JOURNAL OF MATERIALS SCIENCE **34** (1999) 3513 – 3524

Analysis of electron spectroscopy for chemical analysis of the transferred film formed during sliding wear for carbon fibre reinforced polyetheretherketone and its composites

XIANCAN FENG*
Department of Physics, Guangzhou Normal University, People's Republic of China
ZAIPING LU
Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, People's Republic of China
RENJI ZHANG
Department of Mechanical Engineering, Tsinghua University, People's Republic of China
E-mail: xc_feng@163.net

The transferred film formed during sliding of carbon fibre reinforced polyetheretherketone (PEEK) influences greatly its tribological properties. In this paper a study on electron spectroscopy for chemical analysis (ESCA) for the films was carried out. It is indicated in this study that the transferred films formed of the carbon fibre reinforced PEEK composite are thinner, continuous and uniform, and have better tribological properties as compared with neat PEEK and PEEK-PTFE (polytetrafluoroethylene). The compositions of the transferred films are variable along the direction of thickness of the films, this reveals that there is a preferential transform in graphite and PTFE among the films. Based on this study, an adhesive transfer mechanism is proposed for the formation of transferred films during sliding wear. © *1999 Kluwer Academic Publishers*

1. Introduction

Polyetheretherkentone (PEEK) is semicrystalline thermoplastic polymer (Fig. 1). Zhang *et al.* and Kausch introduced systematically its properties of structure and morphology [1, 2]. Recently carbon fibre reinforced PEEK composites have been researched and produced in order to improve mechanical properties of PEEK and they have extensive applications in mechanical industry. For example, they can be used as twist chain in wet environment for textile mechanism, and can be used as wear-resisting parts for mechanism of light industry. Zhang *et al.* have researched tribology of PEEK and its composites and discovered that a polymer transferred film on the steel counterfaces during sliding has been formed and it influences greatly the friction and wear properties of mechanical system [1, 3–5].

Logswell described molecular structure of PEEK [3]. The repeat unit of PEEK contains 19 carbon, 12 hydrogen and 3 oxygen atoms, giving a total molecular weight of 288; it is shown in Fig. 2. The level of crystallinitry of PEEK is several percents to 48% at ordinary temperature. The average molecular weight of PEEK composittes is 30000 and the average degree of polymerization for weight is $D_{\mathrm{pw}} = 104$. Blundell *et al.* study crystalline morphology of the matrix of PEEK [6]. The common structure of PEEK is spherulites and the maximum radial growth rate of the spherulites occur at ∼230 °C with a speed of $\sim 0.2\ \mu\mathrm{m\ s}^{-1}$ (Fig. 3). First, the spherical nucleuses of the crystals with cluster structure of neat PEEK have been formed, the grow up with flowing of atoms molecules and the boundary impingingment takes place for these crystals, which consists of the crystal grain with size of μm, of the PEEK have been formed among them the crystal zone and noncrystal zone with size of nm are connected alternatelly each other.

In this paper, we introduce friction and wear experiments for PEEK and other two composites. We study ESCA of the transferred film formed during sliding wear for carbon fibre reinforced PEEK and its composites. We discuss about transferred films of PEEK composites and that carbon fibre has important effect in the films. And an adhesive transfer mechanism is proposed for the formation of transferred films during sliding wear.

---

* Author to whom all correspondence should be addressed.

0022–2461

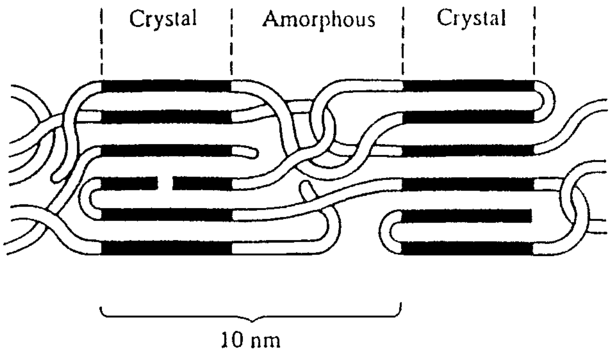


Figure 1 Schematic of crystalline morphology of PEEK.

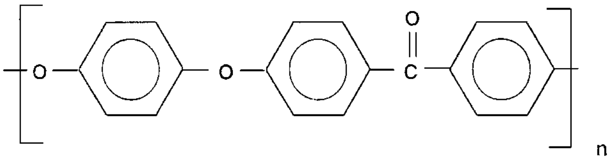


Figure 2 Repeat unit of the PEEK.

2. Friction and wear experiments

2.1. Materials

The material of the steel ring is made from 100 Cr6 steel. The materials of three kinds of polymer pins are:

(1) The neat PEEK material is neat PEEK 150p, its molecular weight is 150×10^6, it is unannealed and is in granulate form, the degree of crystallinity measured by differential scanning calorimetry after injection moulding is 29.3%.

(2) PEEK/TF composite, the mixture of two polymers, PEEK+8%PTFE, the content of PTFE is 8% by weight, PTEF has 13–15 CF_2 basic function clusters and a smooth molecular profile, no branching and no cross-links, it improves tribological properties.

(3) PEEK/FC30 composite, it is a carbon fibre reinforced PEEK composite, it contains PEEK+ 10%PTFE+10%graphite+10%carbon fibres. The diameter of high strength carbon fibres is about 5 μm. The graphite plate spacing is 0.35 nm, the local ordered family of plates thickness is about 5 nm, and graphite plate width is about 3 nm. Because of adding graphite grains and especially carbon fibres, the tribological properties become better.

All the materials were provided by Imperial Chemical Industries (ICI), Wilton, UK.

2.2. Friction and wear tests

Friction and wear test used standard specimen: pin specimens with size $4 \times 4 \times 10$ mm^3, the inside diameter 40 mm and the height H 40 mm, standard test condition were: the local pressure p was 1 MPa, the sliding speed $V = 1$ m s^{-1} and the environmental temperature 25 °C. The results showed that PEEK/FC30 has lowest friction coefficient μ and specific wear rate $\dot{W}_\mathrm{s}$. Table III is comparison of mean sliding friction coefficient $\bar{\mu}$ for the three kinds of specimens. It could be seen from Table III: (1) $\bar{\mu}_\mathrm{PEEK} = 0.42$, it is highest, $\bar{\mu}_\mathrm{PEEK/TF} = 0.36$, second and $\bar{\mu}_\mathrm{PEEK/FC30} = 0.28$, lowest. (2) The $\bar{\mu}$ values of the PEEK/TF disappeared in larger range, it indicated the influence of morphology of friction subsurface on PEEK/TF is larger. Table IV showed comparison of mean specific rate $\dot{W}_\mathrm{s}$ for three kinds of specimens. From Table IV it could be seen: (1) The order of the value of $\dot{W}_\mathrm{s}$ from highest to lowest is like mentioned above, the value of $\dot{W}_\mathrm{s}$ (PEEK/FC30) is one order more of magnitude smaller than of $\dot{W}_\mathrm{s}$ (PEEK). (2) The value of $\dot{W}_\mathrm{s}$ of PEEK/FC30 has larger mean error. This is due to wear mechanism microcutting + delamination wear mechanisms at beginning to delamination wear mechanisms at last (at this time wear dropped down a lot).

According to the tests of $\bar{\mu}$ and $\bar{\dot{W}}_\mathrm{s}$ above, PEEK/FC30 carbon fibres reinforced composites have good friction and wear properties, they can be used as wear-resisting mechanical parts.

The variations of μ and $\dot{W}_\mathrm{s}$ with sliding time t have been tested in Ref. [1]. For PEEK specimen, the value of μ increased from 0.27 to 0.32–0.38, as t increasing the value of μ decreased and the value of $\dot{W}_\mathrm{s}$ increased from lower value to stable value. For PEEK/FC30 specimen, at the beginning of wear test, the value of μ was variable, then increased gradually or oscillated to mean value. At the beginning of sliding the value of $\dot{W}_\mathrm{s}$ was larger, sometimes was larger than initial value, as increasing to $t \geq 4$ h, the value of $\dot{W}_\mathrm{s}$ reached its stable value. The variations of μ and $\dot{W}_\mathrm{s}$ were due to the action of carbon fibres in composite materials.

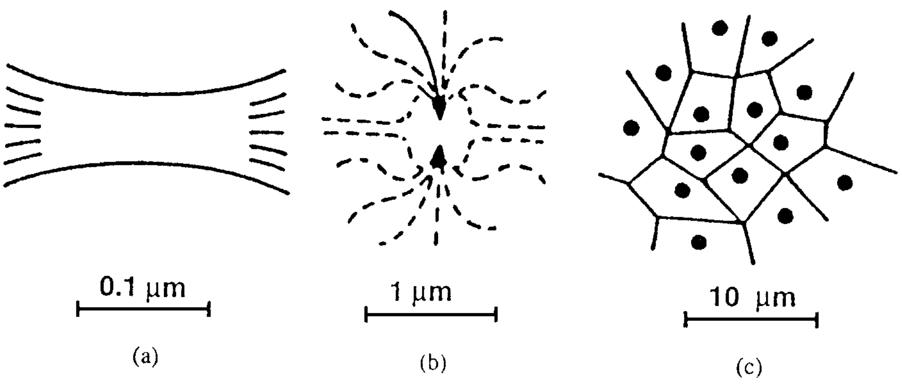


Figure 3 Schematic of spherulite textures of the neat PEEK (a) "Protospherulite" showing sheaf-like structure; (b) Growth pattern; (c) Boundary impingement.

2.3. Fourier transform reflection infra-red spectroscopy (FT-IR) analysis, differential scanning calorimerty (DSC) analysis and SEM observation of the polymer transferred films

The transferred films are formed on the counter-face during sliding for PEEK and its composites. The polymer transferred films are formed for PEEK and PEEK/TF, and the polyme + graphite composites are formed for PEEK/FC30, these films influence greatly tribological properties of a system. In the reference [1], FT-IR analysis and DSC analysis have been carried out for above films, and the SEM observations of the films have been performed. Above analyses and observations indicated:

(1) The back-scattering electron image (BEI) can show both the atomic number contrast and the surface morphology contrast. There was different contrast in the different reasons for the transferred film of PEEK, it meant its continuity and uniformity were poorer. The transferred films of PEEK/TF and PEEK/FC30 were continuous basically.

(2) The second any electron image (SEI) can only show the surface morphology contrast, the observations indicated the transferred film of PEEK/FC30 was most uniform and smooth (after long sliding time).

(3) There were two new carbonyl peaks produced by thermal degradation in the FT-IR spectra of the neat PEEK transferred films, this was due to structure change of the films, which occurred because of thermal effect during sliding. The relative intensities of other peaks had changed a lot. On the contrary, for the PEEK/TF and PEEK/FC30, there were no obvious changes that could be found in the FT-IR spectra.

(4) According to DSC analysis of wear pin top wear debris, we could infer the variation of crystallinity and crystal morphology of all kinds of transferred films. Analysis have showed that the recrystallization content of the film for PEEK was highest, that for PEEK/TF second, and that for PEEK/FC30 lowest. Especially the recrystallization content of PEEK, increased greatly as load pressure increased, this was due to the thermal effect of friction is more serious. In turn, the variation of the transfer films influenced its tribological properties.

3. Analysis of ESCA spectra of the transferred films

In order to investigate the thickness of various transferred films as well as the their structure, we analyzed their ESCA spectra.

3.1. Data table of binding energy

The possible data of binding energy (BE) for our specimens have been summed up in reference [1]. The data of BE for C$_{1s}$, O$_{1s}$, F$_{1s}$ and Fe$_{2p}$ energy bands of ESCA for our transferred films have been listed in Table I. From Table I it can be seen:

TABLE I ESCA peaks for PEEK and PTFE

C$_{1s}$	BE = 285.0 eV (Phenyl carbon atoms not bonded to oxygen in PEEK)
	= 285.9 eV (Phenyl carbon atoms in ether in PEEK)
	= 287.7 eV (-CO- carbonyl group in PEEK)
	= 286.6 eV (C_6F_6)
	= 284.6 eV (Contaminated carbon)
	= 291.5 eV (CF_2 in untreated PTFE)
O$_{1s}$	BE = 532.4 eV (-CO- carbonyl oxygen in PEEK)
	= 533.9 eV (-O- ether oxygen in PEEK)
	= 530.1 eV (O in iron oxide Fe_2O_3)
	= 531.9 eV (O in $SO_4^=$)
	= 531.7 eV (O in H_2O)
Fe$_{2p}$	BE = 707.1 eV (In pure Fe)
	= 710.6 eV (Fe^{3+} in Fe_2O_3)
	= 711.4 eV (Fe^{2+} in FeO and FeF_2)
F$_{1s}$	BE = 689.5 eV (C_6F_6)
	= 683.6 eV (FeF_2)
	= 688.6 eV (CF_2 in PTFE)
	= 691.7 eV (In degraded PTFE)
	= 693.8 eV (In degraded PTFE)
	= 684.8 eV (In metallic fluoride)
	= 684.2 eV (FeF_2)

(1) In the C$_{1s}$ band, the contaminated carbon atom (or carbon atom in graphite) has lowest BE value, others are carbon atoms of the polymers, among them the carbon atom of CF_2 in PTFE has highest BE value.

(2) In the O$_{1s}$ band, BE value of O atom in Fe_2O_3 is lowest, that in absorbing materials ($SO_4^=$ and H_2O) is higher, and that in polymer is highest.

3.2. Thickness analysis of transfer film

In order to estimate the thickness of the transfer films formed on steel counterfaces for PEEK. PEEK+8%PTFE and PEEK+10%PTFE+10% graphite+10%carbon fibre, section analysis of ESCA for the transfer films has been carried out at standard experimental condition ($P = 1$ MPa, $t = 24$ h). The continuous films have chosen. We used multifunction electron spectrograph of Perkin Elmer Company to analyze our specimens. The Mg target was used, the characteristic X-ray photon energy is 1254.6 eV, characteristic width is 680 meV, and the angle of detector is 45°. We estimate the thickness of the transfer films based on areas of peaks of different elements as well as different peaks of same elements.

For the sake of knowing the compositions of the transfer films different depth, we used erosion of Ar iron. The energy Ar^+ is 1 keV and the intensity of iron beam is 2.5 μA/cm^2. We estimated that 2 nm would be eroded per minute for PEEK and PTFE polymers, 0.5 nm for oxide of Fe and 1 nm for boundary plane at above experimental condition. Although the analytical specimens had been cleared in 10 minutes using alcohol, but the contaminated carbon atoms were scattered all over the surface of the specimens, only the peak of contaminated C atom and the weak peak of O$_{1s}$ is appeared in ESCA spectra. After two minutes of ion erosion, higher peak of O$_{1s}$ is appeared, we believed that this ESCA were from beginning surface of transfer films. Went on eroding, the composition of the different depth could be got. After enough erosion of Ar ion, many peaks of Fe in ESCA spectra became stronger, the peak of C was weaker, and the peak of C PEEK/FC30 films was stronger relatively. The thickness of the films could be estimated according to the erosion time.

ESCA spectra of three specimens in different depth are shown in Figs 4–6. Every film has three spectra,

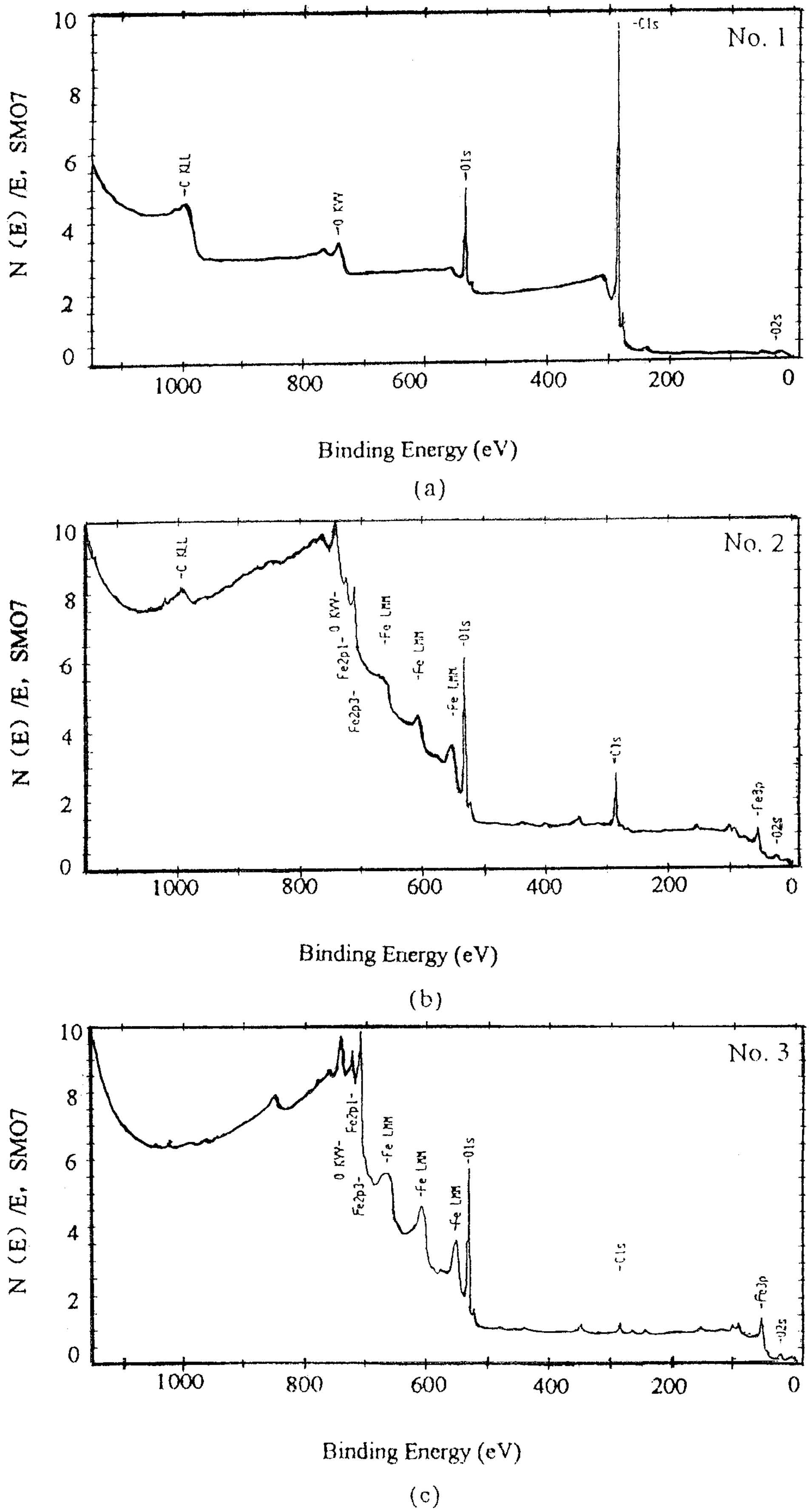


Figure 4 ESCA spectra for PEEK transferred film formed on steel rings surfaces during dry sliding wear (P = 1 MPa, $V = \text{m s}^{-1}$ and $t = 24$ h) (a) No. 1; (b) No. 2; (c) No. 3.

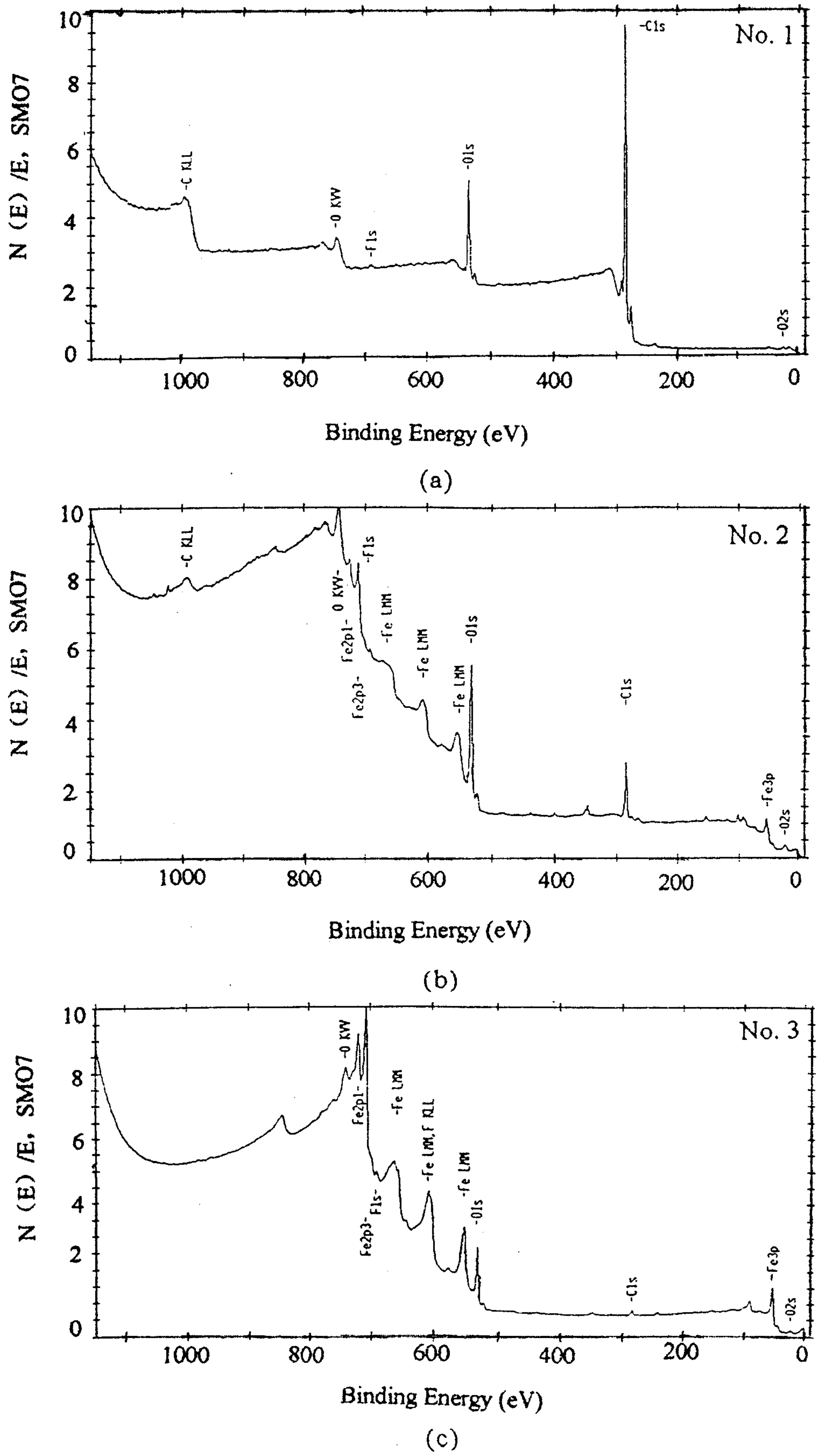
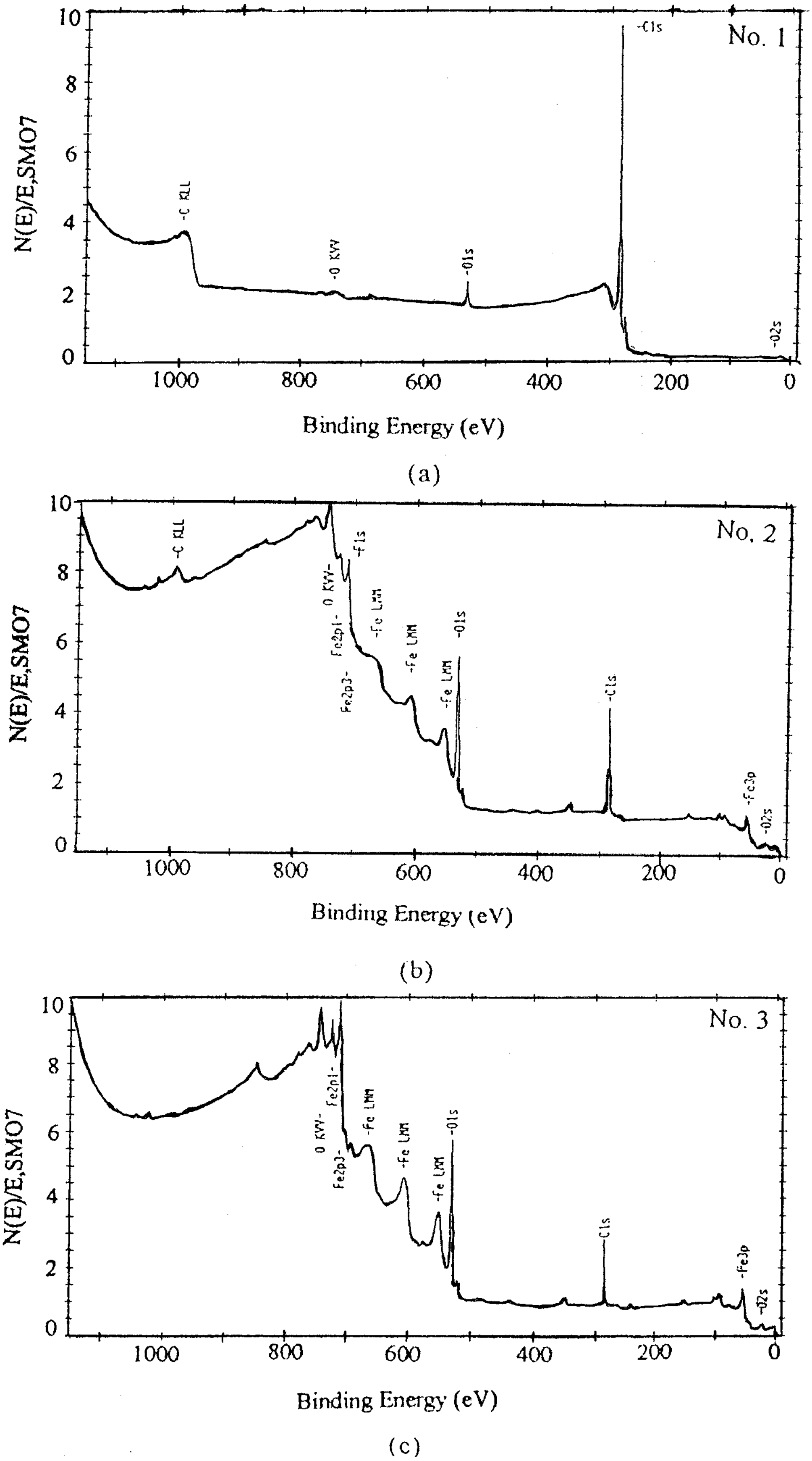


Figure 5 ESCA spectra for PEEK/TF transferred film formed on steeel rings surfaces during dry sliding wear ($P = 1$ MPa, $V = 1$ m s^{-1} and $t =$ 24 h) (a) No. 1; (b) No. 2; (c) No. 3.

one from surface of the film, one from the center and one from the boundary surface between the film and the steel ring. The erosion time estimated depth and estimated compositions are listed in Table II. According to Ref [1], we know that the film of PEEK is thickest and the film of PEEK/FC30 is thinnest, so different erosion time was chosen for different specimens. From Figs 4–6 and Table II, it can be seen.



(a)

(b)

(c)

Figure 6 ESCA spectra for PEEK/FC30 transferred film formed on steel rings surfaces during dry sliding wear ($P = 1$ MPa, $V = \mathrm{m\ s^{-1}}$ and $t =$ 24 h) (a) No. 1; (b) No. 2; (c) No. 3.

(1) One-minute erosion time is not enough for clearing surface. For PEEK and PEEK/TF films, we eroded one minute more, but peak of C_{1s} is still higher, in the same time the peaks of O_{1s} and F_{1s} have appeared, we believe that the surface of the film is analyzed.

(2) After 40 minutes erosion of PEEK film, peak of Fe_{2p3} appeared, we believe the transfer film is analyzed (depth is 80 nm), then the boundary surface between the film and the steel ring is analyzed. 80 minutes erosion later, peak of C_{1s} became very lower, we believe that

TABLE II Concentration analysis of transferred films in ESCA spectra ($p = 1$ MPa, $v = 1$ m s^{-1} and $t = 24$ h)

	Sencitivity factor	PEEK			PEEK/TF			PEEK/FC30		
		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
t_s (min)		2	40	80	2	20	40	1	10	20
d (nm)		4	80	100	4	40	50	2	20	25
Fe_{2p3}	230.574	—	10.18	35.54	—	38.01	52.19	—	13.23	37.29
F_{1s}	122.240	—	—	—	1.11	1.85	1.22	0.66	1.78	1.04
O_{1s}	86.054	13.06	50.38	57.18	12.46	48.22	38.94	3.91	52.76	50.06
C_{1s}	36.864	86.94	39.44	7.28	86.43	11.92	8.10	95.43	32.73	11.61

TABLE III Comparison of mean sliding friction coefficient $\bar{\mu}$ for PEEK, PEEK+8%PTFE and PEEK+10%PTFE+10%graphite+10%carbon fiber pins sliding against steel rings at $P = 1$ MPa, $v = 1$ m s^{-1} and $t = 0.2$ min to 24 h (each has 11 specimens)

No.	1	2	3	4	5	6	7	8	9	10	11	Average
PEEK	0.39	0.39	0.40	0.41	0.41	0.42	0.42	0.43	0.44	0.45	0.46	0.42
PEEK/TF	0.29	0.30	0.32	0.34	0.35	0.36	0.38	0.39	0.40	0.41	0.42	0.36
PEEK/FC30	0.24	0.25	0.27	0.27	0.28	0.28	0.28	0.29	0.29	0.31	0.32	0.28

TABLE IV Comparison of mean specific wear rate $\bar{W}_s$ for PEEK, PEEK+8%PTFE and PEEK+10%PTFE+10%graphite+10%carbon fiber pins sliding against steel rings at $P = 1$ MPa, $v = 1$ m s^{-1} and $t = 0.5$ to 24 h (each has 7 specimens). unit: $\times 10^6$ mm^3/N·m

No.	1	2	3	4	5	6	7	Average
PEEK	8.0	10	11	13	17	27	33	17
PEEK/TF	0.90	3.2	5.3	6.0	7.4	8.2	11	6.0
PEEK/FC30	0.087	0.21	3.0	0.90	1.2	1.5	2.1	0.90

TABLE V Curve fit results of C_{1s} peaks in ESCA spectra for PEEK/FC30 transferred film ($p = 1$ MPa, $v = 1$ m s^{-1} and $t = 24$ h)

Band no.		Peak pos.	Delta	Height	FWHM	Area	% of Total area
a	2	286.40	1.66	7324	1.16	12776	26.76
	1	284.74	0.00	23180	1.42	34961	73.24
b	2	286.96	2.23	881	1.16	1088	6.50
	3	286.21	1.48	2300	1.22	2988	17.85
	1	284.73	0.00	9128	1.30	12661	75.65
c	2	288.10	3.59	837	2.00	1782	14.35
	3	286.15	1.64	1276	1.51	2057	16.57
	1	284.51	0.00	4805	1.68	8574	69.08

the erosion depth had gone to surface of the steel ring, the film thickness of PEEK is estimated at 100 nm. Like this, that of PEEK/TF at 50 nm, that of PEEK/FC30 at 25 nm. This conclusion is agreement with quatitative analysis before.

(3) Even if it is same peak of O_{1s} or O_{1s}, because different linkage has different BE (Table I), so every peak consists of several overlapping peak: Using computer fit program we can know what peak one peak consists of and how much contribution each peak has.

3.3. Curve fit for the peaks of C_{1s} and C_{1s}

For the peaks of C_{1s} and O_{1s} in ESCA spectra of transfer film from PEEK/FC30, we carried out curve fit using computer program provided by the spectrograph. Suppose all constituent peaks are Gauss type, it can be identified by computer that how many peaks one peak consists of, and how many areas each peak is. The criterion is that the curve is agreement with experimental curve of C_{1s} and O_{1s} peaks. Because C_{1s} and O_{1s} peaks listed in Table I have 5–6 peaks and we have not got so many peaks using fit program, so the results from the analysis have only qualitative meaning, they have some error quantitatively. The results are shown in the Figs 7–8 and listed in Tables V and VI. It can be seen from Figs 7–8 and Tables V and VI:

(1) No. 1 spectrum has got after $t_s = 1$ min erosion time (Fig. 6a), highest peak of C_{1s} is contaminated C^+ graphite C atoms. Even so we have found that peak of C_{1s} has a tail at high energy position, a second high peak appears in BE = 286.4 eV position from computer program (Fig. 7a), they are from polymers. It has indicated from Table II that there is oxygen in the films. Peak of O_{1s} is divided into two peaks, one from surface absorbent $SO_4^=$ and H_2O (BE = 531.2 eV), another from polymers mainly (BE = 533.4 eV), Fig. 8a.

(2) No. 2 spectrum (Fig. 6b) has got after $t_s = 10$ min erosion time, the high energy tail of the peak of C_{1s} stretches into higher energy position, the two divided peaks are from polymers. The relative height of the peak of O_{1s} is higher, we estimate the oxygen contents go up over 50%, it indicates that the peak corresponding to

TABLE VI Curve fit results of O_{1s} peaks in ESCA spectra for PEEK/FC30 transferred film ($p = 1$ MPa, $v = 1$ m s^{-1} and $t = 24$ h)

Band no.	Peak pos.	Delta	Height	FWHM	Area	% of Total area
a 2	533.40	2.16	7526	1.62	14163	76.23
1	531.23	0.00	2903	1.43	4417	23.77
b 2	533.03	3.54	2759	1.90	5579	9.76
3	531.59	2.10	10574	1.80	20215	35.35
4	530.75	1.25	6655	1.30	9208	16.10
1	529.49	0.00	12678	1.64	22187	38.80
c 2	532.59	3.14	3962	1.80	7591	13.97
3	531.10	1.65	12357	1.80	23677	43.57
1	529.45	0.00	14004	1.55	23075	42.46

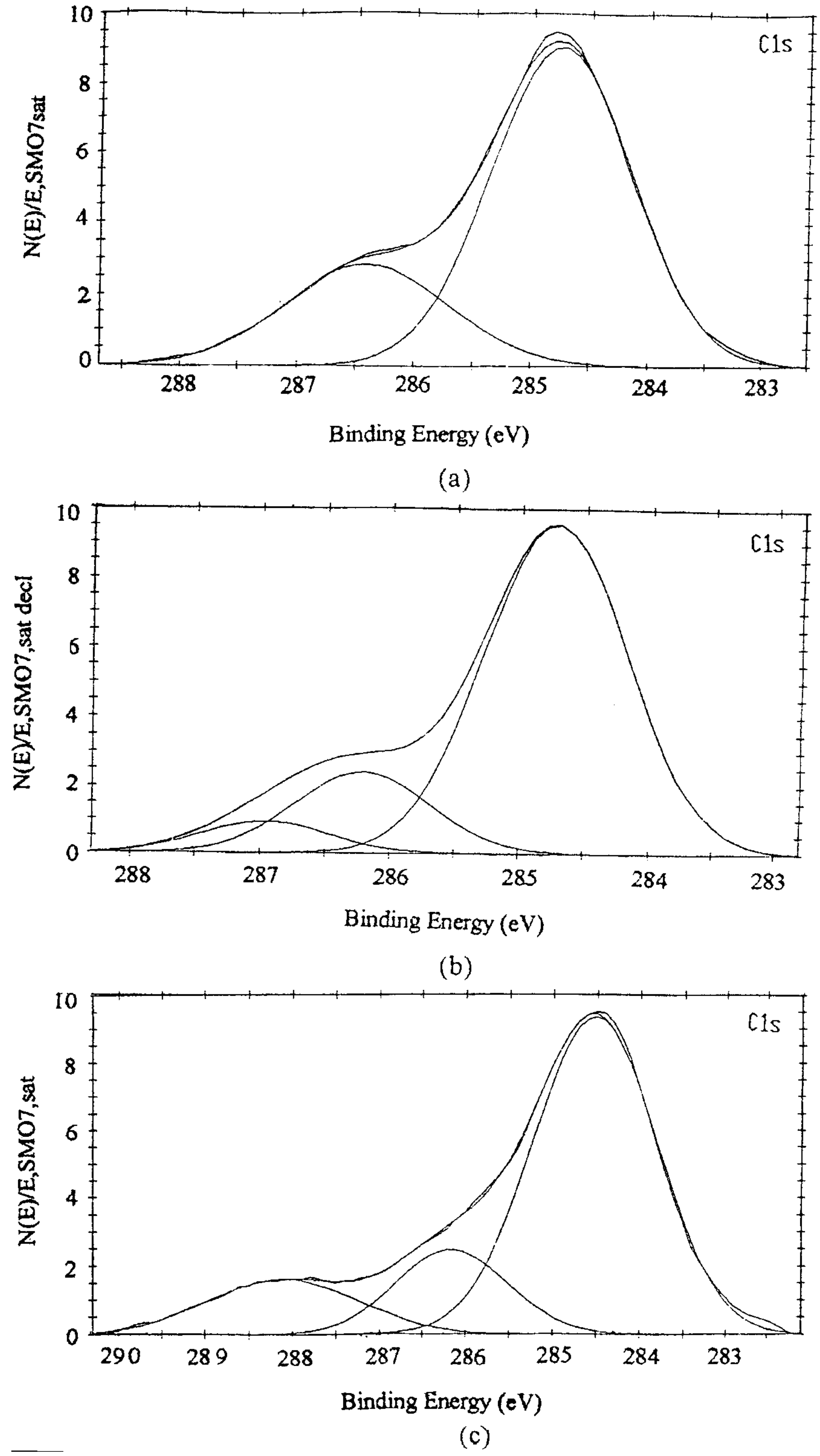


Figure 7 Curve fit of C_{1s} peaks in ESCA spectra for PEEK FC30 transferred film on steel rings during dry sliding ($p = 1$ MPa, $v = 1$ m s^{-1} and $t = 24$ h) (a) No. 1; (b) No. 2; (c) No. 3.

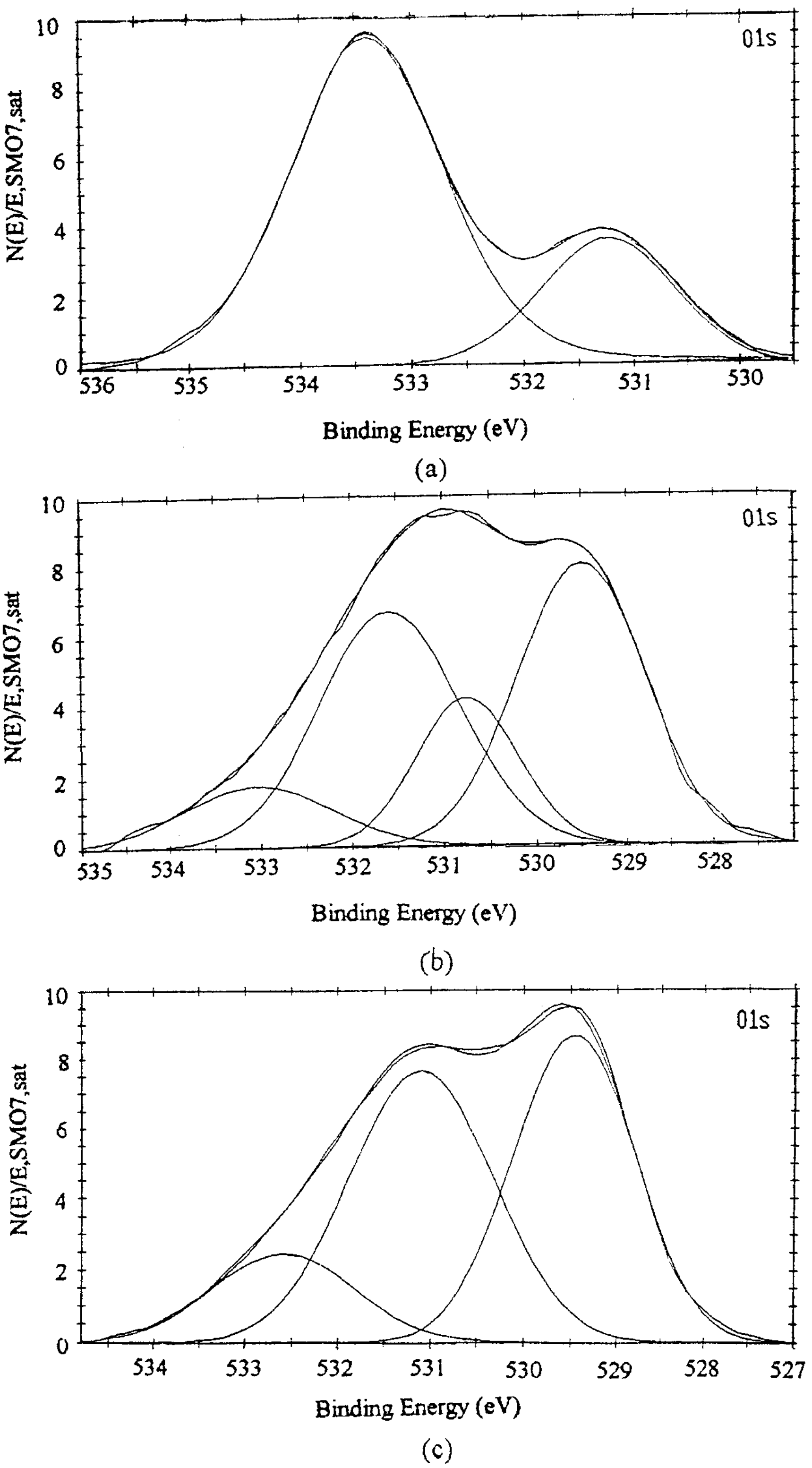


Figure 8 Curve fit of O_{1s} peaks in ESCA spectra for PEEK FC30 transferred film on steel rings during dry sliding ($p = 1$ MPa, $v = 1$ m s^{-1} and $t = 24$ h) (a) No. 1; (b) No. 2; (c) No. 3.

lowest energy is from oxygen of Fe (BE = 530.8 eV) (Fig. 8b), it contains 16% of total areal, other peaks are from polymers. Appeared the peak of Fe indicates that erosion has happened at boundary between the film and the steel.

(3) No. 3 spectrum (Fig. 6c) has got after $t_s = 20$ min erosion time. The peak of C_{1s} is lower and the peak of Fe_{2p3} is higher, it indicates that erosion has happened at boundary. Analyzing carefully divided peaks of the peak of C_{1s}, we have found that there is still two divided peaks at high energy position, it means some signal are from polymers. Especially one peak appears at BE = 288.1 eV position (Fig. 7c), it shows that firstly the transfer film forms from PTFE. Although oxygen contents in the film do not changes very more, but the shapes of the peaks of O_{1s} between No. 2 and No. 3

spectra are different. After fit program we have found that more signals are from Fe_2O_3. The graphite C atom of peak of C_{1s} has high ratio, it shows solid lubricated graphite material transfers preferentially.

4. Formation mechanism of polymer transferred films

The polymer transferred film is formed during sliding against metal counterfaces, it is important tribological property of polymers and its composites, and it decides directly the friction coefficient μ and the specific wear rate $\dot{W}_s$. Usually it is believed that the formation of the transferred films is because of adhesive force on the counterface [8, 9]. According to the analysis of this paper, especially the analysis of ESCA spectra, we not only have known more about existence and properties of the transferred films, but also can discuss the formation mechanism of the polymer-transferred film.

Fig. 9 shows how to form the transfer films on the steel counterface for PTFE and three kinds of PEEK based materials. PTFE transfer film has been studied mostly. Markinson and Tabor [8] pointed out the transfer film is formed on the basis of the banded structure, Tanaka *et al.* proposed the formation mechanism of the transfer film (Fig. 9a) Ref. [9]. The PTFE molecule has 13–15 CF_2 basic functional clusters. It has a smooth molecular profile, no branching and no cross-links. In Fig. 9a by the straight line segment is meant banded structure, and by the broken line segment is meant non-crystalline structure. When the molecule of PTFE along surface of the steel, it's crystal zone intends gradually to arrange along sliding direction the molecules of several layers of PTFE transfer gradually to the surface of the steel, so that the transfer films have formed.

Applying the model of banded structure of the crystallite PTFE, Tanaka *et al.* Pointed out that the fibre-like wear particles is produced first by the serial connection of crystalline slices and then the transferred film of THICKNESS $\delta \sim 20$–30 nm is formed by the lateral connection of adjacent fibres. The molecular orientation in this film is in the direction of the length of the film. It is natural to consider that the amorphous region between crystalline slices has a viscoelastic nature. This concept of the formation of transferred polymer films is consistent with experimental facts, so that it can be used for the PEEK based materials.

The mechanical properties of the neat PEEK is much better than those of PTFE, its Rockwell hardness (R scale) is $\sim$100, its strength is $\sim$60 MN m^{-2} and its uniaxial tension strength is $\sim$90 MN m^{-2}. The common structure of the neat PEEK is spherulites (Fig. 3). The protospherulite is actually a scarf-like structure for the neat PEEK (Fig. 3a). Then the families of crystalline entities initiate from a nucleation point and grow in an approximately spherical manner before impinging with their neighbours (Fig. 3b). Finally, when different crystals meet with each other, the boundary impingingement takes place for these crystals (Fig. 3c). During sliding wear process, these boundaries are destroyed, the crystals at surface near the contact region are deformed, and could be broken down under the adhesion

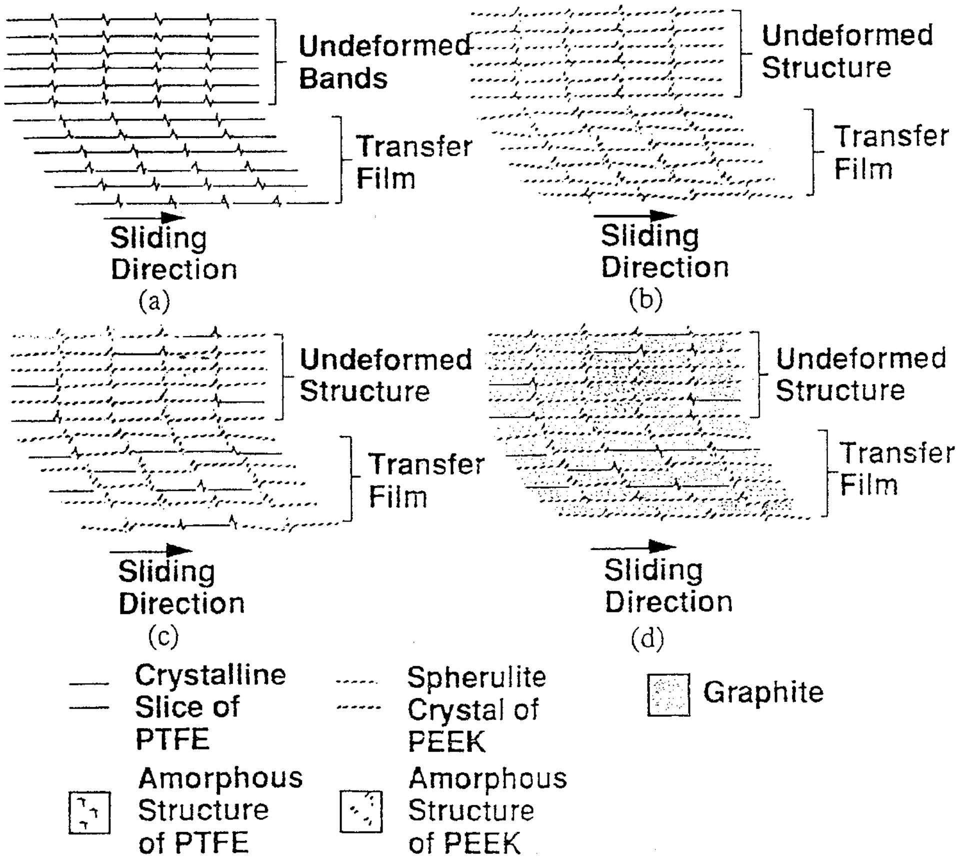


Figure 9 Schematic of mechanisms of the formation of polymer transfer films (a) PTFE; (b) PEEK; (c) PEEK/TF; (d) PEEK/FC30.

action. On one hand, some of them become the wear debris and leave the interface. But others, on the other hand, could transfer to the steel counterface and become the transfer film. Based on this consideration, a mechanism of the formation of the transfer film for the neat PEEK can be proposed (Fig. 9b). The main deference between the mechanisms of the formation of the transferred film for PTFE and PEEK is that the transferred PEEK film consists of spherulite textures. Their orientation is different at the surface region compared to the bulk. The molecules are highly oriented not perfectly as those of a PTFE transfer film. Because of the different structures between the PEEK and the PTFE the thickness, the composition and adhesiveness of the transferred film on the steel counterfaces and back on the worn PEEK surfaces are also different. According to this mechanism, it can be explained that roughness of the steel counterface greatly influences on the formation of transferred film and so specific wear rate $\dot{W}_s$. It is known that the specific wear rate $\dot{W}_s$ of the PEEK is dependent on the steel counterface topography, and a relative minimum of the wear rate occurs under dry, lightly loaded conditions for counterfaces having a rms roughness in the range of 0.1–0.2 μm. If the steel counterface is much smoother than this value, the contact region is too large to avoid severe adhesive wear and the rate of the formation of the transfer film. It can be scraped of rapidly. In the contrary, if the roughness of the counterface is high, the rate of scraping off the transferred film is high enough so that the continuity of the transferred film decreases.

The molecules of PEEK have spherulite structure, when they have cluster structure (Fig. 1). In Fig. 9b by the point line segment is meant its non-crystalline structure. When the molecules slide along the steel surface, the arranging of the crystal zone of PEEK is not so good order like that of PTFE, so a uniform and continuous transfer film can not be easy to form, usually the thickness, at which transfer film appeared, is larger. Because of friction is stronger, the transfer films have thermal effect of friction is stronger, the transfer films have thermal degradation, so the μ and $\dot{W}_s$ for PEEK are higher.

For the PEEK/TF specimen, the main effect of adding 8% PTFE to neat PEEK is the improvement of the solid lubrication. When PTFE is added to PEEK, it would be help to form the uniform and continuous transfer films, and the thickness of the films become thinner (Fig. 9c). The values of μ and $\dot{W}_s$ dropped down more.

For the PEEK/FC30, there is graphite in the specimen which includes graphite and carbon fibres made which are also made of graphite, they are meant by shadow in Fig. 9d. The graphite is also a good solid lubricant. These two kinds of filler as well as the PTFE influence the formation of the transfer film significantly. It can be seen that the specific wear rates $\dot{W}_s$ of the PEEK/TF and PEEK/FC are much smaller than that of the neat PEEK. The transferred films are one of important reasons.

The formation process of the PEEK/FC30 sliding against the steel counterface is like that: first, the carbon fibres on the surface is broken down to very small pieces of the graphite, the fragments of the carbon fibres fill in the spaces between aspirates on the steel counterface, at that stage, the specific wear rate $\dot{W}_s$ of the PEEK/FC30 is large; then the transfer film on the steel counterface is formed by means of the adhesive action between polymer and steel; finally the back transferred film on PEEK/FC30 surface is also formed. After this, the sliding process happens between transferred films. Because these films are stable and have good adhesibility with the bulk materials, the sliding friction coefficient μ and the specific wear rates $\dot{W}_s$ of the PEEK/FC30 become much smaller than those of the neat PEEK. At this time the transfer film formed gradually is thinnest, its uniformity and continuity are best. The composition of the transfer film changed more along the depth direction. This was confirmed by experiment in ESCA spectra of transfer films. Especially based on analysis of fit curve of the peaks of C_{1s} and O_{1s}, We know there is preferential transfer in graphite and PTFE as compared with PEEK.

To sum up, we call this adhesive transfer mechanism.

5. Conclusions

(1) Three kinds of based on materials (PEEK, PEEK/TF and PEEK/FC30) form transferred films on the steel counterface. Different properties of the transferred films decide their different values of μ and $\dot{W}_s$.

(2) The transferred film of PEEK has thermal degradation because of friction thermal effect, its molecular structure changes, its recrystallization content is highest. This kind of effect of another two transferred films is smaller.

(3) The section analysis in ESCA spectra of transfer films indicates that in the continuous area of the films, the film of PEEK are thickest (100 nm), the film of PEEK/TF second (50 nm), and the film of PEEK/FC30 thinnest (25 nm). The change of composition of the films along depth direction indicates that there is preferential transfer in graphite and PTFE for the film of PEEK/FC30. Based on this an adhensive mechanism is proposed.

Acknowledgements

The authors gratefully acknowledge Prof. K. Friedrich of Institute of Composite Materials (IVW) for giving advises in this research. We are indebted to Prof. J. Yong of Analysis Center, Tsinghua University, for the ESCA tests. We would like to thank the German Science Fund and the Tsinghua University Science Fund for their financial support.

References

1. RENJI ZHANG, A. M. HÄGER and K. FRIEDRICH, Polymer Transferred Film on Steel Surfaces for PEEK and its Composites During Sliding Wear IVW Bericht 94-7, University of Kaiser-Slautern, Germany, 1994.
2. H. H. KAUSCH, "Advanced Thermoplastic Composites: Characterization and Processing" (Hauser and Mücher, Germany, 1992).

3. F. N. COGSWELL, "Thermoplastic Aromatic Polymer Composites" (Butterworth-Heineman, UK, 1992).
4. RENJI ZHANG, CAIFEN WANG, A. M. HÄGER and K. FRIEDRICH, *Electron Microscopy Journal* **13** (1994) 452 (in Chinese).
5. R. ZHANG, A. M. HÄGER, K. FRIEDRICH, Q. SONG and Q. DONG, *Wear* **181–183** (1995) 613.
6. D. J. BLUNDELL and B. N. OSBORN, *SAMPE Quarterly* **17**(1) (1985) 1–6.
7. R. ZHANG, A. M. HÄGER and K. FRIEDRICH, Study on Polymer Transferred Film for PEEK and its Composites During Sliding Wear, Advances of Nanometer Tribology (These of 1995 National Symposium of Nanometer Tribology) (Tsinghua Univ. Press. of China, 1996) p. 149 (in Chinese).
8. K. R. MAKINSON and D. TABOR, *Proc. R. Soc. (London), Ser. A* **28** (1964) 49.
9. K. TANAKA, Y. UCHIYAMA and S. TOYOTA, *Wear* **23** (1973) 153.

Received 17 October 1997
and accepted 22 September 1998