

The Mechanical and Tribological Properties of PTFE Filled with PTFE Waste Powders

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ABSTRACT: Polytetrafluoroethylene (PTFE) composites filled with PTFE waste offer interesting combination of tribological properties and low cost. PTFE composites waste was mechanically cut and sieved into powders. PTFE composites filled with PTFE waste powders were prepared by compression molding. Friction and wear experiments were carried out in a reciprocating sliding tribotester at a reciprocating frequency of 1.0 Hz, a contact pressure of 5.5 MPa, and a relative humidity of $(60 \pm 5)\%$. PTFE materials slid against a 45 carbon steel track. Results showed that a PTFE composite (B) filled with 20 wt % PTFE waste exhibited a coefficient of steady-state friction slightly higher than that of unfilled PTFE

(A), while wear resistance over two orders of magnitude higher than that of unfilled PTFE (A). Another PTFE composite filled with PTFE waste and alumina nanoparticles exhibited the highest wear resistance among the three PTFE materials. This behavior originates from the effective reinforcement of PTFE waste as a filler. It was experimentally confirmed that the low cost recycling of PTFE waste without by-products is feasible. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1035–1041, 2007

Key words: polymer composites; polytetrafluoroethylene; recycling; friction; wear; alumina nanoparticle

INTRODUCTION

Recently, a new legislation has been passed in an attempt to minimize industrial waste and to promote recycling. The European Parliament's legislation creates challenges in the materials field by requiring consideration of the full lifecycle of materials (including disposal).¹ Unfortunately, more and more plastics waste is generated by industry and householders. Thus, some polymers and composites that are difficult to recycle become relatively less attractive. For example, plastics waste in municipal solid waste (MSW) in the USA reached 13.2 million tons in 1988 with 21% of MSW by volume.² It is clear now that plastic wastes are becoming a global environmental problem, and local governments worldwide have focused their attention on recycling these plastic wastes to reduce the volume of materials going into landfills. Numerous studies have been performed on recycling of polymers and composites by considering common polymer waste recycling methods such as mechanical recycling and energy recovery.^{3–5}

However, little has been reported on the utilization of polytetrafluoroethylene (PTFE) waste. Actually PTFE

has a currently increasing utility in tribological applications due to its unique properties such as high chemical resistance, low coefficient of friction, and high temperature stability. The manufacture of various PTFE products leads to a considerable amount of waste. PTFE waste is very difficult to dispose because of great chemical resistance. In general, there are two methods that are used to dispose the PTFE waste: the thermal decomposition and ion radiating decomposition. Meissner et al. reported their pyrolysis results of waste PTFE and obtained several useful compounds. The process of PTFE waste disposal is complicated, consequently increasing disposal cost.⁶ Patel et al. reported recycling of plastics in Germany, and proposed that high ecological benefits could be achieved by mechanical recycling if virgin polymers were substituted. The cost effectiveness of reducing energy use and CO₂ emissions is determined by a number of technologies.⁷

In China, over 20,000 tons of PTFE is annually used for industry, and a huge PTFE waste results from manufacturing operation. This article deals with the mechanical recycling of PTFE wastes without any by-products. The PTFE composites waste, from manufacturing operations, was mechanically cut into powders, and then was put into PTFE as the filler. A PTFE composite filled with PTFE waste was therefore expected to be effectively reinforced, without increasing environmental burdens using this low cost way. Our results demonstrated that this method has a new potential for the recycling of PTFE waste.

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EXPERIMENTAL

Materials and sample preparation

Researchers extensively investigated wear properties of polytetrafluoroethylene (PTFE) composites by considering the traditional fillers, such as glass fibers, carbon fibers, and nonferrous metallic powders, as well as some metal oxides, etc.^{8–10} Sawyer et al. filled PTFE with alumina nanoparticles. The addition of less than 20 wt % filler improved the wear resistance by over two orders of magnitude.¹¹ In our work, the pure PTFE was chosen to carry out a comparative investigation, while filling alumina nanoparticles was to further reinforce the new PTFE composite containing PTFE waste.

The PTFE composites waste, from manufacturing operations, was mechanically cut into powders at our laboratory. Because the amount of the waste powders tested was only 500 g, the PTFE waste was mechanically rubbed on a fine file. Then the PTFE composite waste powders with grit sizes from 70 to 90 μm were prepared using a sieve. The pure PTFE powder ($< 90 \mu\text{m}$) was provided by Jinan Chemical Plant, China. Alumina nanoparticle ($< 50 \text{ nm}$) was provided by Taixing nanomaterials Plant in Jiangsu province, China. In the present experiments, three PTFE materials have been prepared (at weight fractions): (i) pure PTFE (A), (ii) PTFE filled with 20% PTFE waste (B), (iii) PTFE filled with 20% PTFE waste, and 15% alumina nanoparticles (C).

The PTFE mixture powders with various filler contents were prepared. The PTFE powders and 20 wt % PTFE waste powders (B) were prepared by a mechanical stirring method, whereas the preparation of PTFE + 20 wt % PTFE waste + 15 wt % Al_2O_3 (Composite C) was as follows. The PTFE and alumina nanoparticles were mixed mechanically, and then fully mixed ultrasonically and dispersed in acetone for ~ 10 min. The PTFE mixture powders were dried at 85°C for 24 h to remove the acetone and moisture. For putting waste PTFE powders into the mixture (PTFE-alumina nanoparticles), the mechani-

cal stirring method was selected. After fully mixing, the mixtures were molded by compression into cuboidal samples. The sizes of cuboidal chamber were 45.0 mm in length, 80.0 mm in width, and 12.0 mm in thickness. A laboratory press was used to consolidate the mixture under a molding pressure of 40 MPa at room temperature in a cuboidal chamber made of 45 carbon steel. The consolidation pressure was held for 30 s. After molding, the samples were heated to 380°C at an average rate of $10^\circ\text{C}/\text{min}$ in a sintering furnace, held for 2 h at 380°C , and then cooled to room temperature in the sintering furnace. The counterface material of a steel track was a 45 carbon steel with chemical composition of C 0.42–0.50 wt %, Mn 0.50–0.80 wt %, Si 0.17–0.37 wt %.

Mechanical properties tests

PTFE and PTFE composites specimens of 115 mm \times 19 mm dimensions were cut from the 3-mm-thick laminates to determine their tensile properties. Tensile tests were performed using a Universal Testing Machine, according to ASTM-638, at a strain rate of 0.005 s^{-1} . Hardness measurements were carried out on 6-mm-thick specimen as ASTM D 224 standards on a shore D scale. Indentations were made at three locations for each specimen and the average hardness value was calculated. The indentation load for each measurement was 22.5 N and hold time was 15 s. All specimens were tested after being equilibrated under standard ASTM condition of 23°C and 50% relative humidity for 24 h.

Friction and wear tests

Sliding experiments were performed in laboratory air using a computer-controlled reciprocating sliding tribotester. Figure 1 is the schematic representation of the part related to loading of the apparatus. The friction force and normal load were measured with the aid of linear variable strain gauges and was recorded automatically throughout the tests con-

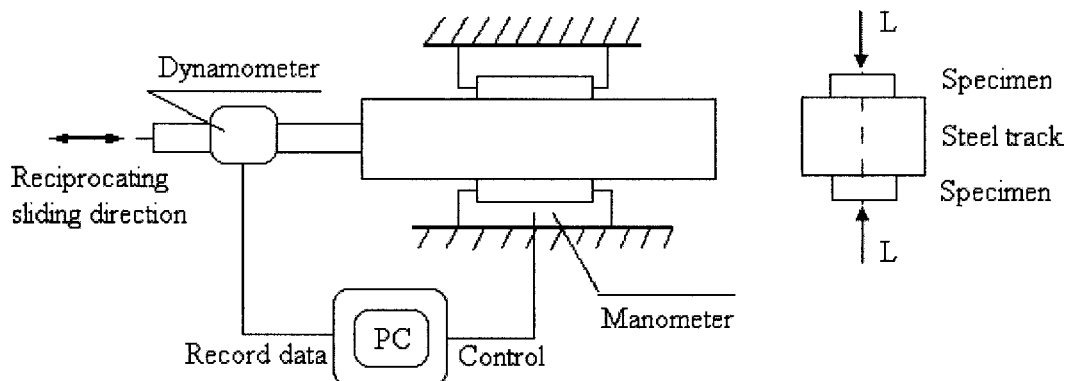


Figure 1 Schematic representation of the part related to loading of the apparatus.

nected to a PC. Surface roughness (R_a) of the 45 carbon steel track was 0.1 μm . The specimens were 43.0 mm in length, 36.0 mm in width, and 10.0 mm in thickness. Surface roughness (R_a) of the composite specimens was 0.2 μm .

Sliding tests were conducted at room temperature in ambient atmosphere ($60\% \pm 5\%$ RH) under dry friction conditions, with a reciprocating sliding frequency of 1.0 Hz and a normal load of 8.8 kN (nominal contact pressure of 5.5 MPa). The stroke length was 14 mm. At the end each test, the specimens and a 45 carbon steel track were cleaned with acetone, followed by drying.

During reciprocating sliding action, the friction coefficient of PTFE and PTFE composites against a 45 carbon steel increases from zero to the maximum value, then decreases from the maximum value to zero. In our work, the maximum value of friction coefficient was recorded during every reciprocating sliding period. At the start of sliding, during the so-called run-in period, PTFE materials exhibited high wear loss, followed by steady-state sliding motion until the wear rate almost remained unchanged. The sliding distance of wear test for each material was 900 m, that is, the sliding distance of 900 m consists of 32,143 cycles of 14 mm forward and 14 mm in reverse. In our work, wear loss was recorded during steady-state sliding period from 300 to 900 m. The amount of wear was measured by interrupting the sliding test at suitable interval for weighing the specimen of PTFE materials to an accuracy of 0.1 mg in a precision balance, and was then converted into volume loss by using the filled PTFE density. The surface temperature of specimen during tests was measured by a thermocouple inserted in a hole of 0.8 mm below the rubbing surface of specimen. Two replicate sliding tests were performed for each specimen with a relative error of $\pm 10\%$, and the averages of the two replicate test results are reported in this article.

Specific wear rate w is defined as the volume loss, Δv , divided by the applied normal load, F_N , per times the sliding distance, S .

$$w = \frac{\Delta v}{F_N S} \quad (1)$$

where the w has the units of volume loss per force per unit distance ($\text{mm}^3/\text{N}\cdot\text{m}$).

X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were taken on a Bruker D8 ADVANCE diffractometer (Germany) with Ni-filtered $\text{Co } k\alpha$ radiation at room temperature. Accelerating voltage and electron current were 40 kV and 40 mA, respectively. The scan-

ning angle ranged from 15° to 60° (2 θ). The mass fraction crystallinities of the PTFE materials were calculated as follows:

$$X_c = \frac{1}{1 + K(S_a/S_c)} \quad (2)$$

where X_c is the mass fraction crystallinity, S_c is the crystalline area, S_a is the amorphous area, and K is the modified coefficient, 0.66.¹²

Morphology observation

The worn surface morphology of specimens for the PTFE materials was observed using a Philip Quanta 2000 scanning electron microscope.

RESULTS AND DISCUSSION

Mechanical properties

The properties of PTFE and PTFE composites are given in Table I.

It can be seen that addition of filler materials to PTFE causes a significant improvement in the hardness. The waste PTFE powders play an important role in increasing hardness (up to 25%). In particular, Composite C exhibited the maximum hardness, which more than likely is due to the presence of the alumina nanoparticles. Such a result is consistent with what has been reported.^{9,13} When the waste PTFE powders were added to PTFE, there was practically a slight decrease in the tensile strength of PTFE composites. With the addition of waste PTFE, the ductility of the composites decreased dramatically. As for the elongation at break, there was a marked decrease with waste PTFE reinforcement. When the material was reinforced, the reinforced composites behaved as brittle materials. Thus, the only effect to be noted here is that waste PTFE reinforcement increased the hardness but reduced ductility of the composite. This behavior of PTFE composite filled with waste PTFE is in good agreement with observations for PTFE filler with other particles. Sole and Ball indicated that rigid fillers have a positive influence on stiffness and creep performance but exhibit a deleterious effect on tensile strength and duc-

TABLE I
Properties of PTFE and PTFE Composites

Properties	PTFE	Composite B	Composite C
Tensile strength (MPa)	19.6	18.2	18.5
Elongation at break (%)	363	28.3	25.5
Hardness (Shore D Scale)	52	58	65
Density (kg/m^3)	2110	2150	2010

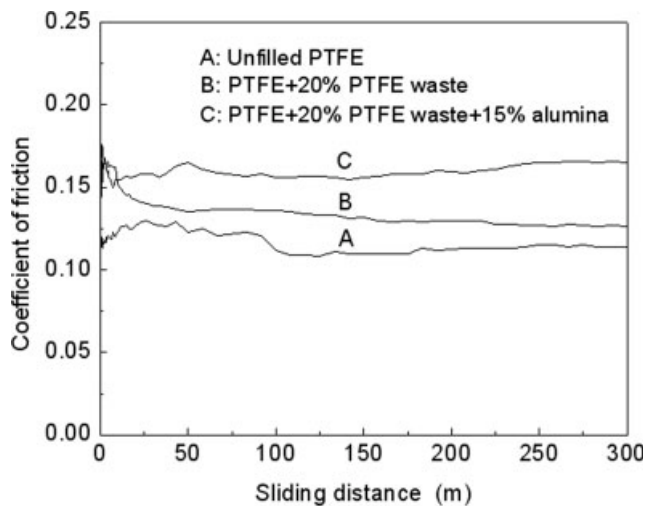


Figure 2 Change of friction coefficient of three PTFE materials with sliding distance at a reciprocating frequency of 1.0 Hz, a contact pressure of 5.5 MPa, and sliding distance of 300 m.

tility.¹⁴ It can be considered that the waste PTFE powders acted as a reinforcing filler.

Friction

Figure 2 shows the change between the friction of PTFE and PTFE composites with sliding distance. At the start of sliding (about 100 m), during the so-called running-in period, all materials exhibited a high coefficient of friction, followed by steady-state sliding motion until the coefficient almost remained unchanged. Varying trend of friction coefficient with sliding distance was in good agreement with the results obtained by Khedkar et al.⁹ It is seen from Figure 2 that unfilled PTFE (A) shows the lowest coefficient of steady-state friction of about 0.11. The highest coefficient of steady-state friction of 0.17 was obtained for Composite C. Composite B exhibited a coefficient of friction of 0.13, which was slightly higher than that of material A, but much lower than that of Composite C. It was also found that friction behavior was in the following order: A > B > C among three materials.

The Composites B and C exhibited a coefficient of friction higher than that of unfilled PTFE because of the addition of PTFE waste. Numerous experimental observations have confirmed that the fillers led to an increase in friction of polymeric composites.^{13,15–17} Coefficient of friction of Composite B was slightly higher than that of unfilled PTFE (A), because the filler of Composite B was PTFE composite waste powders, while the PTFE composite contained the stiff particles, in which they showed a very high coefficient of friction. It is because these filler particles are fairly hard and exhibit plowing, and so they could

have contributed to friction. The alumina nanoparticles in PTFE increased the hardness and stiffness of Composite C, as well as increased the friction of Composite C.

Wear

It is seen from Figure 3 that the addition of filler materials can cause a significant improvement in the wear resistance of PTFE. Composite B showed a wear resistance over two orders of magnitude higher than that of the unfilled PTFE. Composite C exhibited the highest wear resistance among all materials, an improvement of 140 times over that of the unfilled PTFE. This behavior was attributed to the presence of alumina nanoparticles, which can effectively increase the wear resistance of PTFE composites. Comparing the wear resistance of Composites B and C, it can be found that filling alumina nanoparticles in PTFE could increase the wear resistance by about 30%. This was because there existed the stiff particles in the PTFE composites, which were embedded within the matrix and imparted additional strength to the composite. This indicated that addition of alumina nanoparticles to PTFE composite was more effective than that of filling PTFE waste alone. The lowest steady-state wear rate of $1.03 \times 10^{-6} \text{ mm}^3/\text{N m}$ was obtained for PTFE + 20% PTFE waste + 15% alumina composite.

The mass fraction crystallinities of the PTFE materials are listed in Table II. The results show that the crystallinities of the two filled PTFE are higher than that of the unfilled PTFE. Heterogeneous nucleation occurs because of the addition of some impurities such as PTFE waste and alumina nanoparticles. The

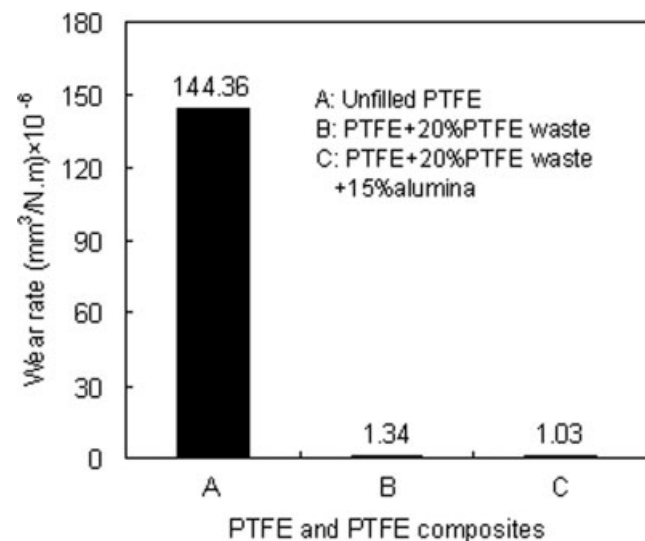


Figure 3 Wear loss of three PTFE materials at a reciprocating frequency of 1.0 Hz, a contact pressure of 5.5 MPa, and a sliding distance from 300 to 900 m.

TABLE II
Calculated Results of WAXD on the PTFE materials

PTFE materials	Amorphous area ($C_{ps} \times 2\theta$ (°))	Crystalline area ($C_{ps} \times 2\theta$ (°))	Crystallinity (%)
A	3168.4	2425.6	53.7
B	3115.7	3521.3	63.1
C	2616.5	2266.6	56.8

filled PTFE composites (Composites B and C) exhibited high wear resistance, perhaps because the PTFE matrix of the PTFE composites has a higher crystallinity.

Worn surface temperature

To further understand the effect of PTFE waste on wear resistance of PTFE composites, worn surface temperature of specimens was monitored during tests as shown in Figure 4. It can be noticed from Figure 4 that by filling with 20 wt % PTFE waste, surface temperature of Composite B increases slightly when compared with that of the unfilled PTFE, with the variation being from 70 to 81°C, while the maximum value of surface temperature for Composite C is up to 88°C, even higher than that of Composite B. For the filled composites, surface temperature tended to increase as the fraction of stiff fillers.⁹ Composite C exhibited the highest surface temperature among the three PTFE materials because of the filled alumina. This was because coefficient of friction increased, leading to an increase in frictional heating. In general, for polymer materials, the mechanical strengths are susceptible to temperature, and they drop drastically with temperature rise. The wear resistance of polymer materials consequently drops with temperature rise. But because PTFE has a high thermal stability, the temperature change of only 20°C slightly affected the wear resistance of PTFE composites. In contrast, fillers dramatically affected wear resistance of PTFE composites. Although Composite C showed a slightly high surface temperature when compared with Composite B, its wear resistance was very good because of the reinforcement of the stiff alumina nanoparticles in PTFE composite.

SEM examination of PTFE materials

Figure 5(a)–5(f) shows the SEM morphology of the worn surface of PTFE and PTFE composites. Figure 5(a), 5(b), and 5(c) shows the worn surface of three PTFE materials at low magnifications. It is observed, from Figure 5(a), that there are obvious abrasion marks on the surface of unfilled PTFE after 900 m comparable to PTFE Composites B and C [see Fig.

5(b) and 5(c)]. The wavy morphology surface with high peaks and deep valleys could also be observed from Figure 5(a). Figure 5(b) shows low peaks and shallow valleys, while the peaks and valleys are hardly observed from Figure 5(c). This is why Composite C exhibited the highest wear resistance, while unfilled PTFE (A) presented very poor wear resistance. Figure 5(d) and 5(e) are the worn surface of Composites B and C at same high magnification of 1000×. It can be observed from Figure 5(d) that there exists the debonding at the interface to the matrix in Composite B at the high magnification during repetitive reciprocating sliding motion. Figure 5(e) shows that there is a small pit of about 10 μm on the surface of Composite C. This is probably because the adhesion bonding between PTFE and PTFE waste was not strong, and the repeated sliding action on this surface was able to pull some of these fragments apart, which would contribute to wear loss. To further understand the worn surface of Composite C, some pits were observed at high magnification of 5000×, as shown in Figure 5(f). This characteristic could be attributed to surface fatigue wear. For Composite B, there existed some pits on the worn surface. Composite C exhibited high wear resistance when compared with Composite B because of reinforcement of alumina nanoparticles.

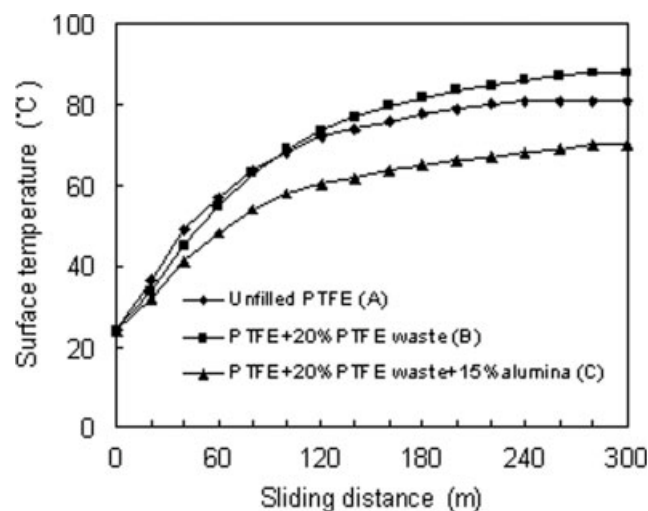


Figure 4 Worn surface temperature of three PTFE materials at a reciprocating frequency of 1.0 Hz, a contact pressure of 5.5 MPa, and a sliding distance of 300 m.

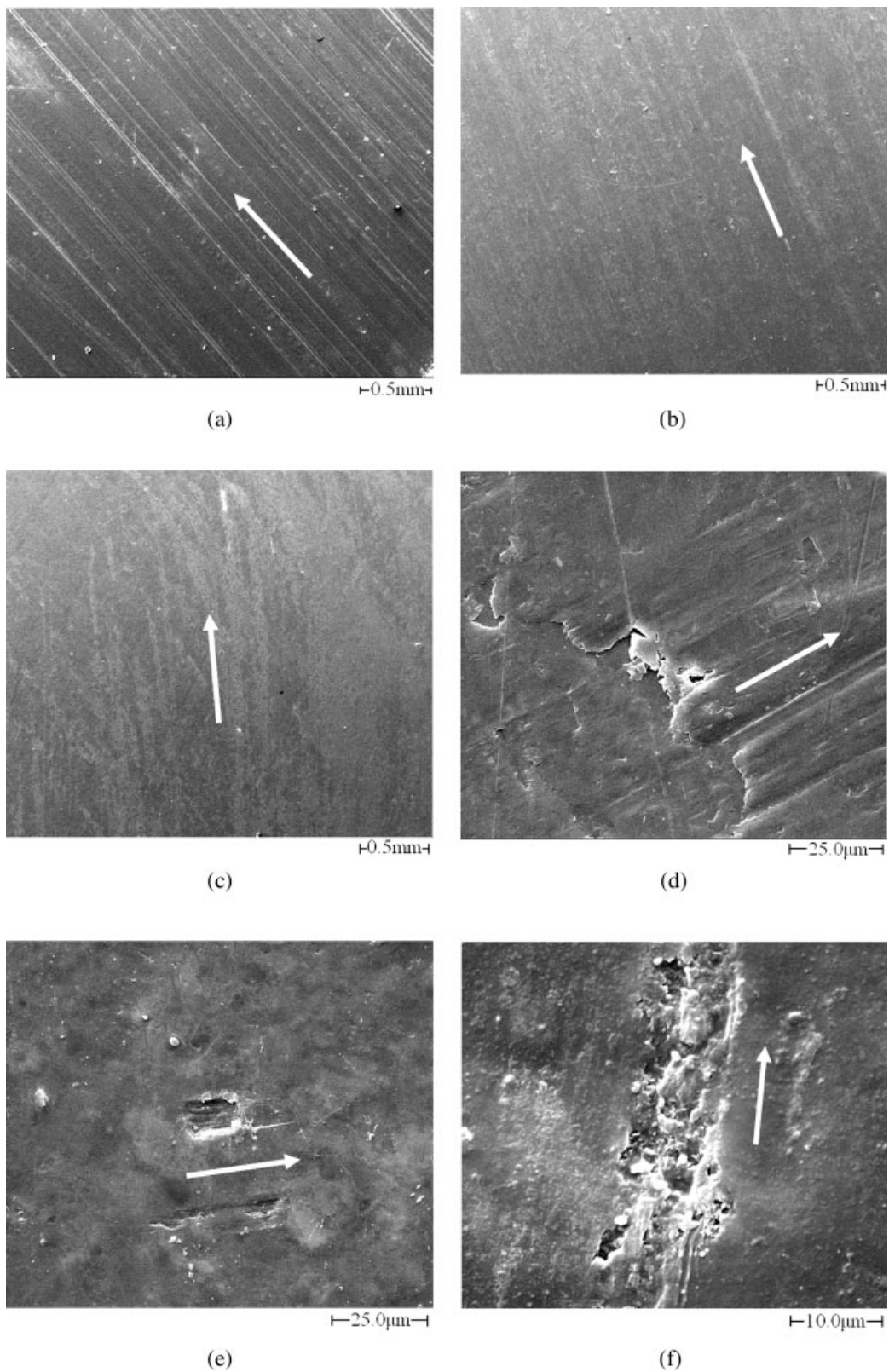


Figure 5 SEM morphology of the worn surface of PTFE and PTFE composites. (a) Unfilled PTFE, (b) PTFE waste filled PTFE composite B, (c) PTFE waste and alumina filled PTFE composite C, (d) Composite B, (e) Composite C, and (f) Composite C. Test conditions: a reciprocating frequency of 1.0 Hz, a contact pressure of 5.5 MPa, and a sliding distance of 900 m.

CONCLUSIONS

PTFE composites filled with PTFE waste (Composites B and C) showed a slightly high coefficient of friction and very high wear resistance when compared with the unfilled PTFE. Comparing Composites B and C, it was found that Composite C presented a slightly high coefficient of friction and high wear resistance. This was because alumina nanoparticles further reinforced PTFE matrix. It was experimentally confirmed that the mechanical recycling of PTFE waste without by-products is feasible. This method demonstrated a new potential for the low cost recycling of PTFE waste.

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