

# Tribological Properties of Micro- and Nanoparticles-Filled Poly(etherimide) Composites

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**ABSTRACT:** It has been found that nano- or micro-sized inorganic particles in general enhance the tribological properties of polymer materials. In the present study, 5 vol % nano-TiO<sub>2</sub> or micro-CaSiO<sub>3</sub> was introduced into a polyetherimide (PEI) matrix composite, which was filled additionally with short carbon fibers (SCF) and graphite flakes. The influence of these inorganic particles on the sliding behavior was investigated with a pin-on-disc testing rig at room temperature and 150°C. Experimental results showed that both particles could reduce the wear rate and the frictional coefficient ( $\mu$ ) of the PEI composites under the applied test-

ing conditions. At room temperature, the microparticles-filled composites exhibited a lower wear rate and  $\mu$ , while the nano-TiO<sub>2</sub>-filled composites possessed the lowest wear rate and  $\mu$  at elevated temperature. Enhancement in tribological properties with the addition of the nano-particles was attributed to the formation of transfer layers on both sliding surfaces together with the reinforcing effect. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1678–1686, 2006

**Key words:** fibers; nanocomposites; nanoparticles; polyetherimide (PEI); fillers

## INTRODUCTION

Nano-<sup>1–7</sup> or micro-sized<sup>8–10</sup> inorganic particles have been widely applied to modify the tribological properties of polymer materials, as recently reviewed by Zhang and Friedrich.<sup>11</sup> Some attempts have been made as well to use them in the traditional wear resistant polymer composites, which include two kinds of fillers—reinforcements, i.e., short carbon fibers (SCF), glass fibers (GF), or Aramid fibers, and internal lubricants, i.e., graphite flakes and polytetrafluoroethylene (PTFE) etc. Zhang et al.<sup>12,13</sup> applied 5 vol % nano-TiO<sub>2</sub> to epoxy composites, which was already filled with SCF, graphite, and PTFE. It was found that the incorporation of nanoparticles enhanced the “limiting  $pv$ ” value (the product of the normal pressure ( $p$ ) and the sliding velocity ( $v$ )) remarkably compared to traditional fillers. A positive rolling effect of the nanoparticles was proposed between the material pairs, which contributed to this enhancement.<sup>12</sup> Bahadur et al.<sup>14–16</sup> added microsize CuS or CuO particles together with PTFE powders into short carbon or glass fabric reinforced polyamide (PA). An optimum wear resistant composition was found as PA with 25 vol % CuO, 11.3 vol % glass fabric, and 10 vol % PTFE. The reason for using the mentioned microparticles was based on the experi-

mental results that the decomposition and physicochemical reactions of the fillers with the counterpart contributed to the formation of a thin, stable, and adherent transfer film.

Polyetherimide (PEI) is an amorphous, high performance thermoplastic. It exhibits outstanding thermostability, excellent mechanical properties, and high temperature resistance. The neat PEI, however, is not favorable for tribo-applications because of its relative low wear resistance, partially due to the lack of its ability to form transfer film on steel counterparts. Therefore, various reinforcements (SCF, GF, and Aramid fibers) and solid lubricants (PTFE, graphite, MoS<sub>2</sub>, etc.) have been introduced into PEI matrix to modify its tribological behavior.<sup>17–23</sup> By using these fillers, the reduction of wear rate and coefficient of friction was achieved. In the present study, inorganic nano- and microparticles were introduced to improve the wear and friction behavior of the PEI composites, which were filled additionally with 10 vol % SCF and 15 vol % graphite flakes. Nano-TiO<sub>2</sub> (300 nm) and two kinds of micro-CaSiO<sub>3</sub> (3.5 and 2.5  $\mu$ m) particles were considered, respectively. The content of the particle was constant as 5 vol %, which was according to the optimum nano-TiO<sub>2</sub> (300 nm) loading for epoxy based nanocomposites with the enhanced wear behavior.<sup>1</sup> The objectives of this study were to explore the possibility to further improve the tribological behavior of the PEI composites by the addition of these inorganic particles, and to understand the influence of particle size and temperature dependency.

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**TABLE I**  
The Fillers and Their Basic Properties

Fillers	Particle size [ $\mu\text{m}$ ]	Density [ $\text{g}/\text{cm}^3$ ]
TiO <sub>2</sub>	0.3	4.05
CaSiO <sub>3</sub>	2.5	2.85
CaSiO <sub>3</sub>	3.5	2.85
Graphite	20	2.25
SCF	$\approx 14.5$ (diameter) $\approx 90$ (length)	1.6

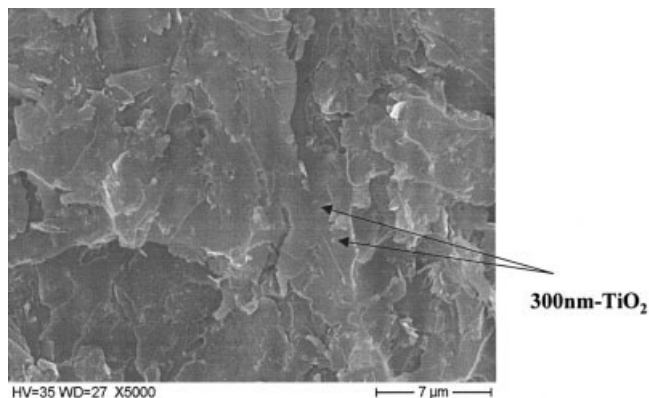
## EXPERIMENTAL

### Material and compounding

A PEI (Ultem 1000, General Electric Plastics GmbH, Rüsselsheim, Germany) was used as the matrix material. Three kinds of inorganic particles, 300 nm TiO<sub>2</sub> (Kronos 2310, Kronos Titan GmbH and Co. OHG, Nordenham, Germany), 2.5 and 3.5  $\mu\text{m}$  CaSiO<sub>3</sub>, (Tremmin, Quarzwerke GmbH, Frechen, Germany) were used, as presented in Table I. The detailed compositions and designations of the materials are given in Table II. The basic composition (denoted as 0-C) was filled with only 10 vol % SCF (M2007s, Krecra Chop, Tokyo, Japan) and 15 vol % graphite flakes (9039, Superior, Chicago, USA), and the others were filled additionally with 5 vol % inorganic particles of different sizes. Compounding of the fillers and PEI matrix was achieved by using a twin-screw extruder (Bertorff GmbH, Hannover, Germany). The screw temperature and the rotation speed were set as 385°C and 100 rpm, respectively. The extrudant was then injection-molded into rectangular plates (4 × 80 × 100 mm<sup>3</sup>). The injection molding temperature was set around 390°C. Figure 1, a fractograph of the nanoparticle-filled composite after impact, shows a relatively uniform distribution of nanosized TiO<sub>2</sub> in the injection-molded samples. The sample pins used for tribological measurements were cut from the plate with a dimension of 4 × 5 × 10 mm<sup>3</sup>.

### Wear test

In this study, wear measurements were performed by a pin-on-disc testing rig (Fig. 2). A polymer pin was pressed against a rotating steel disk (German Stan-



**Figure 1** SEM fractograph of nano-TiO<sub>2</sub> particles reinforced composite after impact, indicating a uniform distribution of nano-TiO<sub>2</sub> in injection-molded samples.

dard 100 Cr 6, HRC 62,  $\mu = 0.1 \mu\text{m}$ ), using a pneumatic cylinder. During wear testing, the specimen's height was recorded with a KISTLER displacement transducer (Ostfildern, Germany), and the torque was measured using a load cell by which the frictional coefficient was calculated. The rotating velocity of the disc was fixed at 1 m/s and a contact pressure of 2 MPa was applied. Additionally, the disc can be heated from the backside, and the temperature of the disc can be adjusted from room temperature up to 250°C. Three measurements were provided for each composition and the average results were reported. The specific wear rate ( $w_s$ ) was calculated by the following equation:

$$w_s = \frac{\Delta m}{\rho F_N L} \quad (\text{mm}^3/\text{N m}) \quad (1)$$

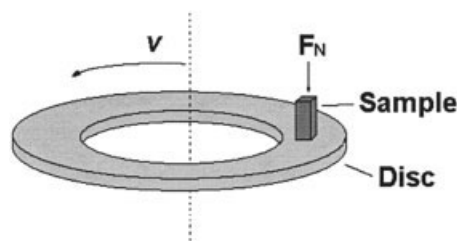
where  $\Delta m$  is the mass loss after wear test,  $L$  is the sliding distance,  $\rho$  is density of the composite, and  $F_N$  is the normal load applied.

### Scanning electron microscopy and optical microscopy

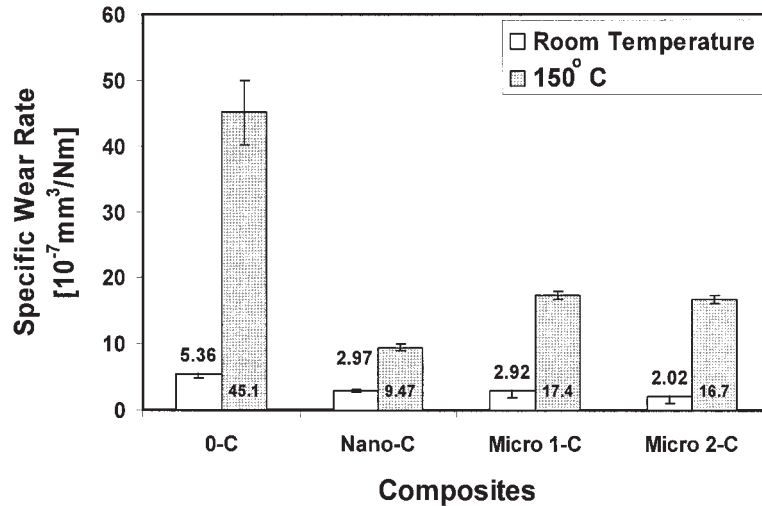
The microphotographs of the worn surface of the samples after wear testing were taken by scanning electron microscopy (SEM, JSM-T330A, Jeol, USA, Inc.

**TABLE II**  
Composites Studied in the Paper

Designation	SCF [vol %]	Graphite [vol %]	TiO <sub>2</sub> [vol %]	CaSiO <sub>3</sub> [vol %]
0-C	10	15	0	0
Nano-C	10	15	5	0
Micro 1-C	10	15	0	5 (2.5 $\mu\text{m}$ )
Micro 2-C	10	15	0	5 (3.5 $\mu\text{m}$ )



**Figure 2** Configuration of pin-on-disc testing rig.



**Figure 3** The specific wear rate of various PEI composites at room temperature or 150°C. Sliding conditions: 1 m/s and 2 MPa.

Peabody, MA). The sliding tracks on the steel counterpart were characterized as well by an optical microscopy (Aristomet, Leiz, Cottonwood, CA).

## RESULTS

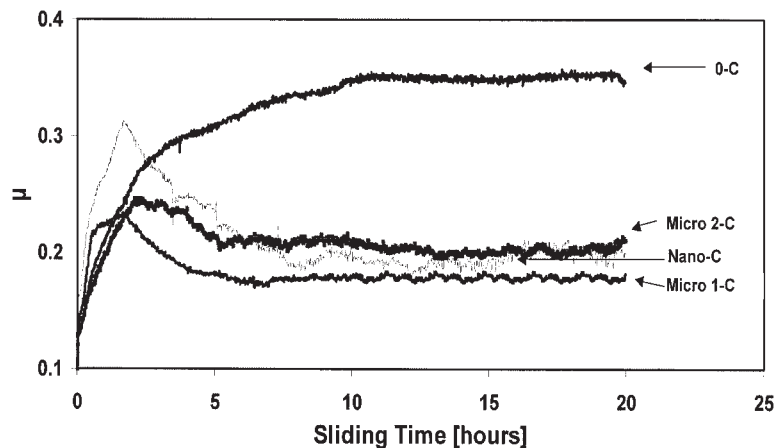
### Wear and friction

The specific wear rate of PEI composites was carried out at room temperature and 150°C, respectively, and the results are summarized in Figure 3. It was found that the addition of inorganic particles to the basic PEI composite (0-C) could significantly enhance the wear resistance at both temperatures. At room temperature, the bigger particles brought in the better wear resistance, which coincides with the results of neat polymer filled only with particles.<sup>10</sup> In this case, micro 2-C exhibited the lowest wear rate (cf. Fig. 3). The increase of the sliding temperature led to a dramatic increase of

the wear rate for all studied composites because of the degradation of mechanical properties of composites.<sup>17</sup> However, the particle size exhibited a different effect compared to that at room temperature. The nanoparticles proved more effective to the wear resistance than the microparticles at elevated temperature. Moreover, the sizes of these two microparticles exhibited negligible effect on the wear rate at 150°C, which was more obvious at room temperature.

Figure 4 gives the recorded frictional coefficient ( $\mu$ ) as a function of sliding time at room temperature. It was found that all three kinds of inorganic particles reduced the  $\mu$  in the steady state from 0.35 of the basic composite (0-C) to around 0.2. No obvious difference between nano- and microparticles was found.

From Figure 4, the running-in time<sup>18</sup> during which  $\mu$  increases with gradually increasing sliding time can also be determined. For 0-C composite, the running-in



**Figure 4**  $\mu$  versus sliding time at room temperature under 1 m/s and 2 MPa.

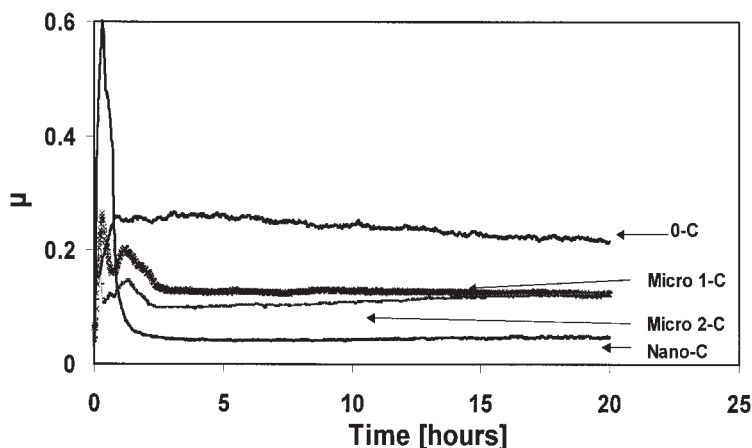


Figure 5  $\mu$  versus sliding time at 150°C under 1 m/s and 2 MPa.

time exceeds 10 h, while the inorganic particles-filled PEI composites show a much shorter running-in time, around 2 h for all three materials. The running-in period is related to smoothing counterface and forming transfer film.<sup>18</sup> The existence of a peak  $\mu$  at the end of the running-in period suggested the formation of an effective transfer film.<sup>6,18</sup> The shorter running-in time for inorganic particles-filled composites indicates that the particles accelerate the formation of the transfer film or accelerate smoothing the surfaces of worn pairs.

The variation of  $\mu$  as a function of sliding time at elevated temperature is presented in Figure 5. All composites showed a lower  $\mu$  in the steady state than that at room temperature. The composite without inorganic particles (0-C) possessed the maximum value of  $\mu = 0.25$ , and the nanocomposite shows the minimum ( $\mu = 0.05$ ), and the microparticles-filled composites have intermediates values ( $\mu = 0.12$ ). It was frequently reported that increased temperature often leads to a decreased  $\mu$  in polymeric composites.<sup>17,24</sup> The possible explanation is that the polymer molecular chain mobility is increased at evaluated temperatures, which may be of help for the formation of the transfer film.<sup>24</sup>

At 150°C, the running-in time is substantially reduced to less than 1 h for all composites (Fig. 5), much shorter than that at room temperature (Fig. 4). This is because the transfer film can be easily formed because of the improved PEI molecular chain mobility at elevated temperature. It is interesting to note that the nanocomposite shows a peak value of  $\mu$  at around 0.6, which is one time higher than that at room temperature ( $\sim 0.3$ ). After that, it reduces sharply to a stable value. This relatively high  $\mu$  peak is supposed to be related with the high real contact area realized in the running-in period, which will be discussed in the following sector. On the other hand, the micrometer-sized particles exhibited a fluctuation in  $\mu$  during the

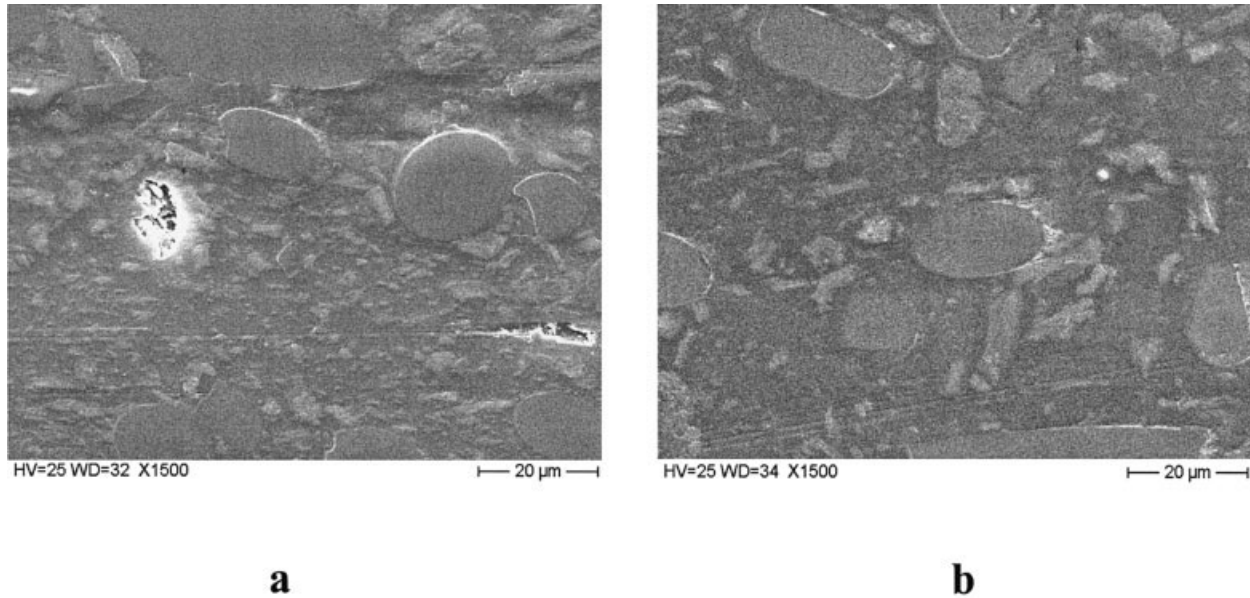
running period, which reflects the inhomogeneity of the materials with bigger hard particles.

#### Characteristics of topography of the worn surfaces

For the SCF reinforced polymeric composites, fibers undertake the main load and wear because of their outstanding mechanical and antiwear performance.<sup>8,25,26</sup> Fiber thinning, fiber crack, fiber breakage or pulverization, as well as debonding between the fiber and the matrix are the main wear mechanisms.<sup>25,26</sup> In Figure 6, all mentioned wear mechanisms could be found on the worn surface of the basic composite (0-C) filled only with graphite and SCF. Besides polished fiber tips, lots of small pieces of fiber fragments lead to an abrasive wear, which was responsible for a relatively high wear rate. At elevated temperature, the cavities due to the fiber pulling-out are not observed while fiber fragments attached on the worn surface still existed [Fig. 6(b)].

Figure 7 shows the worn surfaces of nano-TiO<sub>2</sub>-filled PEI composites at room temperature and 150°C, respectively. In comparison with Figure 6, a distinct characteristic feature of the worn surface was found. At room temperature, no obvious fiber fragments was found, whereas some fiber tips were pulverized. This is expected to diminish the abrasive wear due to the fiber fragments [Fig. 7(a)]. At elevated temperature, a thick, continuous, and compact debris film is observed on the worn nanocomposite surface [Fig. 7(b)], surrounding the fiber tips. This film is expected to protect the substrate of the materials from the asperity of the counter part, and thereafter remains the wear resistance of the composite.

The worn surfaces of the microparticles-filled composites are shown in Figures 8 and 9. At room temperature, there is also no obvious fiber fragments attached on the worn surfaces for both the composites [cf. Figs. 8(a) and 9(a)]. However, more broken fiber

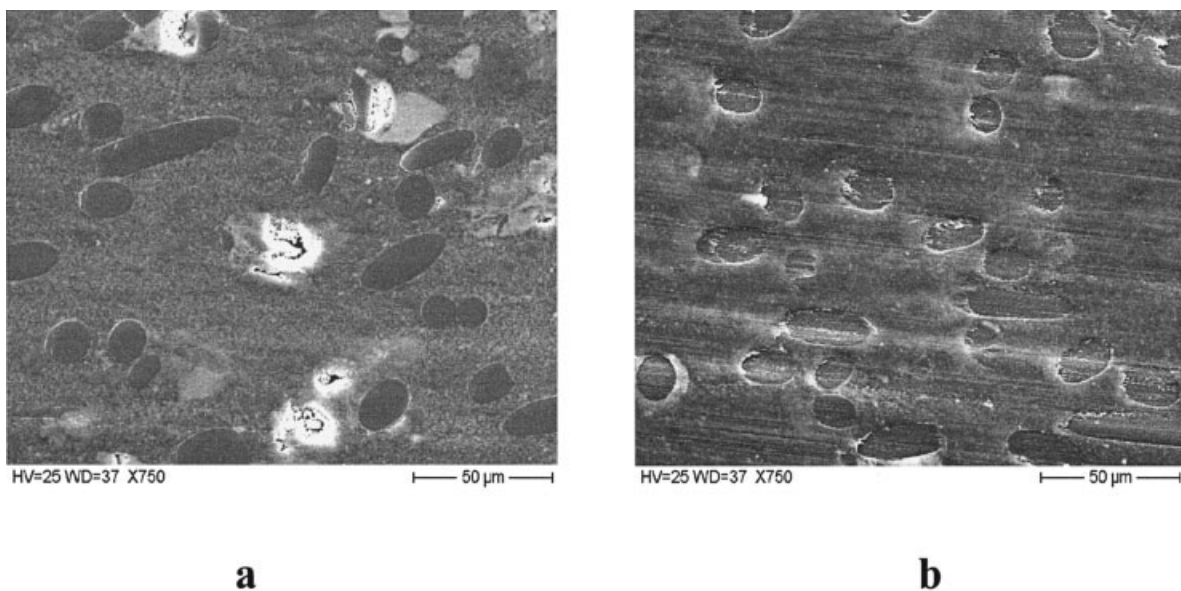


**Figure 6** Worn surfaces of the composite 0-C at room temperature (a) and 150°C (b).

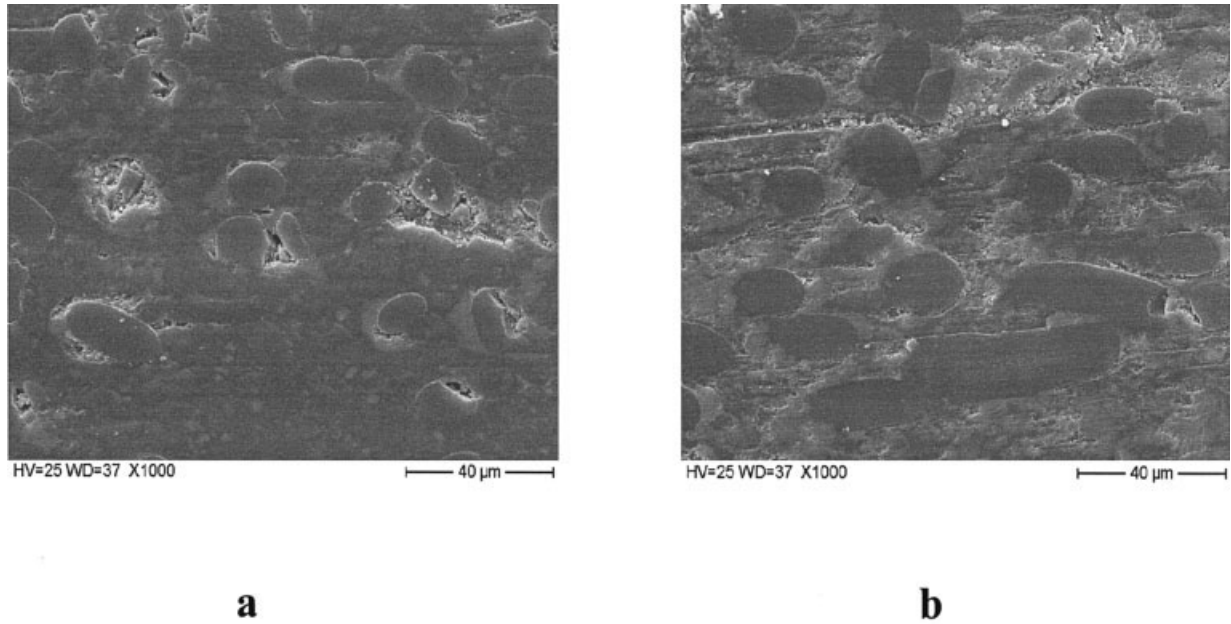
tips are found in comparison to the nanocomposite. At elevated temperature, no compacted debris films can be determined at both worn surfaces [Figs. 8(b) and 9(b)] opposite to that of nanocomposites [Fig. 7(b)]. This may be the reason that the microparticles-filled composites showed worse wear resistance and higher friction coefficient than that of nanocomposite at 150°C.

The worn surfaces of the steel counterpart slid against various composites at room and elevated temperatures are shown in Figures 10 and 11, respectively. Some small patches of flake-shaped compacted debris

distributed on the counterface [Fig. 9(a)] was found for the composite 0-C at room temperature, and the very smooth worn surface was due to the plastic deformation of PEI. Graphite flakes-filled polymers are generally able to form a thick, continuous transfer film on the steel counterpart.<sup>27</sup> The limited transfer film formed by 0-C is attributed to the abrasive effect of the hard fiber tips, which may sweep off the possibly formed transfer film of graphite. The more continuous and thinner transfer film was found for nanocomposites [Fig. 10(b)]. With respect to microparticles-filled composites, counterparts after sliding are also covered



**Figure 7** Worn surfaces of the composite Nano-C at room temperature (a) and 150°C (b).



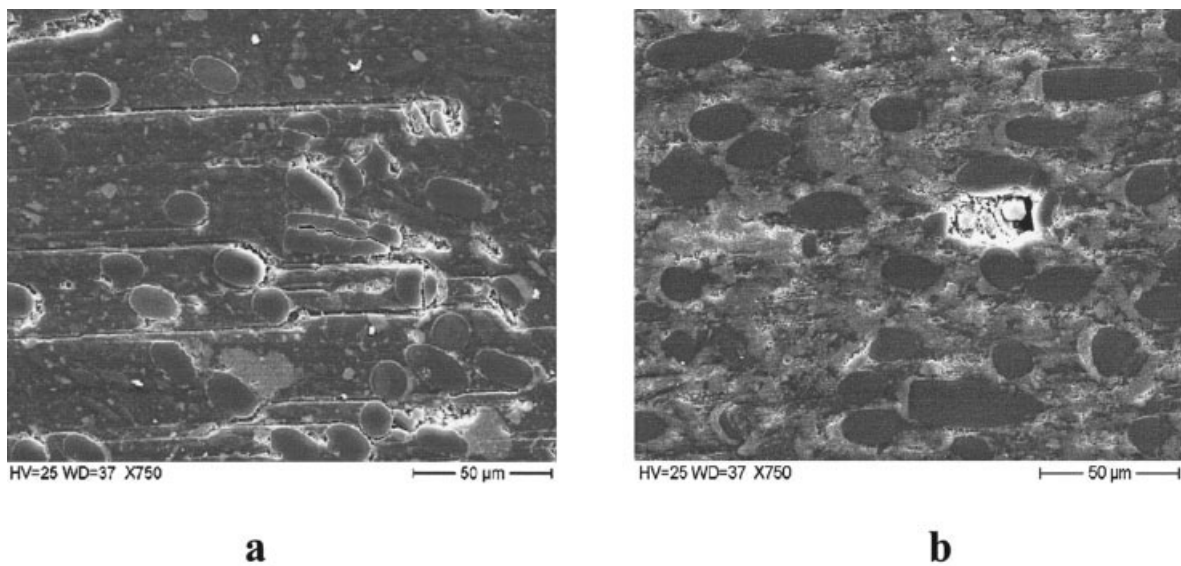
**Figure 8** Worn surfaces of the composite micro 1-C at room temperature (a) and 150°C (b).

with a very thin transfer film similar to the case of nanocomposite [Figs. 9(c,d)], but the transfer film looks less continuous.

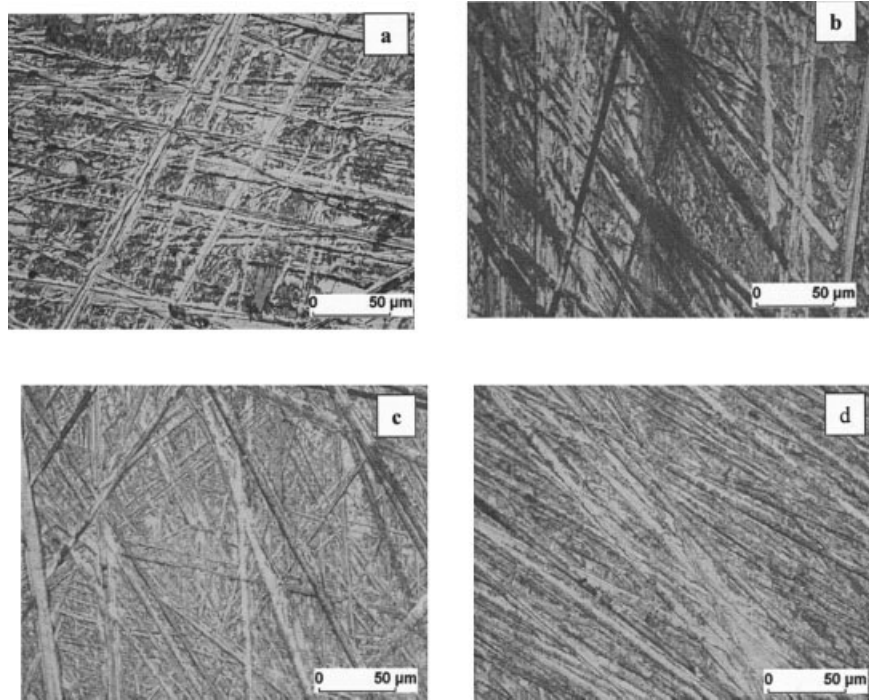
At elevated temperature, thick and continuous transfer films were found on the steel counterparts slid by the basic composite (0-C) or the nanocomposite (Nano-C), as shown in Figure 11(a,b). However, for microparticles-filled composites [Fig. 11(c,d)], more wear debris seems to be transferred onto the counterparts than those at room temperature, even a continuous transfer film was not formed.

**DISCUSSION**

Considering the significant reduction of wear rate and  $\mu$ , nano-TiO<sub>2</sub> and micro-CaSiO<sub>3</sub> particles are very effective in enhancing the tribological behavior of the PEI composites (containing SCF reinforcement and graphite lubricant), especially at elevated temperature. By comparing the results measured at room temperature and 150°C, micro-CaSiO<sub>3</sub> seemed to be more beneficial in reducing the wear and friction at room temperature, while nano-TiO<sub>2</sub> seemed to be more fa-



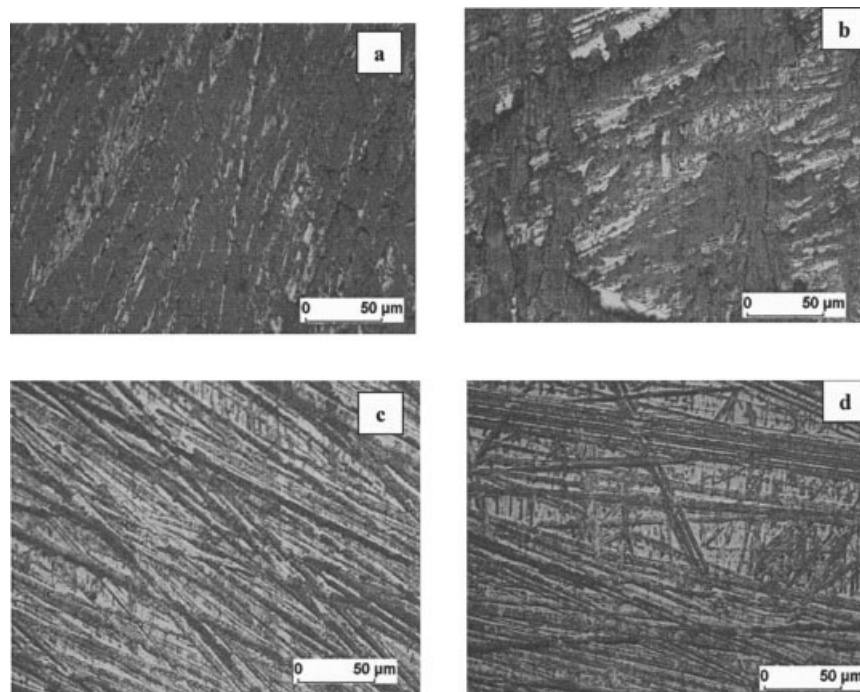
**Figure 9** Worn surfaces of the composite micro 2-C at room temperature (a) and 150°C (b).



**Figure 10** Worn surface of counterface slid by composite 0-C (a), nano-C (b), micro 1-C (c), and micro 2-C (d) at room temperature.

avorable at elevated temperature. The bigger particles leading to better wear behavior at room temperature is consistent with the results on various sized microparticles (5–100  $\mu\text{m}$ )-filled polymeric composite.<sup>10</sup>

The effects of nano- or microparticles on the wear and friction of the PEI composites are ascribed to twofold, reinforcement, and the effect on the formation of the transfer films. Undoubtedly, both nano-



**Figure 11** Worn surface of counterface slid by composite 0-C (a), nano-C (b), micro 1-C (c), and micro 2-C (d) at 150°C.

TiO<sub>2</sub> and micro-CaSiO<sub>3</sub> can bear a part of shear or impact load during sliding. As a result, the fiber is subjected to a less load compared to the basic composite (0-C) under the same conditions, resulting in fewer fibers pulling-out or breakage [Figs. 7(a)–9(a)]. In other words, the fibers were protected by the incorporation of the inorganic fillers. Owing to its bigger size of microparticles, it is expected to be more difficult to be pulled out from the matrix than nanoparticles, and thus it is more effective to share the load.<sup>1</sup> Moreover, the reduced real contact area due to the separation effect of the protruding microparticles from the sliding sample surface contributes to the decreased  $\mu$ . Considering the fact that no uniform and continuous transfer films were formed for all composites at room temperature, microparticles-filled composites exhibited the better wear and friction behavior than nanoparticle-filled counterpart because of its better reinforcing function.

At elevated temperature, PEI tends to undertake a plastic deformation under repeating sliding stress, which benefits the formation of the transfer film on the sliding surfaces through sticking together with the wear debris.<sup>23</sup> Nanoparticles are believed to have less abrasive characteristics, and they did not deteriorate the formation of the transfer layer [cf. Fig. 7(b)] at elevated temperatures. Moreover, the nanoparticles may enhance the cohesion of the transfer film to the counterparts and the cohesion strength of the transfer film on the sliding surface.<sup>4–6</sup> On the contrary, microparticles may be easily pulled out from the matrix because of the softening of PEI at elevated temperature. This may bring in two effects. On the one hand, the reinforcement of the particles will be diminished, and on the other hand the pulled-out particles may serve as abrasive particles. Both of them may contribute negatively to the wear resistance of microparticle-filled composites compared to the nanoparticle-filled composites.

The high  $\mu$  peak of the nanocomposite at elevated temperature (Fig. 5) is ascribed to high real contact area during the running-in period, which can be realized because of the plastic deformation of matrix and the characteristics of nanoparticles. At 150°C, the plastic deformation of PEI can easily occur, and meanwhile the spherical nanometer-sized TiO<sub>2</sub> possesses low abrasive characteristics. At the beginning of the sliding, PEI together with the nanoparticles may be easily transferred to the counterpart filling the grooves, and also the sample surface is smoothed. As a result, the real contact area is increased markedly and leads to a high adhesion stress, forming a high  $\mu$  peak as in Figure 5. Clearly, the easy plastic deformed matrix and less abrasive nanoparticles also make the transfer films to be easily formed. Once the thick and continuous transfer film are formed, the shear stress can be reduced, which is attributed to the sharp re-

duction of  $\mu$ , following the  $\mu$  peak [Fig. 11(b)]. This  $\mu$  peak cannot be found at room temperature (Fig. 4), because PEI is in glassy state exhibiting relatively brittle characteristics, and the contact surface cannot be smoothed markedly in this period. For the other composites (0-C, micro 1-C, and micro 2-C), the contact surfaces also cannot be smoothed like nanoparticle composites because of the abrasiveness of the particles. Consequently, the high  $\mu$  peak cannot be observed.

## CONCLUSIONS

Tribological properties of micro- and nanoparticles-filled PEI composites were carried out in the present study. The following conclusions can be drawn:

1. The introduction of either micro- or nano- inorganic particles can significantly reduce both the wear rate and the coefficient of friction of the PEI composites (filled additionally with both SCF and graphite) at both room temperature and 150°C.
2. At room temperature, the microparticles (Ca-SiO<sub>3</sub>) showed more effectiveness in reducing the wear rate and the coefficient of friction, compared to that of nanometer-sized particle (TiO<sub>2</sub>). Meanwhile, the bigger the size of the particles used, the lower were the wear rate and the coefficient of friction obtained.
3. Once the sliding temperature was increased up to 150°C, all composites showed an increase in the wear rate, but the coefficient of friction reduced remarkably. Nanoparticle-filled composite possessed the lowest wear rate and the coefficient of friction. The variation of microparticle size showed neglected effect to both the wear rate and the coefficient of friction.
4. The beneficial effects of the micro- and nano-inorganic particles on the tribological behavior of PEI composite are attributed to their reinforcement (mainly for microparticles) and assistance in the formation of transfer films (for nanoparticles).

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## References

1. Wetzel, B.; Hauptert, F.; Friedrich, K.; Zhang, M. Q.; Rong, M. Z. *Polym Eng Sci* 2002, 42, 1919.
2. Wetzel, B.; Hauptert, F.; Zhang, M. Q. *Compos Sci Technol* 2003, 63, 2055.



3. Zhang, M. Q.; Rong, M. Z.; Yu, S. L.; Wetzel, B.; Friedrich, K. *Wear* 2002, 253, 1086.
4. Wang, Q.; Xue, Q.; Liu, W.; Chen, J. *J Appl Polym Sci* 2000, 78, 609.
5. Wang, Q.; Xue, Q.; Liu, W.; Chen, J. *J Appl Polym Sci* 2001, 79, 1394.
6. Scharz, C. J.; Bahadur, S. *Wear* 2000, 237, 261.
7. Gregory Sawyer, W.; Freudenberg, K. D.; Bhimaraj, P.; Schadler, L. S. *Wear* 2003, 254, 573.
8. Tanaka, K. In *Friction and Wear of Polymer Composites*; Friedrich, K., Ed.; Elsevier: Amsterdam, 1986; p 205.
9. Xing, X. S. *Wear* 2004, 256, 21.
10. Durand, J. M.; Vardavoulias, M.; Jeandin, M. *Wear* 1995, 181–183, 833.
11. Zhang, Z.; Friedrich, K. In *Polymer Composites—from Nano- to Macro-Scale*; Friedrich, K.; Fakirov, S.; Zhang, Z., Eds.; Springer: New York, 2005; p 169.
12. Zhang, Z.; Breidt, C.; Chang, L.; Hauptert, F.; Friedrich, K. *Compos A* 2004, 35, 1385.
13. Chang, L.; Zhang, Z.; Breidt, C.; Friedrich, K. *Wear* 2005, 258, 141.
14. Bahadur, S.; Gong, D.; Anderegg, J. W. *Wear* 1995, 181–183, 227.
15. Bahadur, S.; Polineni, V. K. *Wear* 1996, 200, 95.
16. Palabiyik, M.; Bahadur, S. *Wear* 2002, 253, 369.
17. Reinicke, R.; Hauptert, F.; Friedrich, K. *Compos A* 1998, 29, 763.
18. Tewari, U. S.; Bijwe, J. In *Advances in Composite Tribology*; Friedrich, K., Ed.; Elsevier: Amsterdam, 1993; *Composite Materials Series 8*, p 159.
19. Bijwe, J.; Indumathi, J.; Rajesh, J. J.; Fahim, M. *Wear* 2001, 249, 715.
20. Bijwe, J.; Indumathi, J.; Ghosh, A. K. *Wear* 2002, 253, 768.
21. Bijwe, J.; Indumathi, J.; Ghosh, A. K. *Wear* 2002, 253, 803.
22. Stuart, B. H. *Tribol Int* 1998, 31, 647.
23. Yoo, J. H.; Eiss, N. S. *Wear* 1993, 162, 418.
24. Samyn, P.; De Baets, P.; Schoukens, G.; Hendrickx, B. *Polym Eng Sci* 2003, 43, 1477.
25. Häger, A. M.; Davies, M. In *Advances in Composite Tribology*; Friedrich, K., Ed.; Elsevier: Amsterdam, 1993; *Composite Materials Series 8*, p 107.
26. Friedrich, K.; Lu, Z.; Hager, A. M. *Wear* 1995, 190, 139.
27. Langlade, C.; Fayeulle, S.; Olier, R. *Wear* 1994, 172, 85.