Tribological Properties of SiO$_2$ Nanoparticle Filled–Phthalazine Ether Sulfone/Phthalazine Ether Ketone (50/50 mol %) Copolymer Composites

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ABSTRACT: SiO$_2$ nanoparticle filled–poly(phthalazine ether sulfone ketone) (PPESK) composites with various filler volume fractions were made by heating compression molding. The tribological behavior of the PPESK composites was investigated using a block-on-ring test rig by sliding PPESK-based composite blocks against a mild carbon steel ring. The morphologies of the worn composite surfaces, wear debris, and the transferred films formed on the counterpart steel surface were examined with a scanning electron microscope, whereas the chemical state of the Fe element in the transfer film was analyzed with X-ray photoelectron spectroscopy. In addition, IR spectra were taken to characterize the structure of wear debris and PPESK composites. It was found that SiO$_2$ nanoparticle filled–PPESK composites exhibit good wear resistance and friction-reduction behavior. The friction and wear behavior of the composites was improved at a volume fraction between 4.2 and 14.5 vol % of the filler SiO$_2$. The results based on combined SEM, XPS, and IR techniques indicate that SiO$_2$ nanoparticle filled–PPESK composite is characterized by slight scuffing in dry sliding against steel and polishing action between composite surface and that of the countpart ring, whereas unfilled PPESK is characterized by severe plastic deformation and adhesion wear. In the former case a thin, but not complete, transfer film was formed on the surface of the counterpart steel, whereas in the latter case, a thick and lumpy transfer film was formed on the counterpart steel surface. This accounts for the different friction and wear behavior of unfilled PPESK and SiO$_2$ nanoparticle filled–PPESK composites. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2136–2144, 2002

Key words: poly(phthalazine ether sulfone ketone); nanoparticle filler; composite; friction and wear behavior

INTRODUCTION

The main advantage of engineering composites over base materials is a better combination of required mechanical properties for a given application. Composites with polymer matrices are very popular in this respect. Polymer-based composites have been finding numerous applications for reducing friction and improving wear resistance.[1–3] Many efforts have been made to investigate the tribological behavior of microscale particle–filled polymer composites, and several mechanisms have been suggested to demonstrate the action mechanisms of fillers.[4–8] However, lit-
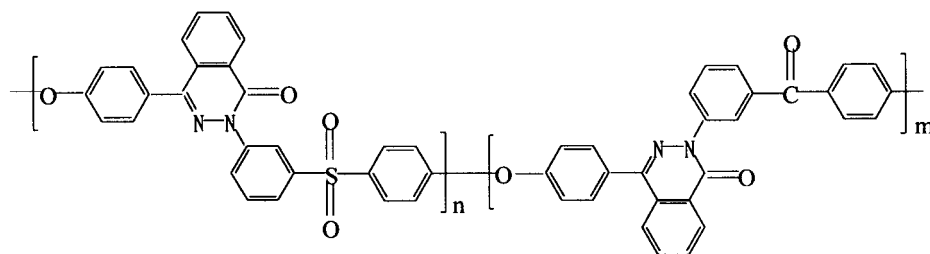
Figure 1 Chemical structure of poly(phthalazine ether sulfone ketone).

erature dealing with nanoparticle-filled polymer for tribological applications[9–11] has been scanty, although what has been reported seems to show promise. Nanoparticles have the ability of blending well with polymer, which could lead to strengthening of the transfer film. Another difference between a nanoparticle and a microscale particle of the same material is that the nanoparticle has a much high surface area–to–volume ratio. This ratio may be important for bonding of the particle to the polymer matrix in the composite. Further, oxide ceramics have been proven to show good resistance to wear, good high-temperature strength, and good dimensional stability; thus they are expected to be attractive candidates as fillers of polymers for the purpose of reducing the friction and wear of polymers.[12]

In recent years there has been growing interest in the development of high-performance polymers for the aerospace, automobile, electrical, and nuclear industries. This is because these types of polymers are technologically important matrices, high-temperature films and adhesives, and cable insulation. Poly(phthalazine ether sulfone ketone) copolymer, with an equivalent molar ratio of sulfone to ketone, coded as PPESK, is an attractive matrix material because of its outstanding high-temperature stability, excellent mechanical properties, radiation and hydrolytic resistance, and easy processing.[13]

This study deals with the friction and wear properties of SiO$_2$ nanoparticle filled–PPESK composites of different filler volume fractions. As a comparison, the tribological properties of unfilled PPESK were also evaluated under dry sliding. It is anticipated that the relevant results would be helpful for better understanding of the function of SiO$_2$ nanoparticle as filler in PPESK and for providing guidance to the tribological application of PPESK in the engineering field.

EXPERIMENTAL

Fine powders of PPESK (diameter, 40 μm) were commercially provided by Dalian University of Technology (China). The PPESK was synthesized from bis(4-fluorophenyl) ketone, bis(4-chlorophenyl) sulfone, and 4-(4-hydroxybenzyl)-2,3-phthalazine-1-one through nucleophilic substitution polycondensation. The chemical structure of PPESK is shown in Figure 1. PPESK contains rigid aromatic rings and has shown very superior mechanical strength, chemical resistance, and a very high glass-transition temperature (T_g).[13] SiO$_2$ nanoparticles (size, 20 nm) were produced by Shandong Zhengyuan Nanomaterial Company of China. The volume fraction of the filler was set from 2.1% to 25.3%, in an attempt to correlate the tribological behavior of the filled composites with the filler volume fraction. The mixture of PPESK and filler was fully mixed, by ultrasonically dispersing them in acetone for about 20 min, and then dried at 100°C for 120 min to remove the acetone. The mixture was then compressed in a mold to a pressure of 30 MPa and temperature 340°C at a rate of 5°C min^{-1} and held at 340°C for 60 min. Finally, the mold was cooled to room temperature in air. After releasing of the mold, the resultant composite blocks in a size of 30 × 7 × 6 mm were obtained.

The friction and wear tests were performed on an MM-2000 model friction and wear tester made by Xuanhua Tester Factory of China. The details of the contact configuration of the frictional pair were previously described elsewhere.[9] The upper block made of PPESK or filled PPESK composites and the lower ring made of mild carbon steel (AISI 1045 steel) were all finely ground with emery paper until a surface roughness of R_a 0.52–0.88 μm was reached. Both the blocks and the rings were cleaned with acetone, then dried and served for friction and wear tests. In this work, a sliding speed of 0.43 m s^{-1}, loads of 100,
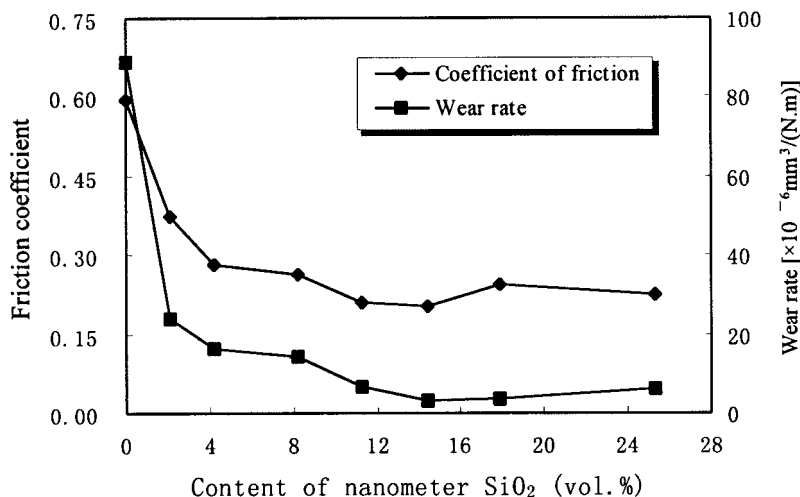
Figure 2   The friction coefficient and wear rate of SiO$_2$/PPESK composites sliding against mild carbon steel with the volume fraction of nanoparticle SiO$_2$ (sliding velocity: 0.43 m/s; load: 200 N).

200, 300, and 400 N, and ambient conditions were used. The friction coefficients of the unfilled PPESK and filled PPESK composites sliding against AISI 1045 steel ring were recorded with a computer connecting with the tester. At the end of each test, a total sliding distance of 3100 m for the steel ring was reached and the widths of wear scar were measured to an accuracy of 0.01 mm on an optical microscope, after which the wear volume loss of the composite specimen was calculated. The wear rate ω of each specimen was calculated from the relationship: $\omega = V/(SP)$, where V is the wear volume loss, S is the sliding distance, and P is the applied load. Three replicate tests were carried out for each specimen, and the average of the three replicate test results is reported in this work. The deviation of the friction and wear test data was 10%. The wear volume loss V is calculated as follows:

$$V = \left[\frac{\pi R^2}{180} \arcsin\left(\frac{b}{2R}\right) - \frac{b}{2} \sqrt{R^2 - \left(\frac{b}{2}\right)^2} \right] B \quad (1)$$

where R is the radius of the steel ring, and b and B are the width of the wear scar and the block, respectively.

The morphologies of the worn composite surface, the wear debris, and the transfer films formed on the counterpart steel ring surface were observed with a JSM-5600LV scanning electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI-5702 photoelectron spectrometer (Physical

Electronics, U.S.A.). The MgK$_\alpha$ radiation was used as the excitation source and the binding energy of C1s (284.6 eV) was used as the reference. The worn composite surface served as the specimen for XPS analysis. IR spectra were taken on a Bio-Rad FTS IR spectrometer (Bio-Rad, Hercules, CA), which operated from 4000 to 500 cm^{-1}, to characterize the structure of wear debris and PPESK composites.

RESULTS AND DISCUSSION

The variation of the friction coefficient and wear rate of SiO$_2$/PPESK composites sliding against mild carbon steel with the volume fraction of nanoparticle SiO$_2$ are shown in Figure 2. It is seen that unfilled PPESK registers a friction coefficient of about 0.59, and the wear rate of pure PPESK is 89.06×10^{-6} mm^3/N · m, which is higher than those of the nanocomposites under the same test conditions. At a filler volume fraction below 4.2%, the friction coefficient and wear rate greatly decrease with an increase of the SiO$_2$ content; then the friction coefficient decreases to a lower value (about 0.28) and the wear rate is 16.08×10^{-6} mm^3/N · m at a 4.2% SiO$_2$ content. When the content of SiO$_2$ in PPESK is between 4.2% and 14.5%, the friction coefficient and wear rate decrease gradually with the increases of the filler content. At a 14.5% volume fraction of the filler, the wear rate of the filled PPESK composites decreases to the lowest value 2.95×10^{-6}
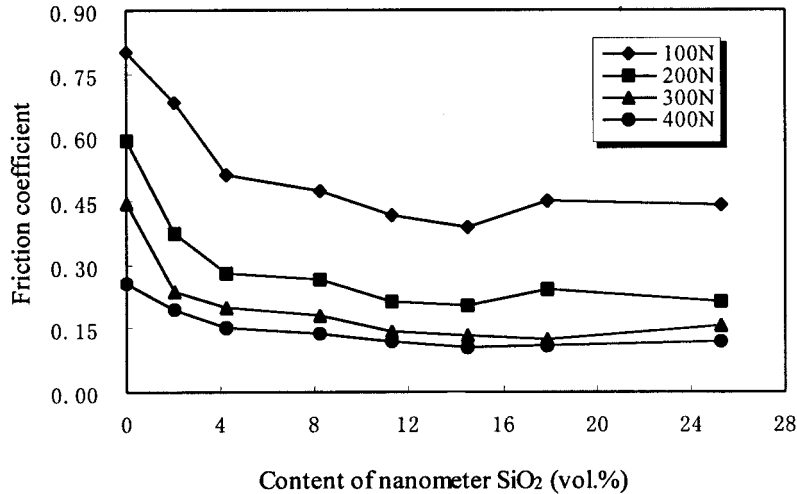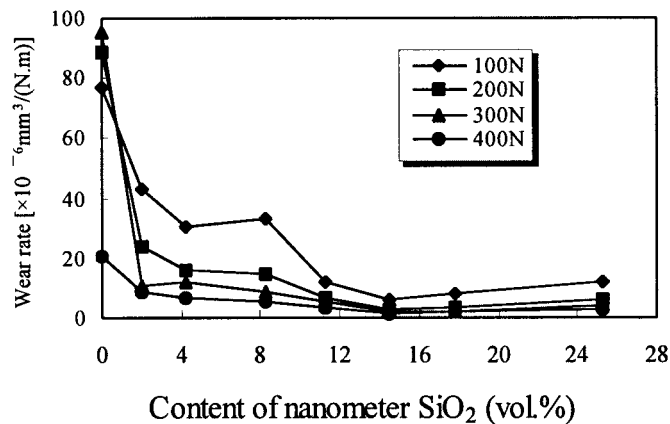
Figure 3 The friction coefficient and wear rate under various loads as a function of the SiO$_2$ volume fraction in the filled PPESK. Sliding velocity 0.43 m/s: (a) friction coefficient; (b) wear rate.

mm^3/N · m. The wear rate of the filled composites can be decreased by one order of magnitude compared to that of pure PPESK in this case. This indicates that SiO$_2$ nanoparticle filler is beneficial to reduce the friction and wear of PPESK.

To investigate the effect of load on the tribological behaviors of the SiO$_2$ nanoparticle filled–PPESK composites, the friction and wear behaviors under different loads were evaluated. Figure 3 shows the variation of the friction coefficient and wear rate of PPESK composites sliding against mild steel under various loads with the volume fraction of SiO$_2$ nanoparticles as filler. It is seen that SiO$_2$ nanoparticles as filler are effective to reduce the friction and wear of PPESK

under different loads; in particular, a lower friction coefficient and wear rate are reached at relatively high load. Meanwhile, the filler content shows a similar tendency to improve the friction and wear properties at different loads. The better friction-reduction and wear-resistant abilities of the filled PPESK composites at higher load are supposed to be related to the strengthened action of the SiO$_2$ nanoparticle filler at higher load. In a combination of the friction coefficient and wear rate, the volume fraction of SiO$_2$ nanoparticles in the composite was recommended as 14.5%.

To understand the effect of SiO$_2$ nanoparticles on the friction and wear behavior of the SiO$_2$–PPESK composite, the worn surfaces of unfilled
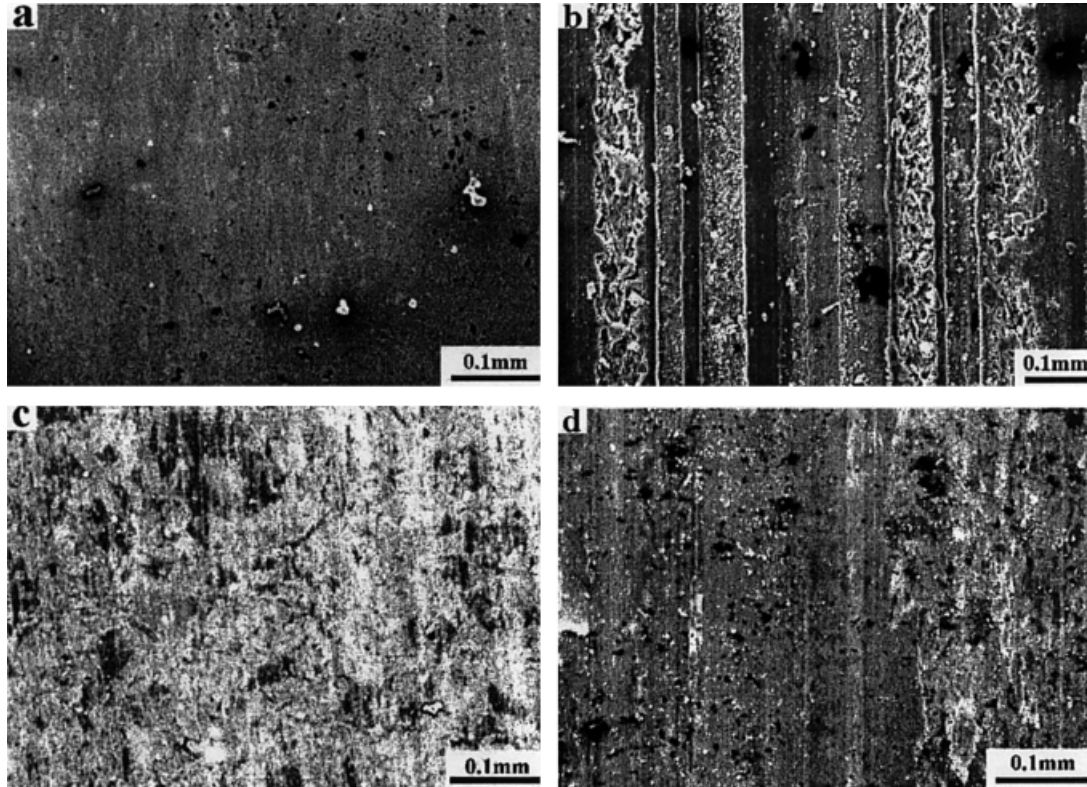
Figure 4 Scanning electron micrographs of (a) original surface of pure PPESK; (b) worn surface of pure PPESK; (c) original surface of PPESK composite; (d) worn surface of PPESK composite (sliding velocity: 0.43 m/s; load: 200 N).

PPESK and 14.5% SiO_2–PPESK composite were analyzed by means of scanning electron microscopy. As a comparison, the original surfaces of unfilled PPESK and SiO_2 nanoparticle filled–PPESK composite were also investigated. As shown in Figure 4(b), the worn surface of the unfilled PPESK shows a significant difference from that of the SiO_2–PPESK composite [Fig. 4(d)]. That is, the wear scar of PPESK filled with SiO_2 nanoparticle is relatively smooth and shows no apparent adhesion and scuffing signs. It is anticipated that the frictional couple for SiO_2 nanoparticle filled composite polished each other compared with the original surface of filled composite. Contrary to the above, the micrograph of the wear scar of unfilled PPESK shows obvious signs of scuffing and adhesion [Fig. 4(b)]. Figure 5 gives the SEM morphologies of the wear debris of unfilled PPESK and SiO_2 nanoparticle filled–PPESK composite. It is seen that the wear debris of the SiO_2 nanoparticle filled–PPESK is obviously smaller in size than that of unfilled PPESK. That is, the wear debris of unfilled PPESK takes a large-flake shape and shows signs of brittle

fracture and large-scale spalling, whereas that of SiO_2 nanoparticle filled–PPESK composite has a granule shape and shows signs of small-scale spalling. This confirms that the dominant wear mechanism for unfilled PPESK is severe plastic deformation and adhesion, whereas that for SiO_2 nanoparticle filled–PPESK composite is slight abrasive wear.

Given that the transfer films in metal–polymer systems play an important role in determining the tribological behavior, the role of the transfer films in this work was thus examined, in an attempt to reveal the essence of the changes in the friction and wear behavior of PPESK composites filled with SiO_2 nanoparticles. It can thus be inferred that SiO_2 nanoparticles as filler in PPESK leads to change of the wear mechanism of the composites. In other words, the wear mechanism of the unfilled PPESK is mainly plastic deformation and adhesion, whereas that of SiO_2 nanoparticle filled–PPESK is mainly slight abrasive wear. As shown in Figure 6, the transfer film of unfilled PPESK is thick and lumpy [Fig. 6(a)]. It shows obvious signs of cracking, which could be an indi-
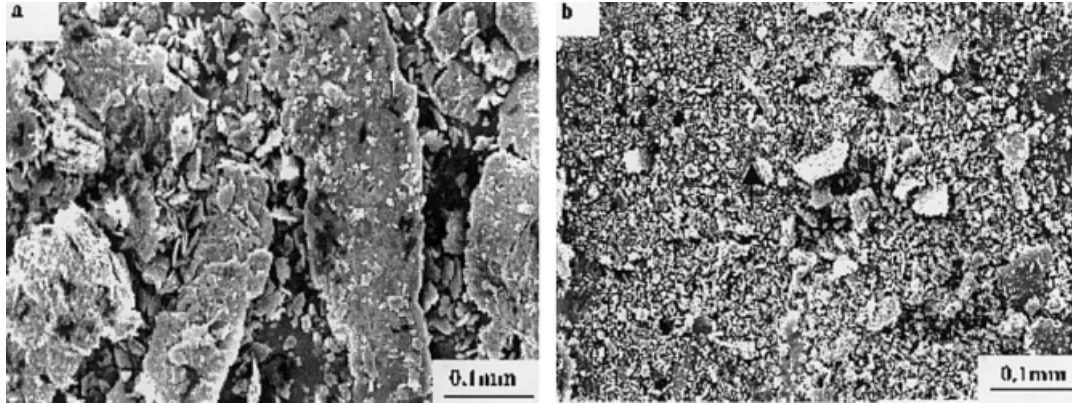
Figure 5 Scanning electron micrographs of the wear debris of (a) unfilled PPESK and (b) SiO$_2$ nanoparticle–filled PPESK composite (sliding velocity: 0.43 m/s; load: 200 N).

cation of their lack of adhesion. The lumpy morphology was generated probably because the patches of transfer film were peeled off and lost during sliding. Thus the large flake shape wear debris was formed for unfilled PPESK during sliding friction [as shown in Fig. 5(a)]. These factors contributed to the high wear rate of unfilled PPESK. Contrary to the above, the transfer film of PPESK filled with SiO$_2$ nanoparticles shows significantly different features from those of unfilled PPESK in terms of the topography and thickness. As shown in Figure 6(b), the transfer film of 14.5% SiO$_2$–PPESK composite becomes fairly thinner, smoother, but could not completely cover the surface of the countpart ring. Also, it is interesting to notice that both worn and unworn PPESK do not have the signal of Fe2p [Fig. 7(a)]. This indicates that no Fe rubbed to the worn surface for the pure PPESK block in sliding

against the mild carbon steel. In other words, the pure PPESK transferred to the surface of countpart steel formed a lumpy transfer layer for unfilled PPESK during sliding friction. On the contrary, as shown in Figure 7(b), the Fe2p at 711.6 eV for the worn surface of SiO$_2$ nanoparticle filled–PPESK indicates that the Fe$_2$O$_3$[14] formed on the worn surface of nanoparticle filled PPESK during the friction process. In this case, the elemental Fe transferred to the composite surface because the transfer film formed on the steel surface is thinner but could not completely cover the surface. This would indicate that the SiO$_2$ nanoparticle filled composite is not easily removed to the counterpart surfaces and has higher strength than that of unfilled PPESK, which makes the countpart steel polish to the composite surface.

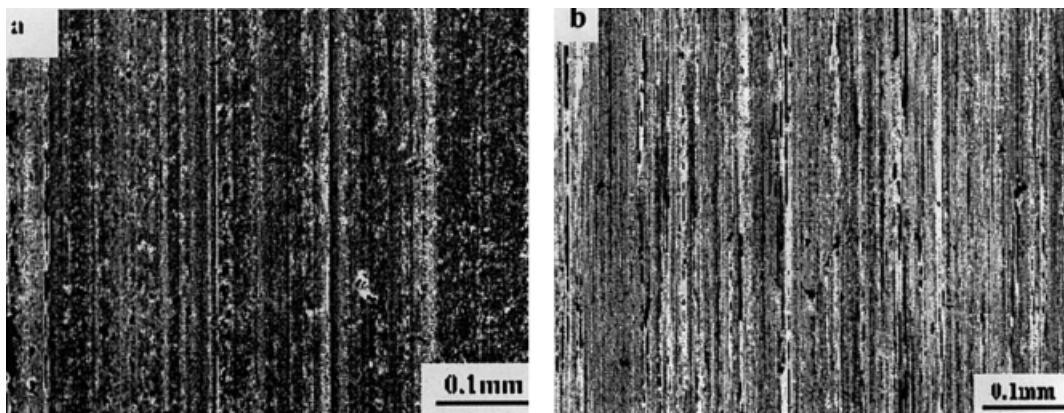Figure 8 shows the FTIR transmission spectra of PPESK and the debris of PPESK. In combina-

Figure 6 Scanning electron micrographs of rings sliding against (a) pure PPESK; (b) SiO$_2$ nanoparticle–filled PPESK composite (sliding velocity: 0.43 m/s; load: 200 N).
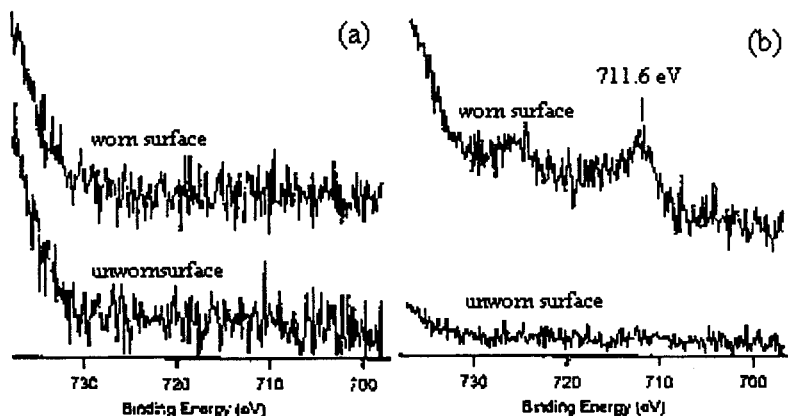
Figure 7 XPS spectra of Fe2p on (a) pure PPESK surface; (b) SiO$_2$ nanoparticle–filled PPESK surface.

tion with the strength of C—O—C stretching vibration peak at 1240 cm^{-1} and Ar—C=O peak at 1666 cm^{-1} (Fig. 8), it can be seen that after friction the C—O—C peak became strong and the Ar—C=O peak became weak. This indicated that the double band in Ar—C=O is active and easily broken during sliding friction. The IR spectra of SiO$_2$ nanoparticle filled–PPESK composite and debris of composite are shown in Figure 9. Contrary to what was observed for SiO$_2$ nanoparticle filled–PPESK, the Ar—C=O peak became weak in debris; it can thus be concluded that the Ar—C=O bond was easily broken during friction. The most obvious change is the disappearance of

the peak at 1099 cm^{-1}, which corresponds to chainlike Si—O—Si stretching vibrations, and the appearance of peaks at 1050 and 1079 cm^{-1} (corresponding to ringlike Si—O—Si). This indicated that the SiO$_2$ nanoparticle causes great variation in the tribological properties of the composite, which is why the amount of composite debris is very small.

Pure PPESK was easily removed from the contact area through the C=O active group counterface, and consequently a higher wear rate was observed in this case. The corresponding wear mechanism was severe plastic deformation and adhesion. As is well known, the nanoparticle has
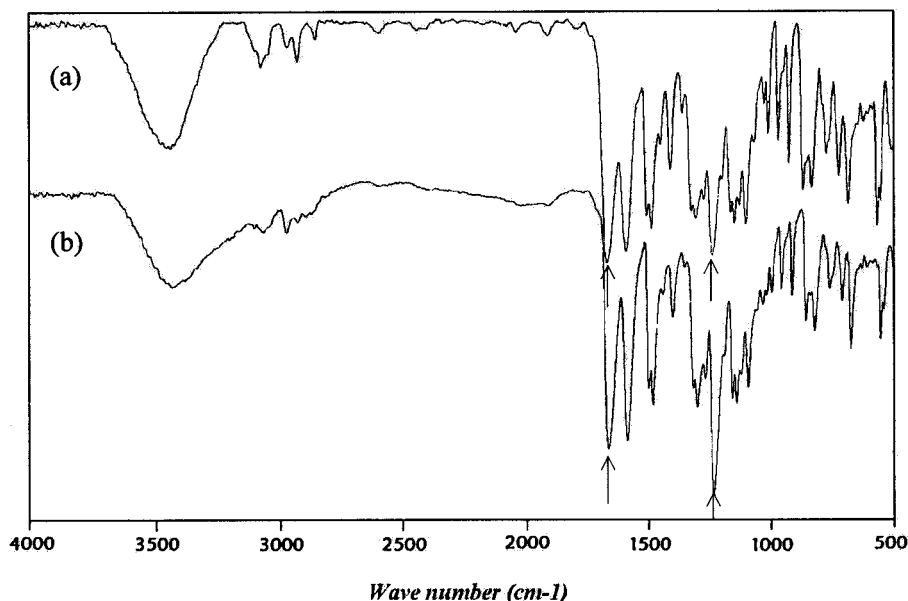

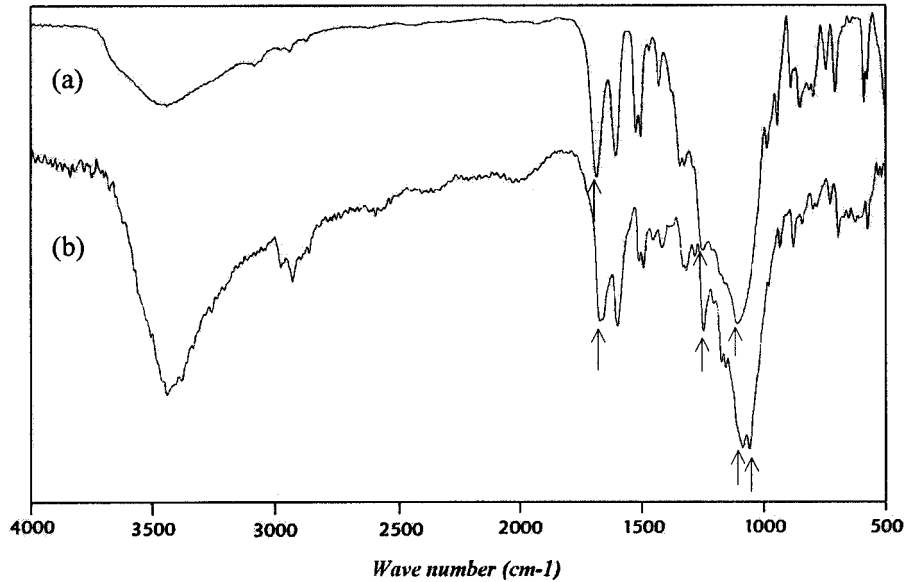**Figure 8** IR spectra of (a) pure PPESK; (b) debris of pure PPESK.

Figure 9 IR spectra of (a) SiO$_2$ nanoparticle–filled PPESK; (b) debris of SiO$_2$ nano-particle–filled PPESK.

a much smaller particle diameter, a much greater surface area–to–volume ratio, and more physical and chemical defects on the surface, all of which could lead to the combination of particle and polymer by either a physical or a chemical pattern. These may be important for increasing the binding of the particle to the polymer matrix at the polymer active position in the composite material. Thus, the carried nanoparticles of the polymer molecular chain were separated at the contact area and, consequently, the adhesion was reduced. The strength of the composite was increased when all of the nanoparticles completely combined with the PPESK active group. The extremely smooth and compact surface profile of the 14.5% SiO$_2$–PPESK composite and the countpart ring correspond well to the lowest wear rate of the composite. However, the strength of the composite decreased with a further increase on the particle content attributed to the aggregate of the nanoparticles, which thus led to the higher wear rate at a filler content above 14.5%.

CONCLUSIONS

From the preceding discussion, the following conclusions can be drawn:

1. The filling of SiO$_2$ nanoparticles into PPESK could greatly increase the wear resistance of PPESK and decrease the friction coefficient at a filler volume fraction below 4.2%. When the volume fraction of SiO$_2$ nanoparticles in PPESK is between 4.2% and 14.5%, the friction coefficient and wear rate decrease gradually with the increase of the filler. Meanwhile, the filler content shows a similar tendency to improve the friction and wear properties at different loads.

2. The worn surface of unfilled PPESK shows signs of severe plastic deformation and adhesion. The corresponding transfer film of unfilled PPESK is thick and lumpy, and the wear debris takes a large-flake shape. Contrary to the above, the worn surface of PPESK filled with SiO$_2$ nanoparticles shows signs of slight abrasion, whereas a thin and uniform transfer film is formed on the counterpart steel ring surface, and the wear debris has a granule shape and shows signs of small-scale spalling. This conforms well with the different friction and wear behaviors of unfilled PPESK and filled PPESK composites.

3. The results based on combined SEM, XPS, and IR techniques indicate that the dominant wear mechanism for unfilled PPESK is severe plastic deformation and adhesion, whereas that for SiO$_2$ nanoparticle filled–PPESK composite is slight abrasive wear.

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