The Effect of Surface Treatments on Wear of Polytetrafluoroethylene

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Synopsis

This paper reports the effect of surface chlorination, oxidation, and phosphatization of carbon steel, copper, and aluminum, and surface treatment with sodium naphthalenide of PTFE on wear of PTFE. It was found that the wear behavior of untreated PTFE is not affected by surface treatments of metals but treatment of PTFE can reduce its wear by a factor of at least 100. The wear mechanism of PTFE is discussed.

INTRODUCTION

It is well known that polymer transfer to the counterface occurs during sliding of polymers on polished metal surfaces and that the transferred material plays an important role in the wear characteristics of polymers. Makinson and Tabor[1] explained the friction and transfer characteristics of polytetrafluoroethylene (PTFE) on the basis of its morphology, which is characterized by a banded structure. Tanaka[2] found that the PTFE film transferred to the counterface and also explained wear characteristics of PTFE on the same theory. Pooley and Tabor[3] observed the lumps transfer of an extremely thin PTFE film, about 2.5 nm thick, and suggested that the low friction and light transfer of PTFE during sliding were essentially due to its smooth molecular profile.

In the sliding of polymers against metal and glass surface, the wear of polymers seems to be dominated by the transfer of softer polymeric material to the harder counterface material. A loss of energy is associated with this process, and this energy loss can be described by means of the surface energies of the materials involved.[4–7] Jain and Bahadur[8] concluded that the material transfer took place from a polymer of low cohesive energy density (i.e., low surface energy) to one of higher cohesive energy density (i.e., higher surface energy). In practice, surface energy can be estimated from the contact angle measurements.[9] Lee put emphasis on role of surface energy in the polymer wear.[10] Briscoe and Tabor[11] suggested that the adhesion of the first layer to the counterface is of critical importance in governing the long-term wear of HDPE and PTFE. Many other workers[12–14] have studied variations in wear and transfer of PTFE with load, speed, and temperature. Tanaka and Yamada,[15] and Sviridyonok et al.[16] have recently noted and studied the effects of properties of counterface on wear of polymers, but up to the present, little attention has been paid to the influence of surface treatment of polymer and counterface on the wear and transfer of polymers.

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In this paper different surface treatments of metals and PTFE and the effect of these treatments on friction, transfer, and wear of PTFE have been studied by observing frictional tracks on metals with optical microscope. Measured change of wetting angles of metals and PTFE before and after these treatments indicates that change of surface energies of metal surface and treated PTFE have taken place. Wear results show that surface treatment of PTFE can reduce its wear by a factor of at least 100.

EXPERIMENTAL

Surface Treatments

To vary surface properties of metal counterface, phosphatization, oxidation of carbon steel and copper, and chlorination of aluminum, copper, and carbon steel have been made. The solution formulations and conditions of these treatments are given as follows:

Phosphated Treatment for Carbon Steel (0.45%C) (Fe): $Zn(H_2PO_4)_2$ 60 kg, $Zn(NO_3)_2$ 90 kg, $NaNO_2$ 0.5 kg, citric acid 0.5 kg, water 1 m^3, temperature 40–50°C, Time 1 min.

Oxidation for Carbon Steel (Fe): NaOH 45.0 kg, Na_3PO_4 10.0 kg, Na_2SO_3 5.0 kg, H_2O 40.0 kg, temperature 130–150°C, time 7–10 min.

Oxidation for Copper (Cu): NaOH 5.0 kg, $K_2S_2O_8$ 10.0 kg, H_2O 85.0 kg, temperature 100°C, time 3–10 min.

Chlorination Treatment for Fe, Al and Cu: HCl 160 kg, H_2O 1000 kg, temperature 20°C, time: Al 10 min, Fe 20 min, Cu 30 min.

It is difficult to treat PTFE with normal chemicals because of its excellent chemical stability. To vary surface properties of PTFE, the following chemical reagents and conditions were used: tetrahydrofuran 1000 M^3, naphthalene 128 kg, metal sodium 23 kg, temperature 15–32°C, time 10–15 min.

Apparatus and Experimental Procedure

To measure wear of PTFE, a pin-block-type reciprocating tester was employed. Experiments were carried out at a average sliding speed of 0.1 m/s with a amplitude of 5 cm under load of 500 N at room temperature (about 18°C). The flat end of PTFE pin, which was 8 mm in diameter, was rubbed against blocks of carbon steel, aluminum, and copper, which were 10 × 14 × 70 mm in dimension. The pin oscillated over the same part of the block repeatedly and a new block and a new pin were used for each experiment. The frictional surface of the block was polished with 700 grade emery paper to a roughness less than 0.06 μm center line average (C.L.A.).

After the PTFE pin specimen was mounted on the specimen holder, the pin was initially rubbed against 700 grade emery paper placed on the block and then rubbed against the block surface for 100 times (except for treated PTFE). This prerubbing treatment allowed uniform contact between the pin and the block. In the wear experiments, the PTFE pins were generally rubbed on the block for 10, 20, 50, 100, 200, 500, and 1000 or more reciprocations. Loss of PTFE pin was weighed after each test.

RESULTS

Wear and Friction Characteristics of PTFE

Figure 1 and Table I illustrate the effect of various surface treatments on wear of PTFE. All treatments of metal surfaces affected no on wear characteristic of PTFE. It is evident from Table I that, regardless of whether the

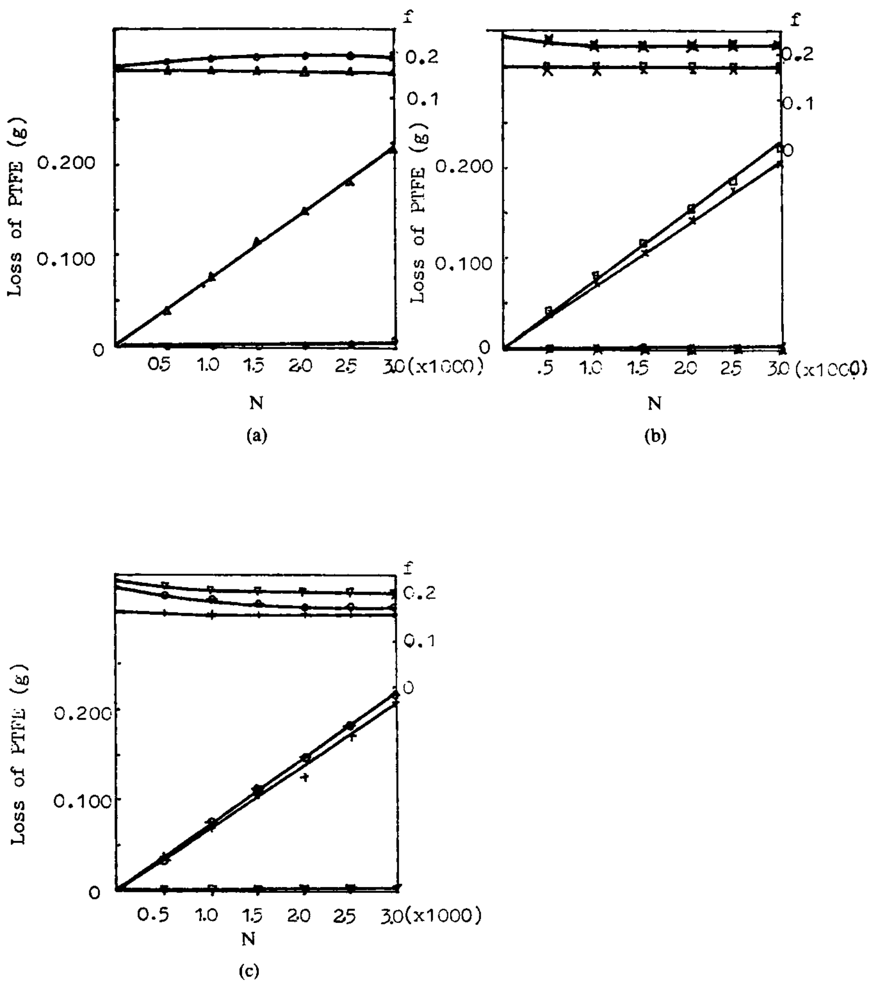

Fig. 1. Variations of wear and frictional coefficient of treated and untreated PTFE rubbing against various metals with number of reciprocation (N). (a) △, untreated PTFE–untreated Al; O, treated PTFE–untreated Al. (b) □, untreated PTFE–untreated Cu; X, untreated PTFE–oxidized Cu; ⊗, treated PTFE–untreated Cu. (c) ⊖, untreated PTFE–oxidized carbon steel; +, untreated PTFE–untreated carbon steel; ∇, treated PTFE–untreated carbon steel. F, frictional coefficient; *N*, number of reciprocations.

TABLE I
Wear of Treated and Untreated PTFE Rubbing against Various Metals Surfaces

Pin	Block	Total number of reciprocations 10	30	80	180	380	880
		Total loss of PTFE pin ($\times 10^{-4}$, g)					
Untreated PTFE	Fe(chlorinated)	7.25	21.5	59.0	131.1	271.7	565.4
	Fe(oxidized)	5.0	18.4	55.3	123.35	263.0	602.0
	Fe(phosphate)	12.7	29.4	69.8	149.0	310.0	718.0
	Al(chlorinated)	8.8	24.7	64.9	140.0	288.2	636.9
	Fe(untreated)	4.4	16.2	52.6	129.5	275.9	587.1
	Cu(untreated)	8.95	23.1	60.2	133.5	266.9	575.5
Treated PTFE	Fe(untreated)	0	0.40	1.17	1.67	1.93	2.58
	Cu(untreated)	0.40	0.70	0.90	1.35	2.0	3.80
		Loss of PTFE pin in each 10 reciprocations ($\times 10^{-4}$, g)					
Untreated PTFE	Fe(chlorinated)	7.25	7.13	7.51	7.20	7.03	5.87
	Fe(oxidized)	5.0	6.7	7.36	6.81	6.99	6.79
	Fe(phosphate)	12.7	8.4	8.08	7.92	8.05	8.16
	Al(chlorinated)	8.8	7.95	8.04	7.51	7.41	6.97
	Fe(untreated)	4.4	5.9	7.28	7.69	7.32	6.22
	Cu(untreated)	8.95	7.08	7.42	7.33	6.67	6.17
Treated PTFE	Fe(untreated)	0	0.20	0.15	0.05	0.013	0.013
	Cu(untreated)	0.40	0.08	0.04	0.05	0.033	0.036

metal surface was treated or untreated, the wear of untreated PTFE under load of 500 N is nearly the same. The result indicates that surface treatments of metals give no effect on the wear behavior of untreated PTFE and with no change of roughness on the metal surface. But when PTFE was treated with naphthalene–sodium liquid and rubbed against various metal surfaces, the wear of treated PTFE is less than wear of untreated PTFE by a factor of at least 100. Wear of treated PTFE in 3000 reciprocations is less than wear of untreated PTFE in 10 reciprocations.

Figure 2 shows the variations in wear of treated and untreated PTFE pins, which were alternately used to rub against the same block of counterface, as a function of the number of block reciprocations. An interesting result is that when using a treated PTFE pin rubbed against a block of metal, wear of PTFE was low. When the treated PTFE pin was replaced by an untreated PTFE pin which was rubbed against the tracks with the transferred treated PTFE layer, wear of the untreated PTFE was high. But when the untreated PTFE pin was replaced by the treated one, a low wear of the treated PTFE pin was again obtained.

Variations in frictional coefficient of treated and untreated PTFE rubbing against various treated and untreated metal surfaces as a function of the reciprocation number of block are shown in Figure 1. It is seen that increase in frictional coefficient of treated PTFE is not high comparing with that of the untreated PTFE.

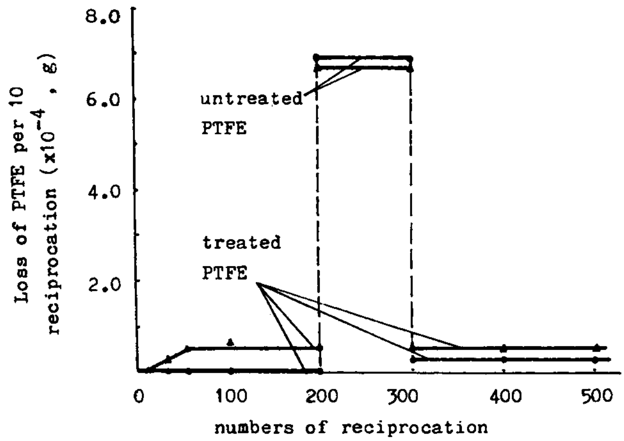

Fig. 2. Wear of treated and untreated PTFE alternately rubbing against carbon steel (▲) and Cu (●).

Change of Properties of Treated Surface

Table II illustrates the change of surface roughness of metals and PTFE through various surface treatments. It is seen that for all treated surfaces (except for phosphatization) surface roughness is almost the same as the untreated one.

The contact angles of various treated and untreated surfaces with water were determined with an apparatus made by Kyowakagaku Co. Ltd in Japan and summarized in Table II. These data show that, for untreated carbon steel and aluminum, contact angles were increased with roughness on these metal surfaces and there is a great change in contact angles between treated and untreated metal surfaces. The contact angles of most treated metal surfaces were reduced by 20–30° compared with these untreated surfaces. The most marked change

TABLE II
Surface Roughness and Contact Angles of Various Materials with Water

Material	Surface roughness R_a (μm)	Contact angle (°)	Material	Surface roughness R_a (μm)	Contact angle (°)
PTFE (untreated)	—	100–103	Al (untreated)	0.280–0.470	90
PTFE (treated)	—	30–34	Al (untreated)	0.650–0.860	94–96
Carbon steel (C.S., untreated)	0.008–0.019	80–82	Al (untreated)	1.25–1.45	97–98
C.S. (untreated)	0.017–0.021	86–88	Al (chlorinated)	0.110–0.135	64–68
C.S. (untreated)	0.158–0.180	90–92	Cu (untreated)	0.043–0.056	97–98
C.S. (untreated)	0.225–0.320	90	Cu (untreated)	0.158–0.175	90
C.S. (oxidized)	0.098–0.160	58–60	Cu (chlorinated)	0.055–0.072	61–64
C.S. (chlorinated)	0.036–0.045	34–36	Cu (oxidized)	0.105–0.168	56–58

of contact angle is between untreated and treated PTFE surface, from 100–103° for untreated surface to 30–34° for treated surface.

Microscopy Examination of the Transferred PTFE Layer

To understand why treated PTFE can greatly reduce its wear and there is little effect of treated metal surfaces on wear of untreated PTFE, optical microscopy examinations were made on the worn tracks with transferred materials. Figure 3 shows optical micrographs of frictional tracks after 800 reciprocations for various treated surfaces. It is seen that untreated PTFE rubbing against

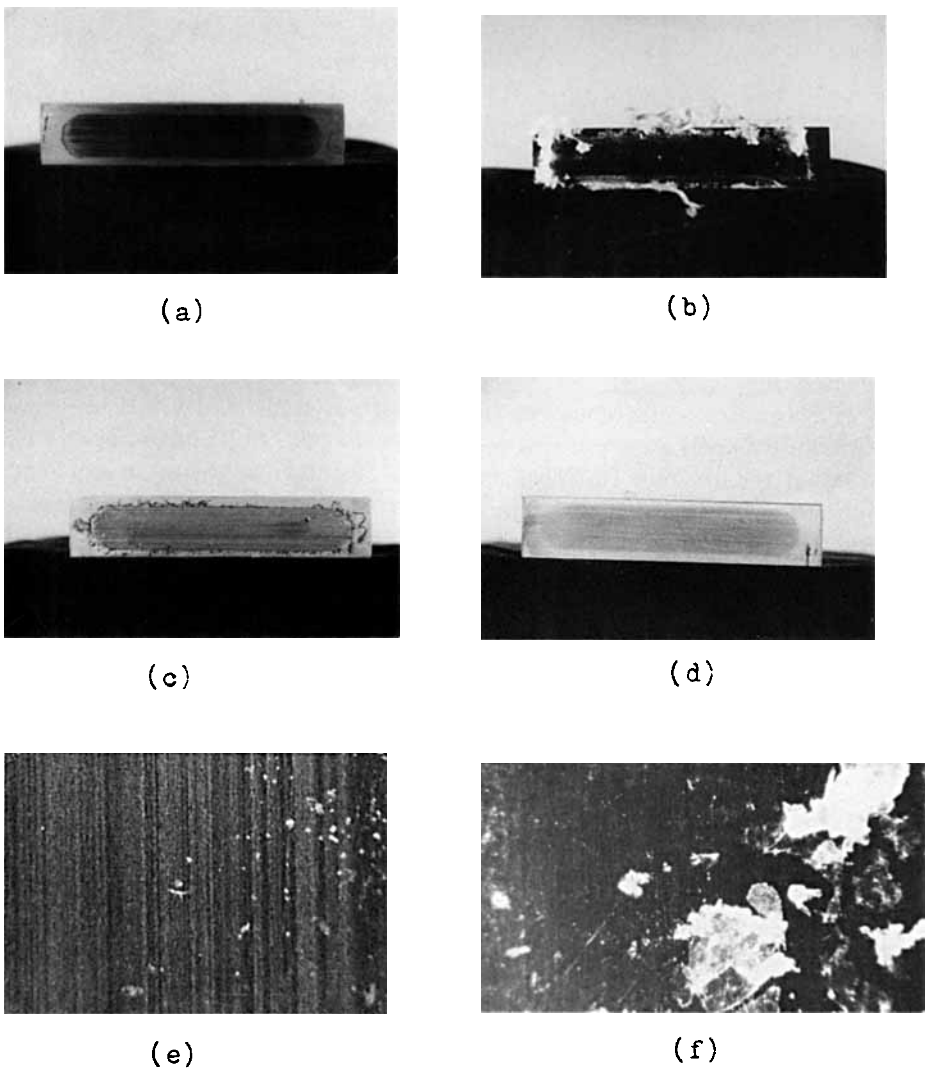

Fig. 3. Pictures of frictional tracks and optical microscopy on surfaces rubbed by untreated and treated PTFE pins for 3000 reciprocations. (a) treated PTFE–untreated Cu; (b) untreated PTFE–oxidized carbon steel; (c) treated PTFE–untreated Al; (d) treated PTFE–untreated carbon steel; (e) treated PTFE–untreated carbon steel; (f) untreated PTFE–untreated carbon steel.

various treated and untreated metal surfaces produced large lump wear debris but treated PTFE produced fine debris.

DISCUSSION

It is interesting that various metal surface treatments can vary surface energy on these surfaces but not change the wear behavior of untreated PTFE rubbing against them. Data of wear of untreated PTFE rubbing against treated metal surfaces in each 10 reciprocations shows that metal surfaces, regardless of whether they were treated or untreated, cannot affect the wear behavior of untreated PTFE. It had been found that after a treated PTFE was rubbed against an untreated carbon steel and copper for 200 reciprocations (wear of the treated PTFE was very small, about 5×10^{-5} g/10 reciprocations) and the treated PTFE pins were replaced with untreated PTFE pins and rubbed against the same block surface covered with the transferred layer of treated PTFE, more wear of the untreated PTFE was obtained. When the treated PTFE pin was rubbed against the block covered with untreated PTFE transferred layer, less wear of PTFE was again obtained (as shown in Figure 2). This means that, for transferred wear, wear of PTFE occurs between PTFE and transferred layer on counterface. This is at variance with the point mentioned by some workers[4] that the adhesion between the first transferred PTFE layer and counterface plays an important role in wear of PTFE. There is no effect of state of the first transferred layer on wear of untreated PTFE, as shown in this experiment.

Change of wetting angles of various metal surfaces with water after treatment indicates that their adhesive work with PTFE during friction test would vary. But the interesting thing is that change of wetting angles of these surfaces do not affect the wear behavior of untreated PTFE. This shows that the interfacial adhesive work is not directly and simply related to the wear of PTFE.

Compared with untreated PTFE surface, wear of treated PTFE has a very low value. The main reason for this appears to be that the mechanism of formation of wear debris for treated PTFE is different from that for untreated PTFE. For treated PTFE, fine wear debris were formed on frictional tracks on block specimen. However, for untreated PTFE large thin lump slices were produced as same as that was characterized by the theory of the band structure. It is reasonable to assume that surface treatment for PTFE can destroy the band structure in the PTFE surface and subsurface region so that it is difficult for treated PTFE to form wear debris of lump slices. Therefore, its wear is greatly reduced.

CONCLUSIONS

On the basis of the above study, the following conclusions may be drawn.

1. Various surface treatments on metal give no change to the wear behavior of untreated PTFE.
2. Surface treatment on PTFE can greatly reduce its wear.

3. Wear of untreated PTFE occurs between PTFE and transferred layer on counterface but not between PTFE and the counterface.

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