Durable Polytetrafluoroethylene Composites in Harsh Environments: Tribology and Corrosion Investigation

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ABSTRACT: The tribological properties and mass loss of polytetrafluoroethylene (PTFE) composites filled with carbon fiber (CF) or potassium titanate whisker (PTW) after the immersion in 30% sulfuric acid solution for 5 or 15 days were studied under different temperatures (25, 50, and 75°C). Results show that PTW/PTFE composites exhibit better anticorrosive and antiwear properties than those of CF/PTFE composites. Acid immersion has no obvious effect on the wear rate of the PTW/PTFE composite. The wear rate of CF/PTFE immersed for 15 days is thrice as much that of untreated composites and 3.6 times as much that of PTW/PTFE composites. Results also indicate that the wear rate of PTFE composites increases with the increasing corrosive mass loss rate and is more dependent on the corrosive mass loss rate rather than the friction coefficient. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4307–4314, 2012

Key words: composites; fillers; polytetrafluoroethylene

INTRODUCTION

Fluid transfer is central to controlling temperature and recycling waste heat in petroleum and chemical industries. Facilities (such as a compressor) providing energy to ensure a continuous fluid cycling require excellent stability of sealing materials, especially in harsh environments such as acid and organic solvent.[1]

The tribological property of polymer composites may degrade in a corrosive solution environment due to the degradation of the polymer matrix and filler as well as the interface between the filler and the matrix.[2] The most significant result of solution absorption in composite materials is matrix plasticization and the lowering of the glass transition temperature yielding a softer and weaker matrix. In addition, nonuniform swelling of the matrix can reduce the mechanical and tribological properties of polymer composites. Meanwhile, the solution will diffuse with less restraint along the fiber fillers and destroy the bond at the fiber–matrix interface. Fiber fillers can be susceptible to the solution damage in the form of stress corrosion cracking due to ion diffusion on the surface of the fibers.[3,4] The tribological and corrosive properties of the polymer composites are also affected by the environmental temperature, immersion time, and solution concentration.[5]

Polytetrafluoroethylene (PTFE) is a promising sealing material in the aforementioned fluid for highly corrosive liquid environments because of its excellent solvent resistant behavior.[6] However, due to its high wear rate at normal friction conditions and poor mechanical properties, extensive efforts have been exerted to improve its antiwear and mechanical properties by incorporating various fillers, such as fibers,[7–9] fine particles,[10–13] whiskers,[14,15] and so on. Among these fillers, the carbon fiber (CF) and glass fiber (GF) are found to be effective fillers for improving the tribological properties of PTFE composites.[16,17] The fibers are able to improve the creep resistance and compressive strength of the PTFE and result in the enhanced wear resistance.
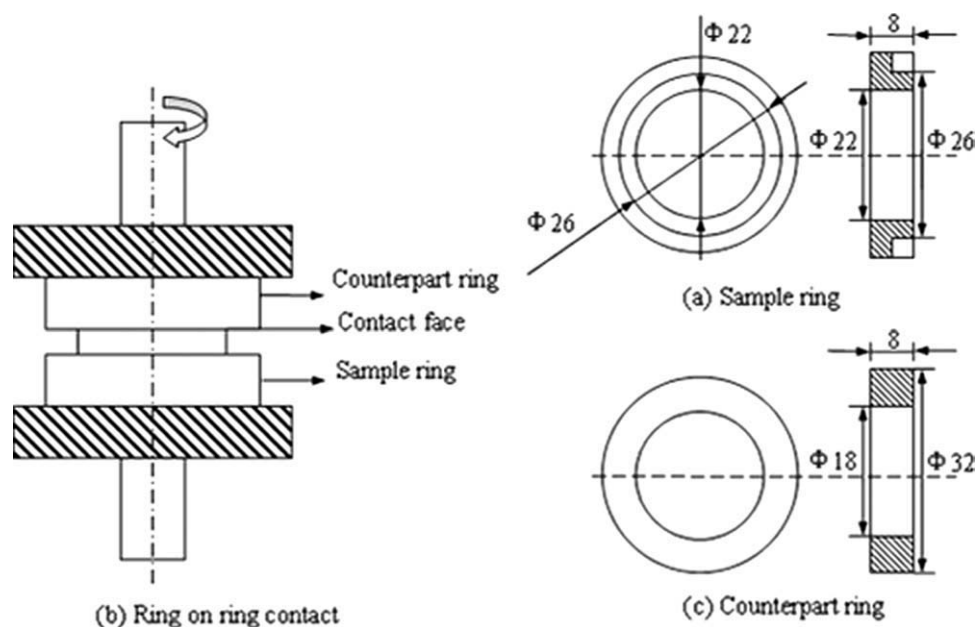
Figure 1 The schematic diagram of wear contact: (a) sample ring, (b) ring on ring contact, and (c) counterpart ring.

Potassium titanate whisker (PTW) has recently been proven a promising structural reinforcement of polymers, metals, and ceramic composites because of its excellent mechanical properties, wear resistance, and thermal stability.[13–15] The PTW has outstanding chemical stability in acid due to its stable tunnel structure. The tunnel structure consists of ribbon sharing at terminal corners with identical ribbons, resulting in an open octahedral framework enclosing tunnels in which the potassium ions are situated.[18,19] Due to its small size, PTW could reinforce micro-regions in composites that conventional fibers (such as CF and GF) are unable to reach.[20]

To the best of our knowledge, most studies on PTFE composites are focused on tribological properties under dry friction conditions. The tribological behavior under fluid conditions, especially corrosive environments, is less reported. In this work, the tribological and corrosive performances of CF- and PTW-filled PTFE composites were comparatively investigated in sulfuric acid solutions. The effects of solution temperature and concentration as well as immersing time on the tribological and corrosive properties of PTFE composites were also examined.

EXPERIMENTAL

Materials and preparation of PTFE composites

The PTFE powder with an average size of 25–100 μm was supplied by Dupont (7A-J, commercial product). The PTW with diameter 0.5–1 μm and an average length of 20 μm was synthesized in our laboratory according to the references.[21,22] The CF with the average diameter of 20 μm and average length ∼ 150 μm was obtained from the Nanjing Fiberglass Research and Design Institute. In the author's previous study,[1] the friction and wear properties of PTFE composites reinforced with various amounts (0, 5, 10, 15, 20, and 25 wt %) of PTW and CF sliding under dry testing conditions were investigated. It was found that, when the content of CF or PTW increased to 15 wt %, the best friction and antiwear properties are obtained. Based the previous studies, the weight fraction of PTW and CF was 15 wt % in each sample.

All the materials were dried in an oven at 120°C for 12 h before use. The preparation method was introduced as follows. First, PTFE and the fibers were blended to produce a well-mixed powder (PTFE: 85%; PTW or CF: 15%). Then, the mixed powder was compressed in the molds under 70 MPa for 5 min. The resulting PTFE composite block was sintered at 380°C for 4 h and cooled to the ambient temperature. For friction and wear tests, the block was cut into a 26 mm in outer diameter, 22 mm in inner diameter, and 2.5–3 mm in shoulder height [Fig. 1(a)].

Immersion corrosion tests

The immersion corrosive tests of the PTFE composites were conducted according to the Chinese National Standards GB11547-89. Table I summarizes the test conditions, and all the reported values are the average of four measurements.

The corrosive mass loss rate, M (%), was calculated by the following equation[5]:

TABLE I
Corrosive Mass Loss Rate Under Different Test Conditions

Test conditions			Corrosive mass loss rate (%)	
Temperatures(°C)	Immersion time (Days)	Sulfuric acid concentration (%)	CF/PTFE	PTW/PTFE
25	5	30	1.0820	0.0300
50	5	30	1.2630	0.0340
75	5	30	1.5275	0.0426
75	15	30	1.7074	0.0437
75	5	20	0.6407	0.0297

$$M = \frac{m_1 - m_0}{m_1} \times 100\%$$

where m is the measured mass of the specimen and the subscripts 0 and 1 stand for the final (after immersion) and initial values, respectively.

Tribological tests

Friction and wear tests were conducted on an MPX-2000 (ring-on-ring model) friction and wear tester [Fig. 1(b)]. The counterpart ring material was AISI1045 steel [Fig. 1(c)]. Sliding was performed under ambient dry friction conditions at sliding velocity of 1.40 m/s and normal load of 150 N. The test time was 60 min. Before each test, the surfaces of each specimen and counterpart ring were polished to an 800-grit finish with a surface roughness of 0.2–0.4 μm Ra and then cleaned with acetone. The frictional force was measured using a torque shaft fixed with strain gauges, and the friction coefficient was calculated from the frictional force. The wear rate was calculated from the weight loss of each specimen.

The specific wear rate, W_r (cm^3/Nm), was calculated by the following equation[23]:

$$W_r = \frac{W}{\rho \times N \times L}$$

where W is the mass loss (g), L is the sliding distance (m), ρ is the density of the composite (g/cm^3), and N is the normal load (N).

Three duplicate friction and wear tests were conducted to minimize the data scattering, and the average of the data was reported. Meanwhile, the friction coefficient value in every test is the average value of the steady-state value. The worn surfaces and transfer films morphologies of the PTFE composites were examined with a scanning electron microscope (SEM, QUANTA-200).

Mercury intrusion porosimetry

Mercury intrusion porosimetry (Poremaster GT-60) was used to determine pore size distribution and porosity. The pore size distribution was measured using the Washburn method. Porosity was evaluated by calculating from the bulk volume of the sample and total volume of mercury intruded up to the maximum pressure. The maximum injection pressure was about 150 MPa. The contact angle and surface tension used for the calculation were 140° and 480×10^{-3} N/m, respectively.

RESULTS AND DISCUSSION

Corrosive properties of CF- and PTW-filled PTFE composites

Table I shows the corrosive mass loss rate of PTFE composites under varied test conditions. It is indicated from Table I that the corrosive mass loss rate of CF/PTFE is much larger than that of the PTW/PTFE composites under different test conditions. The anticorrosive properties of PTW/PTFE composites are ~ 36 times better than those of the CF/PTFE composites (75°C; 5 days; 30% sulfuric acid concentration). In addition, the corrosive mass loss rate of PTFE composites increases with increasing immersion temperature and time. The corrosive mass loss rate of PTW/PTFE stabilizes at 0.0297–0.0437%, which is more stable than that of the CF/PTFE composites (0.6407–1.7174%) under different test conditions. This may be attributed to the small size and stable tunnel structure of PTW, leading to excellent chemical stability and tightly structured network, which is discussed in the effect of corrosive mass Loss rate.

The differential pore volume plot such as dV/d(logd) versus the pore diameter is used to estimate the pore volume contribution arising from individual pore diameters. Figure 2 shows the pore size distribution diagram of the CF- or PTW-filled PTFE composites before immersion. The PTW/PTFE composite curve exhibits two peaks. One lies in the range of 6–8 μm, and the other locates in the range of 8–10 μm [Fig. 2(a)]. However, the CF/PTFE composite curve exhibits three peaks, which lies in ranges of 6–8.5, 9–12, and 30–50 μm, respectively [Fig. 2(b)]. It is obvious from Figure 2 that the CF/
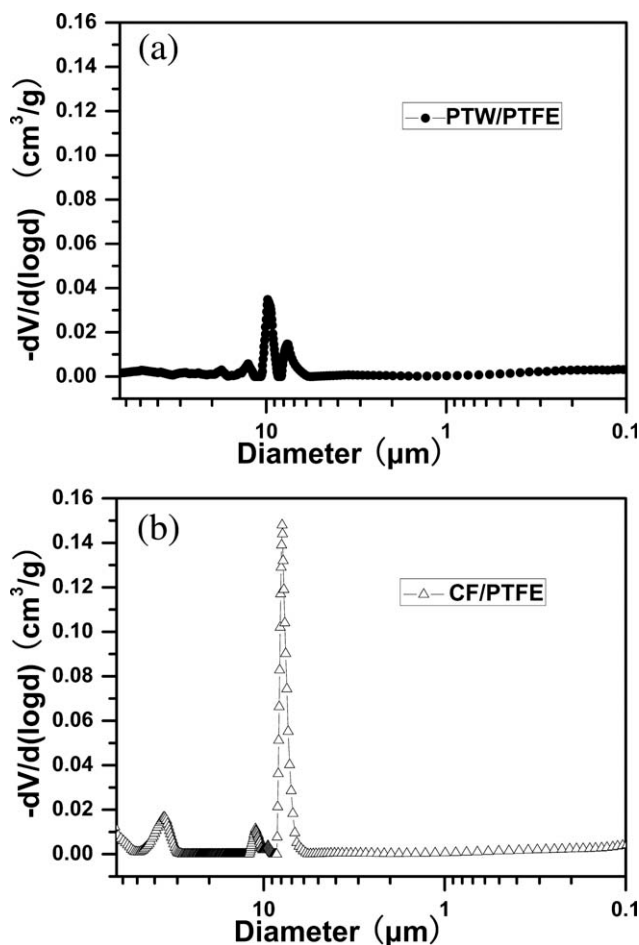
Figure 2 Pore size distribution diagram of PTFE composites before immersion (a) PTW/PTFE composites and (b) CF/PTFE composites.

PTFE composites obtain larger pore size than PTW/PTFE composites. The porosity and pore volume of PTFE composites without immersion are shown in Table II. The pore volume and porosity of the CF/PTFE composites are larger than those of PTW/PTFE composites, signifying that the sulfuric acid may penetrate into the CF/PTFE composites more easily than into the PTW/PTFE composites. This behavior corresponds well to the larger corrosive mass loss rate for the former composites.

Tribological properties

Effect of immersion time

Figure 3 shows the effect of immersion time dependent wear rate and friction coefficient of CF- or PTW-

TABLE II
Porosity and Pore Volume of PTFE Composites Before Immersion

Composites	Pore volume (cm^3/g)	Porosity (%)
CF/PTFE	0.0452	9.0060
PTW/PTFE	0.0200	4.7069

filled PTFE composites. The wear rate of PTW/PTFE composite is lower than those of CF/PTFE composites under the various immersion times. It is indicated from Figure 3 that no significant difference between the friction of CF/PTFE and PTW/PTFE composites is observed under the various immersion times. The wear rate of PTW/PTFE composite is only 40% with compared to that of the CF/PTFE composite after immersing in acid (75°C; 30% sulfuric acid concentration) for 5 days.

The wear rate of CF/PTFE composites increases linearly with the increased immersion time. After 15 days of immersion, the CF/PTFE wear rate is $\sim 4.67 \times 10^{-9}$ cm^3/Nm, which is about thrice as much as its wear rate prior to immersion (1.56×10^{-9} cm^3/Nm). The wear rate of PTW/PTFE composites immersed for 15 days at the same solution condition shows comparable results compared with the original sample. In addition, the wear rate of CF/PTFE composites immersed for 15 days is 3.6 times as much that of the PTW/PTFE composites. This is due to the better anticorrosive properties of PTW/PTFE composites under acidic condition. The wear rate of the CF/PTFE composite is more dependent on the immersion time than the friction coefficient.

Figure 4 shows the typical variation of the friction coefficient of CF/PTFE and PTW/PTFE composites with the sliding time after immersing in acid (75°C; 30% sulfuric acid concentration) for 5 days. The running period of the friction coefficient occurs in most experimental runs.[20] The running period of the friction coefficient for PTW/PTFE composites is shorter than that of CF/PTFE composites.

Effect of solution temperature

Figure 5 shows the effects of solution temperature on the wear rate and friction coefficient of the PTFE
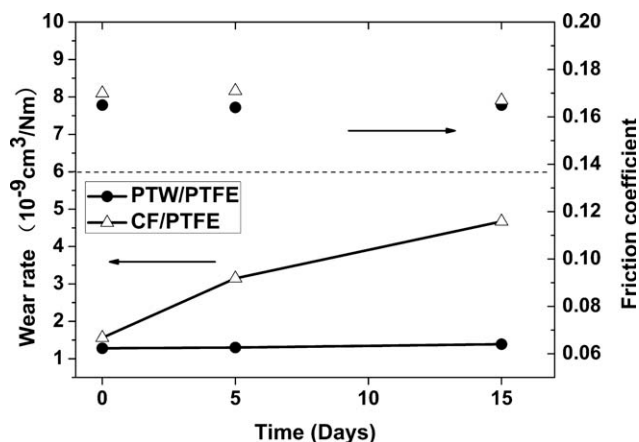

Figure 3 Effects of immersion time on the wear rate and friction coefficient of CF/PTFE and PTW/PTFE composites. (Sliding velocity: 1.4 m/s; Load: 150 N; Immersion temperature: 75°C, 30% sulfuric acid concentration).
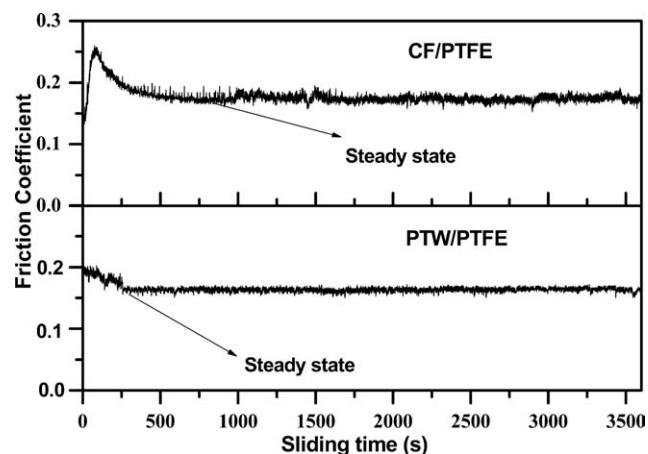
Figure 4 Variation of friction coefficient of CF/PTFE and PTW/PTFE composites with the sliding time (Load: 150 N; Sliding velocity: 1.4 m/s; Immersion times: 5 days, Immersion temperature: 75°C, 30% sulfuric acid concentration).

composites, in which the wear rate of the PTFE composites increases with increasing solution temperature. At relatively higher temperatures, the H_2O molecule move faster, combined with the enhanced segmental motion of the polymer. Thus, sulfuric acid may penetrate into the PTFE composites more easily.[5] Severe swelling may occur due to the penetration of more water molecules and sulfuric acid into the amorphous regions of the polymer reducing in the attractive forces between polymer chains.[24] Absorbed more sulfuric acid and H_2O molecules will also severely attack the fiber-matrix interface, and damage may occur in the form of interfacial microcracks.[25,26] These may lead to the higher wear rate of PTFE composites at an elevated temperature. The wear rate of CF/PTFE composites is about twice as much as that of the PTW/PTFE composites. The
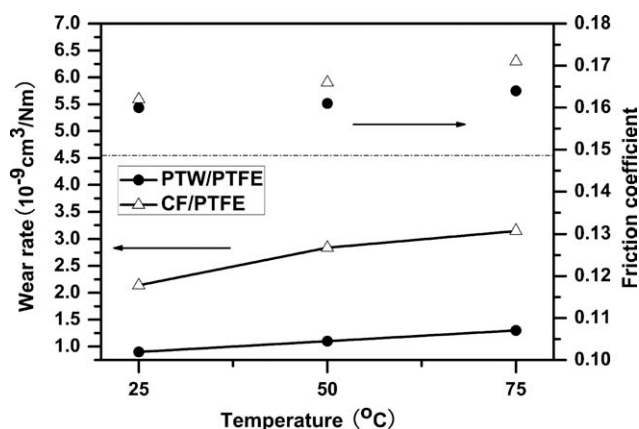
effect of immersion temperature on the friction coefficient of PTFE composites is not obvious.

Effect of sulfuric acid concentration

Figure 6 illustrates the effects of solution concentration on the wear rate and friction coefficient of PTFE composites. The wear rate of PTFE composites increases with increasing sulfuric acid concentration. The sulfuric acid concentration has no obvious effect on the friction coefficient of PTFE composites. In addition, the solution concentration has a stronger effect on the wear rate of CF/PTFE composites than that of PTW/PTFE composites due to the oxidation of the structure in CF when the CF is immersed in highly concentrated sulfuric acid[27,28]; whereas PTW has excellent chemical stability in the sulfuric acid.

Effect of corrosive mass loss rate

The wear rate and friction coefficient of CF- or PTW-filled PTFE composites as a function of corrosive mass loss rate are presented in Figure 7. The friction coefficient is almost unchanged with increasing corrosive mass loss rate. However, the wear rate of PTFE composites increases with increasing corrosive mass loss rate. Therefore, the corrosive mass loss rate can be used as an index to evaluate the wear rate properties in harsh environments. The wear rate of PTW/PTFE composites lays in the small range of 0.8 to 1.4 × 10^{-9} cm^3/Nm, whereas the CF/PTFE locates in a relatively larger range of 2.04 to 4.67 × 10^{-9} cm^3/Nm. This is due to the more stable corrosive mass loss rate of PTW/PTFE composites under different test conditions.

The better tribological and anticorrosive properties of PTW/PTFE compared with CF/PTFE could be explained from the following two aspects. First, the
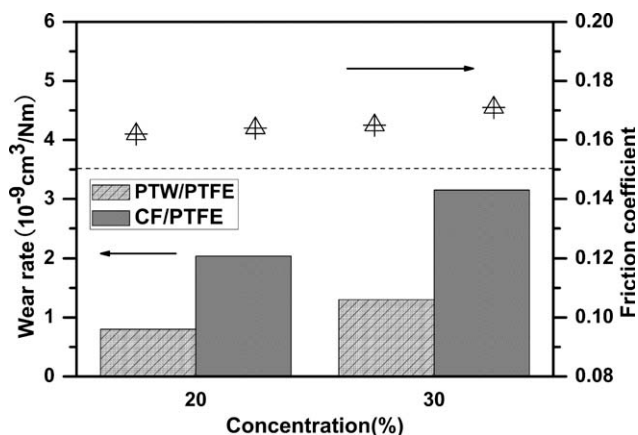

Figure 5 Effects of immersion temperature on the wear rate and friction coefficient of CF/PTFE and PTW/PTFE composites. (Sliding velocity: 1.4 m/s; Load: 150 N; Immersion times: 5 days, 30% sulfuric acid concentration).

Figure 6 Effects of immersion solution concentration on the wear rate and friction coefficient of CF/PTFE and PTW/PTFE composites. (Sliding velocity: 1.4 m/s; Load: 150 N; Immersion times: 5 days, Immersion temperature: 75°C).
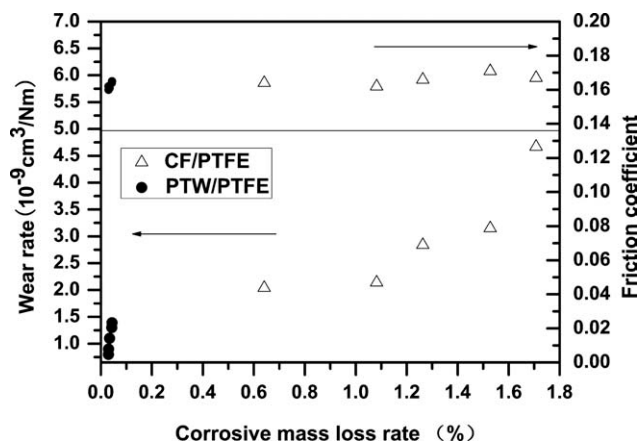
Figure 7 Effects of corrosive mass loss rate on the wear rate and friction coefficient of CF/PTFE and PTW/PTFE composites. (Sliding velocity: 1.4 m/s; Load: 150 N).

small-sized PTW may serve as a nuclear center for developing continuous polymer regions and then interconnect to form a tightly structured network, contributing to the improved antiwear ability and

anticorrosive properties in a sulfuric acid solution.[15] Second, PTW has excellent chemical stability in the sulfuric acid due to its stable tunnel structure. This tunnel structure consists of ribbon sharing at terminal corners with identical ribbons, resulting in an open octahedral framework enclosing the tunnels in which the potassium ions are situated.[18,19] However, oxidation of the structure in CF occurs when the CF is immersed in the sulfuric acid, namely, the aliphatic groups that terminate the graphene sheets would be oxidized.[28] The wear rate of CF/PTFE composites increases after the acid solution immersion, due to the degradation of the fibers and the interface in the surrounding environment. Hence, the PTW/PTFE composites have better anticorrosive properties and antiwear ability than the CF/PTFE composites.

SEM investigation of worn surface and transfer film

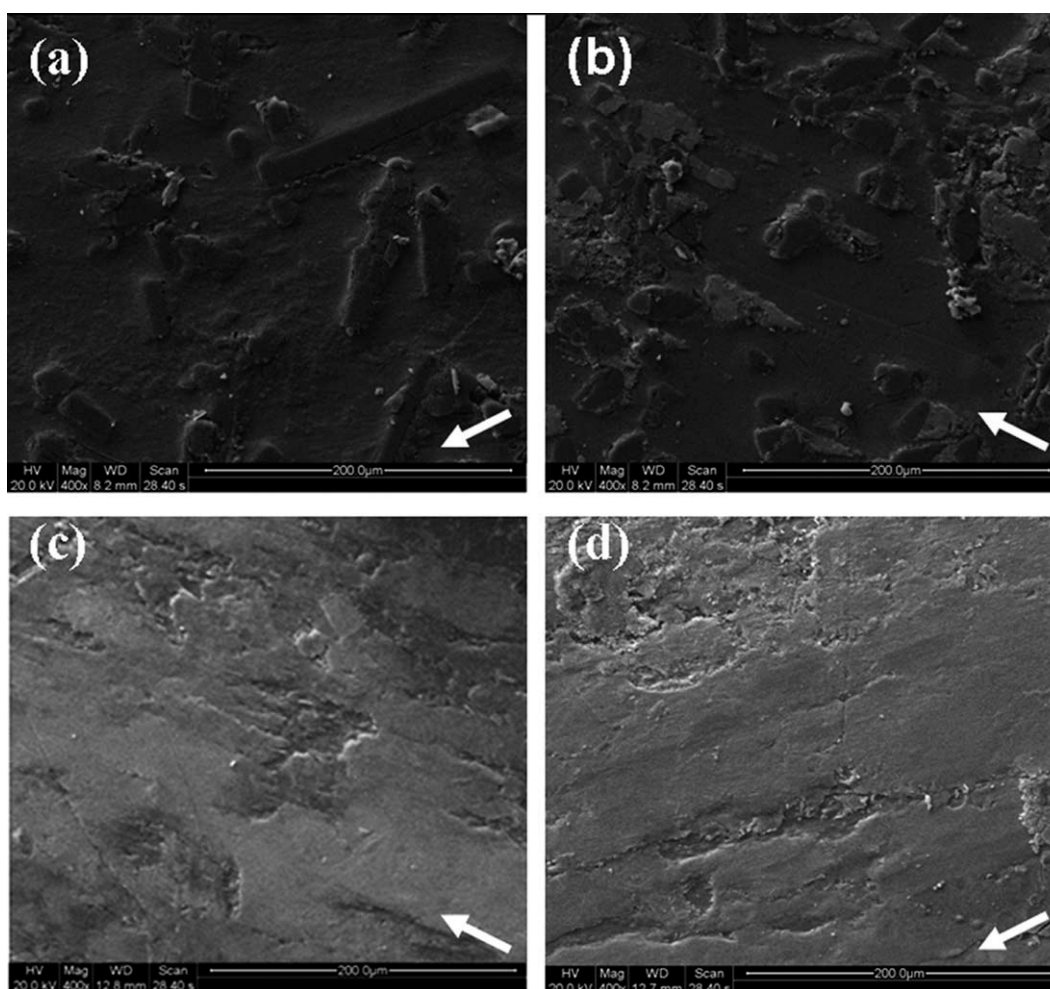To acquire further information on the effects of the fiber fillers on the wear behaviors of the PTFE

Figure 8 SEM micrographs of the worn surface (×400): (a) CF/PTFE-before immersion, (b) CF/PTFE-after immersion, (c) PTW/PTFE-before immersion, (d) PTW/PTFE-after immersion, (Load: 150 N; Sliding velocity: 1.4 m/s; Immersion times: 5 days, Immersion temperature: 75°C, 30% sulfuric acid concentration). White arrows indicate sliding direction.

Figure 9 SEM micrographs of the transfer film (×400): (a) CF/PTFE-before immersion, (b) CF/PTFE-after immersion, (c) PTW/PTFE-before immersion, (d) PTW/PTFE-after immersion, (Load: 150 N; Sliding velocity: 1.4 m/s; Immersion times: 5 days; Immersion temperature: 75°C; 30% sulfuric acid concentration). White arrows indicate sliding direction.
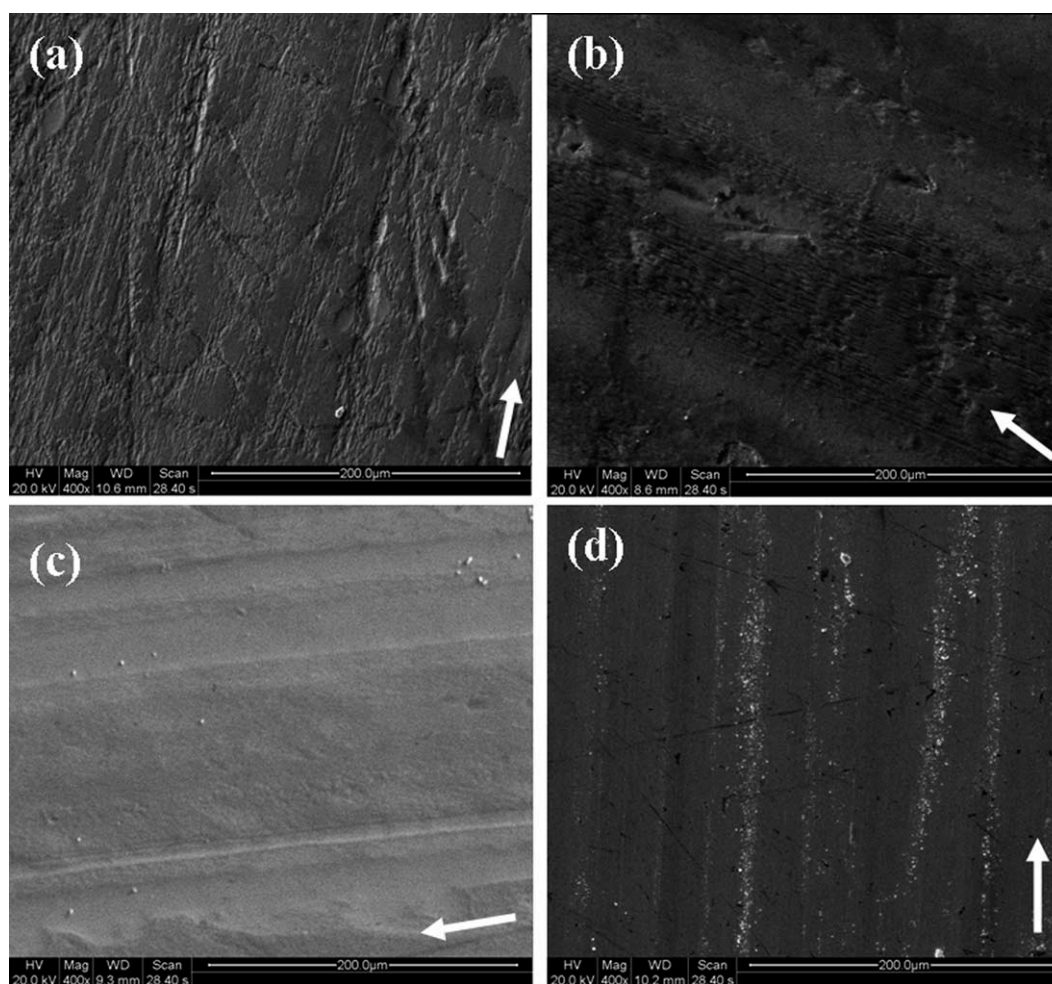
composites after solution immersion, the worn surfaces and transfer films of PTFE composites were studied by SEM, as shown in Figures 8 and 9.

The SEM micrographs of the worn surfaces of the PTFE composites are given in Figure 8. The worn surface of CF/PTFE composites before immersion is characterized by microcracking with the detached CF fibers visible on the worn surface [Fig. 8(a)]. Fatigue might be the main form of wear under dry sliding. After the sulfuric acid immersion, as shown in [Fig. 8(b)], the worn surface of CF/PTFE is relatively rough and the PTFE matrix is significantly peeled, corresponding well to the higher wear rate of CF/PTFE composites. In addition, more microcracking with the detached CF fibers is visible on the worn surface than the one before immersion.

The worn surfaces of PTW/PTFE composites are relatively smooth before [Fig. 8(c)] or after immersion [Fig. 8(d)]. These smooth surfaces directly lead to the lower wear rate of PTW/PTFE composites. Figure 9 shows the SEM micrographs of the transfer

film. In Figure 9(a,b), the transfer film of the CF/PTFE composites is relatively rough. More evident plucked and ploughed marks appear on the transfer film. The transfer film of the CF/PTFE composites after the sulfuric acid immersion is rougher than the one without immersion. In the Figure 9(c,d), the transfer films of the PTW/PTFE composites are smooth independent of the immersion process.

CONCLUSIONS

1. The corrosive mass loss rate of CF/PTFE is much larger than that of PTW/PTFE composites under different test conditions. The corrosive mass loss rate of CF/PTFE is about 36 times larger than those of PTW/PTFE (75°C, 5 days; 30% sulfuric acid concentration), which is due to the larger pore volume, pore size, and porosity of CF/PTFE composites compared with the PTW/PTFE composites.

2. The wear rate of PTFE composites increases with increasing solution temperature and concentration. Acid immersion exhibits no evident effect on the wear rate of the PTW/PTFE composite. While the wear rate of CF/PTFE immersed for 15 days is thrice as much that of untreated composites and 3.6 times as much that of PTW/PTFE composites.

3. The wear rate of the PTFE composites increases with increasing corrosive mass loss rate. Moreover, it is more dependent on the corrosive mass loss rate rather than friction coefficient.

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