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A study on sliding wear mechanism of ultrahigh molecular weight polyethylene/ polypropylene blends

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Abstract

This paper explores anti-wear properties and wear mechanism for ultrahigh molecular weight polyethylene (UHMWPE) and ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) blends, which were prepared by melt extruding through a single-screw extruder, and were conducted sliding wear tests with MM-200 wear tester by sliding against 45# steel ring of a surface roughness about 0.015 μm. Results show that anti-wear properties of UHMWPE are improved notably by blending with appropriated content of polypropylene (PP). The coefficients of friction and wear rate of UHMWPE/PP blend are much lower than those of pure UHMWPE during sliding. Partly oxidized transfer film of UHMWPE is formed on the surface of the steel counterpart. No transfer film but fine powders can be found on the steel ring surface sliding against the UHMWPE/PP blend. Long duration sliding causes fatigue failure of UHMWPE and many big spalls are produced around the counterpart edge, while the amount of debris from UHMWPE/PP blends does not show apparent increase with sliding time. DSC analysis reveals that the surface temperature of UHMWPE is higher than that of UHMWPE/PP blend during sliding. 'Shish-kebab' crystal is formed in the worn surface of UHMWPE/PP blend due to the long time shearing, stretching and annealing effect during sliding. The improvement of wear resistance is probably due to the rod shape debris existing between the contact surface of UHMWPE/PP and the counterpart, which helps to reduce the friction and wear efficiently.

Keywords: Ultrahigh molecular weight polyethylene; Polypropylene; Wear and friction; Fatigue failure

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is a polymer which allows sliding against surface of steel or other materials with very low wear coefficient and a moderate coefficient of friction [1]. There are a large number of reports on the friction and wear behavior of UHMWPE under various conditions [2–7]. Wear of UHMWPE proceeded by two mechanisms: an adhesive process which occurs immediately after sliding begun and a fatigue process which appears after a long period of sliding [6,7]. The wear of UHMWPE is dependent on surface temperature and, when the temperature exceeds a critical value, wear proceeds in a series of discrete steps caused by the sudden loss of a molten or softened layer of polymer. Wear was also influenced by surface roughness. An optimum surface roughness, i.e. a minimum of wear was found at low and medium sliding speeds under dry conditions [1]. Cooper et al. [8] found that two separate types of wear process existed during sliding on relatively smooth counterface. Microscopic wear processes were associated with the very small asperities or the smooth counterface (less than 0.2 μm). Macroscopic polymer asperity wear processes were associated with stress concentrations under the much larger peaks in the polymer surface (amplitude less than 10 μm).

Hashmi et al. [9] found that a small weight fraction of UHMWPE in polypropylene (PP) improved the wear resistance of PP to a significant extent. A PP blend containing 15 wt.% of UHMWPE demonstrate a similar wear behavior of pure UHMWPE. Previous studies by us have shown that appropriate amount of PP added in UHMWPE can improve not only the processability, but also the anti-wear properties effectively. In this paper, we try to investigate the wear mechanism of these materials in detail.

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2. Experimental

2.1. Base materials

UHMWPE(M-II) with an average molecular weight of 2.5×10^6 and a mean particle diameter of about 300 μm was supplied by Beijing No. 2 Auxiliary Agent Factory (Beijing, China). PP(F401) granule was supplied by Lanzhou Chemical Industry Factory (Lanzhou, China) with a MFR = 2.0 g/10 min (230 °C, 2.16 kg load) and grain diameter of about 2 mm.

2.2. Preparation of specimens

All blends were extruded by single-screw extruder (D = 25 mm, $L/D = 25$) through capillary die (D = 3 mm, $L/D = 7$) with the die temperature of 210 °C and the screw rotation speed of 10 rpm. Each blend was blended with a fraction of anti-oxidants and processing aid agents before extrusion. The extrudates were made pellets and compression molded under 195 °C and 13 MPa for 5 min to get 4 mm thick plates. Samples for wear tests were cut from the plates, the size of the wear specimen is 30 mm × 7 mm × 4 mm. Pure UHMWPE specimens were prepared from the original UHMWPE powder without extrusion before molding.

2.3. Wear and friction testing

Sliding wear tests were conducted using a MM-200 wear tester (Shanghai, China) at room temperature according to GB3960-83. The scheme of wear test was shown in Fig. 1. The diameter of the steel ring (45# steel) was 40 mm, the surface smooth was 0.015 μm, the hardness was about 50 HRC, and the rotation speed of the steel ring was 200 rpm during operation. Before the testing, the specimen and the steel ring were washed with acetone and dried naturally. Friction torques (T) were recorded every 5 min, coefficient of friction was calculated by equation as following:

$$\mu_a = \frac{T_a}{MR}$$

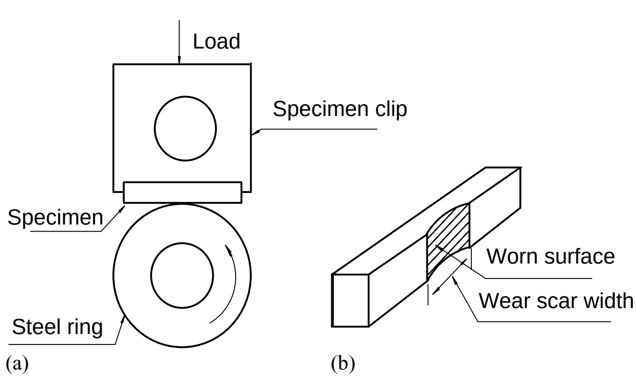

Fig. 1. Schematic diagram of wear testing: (a) scheme of MM200 model friction and wear tester; (b) worn surface of specimen.

where μ_a is the average friction coefficient, T_a the average friction torque (kg cm), M the load (kg), and R the radius of the ring (cm).

The wear scar widths were adopted to evaluate wear-resistance properties.

2.4. Morphology observation

A JSM-5900 LV scanning electron microscope (SEM) was used to observe the worn surface and the steel-counterpart surface. Atomic force micrograph (AFM, SPA400, Seiko Japan) measuring with tapping mode were applied to investigate the micro-topography of the worn surface, silicon nitride (Si_3N_4) cantilever with nominal spring constants of 16 N/m and frequency of 41 kHz was used during observation. Before the AFM observation, the worn surfaces of the specimens were etched in a mixture of 1.3 wt.% $KMnO_4$ dissolved in $H_2SO_4/H_3PO_4/H_2O$ (10:4:1) solution to eliminate the amorphous phase [10].

FT-IR analysis of the debris was carried out with NICOLET-560 FT-IR instrument. Debris from UHMWPE sample were collected directly and heat-pressed into thin film for IR analysis. While the debris from ultrahigh molecular weight polyethylene/polypropylene (UHMWPE/PP) blend must be washed down from the ring surface with alcohol due to the quantity was too small and the particles were very fine.

XPS analysis of the worn surface was performed with XSAM800 (KRATOS, UK) with FRR Analyzer Mode. Thermal characteristics of the worn surface and the bulk of the specimens were studied on NETZSCH DSC 204 with a heating rate of 10 °C/min and temperature interval of 40–200 °C under nitrogen atmosphere. The specimen of the worn surface and the bulk were prepared by careful slicing of the samples at ambient temperature.

3. Results and discussion

Fig. 2 shows the dependence of friction coefficient and wear scar width of UHMWPE/PP blends on the weight fraction of PP during sliding. The results indicate that when PP concentration is lower than 25 wt.%, the friction coefficient and wear scar width of the blend decrease with the increasing of PP content The further increase of the PP content results in the friction coefficient increases abruptly, and wear scar width of the blends increasing.

Fig. 3 shows the SEM of the worn surface of UHMWPE and UHMWPE/PP (80:20) blend. Plenty of microcracks vertical to the sliding direction are clearly observed in the worn surface of UHMWPE, while no long scratches and cracks can be observed in the worn surface of UHMWPE/PP blend.

Fig. 4 shows the morphologies of the steel-counterpart surface after a 30 min sliding. Fig. 4a shows that transfer film is formed on the metal ring surface when sliding against UHMWPE. EDS analysis of the film exhibits

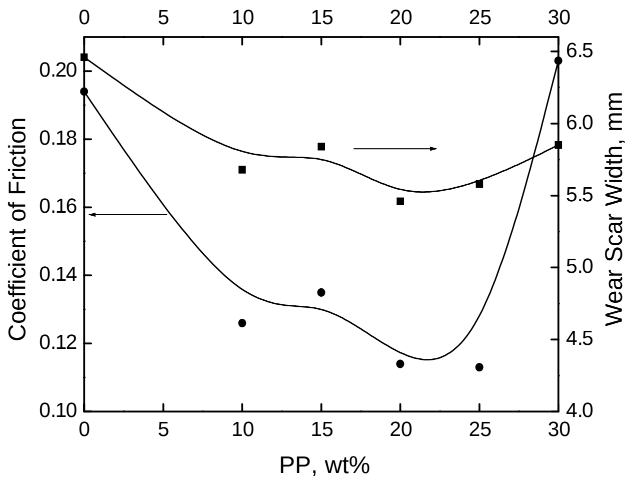

Fig. 2. Variation of coefficient of friction and wear scar width of UHMWPE/PP blend with PP content (load: 30 kg; time: 30 min).

strong oxygen peak as shown in Fig. 5a. The calculated C/O elemental weight ratio is 19.9/32.8, and from naked-eye observation, the film is in brown, which means serious oxidization happened to the film during sliding. No apparent transfer film can be seen on the steel ring surface sliding against UHMWPE/PP (80:20) blend as shown in Fig. 4b. EDS analysis of the ring surface demonstrate only the characteristic of steel base, no oxygen peak can be found as shown in Fig. 5b. Instead, fine powders around the ring surface are formed. Careful observation of these powders shows that they are in the form of long rod formed from the debris by the rolling motion of the steel ring.

A lot of large spalls appear along the edge of the counterpart sliding against UHMWPE when duration time increased to 120 min. IR analysis of the debris shows that they are slightly oxidized UHMWPE (Fig. 6b) as compared with the FT-IR spectrum of the original UHMWPE as shown in Fig. 6c. In the case of UHMWPE/PP (80:20) blend, the amount of debris does not show apparent increase with the increase of duration time. IR analysis shows that the debris is partly oxidized (Fig. 6a). The bands at 3365.93 and 1733.06 cm^{-1} are the characteristic of hydroxyl and carbonyl vibration, respectively.

Table 1
Carbon and oxygen content of the worn surface got from XPS data

Specimen	30 kg, 30 min		30 kg, 120 min	
	C (%)	O (%)	C (%)	O (%)
UHMWPE	99.29	0.71	99.36	0.64
UHMWPE/PP (80:20)	99.18	0.82	96.82	3.18

The XPS wide scan spectra of the worn surface shows very intense C1s peak and weak O1s peak for every sample as shown in Fig. 7. The quantitative XPS analysis is listed in Table 1, which shows that friction causes oxidation of the surface materials. The oxygen content in the worn surface of UHMWPE declines from 0.71 to 0.64% when sliding time increases from 30 to 120 min as shown in the table. SEM observation of the worn surface reveals that long sliding duration cause the fatigue broken of the surface materials and new surface exposed accordingly, therefore the oxygen content of the worn surface did not cumulate with the increase of sliding time. In the case of UHMWPE/PP blend, the oxygen content of the worn surface increases from 0.82 to 3.18 wt.% when the sliding time increases from 30 to 120 min, showing oxidization tendency with sliding time. The all phenomenon demonstrated above indicate that fatigue failure is the major wear mechanism of UHMWPE after a long period of sliding, while the crack resistance properties of UHMWPE/PP blends is much better than that of UHMWPE, which leads to better anti-wear properties.

DSC curves and data of the bulk and the worn surface of UHMWPE and UHMWPE/PP blend after a sliding period of 30 min are presented in Fig. 8 and Table 2. For UHMWPE, the onset and peak melting temperature of the bulk, which are 125.12 and 139.79 °C, respectively,

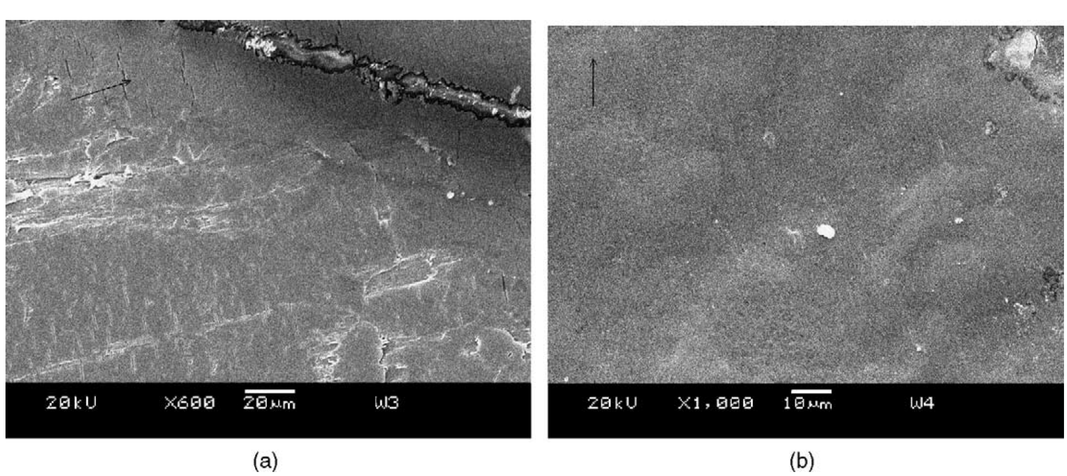

Fig. 3. SEM photography of the worn surface (load: 30 kg; time: 120 min): (a) UHMWPE; (b) UHMWPE/PP (80:20) blend.

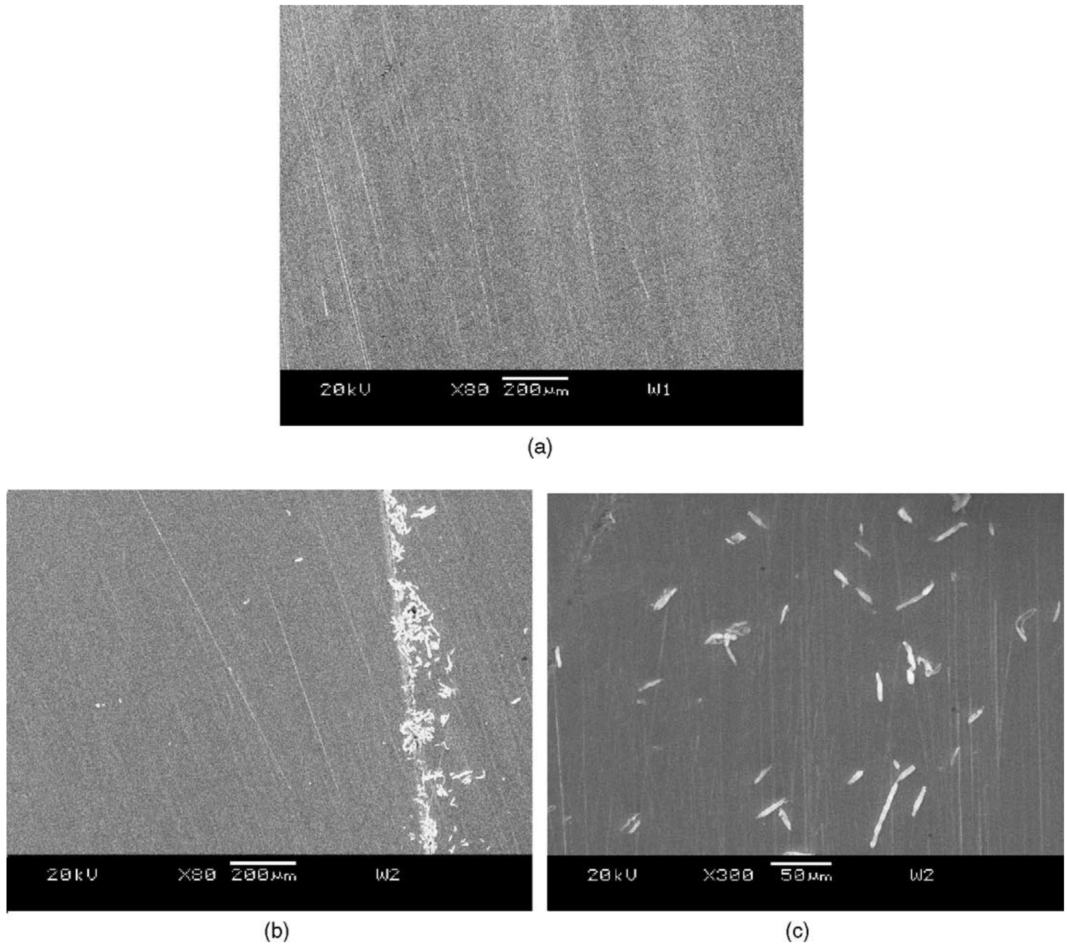

Fig. 4. SEM photography of the steel counterface (load: 30 kg; time: 30 min): (a) sliding against UHMWPE; (b) sliding against UHMWPE/PP (80:20) blend; (c) high magnification of photo (b).

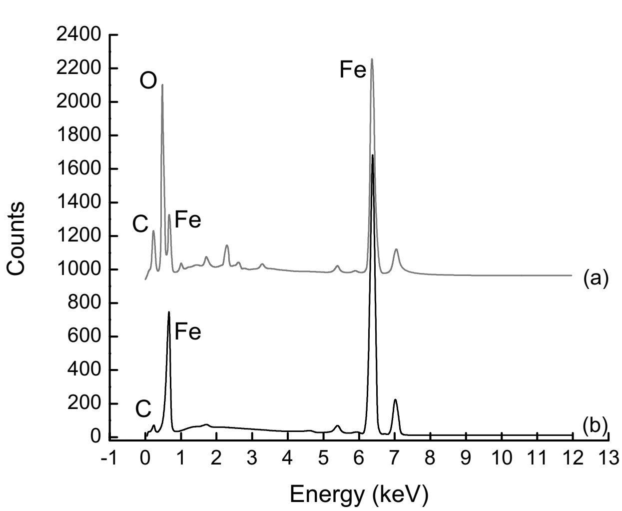

Fig. 5. EDS analysis of the transfer film on the ring surface (load: 30 kg; time: 30 min): (a) counterface sliding with UHMWPE; (b) counterface sliding with UHMWPE/PP (80:20).

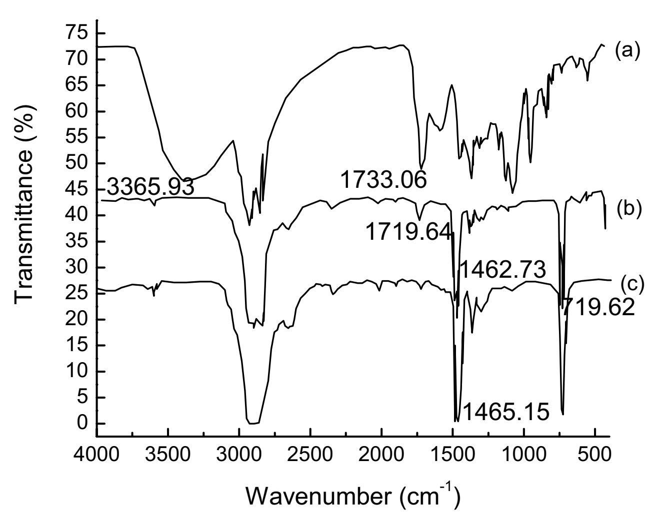

Fig. 6. FT-IR spectrum of wear debris (load: 30 kg; time: 120 min): (a) debris from UHMWPE/PP blend; (b) debris from UHMWPE; (c) original UHMWPE.

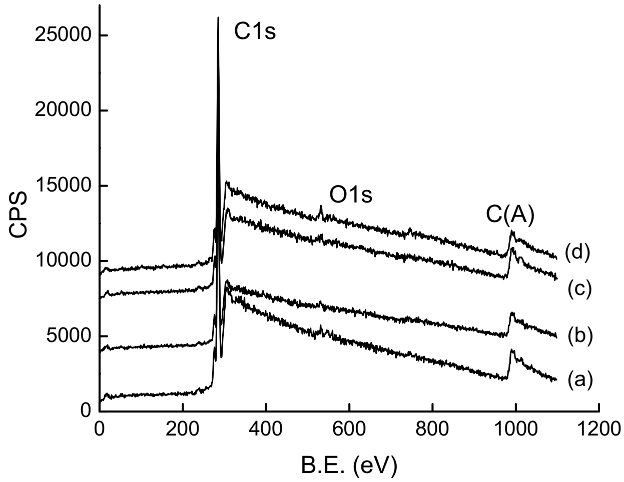

Fig. 7. XPS analysis of the worn surface under different conditions I (30 kg, 30 min): (a) UHMWPE; (b) UHMWPE/PP (80:20) blend; conditions II (30 kg, 120 min): (c) UHMWPE; (d) UHMWPE/PP (80:20) blend.

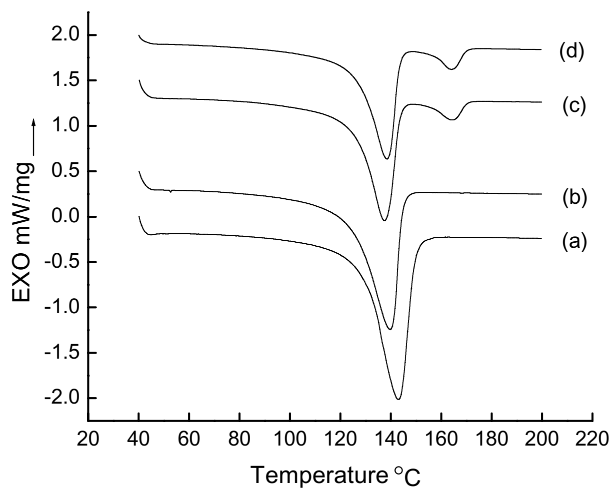

Fig. 8. DSC curves of the bulk and the worn surface of UHMWPE and UHMWPE/PP (80:20) blend (load: 30 kg; time: 30 min): (a) UHMWPE-surface; (b) UHMWPE-bulk; (c) UHMWPE/PP-surface; (d) UHMWPE/PP-bulk.

Table 2
DSC thermogram data of the worn surface and the bulk of UHMWPE and UHMWPE/PP (80:20) blend

Specimen	T_{onset} (°C)[a]	T_{peak} (°C)[b]	X_c (%)[c]
UHMWPE			
Surface	129.47	143.19	59.20
Bulk	125.12	139.79	49.06
UHMWPE/PP (80:20)			
UHMWPE-surface	126.15	137.59	39.44
UHMWPE-bulk	126.54	138.50	34.88
PP-surface	157.16	164.49	26.06
PP-bulk	158.37	164.29	27.46

[a] Temperature at which crystal begin to melt.
[b] Temperature at which crystal melt the fastest.
[c] Relative crystallinity.

are much lower than those of the worn surface, which are 129.47 and 143.19 °C, respectively. And the crystallinity is also increased from 49.0% of the bulk to 59.20% of the worn surface. The increase of crystal melting temperature and crystallinity of the worn surface indicate that the temperature of the friction surface during sliding is high enough to cause UHMWPE to be annealed, which makes the crystal morphology more perfect and the crystallinity higher. As for the UHMWPE/PP (80:20) blend, the changes of crystal melting temperature and crystallinity of the bulk and the worn surface of UHMWPE and PP in the blend is not so apparent as shown in Table 2. This phenomenon reveals that the annealing effect of UHMWPE/PP blend is not so adequate as that of UHMWPE during sliding, which implies that the surface temperature of UHMWPE is higher than that of UHMWPE/PP blend. The rod shape debris between the contact surfaces of steel ring and UHMWPE/PP blend help to decrease the coefficient of friction and hence the surface temperature, therefore improving the wear resistance. Although it is hard to test the surface temperature in situ, we could feel in practice that the ring sliding against UHMWPE is much hotter than that sliding against UHMWPE/PP blend.

AFM observation of the worn surface etched with mixed acid solution shows that the surface crystal morphology of UHMWPE after a sliding period of 120 min is quite different from that of UHMWPE/PP blend as shown in Fig. 9. In the worn surface of UHMWPE/PP blend, 'shish-kebab' crystal is formed. The crystal domains and the adhesion between crystal domains seem larger and stronger than those of UHMWPE. Since UHMWPE/PP blend shows much better wear resistance, no serious wear happened during the operation. Shearing and stretching force are applied to the surface molecular chains, which make the crystal lamellar to be aligned along the moving direction. In the case of UHMWPE, long period of sliding make surface UHMWPE flaking off from the bulk, which causes new surface to be exposed and no 'shish-kebab' crystal can be formed.

3.1. Model of the friction

The wear of UHMWPE is dependent on surface temperature. When the temperature exceeds a critical value, wear proceeds in a series of discrete steps caused by the sudden loss of a molten or softened layer of polymer [1]. The lower is the surface friction coefficient, the less the friction heat will be produced, therefore the surface temperature will be lower, which indicates better anti-wear properties.

Partly oxidized transfer film is formed on the metal ring surface when sliding with UHMWPE. No transfer film but fine powders can be found on the steel ring surface sliding with UHMWPE/PP. Debris of UHMWPE/PP existed between the two friction surface acts as rolling lubricants, therefore reduce the friction coefficient and wear to a much lower level. This friction and wear reduction by interposed

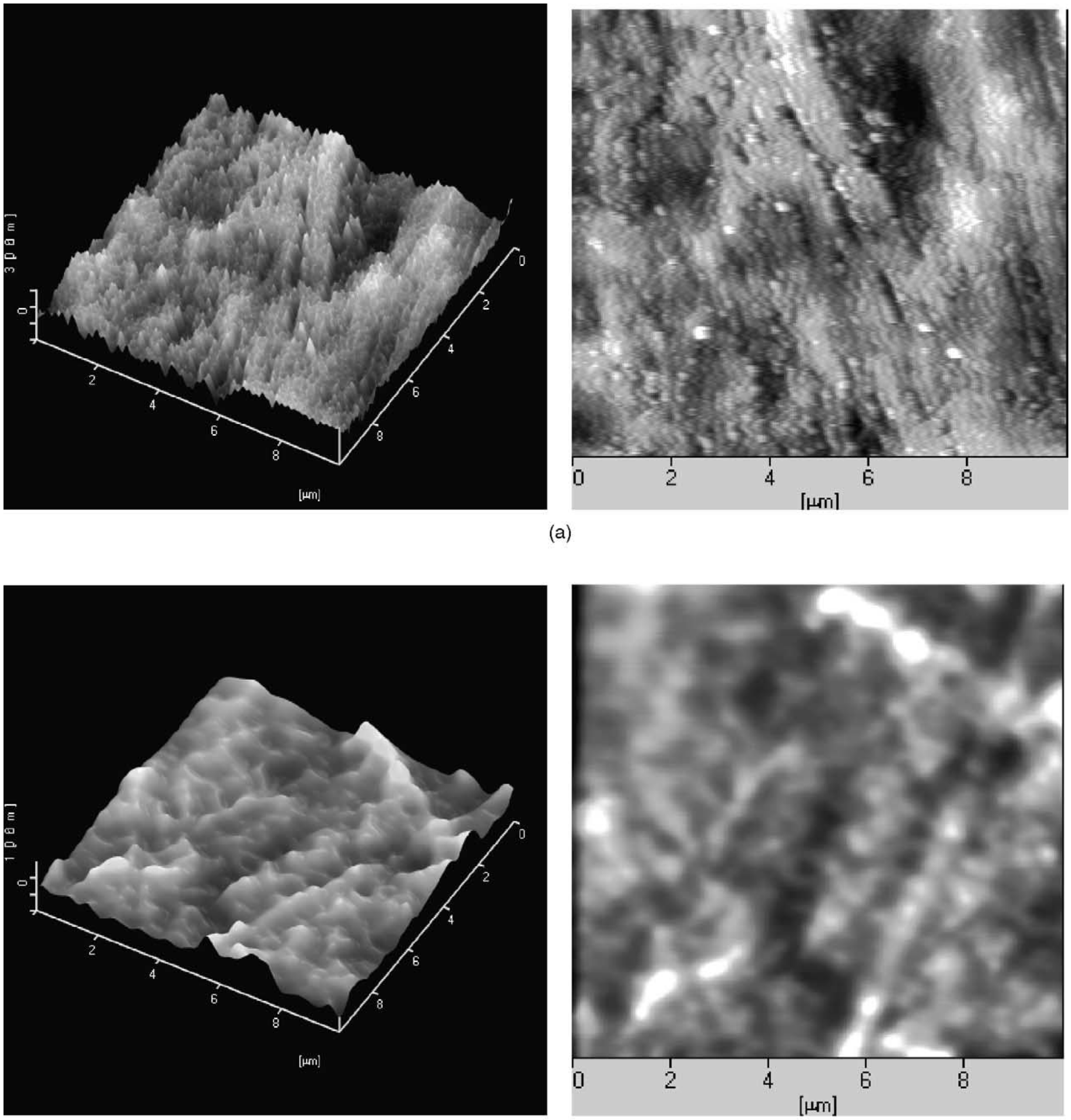

Fig. 9. AFM observation of the worn surface after etching treatment (load: 30 kg; time: 120 min): (a) UHMWPE; (b) UHMWPE/PP (80:20).

debris maybe effect by the same general principle as occurs when a small amount of sand is present between a metal object and a stone floor, if a limited quantity of sand is present, the friction coefficient is smaller than that perfectly devoid of sand. This model is a further application of the principle that in dry sliding there should be a "third body" [11] presented between the sliding surfaces to minimize friction and wear. And loosely attached powdery debris will be more effective in reducing friction and wear and yet be easily lost after testing. This model may be depicted as in Fig. 10.

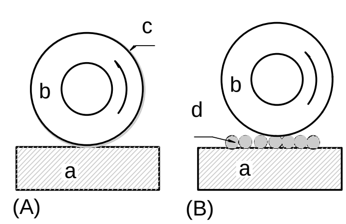

Fig. 10. Models for the sliding wear behavior: (A) sliding with UHMWPE; (B) sliding with UHMWPE/PP blend. (a) Specimen; (b) steel ring; (c) transfer film; (d) debris.

4. Conclusion

1. UHMWPE and UHMWPE/PP blends show very different friction and wear behavior. Appropriate amount of PP added in UHMWPE can improve the anti-wear properties of UHMWPE prominently. Coefficient of friction and wear rate of UHMWPE/PP blend are much lower than those of pure UHMWPE under the same condition.
2. Transfer film on the steel ring surface sliding against UHMWPE is formed and many big spalls are produced after a long period of sliding. While for the case of UHMWPE/PP blend, debris is much looser to the counterface and no transfer film could be formed, only fine powders around the ring surface can be observed.
3. XPS and IR analysis show that oxidization happened to both the worn surface and the debris. DSC analysis of the bulk and the worn surface demonstrates that the surface temperature of UHMWPE is higher than that of UHMWPE/PP blend during sliding.
4. AFM observation of the worn surface after etching the amorphous phase shows that 'shish-kebab' crystal is formed in the worn surface of UHMWPE/PP blend, while no such crystal can be found in the worn surface of UHMWPE, which is consistent with the friction and wear behavior.
5. Under dry conditions, moderate sliding speeds and against a smooth hard counterface, the wear of UHMWPE is dominated by adhesion and fatigue failure. The improving of anti-wear properties of UHMWPE/PP is probably due to the rod shape debris existed between the contacted surfaces, which help to decrease the friction and wear efficiently.

Acknowledgements

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