The Friction and Wear Properties of Nanometer ZrO_2-Filled Polyetheretherketone

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ABSTRACT: Nanometer ZrO_2 filled polyetheretherketone (PEEK) composite blocks with different filler proportions were prepared by compression molding. Their friction and wear properties were investigated on a block-on-ring machine by running a plain carbon steel (AISI 1045 steel) ring against the composite block. The morphologies of the wear traces were observed by scanning electron microscopy (SEM). Results indicated that nanometer ZrO_2-filled PEEK exhibited lower friction coefficient and wear rate in comparison with pure PEEK. The lowest wear rate was obtained with the composite containing 7.5 wt % ZrO_2. The SEM pictures of the wear traces indicated that the plucked and ploughed marks appeared on the wear scar of pure PEEK, while the scuffing on the wear scar of 7.5 wt % nanometer ZrO_2-filled PEEK was obviously abated. Thus, it was inferred that the improvement in the tribological behavior of nanometer ZrO_2-filled PEEK composite was closely related to the improved characteristics of the worn surfaces. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 135–141, 1998

Key words: nanometer ZrO_2; filled polyetheretherketone (PEEK); friction and wear properties; morphologies of worn surfaces; transfer

INTRODUCTION

With its outstanding thermal stability and good resistance to solvent attack and wear, polyetheretherketone (PEEK), a semicrystalline thermoplastic, is becoming a potential candidate for dry friction units under severe conditions, such as bearing components. So far, quite a lot of work about the tribological characteristics of PEEK and its composite has been focused on by many researchers.[1–4] The friction and wear properties of PEEK and its composites filled with fibers, inorganic, and organic compounds were especially emphasized. Friedrich et al.[5] reported that the short glass fibers slightly improved the wear resistance of PEEK, and carbon fibers were superior to glass fibers in enhancing the wear resistance. Briscoe et al.[6] said that by adding polytetrafluoroethylene (PTFE) the friction of PEEK was considerably reduced, with a sacrifice of small loss in wear resistance. Bahadur et al.[7] investigated the action of various copper compounds as fillers on the tribological behavior of PEEK and revealed that CuS and CuF_2 as fillers were very effective in reducing the wear of PEEK when sliding occurred against steel surfaces.

The purpose of the present work is to investigate the friction and wear properties of nanometer ZrO_2-filled PEEK composites with different filler proportions. As a comparison, the friction and wear properties of unfilled PEEK were also evaluated under the identical test conditions. It was believed that this work would be helpful for understanding the function of nanometer ZrO_2 as a

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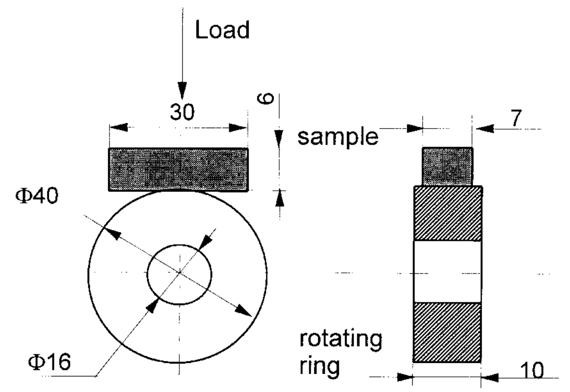

Figure 1 The contact schematic diagram for the frictional couple.

filler in PEEK and for providing guidance to the tribological application of PEEK.

EXPERIMENTAL DETAILS

PEEK fine powders with a diameter of 100 μm were produced by Jilin University of China. The nanometer ZrO_2 (at a size of 10 nm) produced by Shenyang Institute of Metal Research of Chinese Academy of Sciences was used as the filler. The PEEK powder was fully mixed with the nanometer ZrO_2 by ultrasonically dispersing them in alcohol for about 15 min. Then the mixture was dried at 110°C for 6 h to remove the alcohol and moisture. The dried mixture was then heated at a rate of 10°C min^{-1} to a maximum temperature of 340°C. The pressure was held at 5 MPa until the temperature of the mixture increased to 320°C. For the rest of the heating cycle the pressure was raised to 15 MPa. The mixture was held at 340°C for 8 min and was then cooled to 100°C in a mold.

The friction and wear tests were conducted on an M-200 model friction and wear tester. The contact schematic diagram of the frictional couple is shown in Figure 1. During the tests, the friction force between the test block and the steel ring was measured with a torque shaft, provided with strain gauges. Sliding was performed under ambient conditions over a period of 1.5 h at a sliding speed of 0.445 m s^{-1}. The ambient temperature was around 20°C, and the relative humidity was 50 ± 5%. Before each test, the plain carbon steel ring (hardness of HRC 48–50) and the PEEK or its composite block were abraded with No. 900 water-abrasive paper. Then the steel ring was cleaned with cotton dipped in acetone, and the PEEK or its composite blocks were cleaned with acetone followed by drying. At the end of each test, the blocks were cleaned with acetone followed by drying, then provided for wear weight loss measurement. The density of the filled PEEK samples was measured by Archimedes' principle using absolute alcohol as the immersing medium. The weight loss of the filled PEEK specimens was determined on a balance with a sensitivity of 0.05 mg, and was then converted into volume loss by using the filled PEEK density. The wear rate ϖ was calculated from the relationship

$$\varpi = V/(X \cdot L) \quad [\mathrm{mm}^3/(\mathrm{N \cdot m})]$$

where V is the volume loss in cubic millimeters, X is the sliding distance in meters, and L is the applied load in Newtons. Three replicate friction and wear tests were carried out so as to minimize data scattering, and the average of the three replicate test results are reported in this work. The deviation of the data of the replicate friction and wear test was 15%. The morphologies of the wear traces were observed using a JEM-1200EX model scanning electron microscope.

RESULTS

Friction and Wear Properties

Figure 2 shows the friction coefficient and wear rate of nanometer ZrO_2-filled PEEK as a function

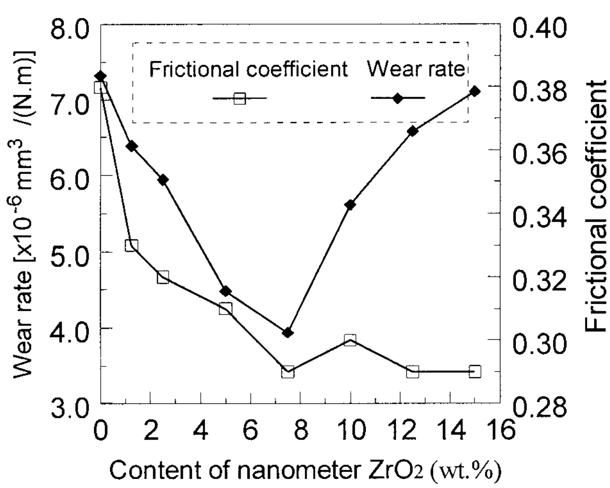

Figure 2 Effect of the content of nanometer ZrO_2 on the friction coefficient and wear rate of the filled PEEK composite (load: 196 N; sliding velocity: 0.445 m s^{-1}).

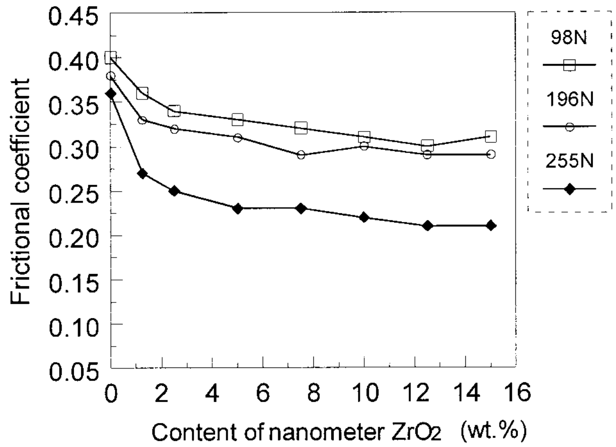

Figure 3 The friction coefficient under various loads as a function of ZrO_2 content in the filled PEEK (sliding velocity: 0.445 m s^{-1}).

of ZrO_2 content. It can be seen that the friction coefficient decreased gradually with the increasing ZrO_2 content when nanometer ZrO_2 content was below 7.5 wt %. Then it reached the lowest value in this work, as the ZrO_2 content was above 7.5 wt %. In the meantime, nanometer ZrO_2-filled PEEK composite exhibited a considerably decreased wear rate than the unfilled PEEK. Here, the relatively higher wear rate of the unfilled PEEK can primarily be understood by considering that the wear debris of pure PEEK was obviously larger in size than that of filled PEEK, as can be seen by the naked eye. Furthermore, it is interesting to notice that the wear rate of the composite was complicatedly affected by the filling of nanometer ZrO_2. In other words, the wear rate decreased sharply as the ZrO_2 content was below 7.5 wt %. Then it came to the lowest value at a ZrO_2 content of 7.5 wt %. When the filler content was above 7.5 wt %, the wear rate almost linearly increased with an increasing ZrO_2 content, although it was still lower than that of the unfilled PEEK. In combination of the friction coefficient and wear rate, it might be rational to suggest that the optimal content of ZrO_2 in the composite should be recommended as 7.5 wt %.

Figures 3 and 4 show the effect of load on the friction coefficient and wear rate of PEEK composites filled with various contents of nanometer ZrO_2. It was found that the friction coefficient of the composites under various loads decreased gradually with an increase of the nanometer ZrO_2 content. Also, the friction coefficient decreased with an increasing load. In particular, the lowest friction coefficient in this work was obtained under a load of 255 *N*. This indicates that nanometer ZrO_2 was more effective for improving the friction-reducing ability of the composite at higher load. On the other hand, the wear rate of the composites under various loads decreased considerably as the content of ZrO_2 was below 7.5 wt %, then it came to the lowest value at a ZrO_2 content of 7.5 wt %. Above a ZrO_2 content of 7.5 wt %, the wear rate turned to increase with an increasing load, but it was still lower than that of the unfilled PEEK. The lowest wear rate in this work was obtained under a load of 98 *N* and the highest wear rate was obtained under a load of 196 *N*. Thus, it can be concluded that nanometer ZrO_2 as a filler in PEEK could not change the friction coefficient and wear rate of the filled composite simultaneously. That is, a low friction coefficient did not necessarily correspond to a decreased wear rate.

Scanning Electron Microscopy (SEM) Observation

To understand the effect of nanometer ZrO_2 on the friction and wear behavior of the filled PEEK, the wear traces and wear debris were studied by SEM. Figure 5 shows the scanning electron micrographs of the worn surfaces of pure PEEK and its composite blocks with various contents of nanometer ZrO_2. It can be seen that the plucked and ploughed marks appeared on the wear scar of the pure PEEK block, while the scuffing in the wear traces on the nanometer ZrO_2-filled PEEK block was obviously abated. Especially for 7.5 wt %

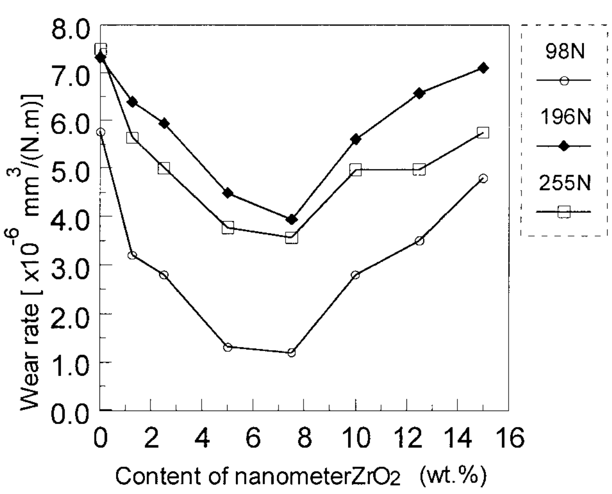

Figure 4 The wear rate under various loads as a function of the ZrO_2 content in the filled PEEK (sliding velocity: 0.445 m s^{-1}).

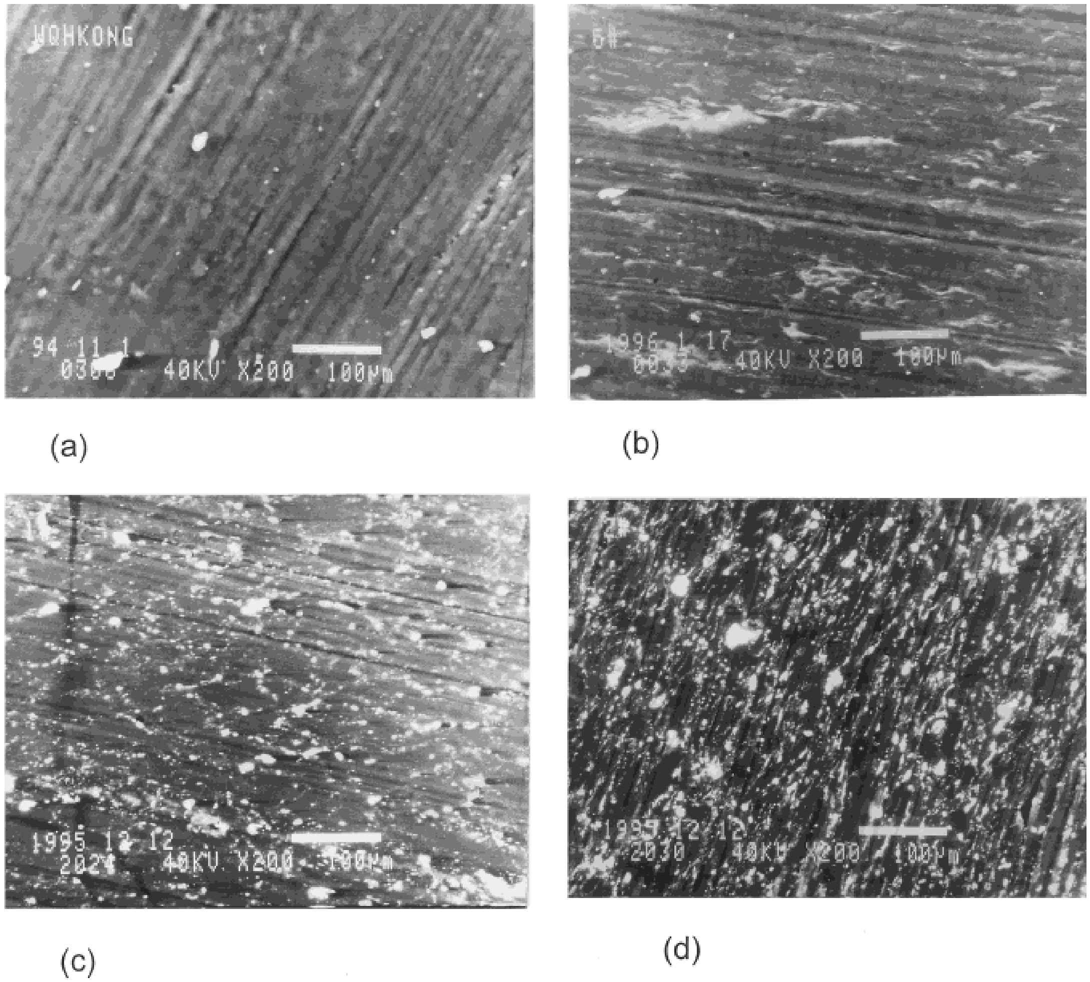

Figure 5 SEM micrographs of the worn surfaces of the pure PEEK and the filled PEEK composites with various contents of nanometer ZrO_2 (load: 196 N; sliding velocity: 0.445 m s^{-1}; test duration: 90 min). (a) Pure PEEK; (b) 1.25 wt % ZrO_2/PEEK; (c) 7.5 wt % ZrO_2/PEEK; (d) 12.5 wt % ZrO_2/PEEK.

ZrO_2-filled PEEK, the worn surface was smoother and only abated scuffing marks could be observed. This is in good agreement with the comments mentioned above. That is, the optimal content of ZrO_2 for the best wear resistance should be recommended as 7.5 wt %. Thus, it can also be inferred that the morphologies of the wear traces are relevant to the wear rates of nanometer ZrO_2-filled PEEK.

The wear trace formed on the steel ring surfaces by running the plain carbon steel ring against the pure PEEK and its composite blocks with different contents of nanometer ZrO_2 are shown in Figure 6. It can be seen that a thick, lumpy, and incoherent transfer film was formed on the counterpart steel ring surface by running the steel ring against the pure PEEK block, while a thin, uniform, and coherent transfer film was formed by running the steel ring against the 7.5 wt % nanometer ZrO_2-filled PEEK composite block. Figure 6(d) indicated that more severely plucked and ploughed marks appeared on the counterpart steel ring surface of 12.5 wt % nanometer ZrO_2-filled PEEK. This indicated that for the 12.5 wt % nanometer ZrO_2-filled PEEK, the counterpart steel ring was worn and ploughed more severely. It is necessary to emphasize again that there exist obvious differences among the morphologies of the wear traces on the pure PEEK and filled PEEK blocks (see Fig. 5). The obvious scuffing on the pure PEEK block indicated the severe ploughing of the polymer surface by the

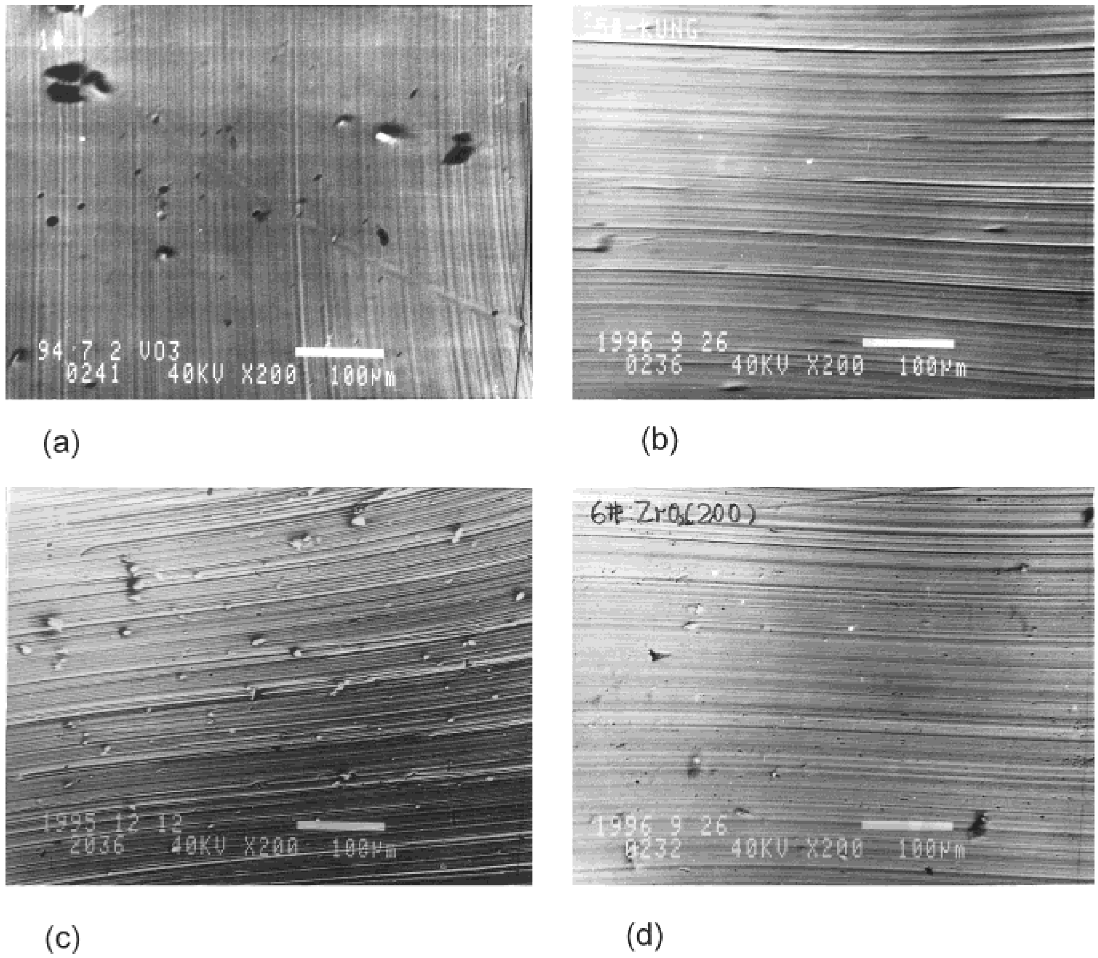

Figure 6 SEM micrographs of the wear traces formed on the steel ring surfaces by running the steel ring against the pure PEEK block and the filled PEEK blocks with various contents of nanometer ZrO_2 (load: 196 N; sliding velocity: 0.445 m s^{-1}; test duration: 90 min). (a) Pure PEEK; (b) 1.25 wt % ZrO_2/PEEK; (c) 7.5 wt % ZrO_2/PEEK; (d) 12.5 wt % ZrO_2/PEEK.

counterpart ring surface during the friction process. In other words, the transfer film concerned was of poor quality. In contrast, only slight scuffing was observed on the surface of the 7.5 wt % nanometer ZrO_2-filled composite block. This also indicated that a uniform and tenacious transfer film was formed on the counterpart ring surface with the frictional couple of steel ring/7.5 wt % ZrO_2-filled PEEK block, being in agreement with what was seen in Figure 5. It was just the transfer film that was responsible for the improved tribological properties of the nanometer ZrO_2-filled PEEK composite.

Figure 7 gives the SEM micrographs of wear debris produced in wear tests of pure PEEK and its composite blocks with various contents of nanometer ZrO_2. It was found that the wear debris of the pure PEEK was multilayer flake, and that the wear debris of the composites were much smaller than that of pure PEEK. The size of the wear debris of nanometer ZrO_2-filled PEEK especially decreased sharply with an increasing of ZrO_2 content.

DISCUSSION

The incorporation of appropriate nanometer ZrO_2 into PEEK caused a considerable improvement in the tribological characteristics. The PEEK filled with 7.5 wt % nanometer ZrO_2 exhibited lower friction coefficient and minimized wear rate. For

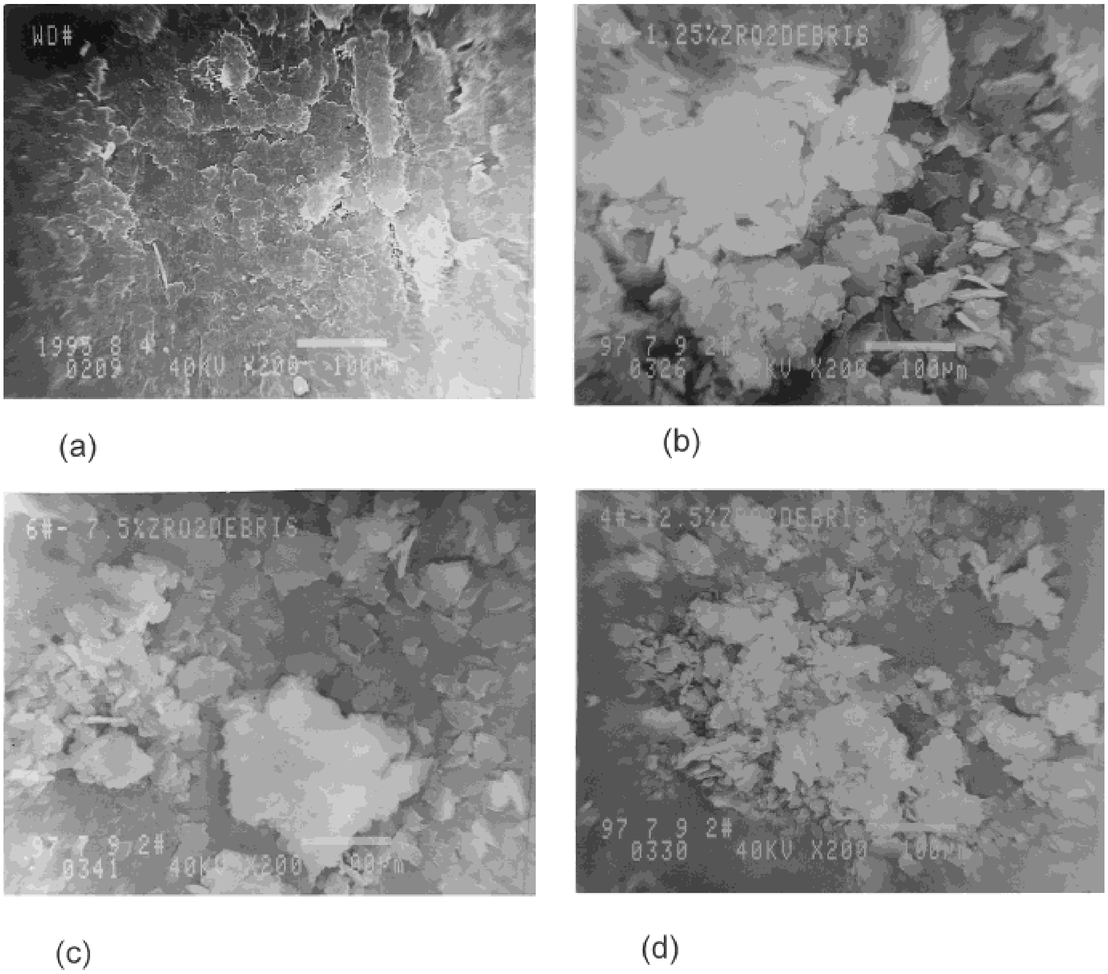

Figure 7 SEM micrographs of the wear debris of the pure PEEK and the filled composites with various contents of nanometer ZrO_2. (a) Pure PEEK; (b) 1.25 wt % ZrO_2/PEEK; (c) 7.5 wt % ZrO_2/PEEK; (d) 12.5 wt % ZrO_2/PEEK.

the pure PEEK specimen, friction-induced fatigue tearing, local melting in the flash temperature zone, chemical degradation, and poor quality of the transfer film are responsible for the higher wear rate.[8] In contrast, for 7.5 wt % nanometer ZrO_2-filled PEEK, a thin and uniform transfer film was formed on the counterpart ring surface during the friction process. That is, with the formation of the uniform and tenacious transfer film, the subsequent sliding occurred between the surface of the 7.5 wt % nanometer ZrO_2-filled PEEK composite block and the transfer film. Consequently, a lowered wear rate was reached. The corresponding wear mechanism was slight transfer wear. However, for the 12.5 wt % nanometer ZrO_2 filled PEEK, too high content nanometer ZrO_2 became wear abrasive during the friction process and the counterpart steel ring was subsequently abraded severely. The abrasive wear caused by the hard wear debris enhanced the wear rate of the composite block filled with 12.5 wt % nanometer ZrO_2.

CONCLUSIONS

From the above, the following conclusions can be drawn: (1) nanometer ZrO_2 as a filler in PEEK can reduce the friction and wear of PEEK. To reach the best comprehensive tribological properties, the optimal content of nanometer ZrO_2 in the filled PEEK should be recommended as 7.5 wt %. (2) The friction coefficient of the nanometer ZrO_2-filled PEEK composite decreased considerably with an increase in load. The wear rate of the composite changed with the increase of applied load in a complicated way and was related to the content of nanometer ZrO_2 in the filled PEEK. (3) With nanometer ZrO_2-filled PEEK, a thin, uniform, and tenacious transfer film was formed on the counterpart steel surface during the friction process. This transfer film contributed to the decreased friction coefficient and wear rate of the filled PEEK composites. (4) With an increasing of nanometer ZrO_2 content, the dominant wear mechanism changed from melting adhesive transfer wear to slight transfer wear, and finally to abrasive wear.

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