Tribological properties of kaolin filled UHMWPE composites in unlubricated sliding[☆]

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Abstract

The two kinds of kaolin filled ultra-high molecular weight polyethylene (UHMWPE) based composites (UHMWPE/kaolin) were prepared by means of polymerization filling and melt mixing, respectively. The unlubricated sliding wear behavior of the composites was tested on an MM200 rig. The effects of sliding speed and load on the sliding wear of UHMWPE were determined. Scanning electron microscopy (SEM) was employed to examine the worn surfaces and the wear mechanisms of the composites discussed. It has been found that appropriate kaolin filling can greatly improve the tribological behavior of UHMWPE. It has also been found that the UHMWPE/kaolin composites prepared by polymerization have much better tribological properties than the ones prepared by mixing with the same components and are promising self-lubricated material candidates for engineering application.
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1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) and its composites are widely used as bearing components, gears, guide rails, in food treatment and medical equipment because of their excellent friction and wear characteristics, corrosion resistance and mechanical properties. With the development of their application as self-lubricated materials, the study of their friction and wear properties under unlubricated sliding condition has caused wide interests. Lots of scholars studied the sliding wear properties and mechanisms of UHMWPE and its composites in recent years [1–7]. Marcus and Allen [8] studied the effect of the fillers on the sliding wear of UHMWPE and sliding behavior of UHMWPE. Cooper et al. [9] considered that there are two wear processes of UHMWPE: microscopic wear and macroscopic polymer asperity wear. Wang [10] developed a theoretical wear model based on the effective frictional work concept for UHMWPE in lubricated multi-directional sliding. The wear of UHMWPE and its composites is complex as other

polymers. The influence of tribosystem parameters on wear for polymers is even stronger than for metals.

It is widely known that the tribological behavior of polymers can sometimes be greatly improved by filling them with inorganic particulate compounds. It has been found that CuO, CuF_2, PbS, Ag_2S are effective as fillers on improving the wear resistance of high density polyethylene (HDPE), polytetrafluoroethylene (PTFE), nylon (PA), and polyetheretherketone (PEEK), while BaF_2, CaF_2, ZnF_2, ZnS, etc. are harmful to the wear resistance of some polymers [11,12]. It is now recognized that the tribological behaviors of polymers and their composites are closely related to their transfer film characteristics, but the mechanisms of filler action are not well understood, and the interactions among the polymer matrices, the fillers, and the counterface active elements have not been adequately studied. Some researchers have suggested that the wear resistance of filled polymers is related to the load-carrying action of fillers and the modification of counterface [1]. However, this supposition has not been found convincing because there does not exist a direct correlation between the filler hardness and its ability to resist wear.

Usually the better frictional performance of the smooth molecular profile polymers can be explained by the ease with which the long chain molecules shear across each other. It is clear that there are close relations among filler or filling method, structure and tribological behavior, but little

attention has been paid to the effect of aggregate structure on the tribological behavior of UHMWPE and its composites [13]. In this paper, the kaolin filled UHMWPE based composites (coded as UHMWPE/kaolin) with different kaolin content were prepared by means of polymerization filling and melt mixing, respectively. The relationship among the mass loss, applied load, sliding speed, filling method and kaolin content of the composites was tested and analyzed. The wear mechanism of UHMWPE/kaolin was explored by using scanning electron microscopy (SEM) to examine the worn surfaces of UHMWPE/kaolin samples. The effect of kaolin particles filled by the two different ways on the structure and further on the friction and wear was studied and compared. The results are useful to guide the application of UHMWPE/kaolin to self-lubricated and wear-resistant component design.

2. Experimental details

2.1. Test materials

Kaolin ($(OH)_8Si_4Al_4O_{10}$, the particle size is 10 μm) was supplied by the State Key Laboratory of Engineering Plastics, the Institute of Chemistry, Chinese Academy of Sciences. $TiCl_4$ (Analytical Reagent Grade) was from Xindai Chemical Plant, PRC. $AlEt_3$ from Germany was diluted to a certain density (129.6 g/l) by *n*-heptane for late use. Ethene (supplied by Beijing Chemical Company, PRC) was polymeric grade. *n*-Heptane (Chemical Reagent Grade, from Beijing Chemical Company) was dried over 4A molecular sieves several times and conserved in an inert gas before use. Hexane (Chemical Reagent Grade, from Xiangyang Yingkou Chemical Company) was dried over 4A molecular sieves several times and conserved in an inert gas before use. Ethanol without water (supplied by Beijing Chemical Company, PRC) was a chemical reagent grade product.

The 30 g pre-treated kaolin and 100 ml heptane were put into a 500 ml reactor with an instillation funnel and a mechanical stirrer, in which the air had been fully displaced with high pure nitrogen before. They were thoroughly stirred for 10 min, and then heated to 60 °C. The 10 ml $TiCl_4$ was slowly instilled into the reactor through the funnel while stirring. After reacted for 3 h at the constant temperature, the solid matter was taken out and separated from the liquid with a filter. The solid matter was washed 10 times with dried hexane and then dried in vacuum. The remaining solid powder was active kaolin carried with $TiCl_4$. The product was kept in nitrogen for future use.

2.2. Sample preparation

A 2 l high pressure reactor was evacuated and then filled with nitrogen and evacuated again, and that was repeated for several times till the air was replaced by nitrogen completely. The 100 ml dried heptane, a designed amount of the active kaolin and $TiCl_4$ were put into the pressure reactor, and then connected with the ethene pipe. The polymerization of ethene was then carried out at the constant pressure (0.2 MPa). After a certain time the polymerization reactor was terminated using ethanol. Then UHMWPE/kaolin powder was gotten after filtered, washed and dried in vacuum. The initial UHMWPE/kaolin powder was pressed to a plate 5 mm thick in a model at the pressure of 19 MPa and the temperature of 200 °C. The sample (so-called as polymerized UHMWPE/kaolin) was cut from the UHMWPE/kaolin plate.

The pure UHMWPE powder with the same molecular weight as in UHMPE/kaolin was produced with the same method but different catalyzer, in which $TiCl_4$–$AlEt_3$ colloid was used as a catalyzer. The UHMWPE powder and the active kaolin were thoroughly mixed with mechanical equipment, and the mixed powder was pressed into a plate and the plate was cut into the samples (so-called as mixed UHMWPE/kaolin) in just the same conditions as described.

The size of rectangular block sample was 12 mm × 10 mm × 4 mm. Before the wear testing, the surfaces of samples were ground with silicon carbide paper (the minimum of grit size: 6 μm), and then polished with cool polishing powder solution. The alumina slurry (the minimum of particle size: 0.25 μm) was used for the UHMWPE/kaolin sample polishing. The UHMWPE/kaolin samples were then ultrasonically cleaned in alcohol and acetone until the surfaces were spotless.

A steel (ASTM 1045) ring was used as a friction counterpart. The outer and inner radius of the circular test ring is 40 and 20 mm, respectively, and its width is 10 mm. The steel sample was treated by quenching and tempering. Its hardness is about HRC50. A finished surface of R_a 0.63–0.82 μm (measured by a surface profilometer) was achieved for the steel specimen by hand polishing.

2.3. The apparatus and the test

The unlubricated sliding wear of the samples was carried out on an MM200 tester. The tester is composed of transfer motion device, frictional torque measuring device, and loading device in which a lever system (the ratio of the lever is 1:3) was adopted for the sake of relatively stable loading force (as shown in Fig. 1). The sliding pair consisted of a tested sample (UHMWPE/kaolin) block and an ASTM 1045 steel ring. The lower sample was UHMWPE/kaolin, and it was fixed on the sample holder. The upper sample was the ASTM 1045 steel ring. The contact pressure of the two samples was applied by the dead weight. The frictional torque was measured by the swing-lever weight regulating system.

The normal load was 105–465 N. The sliding was achieved by the rotation of the ASTM 1045 steel ring, and the sliding speed was 0.42 and 0.84 m/s corresponding with the axes rotation speed of 200 and 400 rpm, respectively. All the tests were carried out at an ambient temperature of 20–25 °C. An analytical electronic balance (AEL-200) was used to measure the mass loss of the polymer samples, and
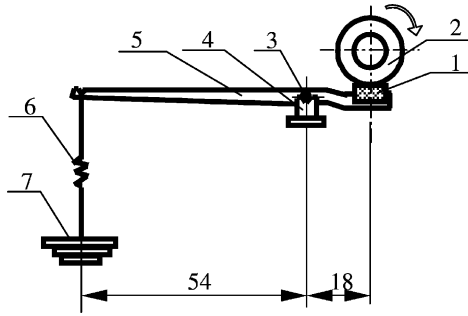
Fig. 1. A schematic diagram of the loading system of MM200 model tester: (1) sample, (2) steel ring, (3) support axes, (4) abutment, (5) lever, (6) spring, (7) weight.

its sensitivity is 10^{-5} g. The mass loss was then transformed into volume loss and the volume loss per sliding distance was taken as an index of wear property (as follows):

$$\omega = \frac{\Delta W}{\rho 2\pi RN} \tag{1}$$

In the above equation, ω represents the wear rate (mm^3/m), ΔW the mass loss (g), ρ the density of the sample (g/mm^3), R the radius of the counterpart (steel ring) (m), and N the number of rotations.

In order to measure the friction coefficient of the pair on the MM200 model tester, the frictional torque was measured. The friction coefficient was calculated according to the following formula:

$$\mu = \frac{T}{RP} \quad \text{or} \quad \mu = \frac{T_H h}{RPH} \tag{2}$$

In the above equation, μ represents the friction coefficient, T the frictional torque (N m), P the normal load (three times the weight) (N), T_H, H and h are parameters of the frictional torque measuring device, T_H the frictional torque when the staff gauge reaches the maximum, which is determined by the weight of the swing-lever weight regulating system, H the efficacious length (80 mm) of the staff gauge and h the actual deviated length from start point on the gauge.

It was observed that there are three wear periods as in [1]: running-in period (about 120 m at 375 N and 0.42 m/s), steady-state period and severe wear period (about 2200 m at 375 N and 0.42 m/s), respectively. In the running-in period, a series of ridges are formed on the UHMWPE/kaolin surface. In the steady-state period, the ridges formed on the UHMWPE/kaolin surface disappear and the wear is relatively steady. In the severe wear period, the heat accumulated in the wear process causes the thermal softening of UHMWPE, and repeated sliding causes massive tearing and rupture of the surface layer. All the data of the wear rate in this paper were obtained after a sample was worn over the distance of 503 m, which is within the steady-state periods. And before the test the sample was pre-worn over the distance of 250 m, which is a little more than the distance of the running-in period. The average friction coefficient in the

last 300 m of the sliding distance 503 m, during which the friction and wear is relatively stable, was taken as the test data.

The sample was treated and tested as follows: cut → pre-worn → cleaned → dried → weighed → worn → cleaned → dried → weighed. The experimental data was taken as the mean value of more than three tests in the same conditions. Statistics showed that the error was less than 8%.

The worn surface morphology was observed by means of SEM. The sample surfaces were sputtered with Au coating to render them electrically conducting, prior to the examination in the scanning electron microscope.

3. Results and discussion

3.1. The friction coefficient

When sliding against ASTM 1045 steel surface, the friction coefficient of UHMWPE/kaolin is a little higher in the beginning of the wear test (first 5 min or 120 m) than afterwards. This is mainly because UHMWPE/kaolin contacts with the steel surface and a series of ridges are formed on the UHMWPE/kaolin surface in the running-in period, while in the steady-state period, the ridges on the UHMWPE/kaolin surface disappear, wear debris cover the surface and the transfer film on the counterpart is formed, and the coefficient of friction is lower as described in [1].

The change of sliding velocity exerts limited influence on the friction coefficient, while the load exerts obvious influence on the friction coefficient as shown in Fig. 2. It can be seen from Fig. 2 that the friction coefficient becomes lower with the load increasing. Basically the load and the friction coefficient are related by following equation:

$$\mu = Kp^{n-1}$$

Here K and n are constants related to the materials, and $2/3 < n < 1$ for the materials tested in this paper.

The filling method and the kaolin content are the other two obvious influential factors. The relations (Fig. 3) were
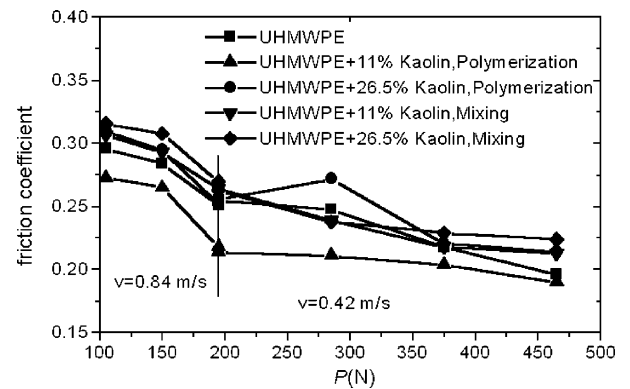

Fig. 2. Friction coefficient–load curves of several UHMWPE/kaolin composite samples with different contents of kaolin.
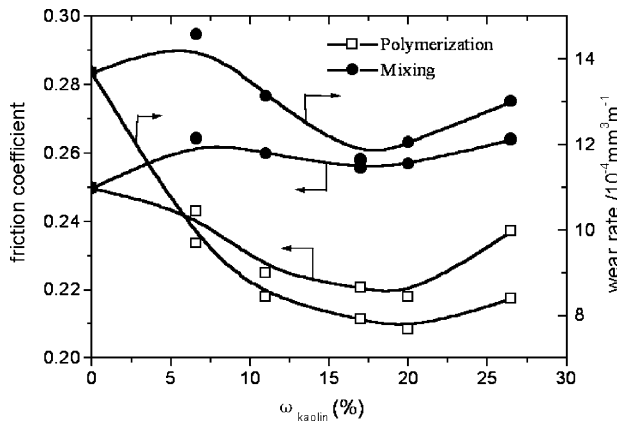
Fig. 3. Variation in wear rate and friction coefficient of UHMWPE/kaolin composites with mass fraction of kaolin.

Fig. 4. Variations of wear rate with load for different UHMWPE/kaolin composite samples.

obtained through regressive analyses to the experimental data, which were gotten according to orthogonal theory under the load from 195 to 465 N. It can been seen from Fig. 3 that the friction coefficient is lower for the polymerization UHMWPE/kaolin than for the mixing UHMWPE/kaolin with the same components. When the content of kaolin is relatively low, the friction coefficient is decreasing as the kaolin content is increasing, while that is opposite when the kaolin content is high. A minimum point of friction coefficient is formed at the kaolin content of about 20% in Fig. 3 and the minimum friction coefficient is 87% that of pure UHMWPE for the polymerization UHMWPE/kaolin. It is not as obvious for mixing UHMWPE/kaolin as for polymerization UHMWPE/kaolin that the friction coefficient changes with the variation of kaolin content.

3.2. Wear properties

The relations between wear rate and the filling method and the kaolin content can be seen from the experimental data shown in Fig. 3. Obviously, the filling method and the kaolin content affect the wear rate. It can been seen from Fig. 3 that the wear rate is much lower for the polymerization UHMWPE/kaolin than for the mixing UHMWPE/kaolin with the same components. Choosing the appropriate content of kaolin can obviously reduce the wear rate of UHMWPE. This strengthening effect of kaolin filled by polymerization is much greater than that by mixing. When the kaolin content is about 20%, the wear rate of the polymerization UHMWPE/kaolin is the lowest, which is only 56% of that of the pure UHMWPE with the same molecular weight. Relatively the influence of kaolin content on the wear rate is not so obvious for the mixing UHMWPE/kaolin, and the lowest wear rate is 85% of UHMWPE at the point of 17% of the kaolin content, while the wear rate is a little higher than the UHMWPE when the kaolin content is about 6.6%.

Fig. 4 shows the curves of the wear rate versus the load at different sliding velocities and for different samples. It
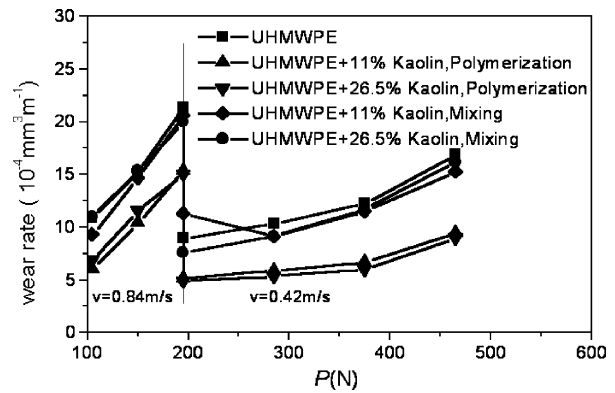
can be seen from Fig. 4 that all the curves have similar shape, and that the wear rate becomes higher with the increase of load or sliding velocity. When the load increases 138% (from 195 to 465 N), and the sliding velocity remains unchanged (0.42 m/s), the wear rate, for polymerization UHMWPE/kaolin as an example, increases 114% (from 4.532×10^{-4} to 9.72×10^{-4} mm^3/m). When the sliding velocity doubles (from 0.42 to 0.84 m/s), and the load remains unchanged (195 N), the wear rate increases by 248% dramatically. From this, it can be seen that the sliding velocity shows greater influence on the wear loss than load.

3.3. Friction and wear mechanisms

Differences in friction and wear properties between polymerization and mixing UHMWPE/kaolin are evidently correspond to the internal structure of these two composites. Their crystal structures of the matrix UHMWPE are different because of the different filling method. The crystal structure of matrix in mixing UHMWPE/kaolin is similar to that in the pure UHMWPE, which is mainly spherical, while in the polymerization UHMWPE/kaolin the crystal structure of matrix is like crossing layers, which is helpful to form a very thin transfer film on the counterpart and a strengthening layer on the wear surface of the composite [14]. This can be proved by a serial of SALS (small angle laser scatter) photos as shown in Fig. 5, in which the pure UHMWPE and the mixing UHMWPE/kaolin have similar four leaved rose shapes (a) and (c), which mean that the matrix of UHMWPE has the spherical crystal structure, while the polymerization UHMWPE/kaolin has circular shape (b).

It can also been seen that the polymerization UHMWPE/kaolin has the smaller crystal grain and stronger interface than the mixing UHMWPE/kaolin as shown in Figs. 6 and 7. Fig. 6 is the frozen fracture surfaces of the composites. The light-colored circular part is the UHMWPE matrix and the dark part is the vestige after kaolin particle is pulled off. When comparing the photos (a)–(b), it is found that kaolin particle is smaller and more regular in the polymerization
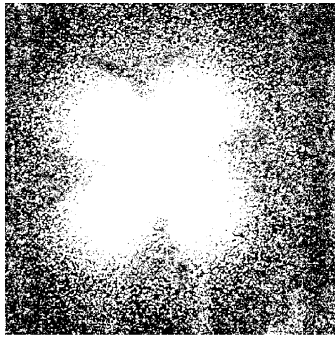
(a)Pure UHMWPE
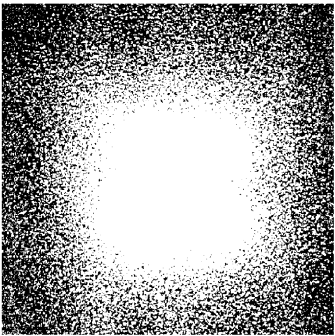
(b) UHMWPE+6%Kaolin, Polymerization
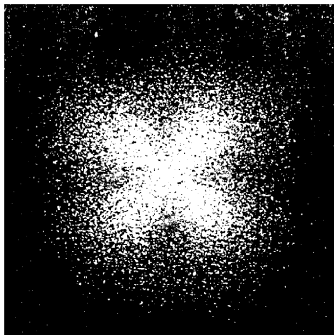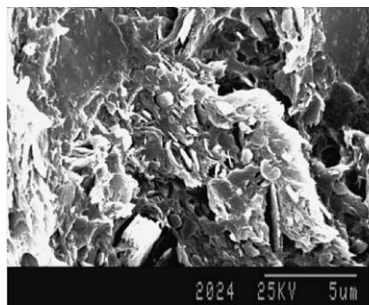

(c) UHMWPE+6%Kaolin, Mixing

Fig. 5. SALS photos of the UHMWPE/kaolin composites.

UHMWPE/kaolin. Fig. 7 shows the stretched fracture surfaces of the composites. The smooth surfaces are the sheared sliding plane, and the light-colored edges are the shear lips. The planes in the photo (b) are smaller than those in photo (a), and the lips in photo (b) are clearer and longer than those in photo (a). It is clear that all these structural differences are the main reasons why the polymerization UHMWPE/kaolin has much better friction and wear behaviors than the mixing one with the same components.

The curves of the friction coefficient or the wear rate versus the kaolin content have the concave shape as in Fig. 3. When the kaolin content exceeds about 17–20%, the friction coefficient or the wear rate becomes higher with the increase of the kaolin content, no longer a simple decrease is expected. This means that the influences of filled kaolin on friction and wear properties of the composites have two sides. Besides the favorable effect related above, the filled kaolin acts as crystallizing kernel, which makes the molecular chain movement difficult and the cross-linking degree increase, so with the increase of the kaolin content the friction coefficient of the composites increases. When the kaolin content exceeds a certain quantity the faults in the composites obviously increase because of the aggregation effect of the kaolin grains, the wear rate becomes higher with the increase of the kaolin content.

The morphology of the worn composite surfaces is smoother than the counterpart surfaces and remains similar under different loadings as in Fig. 8. The relatively less furrowed and scratched surface means that the friction pair do not contact each other directly but instead through a film formed during rubbing on the steel ring surface. The experimental results show that adherent thin film of the composite is formed on the metal surface and the film of the polymerization UHMWPE/kaolin is a little more even and thin than the mixing one. That is one reason why the polymerization UHMWPE/kaolin has the better tribological properties than the mixing one.

At the beginning the surface of UHMWPE/kaolin is cut by the asperities of the steel ring counterpart, micro-furrows are generated on the surface of the composite, and the transfer

(a) UHMWPE+24%Kaolin, Mixing
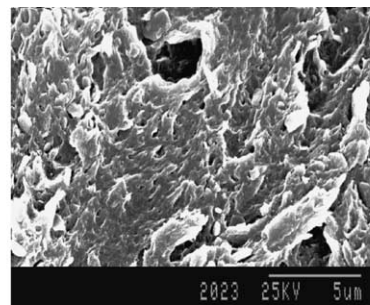
(b) UHMWPE+24%Kaolin, Polymerization

Fig. 6. SEM photos of the frozen fracture surfaces of the UHMWPE/kaolin composites.
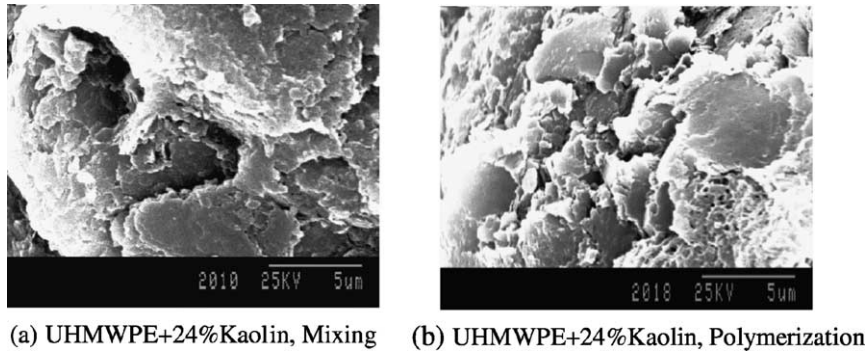
(a) UHMWPE+24%Kaolin, Mixing   (b) UHMWPE+24%Kaolin, Polymerization

Fig. 7. SEM photos of the stretched fracture surfaces of the UHMWPE/kaolin composites.

film is formed on the surface of the counterpart in the meantime. The strength and geometrical property of the film undoubtedly depends on static electric attraction and mechanical embodiment. The chemically bonded points between transfer film and counterface increase gradually as rubbing goes on. Then, the adhesive strength of transfer film to counterface and transfer film area both increase. Elastic and plastic deformations on the surface of UHMWPE/kaolin becomes the main cause of the wear under the effects of the friction force of the pair. The repeated deformation causes cracking on the surface or subsurface of the composite. The cracks extend gradually and tips or cuttings are formed on the surface with continuous rubbing.

Because of the difference of the load and the composites the wear surfaces have different morphology characters as shown in Fig. 8. There are lot of pits, which are mainly caused by adhesive wear or massive tearing, and ridges, which are vestiges remained from plastic material flow of

(a) UHMWPE+6.6%Kaolin
     Polymerization
     Velocity: 0.42 m/s
     Load: 195 N

(b) UHMWPE+6.6%Kaolin
     Mixing
     Velocity: 0.42 m/s
     Load: 195 N

(c) UHMWPE+17%Kaolin
     Polymerization
     Velocity: 0.42 m/s
     Load: 465 N

(d) UHMWPE+17%Kaolin
     Mixing
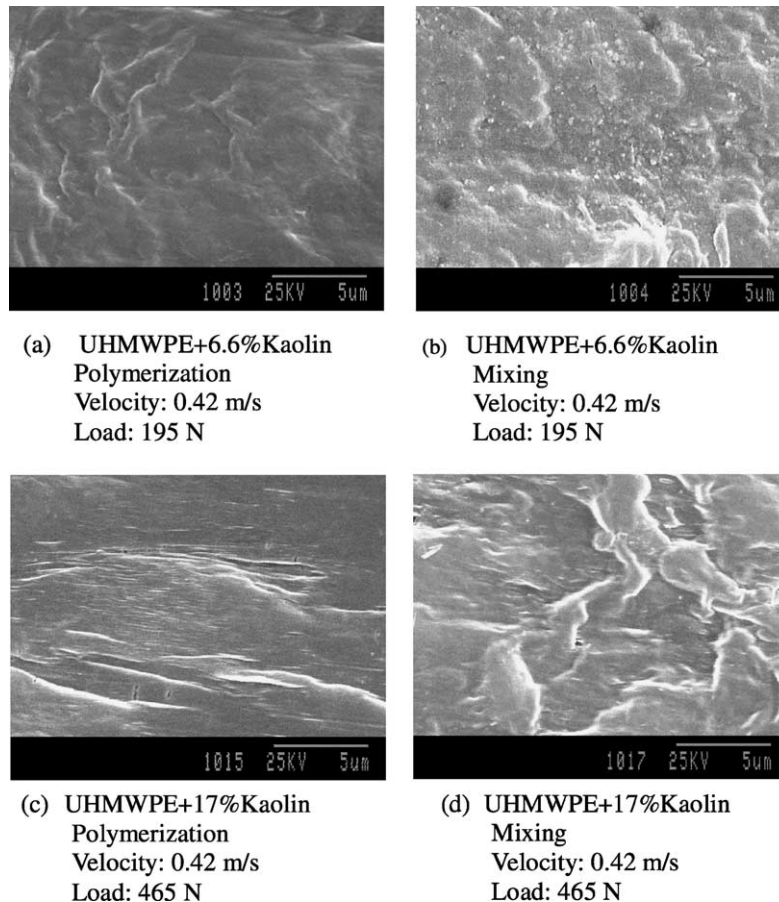   Velocity: 0.42 m/s
     Load: 465 N

Fig. 8. SEM photos of the wear surfaces of UHMWPE/kaolin composites.

the composite in Fig. 8. From Fig. 8 we can see that the pits or ridges are much more obvious and larger on the wear surface of mixing UHMWPE/kaolin than that of the polymerization one. The surface morphology is mainly lifted flakes with white fatigued fracture fringes on the wear surface of polymerization UHMWPE/kaolin, while that is mainly torn pits on wear surface of the mixing one. In a word, fatigue wear, adhesive wear, and massive tearing are the main wear mechanisms of the UHMWPE/kaolin composites when sliding against steel. And fatigue is dominant for the polymerization UHMWPE/kaolin, while adhesive wear and massive tearing cannot be ignored as the main causes for the mixing UHMWPE/kaolin on the same conditions.

4. Conclusions

(1) Kaolin filled at a certain content (about 17–20 wt.%) is very effective to reduce the friction and wear of UHMWPE in sliding against steel. UHMWPE/kaolin composites prepared by polymerization filling are superior to the ones prepared by melt mixing with the same filler content in terms of friction–reduction and reducing wear.
(2) The differences in the transfer film and the crystal structure of UHMWPE matrix account for the different friction and wear properties of the two kinds of UHMWPE/kaolin composites.
(3) Sliding velocity exerts greater influence on the wear of UHMWPE/kaolin composites than the applied load in the sliding against steel.

Acknowledgements

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