

An Investigation of the Friction and Wear Behaviors of Micrometer Copper Particle- and Nanometer Copper Particle-Filled Polyoxymethylene Composites

LAIGUI YU, SHENGRONG YANG, HONGTAO WANG, QUNJI XUE

Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

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ABSTRACT: Micrometer and nanometer copper particle-filled polyoxymethylene composites (coded as POM-micro Cu and POM-nano Cu, respectively) were prepared by compression molding. The compression strength and tensile strength of the composites were evaluated with a DY35 universal materials tester. An RFT-III reciprocating friction and wear tester was used to examine the tribological properties of the composites. The elemental compositions in the transfer films and the chemical states of the elements in the composite-worn surfaces were analyzed with electron probe microanalysis and X-ray photoelectron spectroscopy, while the surface morphologies were observed with scanning electron microscopy. It was found that $\text{Cu}(-\text{CH}_2-\text{O}-)_n$ was produced in sliding of a POM-nano Cu pin against an AISI 1045 steel block and Cu_2O was produced in sliding of a POM-micro Cu pin against the same counterface. POM-micro Cu exhibited higher copper concentration in the transfer film compared with POM-nano Cu, and the transfer film of the former was thick and patchy compared with that of the latter. It was also found that micrometer and nanometer copper particles as fillers in POM exhibit a distinctive size effect in modifying the wear mechanisms of the composites. In other words, the wear mechanism of POM-micro Cu is mainly scuffing and adhesion, while that of POM-nano Cu is mainly plastic deformation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2404–2410, 2000

Key words: nanometer filler; polyoxymethylene; wear mechanism; friction and wear behaviors

INTRODUCTION

As a type of engineering plastic, polyoxymethylene (POM) exhibits good fatigue resistance and creep resistance, high impact strength and elastic modulus, low friction coefficient, and low wear rate.^{1–3} This has attracted much attention in the field of materials science. The mechanical, physical, and tribological properties of POM filled with various fillers have been extensively studied.^{4–7}

The work of Tanaka and coworker may be worth special emphasis.⁸ They reported that POM-carbon composite (POM-C) and polyoxymethylene-polytetrafluoroethylene (POM-PTFE), sliding against mild steel, registered little correlation between the friction coefficient and surface morphology. However, unfilled POM and glass fiber-filled POM exhibited a considerable increase in friction coefficient when the surface roughness R_a was below $0.2 \mu\text{m}$. Kar and Bahadur reported that the friction for pure POM and PTFE-filled POM increased linearly with increasing surface roughness.⁹ Steijin said that unfilled POM and

POM-C exhibited an initial rise in friction at low sliding speed, followed by a decrease with increasing sliding speed, while the friction of filled POM decreased greatly.¹⁰

The reduction in the wear rate of filled polymers sliding against metal counterface is usually attributed to the transfer of the polymer onto the frictional counterface and the subsequent formation of a transfer film. Many efforts have been made to investigate the tribological behaviors of filled polymer composites, and several mechanisms have been suggested to demonstrate the action mechanisms of fillers.^{11–14} These mechanisms can also be applied to the filled POM. However, it should be noticed that some contradictions last in explaining the friction and wear behaviors of POM and filled POM.¹⁵ Especially, little work has been concerned with the tribological investigation of nanometer filler-filled POM.

In this work, micrometer copper particle- and nanometer copper particle-filled polyoxymethylene composites (abbreviated as POM-micro Cu and POM-nano Cu, respectively) were prepared by compression molding. An RFT-III reciprocating friction and wear tester was used to examine the tribological properties of the composites. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to investigate the morphological features and chemical characteristics of the worn surfaces and the transfer films. The wear mechanisms of filled POM composites are discussed.

EXPERIMENTAL

Materials

Chemically pure polyoxymethylene powder (grit size: 60 mesh; melting point: 165°C) was provided by the Shanghai Solvent Factory of China. The analytically pure copper particle, in a grit size of 125 μm , was provided by the Shanghai No. 2 Metallurgical Factory of China. The nanometer copper particle, in a grit size of 10 nm, was provided by Shenyang Institute of Metal Research of China.

Preparation of the Composites

The mixture of POM and filler was first mixed mechanically. Then the fully mixed mixture was compression molded into a cylindrical pin of 8 mm

in diameter and 30 mm in length. The preparation procedures for the samples can be briefly described as follows: surface treatment of raw materials \rightarrow mixing of POM and the filler \rightarrow premolding of the mixture at room temperature \rightarrow compression molding at elevated temperature \rightarrow cooling in air \rightarrow release of the sample from the molder \rightarrow cleaning of the sample in acetone.

In the above procedures, several steps should be especially emphasized. First, a suitable compression ratio should be selected for premolding at room temperature. Second, a relatively low temperature-rising rate should be selected to reach uniform heating. Finally, the temperature should be controlled within a suitable range to rule out the possible decomposition of POM during the preparation process (the decomposition temperature of POM is about 281–283°C).

Determination of the Strength and Microhardness of POM and Its Composites

The relative compressive and tensile strengths of pure POM and filled POM composites were determined on a DY35 universal materials tester made by the Adael Corporation of France. An MVK-1 microhardness tester made by Akashi Seisakusho Ltd. of Japan was used to measure the microhardness of POM and its composites with copper. A load of 1 N, a speed of 0.034 mm s^{-1} , and a loading time of 15 s were used for measurement of the microhardness. The average of five replicate measurements of the microhardness was cited as the microhardness in this article.

Friction and Wear Test

The friction and wear tests were conducted on an RFT-III reciprocating friction and wear tester made by Kyowa R/D Ltd. of Japan. The details of the contact configuration of the frictional pair have been described previously.¹⁶ In this work, a reciprocating speed of 0.2 m s^{-1} , a load of 294 N, and a total cycle number of 5000 were used. The upper pin made of POM or filled POM composites and the lower block made of plain carbon steel (AISI 1045 steel) were all ground finely with abrasive papers in various grit sizes until a surface roughness of Ra 0.20–0.23 μm was reached. Then the pin and block were cleaned in an ultrasonic bath and served for friction and wear tests. Three replicate tests were carried out for each specimen. The friction

Table I The Microhardness and Mechanical Strength of POM and Filled POM

Specimen	Filler Content (wt %)	H_V kg cm^{-2}	Compressive Strength (%)	Tensile Strength (%)
POM	0	19.3	100	100
	10	19.8	120	162
POM-micro Cu	20	21.2	124	156
	30	34.2	140	149
POM-nano Cu	10	26.4	162	176

MVK-1 microhardness tester at a load 1 N, speed 0.034 mm s⁻¹, and loading time 15 s; DY35 universal materials tester with the strength of unfilled POM being set as 100%.

coefficients of the unfilled POM and filled POM composites sliding against AISI 1045 steel were recorded with a relative error of $\pm 7\%$, while the corresponding wear weight loss was measured with a balance to an accuracy of 10^{-7} kg.

Analysis of Wear Surfaces and Transfer Films by SEM, XPS, and AES

A JEM-1200EX electron microscope was used to observe the surface morphologies and worn surfaces. An EPMA-810Q electron probe micro-analyzer was used to determine the elemental distributions in the worn composite surfaces and transfer films. A PHI-550 multifunctional X-ray photoelectron spectrometer was used to determine the chemical states of the typical elements in the wear surfaces of POM composites and the Auger depth profiles of the typical elements in the transfer films. The $K\alpha$ radiation of Mg was used as the excitation source with a pass energy of 50 eV, and the binding energy of contaminated C_{1s} (284.6 eV) was used as the reference. The error for measurement of binding energy is ± 0.30 eV.

RESULTS AND DISCUSSION

The Microhardness and Mechanical Strength of POM and Its Composites

The microhardness and mechanical strengths of POM and filled POM are given in Table I. It can be seen that the lower content of the micrometer copper particle as the filler (below 20 wt %) causes little variation in the microhardness of POM-micro Cu. However, a considerably higher microhardness is obtained when the copper content reaches 30 wt %. This can be attributed to the

effective increase in the load-carrying capacity of micrometer copper-filled POM by the copper filler. In the meantime, nanometer copper-filled POM also exhibits a higher microhardness than POM. It is suggested that the improved bonding between the nanometer copper filler and POM matrix is responsible for the microhardness increase in this case. Moreover, increased compressive strength is obtained with increasing content of micrometer copper filler, but higher content of micrometer copper filler does not necessarily correspond to a higher tensile strength of POM-micro Cu. In other words, although micrometer copper-filled POM always exhibits higher tensile strength than unfilled POM, the tensile strength of micrometer copper-filled POM relatively decreases with increasing filler content. This could be attributed to weakening in the interaction between the polymeric chains of matrix as the filler content increased.

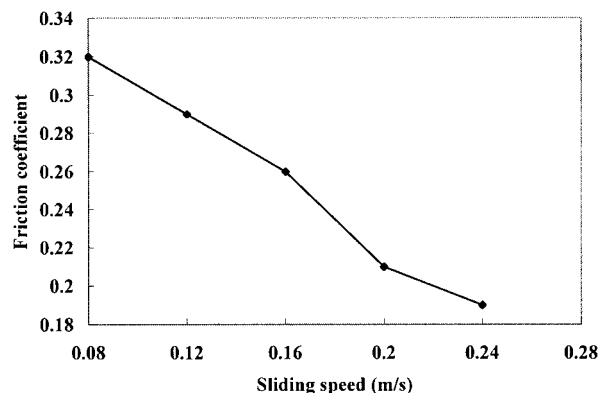


Figure 1 The friction coefficient of pure POM as a function of sliding speed (RFT-III tester, load 294 N, cycle number 5000, POM pin sliding against AISI 1045 steel block).

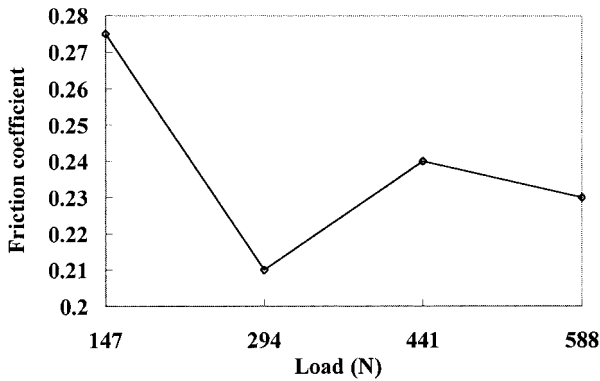


Figure 2 The friction coefficient of pure POM as a function of load applied (RFT-III tester, speed 0.2 m s^{-1} , cycle number 5000, POM pin against AISI 1045 steel block).

Friction and Wear Behaviors of POM and Its Composites

The friction coefficients of POM sliding against AISI 1045 steel as a function of sliding speed and load applied are shown in Figures 1 and 2, respectively. It is seen in Figure 1 that the friction coefficient decreases almost linearly with increasing sliding speed. On the contrary, the friction coefficient changes irregularly with varying the load, and the lowest friction coefficient is reached at 294 N , as shown in Figure 2. It is assumed that at a relatively lower load (147 N), the surface of the POM pin suffers slight abrasion by the hard asperities on the counterpart steel surface, and the transfer film of POM formed on the counterpart steel surface is subsequently incomplete; thus, a relatively higher friction coefficient is observed. The lowest friction coefficient at a load of 294 N is attributed to the formation of a uniform and compact transfer film on the counterpart steel surface, which is effective in protecting the

POM surface from the abrasion of hard asperities on the steel surface. However, this transfer film has a relatively poor load-carrying capacity. In other words, the POM transfer film on the counterpart steel surface may experience severe scuffing or even fracture failure at too high a load, with which the friction coefficient rises to a relatively higher value again. The friction coefficient and wear weight loss of filled POM under identical test conditions are presented in Table II. It is seen that a higher friction coefficient is always obtained with micrometer copper-filled or nanometer copper-filled POM, while a decreased wear weight loss is constantly obtained with both filled POM composites. However, no evident correlation between the friction coefficient or wear weight loss and the content of the micrometer copper was found. Besides, it is interesting to note that nanometer copper-filled POM exhibits a lower friction coefficient and wear weight loss than micrometer copper-filled POM. Such a difference in the wear resistance of filled polymers could be attributed to the different specific surface area and surface reactivity of different fillers, and thereby the different bonding strength between the matrix and the fillers.

Investigation of Wear Mechanisms

The scanning electron micrographs of the worn surfaces of POM-micro Cu and POM-nano Cu are shown in Figure 3. It can be seen that adhesion of copper particles occurs on the worn surface of the composite [see the bright spots in Fig. (3a)] after sliding POM-micro Cu against AISI 1045 steel. At the same time, the scuffing signs in the worn surface of POM-micro Cu indicate that POM-micro Cu underwent somewhat abrasive action during the sliding against plain carbon steel. On the

Table II The Friction Coefficient and Wear Weight Loss of POM and Filled POM

Specimen	Filler Content (wt %)	Friction Coefficient	Wear Weight Loss ($\times 10^{-4} \text{ g}$)
POM	0	0.21	36
	10	0.63	24
POM-micro Cu	20	0.39	19
	30	0.44	27
POM-nano Cu	10	0.38	8

RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000.

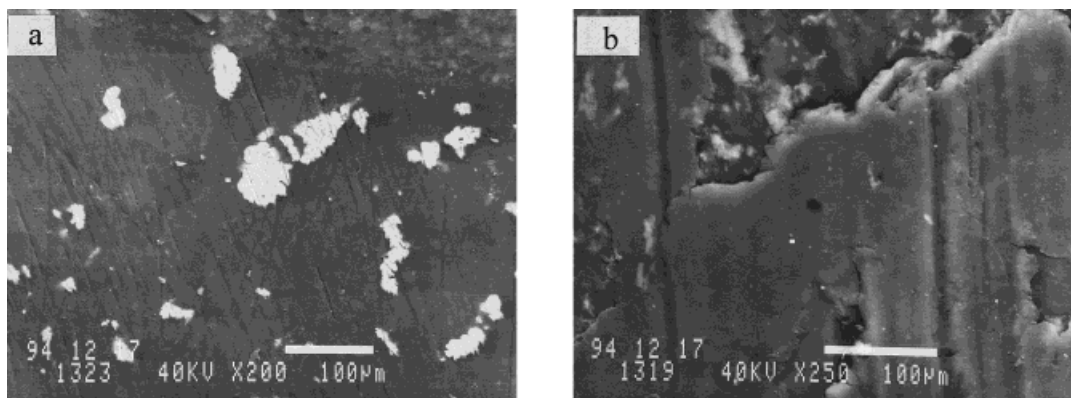


Figure 3 The scanning electron micrographs in the worn surfaces of (a) micrometer copper-filled POM, and (b) nanometer copper-filled POM (RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000).

contrary, the morphology of the worn surface of POM-nano Cu shows obvious signs of plastic deformation [see Fig. (3b)]. Thus, it is concluded that copper particles as fillers in POM exhibit a distinctive size effect in modifying the wear mechanisms of the composites. This can be better understood by taking the transfer film characteristics into consideration. As shown in Figure 4, the X-ray images of the Fe element in the worn surfaces of micrometer copper filled- and nanometer copper-filled POM indicate that more iron transferred onto the surface of the former after sliding micrometer copper-filled POM against the steel counterface. Similarly, as given in Figure 5, more Cu element is detected in the counterface steel surface as well in the sliding of the micrometer copper-filled POM against the steel counterface.

Such a transfer can be more clearly observed from the Auger depth profiles of the transfer films (see Fig. 6). As seen in Figure 6, the transfer film on the steel counterface is thicker and has higher copper concentration for the frictional pair of POM-micro Cu/steel. Thus, the higher wear weight loss with micrometer copper-filled POM can be attributed to the enhanced intertransfer between the filled polymer and steel counterface. It is anticipated that some insight into the difference in the wear mechanisms of the two composites could be obtained from the XPS analysis of the corresponding transfer films. As shown in Figure 7, the binding energy of $\text{Cu}_{2p_{3/2}}$ shifts from 932.4 to 934.0 eV after sliding POM-nano Cu against the steel block, indicating that $\text{Cu}(-\text{CH}_2-\text{O}-)_n$ was likely to generate in the

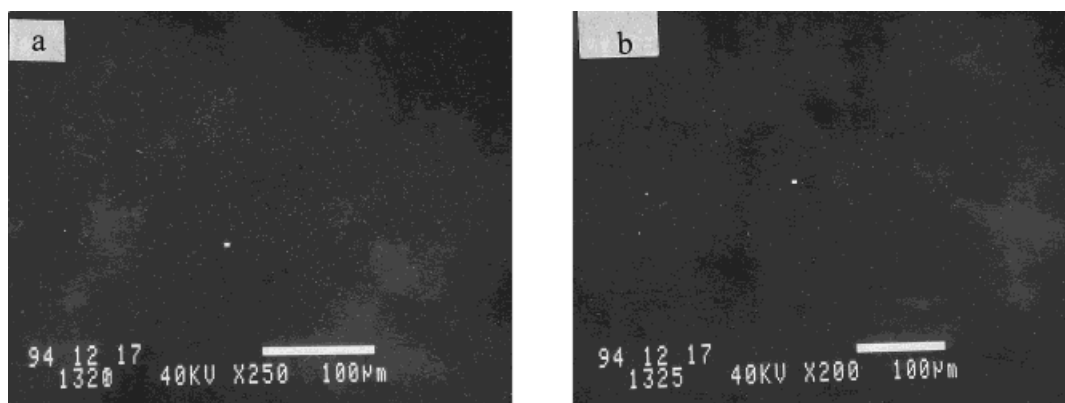


Figure 4 The X-ray images of Fe in the worn surfaces against (a) micrometer copper-filled POM, and (b) nanometer copper-filled POM (RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000).

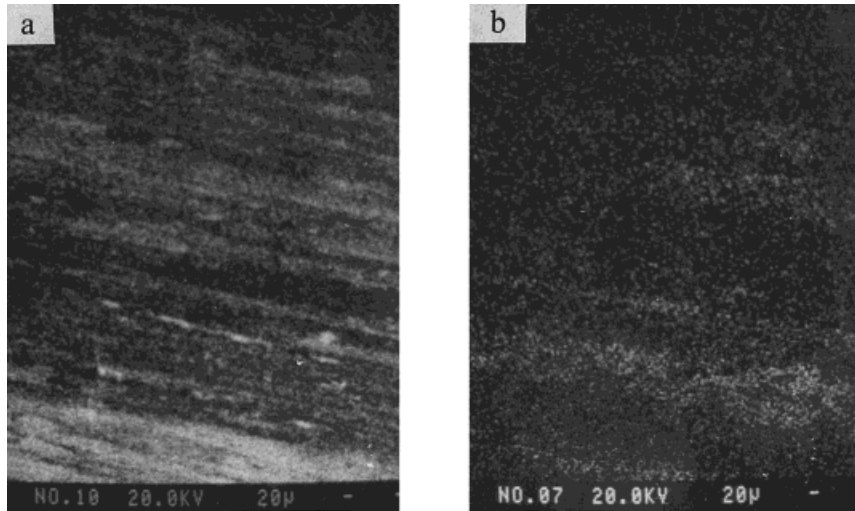


Figure 5 The X-ray images of Cu in the worn surfaces against (a) micrometer copper-filled POM, and (b) nanometer copper-filled POM (RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000).

transfer film by tribochemical reaction. Because $\text{Cu}(-\text{CH}_2-\text{O}-)_n$ has a higher chemical compatibility with the POM matrix than inorganic cupric oxides, such as CuO and Cu_2O , it could be rational to suppose that $\text{Cu}(-\text{CH}_2-\text{O}-)_n$ enhanced the cohesive strength of the transfer film. Subsequently, a lower wear weight loss was obtained with the POM-nano Cu composite. Contrary to the above, the binding energy shift of $\text{Cu}_{2p_{3/2}}$ from 932.4 to 932.0 eV in Figure 7 indicates that Cu_2O was generated by a sliding micrometer copper-filled POM pin against the steel counterface block. Because Cu_2O exhibited relatively severe scuffing action to the counterface, and was easy to be removed from the friction surface, consequently a higher wear weight loss was observed in this case. It is, therefore, inferred that micrometer and nanometer copper particles as fillers in POM exhibit a distinctive size effect in modifying the wear mechanisms of the composites. In other words, the wear mechanisms of POM-micro Cu are mainly scuffing and adhesion, while that of POM-nano Cu is mainly plastic deformation.

CONCLUSIONS

From the above, the following conclusions can be drawn: (1) the microhardness and mechanical strength of POM were increased by filling with micrometer copper particles and nanometer cop-

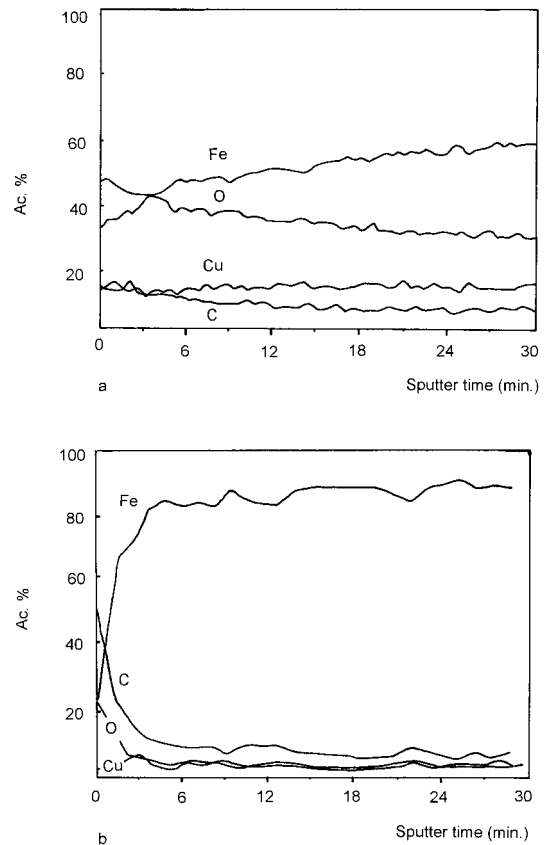


Figure 6 The Auger depth profile of the worn surface against (a) micrometer copper-filled POM, and (b) nanometer copper-filled POM (RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000).

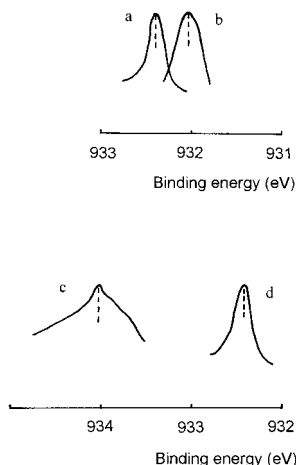


Figure 7 The XPS spectra of Cu in (a) original surface of micrometer copper-filled POM; (b) worn surface against micrometer copper-filled POM; (c) original surface of nanometer copper-filled POM; and (d) worn surface against nanometer copper-filled POM (RFT-III tester, speed 0.2 m s^{-1} , load 294 N , cycle number 5000).

per particles. (2) POM-micro Cu and POM-nano Cu exhibited increased friction coefficients and decreased wear weight loss compared with unfilled POM. (3) POM-micro Cu and POM-nano Cu generated transfer films of different thickness and chemical compositions in sliding against plain carbon steel counterface. The easy transfer of POM-micro Cu contributed partly to its higher wear weight loss. (4) Micrometer and nanometer copper particles as fillers in POM exhibited a distinctive size effect in modifying the wear mechanisms of the composites. Namely, the wear of

POM-micro Cu is characteristic of scuffing and adhesion, while that of POM-nano Cu is characteristic of plastic deformation.

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