

Mechanical and Tribological Properties of PA66/PPS Blend. II. Filled with PTFE

Zhaobin Chen,* Xujun Liu, Tongsheng Li, Renguo Lü

Department of Macromolecular Science, Key Laboratory of Molecular Engineering of Polymer, Ministry of Education, Fudan University, Shanghai 200433, People's Republic of China

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ABSTRACT: The mechanical and tribological properties of 70 vol % PA66/30 vol % PPS blend filled with different content of polytetrafluoroethylene (PTFE) were studied in this paper. It was found that the addition of PTFE impairs the mechanical properties of PA66/PPS blend, but greatly increases the wear resistance and decreases the friction coefficient. When PTFE content exceeds 20 vol %, the friction coefficient of composite is minimum (0.15) and lower than that of pure PTFE under the same conditions (0.22). The lowest wear volume (0.44 mm^3) is obtained with PA66/PPS/30 vol % PTFE composite, which decreased by 91% compared with unfilled PA66/PPS blend (4.99 mm^3). The topography of transfer film and the elemental distribution were investigated by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS), respectively.

Because of the characteristic crystalline structure, PTFE preferentially transferred to the steel ring surface and formed a thin, uniform and firmly adhered transfer layer, which reduced the ability of PA66/PPS blend to transfer and prevent the adhesion between the sample and the counterface. In addition, the superior lubrication of PTFE inhibited the frictional heat melting during sliding. All these aspects are close related to the friction and wear behavior of PA66/PPS/PTFE composite. Upon the addition of PTFE, thermal control of friction regime is not applicable to the PA66/PPS blend. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 969–977, 2006

Key words: polyamide66 (PA66)/polyphenylene sulfide (PPS) blend; composite; friction; wear; surface

INTRODUCTION

Polymeric materials have been replacing metallic materials used as friction and wear parts for many years. It is often found that, however, the single unmodified polymer could not satisfy the demands arising from situations where a combination of good mechanical and tribological properties is required. Therefore, it is necessary for improving polymer to provide it with outstanding properties using different methods, including copolymerizing, blending, filling with fibers and/or fillers, etc. Polymer blending is fascinating in polymer modification because it has simple processing and unfolds unlimited possibilities of producing materials with variable properties. Some researchers studied the tribological properties of polymer blends and pointed out that the friction and wear properties vary continuously with the compositions for most of the polymer blends involved and the optimal properties were obtained at a certain composition, although some data reported were conflicting.^{1–9} Unfortunately,

the studies on the tribological properties of polymer blends are very limited.

Polyamide (PA) and polyphenylene sulfide (PPS) are widely used engineering and high performance plastics. Many studies have been carried out on their tribological properties under dry conditions.^{10–18} When sliding against a metal, the superior wear resistance of PA relative to other polymers has been attributed to its ability to form an adhesive transfer film on counterface, while the lack of this ability leads to the higher friction coefficient and wear of PPS. The addition of internal lubricant (PTFE, silicon oil, etc.) and/or the antiwear fillers (inorganic powders, fibers, etc.) can significantly decrease the friction coefficient and increase the wear resistance of PA and PPS.

To elucidate the friction and wear mechanisms of polymer blends, in previous papers,^{19–21} we selected PA66, PPS, and HDPE as components, which possess different thermal, mechanical, and tribological properties between each other, prepared PA66/PPS and PA66/HDPE blends, respectively, and studied the tribological properties and the effect of phase structure on the friction and wear behaviors of polymer blend. It was found that, for PA66/HDPE blends with different phase morphologies, the better the compatibility between the polymer components the better the tribological properties. The thermal control of friction model is applicable to PA66 blends under severe con-

*Present address: Department of Human Ecology, The University of Texas at Austin, Austin, TX 78712 (wanderer@mail.utexas.edu).

Correspondence to: T. S. Li (lits@fudan.edu.cn).

TABLE I
Data of the Materials Used in This Study

Material	Form	Trademark	Manufacturer	Density (g/cm ³)	Melting point (°C)	Friction coefficient ^a	Wear volume ^a (mm ³)
PA66	Pellet	Zytel® 101L NC010	Du Pont Co. Ltd.	1.14	262	0.67	6.71
PPS	Powder	Ryton® P-4	Chevron Phillips Chem. Co.	1.35	285	0.85	46.4
PTFE	Powder	Aflon G163	Asahi Glass Co. Ltd.	0.33	372	0.22 ²²	371 ²²

^a Block-on-ring configuration, sliding speed: 0.42 m/s; normal load: 196 N, counterface: stainless steel.

ditions, i.e., the friction coefficient of blends is governed by the polymer component with lower melting (or softening) point, independent of the blend composition, while the wear behavior is mainly attributed to the component having higher melting (or softening) point in system.

In this paper, the authors studied the possibility of further improving the tribological properties of PA66/PPS blend by addition of internal lubricant PTFE. On the other hand, the effect of PTFE on the friction and wear mechanisms of PA66/PPS blend was discussed in virtue of SEM observation and EDS analysis.

EXPERIMENTAL

Materials

The data of PA66, PPS, and PTFE used in this study are listed in Table I. The average diameter of PPS powders is in the range of 30–50 μm ; the median particle size is 25 μm .

Sample preparation

In prior work,¹⁹ the authors found that 70 vol % PA66/30 vol % PPS blend with better mechanical properties exhibits lower friction coefficient and the highest wear resistance. On the basis of this, the same blend system was selected as a matrix to study the improvement of PTFE over the PA66/PPS blend and its effect on the friction and wear mechanisms.

To obtain a sufficient homogeneity, two-step processing method in polymer blending was employed. In the first step, the solid lubricant PTFE powders were dispersed in mixture solution of water and ethanol, and then PPS powders were added. The mixtures were vigorously stirred, filtered, and dried under reduced pressure at 100°C for 24 h to remove residual water and ethanol. The received PPS/PTFE powder mixtures were preblended using a HAAKE PTW16/25D corotating twin-screw extruder. The diameter of the die is 3 mm. The temperatures from the feed zone to the die of the extruder were 275, 275, 295, 305, and 295°C, respectively. The screw speed was set at 90 rpm. The extrudate was obtained in the form of a cylindrical rod that was quenched in cold water and then pelletized.

In the second step, PA66 pellets were blended with extruded PPS/PTFE pellets using the same extruder and followed the same procedure, but the temperatures of the barrel were kept at 265, 275, 285, 295, and 285°C, respectively. PA66 pellets were dried at 100°C in vacuum oven for 24 h before compounding.

The specimens for mechanical and tribological tests were injection molded from the blended materials using a SZ-20 reciprocating screw injection-molding machine equipped with a standard test mold. The temperatures maintained in the two zones of the barrel were 280 and 300°C, and in the mold 25°C.

Measurements of mechanical and tribological properties

The tests of tensile strength, flexural strength, impact strength, and Rockwell hardness (HRM) were carried out according to GB/T 16,421–1996, GB/T 16,419–1996, GB/T 16,420–1996, and GB/T 9342–88, respectively.

The friction and wear tests were conducted on an M-200 friction and wear tester, according to GB 3960–83 standard test method. The contact scheme of the frictional pairs is shown in Figure 1. A carbon structure steel ring (No.45, GB 699–88) of 40 mm outer diameter was used as the counterpart. The polymer specimen block was 6 × 7 × 30 mm³. Before each test, the surface was polished with metallographic abrasive paper to Ra 0.17–0.23 μm for the specimen and Ra 0.09–0.11 μm for the counterpart. Then the block and the ring were cleaned ultrasonically in acetone and thoroughly dried. Sliding was performed under ambient conditions (temperature: 20 ± 3°C, humidity: 50 ± 10%) at a speed of 0.42 m/s and a normal load of 196 N. The test duration ranged from 0 to 130 min, and the value of friction force torque was noted after 10 min and later at intervals of 20 min. The transient friction coefficient was calculated from the friction force torque. The average value of transient friction coefficient in the steady state (after 30 min) was used as the friction coefficient of the sample. At the end of each test, the width of the wear scar was measured with a measuring microscope, and the wear volume V of the specimen was calculated from the following formula:²³

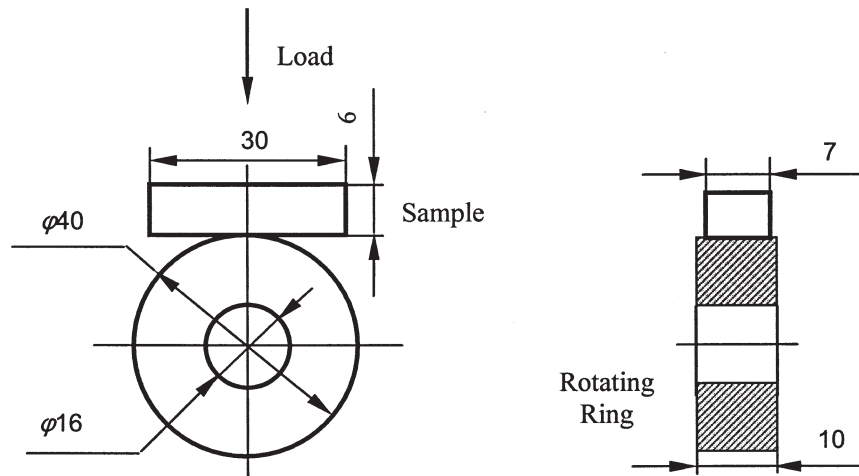


Figure 1 Contact scheme of the frictional pairs (unit: mm).

$$V = B \left[\frac{\pi r^2}{180} \arcsin \left(\frac{b}{2r} \right) - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right] \quad (1)$$

where V is the wear volume (mm^3), B the width of the specimen (mm), r the radius of the steel ring (mm), and b the width of the wear scar (mm). In this work, three replicates of friction and wear tests were carried out.

Surface analysis

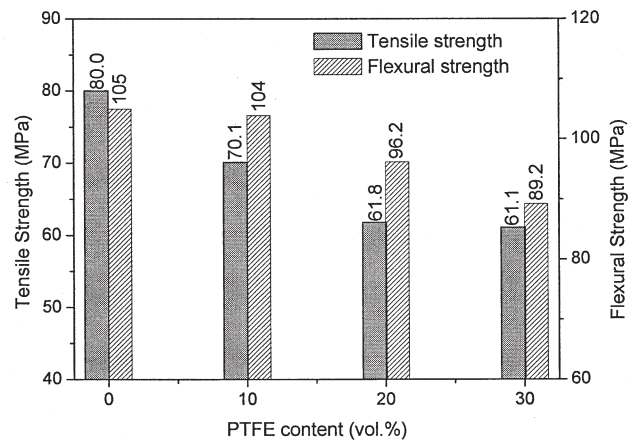
The transfer film formed by the specimen on the ring surface was examined by scanning electron microscopy (SEM, JSM-5600LV). Energy dispersive X-ray spectroscopy microanalysis was performed using an Oxford Instrument 6587 EDS detector attached to the SEM. The X-rays emitted during electron bombardment in SEM were measured to determine the elemental composition and distribution in the transfer film.

RESULTS AND DISCUSSION

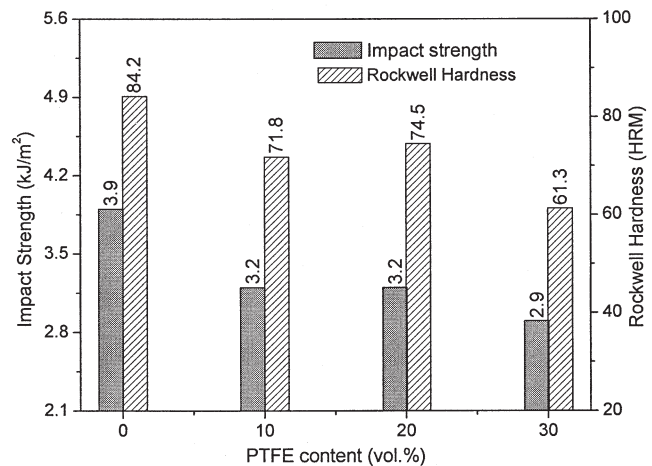
Mechanical properties

The mechanical properties of PA66/PPS blends filled with different content of internal lubricant PTFE are given in Figure 2. From Figure 2(a) it can be seen that the tensile and flexural strengths of PA66/PPS/PTFE composites decrease with increasing PTFE content. The same trend is taken on for the impact strength and Rockwell hardness (HRM), although exceptional values are obtained with the composites containing 10 and 20 vol % PTFE.

PA66/PPS blend can reach satisfactory compatibility at elevated temperature despite of the difference of molecular structure between PA66 and PPS, this may be attributed to the close values of solubility parameters of PA66 (12.7–13.6) and PPS (12.5).^{24,25} PTFE is a



(a)



(b)

Figure 2 Variation in mechanical properties of PA66/PPS blends with PTFE content. (a) Tensile strength and flexural strength. (b) Impact strength and Rockwell hardness.

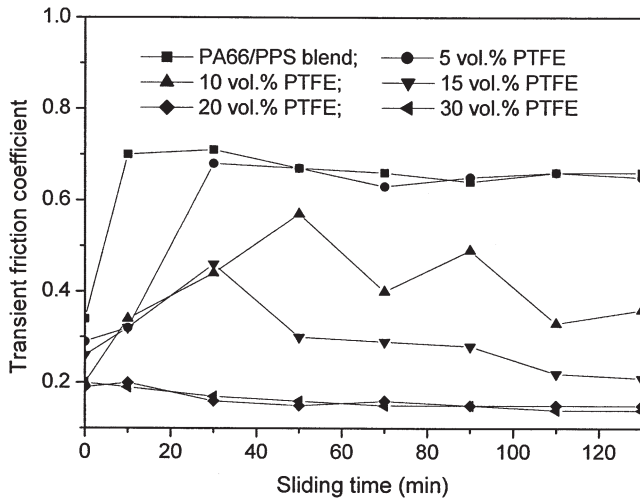


Figure 3 Variation in transient friction coefficient of PA66/PPS blends with different content of PTFE with sliding time.

nonpolar semicrystalline polymer, which has smooth profile of the rigid-rod-like molecule and lower surface tension. In addition, the solubility parameter of PTFE (6.2) is far lower than that of PA66 and PPS.²⁶ Therefore, the introduction of PTFE into the PA66/PPS blend system increases the interfacial tension and deteriorates the compatibility, which results in the impairment of mechanical properties of PA66/PPS/PTFE composites.

Friction and wear

To investigate the influence of lubricant PTFE on the tribological behavior of PA66/PPS blend, the transient friction coefficients were noted during sliding, and their variation with sliding time is shown in Figure 3. The average friction coefficients and wear volumes of samples with different content of PTFE are presented as a histogram in Figure 4. From Figures 3 and 4 it can be seen that the friction behavior of PA66/PPS/PTFE composite greatly depends on the PTFE content in system. As a whole, first, as PTFE content increases, the transient and average friction coefficient of composites markedly decreases. Second, according to the variation in transient friction coefficient with sliding time and the average friction coefficient with PTFE content, all samples can be divided into three groups. In the first group, unfilled PA66/PPS blend and PA66/PPS/5 vol % PTFE composite are included. Their curves of transient friction coefficient vary similarly, which have initial and steady friction periods. During the initial (running-in) period, the friction coefficient markedly increases because of the rapid increase of contact between sample and counterface with sliding time, while during the steady period (after 30 min), it gradually decreases and reaches steady

value. Meanwhile, the average friction coefficient of PA66/PPS blend and its composite with 5 vol % PTFE are nearly the same (about 0.66). These indicate that when the PTFE content is <5 vol %, PTFE does not apparently affect the friction behavior of PA66/PPS blend.

For the second group, the PTFE content is in the range of 5–20 vol %. The initial and steady periods can be roughly distinguished for the variation curves in Figure 3, although the transient friction coefficient fluctuates to some extent. In this range, the average friction coefficient of PA66/PPS/PTFE composites rapidly decreases from 0.65 to 0.15 through 0.43 and 0.26 (Fig. 4), which indicates that the PTFE begins to act as a lubricant and greatly improves the frictional properties of PA66/PPS blend.

In the case of the third group, the PTFE content exceeds 20 vol %. The variation in transient friction coefficient with sliding time is apparently different from that of the first and second groups, i.e., no increase stage of friction coefficient (running-in period) is observed for the PA66/PPS blends with 20 vol % and 30 vol % PTFE, instead, the transient friction coefficient gradually decreases from the beginning and reaches steady stage after 30 min of sliding. This friction behavior is similar to that of the pure PTFE.²⁷ From Figure 4, it can be seen that the average friction coefficient of PA66/PPS/PTFE composite is 0.15 and does not change with the increase of PTFE content, which decreases by 77% compared with that of unfilled PA66/PPS blend. Meanwhile, it is worth noting that the friction coefficient in this case is already lower than that of pure PTFE under the same conditions (0.22).²²

Moreover, Figure 4 shows that the wear volume of PA66/PPS blend decreases monotonically with increasing PTFE content. The minimum value is obtained with PA66/PPS/30 vol % PTFE composite (0.44

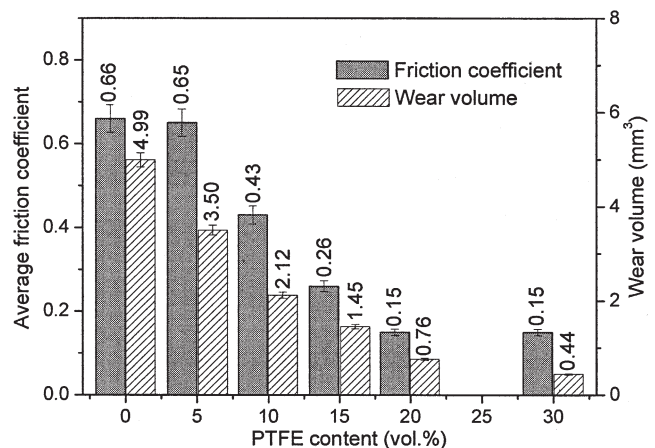


Figure 4 Friction coefficient and wear volume of PA66/PPS blends with different content of PTFE.

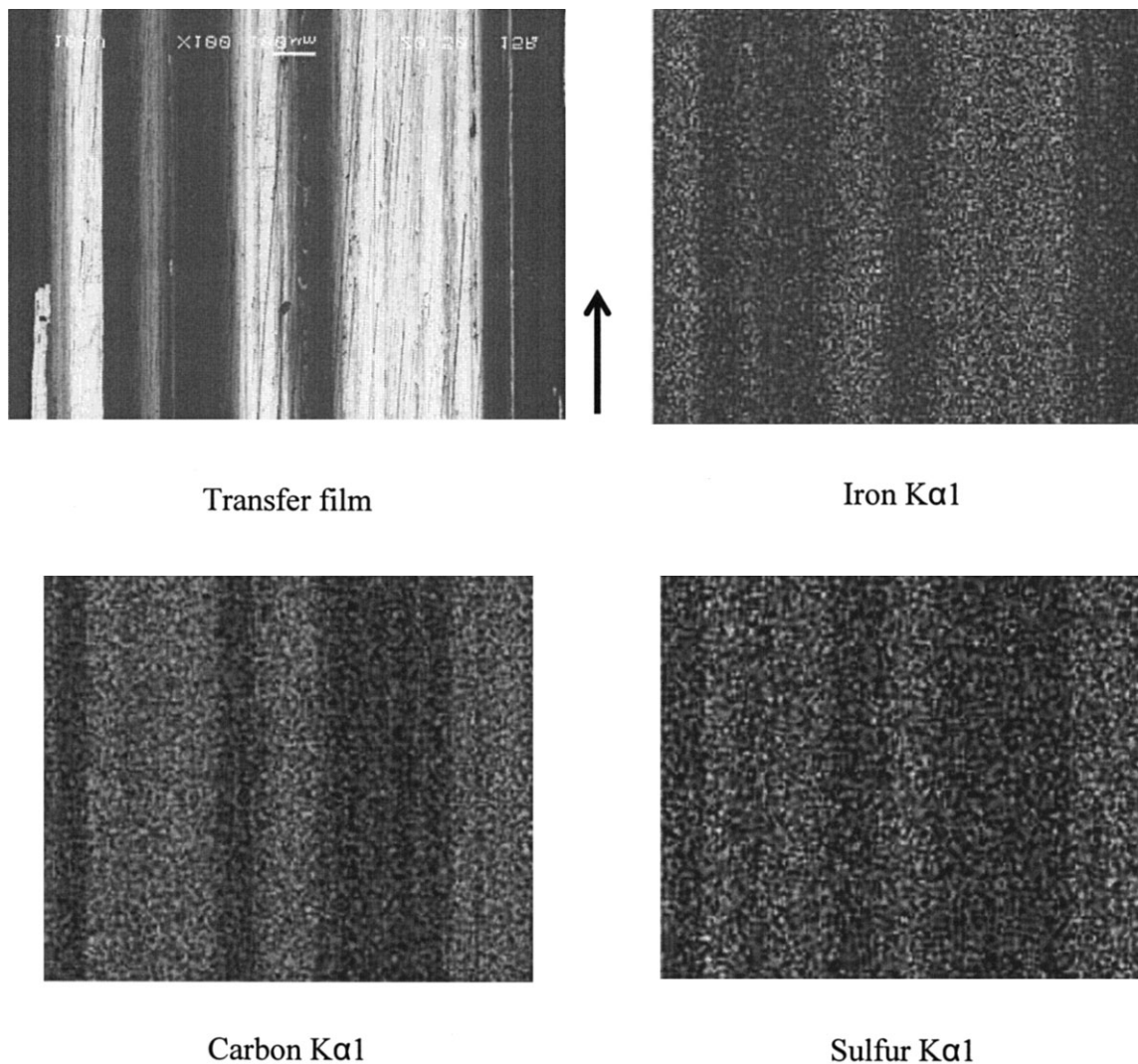


Figure 5 SEM micrograph of transfer film formed by 70 vol % PA66/30 vol % PPS blend and X-ray mapping of the elements. Arrow indicates sliding direction.¹⁹

mm³), which decreases by 91% compared with PA66/PPS blend without PTFE (4.99 mm³).

Surface analysis

It is now well recognized that the friction and wear behavior of a polymer sliding against a metal is strongly influenced by its ability to form a transfer film on the counterface.²⁸ Once a transfer film is formed, subsequent interaction occurs between the polymer and a layer of similar material, irrespective of the composition of the substrate. Because of this, the transfer films formed by samples were investigated with SEM and EDS in this study, and the micrographs are given in Figures 5–8. Among them, Figure 5 showing the SEM and EDS analysis results of the transfer film formed by 70 vol % PA66/30 vol % PPS blend has been reported by the authors in earlier paper¹⁹ and

cited here for comparison with other samples filled with PTFE. For convenience of discussion, the friction and wear mechanisms of the PA66/PPS blend are briefly reviewed as follows.

PA66 forms a belt-like, nonuniform, and discontinuous transfer film on the steel ring surface; PPS has no ability to form transfer film under the same conditions. During the friction process of the PA66/PPS blend, the presence of PA66 enhances the ability of PPS to transfer to the counterface, and the transfer film formed by the blend is belt-like, thick, and discontinuous (as shown in Fig. 5). The “thermal control of friction” regime is applicable to PA66/PPS blend, e.g., the PA66 component in blend melts during sliding because of the accumulation of frictional heat. The molten PA66 forms a low-shear-strength interfacial layer at the sliding surface, which behaves as a lubricant. Therefore, the friction coefficient of PA66/PPS

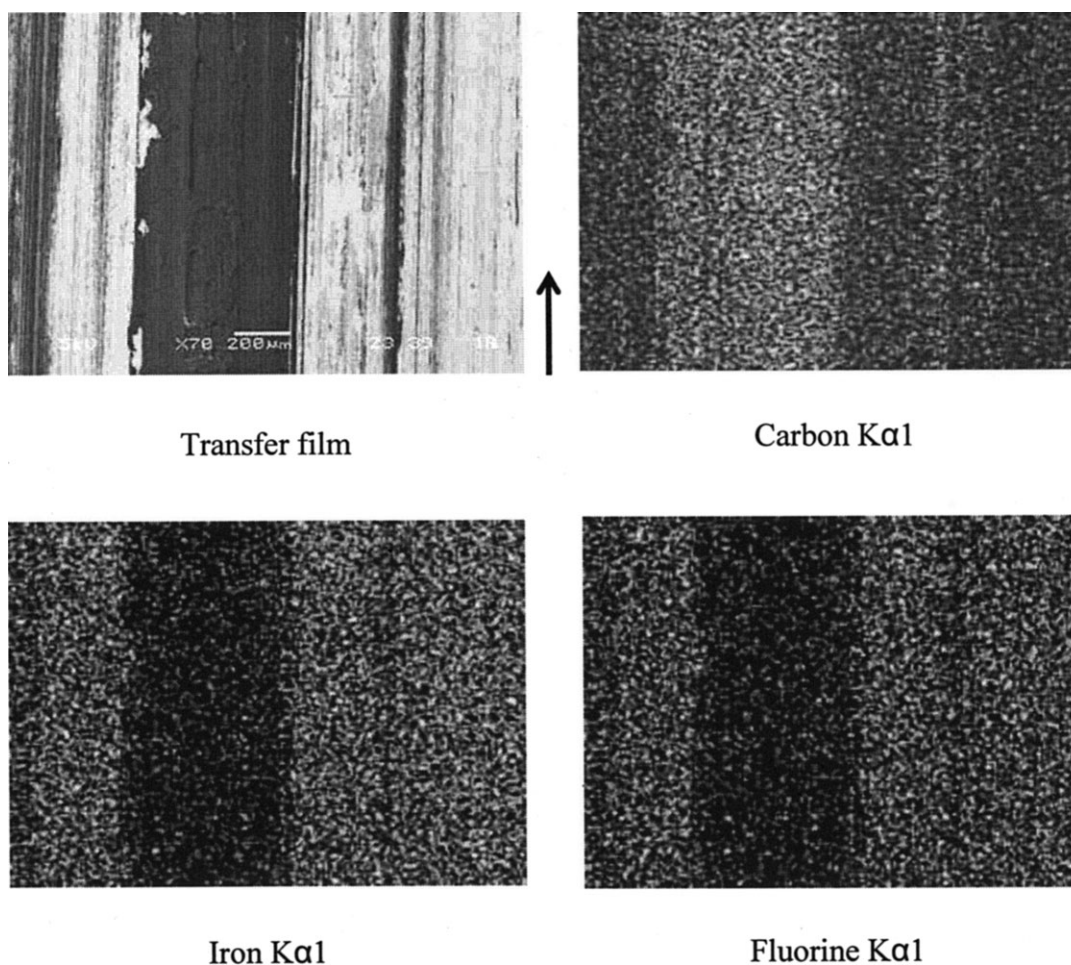


Figure 6 SEM micrograph of transfer film formed by PA66/PPS blend filled with 5 vol % PTFE and X-ray mapping of the elements. Arrow indicates sliding direction.

blends is governed by this interfacial layer, independent of the blend compositions. The wear of PA66/PPS blends mainly results from the melting.

Figure 6 shows the SEM micrograph of the transfer film of PA66/PPS blend with 5 vol % PTFE and the elemental distributions. Compared with Figure 5, it can be seen that the sample forms a belt-like, nonuniform, and discontinuous transfer film on the counterface during sliding, which is similar to that of unfilled PA66/PPS blend. The dark portions of the transfer film (SEM picture) are carbon element enrichment region, which indicates the transfer of PA66/PPS blend onto the metal surface. F-map shows that the bright portions of the SEM picture are covered by an abundant fluorine element, and the iron element is also detected in the same regions. This reveals that the bright portions are not bare steel ring surface, but covered by a thin PTFE layer. This phenomenon is different from that of PA66/PPS blend, for which the bright portions are exposed metal surface, and no other elements can be detected except for iron.

As the PTFE content increases, the topography of the transfer film formed by the composite changes apparently (Fig. 7). The belt-like transfer layer of PA66/PPS matrix disappears, and instead, the dark and stria-like transferred material is observed. The X-ray mapping shows that the carbon element is present in these portions, while iron and fluorine are absent. This means that the dark and stria-like portions are the transferred PA66/PPS matrix. Meanwhile, a large amount of iron and fluorine elements are detected in the rest portions of the ring surface, and they are evenly distributed. That is to say, similar to that of the PA66/PPS/5 vol % PTFE composite, the bright portions of the steel ring surface are covered by a thin and uniform PTFE transfer layer.

In the case of PA66/PPS blend with 30 vol % PTFE, the SEM micrograph of transfer film and X-ray mapping of fluorine element are given in Figure 8. The ring surface covered by the dark portions further decreases, which indicates that the transfer of PA66/PPS matrix is more reduced. At the same time, the entire

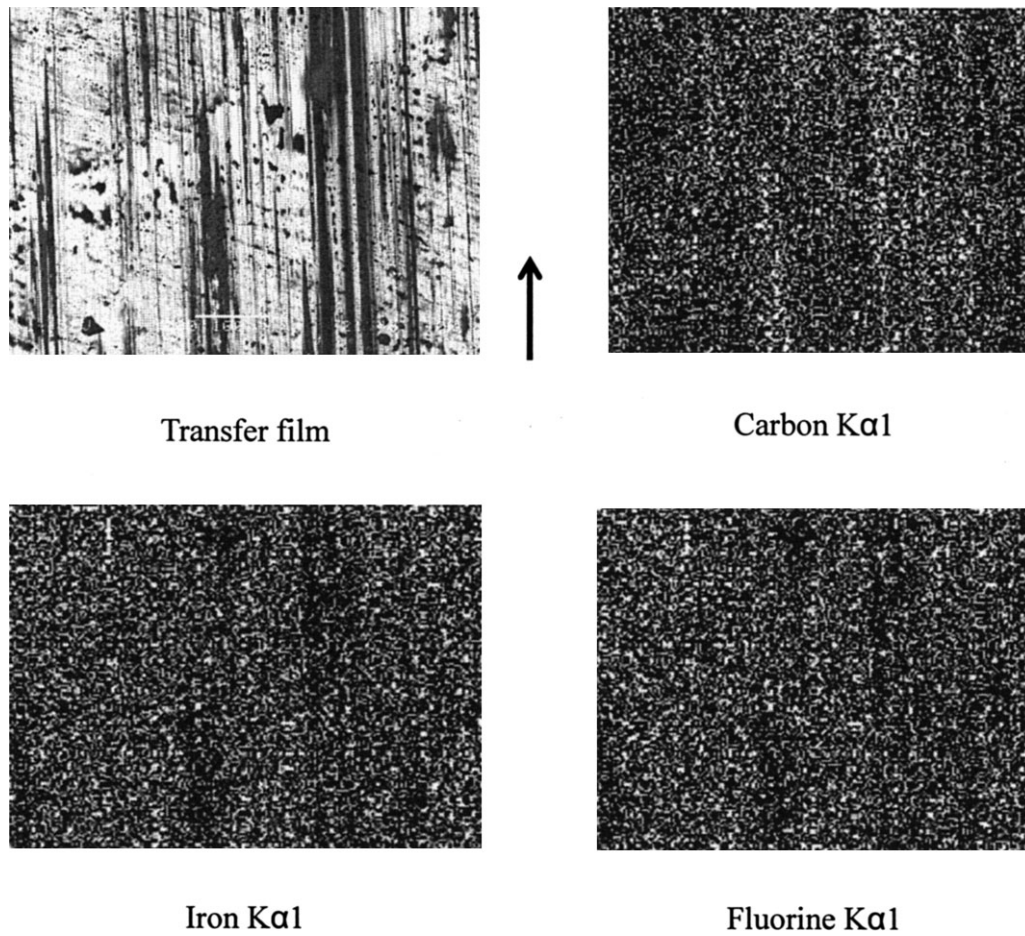


Figure 7 SEM micrograph of transfer film formed by PA66/PPS blend filled with 10 vol % PTFE and X-ray mapping of the elements. Arrow indicates sliding direction.

surface is nearly covered by a mass of fluorine, indicating the presence of PTFE transfer layer.

DISCUSSION

As above-mentioned and reported in Ref. 19, when sliding against a steel ring, the presence of PA66 en-

hances the ability of unfilled PA66/PPS blend to form a transfer film on the counterface. In the case of PA66/PPS/PTFE composite, however, the ability of both PA66 and PPS components to transfer is inhibited by the existence of PTFE. The more the PTFE content, the less the transfer of the PA66 and PPS to the counterpart. On contrast, the amount of transferred PTFE

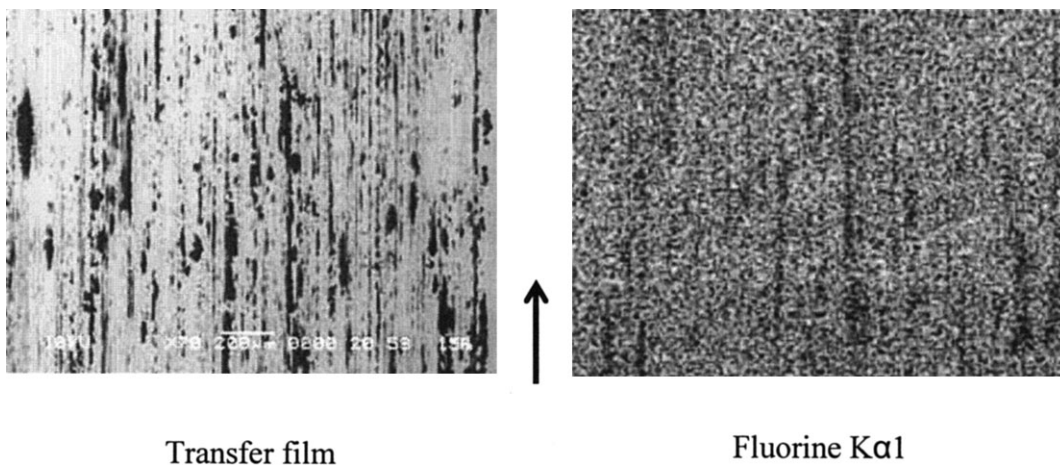


Figure 8 SEM micrograph of transfer film formed by PA66/PPS blend filled with 30 vol % PTFE and X-ray mapping of the elements. Arrow indicates sliding direction.

increases with the increase of PTFE content, and the transferred PTFE forms a thin and uniform layer on the ring surface. The occurrence of this phenomenon is mainly caused by the characteristic crystalline structure of PTFE.²²

PTFE is a semicrystalline polymer containing interdispersed crystalline and amorphous regions; its crystalline region consists of crystalline "slices" microstructure. The adjacent slices are easily slipped and separated by the action of shear and traction force during sliding; therefore, pure PTFE has a very low friction coefficient relative to other polymers. When sliding against a metal, transferred PTFE will form a thin, uniform, and firmly adhered layer on the counterface through chemical bond resulting from the tribochemical interactions between PTFE and the metal substrate.²⁶

For PA66/PPS/PTFE composite sliding against steel surface, because of the characteristic crystalline structure and the frictional behavior, a preferential transfer to the counterface occurs with PTFE, which inhibits the occurrence of the same process with PA66/PPS blend. Moreover, the formation of a thin and uniform PTFE transfer layer on the counterface decreases the contact and adhesion between the polymer and the metal surface. All of these are favorable for the wear resistance of PA66/PPS/PTFE composite. On the other hand, once the PTFE transfer layer is formed, subsequent interaction occurs between the polymer and the PTFE layer, which greatly decreases the friction coefficient of samples and the production of frictional heat, and further avoids melting during sliding. This is the main reason for the decrease in wear volume of PA66/PPS/PTFE composite.

As the PTFE content increases, the effects described above become more prominent. Therefore, the addition of PTFE greatly improves the tribological properties of PA66/PPS blends.

It is worth noting that the friction coefficient of PA66/PPS with >20 vol % PTFE (0.15) is even lower than that of pure PTFE under the same conditions (0.22).²² It is well known that the way to produce an ideal self-lubricating material is to form a solid lubrication film on the surface of a hard substrate, e.g., DU-bearing material. Among them, the presence of the lubrication film decreases the friction coefficient, while the outstanding mechanical properties of substrate improve the wear resistance. In this study, the solid lubricant PTFE forms a thin and uniform transfer layer on the metal surface under tribochemical action, which leads to the interaction between the similar materials during further friction process. On

the other hand, the better mechanical properties are obtained with PA66/PPS/PTFE composite relative to pure PTFE. Therefore, the synergism of the hard substrate and the lubrication film is reached through the addition of PTFE into the PA66/PPS blend, which results in an excellent wear resistance and an extremely low friction coefficient.

Compared with unfilled PA66/PPS blends, the presence of characteristic frictional behavior of PTFE and thus no melting phenomenon during the sliding lead to that the thermal control of friction regime is not applicable to the PA66/PPS/PTFE composite under the same conditions.

CONCLUSIONS

Solid lubricant PTFE greatly improves the tribological properties of PA66/PPS blend. The friction coefficient and wear volume decrease with PTFE content. The lowest friction coefficient (0.15) is obtained for the blend with >20 vol % PTFE, and the minimum wear volume (0.44 mm³) is reached with PA66/PPS/30 vol % PTFE composite. The superior lubrication of PTFE, its preferential transfer to counterface, and the formation of thin, uniform, and firmly adhered transfer layer on the steel ring surface, decrease the contact and the adhesion between the PA66/PPS blend and the metal substrate and prevent the polymer sample from melting. Thermal control of friction regime is not applicable to the PA66/PPS blend filled with PTFE.

All the tests and characterizations were conducted at Shanghai R and D Center for Polymer Materials.

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