Tribological Behavior of Poly(ether ether ketone) Composites Filled with Potassium Titanate Whiskers Sliding in Different Media

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ABSTRACT: The friction and wear properties of poly (ether ether ketone) (PEEK) composites filled with potassium titanate whiskers (PTWs) under alkali, water, and dry conditions were investigated. The wear mechanisms in different lubrication situations were studied on the basis of examinations of the worn and counterpart surfaces with scanning electron microscopy and optical microscopy. The results showed that PTWs could obviously increase the wear resistance and reduce the friction coefficient of the PEEK composites under dry sliding conditions. Only when the PTW content was greater than 35 wt % did the wear resistance and friction coefficient deteriorate. Sliding in water caused increases in the wear rate and friction coefficient of the PEEK composites, and the PTW-filled PEEK composites showed the highest friction coefficient and wear rate under this lubrication condition. On the contrary, sliding in an alkaline solution, the PTW-filled PEEK composites showed the lowest friction coefficient and almost the same level of wear resistance as that found under the dry condition. Furrows and abrasive wear were the main mechanisms for the PTW-filled PEEK composites sliding in water. The transfer onto the counterpart rings was significantly hindered with sliding under water and alkali conditions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1935–1941, 2010

Key words: composites; fillers; high performance polymers; matrix

INTRODUCTION

In the petroleum and chemical industries, in which water, alkalis, acids, and other media are often used, special materials have to be used. Polymers are promising and welcome sealing and wear-resistance materials in such corrosive environments. Poly(ether ether ketone) (PEEK), a semicrystalline polymer, is used as a special engineering plastic because of its excellent mechanical capacity, good resistance to chemical erosion, and thermal stability. However, the high friction coefficient and wear rate of pure PEEK have limited its wider use. To improve its tribological performance, PEEK composites filled with various fillers (e.g., nanometer and micrometer particles and fibers) have been investigated.[1–3]

Among numerous inorganic fillers, potassium titanate whiskers (PTWs; i.e., $K_2O{\cdot}6TiO_2$) have been found to be promising structural reinforcers for polymers, metals, and ceramic composites because of their excellent mechanical properties, wear resistance, and chemical and thermal stability.[4–6] Furthermore, PTWs have excellent alkaline resistance and an excellent capacity for microreinforcement because of their very small size, which is suitable for reinforcing very narrow regions in composites that conventional fibers are unable to reinforce.

However, until now, the effect of PTWs on the friction and wear behavior of PEEK has been unreported. In addition, most published investigations concern the friction and wear properties of polymers sliding against steel under dry conditions, and few researchers have studied the tribological performances of polymers in water;[7,8] almost no information is available about the friction and wear behavior of polymers in alkali.

The purpose of this work was to study the friction and wear properties of PEEK composites reinforced with various amounts of PTWs sliding in alkali, dry, and water lubrication situations and gain some insight into the friction and wear mechanisms in different lubrication situations. This research is also expected to be helpful in the use of outstanding

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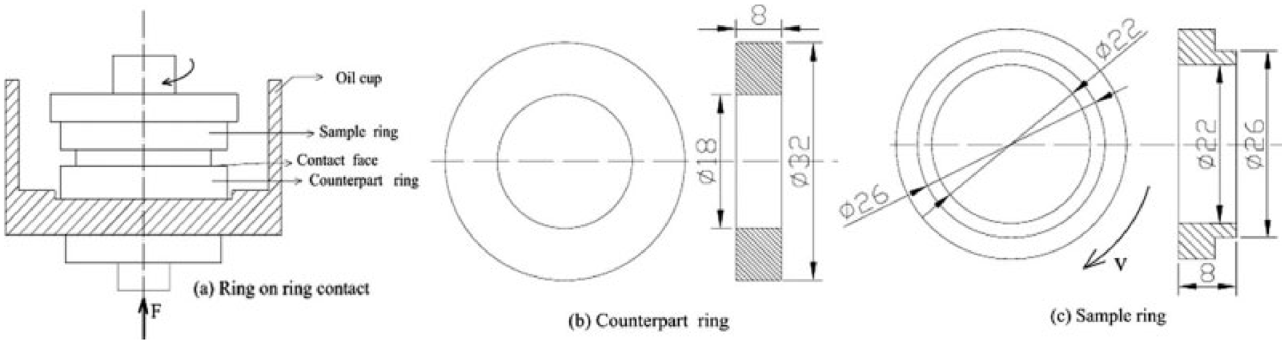

Figure 1 Contact schematic diagram of the wear tester: (a) ring-on-ring contact, (b) counterpart ring, and (c) sample ring.

PEEK composites for bearings, padding, impellers, and so forth in a wider range of applications.

EXPERIMENTAL

Materials and preparation of the PEEK composites

PEEK 450G was supplied by Victrex plc (London, United Kingdom). PTWs with a diameter of 0.5–1 μm and an average length of 20 μm were synthesized by us.[9–11] The PTWs were modified with an amino silane coupling agent.[4,5] Commercial polytetrafluoroethylene (PTFE) powder (7A-J) was supplied by Dupont (Wilmington, DE). The to-be-tested PEEK composites filled with 15 wt % PTFE and various amounts of PTWs were produced by high-temperature compression molding at 370–380°C and 10 MPa for 90 min.[8] Finally, the samples were cut into a shape with an external diameter of 26 mm, an inner diameter of 22 mm, and a shoulder height of 2.5–3 mm [Fig. 1(c)]. The counterpart ring [stainless steel with an external diameter of 36 mm, an inner diameter of 18 mm, and a thickness of 8 mm; Fig. 1(b)] and the sample ring were polished to an average roughness of 0.15–0.3 μm with 900-grit SiC abrasive paper and cleaned. The lubricants were deionized water and a 10 wt % sodium hydroxide alkali solution.

Friction and wear tests

The friction and wear tests were carried out on an MPX-2000 friction and wear tester (Xuanhua Testing Factory, Hebei, China). A contact schematic diagram of the frictional parts is shown in Figure 1. Sliding was performed under ambient conditions (temperature = 25°C, humidity = 50 ± 5%) with a sliding velocity of 1.4 m/s and with loads of 100, 200, and 300 N, respectively. The friction duration was 120 min. The samples were cleaned with acetone and put into an oven at 135°C for 8 h before they were weighed.

The computer recorded the frictional torque data once a second, and the friction coefficient was the average value of the last 60 min. The specific wear rate [Wr (m^3/Nm)] was calculated with the following equation[12]:

$$Wr = \frac{\Delta m}{L \cdot \rho \cdot F_N}$$

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

In this work, three replicated friction and wear tests were carried out to minimize data scattering, and the average of three replicate test results was reported. The microstructure of the worn surface was investigated with a Quanta 200 scanning electron microscope (FEI Co., Eindhoven, Netherlands), and the transfer behavior of the counterpart surface was examined with an optical microscope (Novel Optics Co., Ltd., Nanjing, China).

RESULTS

Friction and wear properties of the PEEK composites

Friction and wear properties of the PEEK composites under dry conditions

The friction coefficient and wear rate of the PEEK composites filled with various amounts of PTWs under the dry sliding condition are shown in Table I

TABLE I
Friction Coefficients and Wear Rates of PEEK Composites Under Dry Conditions (200 N, 1.4 m/s, and 2 h)

	Pure PEEK	15 wt % PTFE/PEEK	15 wt % PTW/15 wt % PTFE/PEEK
Friction coefficient	0.15	0.085	0.07
Wear rate ($\times 10^{-15}$ m^3/Nm)	340	3.05	0.837

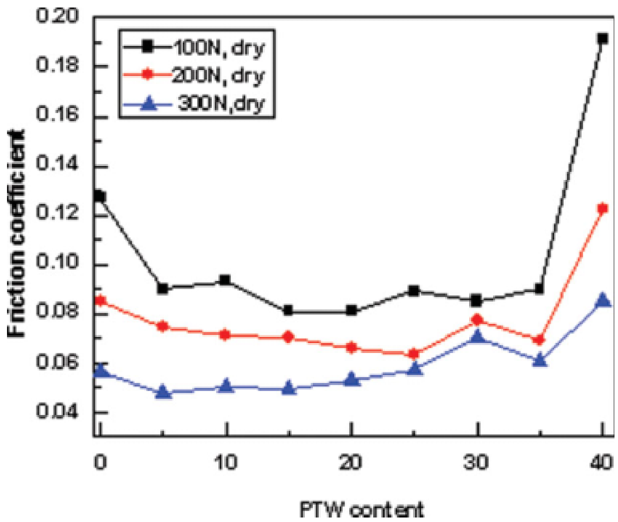

Figure 2 Relationship between the friction coefficient and PTW content of PTW/15 wt % PTFE/PEEK composites in dry sliding at 1.4 m/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and Figures 2 and 3, respectively. As shown in Table I, high frictional heat generated by pure PEEK under this dry sliding condition led to a higher wear rate. PTFE showed a good lubricating effect in the PEEK composites. The friction coefficient and wear rate of PEEK decreased obviously with 15 wt % PTFE added to the pure PEEK. With 15 wt % PTW added to the 15 wt % PTFE/PEEK composite, the friction coefficient and wear rate also decreased. The wear resistance was 3.64 times higher than that of the 15 wt % PTFE/PEEK composite and 406 times higher than that of the pure PEEK under this dry sliding condition. Therefore, the conclusion can be drawn that PTWs have an outstanding ability to reduce the friction coefficient and increase the wear resistance of PEEK composites.

According to Figure 2, the friction coefficient of the PEEK composites decreased obviously when the load increased from 100 to 300 N. With the PTW content increasing, the friction coefficient of the PEEK composites decreased at first and then increased. When the PTW content was between 5 and 35 wt %, the change in the friction coefficient of the PEEK composites was slight. However, the friction coefficient increased sharply when the content exceeded 35 wt %.

Figure 3 also shows that the wear rate of the PEEK composites almost decreased with the load increasing. With the PTW content increasing, the wear rate showed a slight decrease at first, and then it increased. In particular, when the content was more than 35 wt %, it increased rapidly. Therefore, 35 wt % PTW was the critical point for the PEEK composites sliding under this dry condition; after that, the friction and wear behaviors both deteriorated significantly.

This may be attributed to the fact that the size of the PTWs was small and the specific surface area was large. When the amount of PTWs was not too high, they could be dispersed homogeneously in the matrix. The bonding between the PTWs and PEEK matrix was strong. The PTWs improved the tribological performance of the PEEK composites at this time. However, when the PTW content was greater than 35 wt %, this was too much for the matrix to cover. Debonding and detachment of the PTWs from the PEEK matrix took place. Therefore, as far as the friction and wear properties were concerned, the proper amount of PTWs was between 10 and 25 wt %.

Friction and wear properties of the PEEK composites in different media

The results for the friction coefficients and wear rates of the sliding experiments under different lubrication conditions are presented in Figures 4 and 5. The relationship of the friction coefficients of the PEEK composites sliding in different lubrication situations was $\mu_{water} > \mu_{dry} > \mu_{alkali}$. μ_{water} is the friction coefficient of PEEK composites sliding in water; μ_{dryI} is the friction coefficient of PEEK composites sliding in dry condition; and μ_{alkali} is the friction coefficient of PEEK composites sliding in alkali. The distinction was obvious: the friction coefficient was lowest in the alkali and maximum in water. In water, the friction coefficient of the PEEK composites obviously increased with the content increasing. On

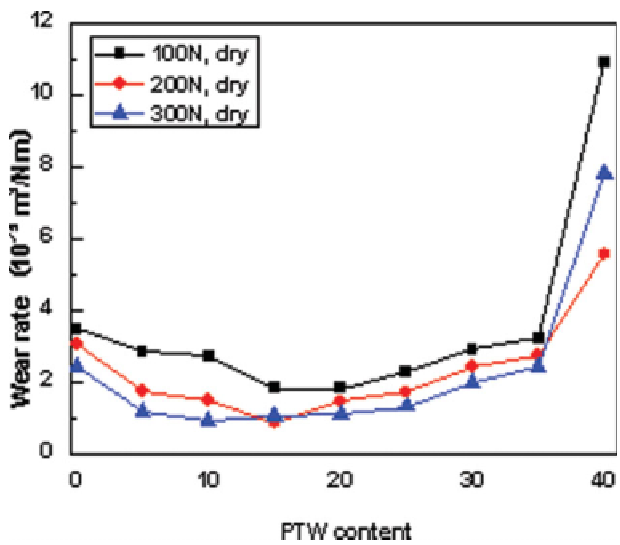

Figure 3 Relationship between the wear rate and PTW content of PTW/15 wt % PTFE/PEEK composites in dry sliding at 1.4 m/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

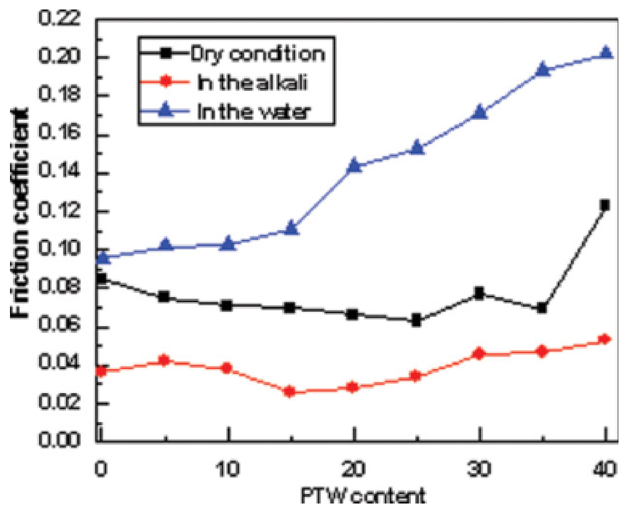

Figure 4 Relationship between the friction coefficient and PTW content of PTW/15 wt % PTFE/PEEK composites in different lubrication situations (200 N and 1.4 m/s). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the contrary, the change in the friction coefficient with the content increasing was slight when they were sliding under alkali and dry conditions.

Figure 5 clearly shows that the wear rates of the PEEK composites with various amounts of PTWs in water were several times higher than those of the PEEK composites under the alkali and dry conditions, and the latter two were almost on the same level. The wear rate increased markedly with the content increasing when the composites were sliding in water.

The friction coefficient and wear rate of the PEEK composites in water both increased obviously with the PTW content increasing. Water degraded the friction and wear properties of the PEEK composites filled with various amount of PTWs. The main reason is that water destroyed the bonding between the PTWs and PEEK matrix, and this caused easier separation between the fillers and matrix.

Scanning electron microscopy micrographs of the worn surfaces

To understand the friction and wear behaviors, the worn surfaces of PEEK composites filled with various PTW contents in different lubricants were studied with scanning electron microscopy (Fig. 6). In the dry condition, slight nicks and obvious adhesion could be seen on the worn surface of the pure PEEK [Fig. 6(a)]. As shown in Figure 6(b), many small PTFE blocks existed on the worn surface of the PEEK composite with the PTW content of 15 wt %. Furthermore, lots of small PTW particles were embedded in each PTFE block. During sliding, these PTFE blocks may also have had a positive effect by having a good lubricating effect and by trapping the broken PTW particles. Therefore, the friction coefficient and microscuffing of PTW particles on the counterpart surface were reduced for these PTFE blocks.

As expected, lots of PTW particles emerged on the worn surface in dry sliding when the content was increased to 40 wt % [Fig. 6(c)]. Moreover, agglomeration and lapping joints could be seen on the worn surface. Deep furrows and severe scuffing appeared on the worn surface after sliding in water [Fig. 6(f)]. Water molecules destroyed the bonding between the PTWs and PEEK matrix. The unstuck PTWs and the broken particles were the main reasons for the severe furrows and scuffing on the worn surface during sliding in water.

Among the three different lubrication conditions, the worn surface of the PEEK composites filled with 15 wt % PTW in the alkali was the smoothest [Fig. 6(d)], and the worn surface became rough when the PTW content was increased to 40 wt % [Fig. 6(e)].

Optical microscopy investigation of the transfer films

Optical micrographs of the transfer films that formed on the counterpart surfaces of the PTW-reinforced PEEK composites in different lubrication situations are shown in Figure 7. Under the dry condition, there were lots of nicks in the length and breadth on the counterpart surface after it was polished with 900-grit SiC abrasive paper [Fig. 7(a)]. The transfer film of the PEEK composite filled with 5 wt % PTW appeared to be discontinuous and thin [Fig. 7(b)]. A uniform transfer film was gained on the counterpart surface when the PEEK composite filled with 15 wt % PTW was sliding under the dry condition [Fig. 7(c)], whereas the 40% PTW-filled

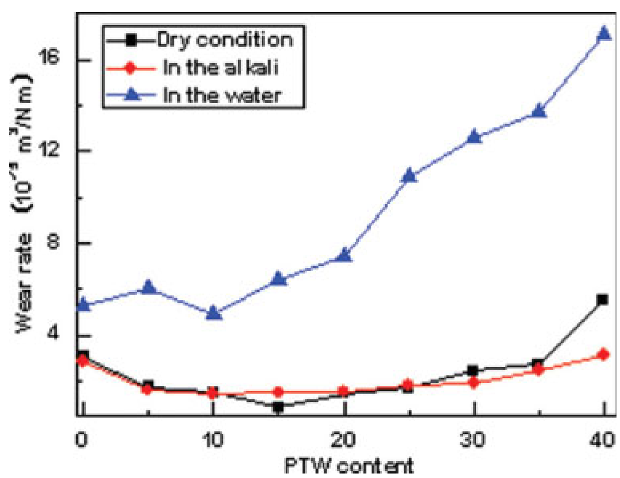

Figure 5 Relationship between the wear rate and PTW content of PTW/15 wt % PTFE/PEEK composites in different lubrication situations (200 N and 1.4 m/s). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

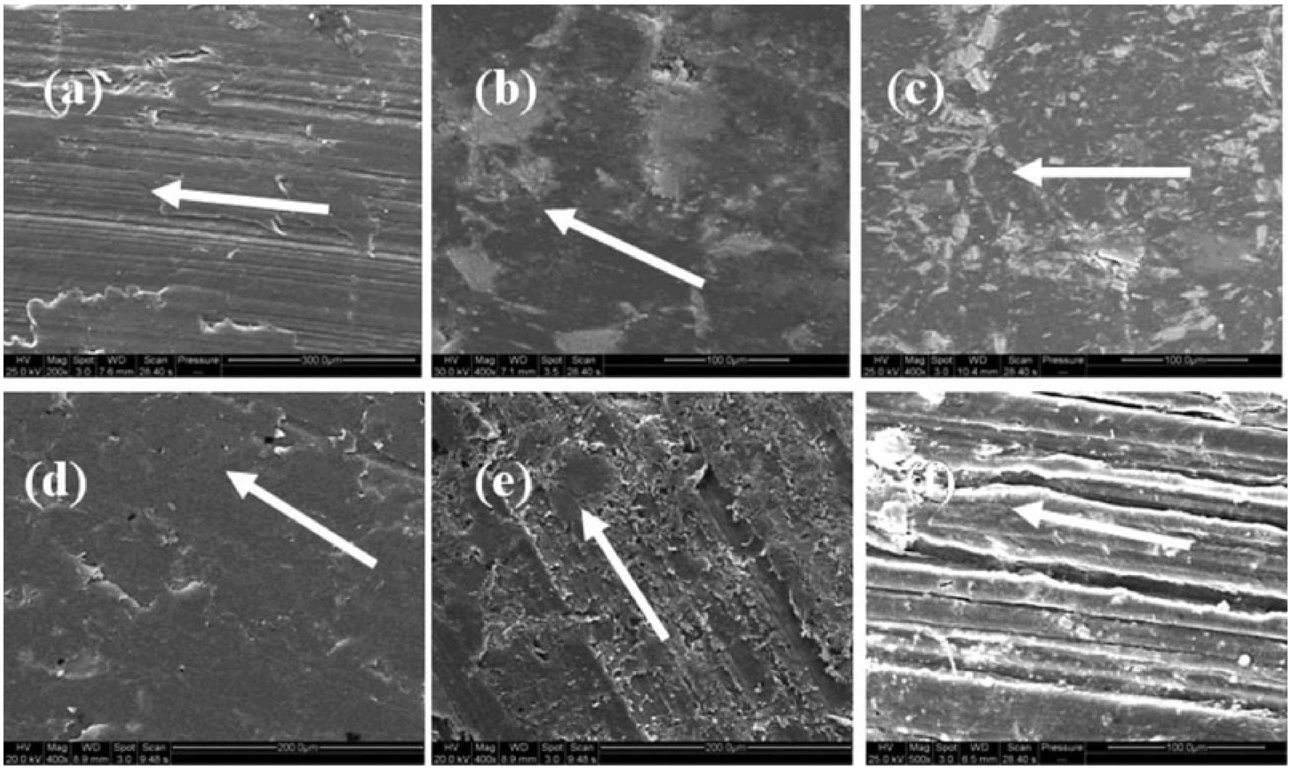

Figure 6 Worn surfaces of PTW/15 wt % PTFE/PEEK composites with various PTW contents in different lubricants at 1.4 m/s and 200 N (×400): (a–c) 0, 15, and 40 wt % PTW under dry conditions; (d,e) 15 and 40 wt % PTW in an alkali; and (f) 15 wt % PTW in water. The arrows indicate the sliding direction.

PEEK composite could not, and obvious furrows could be seen on the counterpart surface.

Some slight furrows could be seen on the counterpart surface when it was sliding in the alkali [Fig. 7(e)]. However, abrasive particles and deep furrows appeared on the counterpart surface when it was sliding in water [Fig. 7(f)]. This meant that transfer films on the counterpart surface were obviously hindered when they were sliding in the alkali and water. Furrows and abrasive wear were the main mechanisms for the PTW-filled PEEK composites sliding in water.

DISCUSSION

Sliding under the dry condition, the PTWs could reinforce PEEK and prevent the composite surface from coming into direct contact with the counterpart, and this accounted for the improvement of the friction and wear behaviors of the PEEK composites. The PTWs could reduce the friction coefficient and increase the wear resistance of the PEEK composites. However, when the amount of the PTWs was excessive (i.e., >35%), agglomeration, lapping joints, and poor fluidity appeared because the dimensions of the PTWs were very small. As a result, poorer wear rates and friction coefficients occurred when the PTW content was more than 35%. With the load increasing, the real contact area and frictional heat increased. Plastic deformation and easy flow of PEEK took place, and this accounted for the reduction of the friction coefficient and wear rate under the dry condition.

We have found that PTWs are hydrophilic inorganic fibers. The silane surface treatment used in this study showed alkalinity, and the hydrolysis tended to be accelerated by water. The penetrating power of the water molecules destroyed the bonding effect of the PTWs and matrix, and this caused easier separation between the fillers and matrix. The furrows and abrasive wear caused the wear rate to greatly increase.[7,13,14] Moreover, water hindered the formation of the transferred film and may have penetrated and corroded the PTW–matrix interface.[15] Furrows and abrasive wear were the main mechanisms for the PTW-filled PEEK composites sliding in water. As a result, although there were some cooling and lubricating effects of water, the friction coefficient and wear rate in water increased significantly in comparison with those in dry friction.

The viscosity of the 10 wt % alkali was 1.77 times higher than that of water at a medium temperature of about 40°C in this test (0.00115 Pa s for 10 wt % alkali and 0.00065 Pa s for water). The thickness of the alkali boundary layer was higher than that of water. The cooling and boundary lubricating effects of the alkaline solution were better than those of

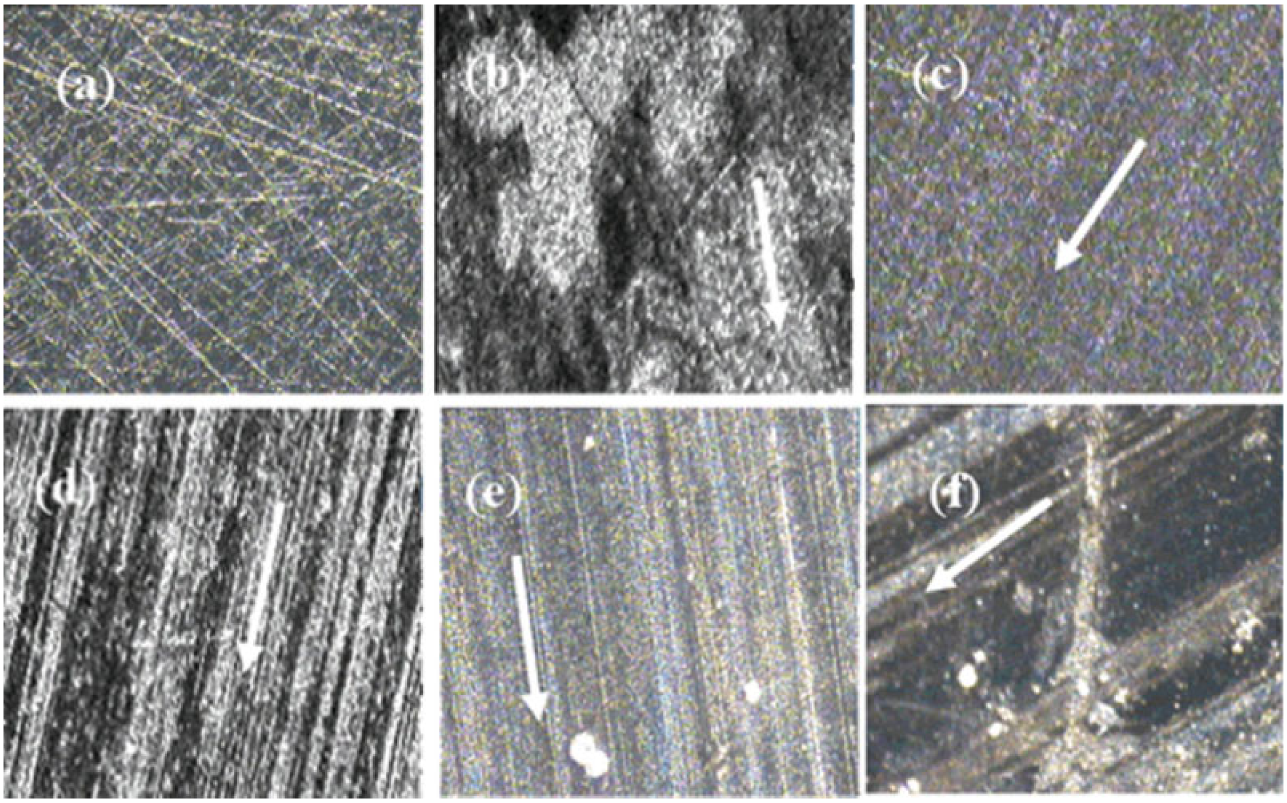

Figure 7 Transfer films of PTW/15 wt % PTFE/PEEK composites with various PTW contents in different lubricants at 1.4 m/s and 200 N (×200): (a) before testing; (b–d) 5, 15, and 40 wt % PTW under dry conditions; (e) 15 wt % PTW in an alkali; and (f) 15 wt % PTW in water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water, and the stability of the PTWs and PEEK matrix in the alkali were good.[16,17] The worn surface and counterpart surface were better than those in water. In addition, the alkali solution had some capacity to wash the surface and remove the debris from the rubbing region, and this reduced the abrasive wear. Therefore, although the transfer behavior to the counterpart surface was hindered, the wear resistance and friction coefficient of the PTW-filled PEEK composites in the alkali were improved greatly versus those of the composites in water.

CONCLUSIONS

The friction and wear properties of PEEK composites reinforced with various amounts of PTWs in alkali, water, and dry lubrication situations were studied. Some insights into the friction and wear mechanisms in the different lubrication situations were also obtained. The following conclusions can be made on the basis of this study:

1. PTWs are excellent-performance whiskers; they could obviously increase the wear resistance and reduce the friction coefficient of the PEEK composites under the dry sliding condition. Only when the PTW content was greater than 35 wt % did the wear resistance and friction coefficient deteriorate.
2. Because of the cooling and boundary lubricating effects of the alkali, PEEK composites filled with PTWs showed lower friction coefficients and much better wear resistance than PEEK composites in water, and they kept almost the same level of wear resistance as that found in the dry condition.
3. Sliding in water degraded the friction and wear properties of the PEEK composites, and the friction coefficient and wear rate of the PEEK composites were highest under this lubrication condition. Furrows and abrasive wear were the main mechanisms for the PTW-filled PEEK composites sliding in water.
4. The transfer onto the counterpart surface of the PTW-filled PEEK composites was hindered obviously when they were sliding in the alkali and water.

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