Friction and Wear Mechanisms of PA66/PPS Blend Reinforced with Carbon Fiber

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

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

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ABSTRACT: The mechanical and tribological properties of carbon fiber (CF) reinforced polyamide 66 (PA66)/polyphenylene sulfide (PPS) blend composite were studied in this article. It was found that CF reinforcement greatly increases the mechanical properties of PA66/PPS blend. The friction coefficient of the sample decreases with the increase of CF content. When CF content is lower (below 30%), the wear resistance is deteriorated by the addition of CF. However, the loading of higher than 30% CF significantly improves the tribological properties of the blend. The lowest friction coefficient (0.31) and the wear volume (1.05 mm^3) were obtained with the PA66/PPS blend containing 30% CF. The transfer film and the worn surface formed by sample during sliding were examined by scanning electron microscopy. The observations revealed that the friction coefficient of PA66/PPS/CF composite depends on the formation and development of a transfer film on the counterface. The abrasive wear caused by ruptured CFs (for lower CF content) and the load bearing ability of CFs (for higher CF content) are the major factors affecting the wear volume. In addition, the improvements of mechanical properties, thermal conductivity, and self-lubrication of bulk CFs are also contributed to the wear behavior of PA66/PPS/CF composite. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 602–608, 2007

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

INTRODUCTION

In recent years, polymer is extensively utilized in sliding components such as gears and cams because of their self-lubrication properties, lower friction coefficient, and higher wear resistance. However, polymer is very rarely used as bearing materials and wear-resistant materials in its pure form, because unmodified polymer could not satisfy the demands arising from the situations where a combination of good mechanical and tribological properties is required. The methods of polymer modification include copolymerizing, reinforcing (or filling), and blending. Among them, polymer blending is fascinating because it has simple processing and unfolds unlimited possibilities of producing materials with variable properties. In polymer tribology, polymer blending is also an effective way to improve the tribological properties of polymers. A different kind of polymer blends has been studied by some researchers,[1–7] and it is found that the friction and wear behaviors of polymer blends vary continuously with compositions, the friction coefficient and wear resistance of blends are superior to those of component polymers and reach optimum at certain compositions, although some reports are conflicting. Unfortunately, some related studies are very limited.

Except polymer blending, the addition of fillers, including internal lubricants, inorganic powders, and reinforcing fibers, is another important method to raise the tribological properties of polymers.[8–13] A great attention was given to the fibrous fillers because of the easy processing and the significant improvement in friction and wear. Although polymeric composites are developed for superior friction and wear properties, this objective often conflicts with the simultaneous achievement of superior mechanical properties. Therefore, developing and producing high quality composite materials with special combinations of mechanical and tribological properties are still the common aim in world wide.[14,15] On the other hand, to our best knowledge, the existing studies have been focused on the wear resistance of fiber-filled homopolymers, no publications dealing with the polymer blends can be searched out, so it is necessary to further study the tribological and mechanical properties of polymer blend composites.

On the basis of the current status of studies on the polymer tribology, in earlier articles,[16–18] the authors selected polyamide 66 (PA66), polyphenylene sulfide (PPS), and high density polyethylene (HDPE) as matrices, systematically studied the friction and wear

Correspondence to: T. S. Li (lits@fudan.edu.cn).
**Present address:* Department of Human Ecology, The University of Texas at Austin, Austin, TX 78712, USA.

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TABLE I
Data of the Materials Used in This Study

Material	Form	Trademark	Manufacturer	Density (g/cm^3)	Melting point (°C)
PA66	Pellet	Zytel® 101L NC010	Du Pont Co. Ltd.	1.14	262
PPS	Powder	Ryton® P-4	Chevron Phillips Chem. Co.	1.35	285
CF	Fiber	–	–	1.74	>1000

behaviors of PA66/PPS and PA66/HDPE blends. It was found that the friction and wear of polymer blends are governed by the components having lower and higher melting (softening) point, respectively; the thermal control of friction regime is applicable to the blend under the conditions used. Further investigations on the mechanical and tribological properties of PA66/PPS blends filled with polytetrafluoroethylene (PTFE) and glass fiber (GF)[19,20] indicate that PTFE greatly decreases the friction coefficient and wear volume of blends but impairs the mechanical properties, the opposite situations are obtained for the GF reinforcement. To further study the possibility of improving the mechanical and tribological properties of PA66/PPS blend and the effect of addition of fibrous fillers on the friction and wear mechanisms, in this article, the authors selected PA66/PPS blend as the base and the carbon fiber (CF) as the reinforcing material, studied the mechanical and tribological properties of PA66/PPS/CF composite, and the friction and wear mechanisms were discussed in terms of scanning electron microscopy (SEM) analysis of the worn surface and the counterface.

EXPERIMENTAL

Materials

The data of PA66 pellets, PPS powders and carbon fibers (CF) 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. The length of CF is 3 mm, diameter of single fiber is 10 μm.

Sample preparation

It has been found that 70% PA66/30% PPS (volume ratio) blend has better mechanical properties with combination of lower friction coefficient and the highest wear resistance.[16] On the basis of this, the same blend system was selected as a matrix blending with different content of CF (5–35 vol %) to prepare the samples to be tested for tribological and mechanical properties.

To obtain a sufficient homogeneity, two-step processing method was employed to produce sample. In the first step, PPS powders and CFs were dispersed in water, vigorously stirred, filtered, and then dried under reduced pressure at 100°C for 24 h to remove residual water. The received PPS/CF mixtures were then 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 265, 275, 285, 295, and 285°C, respectively. The screw speed was set at 70 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/CF pellets using the same extruder and followed the same procedure. Before compounding, PA66 and preblended PPS/CF pellets were dried at 100°C in vacuum oven for 24 h.

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 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 under ambient conditions (temperature: 20°C ± 3°C, humidity: 50% ± 10%). Block-on-ring contact configuration was employed, as shown in Figure 1. The normal load was 196*N*,

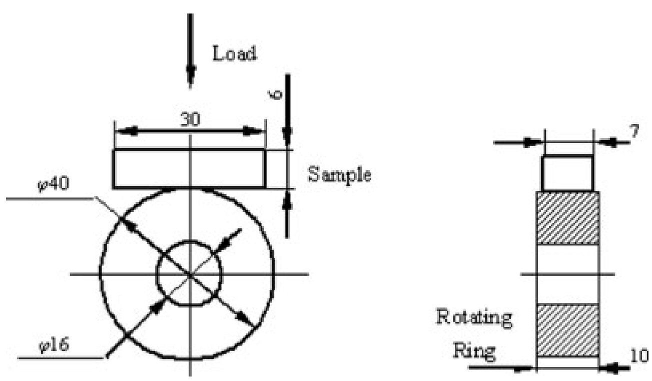


Figure 1 Schematic diagram of block-on-ring configuration.

TABLE II
The Mechanical Properties of PA66/PPS/CF Composites

	Blend	Blend + 5% CF	Blend + 25% CF	Blend + 30% CF	Blend + 35% CF
Tensile strength (MPa)	80.0 ± 2.4	71.0 ± 2.1	94.5 ± 2.8	144 ± 4.3	143 ± 4.3
Flexural strength (MPa)	105 ± 3.2	114 ± 3.4	132 ± 4.0	202 ± 6.1	199 ± 6.0
Impact strength (kJ/m^2)	3.9 ± 0.12	1.4 ± 0.04	1.5 ± 0.05	2.4 ± 0.07	2.3 ± 0.07
Rockwell hardness (HRM)	84.2 ± 2.5	91.6 ± 2.7	95.4 ± 2.9	102 ± 3.1	99.5 ± 3.0

sliding speed was 0.42 m/s, surface roughness of polymer block and steel ring was Ra 0.17–0.23 μm and Ra 0.09–0.11 μm, respectively, by polishing with metallographic abrasive paper. The experimental duration was lasted for 120 min and the frictional force torque was noted down at each interval of 20 min. The transient friction coefficient was derived from the frictional force torque, and the average value in the steady state (after 40 min) was used as the friction coefficient of the sample. The wear property of the sample was denoted by wear volume, which was calculated from following formula[21]:

$$V = B\left[\frac{\pi r^2}{180}\text{aro sin}\left(\frac{b}{2r}\right) - \frac{b}{2}\sqrt{r^2 - \frac{b^2}{4}}\right]$$

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) (determined by measuring microscope). In this work, friction and wear tests were carried out three times for each sample.

Surface analysis

The worn surface of the sample and the steel ring surface (transfer film) were investigated by SEM (SEM, JSM-5600LV). The polymer block was sputter-coated with a gold palladium alloy prior to viewing under the microscope.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of PA66/PPS/CF composites, including tensile strength, flexural strength, impact strength, and Rockwell hardness, are listed in Table II. From this Table it can be seen that the items tested except impact strength are greatly improved by CF reinforcement. As CF content increases, they increase and then slightly decrease when the CF content is 35%. The maximum values of tensile strength, flexural strength, and hardness are obtained with PA66/PPS/30%CF composite, which are increased by 80, 92, and 21%, respectively, relative to the non-reinforced PA66/PPS blend. For impact strength, the same trend also takes place, although the CF reinforcement has a negative effect on it. Considering all these items, it can be deduced that 30 vol % CF reinforced PA66/PPS blend has the best mechanical properties.

Friction and wear

The variation in friction coefficient and wear volume of PA66/PPS blend with CF content is presented as a histogram in Figure 2, the numbers above the bars are the corresponding values. This figure shows that the friction coefficient of PA66/PPS blend is considerably lowered by the addition of CF. As CF content increases, the friction coefficient of composite dramatically decreases and reaches minimum value of 0.31 at 30% of CF concentration, which is decreased by 53% in comparison with neat PA66/PPS blend. The minimum wear volume (1.05 mm^3), which is nearly one seventh of that of unfilled PA66/PPS blend, is also obtained at this point, although it seems that the reinforcement of CF in the range of 5–25% impairs the wear resistance. Further increasing CF content leads to the slight rise of friction coefficient and wear volume. That is to say, the optimum tribological properties of PA66/PPS/CF composite are obtained with 30 vol % CF reinforcement.

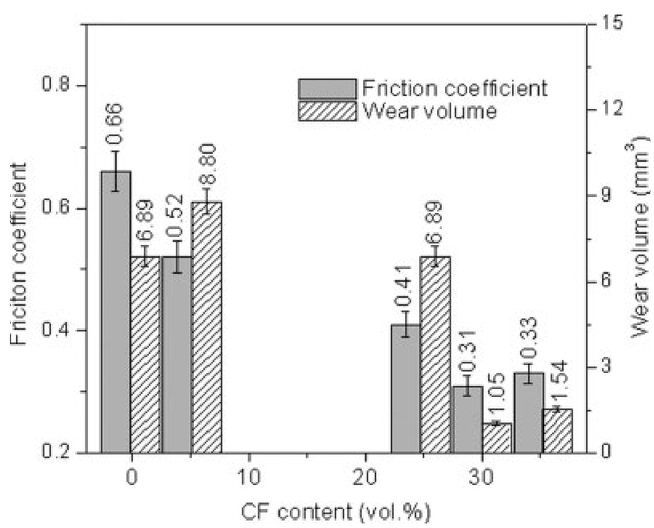


Figure 2 Variation in friction coefficient and wear volume of PA66/PPS blend with CF content.

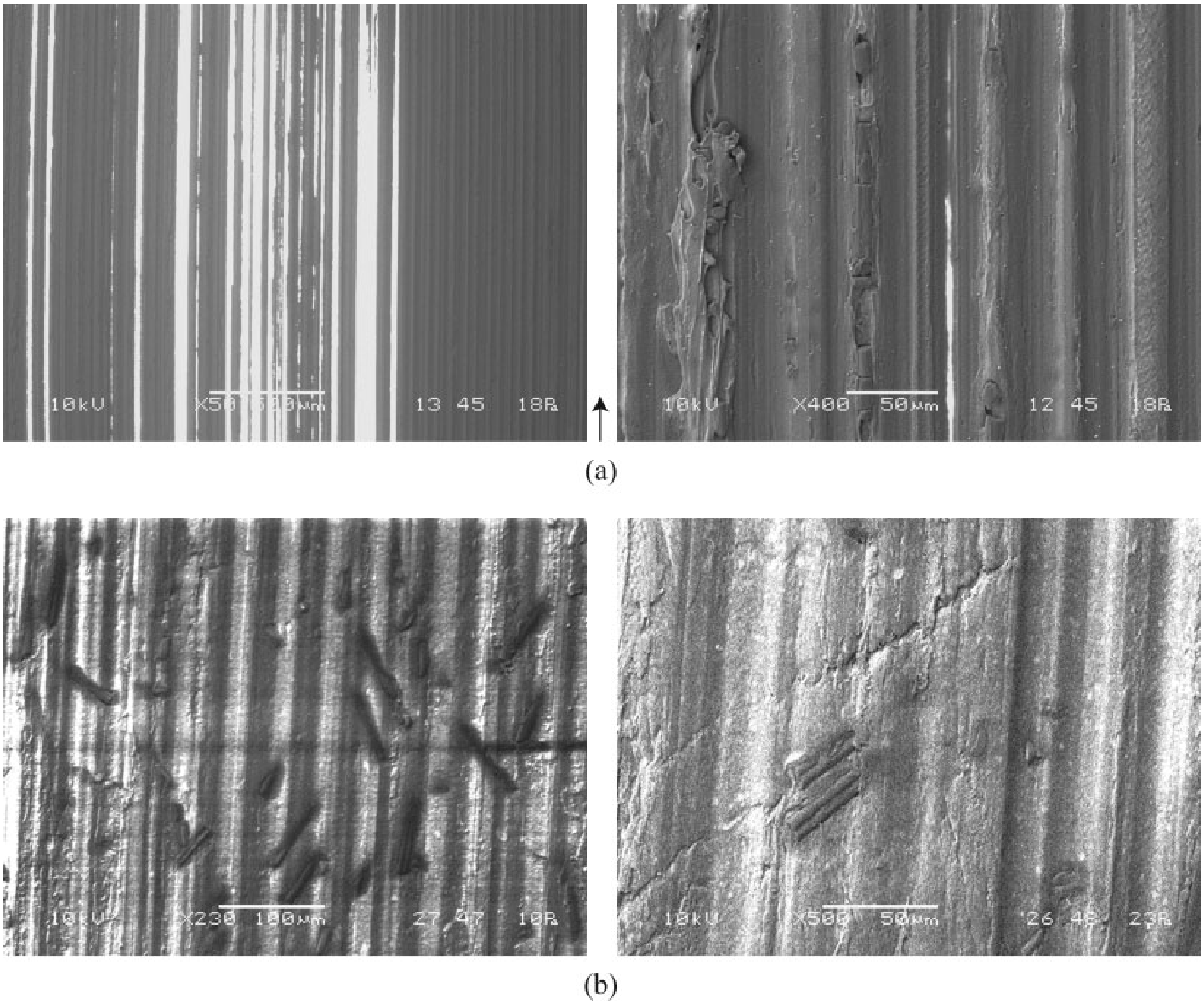


Figure 3 SEM micrographs of transfer film and worn surface fomred by PA66/PPS/5%CF composite. Arrow indicates sliding direction here and thereafter. (a) Transfer film. Left: ×50; right: ×400. (b) Worn surface. Left: ×230; right: ×500.

Surface analysis

It is now fully recognized that the friction and wear behaviors of a polymer sliding against a metal is strongly influenced by its ability to form a transfer film on the counterface.[22,23] The authors' earlier study also shows that the friction and wear mechanisms of PA66/PPS/GF composite can be clearly clarified by SEM analysis.[20] Therefore, the transfer film on the counterface and the worn surface formed by PA66/PPS blend reinforced with different CF content during sliding were investigated using SEM, and the micrographs are listed in Figures 3–5.

Figure 3 gives the topographies of the transfer film and the worn surface of PA66/PPS/5%CF composite. From this figure it can be seen that a nonuniform, belt-like, and thick transfer film was formed during sliding. Typical features can be observed from the picture at higher magnification. Along the sliding direction, the transferred layer on the counterface displays concavo–convex topography. Ruptured fibers of about 50 μm length, which resulted from the frictional shear force and normal load, are also transferred and embedded in the convex ''ridge'' of the layer. In addition, this image shows clear melting traces of polymer matrix.

Corresponding to the transfer film, a lot of furrows parallel to the sliding direction is located on the worn surface of the sample, and a part of fibers exposed at the surface is raised slightly above the plane of the matrix [Fig. 3(b)]. It seems that there is a good adhesion between the matrix and the CF compared with PA66/PPS/GF composite, which is consistent with the Theberge's report.[24] At higher magnification, however, it can be seen that some fibers were pulled out of the frictional surface during

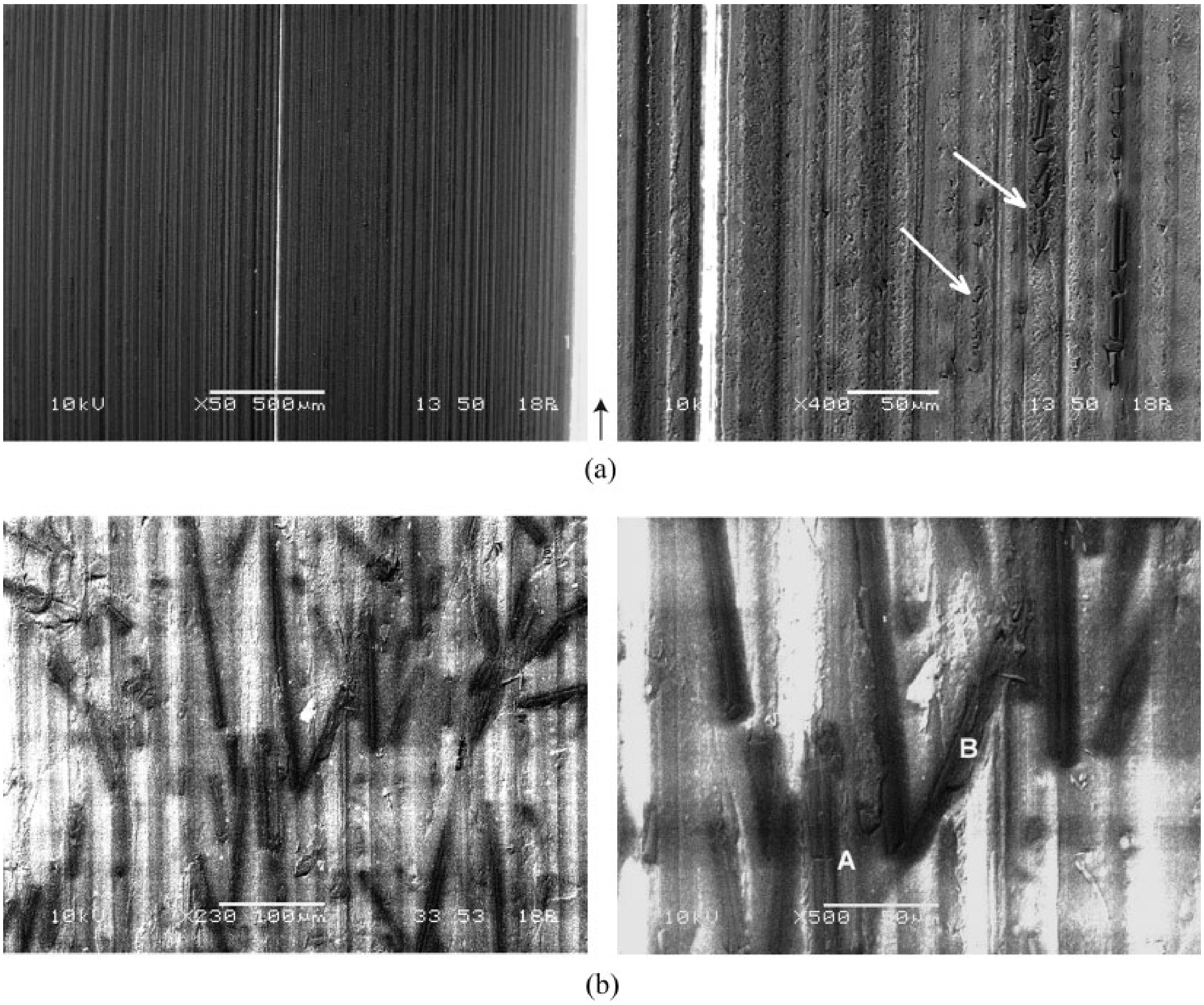
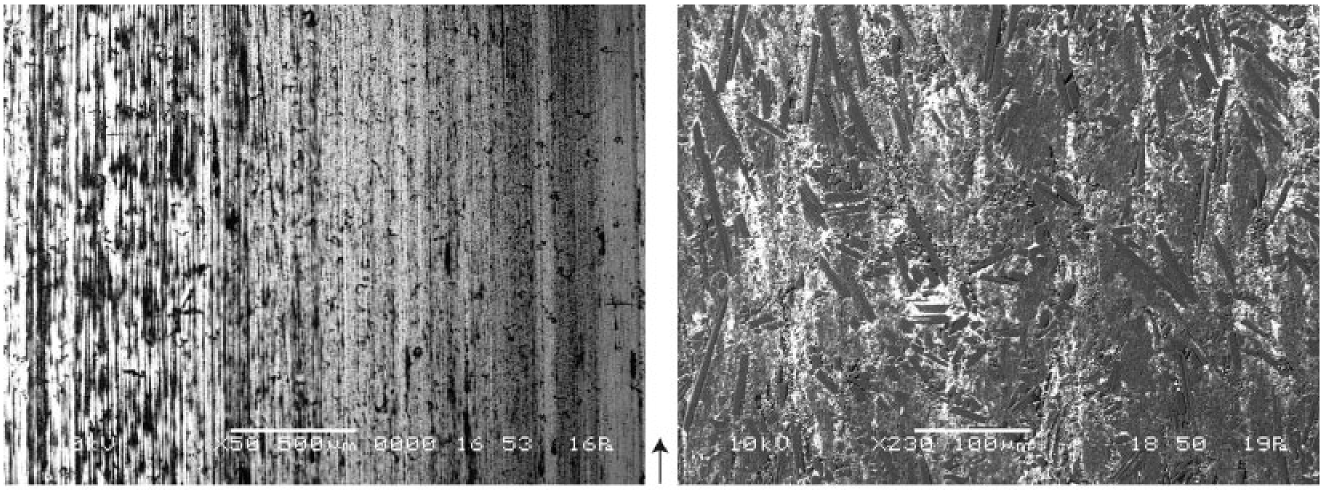


Figure 4 SEM micrographs of transfer film and worn surface fomred by PA66/PPS/25%CF composite. (a) Transfer film. Left: ×50; right: ×400. (b) Worn surface. Left: ×230; right: ×500.

sliding and the cavities left by the debonding process were partially covered by the plastically deformed matrix.

The SEM micrographs of the transfer film and the worn surface formed by PA66/PPS blend reinforced with 25% CF are presented in Figure 4. Figure 4(a) shows that PA66/PPS/25%CF composite formed a more uniform transfer film under the same conditions. In this case, CFs are also broken during sliding and the resultant fibers are much shorter (below 40 μm). Some fibers are pulverized under the action of shear force and normal load (as indicated by white arrows). Compared with the topographies of the transfer film formed by unfilled PA66/PPS blend,[16] the morphologies of the transfer film (rough and porous) and the fibers (pulverized and adhesive to the matrix) allow one to suggest that during frictional process, the pulverized CFs were blended with polymer matrix and both of them together formed the transfer film, and one can also easily deduce that the combination of the CFs with the polymer would improve the mechanical and tribological properties of the transfer film. As the CF content increases, the fraction of the CF exposed at the frictional surface increases, and the plowing action of the worn surface by the hard asperities of the counterface is not crucial as observed for PA66/PPS/5%CF composite in Figure 3(b) [Fig. 4(b)]. The detailed investigations show that the cracking and wear of CFs occurred during sliding (A and B, respectively, in Fig. 4 right-hand). Except the earlier-mentioned, another apparent difference between Figure 3 and Figure 4 is that no melting phenomenon can be observed for the PA66/PPS blend filled with 25% CF.

When CF content is raised to 30%, completely different topographies of the transfer film and the worn



(a) (b)

Figure 5 SEM micrographs of transfer film and worn surface fomred by PA66/PPS/30%CF composite. (a) Transfer film. (b) Worn surface.

surface were obtained by SEM observation, as shown in Figure 5. Figure 5(a) shows that PA66/PPS/30%CF composite did not form a transfer film on the counterface during sliding, the abrasion marks parallel to the sliding direction resulting from the polishing operation before tests can be clearly seen on the steel ring surface. The loading of 30% CF leads to that a large part of the worn surface is covered by the CFs, including broken fibers and pulverized fibers [Fig. 5(b)]. The part of the broken fibers raising above the surface was worn away and pulverized fibers were dispersed around the broken fibers.

Discussion

Although many researchers reported the tribological properties of fiber-reinforced polymers, the existing publications are mainly focused on the wear-resistance of polymer/fiber composite, and the papers dealing with the friction and wear mechanisms of fiber reinforced polymer blend can hardly be searched out. On the basis of the study status, the authors systematically studied the friction and wear behavior of fiber filled PA66/PPS blend composite, the study on the PA66/PPS/GF composite has been made earlier,[20] this article mainly reported the tribological properties of PA66/PPS/CF composite.

From SEM micrographs of the counterface listed in Figures 3 and 4 it can be seen that as the CF content increases, the transfer film becomes uniform. When CF concentration is 25%, the pulverized fibers are blended with polymer matrix to form a transfer film, which improve the mechanical and tribological properties of this layer. Once the transfer film is formed, subsequent interaction occurs between the polymer and a layer of similar materials, therefore, the friction coefficient further decreases. It is worth noting that there is no transfer film on the counterface can be detected for the PA66/PPS blend containing 30% CF, while its friction coefficient is the lowest in the samples (0.31). In this case, the worn surface of the sample is covered by a large amount of fibers, and the abrasive action of the fibers exposed at the surface inhibits the formation of a transfer film. The exposure of CFs changed the frictional contact from metal-polymer to metal-CF, therefore, the friction coefficient of composite depends on that of pure CFs (0.25) and almost does not change when the CF content exceeds 30%. The same results were obtained for some studies on polymer/CF composites reported by Giltrow, in which the friction coefficient is proportional to CF loading and independent of the type of the resins, and almost equivalent to that of pure CF when CF content is higher than 30%.[25]

The friction behavior of PA66/PPS blends reinforced with GF and CF have been reported earlier and in this article,[20] respectively, and it was found that the formation and development of the transfer film greatly affect the friction coefficient of samples. The same relationship between friction coefficient and transfer film is also obtained for the aramid fiber reinforced PA66/PPS blend composite, and the related results will be published later.

The wear mechanism of PA66/PPS/CF composite is relatively complicated and consists of polymer matrix wear and bulk fiber wear. In addition, some other factors, such as mechanical properties of composite, abrasiveness caused by ruptured fibers, characteristics of bulk CFs, including load bearing ability, self-lubrication (lower friction coefficient), excellent thermal conductivity, also affect the wear behavior of sample. The ultimate wear property of PA66/PPS/CF composite is determined by the contributions of these factors.

When CF content is less than 30%, polymer matrix wear is the main wear mechanism of the composite. Although the factors aforementioned are favorable for the wear resistance, the ruptured CFs, which resulted from the frictional shear force and normal load, caused a severe abrasive wear during sliding. Therefore, the wear volume of the samples are higher than that of unfilled PA66/PPS blend (6.89 mm^3), but much lower than that of corresponding PA66/PPS/GF composite,[20] because the CFs are much less abrasive than GFs.[25] The improvements of mechanical properties, thermal conductivity, friction behavior, and the load bearing ability, lead to the increase of the wear resistance of PA66/PPS blend containing 25% CF (6.89 mm^3) relative to that of the PA66/PPS/5%CF composite (8.80 mm^3).

A turning point in wear behavior occurs at 30% CF concentration. Here, the wear volume of the composite (1.05 mm^3) reaches the minimum and is decreased by 85% compared with the unfilled blend. The topographies of the worn surface show that the sample surface is almost completely covered by ruptured and pulverized CFs. That is to say, the wear behavior of PA66/PPS/30%CF composite depends on the wear of bulk CFs, it is almost independent of the polymer matrix. The exposed fibers directly support the significant portion of the applied load during sliding, which results in the highest wear resistance of the sample. Furthermore, the significant improvements of the mechanical properties, thermal conductivity, and the friction behavior are also contributed to the very low wear volume.

The slight increase of wear volume of composite at 35% CF concentration could be caused by the deterioration of mechanical properties and the poor adhesion between polymer matrix and CFs.

CONCLUSIONS

On the basis of previous work, 70 vol %/PA66/30 vol %PPS blend was chosen as matrix and blended with CFs. The mechanical and tribological properties of the composites containing different CF content were tested. It was shown that the mechanical properties of PA66/PPS blend were greatly increased by CF reinforcement. As CF content increases, the friction coefficient of PA66/PPS/CF composite decreases. The loading of 5–25% CF impairs the wear resistance, while CF content higher than 30% significantly improves the wear behavior of the blend. The lowest friction coefficient (0.31) and wear volume (1.05 mm^3) were achieved with the PA66/PPS/30%CF composite, which were reduced by 53 and 85% in comparison with unfilled PA66/PPS blend, respectively. The formation and development of a transfer film is close related to the friction behavior, while the abrasive wear caused by the ruptured CFs and the load bearing ability of the fibers have the crucial effect on the wear volume of the composite. In addition, the improvements of mechanical properties, thermal conductivity, and self-lubrication of bulk CFs have also some contributions to the wear behavior.

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

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