

## A study on the friction and wear behavior of PTFE filled with alumina nanoparticles

W. Gregory Sawyer<sup>a,\*</sup>, Kevin D. Freudenberg<sup>a</sup>, Praveen Bhimaraj<sup>b</sup>, Linda S. Schadler<sup>b</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup> Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

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### Abstract

A solid lubricant composite material was made by compression molding PTFE and 40 nm alumina particles. Prior to compression molding the constituent powders were blended using a jet milling apparatus. Composites from 0 to 20 wt.% were prepared. These composites were tested against a polished stainless steel counterface on a reciprocating tribometer. The experimental conditions were a contact pressure of 6.4 MPa, a stroke length of 50 mm, and a sliding speed of 50 mm/s. The friction coefficient of the composite increased over unfilled samples from roughly  $\mu = 0.15$  to  $\mu = 0.2$ . At filler concentrations of 20 wt.%, the wear resistance improved 600×. The wear resistance of this composite increased monotonically with increasing filler concentration and no optimum filler fraction was found.

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### 1. Introduction

Polytetrafluoroethylene (PTFE) polymer is a widely used solid lubricant. It is commonly used to provide a dry sliding friction coefficient  $\mu < 0.2$  on a variety of counterface types including stainless steel. PTFE is a popular polymer solid lubricant because of its resistance to chemical attack in a wide variety of solvents and solutions, high melting point, low coefficient of friction, and biocompatibility. It is commonly used in bearing and seals applications. Unfortunately, PTFE suffers from poor wear resistance. Gong et al. [6] and Blanchet and Kennedy [3] report unfilled wear-rates of  $7.36 \times 10^{-4}$  and  $7.41 \times 10^{-4}$  mm<sup>3</sup>/Nm, respectively. A hypothesis for the low friction of PTFE is that the long chains of PTFE,  $-(CF_2-CF_2)_n-$ , orient on the transfer surface during sliding, forming a low shear-strength interface with the bulk PTFE bearing material. PTFE has a 13/1 or 15/1 helical molecular structure with the fluorine atoms close enough to form a smooth cylindrical surface against which other molecules can easily slide [2].

Hard particulate fillers made of ceramic or metal particles, and fiber fillers made of glass have been used with a PTFE matrix to dramatically improve the wear resistance, even up to three orders of magnitude. The use of such hard particles

increases the dry sliding friction coefficient and abrades the counterface. Counterface abrasion is not desirable in a solid lubricant bearing system. Novel non-abrasive PTFE systems with wear resistance similar to filled PTFE composites have been made using gamma and electron irradiation by Briscoe and Ni [5] and Blanchet and Peng [4], respectively. With the recent availability of nanoparticles it is hypothesized that composites made with such small fillers will be significantly less abrasive than their micrometer sized counterparts. Perhaps such composites will provide a new family of non-abrasive and wear-resistant solid lubricant bearing materials.

### 2. Review of polymer nanocomposite literature

A polymer nanocomposite is defined as a composite material with a polymer matrix and filler particles that have at least one dimension less than 100 nm. Not included in this review is recent work with layered polymer films that have layer thicknesses less than 1  $\mu$ m.

Wang et al. [13–20], from the Lanzhou Institute of Chemical Physics in China, have filled polyetheretherketone (PEEK) with various weight fractions of SiC, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and ZrO<sub>2</sub>. The addition of the filler in fractions less than 10 wt.% improved the wear resistance and reduced the friction coefficient. The improved wear and friction is attributed

\* Corresponding author. Tel.: +1-352-392-8488; fax: +1-352-392-1071.  
E-mail address: [wgsawyer@ufl.edu](mailto:wgsawyer@ufl.edu) (W.G. Sawyer).

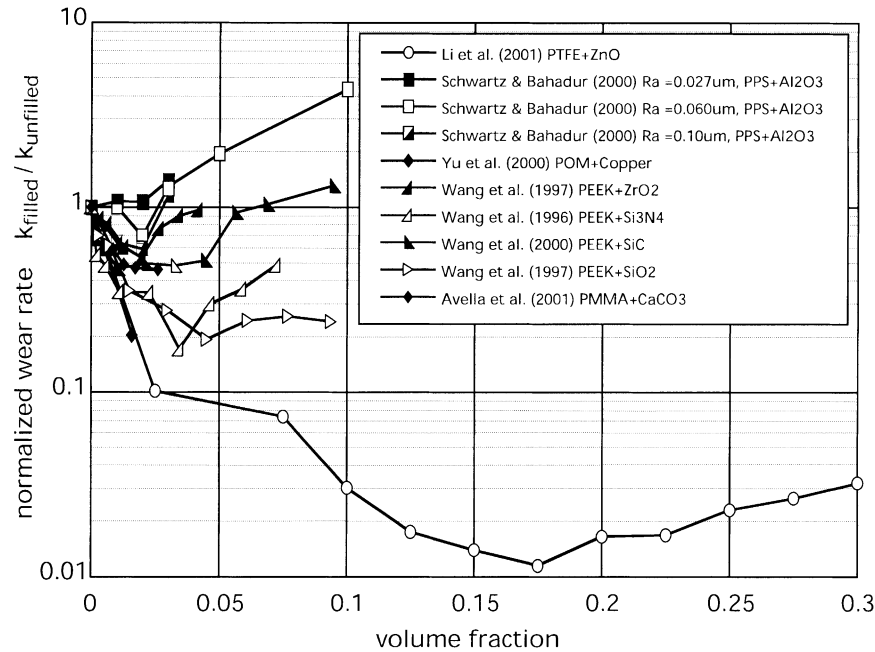


Fig. 1. A plot of normalized wear improvements for polymer nanocomposites as a function of filler volume fraction.

to two factors: the smoothing of the steel counterface, and the development of a transfer film.

Schwartz and Bahadur filled polyphenylene sulfide (PPS) with alumina nanoparticles. Examination of these samples with scanning electron microscopy showed good dispersion of filler particles in the PPS matrix. Wear tests were performed on a four station pin-on-disk tribometer. The roughness of the counterface was varied. It was postulated that this parameter directly relates to the development of the transfer film on the counterface; the rougher surface facilitates transfer film growth. Similar to the previous studies, maximum wear resistance was found at weight percentages below 10. As the percentage of filler increased above this optimum, the composite material experienced more wear than the unfilled counterpart. Unlike the previous work with PEEK, the coefficient of friction increased monotonically with increasing filler concentrations.

Li et al. [8] filled PTFE with nanoparticles of ZnO. Wear resistance was improved by nearly two orders of magnitude with a maximum wear resistance at ZnO concentrations of roughly 15% by volume. In that study, the friction coefficient of the nanocomposite was higher than the unfilled PTFE. Petrovicova et al. [9] filled Nylon 11 with silica. Wear resistance increased with increasing concentrations of nanoscale silica up to 15% by volume. In their study, the friction coefficient of the nanocomposite was lower than that of the unfilled Nylon.

Avella et al. [1] filled polymethylmethacrylate (PMMA) with nanoscale  $\text{CaCO}_3$ . The abrasion resistance increased as the filler content was increased, improving by a factor of 2 with 3%  $\text{CaCO}_3$  by weight. Yu et al. [22] filled polymethylene (POM) with micrometer and submicron cop-

per particles. The nanocomposite had less wear and a lower coefficient of friction than the composites filled with micrometer sized particles of copper and the unfilled POM. It was hypothesized that the increased surface area of the submicron copper filler particles improved the bonding strength at the filler/matrix interface.

In Fig. 1 the reported wear-rates of the nanocomposites are each normalized by the reported wear-rate of the unfilled matrix and plotted versus the volume fraction of filler particles. In Table 1 the wear-rate for the most wear-resistant formulation of each nanocomposite is given. In some studies discussed above not enough information was available to place the data on either such a plot or such a table.

A couple of striking observations are made from this compilation of data. First, the optimum concentrations of nanometer sized filler particles is 2–5% by volume. This is observed repeatedly. A more typical optimum in polymer composites made with micrometer sized filler particles is on the order of 30%. Second is the consistent observation that improvements in wear can be realized with polymer

Table 1

A comparison of the lowest reported wear-rates for various polymer nanocomposites

Reference	Matrix/nano-filler	Lowest wear-rate, $k$ ( $\times 10^{-6} \text{ mm}^3/\text{Nm}$ )
[8]	PTFE/ZnO	13
[10]	PPS/ $\text{Al}_2\text{O}_3$	10.4
[20,21]	PEEK/SiC	3.4
[18]	PEEK/ $\text{Si}_3\text{N}_4$	1.3
[15,19]	PEEK/ $\text{ZrO}_2$	3.9
[13]	PEEK/ $\text{SiO}_2$	1.4

nanocomposites. This is in contrast to models by Tanaka and Kawakami [12] and Lancaster [7] that suggest improvements in wear result from filler particles inhibiting large-scale destruction of the PTFE banded surface, and preferentially supporting load, respectively. Speculation was that nanometer sized filler particles could not prevent large-scale destruction of the banded structure of the PTFE matrix, and were too small to offer any preferential load support. It was assumed the small particles would simply be swept away by the much larger counterface asperities. The origin of wear resistance improvements in polymer nanocomposites is an open question.

### 3. Experimental approach

PTFE powder with a particle size of approximately 20  $\mu\text{m}$  and alumina powder with an average particle size of 38 nm (ranging from 17 to 100 nm) were used in this study. Powder mixtures with mass fractions ( $\lambda = \text{mass}_{\text{Al}_2\text{O}_3} / \text{mass}_{\text{PTFE} + \text{Al}_2\text{O}_3}$ ) of  $\lambda = 0.001, 0.005, 0.01, 0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3$  and 0.5 were prepared and blended using a jet mill. A jet mill is traditionally used to perform size reductions of dry materials and produce powders with sizes between 1 and 10  $\mu\text{m}$ . The jet mill apparatus was not used to mill or reduce the size of any of the constituents; rather, it was used to break apart agglomeration of the individual constituents. The mixtures were passed through the mill three times.

After milling, the mixture was compression molded into a cylindrical sample. A laboratory press was used to consolidate the mixture under 40–50 MPa of pressure at room temperature in a cylindrical chamber made of stainless steel. This consolidation pressure was held for approximately 15 min. The temperature was then ramped at 120  $^\circ\text{C}/\text{h}$  to a maximum temperature of 360  $^\circ\text{C}$ . The temperature was maintained at 360  $^\circ\text{C}$  for 3 h. The chamber was then cooled at a rate of 120  $^\circ\text{C}/\text{h}$  back to room temperature.

After molding a 6.4 mm  $\times$  6.4 mm  $\times$  12.7 mm cuboidal sample was machined from the cylinder. A small portion of the sample was analyzed using thermogravimetric analysis (TGA) to determine the mass fraction of filler in the composite. An amount of 5–10 mg of the sample was heated to 1000  $^\circ\text{C}$  at 10  $^\circ\text{C}/\text{min}$  to burn the polymer. The filler content was obtained by measuring the loss in weight as compared to the pure polymer. The polymer burns completely and the remaining weight fraction is the alumina. The data are presented in Fig. 2 and clearly shows that many fines are lost during the blending process, but a linear fit seems good. Due to the scatter and uncertainty in these measurements, the linear least squares regression line shown in Fig. 2 was used when reporting the composite wt.%.

The crystallinity was measured using a differential scanning calorimeter (DSC). The samples were heated from 25 to 400  $^\circ\text{C}$  at 10  $^\circ\text{C}/\text{min}$ . The heat-of-fusion for the composites was obtained by integrating the melting curve and dividing by the sample mass to get an average heat-of-fusion (J/g) for the sample. The crystallinity is then estimated by taking

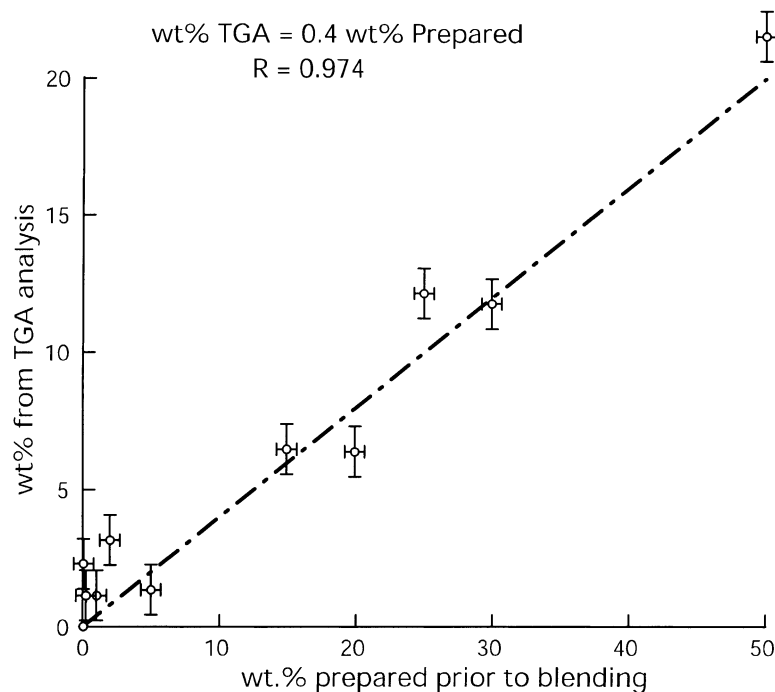


Fig. 2. A plot of the relationship between the measured wt.% of the blended and compression molded composite using TGA and the wt.% prepared prior to blending.

Table 2  
Crystallinity of some PTFE nanocomposite samples obtained from DSC

Al <sub>2</sub> O <sub>3</sub> (wt.%)	Crystallinity (%)
0	20 ± 6
8	42 ± 6
12	34 ± 6

the ratio of the average heat-of-fusion of the sample to the heat-of-fusion of fully crystalline PTFE, which is assumed to be 80 J/g. The crystallinity results are shown in Table 2 and indicate that while there is an increase in crystallinity, due to the presence of nanofillers or due to the process of producing the composite, it is not a monotonic increase with filler wt.%.

The counterface material was 347 stainless steel. The counterfaces were wet sanded with 600 grit paper to an average roughness of  $R_a = 0.1\text{--}0.2\ \mu\text{m}$ , and were cleaned and rinsed with alcohol just prior to testing. Each experiment used a new pin specimen and a new counterface track.

The 6.4 mm × 6.4 mm face of the composite sample was loaded against the stainless steel counterface with an average load of 260 N. This corresponds to a contact pressure of approximately 6.4 MPa. These experimental conditions were similar to those published in other studies, for example: Blanchet and Kennedy [3]. An illustration of the reciprocating tribometer used in this study is shown in Fig. 3. The counterface sample reciprocates below the composite pin with a stroke of 50 mm at a speed of 50 mm/s. The pin is held in a place with a holder that is rigidly mounted to a multi-axis load cell. The load cell is connected to an amplifier/conditioner. The conditioned voltages are read into a computer using a data acquisition system, which monitors both the normal load and friction forces contin-

uously and saves average values to a text file periodically. At the conclusion of each test, the specimens are removed from the sample holder, weighed, and a mass loss is recorded.

#### 4. Results

Prior to beginning tribology experiments with the alumina filled PTFE, two samples were prepared of unfilled PTFE. One of the samples was prepared using the “as received” powders and another was prepared using the previously described jet milling procedure without filler particles. Additionally, a block of already molded “virgin PTFE” was purchased and a cuboidal sample was prepared from this block. All three of these samples were run under the testing conditions and the average friction coefficients, mass loss, and wear-rate are given in Table 3, and compared to the values reported by Gong et al. [6], Blanchet and Kennedy [3], and Li et al. [8]. The unfilled samples in this study have wear resistance and a friction coefficient similar to that reported by others and to the commercial PTFE.

Table 3  
A comparison of the tribological behavior of the prepared unfilled PTFE material with other similar materials and commercially available material

Reference/description	Friction coefficient, $\mu$	Wear-rate, $k$ ( $\times 10^{-4}\ \text{mm}^3/\text{Nm}$ )
[6]	0.16	7.36
[3]	0.20	7.41
[8]	0.20	11.25
Commercial PTFE sample	0.18	6.39
This study—as received PTFE powder	0.18	7.15
This study—jet milled PTFE powder	0.15	4.81

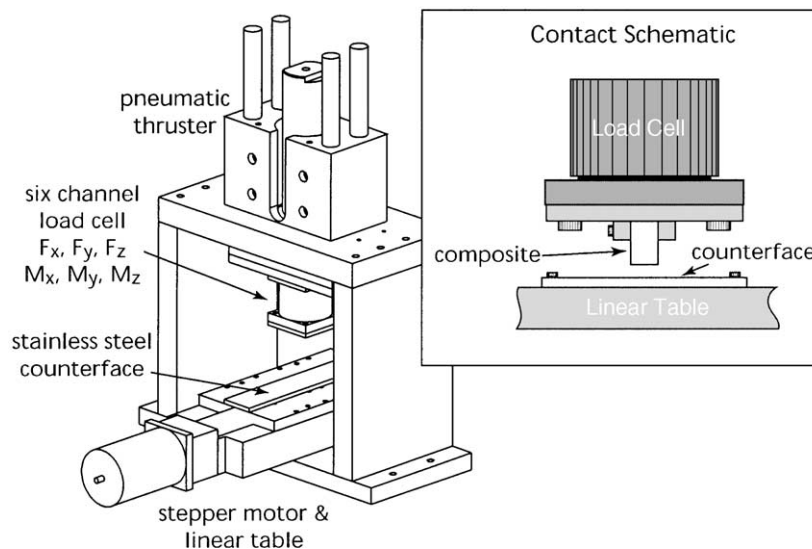


Fig. 3. A schematic of the reciprocating pin-on-disk tribometer.

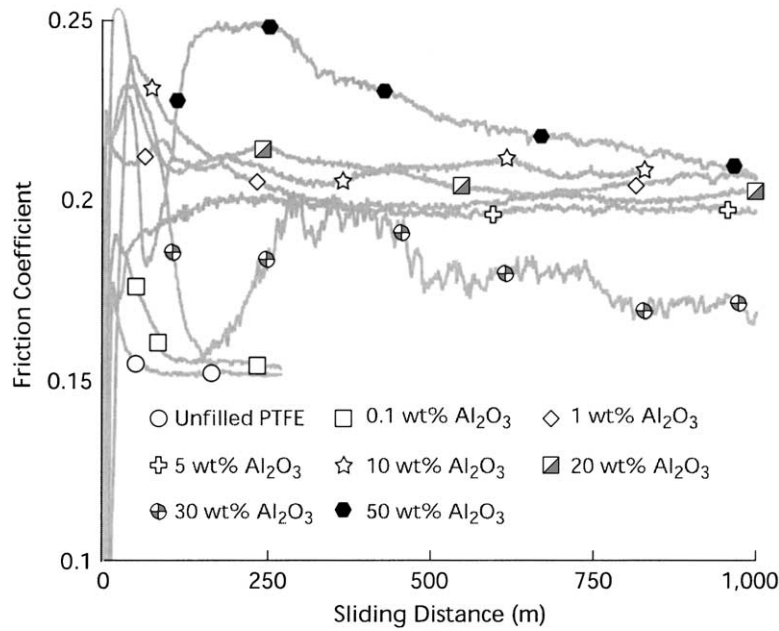


Fig. 4. A record of the friction coefficients as a function of sliding distance for the PTFE nanocomposite with various loading of Al<sub>2</sub>O<sub>3</sub>.

Figs. 4 and 5 show the recorded friction coefficients as a function of sliding distance and the average values as a function of filler wt.%, respectively. The average friction coefficient ( $\bar{\mu}$ ) for each test is calculated using Eq. (1) and the variance ( $\sigma^2$ ) is calculated using Eq. (2). In both the equations  $T$  is the total duration of the test in seconds

$$\bar{\mu} = \frac{1}{T} \int \mu dt \tag{1}$$

$$\sigma^2 = \frac{1}{T} \left( \int \mu dt - \frac{(\int \mu dt)^2}{T} \right) \tag{2}$$

It is clear that the friction coefficient increases due to the presence of the nanofiller, but the increase is small and it plateaus after 0.5 wt.% of filler.

In Fig. 6 the calculated wear-rate  $k$  (mm<sup>3</sup>/Nm) versus filler wt.% is plotted. The mass loss at the end of the tests was

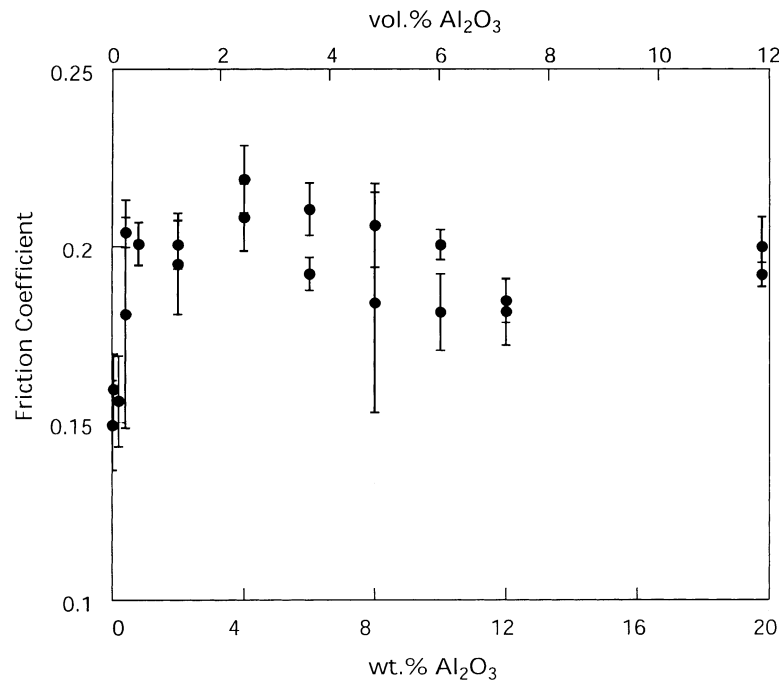


Fig. 5. A plot of the average friction coefficient for the samples as a function of the nanocomposite loading of Al<sub>2</sub>O<sub>3</sub>.

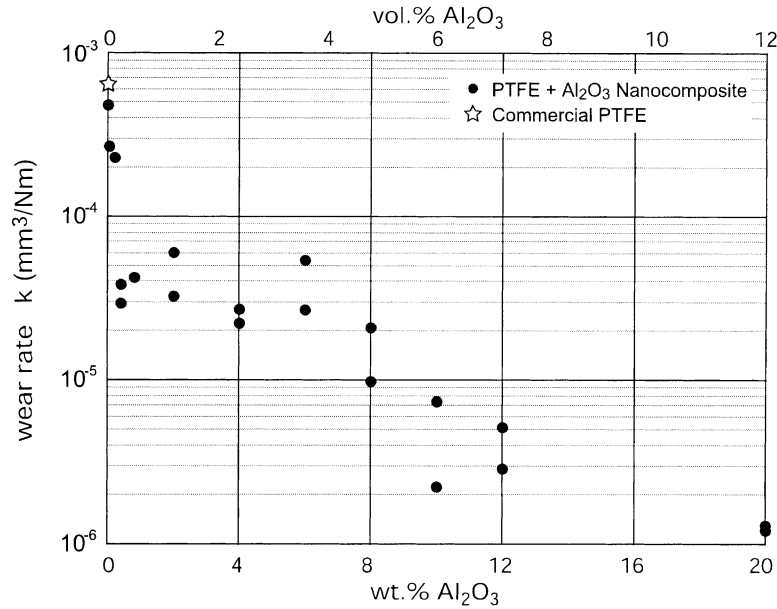


Fig. 6. A plot of the calculated wear-rate  $k$  ( $\text{mm}^3/\text{Nm}$ ) versus filler wt.%.

used to calculate a volume loss and wear-rate. The raw data are given in Table 4.

The lowest wear-rate found in this study was for a PTFE nanocomposite with almost 20 wt.% filler; the lowest wear-rate is  $k = 1.2 \times 10^{-6} \text{ mm}^3/\text{Nm}$ , which means that the nanocomposite is over 600 $\times$  more wear-resistant than the traditional unfilled PTFE. The average friction coefficient for this sample is  $\bar{\mu} = 0.19$ .

A stylus profilometer was used to measure the surface topography across and along the wear tracks after testing. It was not possible to quantify wear on the stainless steel counterfaces using the profilometry data. Qualitatively, visible scratches on the wear surface were observed for all samples with greater than 10 wt.% filler. Hardness measurements were made on all of the composite samples and no quantitative distinction between the samples was obtained.

Table 4  
Average values for the friction coefficient, mass loss, and sliding distance for the various samples<sup>a</sup>

Filler (wt.%)	Friction coefficient	Mass loss (g)	Sliding distance (m)
0.00	0.152	0.0720	270
0.04	0.155	0.0410	270
0.4	0.207	0.0205	1080
0.8	0.197	0.0260	1080
2	0.199	0.0285	1080
4	0.212	0.0155	1080
6	0.202	0.0265	1080
8	0.193	0.0110	1080
10	0.190	0.0060	1080
12	0.182	0.0080	2370
20	0.219	0.0280	30240

<sup>a</sup> All tests were run at a normal load of 260 N and a sliding speed of 50 mm/s.

## 5. Discussion

The microstructure of the composites is shown in Fig. 7. It is clear that there is inhomogeneous distribution of the filler. This is due to the jet milling and compression molding process. The PTFE particles have a characteristic size on the order of 20,000 nm and the alumina filler particles have a characteristic size on the order of 40 nm. The filler particles are roughly 500 $\times$  smaller than the matrix particles. During blending with the jet mill, the filler particles probably decorate the surface of the much larger PTFE particles. After compression molding, the resulting structure is probably cellular, with islands of PTFE surrounded by a continuous casing of alumina rich composite material.

It is offered that the improvements in wear are the result of this casing material interrupting the wear process of PTFE. Under these testing conditions the unfilled samples all show thin, millimeter sized, flaky wear debris, which is indicative of delamination. Perhaps the casing interrupts subsurface crack propagation; thus, it reduces wear by effectively keeping the virgin PTFE islands isolated so damage initiated in one region cannot easily spread into another. Optical inspection of the debris piles showed that the debris particle size decreased rapidly with the inclusion of fillers; however, no quantitative measurement of debris size were made. While it is known that the wear resistance of PTFE increases with increasing crystallinity [11], the changes in crystallinity observed here cannot completely explain the observed behavior because while the wear resistance increased monotonically with filler content, the crystallinity did not.

This PTFE-alumina nanocomposite had friction coefficients on the order of  $\mu = 0.2$ . This is attributed to a transfer film that was on all of the counterfaces when run against

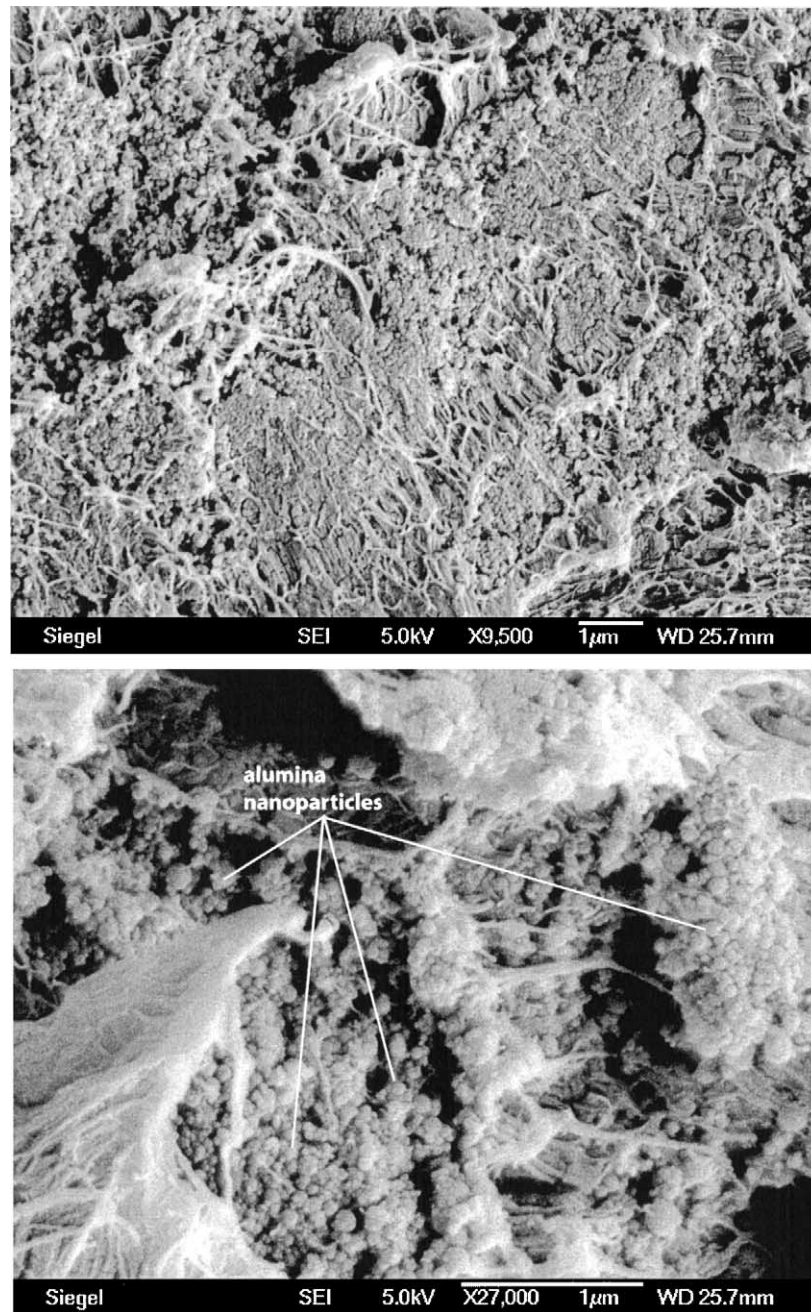


Fig. 7. Cellular structure observed with SEM in 12 wt.%  $\text{Al}_2\text{O}_3$  in PTFE: (a) regions of high and low concentrations of alumina nanoparticles; (b) high concentration region.

filled samples. Qualitatively, the transfer films were well adhered to the surfaces. Optically, they appeared smooth and continuous. For the unfilled PTFE samples, the transfer film was splotchy and easily liberated from the surface. It is hypothesized that the insensitivity of the friction coefficient to filler wt.% is due to the nanofillers being non-destructive to the transfer film, which is at least an order of magnitude thicker than the spherical filler particles.

The monotonic improvements in wear resistance with increasing filler concentration for this PTFE-alumina

nanocomposite is curious. The improvement in wear resistance is monotonic up to an actual filler loading of 20 wt.% which corresponded to our maximum loading. All other research groups have found optimum filler concentrations, and most find them below 10 wt.%. The recent study by Li et al. [8] with PTFE and ZnO found an optimum around 20 volume percent of filler. It is possible that there is something special about the PTFE polymer processing that allows high loading of nanoparticles. The low optimum filler percentages found in other research laboratories may

also be related to incomplete mixing (i.e. agglomerations of filler particles may be molded within the matrix). Most research groups sonicate particles in a solution and then dry the mixture prior to molding.

## 6. Conclusions

- (1) A solid lubricant composite material was made by compression molding PTFE and 40 nm alumina particles that were blended using a jet milling apparatus.
- (2) This composite has slightly increased friction over unfilled samples.
- (3) At filler concentrations of 20 wt.%, this composite has wear resistance over 600× higher than the unfilled samples.
- (4) The wear resistance increased monotonically with increasing filler concentration and no optimum filler fraction was found in the range of a filler wt.% from 0 to 20 (i.e. 20 wt.% was the most wear-resistant).

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