

Investigation of the Influence of CuO Filler and Carbon Fiber on Wear and Transfer Film of Nylon Composites

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ABSTRACT: Nylon 1010 composite specimens were prepared with CuO filler and short carbon fiber (CF) as the reinforcement. Friction and wear behavior of composite materials was investigated in a ring-block wear tester. The results show that carbon fiber was more effective in reducing friction and wear of nylon than CuO filler. Nylon composite with 20% CF and 10% CuO content filler had the lowest wear rate that could not be obtained with any proportion of the fiber or the filler alone. It was found that the transfer film on the counterpart of 20% CF–10% CuO–nylon was thin, continuous, and uniform. These differences in tribological performance have been studied according to the

synergism between the carbon fiber and CuO filler. The tribochemical studies by X-ray photoelectron spectroscopy (XPS) revealed that pure Cu, Cu₂O, and Cu(OH)₂ were produced due to the decomposition of CuO during sliding. Carbon fiber promoted the process of tribochemical reactions of CuO, which generated more pure Cu particle and then self-lubricating transfer film including pure Cu was formed on the steel counterpart. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2397–2401, 2004

Key words: nylon; fillers; fibers; transfer film; tribochemical reactions

INTRODUCTION

Nylon is a good bearing material because of its high strength and good wear resistance, but the friction coefficient and the absorption of moisture is higher than for poly(tetrafluoroethylene) (PTFE) and ultra-high molecular weight polyethylene (UHMWPE) under dry sliding friction conditions. Various studies have demonstrated that the tribological properties of polymers could be further enhanced by the addition of inorganic fillers and fibers. Voss and Friedrich¹ observed that the reinforcement with fibers could improve the wear resistance of nylon, poly(ether ether) ketone (PEEK), and polyethersulfone. The minimum wear rate was obtained with 15–20% fiber proportions. Bahadur and Polineni² found that the wear rate of nylon 11 could be reduced by a factor of five or six with the increasing glass fiber fabric volume proportion up to 20.7%; additionally, it was not possible to prepare good specimens with fiber volume proportions in excess of 20.7%. Kukureka et al.³ found that the aramid-fiber reinforcement did not significantly alter the friction of the nylon 66 matrices. However, wear resistance of the aramid- and carbon-fiber (CF) composite was generally around 10 times greater than that of the unreinforced material. Bahadur et al.^{4–6} and Gong,^{7,8} and Zhang et al.⁹ found that CuO, CuS,

CuF₂, CaO, CaS, PbO, Pb₃O₄, and PbS had the ability to reduce wear of nylon or PTFE. The best wear resistance was usually obtained when 30–35% of the inorganic fillers were used. Contrary to the above, ZnF₂, ZnS, ZnO, CaF₂, and SnF₂ are harmful to the wear resistance of some polymers.^{6,10} In particular, the role of fillers having influence on the wear behavior of polymers is not yet completely understood.

There has been almost no research reported about the contribution of CF in the presence of CuO filler on the tribological behaviors of nylon 1010 composite. The objective of the present work was to look at the effect of the transfer film and tribochemical reactions between the hybrid fillers on the wear of nylon 1010, to find out the important factors related to the wear resistance of composites.

EXPERIMENTAL

The polymer material used in this work was nylon 1010 in the powder form (<175 μm). The CF were 7 μm in diameter and 40–60 μm long. The particle size of CuO filler was smaller than 175 μm. The filler, fiber, and dried nylon 1010 were mixed mechanically and injected into a 6 × 10 × 20 mm block specimen. Friction and wear experiments were run in a ring-block wear tester at the velocity of 0.42 m/s for 2 h, under loads of 100 and 200 N in laboratory atmosphere (relative humidity 45–60%). The material of the steel ring was AISI 1045 steel, which was quenched to a hardness of 40–45 HRC. The composite block and steel ring were ground with 600-grade SiC paper, which

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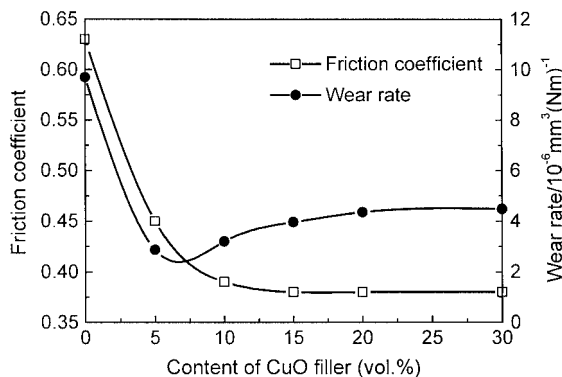


Figure 1 Variation of friction coefficient and wear rate of CuO filler reinforced nylon composites under 100 N normal loads.

provided a surface roughness of $R_a = 0.4\sim 0.6 \mu\text{m}$ and $0.10\sim 0.15 \mu\text{m}$, respectively. The surface of the block and steel ring was cleaned with a soft paper soaked in acetone and dried. Wear mass loss of block was measured to an accuracy of 0.01 mg. The friction force was measured from the output of a strain gauge mounted on a vertical arm that carried the block after successive runs. Each plot value is the mean of the three experimental values. The maximum variation between these experimental values was not higher than $\pm 15\%$.

The transfer films of the composites were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The positions of the XPS peaks were determined with reference to the contaminated carbon peak (henceforth reference to as the C1s peak) at 284.6 eV. The binding energy was measured with the accuracy of $\pm 0.2 \text{ eV}$.

RESULTS AND DISCUSSION

Friction and wear properties

Figure 1 gives the variation of friction coefficient and wear rate for nylon reinforced with varying volume amounts of CuO filler under 100 N normal loads. It may be seen that the friction coefficient and wear rate of nylon were reduced to 0.45 and $2.9 \times 10^{-6} \text{mm}^3 \text{N}^{-1} \text{m}^{-1}$ while 5% CuO filled in nylon block. The friction coefficient approximately kept in steady state when CuO filler content was higher than 15%. The wear rate of 5 and 10% CuO filler-reinforced nylon composites was lower than those for the composites with 15, 20, and 30% CuO filler content. This indicated that there was a critical filler content, which provided a good tribological performance of nylon composite.

Table I gives the test results of tribological properties of nylon and its composites filled with carbon fiber or CuO filler under 200 N normal loads. It was found that pure nylon was intensely worn and the wear debris was not like small particles but instead in the

TABLE I
Test Results of the Friction Coefficient and Wear Volume of Nylon Composite under 200 N Normal Loads

Materials	Friction coefficient	Wear rate/ $10^{-6} \text{mm}^3 (\text{Nm})^{-1}$
Nylon 1010	0.70	Intensely worn
10% CuO	0.56	155
15% CF	0.26	1.90
20% CF	0.25	1.55
30% CF	0.24	1.65

form of large slices after 30~35 min during dry sliding friction. The wear rate of nylon was reduced by the addition of CuO filler or CF, but the friction coefficient and wear rate of 10% CuO-nylon was higher than CF-reinforced nylon composite. The wear rate was the lowest for 20% CF content in nylon and it was higher for both the lower and higher percentage of the fiber. In comparison, the wear resistance of 20% CF-nylon increased by about two orders of magnitude and friction coefficient decreased to half the value of that of 10% CuO-nylon. Factors contributed to the reduction in wear and friction of the fiber-reinforced composite could be as follows. CF have good self-lubricating action, also fibers are known to provide strengthening to the polymer matrix and protrude out of the rubbing surface during sliding so that the major share of normal load will be supported by fibers.

In view of the above study, it was decided to fill CF in nylon with 10% CuO filler, hoping to improve these tribological properties further. The variation of the tribological properties for these composites is given in Figure 2. The results show that the wear rate and friction coefficient of nylon are reduced by a small amount of CF reinforcement. With increased volume proportions of CF, the friction coefficient decreased continuously, and the lowest value of wear rate (which is $1.1 \times 10^{-6} \text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) was obtained with 20% CF. The

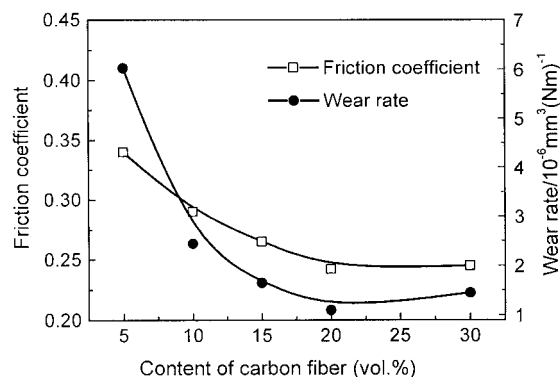


Figure 2 Variation of friction coefficient and wear rate of CF reinforced nylon composites containing 10% CuO filler under 200 N normal loads.

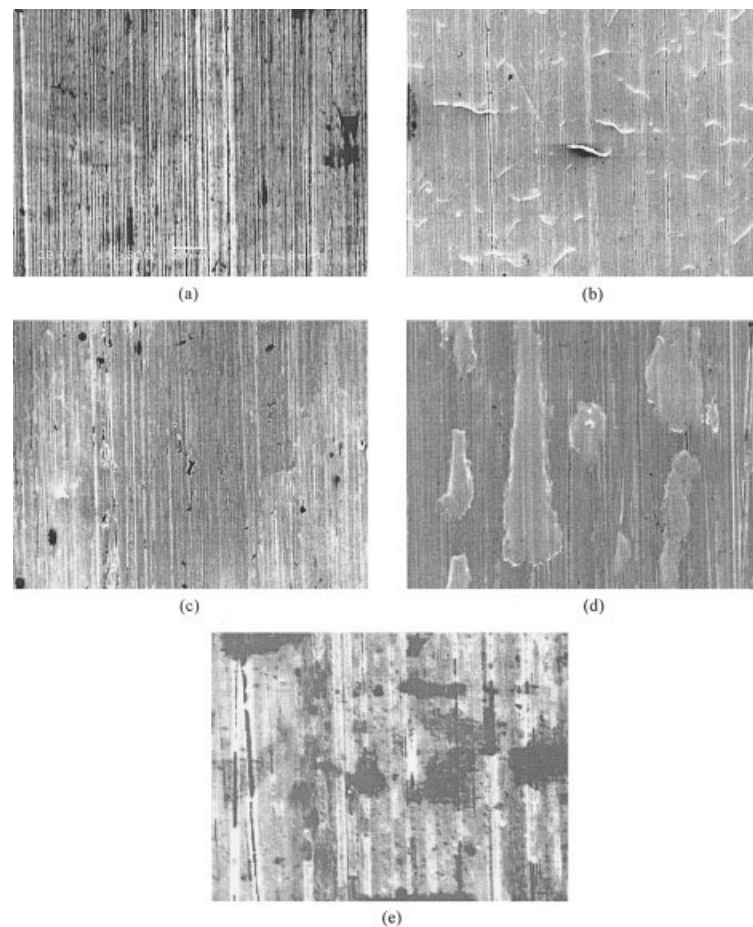


Figure 3 SEM micrographs of the worn surface of the counterpart rubbed against nylon and nylon composite ($\times 600$): (a) nylon, (b) 10% CuO; (c) 20% CF; (d) 5% CF–10% CuO–nylon; (e) 20% CF–10% CuO–nylon.

wear rate of composite increased slightly while the CF content was higher than 20%. The wear reduction was greater when the hybrid filler used was a combination from above experiments. The good wear resistance of 20% CF–10% CuO–nylon could not be achieved with any proportion of the fiber or the filler alone.

Transfer film

The role of CF and CuO filler in the reduction of wear and friction was investigated by examining the transfer film morphologies. The SEM micrographs of the surface of the steel counterpart rubbed against nylon and its composites are shown in Figure 3. A fairly thick film was formed by nylon and the coverage of the counterface surface here was larger and continuous, also lowering tracks were evidently seen in Figure 3(a). The transfer film generated for a CuO–nylon block rubbing against the steel counterpart is shown in Figure 3(b). It may be seen that the presence of CuO filler in nylon has contributed to a uniform and continuous transfer film on the steel counter face. Though metal oxide fillers have been reported^{4,5} to exhibit a general tendency for good adhe-

sion toward iron, there are evident strip debris that detached and existed on the transfer film, therefore, the transfer film concerned here has poor adhesion quality to the counterface surface. Therefore, it would accelerate the film detaching from the steel counterpart.

Figure 3(c) shows a SEM micrograph of transfer film formed by 20% CF–nylon rubbing against the steel counterpart. The transfer film was continuous and tenacious, but was nonuniform in most fields. The reason for this could be the amount of fibers extruded out of the nylon matrix that had scraped the transfer film partially. Meanwhile, CF acted as a promoter of the adhesion between the transferred polymeric material and the steel counterpart, which was basically needed for good wear resistance of the polymer composite. When 10% CuO was added to the composites with 5% CF, the transfer film formed was thin and continuous, and there also existed discontinuous bright patches, which indicated the presence of freshly generated Cu in Figure 3(d). The transfer film of 20% CF–10% CuO–nylon formed on the steel counterpart is shown in Figure 3(e). It was found that the transfer film was thin, continuous, uniform, and tenacious. The

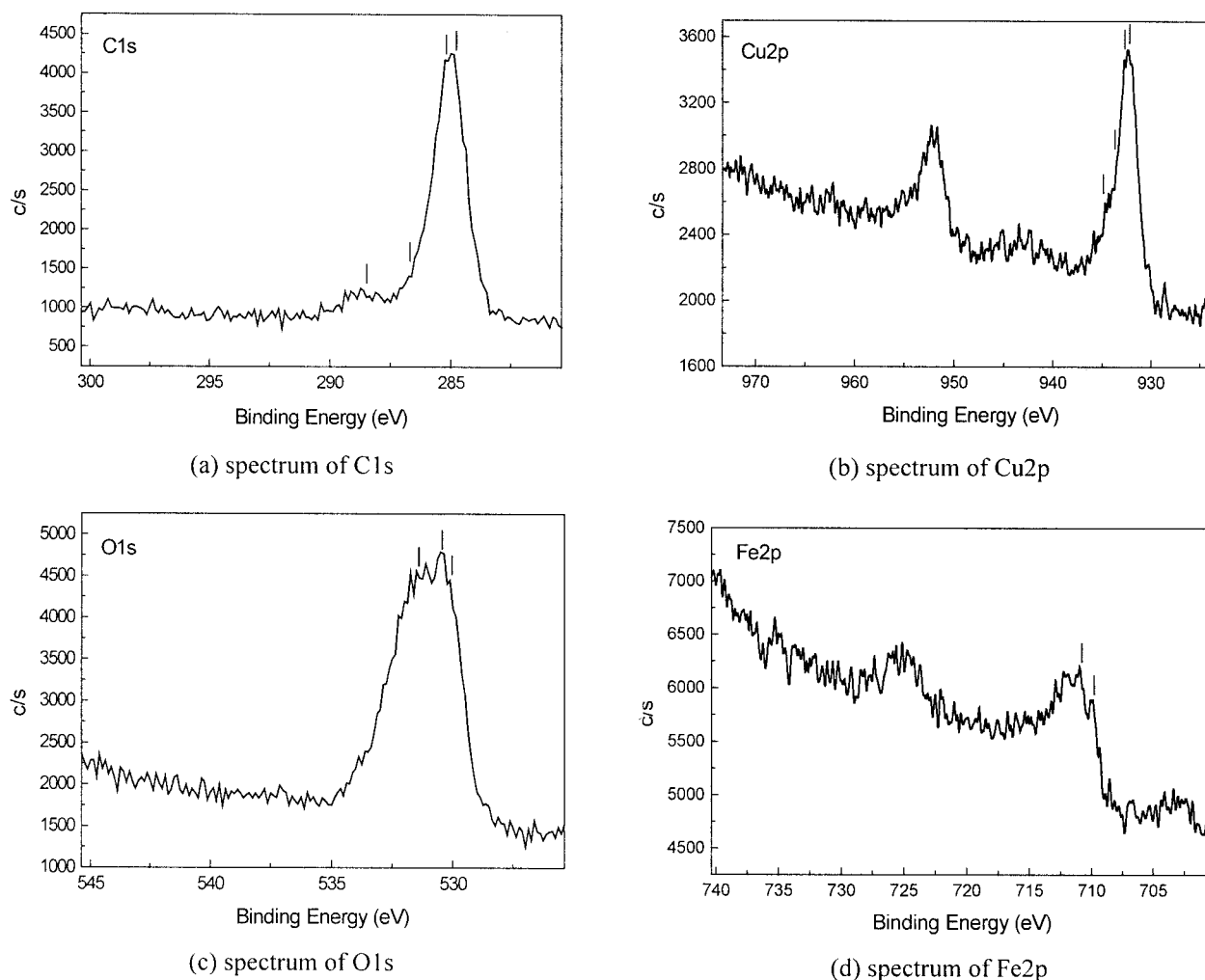


Figure 4 XPS spectra of a typical element of the transfer film formed by 10% CF—10% CuO—nylon rubbing against the steel counterpart under 200 N normal loads.

area of bright patches in Figure 3(e) was larger and almost continuous than that in Figure 3(d). This indicates that the higher proportion of CF in the CuO—nylon composite assists the decomposition of CuO to pure Cu to a larger extent and this generated a thin layer of Cu film over the transfer film. It is reasonable to deduce that pure Cu increased the adhesion between transfer film of the composite and its steel counterpart, which reduced the loss of the transfer film from the counterface surface during repetitive sliding, thereby decreasing the need for replenishment and increasing the wear resistance. Meanwhile, a good self-lubricating transfer film was helpful in protecting the composite surface from damage by the asperities on the hard ridges of the counterface surface in view of other research work.^{11,12}

Tribochemical studies by XPS

The tribochemical reactions during rubbing caused by the presence of CuO filler in nylon composites were

studied. The XPS spectra of the transfer film formed by CuO—CF—nylon rubbing against the steel counterpart are shown in Figure 4. An overlap peak could be seen in the C1s spectrum in Figure 4(a). The peak at the binding energy of 284.6 eV is attributed to the carbon atoms in contaminated carbon and the hydrocarbon in nylon or CF molecules. The peak at 285.2 eV was assigned to the carbon atoms bonded to the —CO— groups and the peak at 286.8 eV bonded to the —NH— group. The peak at 288.5 eV is attributed to —NH—C=O groups of nylon molecules. In the Cu2p spectrum [Fig. 4(b)], the main peak at 932.5 eV corresponds to the pure Cu, and the shoulder peak at 932.7 eV to the copper atoms in Cu₂O, which come from the decomposition of CuO. The peak at 933.6 eV corresponds to the copper atoms in CuO filler, which was filled in nylon compounds. The copper atoms in Cu(OH)₂ attribute to the peak at 935.1 eV. The presence of CuO, Cu₂O, and Cu(OH)₂ is also supported by the peaks at 529.8, 530.5, and 531.6 eV in the O1s spectrum shown in Figure 4(c). In the Fe2p spectrum shown in Figure

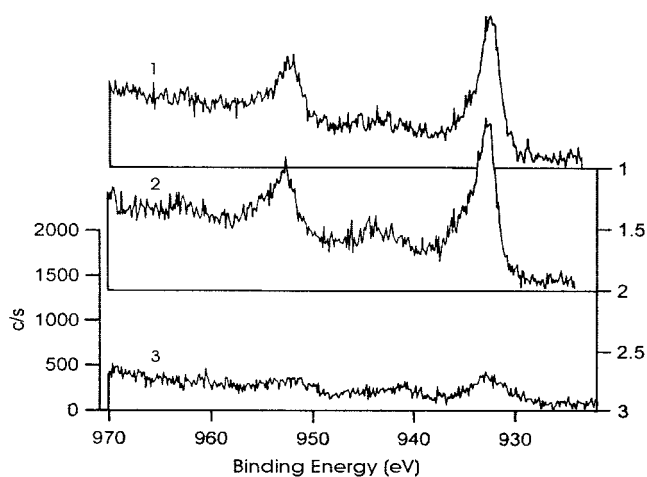


Figure 5 XPS spectra of Cu2p spectra of the transfer film formed by nylon composites rubbing against the steel counterpart: (1) 10% CF–10% CuO–nylon; (2) 20% CF–10% CuO–nylon; (3) 10% CuO–nylon.

4(d), the peaks at 709.4 and 710.9 eV indicate the presence of FeO and Fe₂O₃. The presence of pure Cu, Cu₂O, and Cu(OH)₂ in the transfer film clearly indicates that the CuO filler decomposed during sliding so that these species were generated.

To study the mechanism of the synergistic action described above, Figure 5 shows the Cu2p spectrum of the transfer film formed by nylon composites rubbing against the steel counterpart. The value of Cu2p peak of 10% CuO–nylon was very small, and the main peak at 935.1 eV corresponds to CuO filler, which shows that fewer CuO particles were decomposed to pure Cu or CuO particles were easily removed while rubbing against the steel counterpart. The value of peak of Cu2p of CuO–CF–nylon was higher than that of CuO–nylon. The peak of Cu2p of 20% CF–10% CuO–nylon is higher than the peak of Cu2p of 10% CF–10% CuO–nylon. It is worth noting that the main constituent of the peak of Cu2p was pure Cu. The results confirm that more CuO particles were decomposed and accumulated over nylon matrix for the high proportion of carbon fiber, i.e., a higher proportion of carbon fiber contributes to the decomposition of CuO over a larger area of pure Cu covered over the transfer film. This may be explained by considering that, in the case of fiber-reinforced composites, the matrix polymeric material wears easier than the fiber, and the compressive stress field in the contact area is larger because more fibers support the load. In view of the high temperature rise resulting from the dissipation of

frictional energy,¹¹ it was concluded that, under the combined action of high temperature and compressive stresses conditions, the CuO filler would decompose and generate fresh Cu in these contacting areas.

CONCLUSIONS

1. The wear and friction of nylon were reduced when it was reinforced with CuO. The CuO content for minimum wear rate was 5–10% volume content. The wear resistance of 20% CF–nylon could be increased approximately by two orders of magnitude and friction coefficient decreased to half value compared with that of 10% CuO–nylon.
2. With the increasing proportions of CF with 10% CuO in nylon, the friction coefficient of composites decreased continuously, and the lowest value of wear rate was obtained with the hybrid of 20% CF and 10% CuO in nylon composites, which cannot be achieved with any proportion of the fiber or the filler alone.
3. The presence of CF and CuO in nylon promoted the development of transfer film on the steel counterpart, which was thin, continuous, uniform, and tenacious. A thin and almost continuous layer of Cu film was generated and covered over the transfer film. The latter contributed to increased adhesion between the transfer film and counterface surface and thereby enhanced the wear resistance of CF–CuO–nylon composite.
4. CuO as the filler in nylon filled with CF decomposed during the sliding against the steel counterpart so that pure Cu, Cu₂O, and Cu(OH)₂ were produced. CF promoted the process of tribochemical reaction of CuO, which generated more pure Cu.

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