

CuO nanoparticle 및 fiber 로 구성된 PPS 복합재료의 sliding 조건하의 transfer film 에 관한 연구

조민행[†] · Shyam Bahadur^{*} · 박혜영^{**} · 김윤준^{***}

Study of transfer film in the sliding of nanoscale CuO-filled and fiber-reinforced polyphenylene sulfide (PPS) composites

Minhaeng Cho, Shyam Bahadur, Hye-Young Park, and YoonJun Kim

Key Words : PPS; Wear; Friction; Hybrid composites; Transfer film analysis; Topographical analysis; Filler; Fiber Reinforcement; Back transfer

Abstract

The role of transfer films formed during sliding of polymer composites against steel counterfaces was studied in terms of the tribological behaviors of composites. Four kinds of composites were included in this study: (1) unfilled PPS, (2) PPS+2%CuO, (3) PPS+2%CuO+5% carbon fiber (CF), and (4) PPS+2%CuO+15%Kevlar. The filler material CuO was in nanoscale particulate form and the reinforcing material was in the form of short fibers. The composites were prepared by compression molding at 310°C and sliding tests were run in the 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 m/s and contact pressure of 0.65 MPa. Transfer films formed on the counterfaces during sliding were investigated using AFM and SEM. The results showed that as the transfer film became smooth and uniform, wear rate decreased. PPS+2%CuO+15%Kevlar composite showed the lowest steady state wear rate in this study and its transfer film showed the smoothest and the most uniform characteristics. The examination of worn surfaces of PPS+2%CuO composite using X-ray area scanning (dot mapping) showed back-transfer of 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.

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 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. In polymer-metal sliding systems, especially, it has been widely shown that the variables are closely related to the development of transfer film and so 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, the transfer film is very important in determining the wear resistance. For this reason, an improvement in the mechanical properties does not necessarily result in the enhancement of wear resistance.

Many studies have shown that the formation of transfer film is promoted by the addition of inorganic filler material to the polymer. Also, it has been shown that improved wear resistance is closely related to the characteristics of 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 CaF₂ filler. In the case of CaF₂-filled nylon composite, wear increased linearly with sliding distance and no steady wear state corresponding to a low wear rate was observed. The transfer film was observed to

[†] Department of Mechanical engineering, Iowa State University, 2025 Black Engr. Bldg., Ames, IA 50010
E-mail : mhcho87@iastate.edu
TEL: +1-515-294-0349 FAX: +1-515-294-3261

^{*} Department of Mechanical engineering, Iowa State University, 2025 Black Engr. Bldg., Ames, IA 50010

^{**} Department of Chemistry, Iowa State University

^{***} Department of Materials Science and Engineering, Iowa State University

peel off the substrate which indicated that the adhesion of 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 by covering the metal asperities provides the protection. The studies related to the transfer film are thus important for understanding the friction and wear behavior in polymer-metal sliding.

The dependence of the filler on the characteristics of 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, Ag₂S, NiS, and TiO₂ [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 ZnF₂, CaF₂, PbTe, PbSe, SiC, and ZnO particles and steady state wear rate of the composites in these cases was increased over that of unfilled PPS [3-6].

The fiber reinforcement also affects the tribological behavior of polymer composites. The improvement of wear resistance with the addition of fiber material has been attributed to factors such as the greater load-carrying ability of fiber material and the resistance to surface damage during sliding because of increased shear strength. In respect of the latter, fibers are more effective than the filler particles because of higher aspect ratios which provide for increased adhesion between the matrix and the fiber. Fiber materials are capable of supporting larger loads than the polymeric materials because of much higher strengths and moduli of elasticity. 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 wear rate also decreased because of the factors stated above. With the fiber reinforcement, a smoother transfer film was formed and this was also responsible for increasing 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 in 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 showed that the sliding variables significantly affected the wear and friction of PPS in the running-in period. Wear rate in this period was usually very high. Furthermore, the sliding variables were found to be closely associated with the formation of transfer film during the transient state. However, steady state is not sometimes observed when wear is mostly governed by abrasive action so that wear continues to increase linearly. In other words, no transfer films forms on the counterface, and if it does, it does not adhere to the counterface thereby resulting in its continuous removal

from the counterface. While in transient wear state there is rapid increase in wear with sliding distance accompanied by substantial abrasive action, in steady state 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 the practical reasons.

As stated above, the adhesion of transfer film to the counterface is an important factor to get 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, 11]. In order to investigate the adhesion of transfer film to the counterface and its effect on wear rate, Schwartz and Bahadur [9] performed bond strength measurements on the transfer film of PPS filled with nanoscale Al₂O₃ 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 finished to a surface roughness of 0.027 μm Ra, 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 filler causing abrasion during sliding. Thus, nanoscale particles seem preferable to the microscale particles in this respect. Moreover, smaller particles provide 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 nanometer size filler material, a very small proportion such as 2 vol.% is effective in lowering the wear rate [5] while much larger proportion in the range of 20-30 vol.% are needed for micrometer size filler material [6]. Since excessive filler amounts make the composite fragile, a proper filler amount is important from both the mechanical and tribological considerations.

In the view of the importance of the transfer film for tribological behavior, this paper presents observations related to transfer film studies for PPS, filled PPS, and hybrid composites comprised of both the filler and fiber reinforcement.

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 by Phillips Chemical Company.

Nanoscale CuO particles (16-32 nm in average diameter), which were purchased from the Nanophase Technology Corporation, were used for the filler material. Carbon and Kevlar fiber were used for the reinforcement material. Carbon fibers, which were 7 μm in diameter and 6 mm long, were supplied by the Union Carbide Corporation. Kevlar-29 fibers, 20 μm in diameter and 6 mm long, were supplied by the Du Pont Company.

2.2 Sample preparation and sliding tests

In order to prepare CuO-filled composite specimens, PPS and CuO particles were dried at 125°C for 5 hours. They were then weighed and mixed in the required proportions. Our early work had showed that 2 vol.% CuO provided the lowest steady state wear rate in the PPS-CuO composites [5]. It was, therefore, decided to use the same amount for hybrid composites of PPS, CuO and fiber materials as well. The fiber materials were also dried, weighed, and mixed in 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 per procedure described elsewhere [3-4].

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. In order to measure friction force, strain gauges mounted on the loading arm were used. The loss in weight of the pin sample was measured

Table 1. Steady state wear rates and the coefficients of friction of PPS composites

Compositions	Wear rate, mm^3/Km	Coefficient of friction
Unfilled PPS	0.291	0.48
PPS+2%CuO	0.047	0.52
PPS+2%CuO+5%CF	0.020	0.49
PPS+2%CuO+15%Kevlar	0.014	0.64

with an accuracy of 10 μg and was converted into wear volume loss for the purpose of comparison of data for different composite specimens.

3. Results and discussion

3.1 Wear and friction of 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 detailed on these and other related compositions was reported in our earlier paper [10]. The following observations are important in the context of this paper. Steady state wear rate of unfilled PPS was significantly reduced by the addition of 2 vol.% CuO filler. With the addition of 5 vol.% short carbon fibers to the above composite, steady state wear rate was further lowered, as seen in Table 1. The lowest steady state wear rate was obtained for PPS+2%CuO+15%Kevlar composite. The wear rate in this case was improved by a factor of 20 compared to that of unfilled PPS. The synergism effect

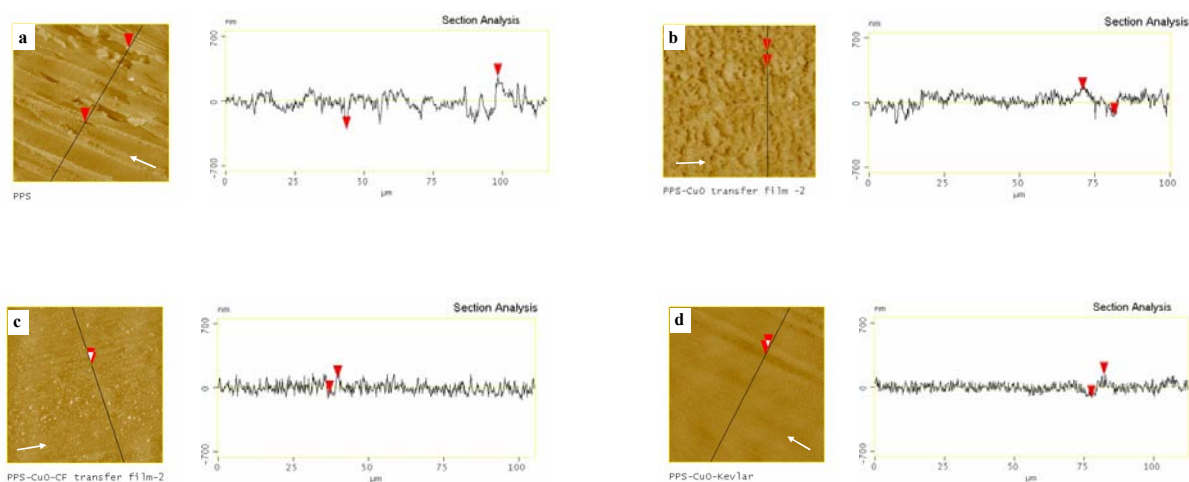


Figure 1. Planar and sectional view of transfer film of (a) unfilled PPS, (b) PPS+2%CuO, (c) PPS+2%CuO+5%CF, and (d) PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction.

when both the filler and reinforcement are added to the polymer was emphasized in our earlier study [10-12]. As seen from Table 1, the coefficients of friction were about the same except for PPS+2%CuO+15%Kevlar composite in which case friction increased slightly.

3.2 Transfer film studies

3.2.1 By Atomic 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 steady wear state is obtained when the film covers the whole wear track. AFM section analyses of the films were performed normal to sliding direction. Figure 1(a-d) show planar topographical images of the transfer films along with their sectional views for all the 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. Wear rate in this case was thus fairly high.

The texture and appearance of transfer film surface were altered by the addition of nanoscale CuO particles to PPS. Figure 1(b) shows the AFM planar view as well as 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 of this, abrasive action was significantly reduced during sliding. Fine wear particles seem to be adhering to the counterface layer by layer. This build-up of the wear particles provided a better coverage of the counterface. Consequently, steady state wear rate decreased significantly in this case as compared to that of the unfilled PPS.

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

The smoothest and the most coherent transfer film in this study was obtained for 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 of transfer films was also carried out in order to examine their texture and make-up. Figure 2(a) shows the transfer film of 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 wear particles blended but not completely so that multilayered structure was developed. The patchy appearance as seen in the AFM planar image (Fig. 1(a)) seems to correspond to the stepped and discontinuous feature of the transfer film. The sharp peaks and valleys observed in the AFM

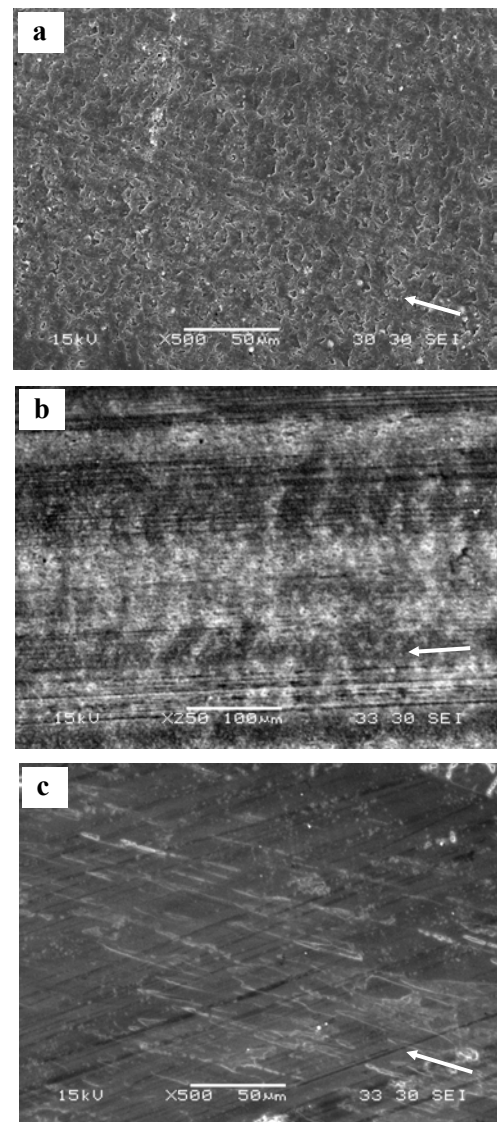


Figure 2. SEM micrographs of transfer films; (a) PPS+2%CuO, (b) PPS+2%CuO+5%CF, and (c) PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction.

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 above were not observed any more. Instead, wear marks with very narrow and compacted feature are clearly seen and this is believed to make jagged

appearance in the AFM sectional view of this composite. The smoothest surface was observed in the case of 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 be seen. The figure also shows highly-compacted wear particles on the surface. These particles were very fine which was necessary for developing a very thin film.

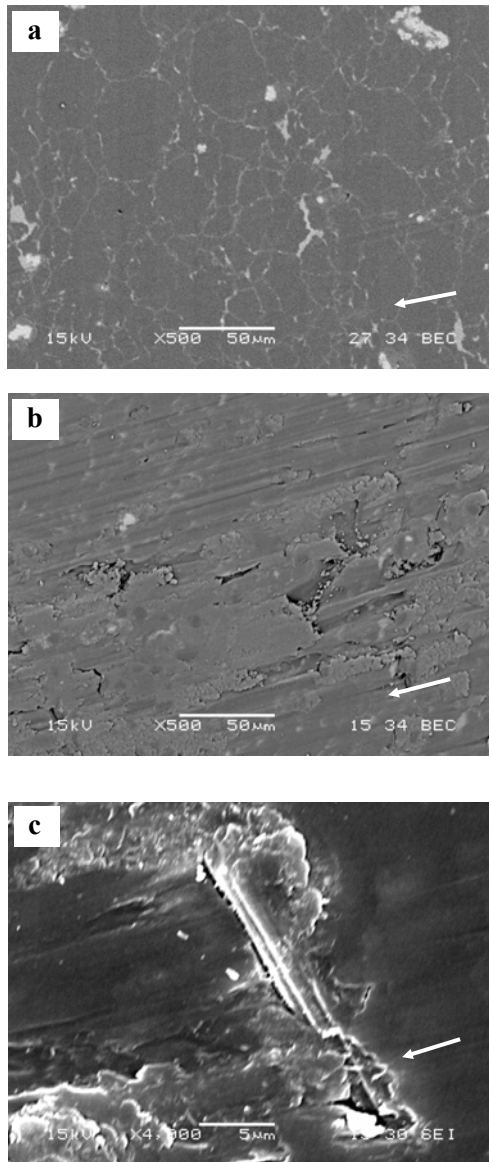


Figure 3. SEM micrographs of worn samples; (a) BSE image of PPS+2%CuO, (b) BSE image of PPS+2%CuO+5%CF, and (c) SE image of PPS+2%CuO+15%Kevlar composites. Arrow indicates sliding direction.

3.3 Examination of worn surfaces

3.3.1 By Scanning Electron Microscopy

SEM micrographs of worn surfaces in the back scattered electron (BSE) mode were taken and analyzed

for PPS+2%CuO and PPS+2%CuO+5%CF composites. As can be seen in Fig. 3(a) for 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. 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. 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. The rupture of worn surface due to fiber-matrix debonding is clearly seen in the case of PPS+2%CuO+15%Kevlar composite. It should be noted, however, that wear particles are strongly adhering to the worn surface, as was found to be the case above. The strong bonding between the matrix and 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 contribute to increased wear resistance.

3.3.2 By X-ray Area Scanning (Dot Mapping)

Dot mapping analysis was done on the worn surface of PPS+2%CuO composite and back-transfer of the counterface material was observed from this analysis. The elements of Fe, Cr, Co, and Ni were detected and were presumably the result of back-transfer during sliding from the steel counterface. It is believed that these elements contributed to the strengthening of the polymer surface. This in turn made the pin surface more wear-resistant.

4. Concluding remarks

1. Nanosize CuO filler particles were effective in developing a transfer film during sliding which had stepped and multilayered structure.
2. The addition of both CuO and short carbon 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.
3. The thinnest and the smoothest transfer film was obtained in the case of PPS+2%CuO+15%Kevlar composite. The lowest steady state wear rate of $0.014\text{mm}^3/\text{Km}$ was also obtained from this composite.
4. 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.
5. EDS 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.

References

- [1] S. Bahadur, The development of transfer layers and their role in polymer tribology, *Wear* 245 (2000) 92-99.
- [2] S. Bahadur, D. Gong, and J. Anderegg, Investigation of the influence of CaS, CaO, and CaF₂ fillers on the transfer and wear of nylon by microscopy and XPS analysis, *Wear* 197 (1996) 271-279.
- [3] Q. Zhao, and S. Bahadur, A study of the modification of the friction and wear behavior of polyphenylene sulfide by particulate Ag₂S and PbTe fillers, *Wear* 217 (1998) 62-72.
- [4] Q. Zhao, and Bahadur, The mechanism of filler action and the criterion of filler selection for reducing wear, *Wear* 225-229 (1999) 660-668.
- [5] C. Sunkara, The role of particulate inorganic fillers on the tribological behavior of polyphenylene sulfide, MS thesis, Iowa State University, Ames, 2000.
- [6] L. Yu, and S. Bahadur, An investigation of the transfer film characteristics and the tribological behavior of polyphenylene sulfide composites in sliding against tool steel, *Wear* 214 (1998) 245-251.
- [7] J. Theberge, and B. Arkles, Wear characteristics of carbon fiber reinforced thermoplastics,
- [8] Q. Zhao, and S. Bahadur, Investigation of the transition state in the wear of polyphenylene sulfide slide against steel, *Tribology Letters*, Vol. 12, No.1, 2002.
- [9] C.J. Schwartz, and S. Bahadur, Studies on the tribological behavior and transfer film-counterface bond strength for polyphenylene sulfide filled with nanoscale alumina particles, *Wear* 237 (2000) 261-273
- [10] Min. H. Cho, and S. Bahadur, A study of the synergism effects in the tribological behavior of nanosize CuO-filled and fiber-reinforced polyphenylene sulfide composites, *Wear* (in progress)
- [11] S. Bahadur, D. Gong, and J. W. Anderegg, Studies of worn surfaces and the transfer film formed in sliding by CuS-filled and carbon fiber-reinforced nylon against a steel surface, *Wear* 181-183 (1995) 227-235
- [12] S. Bahadur, Q. Fu, and D. Gong, The effect of reinforcement and the synergism between CuS and carbon fiber on the wear of nylon, *Wear* 178 (1994) 123-130.