JMEPEG (2009) 18:973–979
DOI: 10.1007/s11665-008-9319-0

Abrasion Mechanism of Stainless Steel/Carbon Fiber-Reinforced Polyether-Ether-Ketone (PEEK) Composites

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(Submitted August 23, 2007; in revised form September 22, 2008)

A new type of composite material, stainless steel fiber and carbon fiber-reinforced polyether-ether-ketone (PEEK), was investigated to study its friction and wear properties and mechanisms. The friction materials containing 11 ingredients were hot-pressed and tested using a pad-on-disc type wear tester under unlubricated sliding friction and wear conditions at a constant sliding speed. The worn surface morphology was observed by Field-emission Scanning Electron Microscope (FE-SEM) and Atomic Force Microscope (AFM). The role of transfer film was studied using X-ray photoelectron spectroscopy (XPS) to investigate the thermal decomposition of the friction material. The fade ratio of the composites was only 4.8%, the recovery ratio 107%, and the total wear ratio was as low as 0.99×10^{-7} cm^3(N m)$^{-1}$, showing the perfect properties of heat stability and recovery, as well as high antiwear ability of the composites. Adherence abrasion and particle abrasion take place at higher temperature. A transfer film is formed, which may improve abrasive resistant performance to get stable friction coefficient and low abrasion value for composite friction materials.

Keywords nonferrous metals, poly-ether-ether-ketone (PEEK), polymer matrix composites, stainless steel fiber, tribology, wear

1. Introduction

The phenolic resin-based composite material possesses advantages such as excellent wear resistance, low environmental pollution, and little damage to counter face. But there are other problems. The friction heating-induced thermal decomposition or liquescence of phenolic resin can cause friction coefficient of this type of material to fade away (Ref 1-3).

The wear of composite materials is a complicated surface damage process, affected by a number of factors, including formulation, microstructure, mechanical properties of the binder and the fillers, loading condition, environmental influence. The role of each ingredient in the friction material has been intensively studied and new ingredients are still being developed to achieve better friction performance (Ref 4-8). Among the ingredients currently available for friction materials, the binder resin and reinforced fibers play a crucial role in determining the friction characteristics.

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When polymer composites serve in tribological environment, a friction layer is formed on the surface of the pad as well as on the disc. The friction and wear performance of multiphase composites is related mostly to the rather thin layer on the interface (Ref 9, 10). The development of a friction material is extremely complicated, not only because the combined effect of the ingredients is unpredictable, but also because the friction and wear performance is influenced by the transfer film (or friction film) formed on the sliding surface between the friction material and its counterpart. It is necessary to understand the structural variation in the worn surfaces for both property prediction and material modification.

The investigation of tribology of sliding surfaces has been active in recent years (Ref 11, 12), but the tribosystem is too complicated and variable to be characterized precisely. There is still much work to do to reveal the relationship between the performance and transfer film. Earlier investigations have involved the mechanism of the formation and deterioration of transfer films (Ref 13, 14). With the aid of X-ray photoelectron spectroscopy (XPS), Wirth et al. (Ref 15) showed that during the abrasive process, a third body was created, which exerts a great impact on the tribological properties of the friction couple. The formation of friction film and its stability are related to the wear debris compaction, which in turn depends on the chemistry of the composites. In addition, the formation and stability of the friction film on the sliding surfaces depend upon the cohesive bond strength between the film and the sliding surfaces.

Nanotribology has been used for the experimental and theoretical investigations of interfacial phenomena on scales ranging from the atomic and molecular to the microscopic in tribological systems (Ref 16). Atomic force microscopy (AFM) technique is increasingly used for tribological studies to evaluate microwear properties of solid surfaces at scales ranging from the atomic and molecular to the microscopic. This technique has been used to study surface roughness, adhesion, friction, scratching/wear, indentation, material transfer, and boundary lubrication for nanoscale surfaces (Ref 17).

To improve the high-temperature performance of a composite friction material and its antifade properties, in this work, a new type of stainless steel/carbon fiber-reinforced polyether-ether-ketone (PEEK)-based friction material was prepared. This was tested on a pad-on-disc type of friction tester to study the friction and wear properties as well as the mechanism of the formation and deterioration of the transfer film.

The main objective of the present work was to investigate the chemical composition, microstructure, and topography of such a friction layer in more detail. Furthermore, studies on how different thermal conditions can affect layer formation and the corresponding tribological properties were also carried out.

2. Experiment Methods

Friction material used in this study were nonasbestos organic type materials containing eleven ingredients comprising PEEK, stainless steel fiber, carbon fiber, solid lubricants, abrasives, cashew nut powder, calcium, and aluminum powder.

The PEEK bonder, produced by Changchun Jida High Performance Materials Co. Ltd., is a new type of semicrystallization aroma group thermoplastic polymer with high performance at high temperature. Its density is 1.32 g/cm^3, granularity 175 um, glass transition temperature 143 °C, melting point 334 °C, and the decomposition temperature 590 °C. The stainless steel fibers, provided by Northwest Institute for Nonferrous Metal Research, with a composition of 0.03% C, 17.03% Cr, 8.34% Ni, had an average diameter of 0.025 mm and an average length of 1-3 mm. The carbon fiber, purchased from Changzhou Wujin Huadong particular kind fiber manufacture Co. Ltd., had an average diameter of 0.009 mm with a tensile strength of 4200 MPa. The conventional particles, such as chromite, barite, graphite, sulfide stibium, were selected as additional fillers to modulate the friction and wear performance.

PEEK, stainless steel fiber, carbon fiber, cashew nut powder, and fillers were chosen as the most important five factors affecting the properties of the material. The uniform design method was used to design the composition of the composite materials. Specimens were manufactured by the conventional procedure for friction linings, comprising mixing, preheating, hot pressing, and heat treatment. The compounding of polymer matrix with different fibers and fillers was achieved by a high-speed mixing machine. The wear specimens were hot-pressed at 320 °C and 25 MPa on a WE-10A hydraulic all-purpose machine. Then, the molded specimens were postcured at 80, 150, and 270 °C for 30 min each and at 310 °C for 12 h. Dry sliding wear tests were carried out on a pad-on-disc machine under different temperatures to evaluate the durability of materials at elevated temperatures. Two specimens ($25 \times 25 \times 6$ mm^3) were run against a polished gray cast iron disc with a contact pressure of 0.98 MPa and a constant sliding speed of 480r/min. The gray cast disc was of pearlite structure, with Brinell hardness of HB180-220 and an initial surface roughness of 0.5 μm. The disc was heated and the temperature controlled by a heating device. The friction interface temperature was monitored by a thermocouple positioned on the edge of the disc with a contact force of 0.1-0.2 N and the temperature variation in the steady stage was less than ±5 °C. During the test, the friction force was recorded by a PC-based data acquisition system at 100, 150, 200, 250, 300, and 350 °C. The friction coefficient was calculated by a ratio between the friction force and the normal load. The specific wear rate was obtained by measuring the reduction in the height of the specimen with a displacement transducer after the test. Each result is an average value of at least three experimental data, and the friction coefficient and temperature of the disc are mean values during the steady stage of the sliding process. Ingredients of the specimens and the physical properties are shown in Table 1.

To understand the friction mechanism and to reveal tribologically induced surface films of the composites, the wear surface morphology after abrasion was observed by Field-emission Scanning Electron Microscope (FE-SEM, S4800-I) and Atomic Force Microscope (AFM, PICO SCAN 2500 TM, MI co.). PPP-CONT AFM tip produced by NANOSENSORS™ Corporation with a radius of curvature less than 7 nm and force Constant 0.2 N/m were used.

X-ray photoelectron spectroscopy (XPS, MICROLAB MK II) was used to evaluate the surface chemistry and analyze the surface structure of the material before and after wear test. An Al-Kα X-ray source was used and a binding energy range of 0 to 1200 eV was selected for the analysis. High-resolution spectra of C 1s were recorded at 0.2 eV steps between 295 and 270 eV. To help identify each characteristic peak, curve fitting was performed assuming a Gaussian peak shape.

3. Results and Discussion

3.1 Properties and Abrasion Mechanism

Figure 1 shows the variation of friction coefficient and temperature with numbers of sliding passes. It can be seen that, in the whole sliding process, the friction coefficient remains stable at 0.4 with little fluctuation for a long period of 5000 passes at different temperatures. The average values of friction coefficient μ and wear rate ω at different temperatures were measured and are shown in Table 2. It is obvious that the friction coefficient changed smoothly from room temperature to 350 °C and could be restored to a value of 0.44 when the temperature dropped to 100 °C, while the wear rate was low when the temperature increased.

The friction coefficient μ decreases temporarily with increasing temperature and should be regained after a decrease in the temperature. This phenomenon is called fade and

Table 1 Composition (wt.%) and properties of specimen

PEEK	Stainless steel fiber	Carbon fiber	Cashew powder	Barite powder	Chromite powder	Graphite + sulfide stibium	Aluminum powder	Kaolin + fluorite	Light calcium	Hardness, HRR	Density, g cm^{-3}
16.07	4.67	12.50	13.16	11.11	5.09	11.47	6.16	10.68	2.0	99.3	2.54

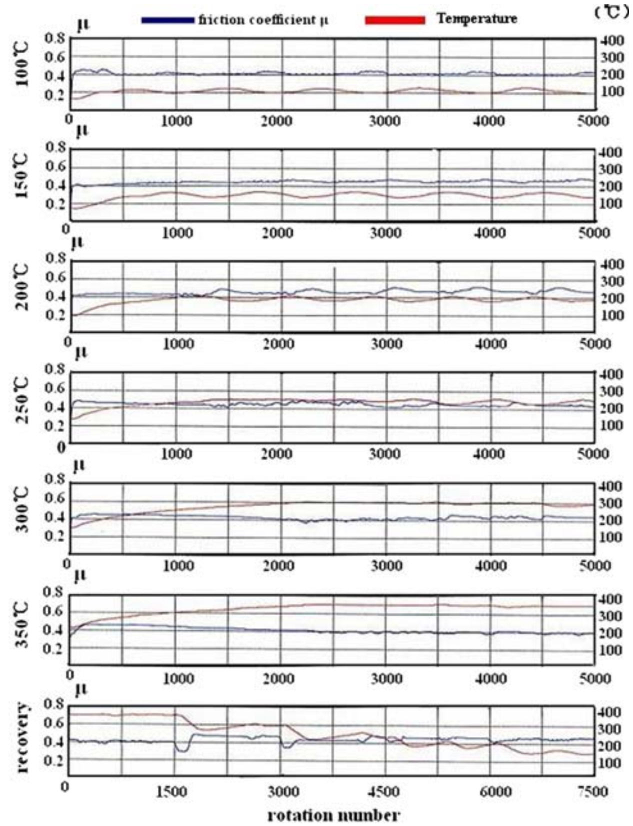

Fig. 1 The variation of friction coefficient as a function of sliding cycles

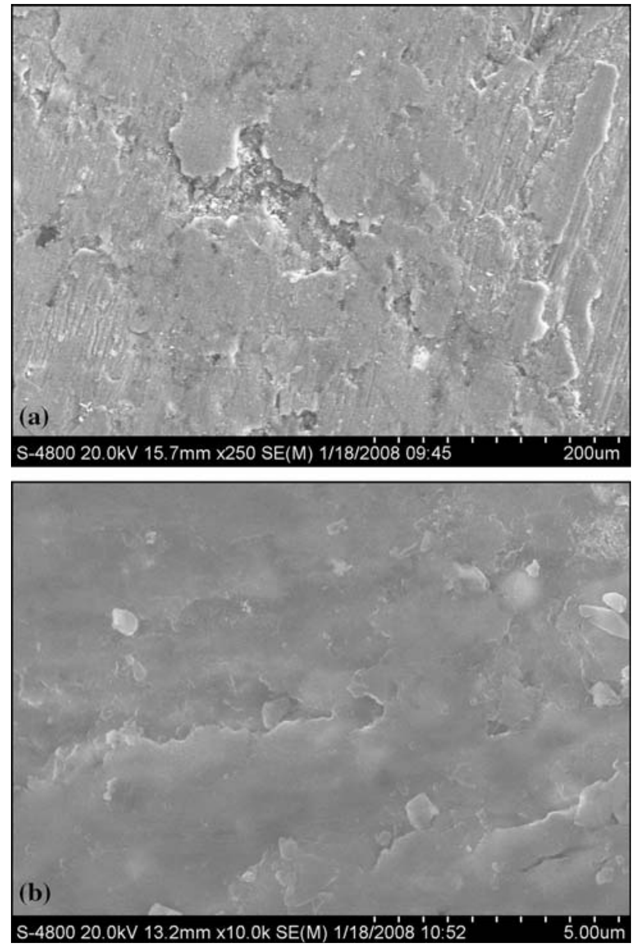

Fig. 2 FE-SEM morphology after abrasion at 350 °C

Table 2 Friction and wear performance at different temperatures (test condition: load 0.98 MPa, sliding speed: 480r/min)

Temperature, °C		100	150	200	250	300	350
μ	Elevated	0.414	0.458	0.476	0.446	0.430	0.394
	Descending	0.442	0.455	0.459	0.443	0.463	0.400
$\omega/10^{-7}$ cm^3, N m^{-1}		0.064	0.078	0.084	0.178	0.276	0.310

recovery and is essential for repeatable friction performance. The fade and recovery ratio can be expressed by:

$$F = \frac{\mu_{F100\,^\circ\mathrm{C}} - \mu_{F350\,^\circ\mathrm{C}}}{\mu_{F100\,^\circ\mathrm{C}}} \times 100\% \qquad \text{(Eq 1)}$$

$$R = \frac{\mu_{R100\,^\circ\mathrm{C}}}{\mu_{F100\,^\circ\mathrm{C}}} \times 100\% \qquad \text{(Eq 2)}$$

where F and R are fade and recovery ratios, and the subscripted F and R stand for the process of temperature ascending (fade) and descending (recovery), respectively. The fade ratio of the composites was only 4.8% and the recovery ratio 107%, indcating the perfect properties of stability and recovery. The total wear ratio by adding the wear values of each temperature is as low as 0.99×10^{-7} cm^3(N m)$^{-1}$, showing the high antiwear ability of the composites.

The composites developed based on PEEK resin show better heat stability and no fading at 350 °C. According to detailed discussion and SEM morphology observation in earlier publications (Ref 18, 19), the predominant wear mechanisms of composites have been ascribed to abrasion and adhesion. Adherence straps can increase friction coefficient and maintain it steadily. In this paper, the worn surfaces at 350 °C was researched further to explore the friction and wear mechanisms. FE-SEM micrographs are shown in Fig. 2. The even and compact adherence straps are visible on the worn surface, showing obvious adherence abrasion. Along the sliding direction, a series of parallel shallow grooves accompanied by the generation of small particles on the adherence straps shows the particle abrasion. When temperature was increased to 350 °C, a great deal of uniform films was formed on the friction surface, which accounts for the abrasive wear of the materials, and the resultant high friction coefficient and slight abrasive wear.

In general, the friction properties depend on the changes of the real contact area at the friction interface, the strength of the binder resin, and the frictional properties of the ingredients at elevated temperatures. The organic constituents in the friction material, such as binder resin, organic fibers, and other friction modifiers, play crucial roles in the wear of the friction material (Ref 20). It is known that resin changes its properties above the glass transition temperature and transforms into char at the thermal decomposition temperature. The property of high heat resistance of PEEK makes it possible for the composites based on PEEK to possess better stability at high temperature. The stainless steel wool is fiber reinforced with good friction

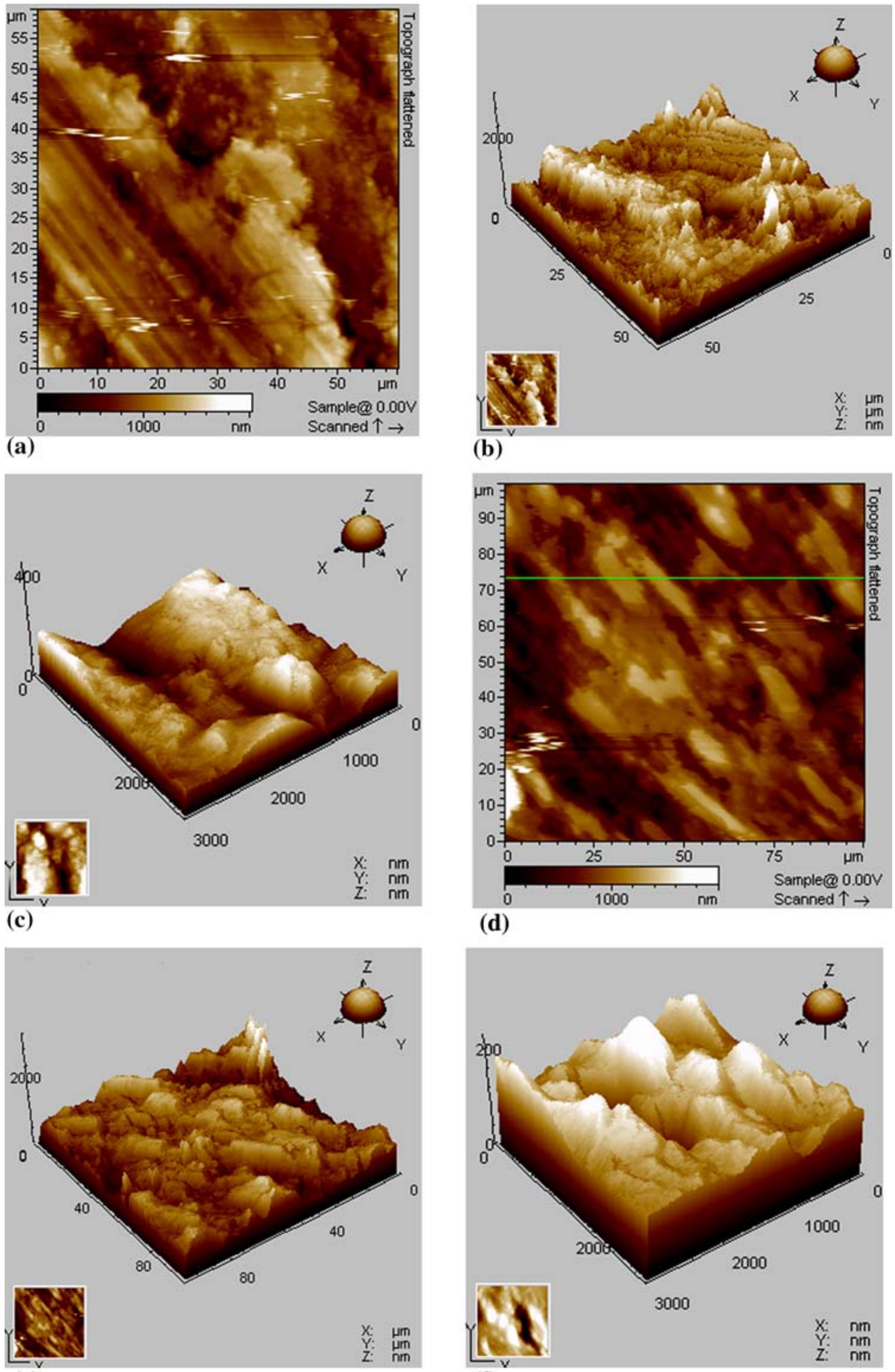

Fig. 3 AFM topographies of wear surface of counter disc and friction pad. (a) 2D configuration of pad (b) 3D configuration of pad, 50 μm^2 area. (c) 3D configuration of pad, 3 μm^2 area (d) 2D configuration of disc (e) 3D configuration of disc, 80 μm^2 area (f) 3D configuration of disc, 3 μm^2 area

performance and without the problem of rustiness faced in the case of the carbon steel wool. Its high conductivity of heat helps in decreasing the temperature of friction interface and prevents decomposing of PEEK. The carbon fibers, with high wear resistance and self-lubricating ability, make the composites have stable friction coefficient and low wear rate at high temperature.

3.2 Analysis of Transfer Film

The tribological behaviors of films were experimentally investigated at the nanoscale using atomic force microscope (AFM). Figure 3 is AFM topographic image (2D and 3D) of wear surface of counter disc and friction material. The worn surface of samples is covered with adherence straps and rough sliding tracks (Fig. 3a). It is evident that the worn material forms debris particle, which plows the surface; pile-up was seen on the sides of shallow grooves.

The thin amorphous layers and films were also observed at the surface of the counterpart. The surface morphology of counter disc is shown in Fig. 4. The counter disc is made from cast iron and its microstructure comprises graphite flakes in a pearlitic matrix. The AFM image reveals that, after wear test, the disc surface is covered with a gray friction layer (Fig. 3d). A significant amount of counter face material is transferred onto the sample surface during the sliding. In sliding process, plate-shaped microcontact areas are a compositional mix of all components of the mating materials. The results of X-ray energy and diffraction analysis (XRD) showed that compounds of barium, iron, and sulfur formed on the surface (Fig. 5).

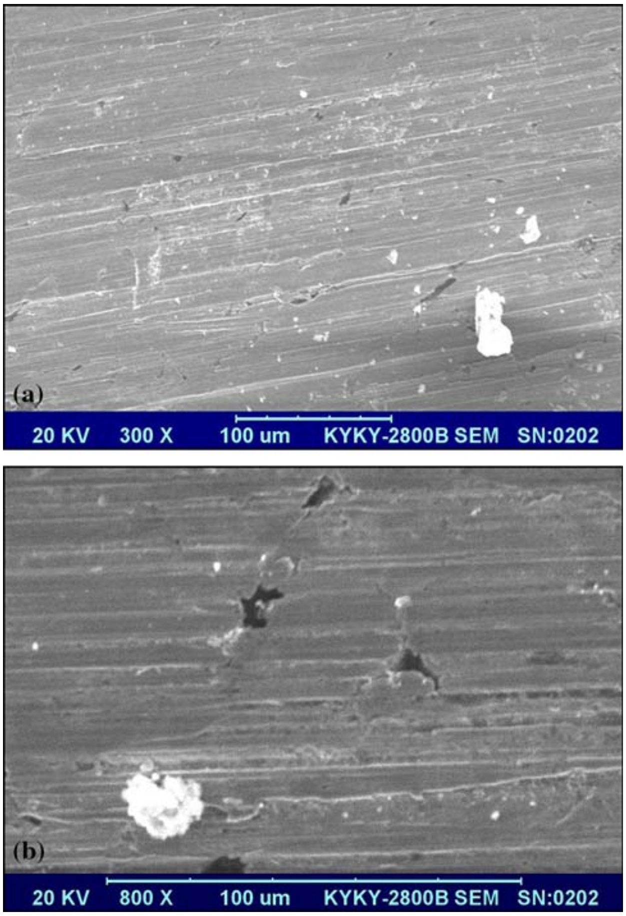

Fig. 4 SEM morphology of counter disc after abrasion at 350 °C

The wear resistance of a surface film is directly related to the interfacial bonding strength. A tenacious, long-lasting film can reduce the fracture of film and improve tribological durability and stability (Ref 21). Figure 6 shows the XPS spectra of counter disc and sample surface before and after friction test. The shift of binding energy (BE) of XPS is that the charge accumulated on the surface of sample when irradiated with X-rays and the BE higher than normal. The BE peaks were corrected by setting the C 1s (BE) at a value of 284.6 eV. After spectra deconvolution, every carbon environment is shown in Table 3, including binding energy, atom percentage, and ratio of peak area of each component over C 1s total area. At least three different carbon environments are found: carbon atoms of C-C bonds at 285.0 eV, and carbon atoms of C-O bonds at 286.0 eV, carbon atoms of C=O bonds at 287.1 eV. The main groups of PEEK molecular system are benzene, ketone, and aromatic aether bond. It can be seen from Fig. 6 and Table 3 that, after abrasion, the percentage of carbon atoms in C-C bonds increases; at the same time, the percentage of C-O and C=O bonds decreases. These indicate that, during the photon-chemical processes associated with the energy transitions, diversion, and dissociation of bonds in the interaction, C-O and C=O bonds can rupture more easily than C-C bonds, resulting in the breakaway of ketone and aromatic aether groups from the polymer molecules.

As shown in Fig. 6(c), the intensity and atom percentage of C-O and C=O bonds of counter disc increased. It can be concluded that pure PEEK transforms discontinuous surface film and transfers to the surface of the counterpart. Otherwise, the carbon fibers rub into graphite powder and ingress films, with layer structured graphite acting as a favorable solid lubricant (Ref 22).

Wear, in general, relies on many factors such as temperature, applied load, sliding velocity, properties of mating materials, and durability of the transfer layer. Due to the effect of the heat

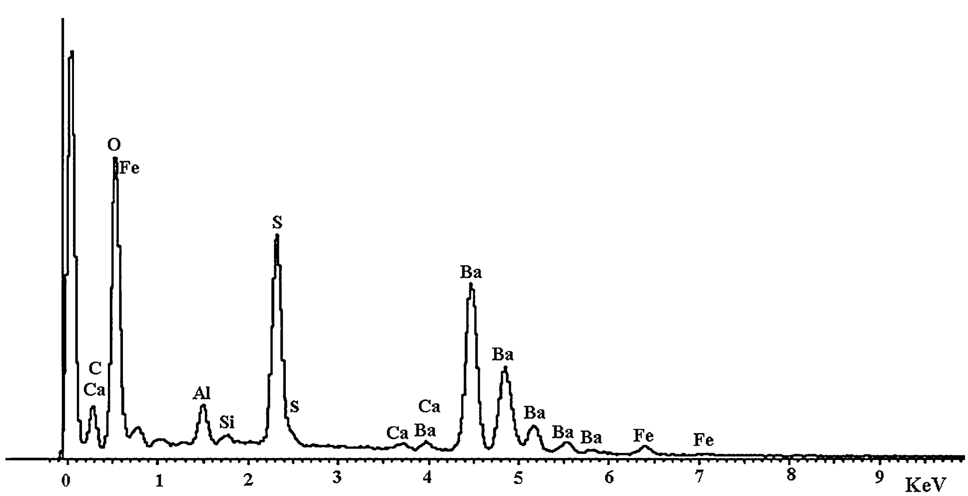

Fig. 5 EDS analysis of counter disc after abrasion at 350 °C

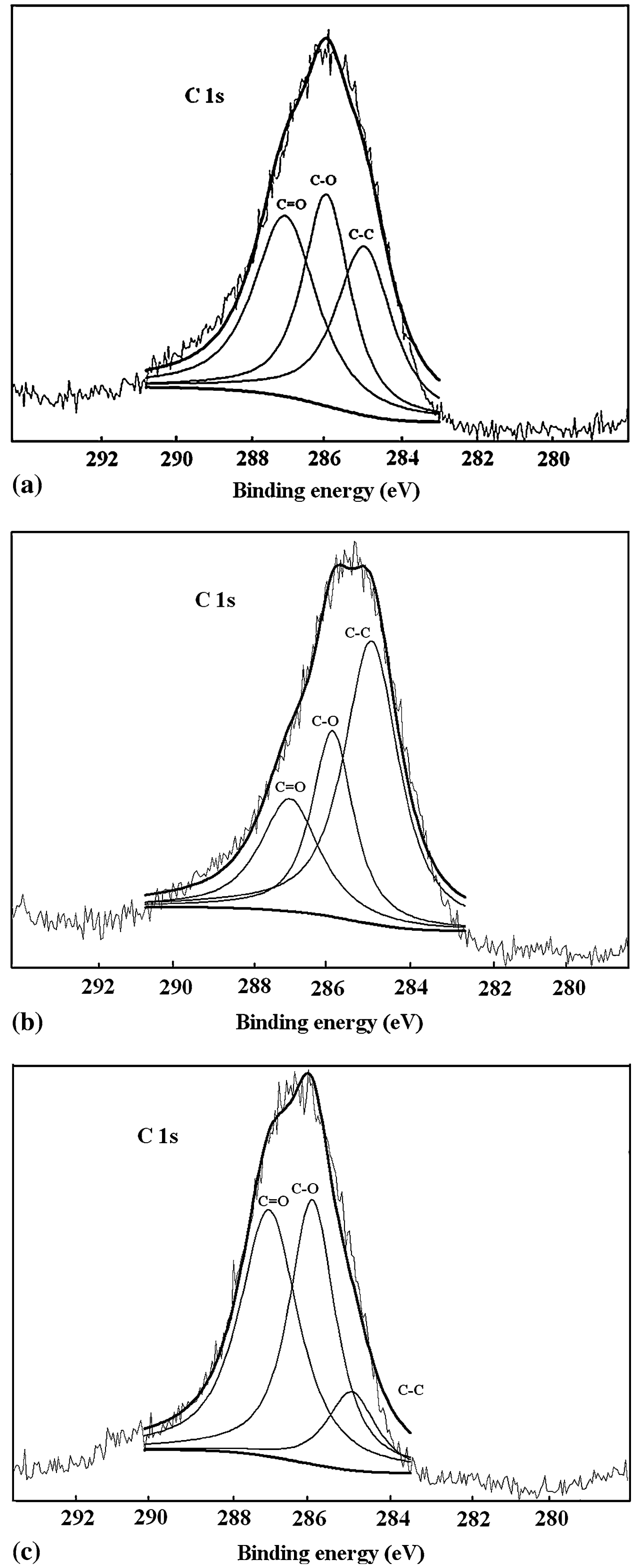

Fig. 6 XPS spectra in the C 1s region for PEEK. (a) before abrasion (b) after abrasion (c) Counter disc after abrasion

generated during grinding process and the friction force, the friction material undergoes continuous mechanical abrasion, deformation, delamination, fatigue, and wear. When the stress generated under friction in the film exceeds the adhesion force

Table 3 Data from XPS for C 1s electrons of PEEK

Atom	Wear	Position	Area	at.%
C-C	Before wear	285.0	9275.88	30.93
	After wear at 350 °C	285.0	12462.70	52.02
	Counterpart	285.0	2980.41	12.76
C-O	Before wear	286.0	9693.20	32.31
	After wear at 350 °C	286.0	6182.16	25.80
	Counterpart	286.0	9359.18	40.07
C=O	Before wear	287.1	11024.96	36.76
	After wear at 350 °C	287.1	5312.77	22.18
	Counterpart	287.1	11016.14	47.17

of the film, the film will begin to peel and result in abrasion. But if the films have strong bonding strength to the substrate, it can withstand the shear force caused by frictional force at high temperature. For the developed friction materials, PEEK was taken as adhesive because of its high decomposing temperature. It can be concluded that the structure of surface was little changed after wear testing and the PEEK is stable at high abrasion temperature of 350 °C. It was evident that the better friction stability of the friction material in Fig. 1 is attributed to the higher heat resistance of the binder resin PEEK. PEEK may have important influence on preventing the generation and propagation of microcracks at extended sliding passes (Ref 23). The high-temperature friction behavior might be improved to a certain extent by adding different kinds of powders and stainless steel fibers into the material.

4. Conclusions

The tribological behaviors of stainless steel fiber and carbon fiber-reinforced PEEK composite materials were studied by AFM, FE-SEM, and XPS. Based on the experimental data and analysis, the following conclusions are drawn:

(1) The wear mechanism of adherence abrasion as well as particle abrasion occurred at higher temperature. The formation of transfer layer plays a crucial role in improving abrasive resistant performance of PEEK-based friction materials.
(2) PEEK with high decomposing temperature and stainless steel fiber could enhance the cohesive strength between fiber and matrix to get stable friction coefficient and low abrasion value for friction materials.

Acknowledgment

The authors would like to acknowledge the financial support of the Science and Technology Plan of Shijiazhuang, China (04108231A).

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