

# Study on Tribochemical Interaction of Metals or Metal Oxides with Polytetrafluoroethylene by X-ray Photoelectron Spectroscopy

DE-LI GONG, BING ZHANG, QUN-JI XUE, and HONG-LI WANG,  
*Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics,  
Chinese Academy of Sciences, Lanzhou, Gansu, People's Republic of China*

## Synopsis

Tribochemical reactions of PTFE with aluminum, silicon, and iron during rubbing were detected by ESCA. No apparent relationship between this chemical reaction of the fillers with the PTFE in the composite and the wear-reducing action of those fillers on the composite material was found.

## INTRODUCTION

In tribology there has been extensive activity dealing with the influence of friction conditions on the tribochemical behavior of polymers and their composites. Richardson<sup>1</sup> reviewed the work on chemical and physical changes reported in the literature at sliding interfaces. Gao et al.<sup>2</sup> studied the reactions of metal oxides with PTFE using differential scanning calorimetry (DSC), thermogravimetry (TG) and X-ray photoelectron spectroscopy (XPS). The work was done under heating but not rubbing conditions, and it was found that a chemical interaction occurred between PTFE and aluminum, lead oxides. Cadman et al.<sup>3-6</sup> examined the interaction of PTFE transferred film with metals by XPS, and the chemical interaction between the F atoms in PTFE and iron as well as tin was detected. Pocock et al.<sup>7</sup> studied the mixtures of PTFE with metals or metal oxides by DSC and revealed a reaction between tin and PTFE. Buckley and others<sup>8-12</sup> studied chemical phenomena occurring at the interface between polymer and metal by using FIM, XPS, SIMS, and AES and obtained the important conclusion that strong adhesion between metal and polymer occurs under ultra high vacuum. Although some progress in studying the wear-reducing action of fillers has been made and some polymers, such as nylon filled with molybdenum disulfide, PTFE filled with many kinds of fillers (bronze, lead, glass fiber, carbon fiber, etc.), have been used in commercial 'wear' applications, little is really understood on the intrinsic chemical and physical wear mechanisms. Moreover, the relationship between chemical reaction of metal and polymer in composite materials and the role played by the metallic fillers on the wear-reducing action has not been found.

The purpose of this study is to explore the relation between the tribochemical reaction of metal oxides or metallic fillers with PTFE during rubbing and the wear rate of the PTFE-based composite filled by these fillers, and to search for the most effective filler in reducing the wear rate of PTFE.

## EXPERIMENTAL

### Specimens

The pins of PTFE-based composites filled by metallic powders, metal oxides, or stainless steel or copper net, vertically inserted into the end surface of the pins, were made by incorporating PTFE powder with the filler and sintering the mixture at 380°C for 1 h and then cooling down within the furnace to room temperature. The diameters of the metallic powders used in this experiment are in the range from 0.5 to 34.5  $\mu\text{m}$ .

Metallic blocks used as the frictional counterface for these pins were made of 45 carbon steel (C: 0.42–0.50%, Si: 0.17–0.37%, Mn: 0.50–0.80%, P:  $\leq$  0.040%, and S:  $\leq$  0.040%) or pure aluminum (Al:  $>$  97%). Before the experiment started, the blocks were polished with 500 grade emery paper to give surface roughness less than 0.12  $\mu\text{m}$  in CLA.

### Experiments of Friction and Wear

All experiments of friction and wear were carried out on a RFT-III reciprocating tester, made in Japan, under a load of 250 N at an average sliding speed of 0.2 m/s under ambient conditions. A pin,  $\phi$  8  $\times$  30 mm in dimension, was mounted into the pin holder and initially rubbed on a metallic block that is 14  $\times$  10  $\times$  70 mm in size for 500 times to ensure good contact between the pin and the block. Before the wear test started, the pin and the block surfaces were cleaned by rubbing with a soft cloth dipped in pure ethyl alcohol. In each test, a new pin and a new block were used, and the pin was rubbed on the same track with a reciprocating distance of 50 mm on the block for 1000 times (100 m in sliding distance). The total reciprocating number for each pin was 12,000 times (1200 m). The weight loss of the pin was measured after every 1000 cycles. The metallic block rubbed was immediately analyzed by ESCA.

### ESCA Analysis

The block covered with the transferred film of PTFE-based composite was analyzed by ESCA on a commercial PHI-550 electron spectrometer with a Mg  $K\alpha$  X-ray anode operated under a voltage of 8 kV with a current of 40 mA.

## RESULTS AND DISCUSSION

Figure 1 gives the results of the effect of different fillers on the wear rate of PTFE. It is seen that all fillers decrease the wear of PTFE and the most effective one is  $\text{SiO}_2$ —it reduces the wear of PTFE by a factor of nearly 1000. For metal nets used as filler, stainless steel net is more effective in wear-reducing than copper net.

ESCA spectra of (1) an unrubbed pin, (2) a rubbed pin, (3) a rubbed and then scraped pin of PTFE-based composite filled by aluminum powder, (4) the frictional track on the block covered with the transferred film of the composite, and (5) the block on which the transferred film was scraped off with a razor blade are shown in Figure 2. No chemical shift was found in C(1s) spectra of the pins [shown in Fig. 2(a)]. But a change of ratio of the C(1s) peak height

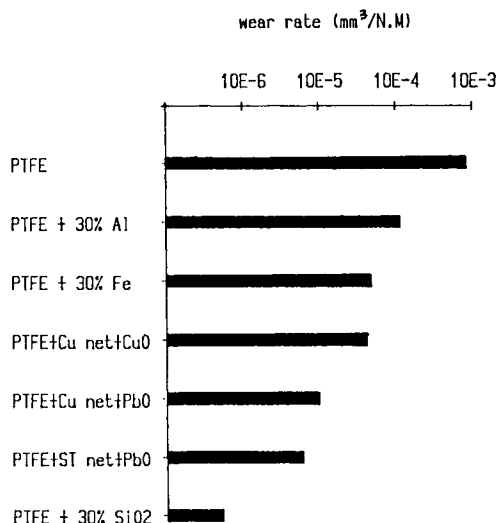


Fig. 1. Wear rate of various PTFE-based composites under a load of 250 N at an average sliding speed of 0.2 m/s under ambient conditions.

of PTFE at 292 eV to the C(1s) peak height of amorphous carbon at 284.6 eV was observed. The peak height ratio in the spectra of the rubbed pin and the scraped block is lower than that in the spectrum of the scraped pin. This means that fluorine was consumed during the rubbing. In the fluorine F(1s) spectra of pins [Fig. 2(b)] no sign of chemical change was visible. But in the case of the rubbed and scraped block, its F(1s) peak was significantly broadened. This broadening may be understood with the formation of aluminum fluoride ( $\text{AlF}_3$ ) and possibly  $\text{AlF}_3 \cdot \text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ , as well as aluminum fluoride oxide ( $\text{AlFO}$ ) during the rubbing process. In correspondence to this negative chemical shift of about  $-2.6$  eV in F(1s) spectra, a new broad peak at 75.8 eV with a chemical shift of  $+1.2$  eV [relative to Al(2p) peak of  $\text{Al}_2\text{O}_3$ ] in the aluminum Al(2p) spectrum of the rubbed and scraped blocks was observed.  $\text{Al}_2\text{O}_3$  was actually present or formed on rubbing. This also suggests that more than one species containing aluminum as well as fluorine were formed under these rubbing conditions. Furthermore, this  $\text{AlF}_3$  compound appears to concentrate at the interface between the block and the transferred film, but not on the surface of the transferred film.

Figure 3 shows C(1s), F(1s), and Si(2p) spectra of (1) the rubbed pin, (2) the rubbed and scraped pin of PTFE-based composites filled by silicon dioxide powders, (3) a block covered with transferred film of the composite, and (4) the block scraped by a razor blade after rubbing. The same phenomena as in Figure 2 were observed in the C(1s) and F(1s) spectra of the pins. For the C(1s) and F(1s) spectra of the blocks, the disappearance of the C(1s) peak at 292 eV belonging to the C in PTFE was accompanied by the emergence of a new F(1s) peak at 684 eV with a chemical shift of  $-4.4$  eV with respect to PTFE. In the Si(2p) spectrum of the scraped block a new peak at 101.7 eV, corresponding to  $-\text{SiF}-$ , was observed. This suggests that  $-\text{SiF}-$  was formed at the interface between the block and the transferred film when a pin of  $\text{SiO}_2$ -containing composite was rubbed on a carbon steel block.

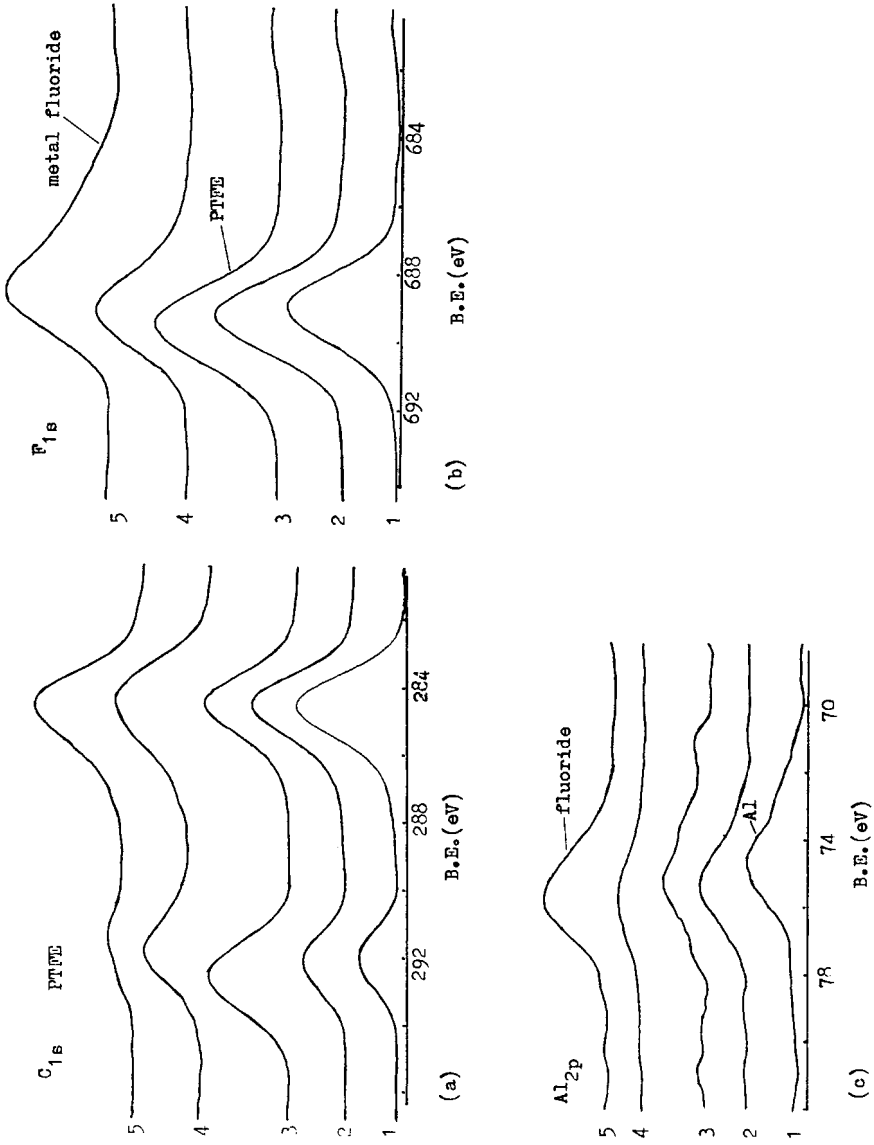


Fig. 2. ESCA spectra of (a) C(1s), (b) F(1s), and (c) Al(2p) of various samples. (1) Unrubbed pin of Al-containing PTFE composite, (2) rubbed pin of Al-containing PTFE composite, (3) rubbed and then scraped pin of Al-containing PTFE composite, (4) rubbed block covered with the transferred film of Al-containing PTFE composite, and (5) rubbed block on which the transferred film was scraped off.

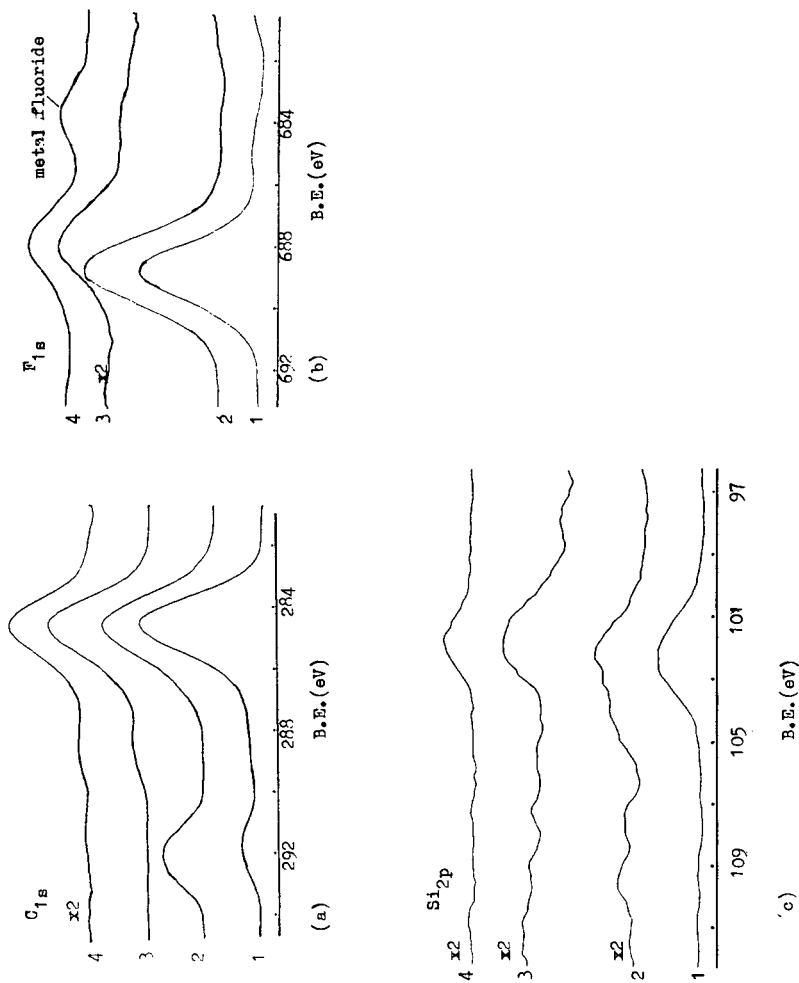


Fig. 3. C(1s), F(1s), and Si(2p) spectra of ESCA analyses on various samples. (1) Rubbed pin of SiO<sub>2</sub>-containing PTFE composite, (2) rubbed and scraped pin of SiO<sub>2</sub>-containing PTFE composite, (3) rubbed block with a transferred film of SiO<sub>2</sub>-containing PTFE composite, and (4) rubbed block on which the transferred film of SiO<sub>2</sub>-containing PTFE composite was scraped off.

Figure 4 illustrates the change of ESCA spectra of C(1s), F(1s), and Fe(2p) of (1) an unrubbed pin, (2) a rubbed pin, (3) a rubbed and scraped pin of PTFE-based composite filled by iron powders, (4) a rubbed carbon steel block, and (5) the rubbed and scraped block covered with the transferred film of the composite. In correspondence to a marked decrease of the peak height of the C(1s) peak of PTFE at 292 eV, a new F(1s) peak at 685.4 eV was observed on the F(1s) spectrum of the rubbed and scraped block. This is consistent with the idea that  $\text{FeF}_2$  was formed at the interface between the carbon steel block and the transferred film during the rubbing process.

It is seen from this discussion that tribochemical reaction of PTFE with aluminum, silicon, and iron during frictional process was detected by ESCA in this study. However, there was apparently no relation between the reaction and the wear-reducing action of the filler. For the case of aluminum, the wear-reducing ability of the composite containing aluminum was not principally due to the tribochemical reaction of PTFE with aluminum. The change of crystalline structure in this case is probably more important as mentioned in Ref. 13. In

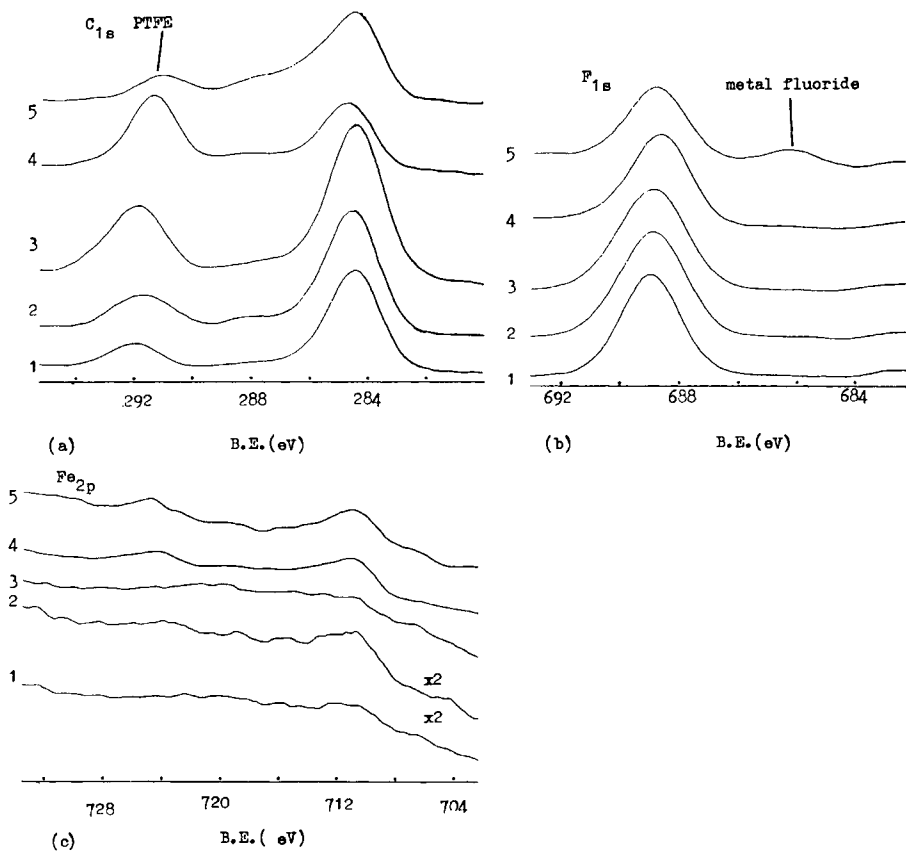


Fig. 4. ESCA spectra of (a) C(1s), (b) F(1s), and (c) Fe(2p) of various samples. (1) Unrubbed pin of PTFE-based composite with iron filler, (2) rubbed pin of PTFE-based composite with iron filler, (3) rubbed and scraped pin of PTFE-based composite with iron filler, (4) block rubbed by a PTFE + Fe pin, and (5) block rubbed by a PTFE + Fe pin and then scraped by a razor blade.

other words, tribochemical reaction of PTFE with metal aluminum cannot improve the wear behavior of aluminum-incorporated PTFE composite, its wear rate being still as high as  $1.16 \times 10^{-4}$  mm/N.M. The lower wear rate of PTFE filled with silicon dioxide (wear rate is  $1.19 \times 10^{-6}$  mm/N.M) is probably not due to the tribochemical reaction of PTFE with silicon but rather due to the load-supporting action of silicon dioxide. The observation that the stainless steel net added into PTFE is more effective in wear reduction than the copper net is another indication for the load-supporting role played by the filler in wear reduction.

## CONCLUSIONS

1. The tribochemical reactions of PTFE with aluminum, silicon, and iron in the rubbing region was detected by ESCA when a pin of PTFE-based composite filled by aluminum, silicon dioxide, or iron powders was rubbed on a carbon steel block.
2. Although the tribochemical reaction of PTFE with aluminum takes place, the wear-reducing action of aluminum in PTFE is not as effective as that of silicon dioxide or stainless steel net when incorporated into PTFE.
3. No relation between the tribochemical reaction of PTFE with metal fillers and the wear-reducing action of these fillers was found.

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