



Thermal Stability of Poly(ether ether ketone) Composites under Dry-sliding Friction and Wear Conditions

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A B S T R A C T

By using X-ray diffraction (XRD), infrared spectrometry (IR), scanning electron microscope (SEM) and transmission electron microscope (TEM), the worn specimens of poly(ether ether ketone), (PEEK), composites tested under unlubricated sliding friction and wear conditions at a constant sliding speed were investigated in order to reveal structural changes of polymer as well as wear mechanisms as a function of temperature. The results showed that the PEEK composites exhibited stable friction coefficient and lower wear ratio. The wear mechanism is that the particle abrasion occurs at low temperature, the adherence abrasion and particle abrasion take place at the temperature between 200~350°C as revealed through wear morphology and wear debris analysis. The thermal degradation of PEEK does not occur until its temperature rises to higher than 350°. The stainless steel and carbon fibres bind strongly with the matrix PEEK and may be responsible for improving stability of the friction coefficients of the materials. Surface film, transition layer and matrix composed the superficial structure of friction material after wear test. Two kinds of surface film structures are formed: one is cystiform microstructure with PEEK matrix surrounded by single or multi-crystal powder of fillers; the other is meshwork generated by resin base and friction fillings.

Key Words:

poly(ether ether ketone);
composite material;
thermal stability;
wear;
fibre.

INTRODUCTION

It has been demonstrated that friction and wear performance are related mostly to the rather thin layer of a rubbing surface when a bulk polymer composite serves in tribological environment, leading to consequent mechanophysical and mechanochemical changes in the surface layer [1, 2]. As a com-

posite formulation and structure exert a critical influence on the wear mechanisms and friction performance of the polymer composites, it is necessary to understand structural variation in worn surfaces for both property prediction and material modification. The demands of multiphase composites

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with higher anti-wear properties have gradually increased for the development of economical and high-efficient technology. The friction composites normally consist of more than 10 ingredients, including resin matrix, reinforcing fibers, solid lubricants, abrasives and other friction modifiers [3]. A considerable amount of research work has been focused on the role of each ingredient, such as fibres [4-7], functional fillers [8] and resin matrix [9,10], and new ingredients are still being developed to achieve better friction performance [11]. Among the ingredients currently available for friction materials, the binder resin and reinforced fibres play a crucial role in determining the friction characteristics. The friction heat generated during the brake process easily raises the temperature at the friction interface above the decomposition temperature of the binder resin, resulting in the abrupt change of friction force during braking. The interaction of hybrid fibres provides the performance that each single fibre does not have. The development of a friction material is extremely complicated, not only because the combined effect of the ingredients is unpredictable, but also, the friction and wear performance is influenced by the transfer film (or friction film) formed on the sliding surface between friction material and counterpart. The investigation in tribology of sliding surfaces has been conducted actively in recent years [11,12], but the tribo-system 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 between the two counterparts [13,14]. The formation of friction film and its stability are related to the wear debris compaction, which in turn depends on the mechanophysical and mechanochemical changes of the composite. In addition, the formation and stability of the friction film on the sliding surfaces depend upon the stability of resin bonder as well as the cohesive strength between the film and the sliding surfaces.

This paper is focused on a research of the worn surface layer with the objective of revealing structure information about the polymer during wear processes. In particular, polyetheretherketone (PEEK), a typically high performance semi-crystalline polymer whose

composites have been reported to exhibit excellent potential for tribo-applications and widely act as a slider material [15-18], is employed as a bonder for stainless steel/carbon fibre reinforced poly(ether ether ketone), PEEK, resin based composite in this study.

EXPERIMENTAL

Composite material used in this study contains several ingredients including poly(ether ether ketone), PEEK, stainless steel fibre, carbon fibre and fillers. Commercially available PEEK powder was used as matrix material. The stainless steel fibre, with composition of 0.03% C, 17.03% Cr, 8.34% Ni, is 0.025 mm in average diameter and short cut to 3 mm in average length. The average diameter of carbon fibre is approximately 0.009 mm, with the tensile strength of 4200 MPa. The conventional particles (such as chromite, barite, graphite, sulfide stibium, etc) were selected as additional fillers to modulate the friction and wear performance. The composition was selected as the optimum content on the basis of our earlier work on evaluating the wear performance of series of polymer composites with different ingredients [19]. The compounding of polymer matrix with different fibres and fillers was achieved by a high speed mixing machine. The wear specimens were produced by the conventional hot-press procedure at the temperature of 320°C and the pressure of 25 MPa on a WE-10A hydraulic all-purpose machine. Then the moulded specimens were post-cured at 80°C, 150°C, 270°C for 30 min respectively and 310°C for 12 hours.

Dry sliding wear tests were carried out on a pin-on-disc apparatus under different temperatures to evaluate the durability of materials at elevated temperatures. Two specimens (25×25×6 mm³) were run against a polished gray-cast iron disc with contact pressure of 0.98 MPa and constant sliding speed of 480 r/min. The counter disc, with pearlite structure and Brinell hardness of HB180-220 and an initial surface roughness of 0.5 μm, were pre-worn to average surface conditions and reduce the running-in period. The disc was heated and the temperature was controlled by a heating device. The variation in the temperature of the cast disc in the steady stage was less than ±5°C. 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.

During the test, the friction force was recorded by a PC-based data acquisition system at 100°C, 150°C, 200°C, 250°C, 300°C and 350°C, respectively. The friction coefficient was calculated by a ratio between the tangential 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.

To understand the friction mechanism of the semi-metallic composites, the wear surface morphology after abrasion test was observed by scanning electron microscopy (SEM, KYKY2800B) and X-ray diffraction (XRD, D8 Advance). Transmission electron microscope (TEM) and infrared spectrometry (IR, Nicolet AVATAR330) were used to analyze the surface structure before and after wear abrasion test. Thermal analysis (TGA/DTA) was performed to investigate the thermal decomposition of the friction material using a thermal analyzer (Mettler model TGA/SDTA851^o) at 10°C/min of heating rate up to 800°C.

RESULTS AND DISCUSSION

Friction and Wear Properties

Figure 1 shows the variation of friction coefficient μ and the specific wear rate W with elevated temperature, f_1 and f_2 instead μ of temperature ascending and falling process, respectively. It is clear that the friction coefficient was 0.41 at 100°C and went up to the maximum value 0.47 with temperature rising to 200°C. At 350°C the μ was descending to 0.39. The specific wear rate was between $0.06\text{--}0.31 \times 10^{-7} \text{ cm}^3(\text{N.m})^{-1}$ with temperature rising. While temperature falling from 350°C to 100°C, the μ resumed to 0.44. These results showed that the friction coefficient was steady and changed smoothly from room temperature to 350°C, while the wear rate was low with temperature ascending.

With the temperature rising, the friction coefficient μ of an organic composite material decreases tem-

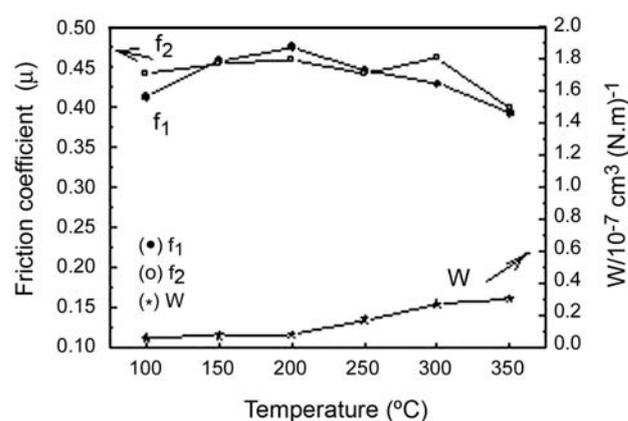


Figure 1. Effect of temperature on friction coefficient and wear rate of composites (load: 0.98 MPa, and sliding speed: 480 r/min).

porarily and this phenomenon is called fade. After the material is engaged at high temperature, pre-fade μ should be regained at lower temperature and this characteristic is termed as recovery that is essential for repeatable friction performance [20]. In general, the change of friction coefficient during sliding process depends on the changes of the real area of contacts at the friction interface, the strength of the binder resin, and the frictional properties of ingredients at elevated temperatures. It is known that resin changes its properties above the glass transition temperature and transforms into char at the thermal decomposition temperature. Wear, in general, relies on many factors such as temperature, applied load, sliding velocity, properties of mating materials and durability of the transfer layer. The organic components in the friction material, such as binder resin, organic fibres and other friction modifiers, play crucial roles in the wear of the friction material. This is because the heat generated during grinding process raises the temperature of the friction material beyond the transformation temperatures of the organic constituents. It is shown in Figure 1 that the developed PEEK compound has better thermal stability and no degradation has occurred at high has temperature as 350°C.

Structure Analysis of Surface Layer

Figure 2 shows the infrared spectrum of pure PEEK and surface of sample before and after friction test. The main groups of PEEK molecule are benzene, ketone and aromatic ether bond. The wavenumbers of

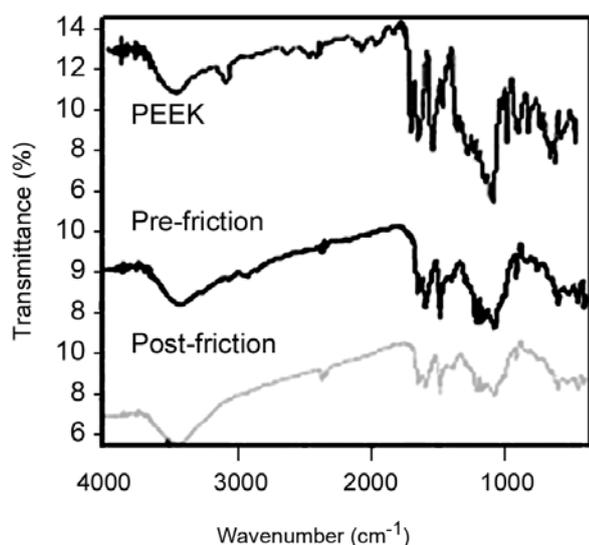


Figure 2. FTIR Spectrum of friction materials before and after wear test.

carbon-hydrogen ($=C-H$) extension vibration are 3030 and 3070 cm^{-1} , the aromatic ring ($C=C$) 1500 cm^{-1} and 1600 cm^{-1} , ketone ($C=O$) 1660 cm^{-1} and 3420 cm^{-1} , aromatic ether bond ($C-O-C$) 1050 cm^{-1} and 1220 cm^{-1} , and peak 1050 cm^{-1} is strong.

After solidifying, the peak of carbon-hydrogen ($=C-H$) extension vibration 3030 and 3070 cm^{-1} are disappeared. The peak strength of aromatic ether bond ($C-O-C$) at 1050 cm^{-1} and benzene ring ($C=C$) 1500 cm^{-1} and 1600 cm^{-1} are weakened after wear test, the hydroxy peak of 3420 cm^{-1} changed little before and past friction. It can be concluded that the structure of surface changes slightly after wear testing and the PEEK is stable at high abrasion temperature of 350° . It was evident that the better friction stability of the friction material in Figure 2 is attributed to the higher heat resistance of the binder resin PEEK.

Analysis of Heat Affected Zone

The evident rise of the friction coefficient in the beginning in Figure 1 seems closely related to the change of real contacts at the friction interface and the change of the mechanical properties of PEEK above the glass transition temperature. G. Zhang [18] invested the tribological characteristics of pure PEEK coating under dry sliding conditions and the result showed that before crystallization of the PEEK, the

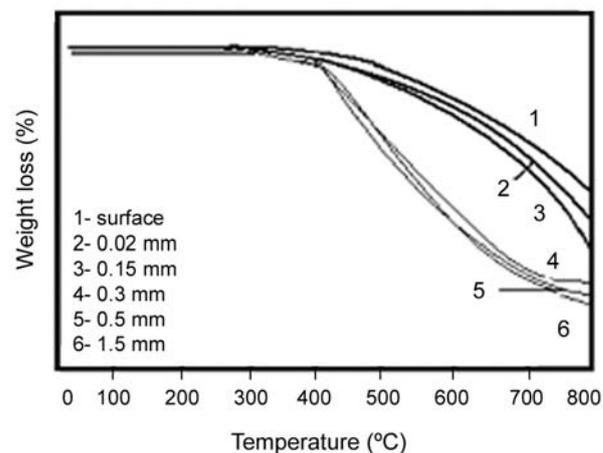


Figure 3. TGA Thermograms of different layers of friction materials.

friction coefficient increased with increasing temperature and the PEEK exhibits the biggest friction coefficient at a temperature slightly higher than the PEEK crystallization point. The slower decline of the friction coefficient above 200°C in Figure 1 indicates the formation of reaction products at the friction interface and the development of a heat affected zone in the sub-surface of the friction material at high temperatures.

Thermal analyses were performed to examine the difference in heat resistance of friction materials. Figure 3 shows the thermogravimetric analysis (TG) curves of the composites from surface to sub-layers by 0.02 , 0.15 , 0.3 , 0.5 , 1.5 mm depth. It is revealed that the heat-affected zone is about 0.3 mm depth from surface. Figure 4 displays a schematic structure of the heat affected zone of the composite during sliding friction. The heat affected sub-surface layer of the friction material appears important in the stabilization

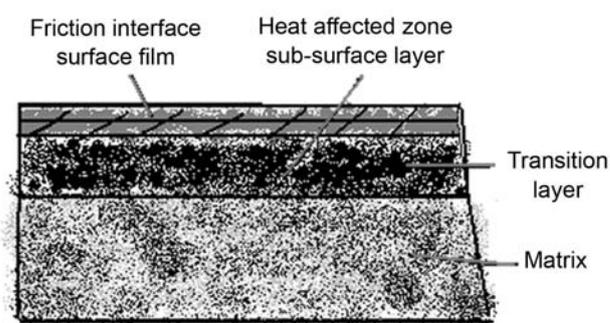


Figure 4. A schematic display of the composite structure.

of the friction coefficient at elevated temperatures and the layer is produced incessantly by maintaining a certain thickness while the material at the top surface is removed during sliding. The reaction products at the friction interface are composed of carbonaceous reaction products, unreacted constituents, and oxides from metallic ingredients act as a buffer layer for the rapid change of the friction coefficient.

Analysis of Friction and Wear Mechanism

Figure 5 shows SEM morphology after abrasion at corresponding temperatures. The composite materials undergo mechanophysical and mechanochemical changes during the wear test due to the relatively long period of sliding. During the onset of friction, the surface is coarse and the interface temperature is low. It is clear that shallow grooves parallel to the sliding direction are formed as a result of friction and abrasion, cracks are produced as a result of disruption on the plane subjected to compression and shear force [21], and debris are products of fracture (Figure 5a). These grooves were possibly caused by embedded hard particles, which engendered a three-body abrasive wear mechanism. The friction surface is nicked

by abrasive debris and hard particles, and hard particles are the main factor deciding the abrasive value, so the wear mechanism is particle abrasion at this stage of abrasion. It can be seen that stainless steel fibres were outcropped on the surface, showing lathy shape subjected to friction force after abrasion at 100°C.

When the temperature ascended to 150°C, the resin matrix started to be softened and resulted in an increase in real contact area. The asymmetrical distributing contact points between PEEK matrix and mating disc formed locally adhering points at friction interface due to high temperature and high pressure. Meanwhile, when the adhering points went on gliding at the effect of friction and shear force, an even film was gradually formed on the friction surface, and this film was called "transferred film". Because of the keeping physical and chemical effects between transferred film and counter disc, the real contact and adherence were produced at the interface of two surfaces. When the shear force within the adhering points exceeded the flow limit between the film and the matrix, the film was broken and resulted in abrasion. Thus the friction surface had produced a number of

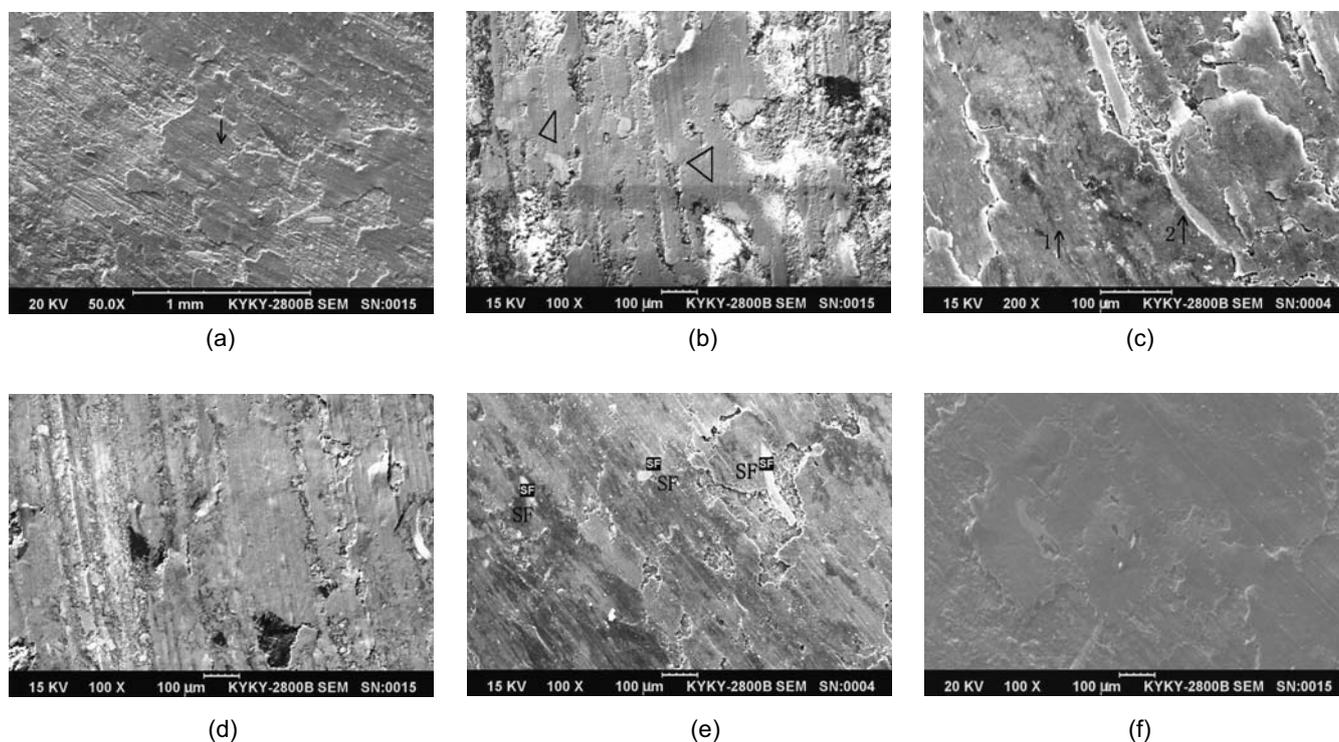


Figure 5. SEM Morphology after abrasion at: (a) 100°C, (b) 150°C, (c) 200°C, (d) 250°C, (e) 300°C, and (f) 350°C SF (stainless steel fibre).

adherence straps showing that the adherence abrasion occurred (Figure 5b).

At 200°C, the even and compact adherence straps were gradually formed on the friction surface, showing obvious adherence abrasion (Figure 5c). With the proceeding of attrition, the part of transition layer contacted with surface film was continuously translated to superficial film by double effect of friction heat and mechanical force. The early-formed surface film was shorn and grind continuously and spread to agglomerate film dispersed. Adherence straps can increase friction coefficient and keep it steadily (Figure 1). G. Zhang [18] suggested that a stick-slip motion between the two counterparts, together with the strain-hardening effect of the PEEK surface layer, results in a periodic material stack on the worn track. Along sliding direction, a series of parallel shallow grooves on the adherence straps shows the particle abrasion (Figure 5c, Arrow 1), with stainless steel fibres unfolding on the surface and a few of them being pulled out (Figure 5c, Arrow 2). Particle and adherence abrasion occurred at this temperature.

When temperature was as high as 250°C-350°C, a great deal of uniform films was formed on the friction surface (Figures 5d-5f). A number of experiments have shown that pure PEEK transforms to a discontinuous surface film in the sliding friction process and the carbon fibres rub in to graphite powder and ingress films with layer structure graphite acting as a favourable solid lubricant [22-24].

When the shear force within the adherence points exceeded the flow limit between the film and the matrix, the film was broken and resulted in abrasion. So the abrasion in this stage was dependent on the cohesive strength of the composites and the heat-resistant property of resin matrix. For the developed friction materials, PEEK was taken as adhesive because of its high decomposing temperature (above 500°C). This excellent property of PEEK composites was attributed to their crystallized phase, which remains immobile across the glass transition at elevated temperature and confers on the material excellent thermal stability and a high continuous service temperature. And the stainless steel fibres enhanced the cohesive strength between fibre and matrix and resulting in stable friction coefficient and low abrasion value for the composites.

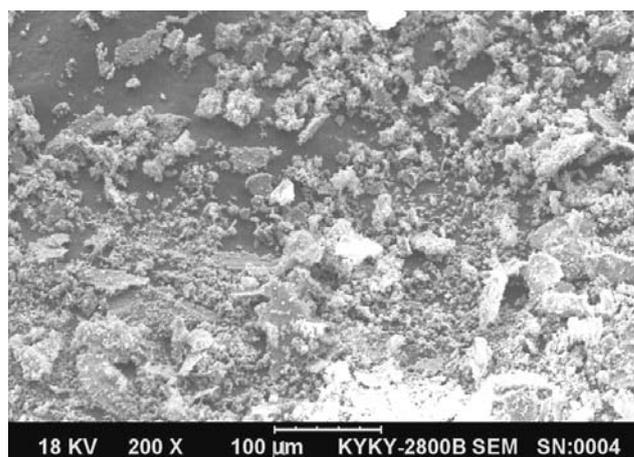


Figure 6. SEM Morphology of composites after abrasion at temperature of 350°C.

The friction characteristics observed for organic brake pads against cast iron discs can be explained by the formation of contact plateaus [22]. The plateaus are subdivided into primary and secondary plateaus. The primary plateaus consist of the wear resistant components of the composite and form nucleation sites for the secondary plateaus. The secondary plateaus are formed by wear debris, compacting in front of the primary plateaus.

SEM morphology of debris particles collected after wear test at the temperature of 350°C is shown in Figure 6. It reveals the general pattern, distribution and their agglomerates of extracted particles. Most of the debris was found flake-like and clustered as loose particles. The abrasion mechanism can be conferred from the morphology of scraps. Grain, stick and flake shape debris stand adherence abrasion and sector debris maybe the effect of severe fatigue wear [25]. Flake and little stick straps showed the effect of adherence abrasion (Figure 6). Most of the debris was fine, showing that the PEEK matrix had not decomposed at high temperature of 350°C and the film possessed well smooth function. No stainless steel fibres were observed to be rubbed off, indicating that the coherence strength between fibres and matrix is higher. This result is consistent with that of SEM morphology analysis.

Analysis of Transfer Film

During the friction and wear process, a polymeric film can be formed and transferred to the steel counterpart,

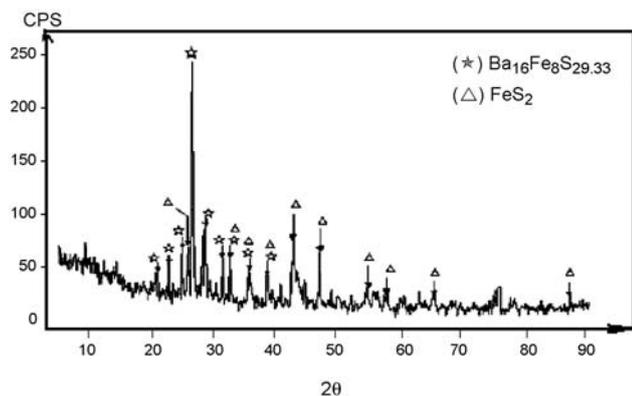


Figure 7. XRD Spectrum of composites surface after wear at 350°C.

which results a new counter-surface and producing primarily an adhesive wear mechanism. After continuous grinding, the transfer film becomes more even, and its strength, hardness and toughness become higher. Iron and iron oxides transfer from cast iron disc to friction materials, and self-organization structure is formed due to mechanical-chemical and thermo-

chemical actions on friction interface [25]. The results of X-ray energy and diffraction analysis (XRD) showed that compound of barium, iron and sulphur formed on the surface (Figure 7). Transfer layer is composed of new phases, mainly various oxides from metals, metal sulphides and inorganic compounds [26]. In most cases, the formation mechanism of the film is considered by debris generated from two sliding contact surfaces filled into the friction materials or diffused into cast iron disc [27]. An efficient transfer layer can improve friction performance, and improve wear resistance or stability of friction coefficient.

The macrostructure of friction material is asymmetric due to multi-ingredient hybrids. However, after long running wear test at elevated temperature, the transfer film is formed under the action of force and heat together. From the results of face scanning by energy diffraction spectrum, the composition of surface film is basically uniform and thus the microstructure of film could be investigated using TEM.

Figure 8 showed the Transmission Electron Microscope (TEM) morphology and diffraction pattern of the surface film.

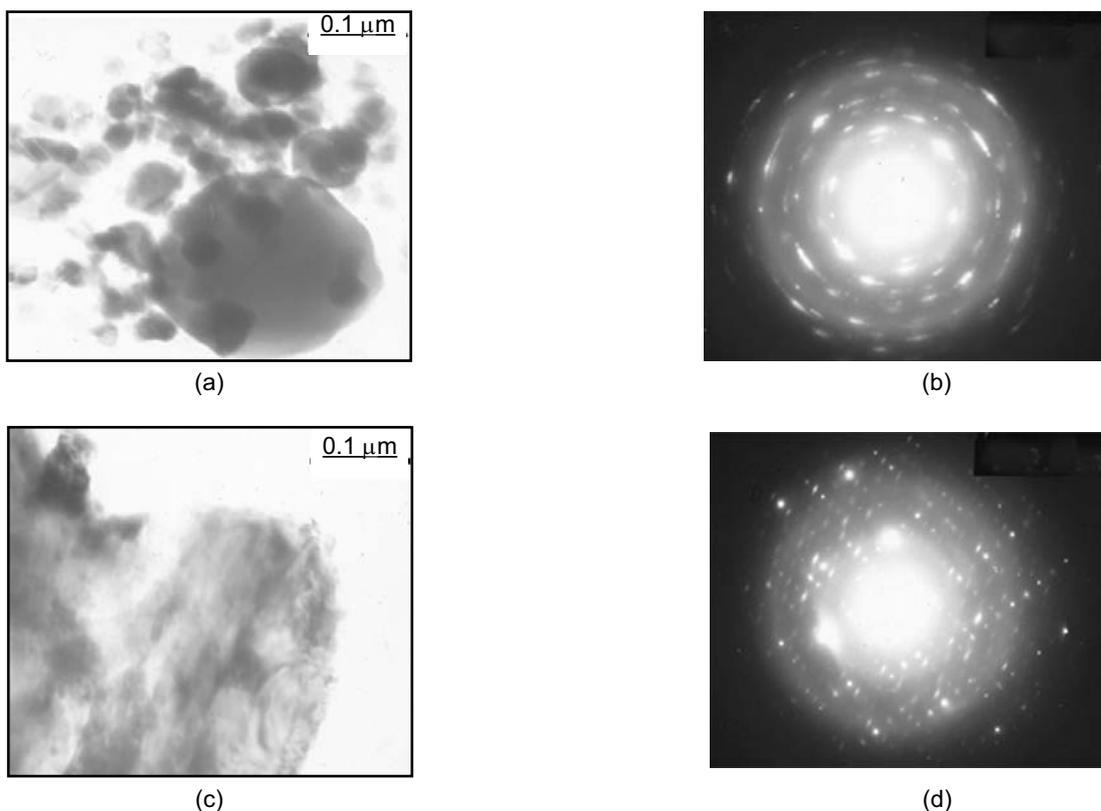


Figure 8. TEM Morphology and diffraction ring or spot of the surface film (a) film morphology, (b) diffraction ring for (a), (c) film morphology, and (d) diffraction ring for (c).

Table 1. The results of elemental analysis.

Element	Fe	Ca	Ba	Cr	Si	Al	S	Sb
wt%	26.34	6.06	20.45	20.68	9.21	7.46	3.45	4.35

tern of surface film. In Figure 8a, the cystiform microstructure of the film is shown and no diffraction spots or ring were produced by this structure. These results showed that the structure of PEEK matrix is non-crystal. Figure 8b showed the diffraction ring produced by interface and Table 1 is the result of elemental analysis. It can be concluded that all composition of the mineral fillers is contained in this region and the diffraction ring is produced by powder of these fillers.

Another kind of mesh structure of surface film can be seen in Figure 8c. The diffraction ring or spots were produced by the black venation (Figure 8d), while the results of elements analysis is similar as Table 1. It can be inferred that the white region is PEEK matrix and the black is powder of friction fillers. Therefore, two kinds of surface film structures are formed: one is cystiform microstructure with PEEK matrix surrounded by single or multi-crystal powder of fillers; the other is meshwork generated by resin base and friction fillings.

CONCLUSION

The thermal stability of Poly-ether-ether-ketone (PEEK) Composites under dry-sliding friction and wear conditions was studied and the following conclusion have been drawn from the above investigations:

- PEEK with high decomposing temperature and the stainless steel fiber could enhance the cohesive strength between fiber and matrix to get stable friction coefficient and low abrasion value for friction materials.

- The wear mechanism was a complex process, particle abrasion took place at low temperature, and 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.

- The superficial structure of friction material after wear test is composed of three layers. The first is surface film that was worn and torn continually during abrasion process as a result of friction force and heat. The second is transition layer with a thickness of about 0.3 mm and could be translated into film incessantly. The third layer is friction material keeping the initial state before abrasion test.

- Two kinds of surface film structure are formed: one is cystiform microstructure with PEEK matrix surrounded by single or multi-crystal powder of fillers; the other is meshwork generated by resin base and friction fillings.

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