Mechanical Properties and Sliding Wear Behavior of Potassium Titanate Whiskers-Reinforced Poly(ether ether ketone) Composites Under Water-Lubricated Condition

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ABSTRACT: Polyetheretherketone (PEEK) composites reinforced with potassium titanate whiskers (PTW) were compounded using a twin-screw extruder followed by injection molding. The effects of PTW on the mechanical properties, crystallization performances and wear behaviors of PEEK under water lubrication have been investigated. It was denoted that the yield strength, Young's modulus, and microhardness of the composites increased with increasing whisker content, but the elongation at break and the impact strength showed decreasing trend. It was revealed that the inclusion of PTW could effectively reduce the friction coefficient and enhance the wear resistance of the PEEK. The DSC tests showed that the crystallinity of the composite slightly decreased with the addition of PTW, which might imply that the crystallinity of PEEK was not the dominant factor that influenced the wear properties of the composites. The enhancement on the wear resistance was attributed to the reinforced effect of PTW on PEEK. The wear mechanism changed from fatigue wear into mild abrasive wear when the PTW was added into PEEK. The lowest wear rate 9.3×10^{-8} mm^3/Nm was achieved at 10 wt % PTW content. However, excessive whiskers would cause severe abrasive wear to the composite. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 186–193, 2010

Key words: mechanical property; sliding wear; water lubrication; poly (ether ether ketone); potassium titanate whisker

INTRODUCTION

With its outstanding mechanical properties, thermal stability and good wear resistance, polyetheretherketone (PEEK) has been widely used for applications of dry sliding conditions. However, in some cases of the applications, the material was with water lubrication or contamination with water. Generally, the influencing factors on the wear rate in the aqueous condition for the polymer matrix material included counterface material, counterface roughness, sliding velocity and contact stress.[1–4] The presence of water in the friction surface could result in fluid film lubrication, boundary lubrication, or a mixture of the two.[5] Therefore, the friction coefficient in water lubrication always showed lower value than that in dry sliding.[6,7] Moreover, water also interacted with polymeric materials in some other ways. They were: the capability of washing the surface and wear debris, which caused the inhibition of the transfer film formation[8,9]; working as a cooling agent[6,7]; deterioration on the combination between the fillers and polymer matrix[9]; absorption of water, which soft-ened the surface layers and resulted in an easier deformation of the matrix.[2,10] Thus, it is necessary to identify the wear behavior for PEEK and its composites in aqueous condition. Although the hardness of PEEK did not decrease only by immersing in water, the hardness of sliding surface could still decreased after the test in water lubrication,[11] so that the water might facilitate an easy detachment of neat PEEK. It was believed that the harder, stronger materials have the ability to resist deformation during the friction process.[2] In this point, higher performances in mechanical properties may lead to a higher wear resistance for some polymer-based materials. This has been achieved successfully by using special fillers, such as carbon fiber,[12] nanometer SiC,[13] glass fiber.[3] Normally, the carbon fiber reinforced composites showed superior wear resistance in the water lubrication. Nevertheless, the PEEK-CF composite might not the optimal counter pair for stainless steel for some conditions, since Davim et al.[14] found that the carbon fiber-reinforced PEEK composite would abrade the counterface in the friction process. Therefore, it is necessary to develop a kind of high performance composite with low wear rate under water condition and less abrasiveness to the counterpart.

Potassium titanate whiskers (PTW) have been widely used as promising reinforcement fillers. This kind of whiskers has been proved to improve not

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only the mechanical properties[15] but also the wear resistance of PTFE in dry sliding condition[16] and under the oil lubricated condition.[17] Especially, the wear rate of PTFE was decreased by two or three orders of magnitude by the addition of the PTW. Zhuang et al.[18] incorporated PTW into PEEK to develop a composite with high mechanical properties, which demonstrated the significant reinforcement effect of PTW. On the other hand, the hardness of the PTW is not as high as that of carbon fiber (the Mohs hardness of PTW is 4). This implies that the PTW filled composite might not promote a severe abrasion to the counterface as the carbon fiber did. Therefore, it may be a good way to compound PTW into the PEEK to achieve a high wear resistance material under water lubrication. In this work, to understand the effect of PTW on the wear behaviors of PEEK/PTW composites in aqueous environment, the PEEK/PTW composites filled with various loadings of PTW were prepared. The mechanical performances, crystallization behaviors and tribological properties were investigated. The relationship between mechanical properties and wear behavior were also discussed.

EXPERIMENTAL

Materials

The PEEK (VESTAKEEP 4000G) used in this study was produced by Degussa Co. Ltd. Potassium titanate ($K_2Ti_6O_{13}$) whiskers (PTW) were supplied by the Jinjian Co. Ltd. (Shenyang, China). The diameters of the PTW are from 0.1 μm to 1.0 μm. The strength and modulus of PTW are 7 and 280 GPa, respectively. The density of the PTW is about 3.3 g/cm^3.

Specimen preparation

All the materials were dried in an oven at 150°C for 6 h before melt processing. The PTW were compounded into PEEK by using twin-screw extruder with a screw speed of 360 rpm under processing temperature of 390°C. The extrudate was continuously cooled by water and palletized. The pellets were dried in oven at 150°C for 6 h ready for injection molding. Standard test bars were injection molded with mold temperature at 180°C. The contents of PTW were controlled to be 5, 10, 15, 20, and 25 wt %, respectively. For the purpose of comparison, neat PEEK specimens were also injection molded.

Characterization

The wear tests were performed on MM-W1A universal wear testing machine (Jinan Shijin Co. Ltd.) with

three-pin-on-disk configuration. The cylindrical specimen pins (4.8 mm diameter and 12.8 mm length) and the stainless steel disk were polished with 1500 grit SiC water-abrasive paper. The average roughness of the counterface (R_a) is 0.051 μm. All of the tests were carried out at ambient temperature with sliding velocity of 2.0 m/s and the duration of 2 h. The applied load was 1.0 MPa. The polymer-metal interface was immersed in tap water. Before and after the test, the pins were ultrasonically cleaned and dried at 150°C for 6 h for weighing. Then the mass loss of the composite pins was measured by electronic balance (Mettler AE240, accuracy 0.01 mg) for the specific wear rate calculation. The specific wear rate was calculated from the following equation:

$$K = \frac{\Delta m}{\rho F_N L} \tag{1}$$

where Δm is the mass loss of the pins (mg), ρ is the density of the pins (g/cm^3), F_N is the applied load (N) and L is the total sliding distance (m). The average of the three replicate test results for each point is reported.

Tensile tests were carried out according to ASTM D638 on a universal testing machine with a crosshead speed of 5.0 mm/min. A load cell of 20 kN and an extensometer with a gage length of 25 mm were used. Notched Charpy impact tests were carried out on a JJ-5 pendulum impact apparatus according to ASTM D6110. For each specimen, the data reported here represent the average result of at least five successful tests. The microhardness was measured by FUTURE-TECH FM-700e Vickers microhardness tester (Japan). A load of 50 gf with a loading time of 10 s was applied. A minimum of 10 data points were collected to calculate the microhardness value for each specimen.
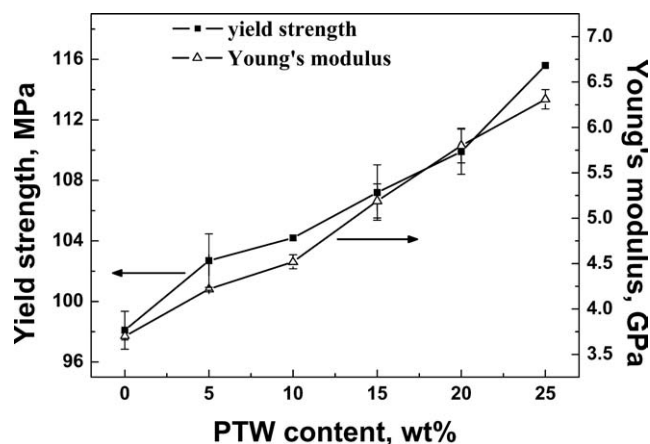

Figure 1 The variation of yield strength and Young's modulus with PTW content for PEEK/PTW composites.

TABLE I
The Microhardness of the PTW Reinforced PEEK Composites

PTW content (wt %)	0	5	10	15	20	25
Microhardness (kg/mm^2)	22.0 ± 0.4	22.5 ± 0.4	23.6 ± 1.1	25.2 ± 0.6	25.7 ± 0.8	26.1 ± 1.0

Differential scanning calorimetry (DSC) analysis was taken on a TA DSC Q20 instrument (USA) protected by nitrogen atmosphere. After being dried under vacuum at 150°C for 24 h, the samples were melted at 380°C for 5 min to eliminate the thermal history. Then they were cooled to 40°C and reheated to 380°C, both the heating and cooling rates were 10°C/min.

After the test, the counterfaces and the worn surfaces of the composite were coated with a thin layer of gold and then observed by JSM-6301F scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Mechanical properties

The variations of the yield strength and Young's modulus of the composites with the PTW content are shown in Figure 1. It can be seen that the yield strength and the Young's modulus are enhanced by the addition of the PTW due to the superior mechanical properties of the PTW. The yield strength almost linearly increases from 98 MPa for neat PEEK to 116 MPa for the 25 wt % PTW filled composite. The Young's modulus increased by 70% when the PTW loading was 25 wt %, due to the high modulus of PTW as 280 GPa. The microhardness measurements were performed on well-polished PEEK/PTW composite samples. From the microhardness data listed in Table I, an ascending trend of the microhardness with PTW content is observed. Those results demonstrate that the PTW could effectively enhance the mechanical properties of PEEK matrix. In contrast, the tensile elongation at break of the composite drops sharply with the rise of PTW content as shown in Figure 2. Generally, the incorporation of the inorganic filler into the polymer matrix might sacrifice the ductility of the polymer,[19] due to the restriction effect of the fillers on the motion of polymer chains physically or chemically.[20] Therefore, the tensile ductility decreased sharply with the addition of the PTW in the present case. The gradual decrease in strain at break indicates the transition of fracture modes from ductile fracture to brittle fracture. This statement is consistent with the micro-morphologies observed on the tensile fracture surfaces in Figure 3. It is easy to find the ductile fracture features for

neat PEEK resin because large scale of neck-shrinkage is observed accompanied with elongation increasing. When PTW are added into PEEK, the neck-shrinkages still appear during tensile tests but are limited to some local sections. The ductile and brittle fracture morphologies exist simultaneously in all the filled composites.[18] The only difference is the relative proportion of ductile fracture regions decrease gradually with the increasing whisker content.

The results of notched impact strength are also given in Figure 2. It is apparent that the impact strength of the composite reduces slightly when the whisker content is below 10 wt %. Afterwards, the impact strength levels off when the whisker content exceeds 15 wt %. Generally, the impact energy consists of two parts. One is consumed for the crack surfaces opening, and the other is consumed for the plastic deformation. For the case of PTW reinforced composites, on one hand, the PTW whiskers reinforced PEEK and thus enhanced the crack opening resistance. On the other hand, the whiskers restrained the plastic deformation of PEEK and thus reduced the plastic energy consumption. The total impact strength depends on these two competitive factors. At low loading up to 10 wt %, both reinforcement and restraint effects of PTW are not significant. Therefore, the impact strength is kept in a balance at a relative high level. With further
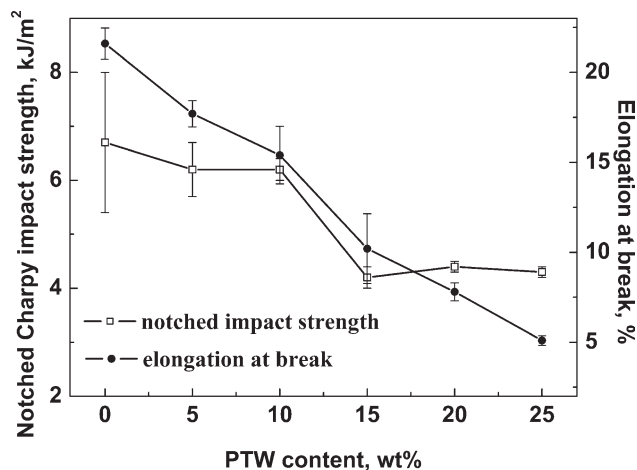

Figure 2 The variation of elongation at break and notched Charpy impact strength with PTW content for PEEK/PTW composites.
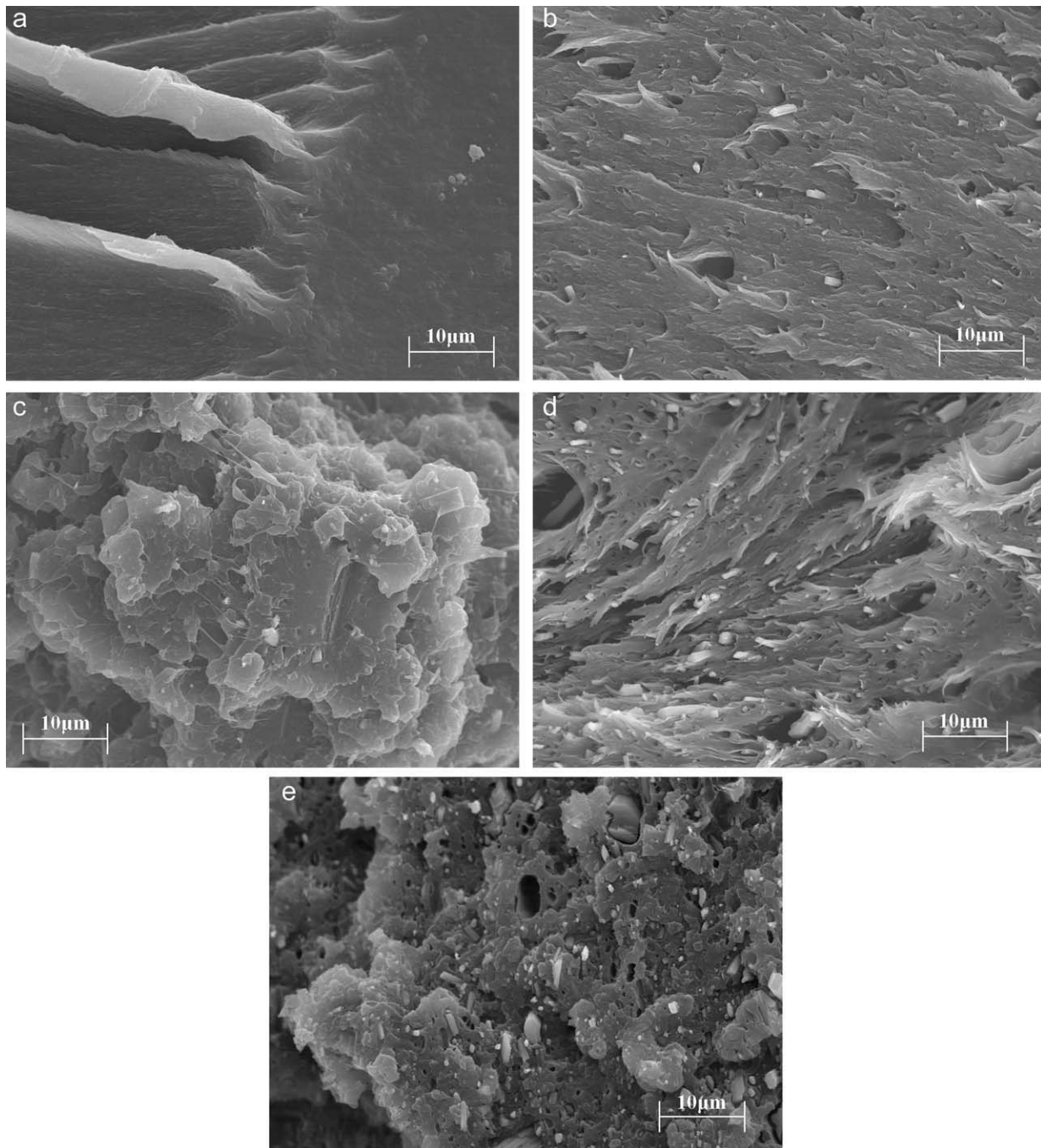
Figure 3 The representative SEM micrographs of the tensile fracture surfaces of neat PEEK and PEEK/PTW composites. (a) ductile fracture feature for PEEK, (b), (c) ductile and brittle fracture features for PEEK/5% PTW composite; (d), (e) ductile and brittle fracture features for PEEK/20% PTW composite.

increase of the PTW loading the restraint effect dominates, which results in a drop of the impact strength until 15 wt % when a new balance between the reinforcement and the restraint effects is setup. With the PTW loading at 15 wt % and up, the impact strength is kept in a balance at a relative low level. Therefore, a ductile-brittle transition is seen obviously at the PTW loading from 10 to 15 wt%.

Wear and friction performances

Figure 4 presents the results of the friction coefficient and wear rate of the PTW filled PEEK against stainless steel as a function of PTW content under water lubrication. It is evident that the friction coefficient significantly decreased as the PTW incorporated into the composites. As shown in Figure 4, the PEEK composite with a weight fraction of 5% filler
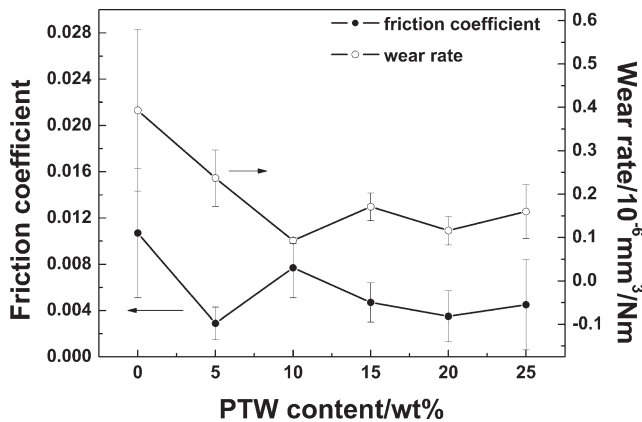
Figure 4 Relationships of the friction coefficient and wear rate of the PEEK/PTW composites versus the content of PTW. Test conditions: sliding velocity 2 m/s; sliding duration 2 h; applied load 1 MPa.

gives the lowest friction coefficient under water lubrication. The friction coefficients of those composites with higher filler loadings are around 0.005, slightly higher than that of 5 wt % PTW filled composite. As for the sliding of polymers against metallic counterparts, the friction component resulting from adhesion equals the product of the real contact area and the shear stress of the softer material. As the PTW filled in, the elastic modulus of the composites increases due to the reinforcement effect of PTW. As a result, the real contact area between composite and counterface drops, and this will lead to a decrease of the friction coefficient. On the other hand, the reinforced composites exhibit dramatic improvement in wear resistance. The wear resistances of all composites are enhanced as the PTW added in. The wear rate of the filled composite sliding against stainless steel under aqueous condition decreased linearly with increasing whisker content up to 10%. The wear rate of 10 wt % PTW filled composite is as low as 9.3×10^{-8} mm^3/Nm, which is only about a quarter of that for PEEK. However, the variation of the wear rate is indistinctive when the PTW content is above 10 wt %.

The effects of load on the friction coefficient and wear rate of PEEK/5% PTW composite were displayed in Figure 5. The results revealed that the friction coefficients of the PEEK/5% PTW composite at different load were all at a level lower than 0.01 and did not vary greatly with the applied load. However, the wear rate of the PEEK/5%PTW composite decreased gradually with the increasing load. The lowest wear rate achieved 1.08×10^{-7}mm^3/Nm at 4 MPa, only 50% of that at 1 MPa. The 5 wt % PTW

filled composite exhibited dramatic wear performance with load.

To identify the effect of PTW on the wear resistance of the composite, the worn surfaces of the composites were observed by the SEM. The morphologies of the worn surfaces for PEEK and PEEK/PTW composites are shown in Figure 6. One can find that there are some flakes on the worn surface of the neat PEEK from Figure 6(a), which implies that the wear mechanism of the PEEK is fatigue wear in present case. For the worn surface of PEEK/10% PTW, only few mild plowing tracks and microcracks can be detected from Figure 6(b). This indicates that the fatigue wear mechanism is greatly inhibited by the addition of the PTW. In this way, the wear rate of the composite dramatically decreased with the addition of the PTW. Therefore, the PTW are thought to be efficient filler to enhance the wear resistance of PEEK. However, the whisker would be worn out from the composite during the friction process to facilitate the grain abrasion, which might increase the wear rate of the composite. For the composite with high PTW content, more whiskers were likely to be worn out of the composite pin and became third-body abrasive. This is confirmed by the SEM observation in Figure 6(c). It is obvious that there were more plucked and ploughed marks on the worn surface of PEEK/25% PTW composite, which suggests that the abrasive wear is aggravative at high PTW content. Therefore, compared with that of PEEK/10% PTW composite, PEEK/25% PTW shows high wear rate. This further indicates that as filler for PEEK, a much higher content of PTW is unfavorable for the improvement on the wear resistance.

When sliding on the steel counterface in dry condition, the formation of the transfer film was always thought to be an important factor to enhance the
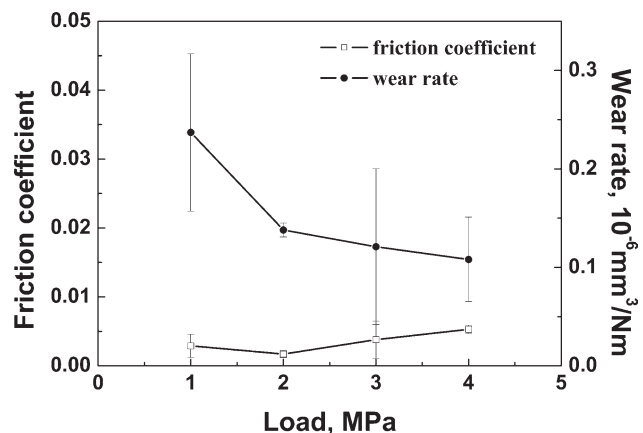

Figure 5 The relationship of the friction coefficient and wear rate of 5 wt % PTW filled composite versus the load. Test conditions: sliding velocity 2 m/s; sliding duration 2 h.
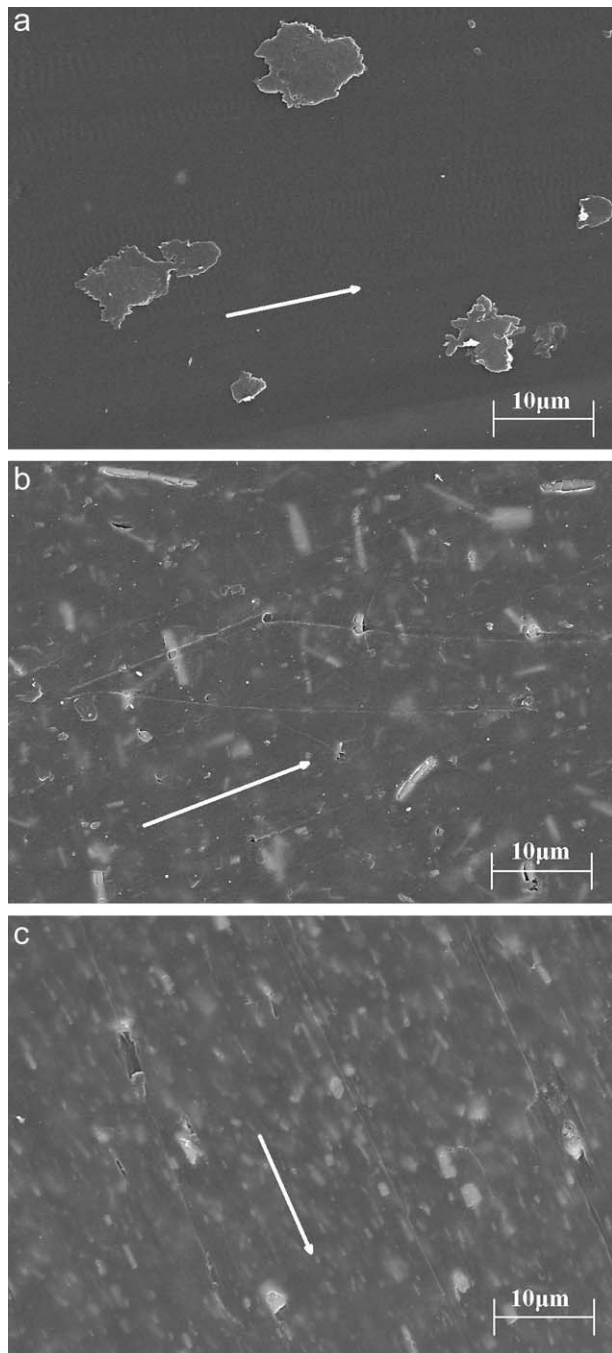
Figure 6 The morphologies of the worn surfaces for (a) PEEK, (b) PEEK/10% PTW, and (c) PEEK/25% PTW composite. Test condition: sliding velocity 2 m/s; sliding duration 2 h; applied load 1.0 MPa. The white arrow indicates the sliding direction.

wear resistance of the polymer composite.[21] However, for the case in aqueous environment, the transfer film had smaller effect on the tribological behavior.[7] In fact, the counterface was hard to modify by the transferred polymer materials.[8,9] The typical morphology of the counterpart surface of the composite was examined by SEM in Figure 7, and no transfer film could be observed on the counterface.

It is confirmed again that the transfer film is not the main reason for the enhancement of the wear resistance in water lubrication.

On the crystallinity of PEEK matrix

The crystallization performances of the polymer matrix usually have been recognized to have significant influences on the wear behavior of the polymer composite. Therefore, it is necessary to clarify the effect of the PTW on the crystallization behavior of PEEK matrix. This has been achieved by DSC measurement. The crystallinity (X_c) for PEEK and PEEK composite was calculated from the enthalpy evolved during crystallization based on the cooling scans using the following formula:

$$X_c(\%) = \frac{\Delta H_c}{\phi \Delta H_m^o} \times 100 \qquad (2)$$

where ΔH_c is the apparent enthalpy of crystallization of sample, ΔH_m^o is the extrapolated value of the enthalpy corresponding to the melting of 100% crystalline PEEK, which is taken as 130 J/g,[22] and ϕ is the weight fraction of PEEK in the composite.

The results obtained from DSC are given in Table II. It can be found that the crystallization temperature of the composites shift to a lower temperature with the incorporation of the PTW, which indicates that the crystallization temperature (T_c) decreases with the addition of PTW. In addition, the crystallization degree of the filled composite slightly reduces according to Table II. In general, the inorganic fillers have two inconsistent influences on the crystallization of the semi-crystalline polymers. On the one hand, they act as heterogeneous nucleating
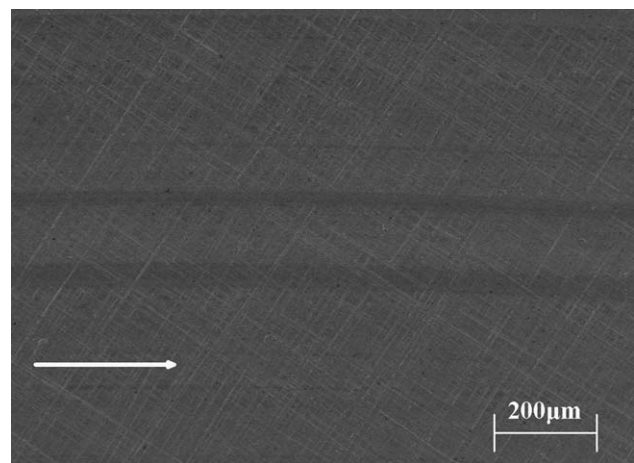

Figure 7 The surface morphology of the steel counterface after test with the PEEK/10% PTW composite. Test condition: sliding velocity 2 m/s; sliding duration 2 h; applied load 1.0 MPa. The white arrow indicates the sliding direction.

PTW content (wt %)	0	5	10	15	20	25
T_c (°C)	291.4	289.2	286.5	285.8	277.8	277.9
ΔH_c (J/g)	48.5	43.7	39.6	40.1	35.9	33.0
X_c (%)	37.3	35.4	33.9	36.2	34.5	33.8

T_c, the temperature of crystallization; ΔH_c, the apparent enthalpy of crystallization; X_c, the degree of crystallinity.

agents to facilitate the crystallization of polymers; on the other hand, they hinder the motion of polymer chain segments to retard the crystallization of polymers.[20] In the present work, the hindering effect of PTW dominates and thus results in a lower crystallinity of the reinforced PEEK.

It has been reported in some works that the increase in crystallinity reduced the wear rate of the polymer-matrix composite.[23,24] Those results believed that the PEEK composite with a higher crystallinity could achieve a better wear resistance. However, in the present case, as seen in Table II, the addition of the PTW slightly reduces the crystallinity of PEEK. In contrast, the wear rate of the composite decreases with the increasing PTW. This is similar to that of the carbon-nanofiber reinforced PEEK,[25,26] in which the degrees of crystallinity of the matrix were all about 30%, but the wear resistance was improved when the nanofibers were added in. This implies that the influence of the crystallization behavior, caused by the addition of the PTW, is not the dominant factor for the enhancement of the wear resistance in present case.

The correlations between mechanical and tribological properties

There have been some works focusing on the relation between the mechanical properties and the tribo-performance of polymer matrix composite.[27–29] It is recognized that some mechanical properties of the composite, such as hardness, elongation at break, flexural modulus, tensile strength, or the product of these factors, usually have significant influences on the wear behaviors of the composite. According to Clarke and Allen's opinions,[2] materials with high hardness and high strength would possess ability to resist deformation or absorb energy prior to fracture,

and therefore might achieve lower wear rate. It is believed that the wear rate is a function of mechanical, tribological and material parameters. A theoretical expression for wear rate under lubricated condition was derived from the concepts of crack propagation, damage accumulation, and classical mechanics by Lhymn.[30] According to this expression, the wear rate is proportional to the crack propagation velocity (V_c), and inversely proportional to the product of hardness (H), Young's modulus (E), yield strength (σ) and elongation at break (ε). As for the present case, on the one hand, the product of $HE\sigma\varepsilon$ decreases with the increasing PTW content. On the other hand, the crack propagation is greatly restricted by the addition of the whiskers; so V_c might decline with the increasing of the whisker content. The wear rate of PEEK/PTW composite gradually reduces with the whisker content increasing until 10 wt %, since the inhibition effect of the whisker on the crack propagation dominates. This could be confirmed by the SEM observations in Figure 6, in which the wear mechanism changes from fatigue mechanism for neat PEEK into mild abrasive mechanism for the filled composites. Obviously, this kind of reinforcement of the PTW is beneficial to the improvement on the load-carrying capacity of the composite, which is attributed to the main reason for the enhanced wear resistance. However, when the whisker content exceeds a critical value, the product of $HE\sigma\varepsilon$ sharply drops, as listed in Table III. Therefore, it is easy to understand why the wear rate of the composite slightly increases as the PTW loading up to 15 wt %. In this condition, more PTW would be brushed off easily and enhanced the grain abrasion, which deteriorates the wear resistance.[16] Therefore, the wear rate of the composite slightly increases when the PTW content is more than 10 wt %. For this reason, it might be

TABLE III
The Products of Hardness, Young's Modulus, Yield Strength, and Elongation at Break

PTW content (wt %)	0	5	10	15	20	25
$HE\sigma\varepsilon$	1724.8	1726.0	1711.7	1444.1	1277.8	971.0

H, the hardness (kg/mm^2); E, the Young's modulus (GPa); σ, yield strength (MPa); ε, the elongation at break ($\times$100%).

rational that the optimal content of PTW in the composite is recommended as 10 wt %.

CONCLUSIONS

This study has shown that the PTW could be used as an effective reinforcement for PEEK matrix. The strength and stiffness of PEEK composite were enhanced by the addition of PTW. However, the filled of PTW slightly decreased the crystallinity degree and the temperature of crystallization for PEEK. Under water-lubricated condition, PTW could greatly improve the wear resistance and reduce the friction coefficient of the PEEK composites due to the reinforcement of the PTW. The main wear mechanism changed from fatigue wear for neat PEEK into mild abrasive wear for the filled composites.

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