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The role of transfer film and back transfer behavior on the tribological performance of polyoxymethylene in sliding [†]

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Abstract

The role of transfer films formed during the sliding of polymer composites against steel counterfaces was studied in terms of the tribological behaviors of the composites. The composites were prepared by compression molding and sliding tests were run in pin-on-disk sliding configuration. The counterface was made of tool steel hardened to 55-60 HRC and finished to a surface roughness of 0.09-0.10 μm Ra. Wear tests were run for 6 hrs at the sliding speed of 1.0 m/s and contact pressure of 0.65 MPa. Transfer films formed on the counterfaces during sliding were investigated using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The results showed that as the transfer film became smooth and uniform, the wear rate decreased. The examination of worn surfaces using Energy Dispersive Spectroscopy (EDS: dot mapping mode) showed the back-transfer of the steel counterface material to the polymer pin surface. This behavior is believed to strengthen the polymer pin surface during sliding thereby contributing to the decrease in wear rate.

Keywords: AFM; Back transfer; Friction; Transfer film; Wear

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1. Introduction

The formation of transfer film on the counterface during sliding plays an important role in the wear and friction of polymeric materials [1]. It is also known that the addition of a particulate filler material or reinforcement material to the polymer affects the formation of transfer film. Thus, the transfer film is equally important for the tribological behavior of polymer composites. In other words, unlike other mechanical properties, the tribological properties of materials are not intrinsic but are instead specific to the sliding system and are modifiable by the sliding variables such as sliding speed, counterface roughness, and applied load. Especially, in polymer-metal sliding systems, it has been widely shown that the variables are closely related to the development of transfer film and so they affect the wear resistance of polymer composites. Since material transfer occurs from the soft polymer material to the hard metal counterface, later sliding occurs between the polymer and its transfer film. Thus, this transfer film is very important in determining wear resistance. For this reason, an improvement in mechanical properties does not necessarily result in the enhancement of wear resistance.

Many studies [2-6] have shown that the formation of a transfer film is promoted by the addition of an inorganic filler material to the polymer. Also, it has been shown that improved wear resistance is closely related to the characteristics of the transfer film. For example, Bahadur et al. [2] reported that the formation of thin and uniform transfer films on the steel counterface during sliding was observed in the case of nylon 11 filled with CaS and CaO, but not with CaF_2 filler. In the case of CaF_2-filled nylon composite, the wear increased linearly with sliding distance and no

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steady wear state corresponding to a low wear rate was observed. The transfer film was observed to peel off the substrate which indicated that the adhesion of the transfer film to the counterface was poor. The protection of soft polymer surface from hard metal asperities in contact is necessary and is believed to lower the wear of the polymer material. The transfer film provides the protection by covering the metal asperities. Studies related to the transfer film are thus important to understand the friction and wear behavior in polymer-metal sliding.

The dependence of the filler on the characteristics of the transfer film and the dependence of the latter on wear resistance has been extensively studied. For example, continuous, thin, and uniform transfer films have been reported for PPS composite filled with micro particles of CuS, CuO, Ag_2S, NiS, and TiO_2 [3-6]. Such transfer films increase the wear resistance. Contrary to this, discontinuous and patch-like transfer films were reported for the composites filled with ZnF_2, CaF_2, PbTe, PbSe, SiC, and ZnO particles and the steady state wear rate of the composites in these cases was increased over that of unfilled PPS [3-6].

Fiber reinforcement also affects the tribological behavior of polymer composites. The improvement in wear resistance with the addition of fiber material has been attributed to factors such as the greater load-carrying ability of the fiber material and the resistance to surface damage during sliding because of increased shear strength. With respect to the latter, fibers are more effective than filler particles because of their higher aspect ratios which provide for increased adhesion between the matrix and the fiber. Fiber materials are capable of supporting larger loads than polymeric materials because of their much higher strengths and moduli of elasticity. A study [7] on carbon fiber-reinforced PPS composites showed that the coefficient of friction decreased due to low coefficient of friction characteristic of the carbon fiber and the wear rate also decreased because of the factors stated above. With the fiber reinforcement, a smother transfer film was formed and this was also responsible for the increase in wear resistance.

It is known that there are two states in wear: transient state and steady state. The early period of wear is known as the transient state and abrasive action during this period on the polymer surface from hard metal asperities is dominant. Zhao and Bahadur [8] performed an extensive study of the running-in wear state of PPS by varying sliding variables such as sliding speed, counterface roughness, and contact pressure. They found that the sliding variables significantly affected the wear and friction of PPS in the running-in period. The wear rate in this period was very high. Furthermore, the sliding variables were found to be closely associated with the formation of a transfer film during the transient state. However, the steady state is sometimes not observed when the wear is mostly governed by abrasive action so that wear continues to increase linearly. In other words, no transfer films are formed on the counterface, and if they are, they do not adhere to the counterface. This thereby results in their continuous removal from the counterface. While in the transient wear state there is rapid increase in wear with sliding distance accompanied by substantial abrasive action, in steady state a low wear rate is observed along with the transfer film on the counterface. Most studies have focused on the steady state instead of the transient state because of practical reasons.

As stated above, the adhesion of the transfer film to the counterface is an important factor to obtain a reduced wear rate. It is well known that adhesion is promoted by two factors: mechanical interlocking of fine wear particles into deep and narrow metal asperities, and chemical reaction between the transfer film and metal substrate [4, 9]. To investigate the adhesion of the transfer film to the counterface and its effect on wear rate, Schwartz and Bahadur [10] performed bond strength measurements on the transfer film of PPS filled with nanoscale Al_2O_3 particles formed on the steel counterface finished to 0.027-0.100 μm Ra. They reported that wear decreased as the bond strength increased and this was closely associated with a thin and uniform transfer film formed during sliding. On the other hand, when the counterface was made smoother and finished to a surface roughness of 0.027 μm Ra, the wear rate increased due to the lack of mechanical bonding between the transfer film and the counterface.

Filler size also affects significantly the tribological behavior of polymer composites. It is known that as particle size increases, the angularity also increases, resulting in the possibility of the filler causing abrasion during sliding. Thus, nanoscale particles seem preferable to the microscale particles in this respect. Moreover, smaller particles provide a larger surface area-to-volume ratio which increases the likelihood of greater bonding between the filler and the matrix material. Furthermore, they also provide the mechanism for stronger bonding between the transfer film and the counterface by virtue of the interlocking of fine particles into metal asperities. In the case of a nanometer-sized filler material, a very small proportion such as 2 vol.% is effective in lowering the wear rate [5] while a much larger proportion in the range of 20-30 vol.% is needed for a micrometer-sized filler material [6]. Since excessive filler amounts would make the composite fragile, an appropriate filler amount is important from both the mechanical and tribological perspectives

In view of the importance of transfer film in tribological behavior, this paper presents the observations related to transfer film studies for PPS, filled PPS, and hybrid composites comprised of both the filler and fiber reinforcement. In addition, back-transfer behavior for a typical composition is also presented to support the wear resistance mechanism of the composites.

2. Experimental details

2.1 Materials

Polyphenylene sulfide was used as the matrix material because of its high temperature capability and excellent mechanical properties. It was supplied in the form of powder from Phillips Chemical Company. Nanoscale CuO particles (16-32 nm in average diameter), which were purchased from Nanophase Technology Corporation, were used for the filler material. Carbon and Kevlar fiber were used for the reinforcement material. Carbon fibers (CF), which were 7 μm in diameter and 6 mm in length, were supplied by Union Carbide Corporation. Kevlar-29 fibers, 20 μm in diameter and 6 mm long, were supplied by Du Pont Company.

2.2 Sample preparation and sliding wear tests

To prepare CuO-filled composite specimens, PPS and CuO particles were dried at 125°C for 5 hours. They were then weighted and mixed in the required proportions. Our previous work showed that 2 vol.% CuO provided the lowest steady state wear rate in the PPS-CuO composites [5]. It was therefore decided that the same amount for hybrid composites of PPS, CuO and fiber materials should be used as well. The fiber materials were also dried, weighed, and mixed in the right proportions with PPS and CuO particles in an ultrasonic bath of acetone. This allowed PPS and CuO particles to cover fiber surfaces effectively. The mixture was then dried and used for compression molding as described elsewhere [3, 4].

Table 1. Steady state wear rates the coefficient of friction of PPS composites [11].

Compositions	Wear rate [mm^3/km]	Friction coefficient
Unfilled PPS	0.291	0.46
PPS+2%CuO	0.047	0.52
PPS+2%CuO+5%CF	0.020	0.49
PPS+2%CuO+15%Kevlar	0.014	0.59

Note: The coefficient of friction was taken from the steady wear state and was later averaged.

Sliding tests were performed in the pin-on-disk configuration. The counterface was made of quenched and hardened tool steel (55-60 HRC) and was finished by abrasion to a surface roughness of 0.09-0.10 μm Ra. The polymer composite pin with a nominal contact area of 5 mm x 6 mm was also finished and loaded on the rotating steel disk with a nominal contact pressure of 0.65 MPa. Sliding tests were run for 6 hours which provided steady state sliding. To measure friction force, strain gauges mounted on the loading arm were used. The loss in weight of the pin sample was measured with an accuracy of 10 μg and was converted into wear volume loss for the purpose of comparison of data for different composites.

3. Results and discussion

3.1 Wear and friction of the PPS composites

Table 1 gives the steady state wear rate and the coefficient of friction data for four polymer compositions. The latter are unfilled PPS, PPS+2%CuO, PPS+2%CuO+5%CF, and PPS+2%CuO+15%Kevlar. More details on these and other related compositions were reported in our earlier paper [11]. In addition, some of the related observations quoted from the paper are provided in order to correlate the transfer film and back transfer behavior study done in this paper with the tribological behavior of the above composites. The following observations are important in the context of this paper. The steady state wear rate of the unfilled PPS was significantly reduced with the addition of 2 vol.% CuO filler.

With the addition of 5 vol.% short carbon fibers to the above composite, the steady state wear rate was further lowered, as seen in Table 1. The lowest steady state wear rate was obtained for the PPS+2%CuO+ 15%Kevlar composite. The wear rate in this case was improved by a factor of 20 as compared to that of unfilled PPS. The synergism effect when both the filler and reinforcement are added to the polymer was emphasized in our earlier study [11, 12]. As seen from Table 1, the coefficients of friction were about the same except for the PPS+2%CuO+15%Kevlar composite in which case friction increased slightly.

3.2 Transfer films studies

3.2.1 By atomic force microscopy

PPS is known to form a good transfer film during sliding, but the film is somewhat thick and grainy in structure. It develops gradually in the transient wear state and the steady wear state is obtained when the film covers the whole wear track. AFM section analyses of the films were performed in the normal to sliding direction. Fig. 1(a-d) show the planar topographical images of the transfer films along with their sectional views for all compositions included in this study. The sectional view of the transfer film of unfilled PPS in Fig. 1(a) shows deep and wide furrows, which are the result of abrasive finishing of the hard metal counterface. The transfer film did not cover the steel counterface adequately and so some abrasive action occurred during sliding. The wear rate in this case was thus fairly high.

The texture and appearance of the transfer film surface were altered by the addition of nanoscale CuO particles to PPS. Fig. 1(b) shows the AFM planar view and the sectional view of the transfer film for CuO-filled PPS. The wide and deep furrows disappeared in this case and the surface became more uniform. As a result, abrasive action was significantly reduced during sliding. Fine wear particles seem to adhere to the counterface layer by layer. This build-up of wear particles provided a better coverage of the counterface. Consequently, the steady state wear rate decreased significantly in this case as compared to that of the unfilled PPS.

The AFM results for the PPS+2%CuO+5%CF composite are given in Fig. 1(c). As can be seen, high peaks and deep valleys are no longer visible here. The surface of the transfer film is much more uniform and coherent than in the earlier two cases. It is also much smoother. Owing to the smoother and more uniform transfer film, the steady state wear rate of this composite was further reduced.

The smoothest and most coherent transfer film was obtained for the PPS+2%CuO+15%Kevlar composite, as seen in Fig. 1(d), and the reduction in wear rate was also the largest in this case. The film in this case was very effective in reducing the damage on the soft polymer surface from hard counterface asperities during sliding.

3.2.2 By scanning electron microscopy

Scanning electron microscopy for the transfer films was also carried out to examine their texture and make-up. Fig. 2(a) shows the topographical image of the transfer film of the PPS+2%CuO composite.

It shows stepped structures along the sliding direction which is indicated by an arrow. These structures were formed by the compaction of wear particles on the counterface under high pressure and temperature. In the process, the boundaries of the wear particles blended but not completely so that a multilayered structure was developed. The patchy appearance as

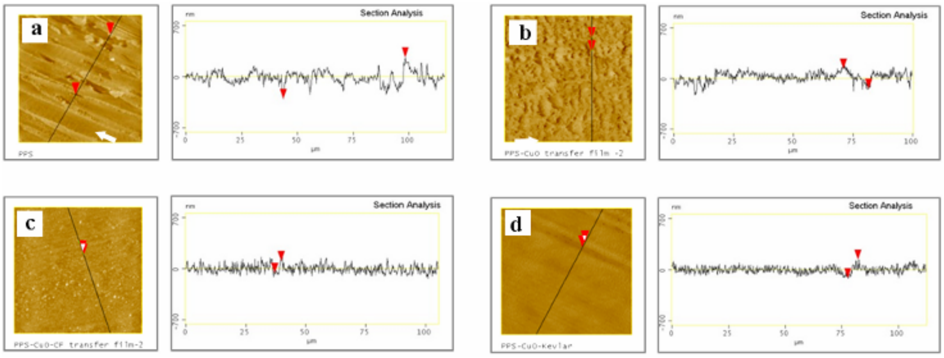

Fig. 1. Planar and sectional view of the transfer films of (a) unfilled PPS, (b) PPS+2%CuO, (c) PPS+2%CuO+5%CF, and (d) PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction.

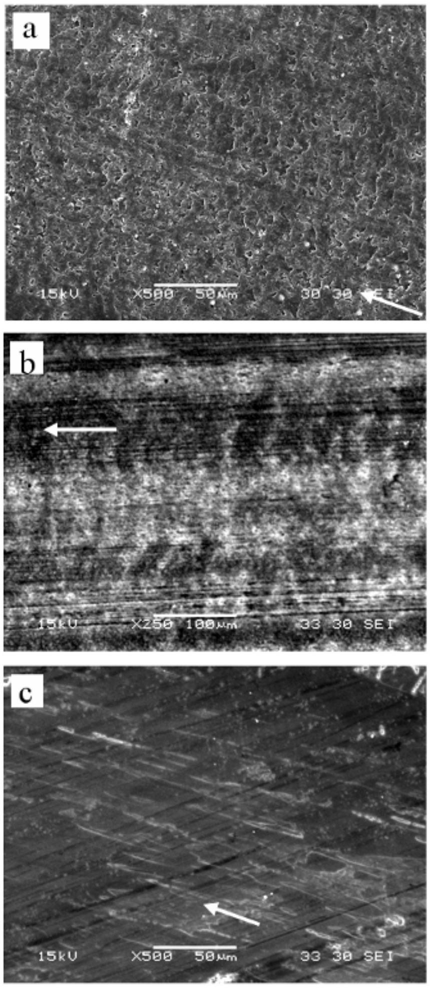

Fig. 2. SEM micrographs of the transfer films; (a) PPS+2% CuO, (b) PPS+2%CuO+5%CF, and (c) PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction.

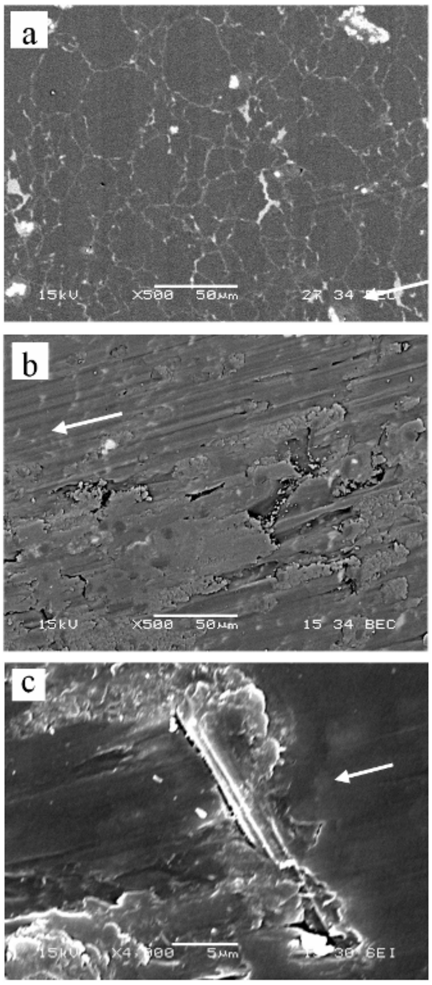

Fig. 3. BSE micrographs of worn samples; (a) PPS+2%CuO, (b) PPS+2%CuO+5%CF. SEM in secondary electron (SE) image of worn sample of (c) PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction. Note: BSE and SE images have different magnification.

seen in the AFM planar image (Fig. 1(b)) seems to correspond to the stepped and discontinuous feature of the transfer film. The sharp peaks and valleys observed in the AFM sectional view were presumably because of this structure.

The transfer film for PPS+2%CuO+5%CF became much smoother and coherent and the stepped structures seen in the above were not observed any more. Instead, wear marks with very narrow and compacted feature are clearly seen and this is believed to make a jagged appearance in the AFM sectional view of the composite. The smoothest surface was observed in the case of the PPS+2%CuO+15%Kevlar composite, as seen in Fig. 2(c).

The transfer film here was so thin that the abrasion finishing marks on the counterface may also be seen. The figure also shows highly-compacted wear particles on the surface. These particles were very fine, and they were necessary for developing a very thin film.

3.3 Examination of worn surfaces

3.3.1 By scanning electron microscopy

The SEM micrographs of the worn surfaces in the backscattered electrons (BSE) image were taken and analyzed for the PPS+2%CuO and PPS+2%CuO+5%CF composites. As can be seen in Fig. 3(a) for the

PPS+2%CuO composite, sliding tracks and white dots are seen. There was no apparent damage to the surface in this case and so it is believed that wear occurred mainly due to fatigue and the depletion of transfer film in repeated sliding. In other words, since BSE is known to produce a depth image rather than surface topography, worn surface with no severe damage under BSE analysis indicates that sliding took place mostly near the sliding interface. In addition, since BSE micrograph could not tell the elemental information, X-ray area scanning (dot mapping) was performed for this purpose, which is presented in the next section. On the contrary, Fig 3(b) for PPS+2%CuO+5%CF composite shows highly-compacted wear particles. Extensive plowing action from carbon fibers is more clearly seen. This indicates that the sliding action affected the sliding interface, as well as the inside of the sample. Wear marks along the sliding direction are significantly pronounced. Also, the rupture of the worn surface due to fiber-matrix debonding is clearly seen in the case of PPS+2%CuO+15%Kevlar composite, which is secondary electron (SE) image. It should be noted, however, that wear particles strongly adhere to the worn surface, as was found to be the case above. The strong bonding between the matrix and the Kevlar fibers prevented the loss of matrix material due to matrix cracking and/or fiber-debonding. In this respect, the reinforcement by fibers and the consequent improvement in mechanical properties of the composite contributed to the increased wear resistance.

3.3.2 By dot mapping analysis

It has been widely reported that a chemical reaction due to high pressure and temperature at the sliding interface during sliding occurs, thereby contributing to the enhanced bonding of the polymeric transfer film to the steel counterface [2-3,9]. For example, X-ray photoelectron spectroscopy (XPS) analysis performed for the transfer film of PPS composite filled with CuS particle showed that the CuS filler in PPS matrix decomposed to Cu and S during sliding and later the S element from the decomposition of CuS reacted with Fe element of the steel counterface, producing $FeSO_4$ [9]. It has been reported that S element was not from the decomposition of PPS containing S element. The generation of $FeSO_4$ is shown to increase the bonding of transfer film to the steel surface. In addition, intensity of $FeSO_4$ was much pronounced closer to the steel surface, indicating that chemical reaction between CuS filler and steel counterface took place rigorously.

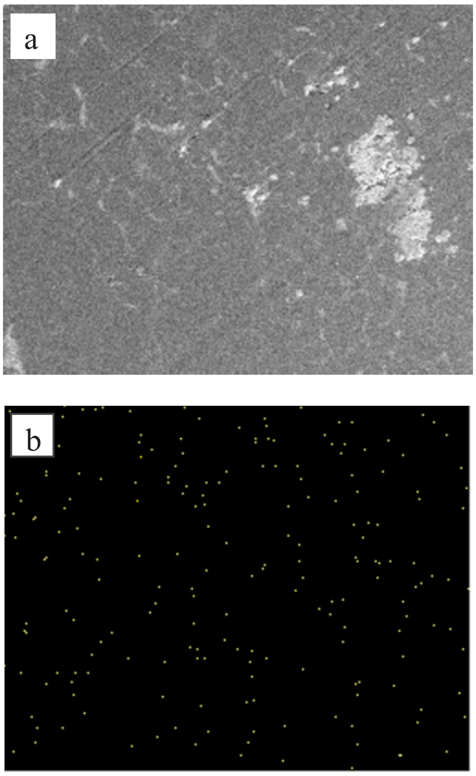

Fig. 4. (a) BSE image of the worn pin surface of PPS+2%CuO composite, (b) Fe-K element detected by dot mapping analysis for the same composition.

However, this behavior shows only the effect of matrix material and/or filler material to the counterface material and explains why a certain transfer film is highly adherent to the counterface while some are not. To investigate the opposite phenomenon, which reveals the transfer of counterface constituents to the specimen surface, chemical analysis should be done to examine the presence of other constituents other than the matrix and filler material. For this, dot mapping analysis was done on the worn surface of PPS+2%CuO composite and Fig. 4 shows Fe-K element detected by dot mapping analysis. From this analysis, back-transfer of the counterface material was observed. The elements Fe, Cr, Co, and Ni which are the typical tool steel elements used as counterface material in this study were detected. They were presumably the result of back-transfer behavior during sliding from the steel counterface. It is generally known that material transfer occurs from a soft material to a hard material because the latter can easily plow the former and generate a number of wear grooves. It is not a surprising observation, however, that back-transfer was observed from the soft PPS composite because this composite contained a hard filler material, CuO. In other words, the contact between CuO and metal asperities took place during sliding and this resulted in the removal of metal asperities. Subsequently, the loose metal fragments would either be embedded in the polymer matrix or remain at the sliding interface, causing the two-body or three-body abrasion. However, abrasivity was not significant in this case because the angularity of the filler particle decreases with the decrease in particle size. In this respect, nanoscale particles are preferred to micro scale particles in many cases. In addition, it is believed that these back-transferred elements contributed to the strengthening of the polymer surface. This in turn made the pin surface more wear-resistant. However, whether or not the chemical reaction between the back-transferred material and the PPS composite took place during sliding is unknown.

4. Conclusions

Nanoscale CuO filler particles were effective in developing a transfer film during sliding which had stepped and multilayered structure.

The addition of both CuO and short fibers to PPS resulted in the formation of a more uniform and thinner transfer film compared to both the unfilled PPS and CuO-filled PPS composite.

The formation of thin and uniform transfer film on the counterface during sliding was the main factor in governing the wear resistance of the compositions studied in this work.

Dot mapping analysis showed the back transfer of material because elements such as Fe, Cr, Co, and Ni were detected on the worn surfaces. This exposes the possibility of the transfer film being composed of a mixture of the polymer composite ingredients and the elements in the steel counterface.

Back-transfer of metallic fragments to the polymer matrix is believed to enhance the wear resistance of PPS composite by strengthening mechanism.

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