

Action of Transfer Film in Improving Friction and Wear Behaviors of Iron- and Copper-Filled Poly(ether ether ketone) Composites

LAIGUI YU,¹ SHENGRONG YANG,¹ WEIMIN LIU,¹ QUNJI XUE,¹ S. BAHADUR²

¹ Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

² Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011

ABSTRACT: The composites of poly(ether ether ketone) (PEEK) filled with micrometer-sized Cu and Fe particles were prepared by compression molding. The friction and wear behaviors of the composites were examined on a pin-on-disc friction-and-wear tester by sliding PEEK-based composites against tool steel at a sliding speed of 1.0 m s^{-1} and a normal load of 19.6 N . Optical microscopic analysis of the transfer film and of the worn pin surfaces and wear debris was performed to investigate the wear mechanisms of the composites. It was found that Cu and Fe used as filler considerably decreased the wear rate of PEEK. A thin, uniform, and tenacious transfer film was formed when Cu was used as the filler, and a nonuniform and thick transfer film was formed when Fe was used as the filler. The transfer film played a key role in increasing the wear resistance of the PEEK composites. Plastic deformation was dominant for wear of PEEK-Cu, while abrasion and adhesion were dominant for wear of PEEK-Fe. Because of the strong affinity between Fe as filler and its identical counterpart in the counterface tool steel surface, the adhesion between the PEEK-Fe composite surface and the counterface tool steel surface was thus severe. This contributed to the generation of a thicker transfer film for PEEK-Fe. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 179–184, 2000

Key words: poly(ether ether ketone); composite; wear resistance; transfer film

INTRODUCTION

Polymers and polymer-based composites have found numerous applications for reducing friction and improving wear resistance.^{1–4} Recently, high-performance polymers such as PI, PEI, PBI, LCP, and PEEK have been finding greater acceptance in some special tribological applications in which high service temperature is a critical issue. As a typical example, poly(arylether ketones) are attracting much attention since they allow tailoring of their glass transition and melting range by the variation of ether and ketone groups in the

polymer molecule chain. Inorganic particulate fillers are of considerable interest not only from an economic viewpoint but also as modifiers of the physical and mechanical properties of polymers. With a few exceptions, fillers can improve the physical and mechanical properties of polymers and are usually beneficial, often dramatically so, in reducing the wear of polymers under adhesive wear conditions. This is related to the formation and characteristics of the transfer film formed on the counterface surface during the sliding process.^{5–7} Our previous work showed that unfilled PPS exhibited much higher transient wear and that the tribochemical interactions among the polymer matrix, the fillers, and the counterface Fe are important in increasing the wear resistance of filled PPS composites.^{8–9} The friction and

Correspondence to: L. Yu.

Journal of Applied Polymer Science, Vol. 76, 179–184 (2000)
© 2000 John Wiley & Sons, Inc.

wear properties of nanometric-sized ZrO_2 -filled PEEK and the effect of SiC whisker reinforcement on the tribological properties of PEEK were reported by Wang et al.^{10–11} However, it is still not well understood how the friction and wear behaviors of polymer-based composites are governed in the absence of the above-mentioned tribochemical interactions. With this perspective in mind, micrometric-sized particles of copper and iron were selected as the fillers for PEEK because they are not expected to react chemically with the counterface steel during the sliding process.⁹ Accordingly, the different friction and wear behaviors of PEEK composites filled with Cu and Fe, if any, should be attributed to their different wear mechanisms.

This article reports the effect of Cu and Fe as fillers on the friction and wear behaviors of PEEK, with emphasis on examining the features of worn surfaces and wear debris and on revealing the action of the transfer film in increasing wear resistance.

EXPERIMENTAL

Commercial PEEK powders (grit size 150 mesh) were used as the matrix material, and analytically pure metallic powders of Cu and Fe in a size of $50\ \mu\text{m}$ were used as the fillers. Cu was selected because a lot of its compounds have been found to be effective in increasing the wear resistance of various polymer composites.^{5–7} Fe was selected with the aim of revealing whether it had a different action compared to Cu. Fillers in varying proportions, from 10 vol % to 30 vol %, were used, based on the work of Bahadur et al.⁵ The polymer and the filler were first mixed mechanically and then compressed in a mold to a pressure of 56 MPa. During the compression process the mixture was heated to 340°C at a rate of $5^\circ\text{C}\ \text{min}^{-1}$ and held at that temperature for 30 min. Finally, the mold was cooled to room temperature in air. Since the pressure decreased with the melting of PEEK, the pressure was kept at 28 MPa when the temperature rose to 340°C . It was then raised to again 56 MPa at about 300°C during the cooling session. The size of the molded slabs was $35\ \text{mm} \times 30\ \text{mm} \times 6\ \text{mm}$. Pins that were $5\ \text{mm} \times 6\ \text{mm}$ in cross section and 25 mm long were cut out of the molded slabs and used for friction and wear tests. Before testing the composite pins were abraded against a 320-grade emery paper that was mounted on a rotating flat disc surface. This

preparation ensured a good contact between the pin and the disc surface during sliding.

The sliding friction and wear tests were performed in a pin-on-disc configuration at a sliding speed of $1.0\ \text{m}\ \text{s}^{-1}$ and a normal load of 19.6 N. The composite pin was held in a specimen holder on a loading arm that had two strain gauges to record the friction force. Wear mass loss was measured by weighing the pin to an accuracy of 10^{-8} kg and was converted into volume loss by accounting for the density of the tested composite. The coefficient of friction was also measured at the same intervals as the wear mass loss. Three replicate tests were performed for each composite sample, and the resulting average values of wear mass loss are used in this article. The coefficients of variation among the corresponding wear and the coefficients of friction values were within 15%. Tool steel (composition 0.9% C and 1.6% Mn, balance Fe; HRc 58) discs 5 mm thick and 75 mm in diameter were used as the counterface. The discs were ground by abrasion to provide an initial surface roughness of $0.10\ \mu\text{m}\ \text{Ra}$. Both the pins and the discs were cleaned with soap and water, flushed with acetone, then dried and used for friction and wear tests.

The morphologies of the transfer films, worn composite surfaces, and the wear debris for PEEK–35 vol % Cu and PEEK–35 vol % Fe were observed with an optical microscope, and the arrows on the micrographs show the sliding direction.

RESULTS

The Friction and Wear Behaviors of PEEK–Cu and PEEK–Fe

The relationship between the friction coefficients of the composites and the sliding distance is shown in Figure 1 (the proportions of the fillers are 35 vol % in Figs. 1 and 2). The friction coefficient of unfilled PEEK stabilized at a sliding distance of about 10 km can be seen. This suggests that a transfer film was formed after sliding an unfilled PEEK pin against a tool steel disc for about 2.8 h. The addition of Cu and Fe in PEEK increased the friction coefficient to some extent, but PEEK–Cu and PEEK–Fe have almost the same friction coefficients under the same testing conditions. The increase in the friction coefficients of PEEK–Cu and PEEK–Fe composites could be governed by their increased shear strength and the abrasion action of the harder

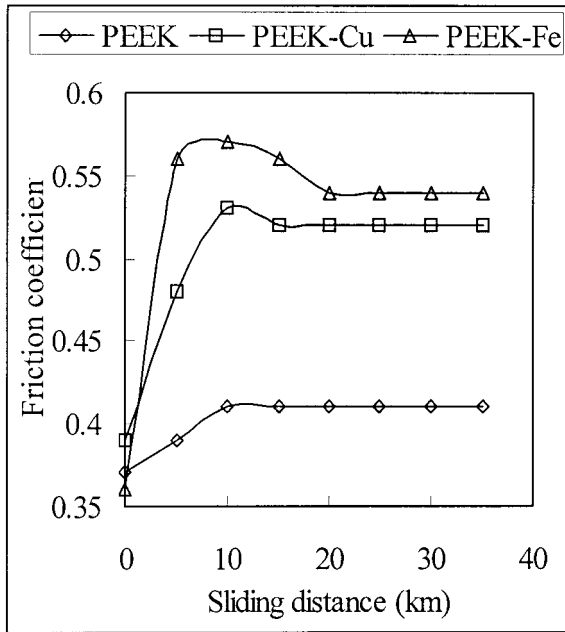


Figure 1 The friction coefficient as a function of sliding distance.

filler particles. This was caused by the abrasion action of the transferred metal particles that increased the adhesion and deformation of the polymer matrix. The relationship between the wear volume loss of PEEK composites and the sliding distance is shown in Figure 2. It can be seen that the addition of Cu and Fe in PEEK considerably increases the wear resistance of PEEK. This indicates that metallic particulate fillers are effective reinforcements for increasing the wear resistance of PEEK. Moreover, no significant difference in the wear resistance is observed for both PEEK-Cu and PEEK-Fe, though they may have different wear mechanisms, as discussed below.

Optical Microscopic Observation of the Transfer Films, Worn Surfaces, and Wear Debris

The optical micrographs of the worn surfaces of PEEK-Cu and PEEK-Fe pins are given in Figure 3. It can be seen that wear of PEEK-Cu is characteristic of deformation of the polymer matrix and that of PEEK-Fe is characteristic of abrasion and adhesion. The obvious signs of abrasion and adhesion on the worn surface of PEEK-Fe composite could be closely related to the stronger affinity between the filler Fe in the composite pin and the counterface Fe and its oxides originated from the substrate tool steel. However, such dif-

ferences in the wear mechanisms of PEEK-Cu and PEEK-Fe composites do not necessarily lead to significant differences in the wear resistance, as shown in Figure 2.

The optical micrographs of the transfer films after 0.5 and 10 h sliding of a PEEK-Cu pin against a tool steel disc are shown in Figure 4. The micrograph after 10 h sliding of a PEEK-Fe pin against a tool steel disc is shown in Figure 5. It can be seen that a thin and uniform transfer film is formed even after 0.5 h sliding of PEEK-Cu against a tool steel. Since the transfer film after 10 h sliding could have better uniformity and compactness, therefore PEEK-Cu could have better wear resistance after a longer test duration. On the contrary, however, the transfer film formed after 10 h sliding of a PEEK-Fe pin against a tool steel disc was thick and nonuniform. Because of the stronger mechanical interaction between the filler Fe and its identical counterpart in the substrate tool steel surface, the adhesion and abrasion between the transfer film and the composite sliding surface were enhanced.

The optical micrographs of the wear debris are shown in Figure 6. It was found that the wear debris for PEEK-Cu is relatively smaller and more uniform, while that for PEEK-Fe is larger and nonuniform. The larger wear debris could not be well entrapped in the transfer film and had a stronger abrasion action to the polymer composite

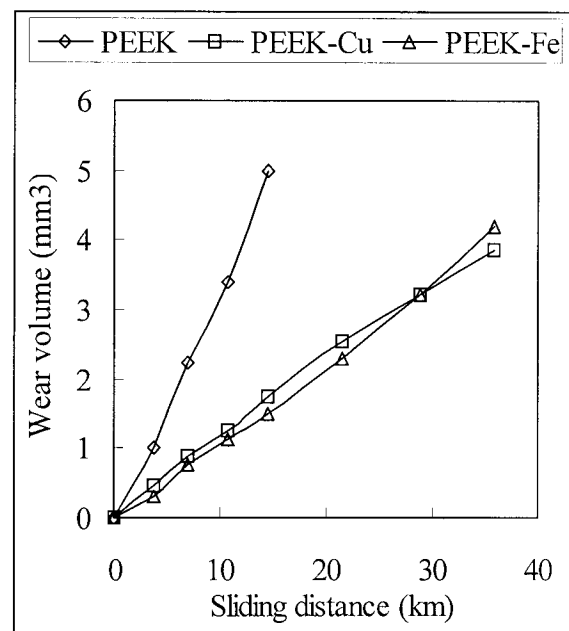
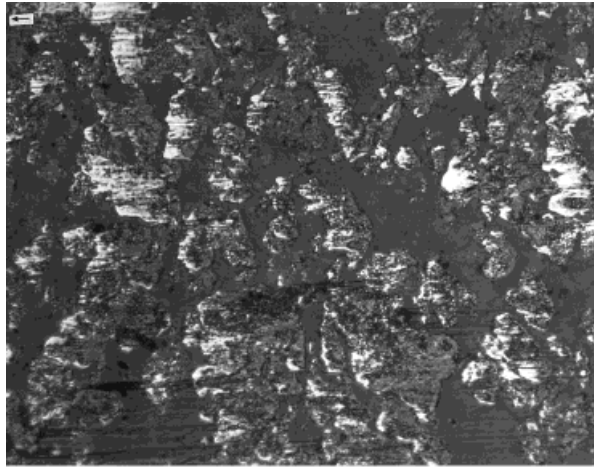
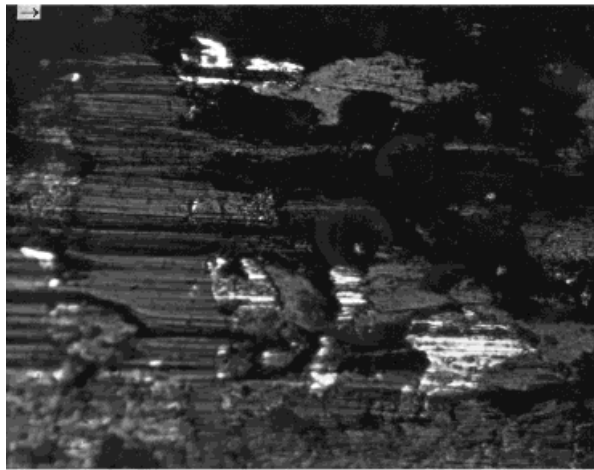


Figure 2 Wear volume loss as a function of the sliding distance.



(a)



(b)

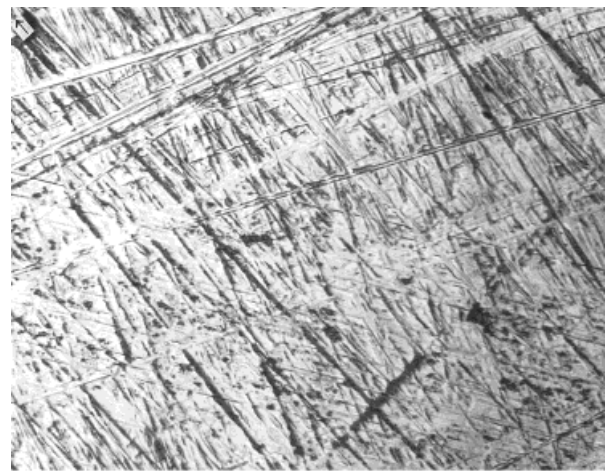
Figure 3 Optical micrographs of worn surfaces of (a) PEEK-Cu and (b) PEEK-Fe pins at 10 h sliding (pin-on-disc tester, load 19.6N, speed 1 m s⁻¹, arrow shows sliding direction).

surface; thus, differences in the worn surfaces of PEEK-Cu and PEEK-Fe were observed, as shown in Figure 3, though little difference in the wear resistance was found.

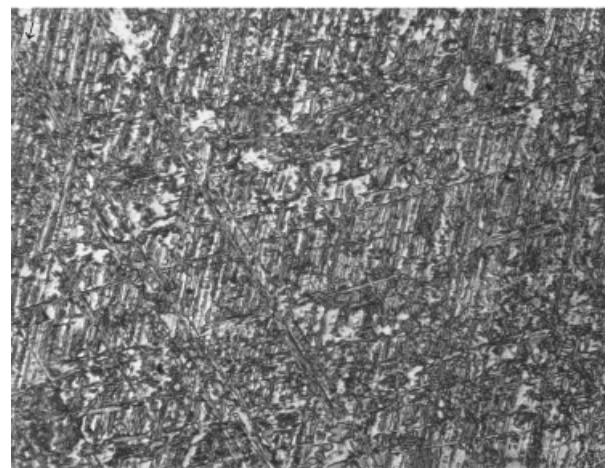
Investigation of the Action of Transfer Films in Reducing Wear

In order to investigate the action of transfer films in reducing wear, a pin made of unfilled PEEK and a pin made of tool steel were slid against the transfer films formed by unfilled PEEK and its composites on the tool steel disc surface under the

same test conditions. The wear rates of the PEEK pin and that of the steel pin at 0.5 h sliding are presented in Table I. It can be seen that the PEEK pin sliding against its identical transfer film had the same wear rate as it did sliding against the transfer films of PEEK-CuF₂ (35 vol %) and PEEK-CuS (35 vol %). The wear rate was almost the same when the PEEK pin slid against the transfer film of PEEK-Cu (35 vol %). The lowest wear rate was obtained when the PEEK pin slid against the transfer film of PEEK-CuO (35 vol %). This is because CuO as filler could react easily with counterface Fe, thereby increas-



(a)



(b)

Figure 4 Optical micrographs of transfer films of PEEK-Cu after (a) 0.5 h and (b) 10 h sliding (conditions same as in Fig. 3).

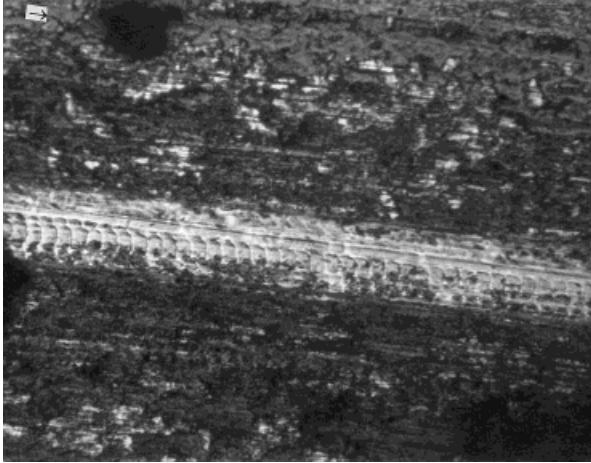


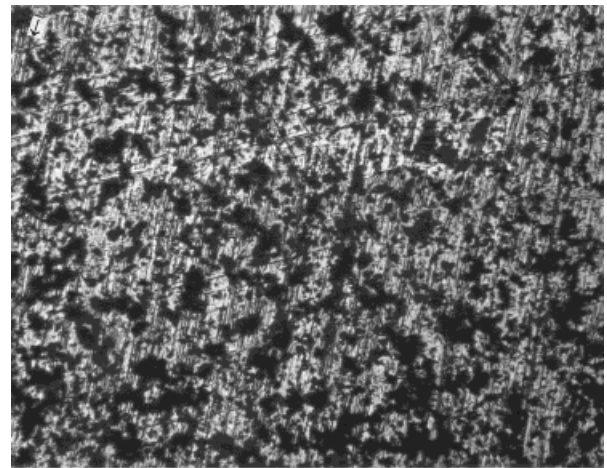
Figure 5 Optical micrograph of transfer film of PEEK-Fe after 10 h sliding (conditions same as in Fig. 3).

ing the bonding strength of the transfer film to the steel substrate.⁹ Subsequently, the adherent transfer film with high bonding strength contributed to the good wear resistance of PEEK-CuO. The considerably higher wear rate for the tool steel pin sliding against its identical counterface indicates that the transfer film formed by sliding polymer or its composites against steel counterface is very important and effective in reducing wear. The wear rate of the steel pin sliding against the transfer film of PEEK and PEEK-CuS (35 vol %) is virtually the same. It was also the same as that of a PEEK pin sliding against the transfer film of PEEK-CuO (35 vol %). In combination with the above mentioned observation that a steel pin sliding against its identical counterface exhibits a much higher wear rate, it is rational to conclude that the transfer film of polymer and/or its composites has acted to reduce wear even when the contact configuration of the friction pairs is changed.

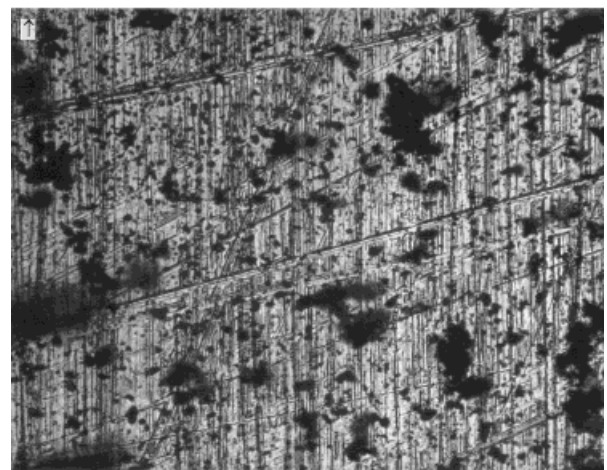
DISCUSSION

During the experiments, it was noticed that metallic fillers were transferred along with polymers onto the counterface to form a transfer film. Since the transfer film is composed of both filler and polymer materials, its action in reducing wear depends on the properties of both the filler and the polymer matrix. Generally speaking, fillers help in increasing the wear resistance of polymer composites in two ways: fillers can increase the wear resistance of polymers by increasing the bonding strength of the transfer film to its coun-

terface substrate; and they can also improve the wear resistance of polymers by increasing the shear strength of the composite as compared to unfilled polymers. Since pure metal fillers are initially in the contaminated state, they are not reactive with the frictional counterface steel. During sliding, with the removal of the outer contaminated layer on the metal filler surface and the exposure of fresh metal surface, the oxidation of the metal fillers is enhanced, so the possibility of a chemical reaction between the transfer film and the counterface steel is further reduced. Thus it has been deduced that only mechanical action



(a)



(b)

Figure 6 Optical micrographs of wear debris of (a) PEEK-Cu and (b) PEEK-Fe pins at 10 h sliding (conditions same as in Fig. 3).

Table I Wear Rate of a PEEK Pin and a Steel Pin Sliding Against the Transfer Films of PEEK and Its Composites at 0.5 h Sliding

Pin	Transfer Film	Wear Rate ($\times 10^{-6}$ mm ³ /N m)
PEEK	PEEK	6.5
PEEK	PEEK-Cu (35 vol %)	7.4
PEEK	PEEK-CuF ₂ (35 vol %)	6.6
PEEK	PEEK-CuS (35 vol %)	6.4
PEEK	PEEK-CuO (35 vol %)	4.3
Tool steel	—*	24.7
Tool steel	PEEK	4.4
Tool steel	PEEK-CuS (35 vol %)	4.5

* No transfer film formed in this case.

contributes to the bonding between the transfer film and the counterface steel for the metal filler-PEEK-tool steel system. The subsequent change in the shear strength of the composites by inclusion of metal fillers is assumed to be responsible for the change in the wear resistance. If the filler is stronger than the polymer matrix, the shear strength of the composite would be higher than that of the polymer alone. This is so because at this point the shear occurring in any plane of the composite would be resisted by the stronger filler particles present in that plane. Accordingly, it can be rationally understood why Cu or Fe as filler in PEEK increases the wear resistance considerably. Since PEEK has an extremely low shear strength, it would exhibit excessively high wear in sliding against a steel counterface that could abrade the soft PEEK away in the form of large wear debris. Contrary to the above, the inclusion of metal fillers in PEEK increases the shear strength of the composite; the composite would subsequently be more abrasion resistant in comparison to unfilled PEEK and would undertake wear in the form of minute wear debris. Since the wear debris could bond mechanically well to and be entrapped in the counterface surface, a good transfer film would be able to develop, thereby decreasing the wear rate of the composites.

CONCLUSIONS

From the above, the following conclusions can be drawn:

1. Cu and Fe as fillers decreased the wear rate of PEEK considerably but increased the friction coefficient to some extent.
2. A thin, uniform, and compact transfer film

was formed in the sliding of PEEK-Cu against tool steel, and a nonuniform, patchy, and thick transfer film was formed in the case of PEEK-Fe sliding against a tool steel counterface.

3. The transfer film plays a key role in increasing the wear resistance of filled PEEK composites. The action of the polymer-composite transfer film remains even when the contact configuration of the frictional pairs is changed. This together with the increased shear strength determines the low wear rate of PEEK composites sliding against a steel counterface.
4. Plastic deformation is dominant for wear of the PEEK-Cu composite, and abrasion and adhesion are dominant for wear of the PEEK-Fe composite.

REFERENCES

1. Voort, J. V.; Bahadur, S. *Wear* 1995, 212, 181.
2. Bazhenov, S. *Polymer Engineering and Science* 1995, 35, 813.
3. Zhuk, A. V.; Knunyants, N. N.; Oshmyan, V. G. *J Materials Science* 1993, 28, 4595.
4. Durand, J. M.; Vardavoulias, M.; Jeandin, M. *Wear* 1995, 833, 181.
5. Bahadur, S.; Gong, D.; Anderegg, J. W. *Wear* 1993, 165, 205.
6. Bahadur, S.; Gong, D.; Anderegg, J. W. *Wear* 1993, 160, 131.
7. Voort, J. V.; Bahadur, S. *Wear* 1995, 212, 181.
8. Yu, L. G.; Liu, W. M.; Xue, Q. J. *J Appl Polym Sci* 1998, 68, 1643.
9. Yu, L. G.; Liu, W. M.; Xue, Q. J. *J Appl Polym Sci* 1998, 69, 1099.
10. Wang, Q. H.; Xue, Q. J.; Shen, W. C. *J Appl Polym Sci* 1998, 69, 2341.
11. Wang, Q. H.; Xue, Q. J.; Shen, W. C.; Zhang, J. Y. *J Appl Polym Sci* 1998, 69, 135.