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Thermal, Crystalline, and Tribological Properties of PEEK/PEI/PES Plastics Alloys

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ABSTRACT: PEEK/PEI/PES plastics alloys in weight ratios of 70/30/0, 70/25/5, 65/30/5, 60/30/10, 60/35/5, and the three kinds of single high performance engineering plastics 100/0/0, 0/100/0, 0/0/100 were prepared by twin-screw extrusion molding. A single glass-transition temperature (T_g) of each alloy in the former five kinds of the plastics alloys could be measured by DSC and always rose to higher one than that of the pure PEEK by about 20°C. The crystalline degrees of these alloys could also ascended to more than 35.81% higher than that of the pure PEEK, especially for the alloy of the ratio 60/30/10 reached the maximum crystalline degree 37.76%. Adding PEI or PEI and PES, the crystalline temperatures of the PEEK alloys were decreased. The wear resistances of the alloys under dry sliding condition were considerably improved compared with pure PEI or PES, and the specific wear rate of the pure PEI or PES were four to six times as large as that of the alloys. However, the specific wear rates of the alloys were six to eight times larger than that of the pure PEEK, and the friction coefficients of the alloys were higher than that of the pure PEEK for 0.2–0.3. The polymeric transferred film on the steel ring surface against the alloys could be found, but no film on that against pure PES or PEI was found. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: poly (ether ether ketone) (PEEK); poly (ether imide) (PEI); poly (aryl ether sulfone) (PES); plastics alloy; crystallization; tribological property

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INTRODUCTION

Because of the possibility of tailoring and reinforcing the properties of thermoplastic composites with special fillers or short fibers, these materials could be widely applied for numerous purposes such as seals, gears, and bearings or providing light weight alternatives to the original metallic components in the past decades.[1–3] Polymer blends, especially plastics alloys, such as poly (ether ether ketone) (PEEK) blend with poly (ether imide) (PEI) or poly (aryl ether sulfone) (PES) could be also developed with great interesting.[4–6] PEEK, a kind of semicrystalline high performance engineering plastics, has prominent advantages in mechanical strength, thermal stability, high melting point (T_m: 334°C), electrical insulativity and chemical stability, but its glass-transition temperature (T_g: 143°C) lower. The both amorphous high performance engineering thermoplastics, PEI and PES, display high heat resistance, high glass-transition temperature (T_g: 215°C, 220°C), high strength and modulus, and good electrical insulativity[4,7,8]; however, PEI has a low chemical resistance,[5,6] and PES has a poor organic solvents resistance. It was also well known that plastics alloys with excellent comprehensive performance could be obtained by blending. However, only two components alloys among these three plastics such as the alloy of PEEK and PEI or PES, were investigated reported in literatures.[8,9] Few research reports emphasized on the three components alloys based on PEEK. In this paper, some ternary plastics alloys of PEEK, PEI, and PES with lower cost were prepared by blending, which could be used for insulating sheath of the special cable in nuclear power engineering, and crystalline and tribological properties of these ternary alloys were investigated, compared with that of pure PEI, PES, or PEEK.

EXPERIMENTAL

Materials

The type of PEEK 012P, which number-average molecular weight (M_n) was 60,000, and PES, M_n 65,000, which powder of 250 μm in diameter, were supplied by Changchun Jida

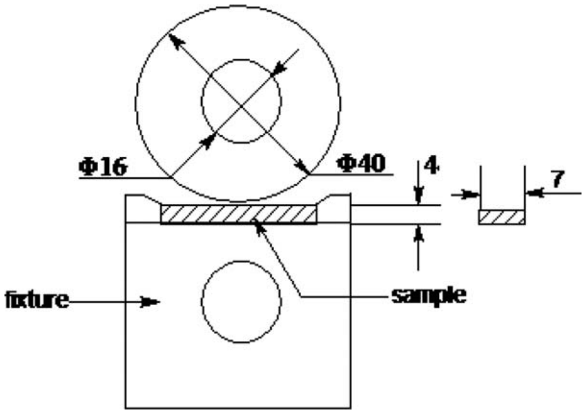

Figure 1. The testing samples and the fixtures device in the sliding wear apparatus.

Engineering Plastics Research, in which PEEK material had a T_g of 143.3°C and a T_m of 335°C, and PES had also a T_g of 230.2°C. PEI, M_n 50,000, had a T_g of 216.5°C, its powder of Ultem1000 was supplied by SABIC.

Preparation of Polymer Specimens

PEEK, PEI and PES were blended in weight ratios of 70/30/0, 70/25/5, 65/30/5, 60/30/10, 60/35/5, 100/0/0, 0/100/0, and 0/0/100, respectively, by TSE-30A twin-screw extruder supplied by Nanjing RuiYa Polymer. Before blending, the three polymers were completely dried overnight in an air-circulated oven at 150°C. Extrusion processing parameters: temperatures of extruder sections for 310–370°C, screw speed 10–30 r/min, head pressure 9–11 MPa. Compression molding was used to prepare the specimens in test, which parameters: molding temperature for 370°C, molding pressure for 5 MPa at 350–370°C and for 10 MPa at 275–350°C, holding molding pressure temperature of 370°C for 20 min, stripping temperature 150°C.

Differential Scanning Calorimeter Analysis

A Q2000 Type PerkinElmer differential scanning calorimeter (DSC) made by TA Instruments was used to measure the thermograms of the alloys of PEEK/PEI/PES and pure PEEK, PEI, PES. The samples with a nitrogen atmosphere and 50–400°C testing temperature were heated at 10°C min^{-1}, then cooled at −10°C min^{-1} to room temperature. All kinds of the sample materials were analyzed two times. Their T_g, T_m, crystallization temperature (T_c) and enthalpy of melting (ΔH^*m) were evaluated. Degree of crystallinity (X_c) would be positive with mechanical properties of materials and could be calculated as eq. (1).

$$X_c(\%) = \frac{\Delta H_c}{\Phi \Delta H_m} \times 100\% \quad (1)$$

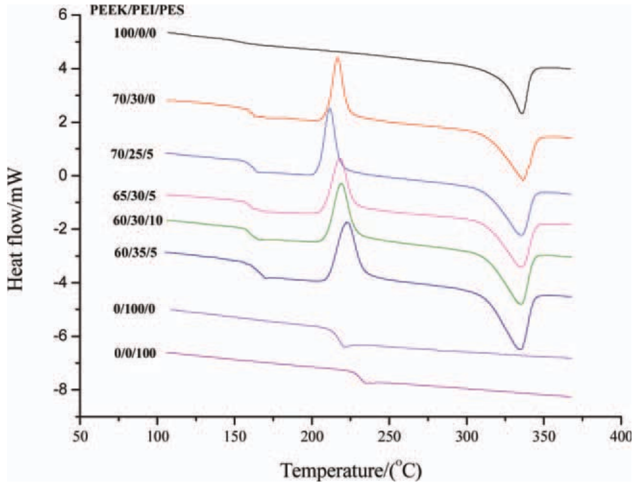

Figure 2. DSC curves of rising temperature for the alloys of different contents of PEEK/PEI/PES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Where the crystallization enthalpy (ΔH_c) can be obtained from the area enclosed by the peak of DSC melting curves and the baseline, and ΔH_m, the melting enthalpy while the degree of crystallinity is 100%, is 130 J/g,[10,11] and Φ is the weight fraction of PEEK.

Friction and Wear Test

The testing apparatus for friction and wear properties of the plastics alloys under sliding condition against the steel rings, M-2000A Type Wear Tester made by Zhangjiakou Xuanhua Kehua Tester (Shanghai City, China) was used, and the testing samples and the fixtures in this tester were outlined in Figure 1. The steel rings in the sliding friction wear device were made of 30CrMnSiA, which surface hardness was HRC 50-55. The friction wear tests without lubricant in laboratory at room temperature and relative humidity of about 50 ± 10% were conducted. The plastics alloy specimen was a block with dimensions of 30 mm × 7 mm × 4 mm, the testing load was 200 N, the rotating speed was 200 r/min, the testing cycle was 120 min, but that of pure PEI or PES was 20 min. The wear scar width on the plastic specimen could be measured respectively by the JC-10 optical microscope with micro scale supplied by Shanghai Fifth Optical.

Dynamic curves of friction and the friction coefficient were calculated with eq. (2).

$$\mu = M/(r \cdot F) \quad (2)$$

where μ is the friction coefficient, M is the average friction torque, F is the vertical load, and r is the radius of the steel ring.

Table I. T_g of the Alloys of PEEK/PEI/PES

Ratios(w/w)	100/0/0	70/30/0	70/25/5	65/30/5	60/30/10	60/35/5	0/100/0	0/0/100
T_g/°C	143.3	160.6	161.2	163.0	163.2	164.5	216.5	230.2
T_g^a/°C	-	159.8	159.6	162.6	166.1	165.7	-	-

$^a T_g$ were calculated by the Fox equations with the tested T_g of pure PEEK, PEI and PES.

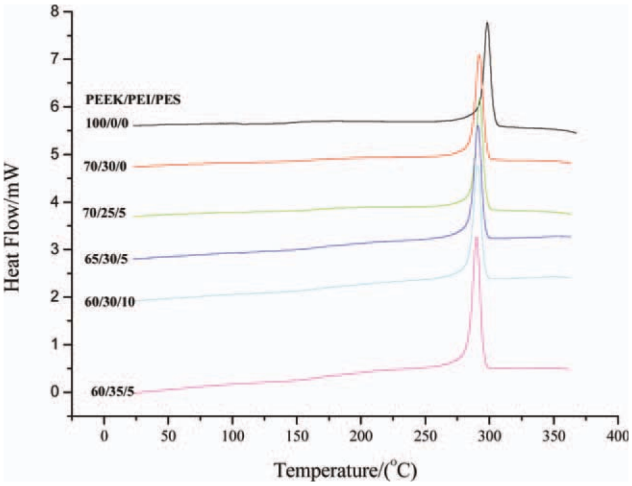

Figure 3. DSC crystallization curves of dropping temperature for the alloys of different contents of PEEK/PEI/PES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

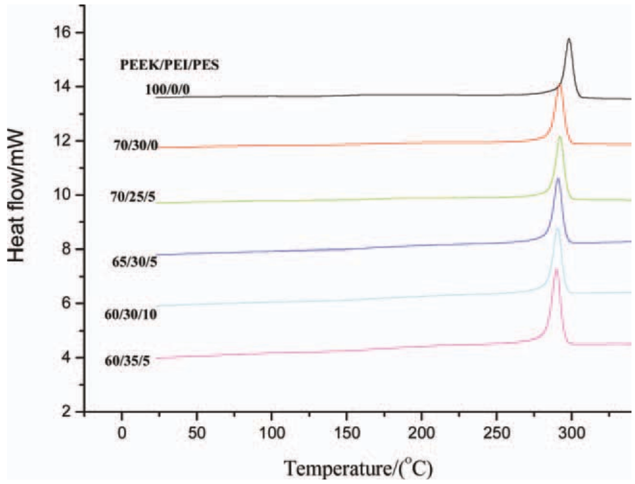

Figure 4. DSC crystallization curves of annealing for the alloys of different contents of PEEK/PEI/PES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The wear volume (V_s) was calculated in cubic millimeters as given in eq. (3) and the specific wear rate (W_s) was calculated by eq. (4).[12]

$$V_s = 7 \cdot [(\pi r^2/180) \cdot \arcsin(B/2r) - B\sqrt{4r^2 - B^2}/4] \quad (3)$$

$$W_s = V_s/L \cdot F \quad (4)$$

where L is the sliding distance, B is the width of wear scar. For each testing condition, three parallel tests were performed and the average results were employed.

RESULTS AND DISCUSSION

Thermal Properties of the PEEK/PEI/PES Plastics Alloys and Compatibility between the Component Plastics

In Figure 2 and Table I the T_g of pure PEEK, pure PEI, and pure PES could be measured for 143.3, 216.5, and 230.2°C, respectively; however, only a single T_g for the five alloys of PEEK/PEI/PES could exhibit from 160.6 to 164.5°C. The alloy of PEEK/PEI/PES in a weight ratio of 70/30/0 presented the minimum T_g for 160.6°C, but the other alloy of PEEK/PEI/PES in the ratio of 60/35/5 had the maximum T_g for 164.5°C. It would be presented in the results that T_g of PEEK would be raised with adding PEI or PEI and PES, to reach higher than that of pure PEEK about 20°C, which could reveal that PEEK, PEI, and PES had a good compatibility and could be blended to a certain extent at high temperature.

It had been reported that there could be an intense reciprocity between PEI and PES that have a good compatibility,[13] and two closed Tg of the PEEK/PES blends, which would display only a partial compatibility, would be measured,[14,15] and the blends of PEEK and PEI would present a good compatibility between the both plastics.[16] Therefore, it can be inferred that PEI as a coupling agent could improve the compatibility between PEEK and PES, and only a single T_g for the alloys of PEEK/PEI/PES have been obtained in these tests.

It is known that adding a small amount of low molecular weight diluent, commonly known as a plasticizer, to plastics, the free volume in the system of plastics can be increased and T_g subsequently decreased.[17] Fox equation as eqs. (5) and (6) could serve a model for revealing T_g change of plastics over a given molecular weight range. Fox equations are described in the following.

$$\frac{1}{Tgb} = \frac{w1}{Tg1} + \frac{w2}{Tg2} \quad (5)$$

$$\frac{1}{Tgb} = \frac{w1}{Tg1} + \frac{w2}{Tg2} + \frac{w3}{Tg3} \quad (6)$$

where T_gb is T_g of the blends, and w_1, $w_{2,}$ and w_3 are the weight fractions of components 1, 2, and 3, respectively. T_g1, T_g2, and T_g3 are T_g of components 1, 2, and 3, respectively. It can be seen in Table I that with increasing of the weight fractions of PEI and PES from 30 to 40%, T_g of the PEEK/PEI/PES alloys

Table II. Thermal Property Parameters for the Alloys of PEEK/PEI/PES and the Pure PEEK

Ratios (w/w)	100/0/0	70/30/0	70/25/5	65/30/5	60/30/10	60/35/5
ΔH_c (J/g)	43.77	32.75	32.87	31.40	29.45	27.93
T_C/°C	298.36	291.89	292.27	290.94	290.55	289.97
T_m /°C	336.44	336.29	335.51	335.15	335.14	334.36
ΔH^*_m (J/g)	36.31	26.56	26.66	24.51	24.68	22.55
X_c	33.67	35.99	36.12	37.16	37.76	35.81

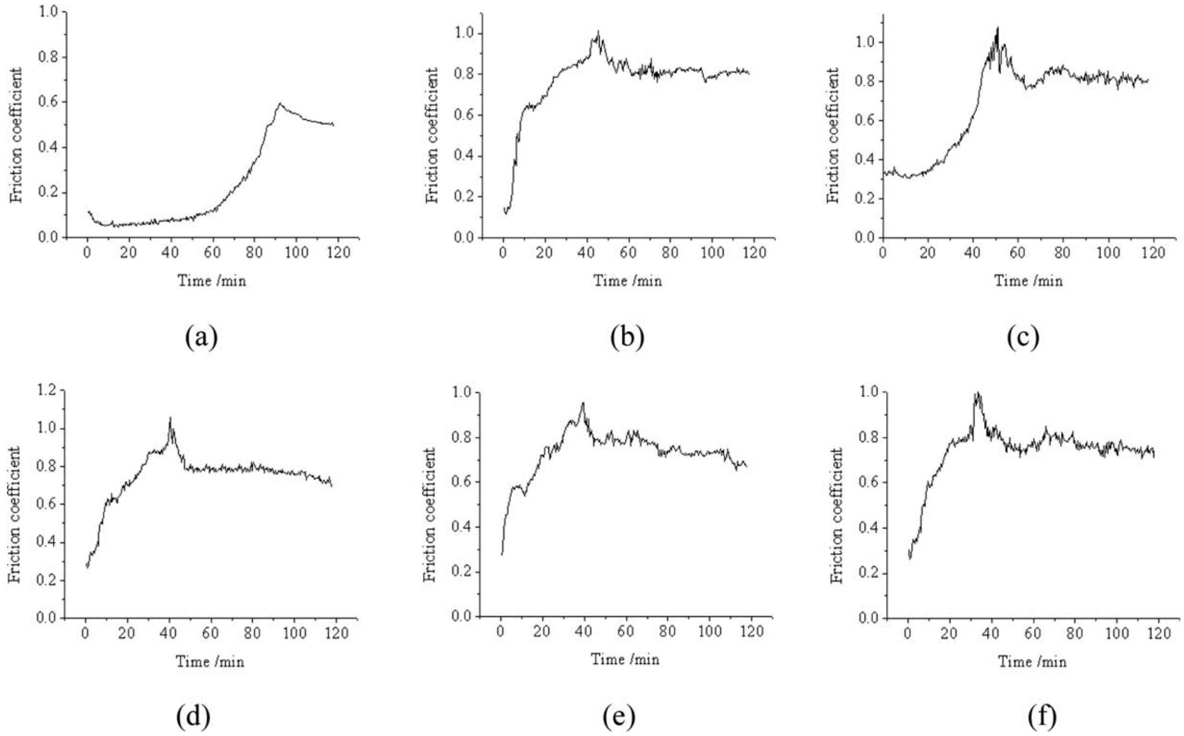

Figure 5. Variations of friction coefficient with time for the alloy plates of PEEK/PEI/PES: (a) 100/0/0, (b) 70/30/0, (c) 70/25/5, (d) 65/30/5, (e) 60/30/10, (f) 60/35/5.

will be increased from 160.6 to 164.5°C. For the miscible blends system, there are many theoretical equations to interpret the relationship between blend compositions and T_g,[18] and Fox equations can be used to determine the phase compositions of the PEEK/PEI/PES alloys here. In fact, T_g can be measured by DSC and would comply with Fox theory equations approximately, but T_g^* are higher than T_g of alloys obtained by experiments. However, addition of PES with the higher T_g would influence on T_g^* more seriously than that of PEI, but there are not any line relationship between the T_g^* and the content of PEI or PES or PEI and PES. It also may be inferred by the fact that the compatibility of PEEK and PES can be improved by adding PEI, because PEI have an intense reciprocity to PES, and PEEK and PEI in the blends have a good compatibility.[13,16]

Crystallization Behavior of the PEEK/PEI/PES Plastics Alloys

It is shown in Figure 3 that adding PEI or PEI and PES can make the crystallization temperature of the alloys deviate from the higher temperature to lower one. Therefore it may be inferred that adding PEI or PEI and PES, though the both are amorphous polymers, the crystallization temperature of alloys would be influenced.

It was reported that the interlamination fluidity of blends could be increased by addition of amorphous diluent, to form easily the order arrangement of chain segments and result in increase of crystallinity degree.[19] In Table II it was shown that the crystallinity degree of the alloys appeared from 35.81 to 37.76%, which all were higher than that of pure PEEK, and the crystallinity degree of the alloy in the ratio of 60/30/10 reached the maximum value of 37.76%. Therefore, it can be proved that PEI or PEI and PES in PEEK based alloys could play the role of the amorphous diluent and increase interlamination fluidity of the alloys, resulting in avail to order arrangement of PEEK chain segments and increase of their crystallinity degree. However, the temperature of crystallization for the alloys would be lower than that for pure PEEK.

DSC crystallization curves of annealing for the alloys of PEEK/PEI/PES with different component contents were measured in Figure 4, and it was shown that the morphology of the crystallization curves of annealing were similar to that of dropping temperature. It could also be proved by the results that addition of PEI or PEI and PES would influence on the crystallization temperature of the PEEK-based alloys.

Friction Behaviors of the PEEK/PEI/PES Plastics Alloys

It was shown in Figure 5(a) that the friction coefficient of the pure PEEK would increase rapidly after testing period of 60 min and reach to the maximum value about 0.6 after 90 min,

Table III. Specific Wear Rate for the Alloys of PEEK/PEI/PES

Ratios (w/w)	100/0/0	70/30/0	70/25/5	65/30/5	60/30/10	60/35/5	0/100/0	0/0/100
$W_s/10^{-5}mm^3/Nm$	0.7005	5.1334	5.2463	5.3518	6.4279	5.6989	24.992	31.255

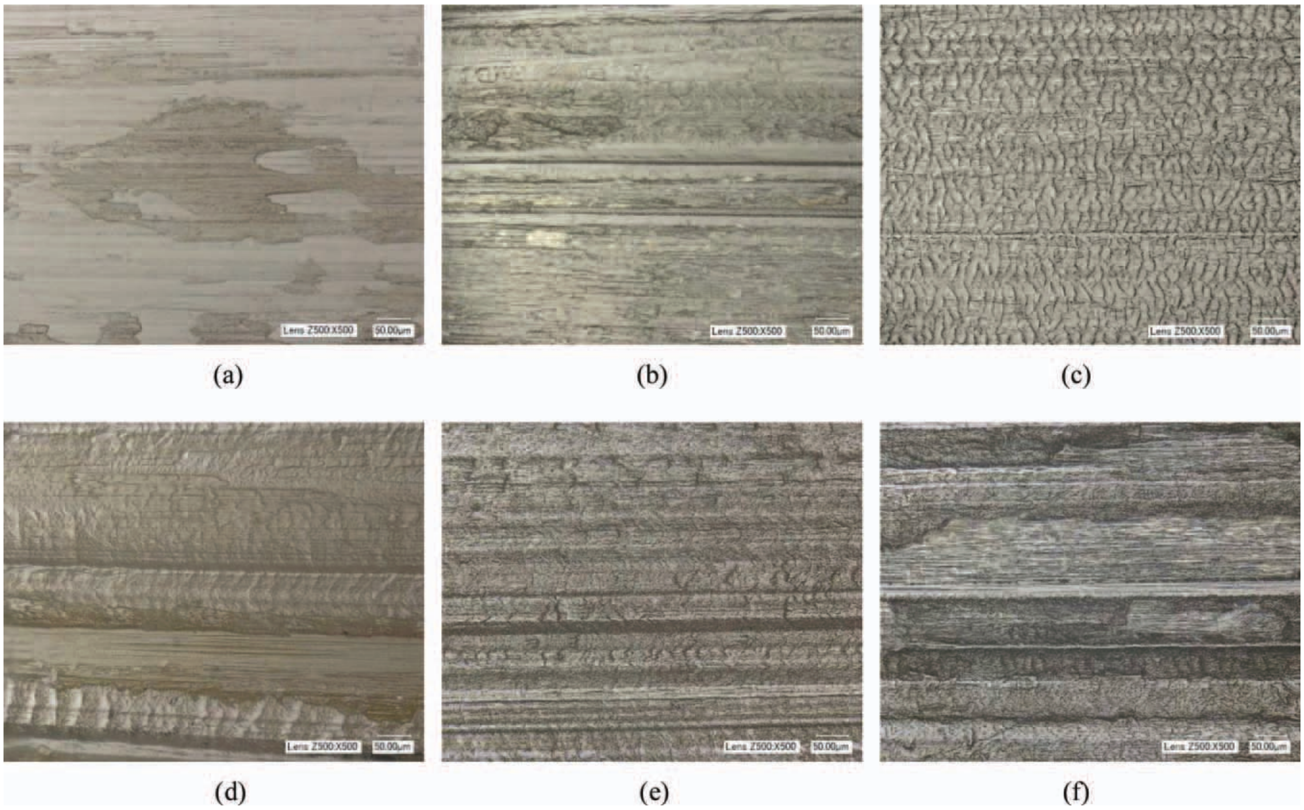

Figure 6. The worn surface micrographs of the PEEK/PEI/PES plastics alloy plates: (a) 100/0/0, (b) 70/30/0, (c) 70/25/5, (d) 65/30/5, (e) 60/30/10, (f) 60/35/5.

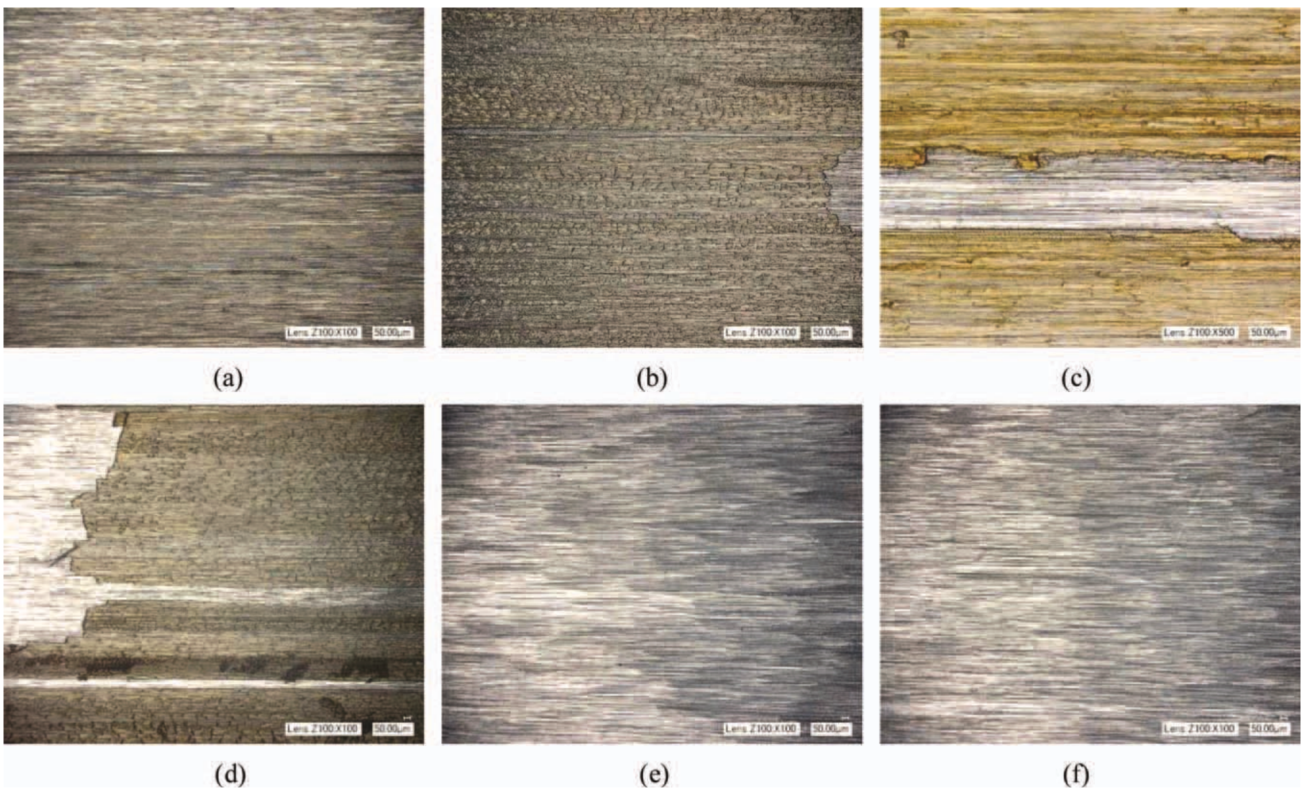

Figure 7. The worn surface micrographs on the steel ring sliding against the plastics or alloys specimens: (a) 100/0/0, (b) 70/25/5, (c) 65/30/5, (d) 60/30/10, (e) 0/100/0, (f) 0/0/100. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but the friction coefficient for all alloys of PEEK/PEI/PES would rise rapidly at the beginning period, as shown in Figure 5(b–f), then the maximum one would usually occur after about 40 min, and that of the alloys would reach to the balance value about 0.7–0.8, which are higher than that of pure PEEK.

During sliding friction and wear of alloys of PEEK/PEI/PES in the beginning period, the contacting areas of the friction pairs would increase obviously, and friction heat would be produced greatly, therefore intensive adhesion action between the surfaces of the friction pair would occur and the friction coefficient of the alloys of PEEK/PEI/PES would rise rapidly in the beginning period.[20,21] When the temperature and the contacting area of the friction pair had reached to the balance value, the friction coefficient would also reach the balance value. For the pure PEEK, the contacting area of the friction pairs would be relative small and adhesion action weak, then the friction coefficient would increase slowly before 60 min, but with increasing contacting area and adhesion action of the friction pairs after 60 min, the friction coefficient also reaches a balance high value.

Wear Resistances of the PEEK/PEI/PES Plastics Alloys

In Table III it was showed that the specific wear rate of the pure PEI or PES were four to six times as large as that of the PEEK/PEI/PES alloys, and the latter was also larger than that of the pure PEEK for six to eight times, by which it would be proved that with adding of PEI or PEI and PES, the wear resistance of the alloys is considerably better than that of the pure PEI or PES, but inferior to that of the pure PEEK.

In Figure 6(a) some stripping scar in part area on the worn surface of the pure PEEK specimen would be observed, and it can be inferred that friction heat would occur in lower scale and in part region and wear mechanism should mainly display adhesion wear. However, in Figure 6(b–f) wear scar as striations even several deep furrows in the worn surface of the PEEK/PEI/PES alloys could be seen; therefore, it would be shown that friction heat of the PEEK/PEI/PES alloys is higher and wear more serious than that of the pure PEEK, and wear mechanism of the PEEK/PEI/PES alloys should also present adhesion wear.

In Figure 7(a) a thin symmetrical and tough transferred film on the worn surface of the steel rings sliding against the pure PEEK specimen would be found, which could result in remission of friction action and decrease of friction heat to avail wear resistance of the pure PEEK specimen. However, in Figure 7 (b–d) the thicker transferred films, in which some part stripping scar occurred, on the steel ring surfaces against the plastics alloys of the weight ratio such as 70/25/5, 65/30/5, and 60/30/10 would be observed, and in Figure 7(e,f) no transferred film on the steel ring surfaces against the pure PEI or PES could be seen, therefore it would be inferred that adding PEI or PEI and PES to PEEK would be adverse to formation of stable transferred films on steel counterface and rise the wear amount of plastic specimens.[22]

CONCLUSIONS

1. In the prepared PEEK/PEI/PES plastics alloys every one exhibited only a single glass-transition temperature and a good compatibility between the components of the alloys, and adding PEI or PEI and PES T_g of the alloys can be increased about 20°C higher than that of pure PEEK.
2. The crystallinities of the alloys appeared between 35.81% and 37.76% and were higher than that of pure PEEK, and the crystallinity of the 60/30/10 alloy had the maximum value of 37.76%; however, adding PEI or PEI and PES, the crystalline temperatures of the PEEK alloys were decreased.
3. The friction coefficients of the PEEK/PEI/PES alloys were higher than that of the pure PEEK for 0.2–0.3, and the specific wear rate of the alloys were six to eight times larger than that of the pure PEEK, however, the specific wear rates of the pure PEI or PES were four to six times as large as that of the alloys. Adding PEI or PEI and PES to PEEK would be adverse to formation of stable transferred films on the steel ring surface and wear resistance of plastic specimens.

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