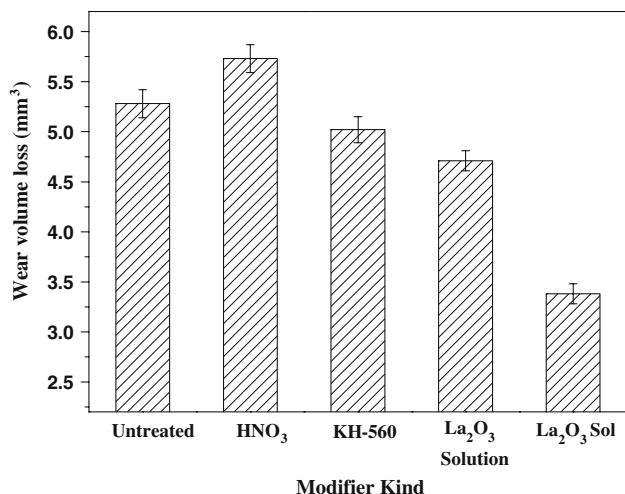
Fig. 6 The wear volume loss of PTFE composites filled with the CF treated by different modifiers

fibers presents the highest friction coefficient. Friction coefficient of the PTFE composite filled with untreated CF, KH-550 treated CF and La_2O_3 solution treated CF are the second, the third and the fourth, respectively.

The change of the wear volume loss of the PTFE composites filled with untreated and different modified CF is very similar to that of the friction coefficient (Fig. 6). The PTFE composite filled with La_2O_3 sol treated CF shows the lowest wear volume loss, which is about 35% lower than that of the PTFE filled with the raw CF. While the composite filled with concentrated HNO_3 treated CF presents the highest, which is about 10% higher than that of the PTFE filled with untreated CF. Thus the PTFE composite filled with La_2O_3 sol treated CF is the best from both friction and wear point of view. This indicates that rare earth surface modification is more effective to improve wear resistance of CF/PTFE composite than concentrated HNO_3 and silane coupling agent.

Generally, concentrated HNO_3 can react with CF, which decreases the mechanical strength of CF. Thus the load support capacity of the CF filled in PTFE is decreased, which increases the friction coefficient and the wear volume loss of PTFE composites. Silane coupling agent can improve the adhesion between CF and PTFE matrix. Thus CF will be

peeled off from PTFE matrix with large difficulty during sliding resulting in the decrease of the friction coefficient and the wear volume loss. According to chemical bonding theory and interdiffusion theory, rare earth is adsorbed onto the CF surface and creates a distorted region near the fiber surface through chemical bonding and physical adsorption. These adsorbed rare earths on the CF surface improve the CF-PTFE adhesion in composites [19]. So during sliding CF will not be peeled off from PTFE matrix easily. Thus, the abrasive wear of PTFE composites is reduced. As a result, the wear volume loss of CF/PTFE composites is decreased. Based on the test results, the conclusion that the CF-PTFE adhesion strength for rare earth is stronger than that for silane coupling agent can be drawn.

SEM and EDS investigation of the surface of La_2O_3 sol treated CF

Figure 7 shows the SEM morphologies and the EDS analysis of the surfaces of untreated and La_2O_3 sol treated CF. It can be seen from Fig. 7a, b, there is something coated on the surface of CF after the treatment of La_2O_3 sol. At the same time, EDS analysis shows that La and O elements exist on the surface of La_2O_3 sol treated CF. Thus it can be concluded that La_2O_3 is successfully coated on the surface of CF.

SEM investigation of worn surfaces

SEM images of the worn surfaces of PTFE composites filled with differently surface treated CF are shown in Fig. 8. For the PTFE composite filled with unmodified carbon fibers, there are some cracks and peelings of fibers are noticed on the worn surface, as seen in Fig. 8a. This reveals that the interfacial adhesion between CF and PTFE is relatively poor without the surface treatment of the CF, which results in the ineffective reinforcement of carbon fiber in PTFE and decreases the wear properties of the PTFE composites. It is seen in Fig. 8b that some peelings are also noticed on the worn surface of the PTFE composite filled with HNO_3-oxidated CF. Moreover, many broken fibers are appeared on the worn surface. This shows that the interfacial adhesion between CF and PTFE is not strong.

Fig. 7 SEM micrographs of the untreated and La_2O_3 sol treated CF surfaces: (**a**) untreated, (**b**) La_2O_3 sol treated, (**c**) EDS spectrum of the La_2O_3 sol treated CF surface

(a) (×5000) **(b)** (×5000) **(c)** (EDS)
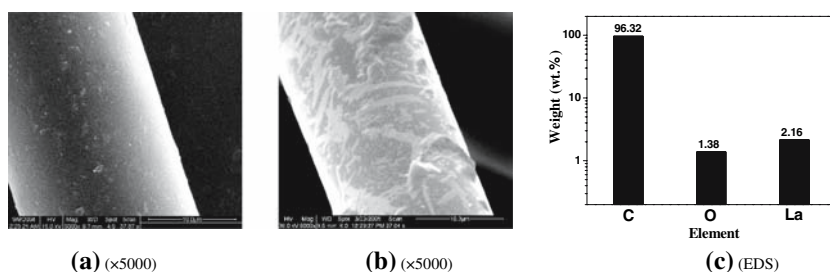
Fig. 8 SEM micrographs of worn surfaces: (**a**) untreated, (**b**) HNO$_3$ treated, (**c**) KH-560 treated, (**d**) La$_2$O$_3$ solution treated, (**e**) La$_2$O$_3$ sol treated

(**a**) (×400)   (**b**) (×400)   (**c**) (×400)

(**d**) (×400)   (**e**) (×400)
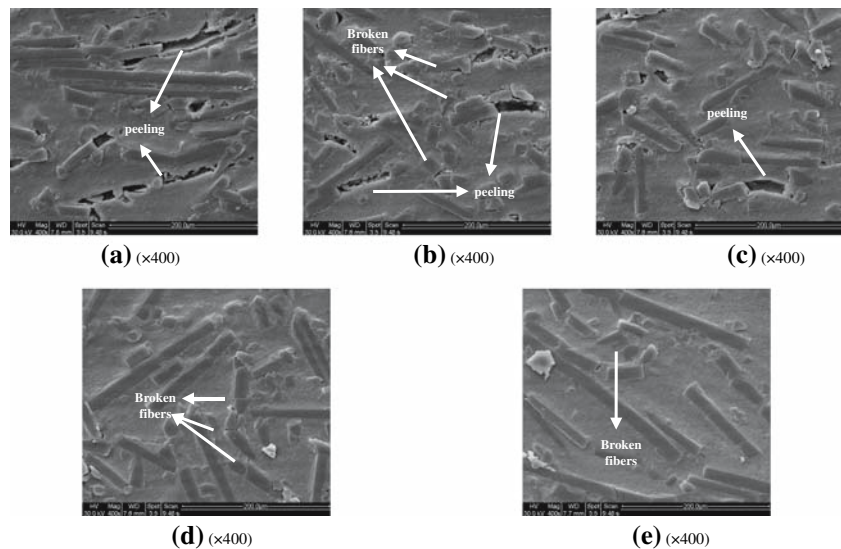
Moreover, the load support capacity of CF is decreased. There are a few peelings of fibers are noticed on the worn surface KH-550 treated CF filled PTFE (Fig. 8c). This indicates that the interfacial adhesion between CF and PTFE is not strong enough, even though the surface of CF is modified by silane coupling agent.

It can be seen in Fig. 8d that the worn surface of PTFE composite filled with La$_2$O$_3$ solution treated CF is comparatively smooth. Only some broken fibers are observed on the worn surface. This reveals that the interfacial adhesion between CF and PTFE is improved when carbon fibers are treated by La$_2$O$_3$ solution. It is seen in Fig. 8e that the worn surface of PTFE composite filled with La$_2$O$_3$ sol treated CF is quite smooth. Peelings are not visible on the worn surface and only several broken fibers are found. This indicates that there is a strong interfacial adhesion between CF and PTFE after La$_2$O$_3$ sol surface treatment, and the load support capacity of CF is increased. The strong coupling between CF and PTFE matrix prevents the rubbing-off of PTFE and large-scale transfer, and then reduces the wear of composites. Therefore, wear resistance of the PTFE composites filled with CF is improved after rare earth surface treatment.

Conclusions

1. Rare earth can be successfully coated on the surface of CF.
2. The wear volume loss of the rare earth sol treated CF filled PTFE composites reaches the lowest value when the modifier concentration is 10 wt%. It is only about 65% of the wear volume loss of the PTFE filled with untreated CF.
3. Among all the treatments to CF, rare earth sol treatment is the most effective and the lowest friction and wear volume loss of CF/PTFE composite is exhibited in this case.
4. After rare earth treatment, CF is not easy to detach from the PTFE matrix and rubbed-off of PTFE are restrained, which results in the increase of the friction and wear properties of the PTFE composite.

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