

# Tribological Behavior of the Polyamide Composite Coating Filled with Different Fillers under Dry Sliding

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**ABSTRACT:** The polyamide (PA) composite coating filled with the particles of microsized MoS<sub>2</sub>, microsized graphite, and nano-Al<sub>2</sub>O<sub>3</sub>, respectively, were prepared by flame spraying. The friction and wear characteristics of the PA coating and composite coating filled with the varied content of filler under dry sliding against stainless steel were comparatively investigated using a block-ring tester. The morphologies of the worn surfaces and transfer films on the counterpart steel ring were observed on a scanning electron microscope. The result showed that the addition of fillers to the composite coatings changed significantly the friction coefficient and wear rate of the coatings. The composite coatings filled with a low level content of fillers showed lower wear rate than did pure PA coating under dry sliding; especially the MoS<sub>2</sub>/PA composite coating had the lowest wear rate

among these composite coatings. The composite coatings with a high level content of fillers had higher wear rate than did pure PA coating, except of the Al<sub>2</sub>O<sub>3</sub>/PA composite coating. The bonding strengths between the polymer matrix and fillers changed with the content of the fillers, which accounted for the differences in the tribological properties of the composite coatings filled with the varied content fillers. On the other hand, the difference in the friction and wear behaviors of the composite coatings and pure coating were attributed to the difference in their worn surface morphologies and transfer film characteristics. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2554–2560, 2007

**Key words:** polymer coatings; fillers; PA; flame spraying; friction and wear

## INTRODUCTION

Polymer coatings have many good properties such as surface decoration, corrosion protection, low noise, insulation, and wear resistance, and so they are widely used in many fields of aviation, spaceflight, medicine, and so on.<sup>1,2</sup> Many kinds of preparation technologies such as electrostatic powder coating, electrostatic fluidized-bed coating, painting, and flame spraying have been widely used in the preparation of various polymer coatings. Of those methods, flame spraying has been attracting increased attention, owing to the advantages of cost-effective, low-pollution, and physically portable process for thermoplastics.<sup>3,4</sup> Therefore, flame spraying has been used to prepare various kinds of polymeric coatings such as polyetheretherketone, polyphenylenesulfide,<sup>5,6</sup> polyethylene, polyethyl-

ene copolymers, polymethylmethacrylate, polytetrafluoroethylene, and nylons.<sup>7,8</sup> However, most of the reported work in this area is confined to the physical properties or the friction and wear behaviors of the flame-sprayed neat polymer coating,<sup>9,10</sup> and little has been focused on the tribological investigation of flame-sprayed polymer-based composite coatings filled with fillers. This is hindering the potential of various fillers in the tribological application of flame-sprayed polymer-based composite coatings. It has been found that many kinds of polymer-based composites filled with various inorganic particulates show dramatically increased wear-resistance than do the polymer matrices,<sup>11</sup> owing to the increased mechanical strengths and improved friction-reducing and antiwear abilities in the presence of the particulate fillers. Such a kind reinforcing action of the fillers in the bulk polymeric composites can also apply to the polymeric composite coatings.

With those perspectives in mind, the inorganic fillers reinforced PA composite coatings were prepared by flame spray process and the tribological property of the composite coating under dry sliding condition was investigated. Polyamide (PA) is a good material because of its high strength and good wear resistance. However, it has high friction coefficient under dry sliding. The objective of the present work is look at the effects of the

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inorganic fillers on the tribological properties of PA coating and expected to broaden the application of PA material in surface coating technology.

## EXPERIMENTAL

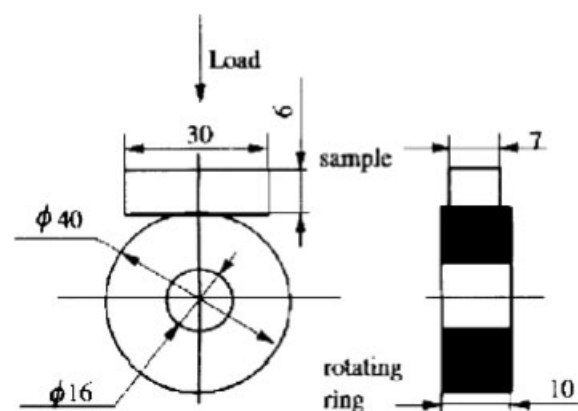
### Coating preparation

PA powders of diameter about 80  $\mu\text{m}$  were provided by Xindi Surface, Beijing, China. Nanometer  $\text{Al}_2\text{O}_3$  (nano- $\text{Al}_2\text{O}_3$ ) of a diameter about 40 nm was commercially available domestically.  $\text{MoS}_2$  and graphite (GF) particulates (<38  $\mu\text{m}$ ) were produced by Shanghai Colloid Chemical Plant, China. The filler particulates at proper mass fraction were dispersed in ethanol solvent for 1 h mixing with PA matrix powders, with mechanical stirring on an electromagnetic cooker under 100°C, and dried at a temperature 90°C to remove the solvent in the oven for 3 h. To improve the bond strength between polymer matrix and fillers, the amount of silane was kept at 5% by weight of fillers in ethanol solvent. Finally, the dried powders were sprayed on the AISI 45 steel (composition: 0.42–0.50% C, 0.17–0.37% Si, 0.50–0.80% Mn, 0.035% max P,  $\leq 0.035\%$  max S, 0.25% Cr, 0.25% max Ni, 0.25% max C, and balance Fe at weight fraction) substrate of size 30  $\times$  7  $\times$  6 mm<sup>3</sup>.

Flame spraying process was carried out by the CMD-PS equipment made in China. A flame spray pistol was used both for preheating the substrate and for spraying the coating. Acetylene and compressed air were used to produce the combustion flame; the compressed air was also used to fluidize the powders and transport the powders from the fluidized bed to the torch. The substrate was sand-blasted using  $\text{SiO}_2$  grit and cleaned with ethanol in an ultrasonic bath. Then it was preheated to about 100–150°C by traversing the spray gun over the substrate surface. And finally, the PA-based composite coating of a thickness 250–350  $\mu\text{m}$  was deposited.

### Friction and wear test

The friction and wear behaviors of the resulting coatings sliding against the stainless steel ring were evaluated on an MM-200 model ring-on block test rig. The contact schematic diagram of the frictional pair is shown in Figure 1. The block in a size of 30  $\times$  7  $\times$  6 mm<sup>3</sup> was made of the AISI 45 steel, on which the coating was prepared, and the ring of  $\phi 40 \times 10$  mm<sup>2</sup> was made of stainless steel (composition: 0.47–0.57% C, 0.25% Si, 8–10% Mn, 20–22% Cr, 2.5–4.5% Ni, 0.02% Ti, and balance Fe at weight fraction; HB = 1.48 GPa). The tests were carried out at a linear velocity of 0.43 m/s, loads from 50N to 200N, ambient temperature around 20°C, relative humidity 50  $\pm$  5%, and duration of 60 min. Before each test, the stainless steel



**Figure 1** Contact schematic diagram for the frictional couple (unit : mm).

ring and the coating were abraded with No. 900 water-abrasive paper to reach surface roughness  $R_a$  of 0.1  $\mu\text{m}$  and 0.1–0.2  $\mu\text{m}$ , respectively. The friction force was measured with a torque shaft equipped with the strain gauges. The wear track widths of the coatings were measured with a digital-reading microscope to an accuracy of 0.01 mm. Then the wear volume loss  $V$  of the coating was calculated from the relationship:

$$V = B \left[ \frac{\pi r^2}{180} \arcsin \left( \frac{b}{2r} \right) - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right] \quad (1)$$

where  $V$  is wear volume loss (mm<sup>3</sup>);  $B$ , width of the substrate (mm);  $r$ , radius of the stainless steel ring (mm); and  $b$ , width of the wear track of the coating (mm). The specific wear rate ( $K_0$ ) was calculated from the volume loss using the following equation:

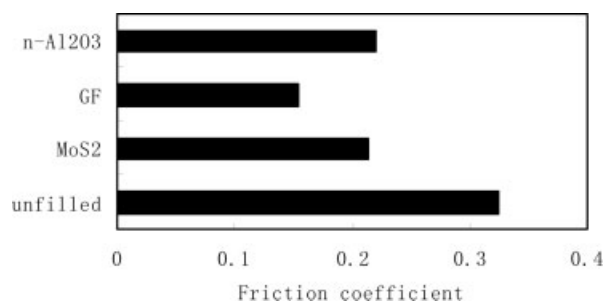
$$K_0 = V / (Ld) [\text{mm}^3 (\text{Nm})^{-1}] \quad (2)$$

where  $d$  refers to the sliding distance in meter and  $L$  to the load in Newton. Three replicate tests were carried out for each pure PA coating and composite coating, and the average of the three replicate test results was reported. The wear tracks of the coatings were examined on a JEM-5600LV scanning electron microscope (SEM). To increase the resolution for the SEM observation, the wear tracks of the coatings were ion-plated with gold to increase the electric conductivity.

## RESULTS AND DISCUSSION

### The friction and wear behaviors of the PA composite coatings

Figure 2 shows the friction coefficient obtained for various specimens sliding against the stainless ring under 100N and 0.43 m/s. It is seen that the friction coefficients of the composite coatings were lower than

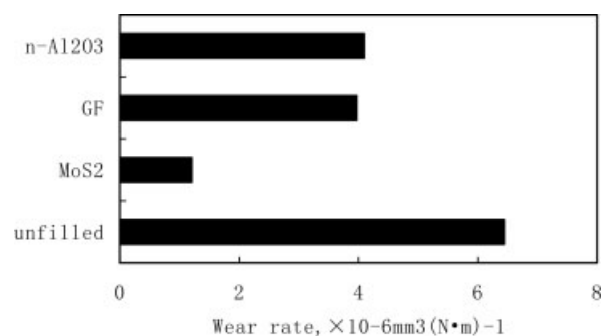


**Figure 2** Variations in friction coefficient of the composite coating with the different fillers at a sliding speed of 0.43 m/s under 100N.

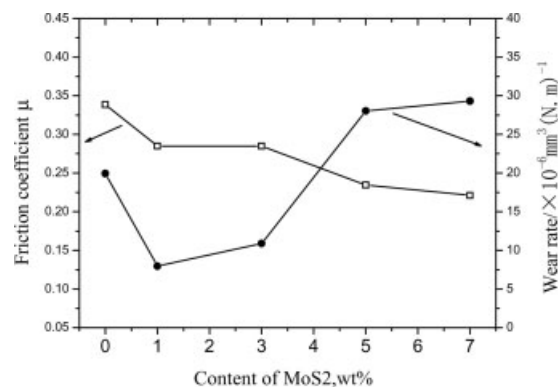
that of the neat PA coating, which is attributed to fillers being good traditional solid lubricants. It can also be seen that the PA composite coating filled with GF showed the lowest friction coefficient than the others, a value of about 0.15.

Figure 3 shows the wear rates for various specimens sliding against the stainless ring under 100N and 0.43 m/s. By comparing with the PA coating without filler, it can be observed that the addition of filler decreased the wear rate of the composite coating. In particular, the incorporation of the MoS<sub>2</sub> particulates contributed to dramatic decrease in the wear rate of the PA coating by six times. The other kinds of the composite coatings had similar wear rate, which was about four times as large as that of MoS<sub>2</sub>/PA coating.

Figure 4 shows the effect of MoS<sub>2</sub> content on the friction coefficient and wear rate of the MoS<sub>2</sub>/PA composite coating under dry sliding at 200N and 0.43 m/s. The friction coefficient of the MoS<sub>2</sub>/PA composite coating decreased quickly with increasing MoS<sub>2</sub> content from 1 to 7 wt %. At a low level content of MoS<sub>2</sub> (1–3 wt %), it was stable. As compared with the friction coefficient, this change for the wear rate was complex. The low level content (1–3 wt %) of MoS<sub>2</sub> particulates lead to a significant decrease in the wear rate of the composite coating. However, the composite coating containing high level content (above 5 wt %) of



**Figure 3** Variations in the wear rate of the composite coating with the different fillers at a sliding speed of 0.43 m/s under 100N.



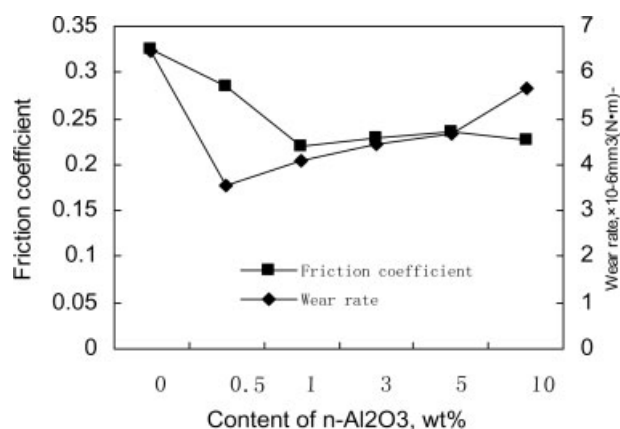
**Figure 4** Variation of the friction coefficient and wear rate of the MoS<sub>2</sub>/PA composite coating with MoS<sub>2</sub> content under dry sliding at 200N and 0.43 m/s.

MoS<sub>2</sub> particulates had much larger wear rate than that of the neat PA coating, which could be attributed to the weakened adhesion between the fillers and polymer matrix in the presence of an excessive amount of MoS<sub>2</sub> particulates.

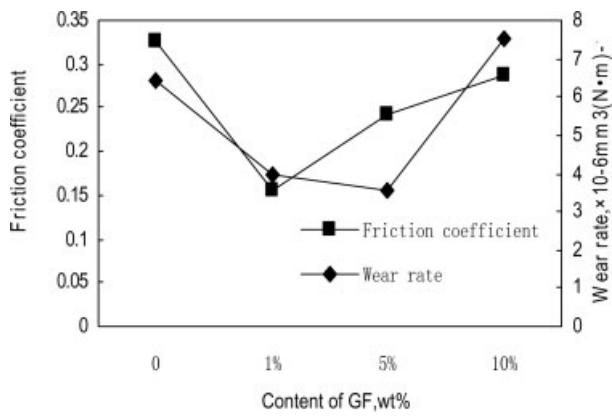
The effect of the filler content on the friction and wear behaviors of nano-Al<sub>2</sub>O<sub>3</sub>-filled PA composite coating was similar to that of the MoS<sub>2</sub>/PA one, except that the composite coating containing a high level content of nano-Al<sub>2</sub>O<sub>3</sub> had larger wear rate, which is lower than that of the PA coating without fillers (Fig. 5).

For the GF filled composite coating, the variation of the wear rate with the content of filler was similar to that of the MoS<sub>2</sub>/PA one, while the friction coefficient decreased with the content of fillers below 1 wt %, then increased quickly with the content of fillers above 1 wt % (Fig. 6).

Based on these results, it could be postulated that the level of the filler can affect the matrix hardness and bonding strength between the filler and polymer matrix.<sup>12</sup> A high level of filler may decrease the hard-



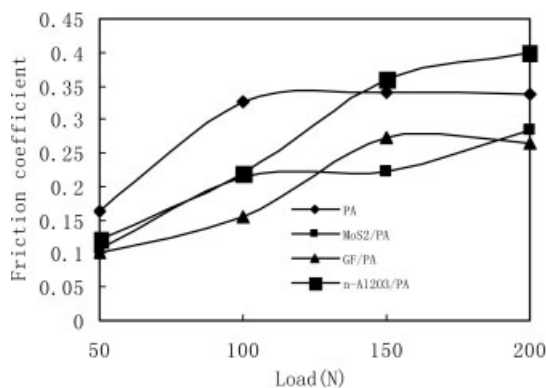
**Figure 5** Variation of the friction coefficient and wear rate of the Al<sub>2</sub>O<sub>3</sub>/PA composite coating with Al<sub>2</sub>O<sub>3</sub> content under dry sliding at 200N and 0.43 m/s.



**Figure 6** Variation of the friction coefficient and wear rate of the GF/PA composite coating with GF content under dry sliding at 200N and 0.43 m/s.

ness of the matrix and weaken the adhesion between the filler and polymer matrix. The weak bond led to the filler particles detaching from the matrix and the matrix pulling out more easily, which could increase the wear rate of the composite coating. At the same time, the composite coating with a high level of the filler showed many voids and unmelted particles, which was harmful to the wear-resistance of the composite coating. So, a high level of the filler led to the high wear rate of the composite coating. On the other hand, a low level of filler may increase the hardness of the matrix and the bonding strength between the filler and polymer matrix. This should result in fewer polymer matrices being pulled out and reduced the wear rate. The filler as a kind of strength phase was distributed throughout the coating and carried the load. So, the fresh lubricant was continuously being exposed as the surface wears.

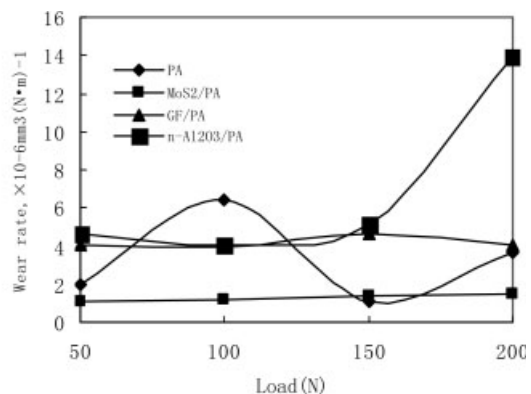
Figure 7 shows the variations of the friction and the wear behaviors of the coatings with the load. It is seen that the load had a great effect on the friction coefficients of the coatings. They increased gradually with the increase of the load up to 200N except that the fric-



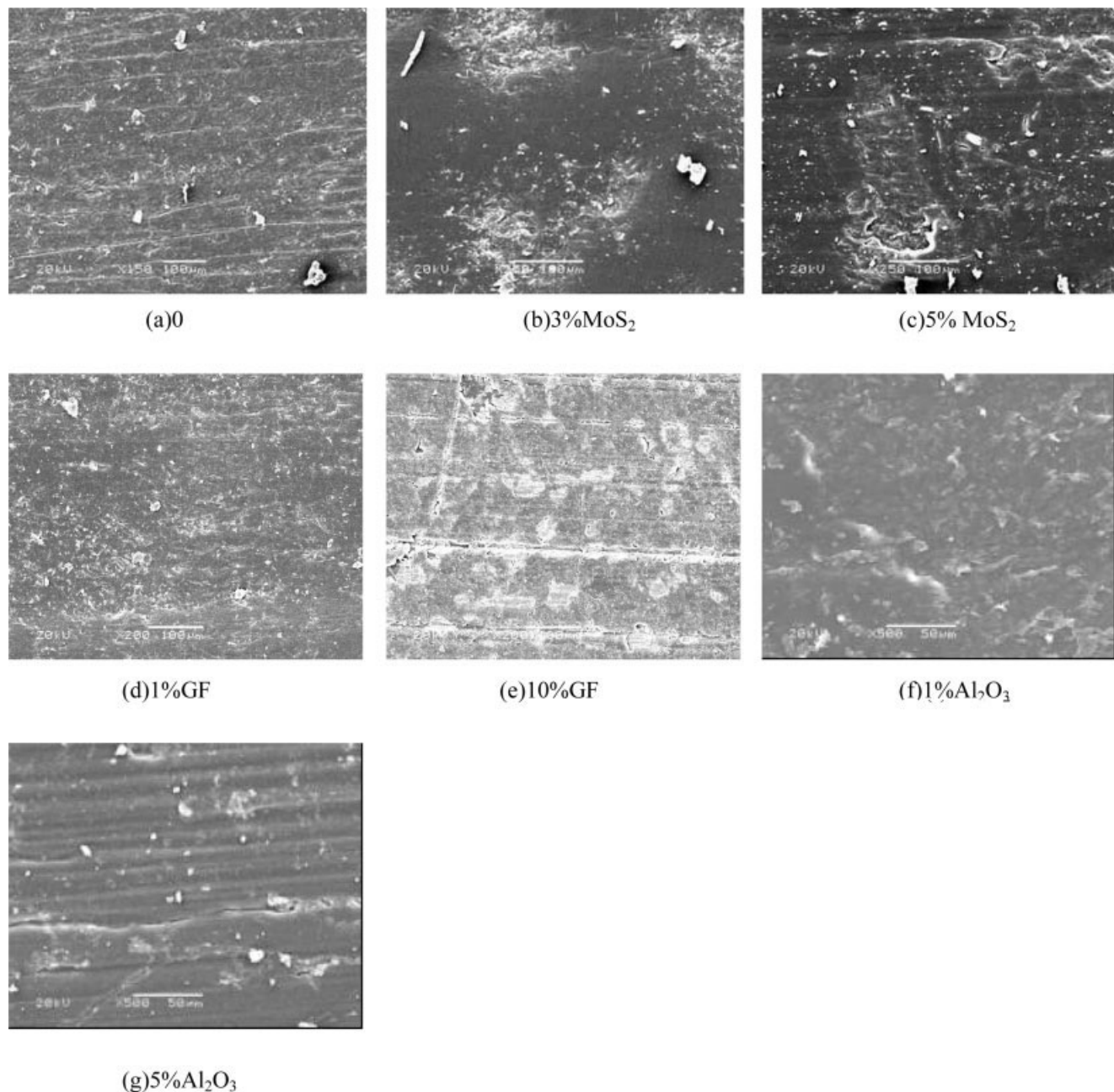
tion coefficient of the pure PA coating kept almost unchanged within the load from 100 to 200N. It was inconsistent that the load affected on the wear rate of the different composite coating. The load had almost no effect on the wear rate of the MoS<sub>2</sub>/PA and GF/PA composite coatings. For the nano-Al<sub>2</sub>O<sub>3</sub>/PA coating, it was almost unchanged below the load of 150N and then sharply rose at the load of 200N. Therefore, the nano-Al<sub>2</sub>O<sub>3</sub>/PA composite coating was not suitable for the high load tribological application. Moreover, the pure PA coating showed the good wear-resistance at the load of 150N.

**SEM investigation of the worn surfaces**

Figure 8 shows the SEM morphologies of worn surfaces of the composite coatings with different filler content sliding against the steel ring at normal load of 200N and velocity of 0.43/m/s. It can be seen that the worn surface of the unfilled PA coating showed many broad and deep furrows characterized by severe abrasive wear [see Fig. 8(a)], which indicated that PA coating was brittle and easier to be scuffed and abraded by the asperity tips on the counterpart steel ring.<sup>13</sup> Contrary to the above, the worn surface of the composite coating with 3 wt % MoS<sub>2</sub> was flat and smooth and showed light adhesive wear [see Fig. 8(b)]. This indicated that the MoS<sub>2</sub> particles incorporated in the composite coating effectively acted as a strength phase to restrain the direct contact between the brittle polymer matrix and the hard counterpart steel ring; thus, the friction and wear considerably decreased, owing to their good solid-lubricating action. However, when the content of MoS<sub>2</sub> rose to 5 wt %, fatigue wear of the matrix material was the main wear mechanism [see Fig. 8(c)]. The matrix material was fractured and removed, which was in agreement with the high wear rate shown in Figure 4. The worn surface of the composite coating filled with 1 wt % GF had similar property as that of the low level nano-Al<sub>2</sub>O<sub>3</sub> filled one char-



**Figure 7** Variations in friction coefficient and wear rate of the composite coating with the loads at a sliding speed of 0.43 m/s under 200N.

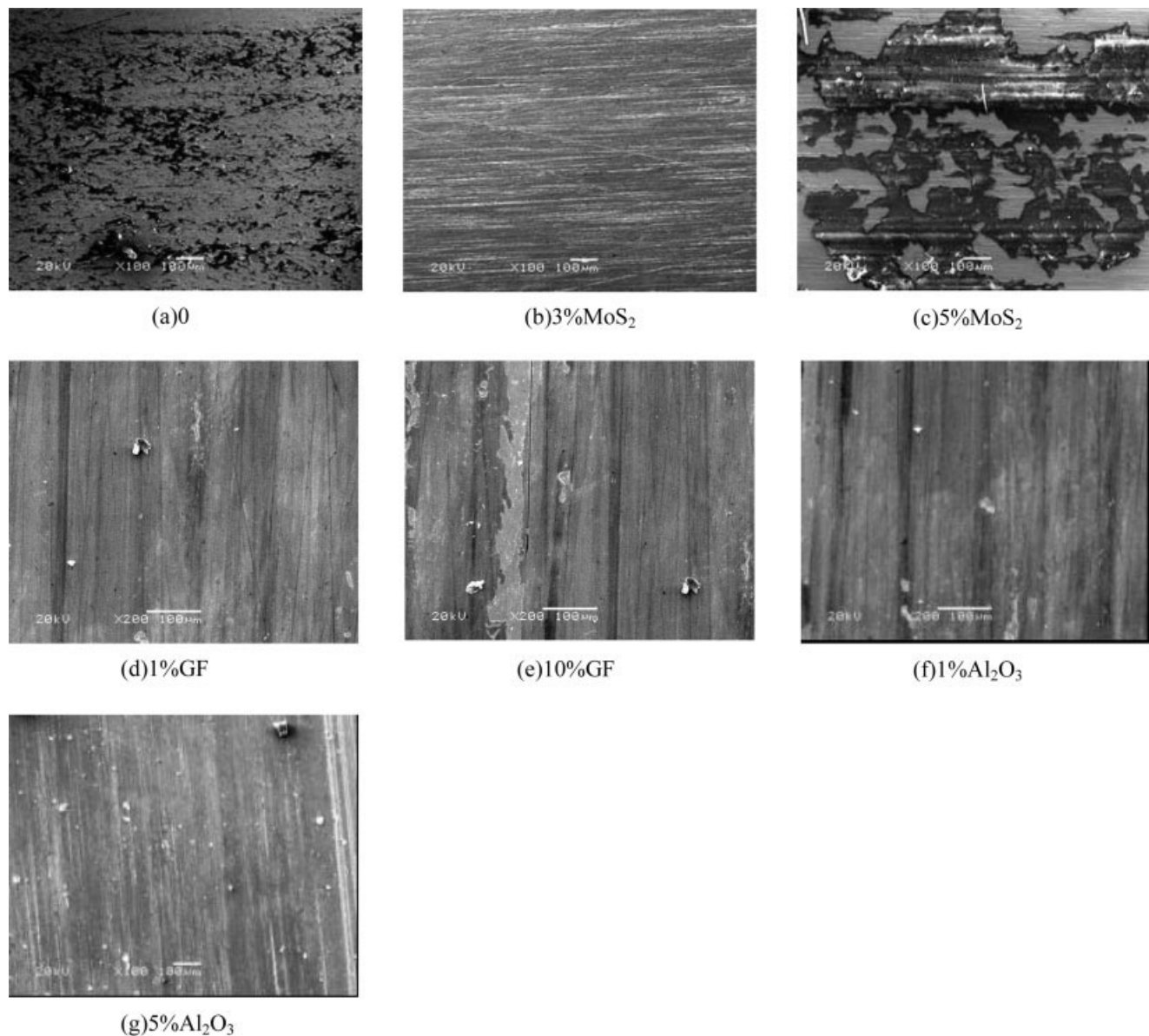


**Figure 8** SEM morphologies of worn surfaces of the composite coatings with different filler content sliding against the steel ring at normal load of 200N and velocity of 0.43/m/s.

acterized by light adhesion and plastic deformation [see Fig. 8(d,f)], which conformed to be next to the MoS<sub>2</sub> filled one in term of wear rate of the composite coatings. While the composite coatings with a high level content of filler showed the different SEM morphologies. For the composite coating with 10 wt % GF, severe microcracking and microploughing could be seen as the main wear mechanisms [see Fig. 8(e)]. Microcracking initiated from the filler particles and the crack propagated into the matrix; the microploughing furrows were deep and wide paralleled to the wear direction, which was responsible for the high

wear rate exhibited in Figure 6. The worn surface of the composite coating with 5 wt % nano-Al<sub>2</sub>O<sub>3</sub> filler showed signs of much more severe scuffing, lowing, and plastic deformation [Fig. 8(g)].

The SEM morphologies of the worn surface of the counterpart steel ring sliding against the composite coatings under 200N and 0.43 m/s are shown in Figure 9, in an attempt to elucidate the effect of the filler content on the transfer film characteristics. It is seen that the worn surface of the counterpart steel ring sliding against the composite coatings seemed to be polished to different degrees, with the formation of the



**Figure 9** SEM morphologies of the worn surface of the counterpart steel ring sliding against the composite coatings at normal load of 200N and velocity of 0.43/m/s.

transferred layers with varied thickness and uniformity. This could partly account for the different wear resistance of the composite coatings. The counterpart worn surface sliding against the unfilled coating seemed to have a thick and loose transferred layer [see Fig. 9(a)]. This indicated that PA matrix was softened and easily transferred to the counterpart surface forming thick layers. The thick transferred materials were harmful to the antiwear of PA coating. While those sliding against the composite coatings with low level content of fillers looked smooth and seemed to have uniform, thin, and continuous transferred layers [see Fig. 9(b,d,f)]. It can be concluded that the low level content of fillers may help to form a good and tenacious transfer film on the counterpart surface, which resulted in the antiwear of the composite coat-

ings. On the other hand, the thick and uneven transferred films were formed on the counterpart worn surface sliding against the composite coatings with high level content of MoS<sub>2</sub> and GF fillers [see Fig. 9(c,e)], which agreed well with their high wear rates as compared with that of the composite coating filled with a low level content of fillers and even to the unfilled PA coating. The agglomerated abrasives on the transfer film of 5 wt % Al<sub>2</sub>O<sub>3</sub>/PA composite coating also contributes to the larger wear rate [see Fig. 9(g)].

Above all, it can be concluded that the differences in the worn surface morphologies, and transfer film characteristics of the PA composite coatings accounted for their different friction and wear behaviors in sliding against the stainless steel ring.

## CONCLUSIONS

From the above, the following conclusions can be drawn:

- a. the PA composite coatings were prepared successfully by flame spraying optimizing the craft parameter.
- b. The addition of fillers to the composite coatings changed significantly the friction coefficient and wear rate of the coatings. The composite coatings filled with a low level content of fillers showed lower wear rate than pure PA coating under dry sliding. While the composite coatings with a high level content of fillers had higher wear rate.
- c. The bonding strengths between the polymer matrix and fillers changed with the content of the fillers, which accounted for the differences in the tribological properties of the composite coatings filled with the varied content fillers. On the other hand, the difference in the friction and wear behaviors of the composite coatings and pure coating were attributed to the difference in their worn surface morphologies and transfer film characteristics.

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