Effects of Various Kinds of Fillers on the Tribological Behavior of Polytetrafluoroethylene Composites Under Dry and Oil-Lubricated Conditions

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ABSTRACT: Polytetrafluoroethylene (PTFE)-based composites filled with various inorganic fillers in a volume fraction of 30% were prepared. The tribological behavior of the PTFE composites sliding against AISI52100 steel under dry and liquid paraffin-lubricated conditions was investigated on an MHK-500 model ring-on-block test rig. The morphologies of worn surfaces and wear debris were observed with a scanning electron microscope (SEM) and an optical microscope. As the results, different fillers show different effects on the tribological behavior of the PTFE composites, while the composite shows much different tribological behavior under lubricated conditions as compared with dry sliding. The tribological behavior of the PTFE composites under dry sliding is greatly related to the uniformity and thickness of the transfer films. Only the PTFE composites with a transfer film of good uniformity and proper thickness may have excellent tribological behavior. The PTFE composites show much better tribological behavior under lubrication of liquid paraffin than under dry sliding, namely, the friction coefficients are decreased by 1 order of magnitude and the wear rate by 1–3 orders of magnitude. Observation of the worn composite surfaces with SEM indicates that fatigue cracks were generated under lubrication of liquid paraffin, owing to the absorption and osmosis of liquid paraffin into the microdefects of the PTFE composites. The creation and development of the fatigue cracks led to fatigue wear of the PTFE composites. This would reduce the mechanical strength and load-supporting capacity of the PTFE composites. Therefore, the tribological behavior of the PTFE composites under lubrication of liquid paraffin is greatly dependent on the compatibility between the PTFE matrix and the inorganic fillers. In other words, the better is the compatibility between PTFE and fillers the better is the tribological behavior of the composites.
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Key words: polytetrafluoroethylene; inorganic fillers; composite; tribological behavior

INTRODUCTION

The incorporation of mineral fillers into thermoplastics has been widely practiced in industry to extend them and to improve the performance of polymeric products.[1,2] As a typical example, the friction and wear behaviors of polymers can be effectively improved by filling them with the desired inorganic particulate compounds. It was found that CuO, CuS, CuF_2, PbS, and Ag_2S as fillers are effective in increasing the wear resistance of high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), nylon (PA), and poly(ether ether ketone) (PEEK). Contrary to the

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Table I Typical Characteristics of Liquid Paraffin

Viscosity ($\times 10^{-6}$ m^2 s^{-1})					
40°C	100°C	Viscosity Index	Flash Point (°C)	Boiling Point (°C)	Main Composition
21.49	4.42	117	226	> 300	Paraffin

above, BaF_2, CaF_2, ZnF_2, SnF_2, ZnS, SnS, ZnO, and SnO are harmful to the wear resistance of some polymers.[3–7] The tribological behaviors of polymers and polymer-based composites are closely related to the transfer film characteristics. However, the mechanisms for filler action is not well understood, and little has been available on the effects of fillers on the tribological behavior of PTFE composites under oil-lubricated conditions. Our previous work indicated that PTFE and its composites filled with various inorganic fillers registered a considerably high friction coefficient and/or wear at a certain high load.[8,9] It was suggested that under lubrication with liquid paraffin the absorption and osmosis of liquid paraffin into the microdefects in the PTFE composites reduces the mechanical strength and load-supporting capacity of PTFE composites.[10–12] This would lead to the deterioration of the tribological behavior of PTFE composites under higher loads as lubricated by liquid paraffin. However, more evidence is needed to verify this supposition. As found in our previous tentative research work, it was likely that the different compatibility between the PTFE matrix and various inorganic fillers played a key role in determining the tribological behavior of PTFE composites under higher loads.[13,14]

The purpose of this work was to study the effects of various kinds of fillers on the tribological behavior of PTFE composites under both dry and oil-lubricated conditions and to give some insight into the friction and wear mechanisms of the PTFE composites under oil-lubricated conditions. It was expected that this study would provide guidance for the application of PTFE composites filled with various inorganic fillers in practice.

EXPERIMENTAL

The materials used for preparing the PTFE composites include PTFE powder in a grit size of about 30 μm; metal powders Pb (45 μm), Cu, and Ni (76 μm); metal oxides Pb_3O_4, PbO, and Cu_2O (76 μm); metal sulfides MoS_2, PbS, CuS, and graphite (abridged as GR, 76 μm); ceramic particles SiC, Si_3N_4 (76 μm), BN, and B_2O_3 (154 μm); potassium titanate ($K_2Ti_6O_{13}$) whisker (coded as PTW) of diameter 0.2–1.0 μm and length 10–80 μm; and carbon fibers (CF) and glass fibers (GF) of diameter 20–30 μm and length 30–300 μm. The proportion of the fillers in PTFE was 30% by volume in each case.[10] The fillers were mixed fully with the PTFE powder. Then, the mixtures were molded into a block specimen of size $12.3 \times 12.3 \times 18.9$ mm^3 by compression molding under a pressure of 50 MPa. Finally, the composite blocks were sintered at 380°C for 3 h in air and then cooled in air to room temperature. Eighteen kinds of PTFE-based composites were prepared in this work.

The friction and wear tests were carried out on an MHK-500 model ring-on-block test rig (similar to a Timken friction and wear tester) by rotating a steel ring (AISI52100 steel; outer diameter 49.2 mm; thickness 13.0 mm) against the PTFE composite block. The ring was polished with No. 900 grade SiC abrasive paper to a surface roughness of R**a** = 0.15 μm, while the PTFE composite blocks were polished with No. 800 grade SiC abrasive paper to a surface roughness of R**a** = 0.2–0.4 μm. Chemical reagent liquid paraffin was used as the lubricating base stock. The properties of liquid paraffin are listed in Table I. The lubrication of the frictional pair was realized by dropping the liquid paraffin onto the rubbing surfaces at a rate of 30 drops per min.

The friction and wear tests were performed at room temperature in an ambient atmosphere (relative humidity 35–40%) for a test duration 30 min. The sliding speed is 1.5–2.5 m/s and loads 100–1200 N. Before each test, the rubbing surfaces of the PTFE composite blocks and the steel ring were cleaned with acetone and then dried in air. The wear mass losses of the composites were determined by weighing the composite blocks before and after the friction and wear tests to an

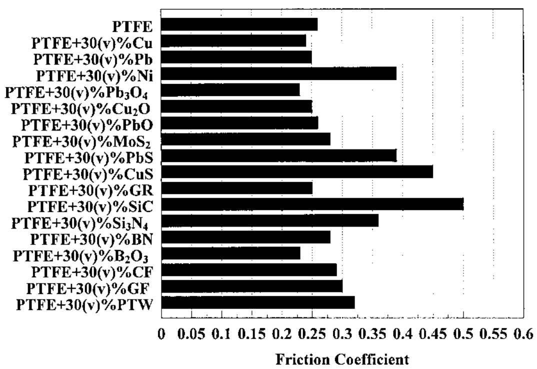

Figure 1 Friction coefficients of the PTFE composites filled with various kinds of fillers under dry-friction conditions (sliding speed, 1.5 m/s; load, 100 N).

accuracy of 0.1 mg. The friction coefficient was determined by accounting for the normal load and the friction torque, where the latter was determined with a torque gauge equipped with the test rig. Three replicate tests were conducted for each composite specimen and the averaged friction coefficients and wear mass losses of the replicate tests are reported in this article. The relative errors of the friction coefficients and wear mass losses for the replicate tests are about 10 and 5%, respectively.

The wear debris and the worn surfaces of the PTFE composites were examined with a JEM-1200EX/S scanning electron microscope (SEM). The transfer films of the PTFE composites on the counterpart steel surface were observed with an optical microscope.

RESULTS AND DISCUSSION

Effects of Fillers Under Dry Sliding

The friction coefficients and the wear rates of the PTFE composite blocks in dry sliding against an AISI52100 steel ring are shown in Figures 1 and 2. It is seen that, under the given conditions in this work, CF, GF, and PTW as the fillers slightly increase the friction coefficients; Ni, PbS, CuS, SiC, and Si_3N_4 as the fillers increase the friction coefficient considerably; while the other fillers including Cu, Pb, Pb_3O_4, Cu_2O, PbO, MoS_2, graphite, BN, and B_2O_3 have almost no effect on the friction coefficients, if one takes into account the scattering of the friction and wear test data. Moreover, the wear rates of various PTFE composites are much lower than that of unfilled PTFE (which is as high as 1427.4×10^{-6} mg N^{-1} m^{-1} and is not presentable in Figure 2 at the same scale). The wear rate of the PTFE–PbO composite (465.2×10^{-6} mg N^{-1} m^{-1}) is not given in Figure 2 either, also because of the difficulty in expressing it at the same scale in Figure 2. Excluding the PTFE–PbO composite, the wear rate of the other PTFE composites is reduced by 1–3 orders of magnitude. However, the wear-reducing action of different fillers in PTFE varies greatly from each other. Of the fillers used in this work, PbO shows the lowest wear-reducing ability, followed by B_2O_3 and Pb. The fillers such as Cu, Pb_3O_4, and Si_3N_4 are much more effective in reducing wear than the other fillers, and the highest wear-reducing ability is attributed to Pb_3O_4.

In combination of the results shown in Figures 1 and 2, it is interesting to note that the friction-reduction capability of a filler does not necessarily to conform with its antiwear ability. For example, although Si_3N_4 as the filler in PTFE increases the friction coefficient greatly, it registers a considerably decreased wear rate. Almost all the fillers used in this experiment can greatly reduce the wear rate of the PTFE composites, but some of them greatly increase the friction coefficients of the PTFE composites. Since Pb_3O_4 as the filler in PTFE shows almost no effect on the friction coefficient of the PTFE–Pb_3O_4 composite and reduces the wear rate of the composite by nearly 3 orders of magnitude, the PTFE–Pb_3O_4 composite thus is anticipated to find promising application in practice as a good candidate for friction-reducing and wear-resistant material in dry-friction conditions.

Effects of Fillers Under Oil-lubricated Conditions

The friction coefficients and the wear rates of the PTFE composites filled with various kinds of fill-

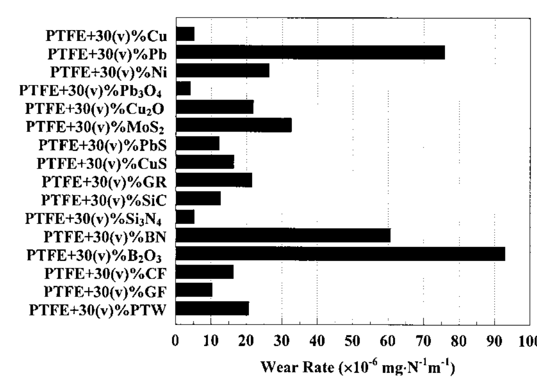

Figure 2 Wear rate of the PTFE composites filled with various kinds of fillers under dry-friction conditions (sliding speed, 1.5 m/s; load, 100 N).

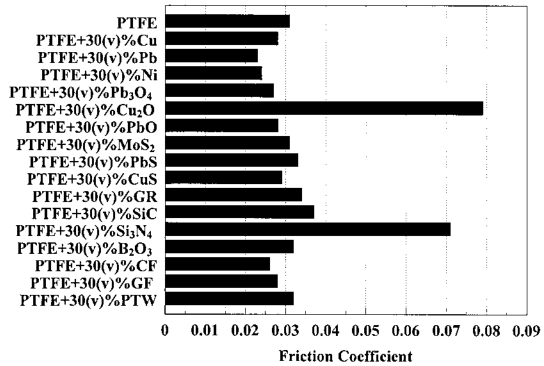

Figure 3 Friction coefficients of the PTFE composites filled with various kinds of fillers under lubrication of liquid paraffin (sliding speed, 2.5 m/s; load, 600 N).

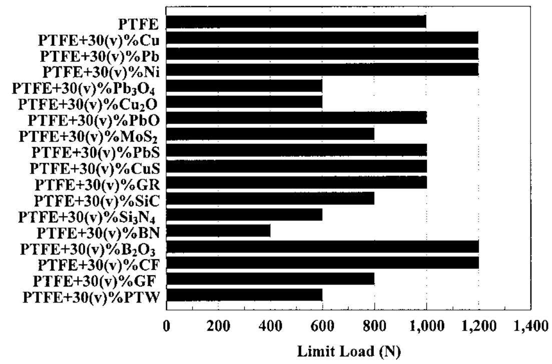

Figure 5 Limit loads of the PTFE composites filled with various kinds of fillers under lubrication of liquid paraffin (sliding speed, 2.5 m/s).

ers sliding against AISI52100 steel under lubrication of liquid paraffin are shown in Figures 3 and 4. It is seen that the composites show considerably decreased friction coefficients and wear rates under lubrication with liquid paraffin than under dry sliding, namely, the friction coefficients under lubrication can be decreased by several factors or even 1 order of magnitude as compared with the dry-sliding condition, while the wear rates by several factors to 1 and even nearly 3 orders of magnitude except that PTFE/Si_3N_4 shows almost unchanged wear rates under both lubricated and dry-sliding conditions and PTFE/Pb_3O_4 registers a slightly decreased wear rate under the lubricated condition. Thus, it can be concluded that lubrication with liquid paraffin has little effect on the decreasing wear of PTFE/Si_3N_4 and PTFE/Pb_3O_4 composites, although considerably decreased friction coefficients are obtained in these two cases. This also indicates that the friction-reduction capability of a lubricant does not necessarily conform with its antiwear ability, as seen above in the friction-reduction capability and the antiwear ability of a filler.

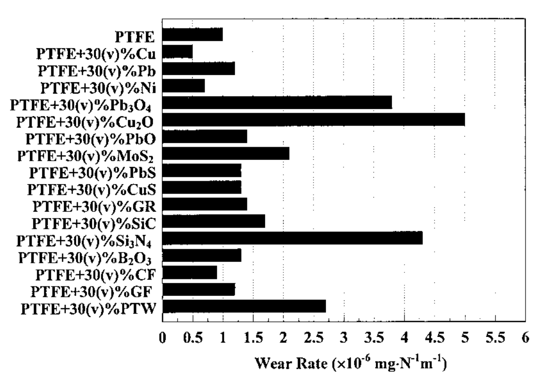

Figure 4 Wear rate of the PTFE composites filled with various kinds of fillers under lubrication of liquid paraffin (sliding speed, 2.5 m/s; load, 600 N).

As is well known, there exists a load limit for various polymer-based composite materials under oil-lubricated conditions. Under such a load, some signs of serious deformation or cracks can be observed on the worn surfaces of the composites. Figure 5 gives the load limits of the PTFE composites sliding against AISI52100 steel under the lubrication of liquid paraffin. It is seen that under the lubrication of liquid paraffin different fillers have different effects on the load-carrying capacity of PTFE, namely, the fillers Cu, Pb, Ni, B_2O_3, and carbon fibers (CF) increase the load limits of PTFE to some extent, the fillers PbO, PbS, CuS, and graphite (GR) have little effect on the load limits, and the fillers Pb_3O_4, Cu_2O, MoS_2, SiC, Si_3N_4, BN, glass fibers (GF), and $K_2Ti_6O_{13}$ whiskers reduce the load limits of PTFE. In terms of improved friction and wear behavior as well as increased load limit, Cu should be the first choice as the filler of PTFE.

SEM Investigation of Wear Debris

Figure 6 shows electron micrographs of the wear debris of several PTFE composites under the dry-sliding condition. Those for the other PTFE composites in this work have similar features and, hence, are not presented as a whole in this article. It is seen that the wear debris of pure PTFE and Pb-, BN-, B_2O_3-, Cu-, and Pb_3O_4-filled PTFE composites all appear as flakelike pieces, although the sizes of the flakelike pieces vary from each other, namely, the wear debris of the filled PTFE composites is much smaller than that of unfilled PTFE. This indicates that the fillers in PTFE can

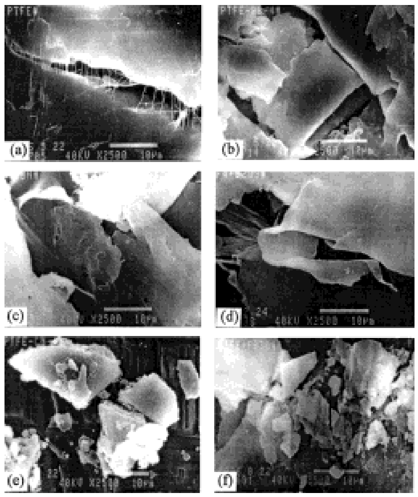

Figure 6 Electron micrographs of the wear debris of PTFE composites under dry-friction conditions (sliding speed, 1.5 m/s): (a) PTFE, 100 N; (b) PTFE + 30 (v) % Pb, 400 N; (c) PTFE + 30 (v) % BN, 400 N; (d) PTFE + 30 (v) % B_2O_3, 400 N; (e) PTFE + 30 (v) % Cu, 400 N; (f) PTFE + 30 (v) % Pb_3O_4, 400 N.

restrain and/or abate large-scale destruction and peeling off of the banded structure of PTFE. In other words, unfilled PTFE is liable to delaminate and peel off during the friction process, while such delamination and peeling off are effectively restrained by incorporation of inorganic fillers in PTFE. Subsequently, PTFE composites show greatly decreased wear rates than those of unfilled PTFE. It is also interesting to note that the wear debris of Cu- and Pb_3O_4-filled PTFE composites is much smaller than that of Pb-, BN-, and B_2O_3-filled PTFE composites, indicating that Cu and Pb_3O_4 as fillers could be more effective in inhibiting the large-scale destruction of the banded structure of PTFE, as compared with the fillers Pb, BN, and B_2O_3. This is in agreement with the lower wear rates of Cu- and Pb_3O_4-filled PTFE composites as compared with Pb-, BN-, and B_2O_3-filled PTFE composites under dry sliding.

Optical Microscope Investigation of Transfer Films

The optical micrographs of the transfer films formed on the surface of AISI52100 steel for the PTFE composites filled with several fillers under dry-friction conditions are shown in Figure 7. Similar to above, those for the other PTFE composites in this work have similar features and, hence, are not presented as a whole in this article either. It is seen that tenacious and uniform transfer films are formed on the steel surface in sliding against Cu-, Pb_3O_4-, CuS-, and Ni-filled PTFE composites. The transfer film of SiC–PTFE composite shows some patchy signs, while almost no transfer film is formed in the sliding of unfilled PTFE against AISI52100 steel. By correlating the above investigations with the results of friction and wear tests under dry-friction conditions, it can be deduced that the fillers (such as Cu, Ni, Pb_3O_4, CuS, and SiC) in PTFE enhance the adhesion of transfer films to the surface of AISI52100 steel and promote the transfer of the PTFE composites to the surface of AISI52100 steel. Therefore, they greatly reduce the wear of the PTFE composites.

It is interesting to notice that the transfer films of Cu- and Pb_3O_4-filled PTFE composites are much more uniform and tenacious than those of Ni-, CuS-, and SiC-filled PTFE composites. This indicates that Cu- and Pb_3O_4-filled PTFE composites may have better wear-resistance than that of the other filled composites under dry sliding, as mentioned above in Figure 2. It can thus be inferred that the adhesion between the surface of AISI52100 steel and the transfer films of Ni-, CuS-, and SiC-filled PTFE composites is weak while that of Cu- and Pb_3O_4-filled PTFE composites is of high bonding strength. With the formation of uniform and tenacious transfer films on the surface of AISI52100 steel, the friction be-

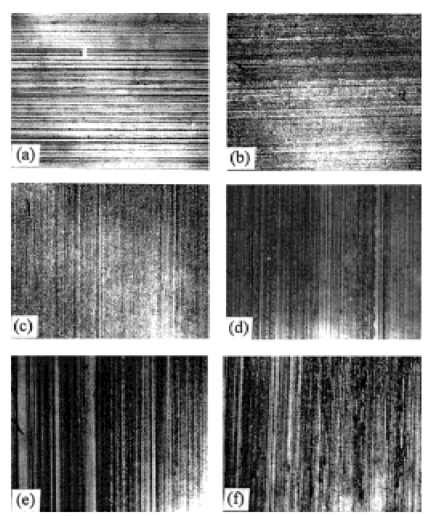

Figure 7 Optical micrographs of the transfer films of PTFE composites formed on the surface of AISI52100 steel under dry-friction conditions (magnification, 128×; sliding speed, 1.5 m/s; load, 100 N): (a) PTFE; (b) PTFE + 30 (v) % Cu; (c) PTFE + 30 (v) % Pb_3O_4; (d) PTFE + 30 (v) % CuS; (e) PTFE + 30 (v) % SiC; (f) PTFE + 30 (v) % Ni.

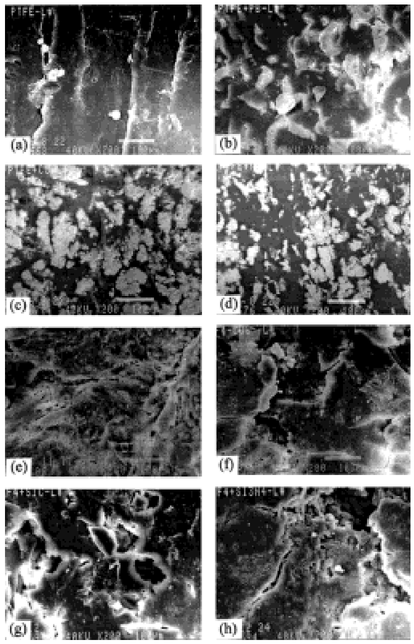

Figure 8 Electron micrographs of the worn surfaces of PTFE composites under lubrication of liquid paraffin (sliding speed, 2.5 m/s): (a) PTFE, 1000 N; (b) PTFE + 30 (v) % Pb, 1000 N; (c) PTFE + 30 (v) % Cu, 1000 N; (d) PTFE + 30 (v) % Ni, 1000 N; (e) PTFE + 30 (v) % Pb_3O_4, 600 N; (f) PTFE + 30 (v) % CuS, 1000 N; (g) PTFE + 30 (v) % SiC, 800 N; (h) PTFE + 30 (v) % Si_3N_4, 600 N.

tween PTFE composites and AISI52100 steel transforms to the friction between the PTFE composites and its transfer films. Subsequently, considerably decreased wear rates are recorded for Cu- and Pb_3O_4-filled PTFE composites as compared with Ni-, CuS-, and SiC-filled PTFE composites under dry-friction conditions. Therefore, it can be deduced that the tribological behavior of the PTFE composites are greatly related to the uniformity and thickness of the transfer films of the PTFE composites on the counterface. Only when the transfer films of the PTFE composites are more uniform and in a proper thickness may the PTFE composites exhibit excellent tribological behavior under dry-friction conditions.

SEM Investigation of Worn Surfaces

Figure 8 gives electron micrographs of the worn surfaces of the PTFE composites filled with different kinds of fillers sliding against AISI52100 steel under the lubrication of liquid paraffin. It is seen that the worn surface of unfilled PTFE shows obvious signs of adhesion, plastic deformation, and bandlike extruded agglomeration as well. Those for the filled PTFE composites show obvious differences as compared with that for unfilled PTFE, namely, obvious cracks are observed on the worn surfaces of Pb_3O_4-, CuS-, SiC-, and Si_3N_4-filled PTFE composites, while the worn surfaces of Cu-, Pb-, and Ni-filled PTFE composites show signs of adhesion and fatigue wear, with formation of small or even tiny wear debris on the worn surfaces. This indicates that the wear mechanisms of PTFE under the lubricated condition can be changed largely by the incorporation of an inorganic filler as well; thereby, the wear resistance be lowered greatly, similar to that observed under the dry-sliding condition.

It is well known that filling any kinds of fillers to PTFE can produce some microdefects in the PTFE composites. Meanwhile, the difference of solid compatibility between PTFE and the fillers can result in the difference of microdefects in the PTFE composites. It is thus rational to suppose that the absorption and osmosis of liquid paraffin into the microdefects in the PTFE composites would contribute to initiate fatigue cracks on the worn surfaces of various PTFE composites. Such an initiation and development of fatigue cracks under a load would then lead to fatigue wear of the PTFE composites. This, in turn, reduces the mechanical strength and load-supporting capacity of PTFE composites and, hence, deteriorates the tribological behavior of the PTFE composites under higher loads.[10–12] Accordingly, it was supposed that the good solid compatibility between PTFE and metal powders (such as Cu, Pb, and Ni) as fillers accounts for the excellent tribological behavior of Cu-, Pb-, and Ni-filled PTFE composites.

CONCLUSIONS

1. Fillers contained in PTFE have different effects on the tribological behavior of the PTFE composites under dry-friction conditions. All the fillers tested in our work greatly reduce the wear rates of PTFE under both dry-sliding and liquid paraffin-lubricated conditions, but some of them greatly increase the friction coefficients under dry sliding.
2. The tribological behavior of the PTFE composites are greatly related to the uniformity and thickness of the transfer films on the counterface under dry-friction condi-

tions. Only when the transfer films of the PTFE composites are more uniform and in a proper thickness may the PTFE composites exhibit excellent tribological behavior.

3. The wear rates and friction coefficients of PTFE composites filled with various inorganic fillers under lubrication with liquid paraffin can be decreased by several times to 1 or even 3 orders of magnitude as compared with dry sliding. The exceptions are that PTFE/Si_3N_4 shows almost unchanged wear rates under both lubricated and dry-sliding conditions and PTFE/Pb_3O_4 registers a slightly decreased wear rate under the lubricated condition.
4. In terms of improved friction-reduction and antiwear behaviors and increased load limits as well, Cu should be the first choice as a filler for PTFE.
5. The incorporation of various inorganic fillers in the PTFE matrix causes transformation in the wear mechanisms under both dry-sliding and lubricated conditions. All the inorganic fillers function to restrain and abate the large-scale destruction and peeling off of the banded structure of PTFE and therefore to increase the wear resistance of the PTFE composites.
6. Under lubrication of liquid paraffin, the absorption and osmosis of liquid paraffin into the microdefects of the PTFE composites contribute to initiate fatigue cracks in the worn surfaces of the PTFE composites. The initiation and development of these fatigue cracks under loads lead to fatigue wear of the PTFE composites. This is why filled PTFE composites assume different wear mechanisms as compared with unfilled PTFE under a lubricated condition.

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