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Wear 260 (2006) 915–918

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Technical note

Improved wear resistance in alumina-PTFE nanocomposites with irregular shaped nanoparticles

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Received 25 March 2005; received in revised form 14 June 2005; accepted 27 June 2005
Available online 1 August 2005

Abstract

Past studies with PTFE nanocomposites showed up to 600× improvements in wear resistance over unfilled PTFE with the addition of Al_2O_3 nanoparticles. Irregular shaped nanoparticles are used in this study to increase the mechanical entanglement of PTFE fibrils with the filler. The tribological properties of 1, 2, 5 and 10 wt.% filled samples are evaluated under a normal pressure and sliding speed of 6.3 MPa and 50.8 mm/s, respectively. The wear resistance was found to improve 3000× over unfilled PTFE with the addition of 1 wt.% nanoparticles. The 5 wt.% sample had the lowest steady state wear rate of $K = 1.3 \times 10^{-7}$ mm^3/N m and the lowest steady friction coefficient with $\mu = 0.21$.

Keywords: Solid lubricants; Nanocomposites; Friction; Wear; PTFE; Nanoparticles

1. Introduction

Polytetrafluoroethylene (PTFE) exhibits many desirable tribological characteristics, including low friction, high melting temperature and chemical inertness. PTFE is a frequently used solid lubricant both as filler and matrix. As a matrix, it has been successfully filled with nanoparticles of alumina, zinca, and carbon nanotubes. Sawyer et al. [1] used 38 nm Al_2O_3 filler to improve the wear performance of PTFE, and the wear resistance of this nanocomposite increased monotonically with filler wt.%, eventually being 600 times more wear resistant than unfilled PTFE at a loading of 20 wt.%. Burris and Sawyer [2] and Li et al. [3] have found similar improvements for metal-oxide nanocomposites of PTFE at high weight percents of filler. The promise of nanocomposites, however, was that low weight percents could provide such improvements. This study is the first in which low weight percentage of filler particles are shown to provide over 1000× improvements in wear rate. The difference between these composites and previous nanocomposites of PTFE is that the nanoparticles are irregular in shape, as opposed to the spherical shape of previous composites.

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0043-1648/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.wear.2005.06.009

2. Experimental details

The processing of ceramic nanoparticle filled PTFE follows the procedure described in [1,2], and uses the same PTFE powders. The Alumina powder used in this study is shown in Fig. 1. In contrast to the particles used in the previous studies these particles are very irregular in shape. Composites of 1, 2, 5 and 10 wt.% filler were prepared and 6.3 mm × 6.3 mm × 12.7 mm pin samples were machined from the compression molded parts.

A reciprocating pin-on-disk tribometer was used to test the wear and friction of the samples. This testing apparatus and an uncertainty analysis of the friction coefficient and wear rate are discussed in detail in Schmitz et al. [4] and Schmitz et al. [5], respectively. The counterfaces are lapped plates of AISI 304 stainless steel and are described in detail in Burris and Sawyer [2]. A normal force of 250 N (6.3 MPa), a reciprocating length of 25.4 mm and an average sliding speed of 50.8 mm/s are used for these tests. Experiments are interrupted periodically and mass loss measurements are converted to wear volume loss as a function of the sliding distance. Uncertainty intervals shown on the wear volume and wear rate data are calculated following Schmitz et al. [5].

3. Results and discussion

The TEM micrographs in Fig. 1 show the shape variation between the nanoparticles used in previous studies [1,2] and the more irregular nanoparticles used in these experiments. These ‘80 nm’ particles are clearly larger than their reported size and are much more faceted than the more spherical ‘38 nm’ and ‘44 nm’ particles. These particles produced statistically significant increases in friction coefficient and reductions in wear rate over previous metal-oxide filled nanocomposites.

Fig. 2 plots the friction coefficient of each sample as a function of sliding distance under a normal load of 250 N. Initially, the friction coefficient of each sample was low, ranging from $\mu = 0.15$–0.2. The friction coefficient of the 10 wt.% sample quickly increased to a higher steady value of $\mu = 0.32$, while the 1 wt.% sample experienced nearly a kilometer of sliding distance before increasing to a similar value. Generally, the length of this transient period increased with decreasing particle loading. This transient behavior is consistent with filler particle accumulation at the sliding interface [6,7]. It is interesting to note that the friction coefficient of the 5 wt.% sample did not follow this trend, but stayed low at $\mu \sim 0.22$ for the entire test. The steady values of friction coefficient for the 1, 2 and 10 wt.% samples were similar at $\mu \sim 0.3$.

The wear volume of each sample is plotted as a function of the sliding distance in Fig. 2. The less filled samples showed high wear rates at the beginning of the tests that occur in concert with the initial transients in friction coefficient. The total wear volume decreased with increasing filler concentration, but the steady state wear rate was relatively insensitive to the filler loading. Fig. 3 shows the steady state wear rates as a function of filler particle loading for four different PTFE + metal-oxide nanocomposites. The irregularly shaped nanoparticles provide substantial reductions in steady state wear rate over the other PTFE nanocomposites. With the addition of 1 wt.% irregular shaped nanoparticles, the wear resistance is improved 3000× over unfilled PTFE. Prior to this study, the lowest wear rate for PTFE nanocomposites was $K = 1 \times 10^{-6}$ mm^3/N m for a 20 wt.% ‘38 nm’ alumina

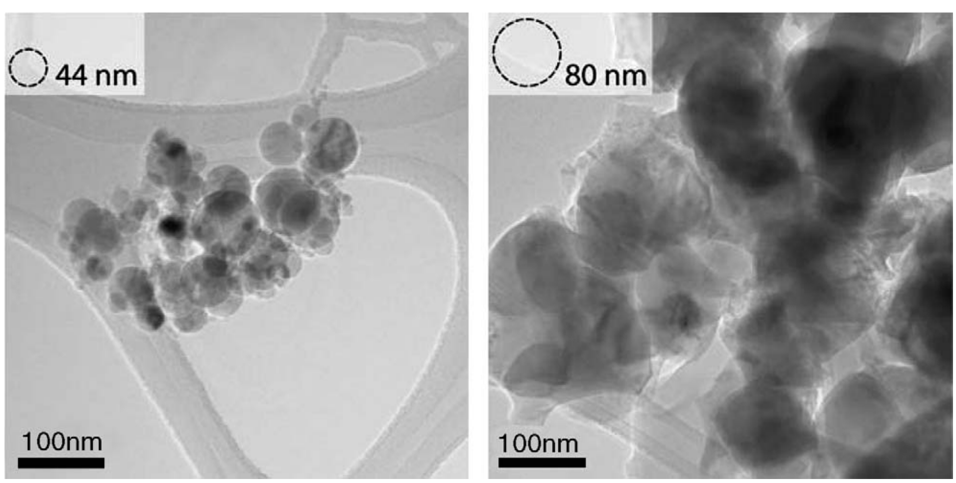

Fig. 1. TEM images of the two alumina particles evaluated. The manufacturer reported mean particle size is indicated on the upper left of each image. The crystal phase of the spherical 44 nm particles is reported to be 70% delta and 30% gamma; the more irregular 80 nm particles are reported to be 99% alpha.

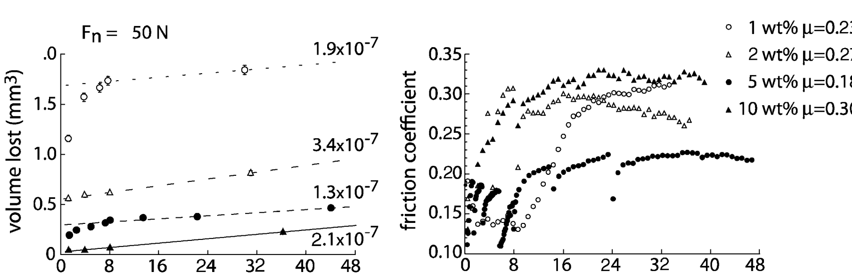

Fig. 2. Plots of wear volume and friction coefficient as a function of sliding distance. The experiments were run under a load of 250 N, a sliding speed of 50 mm/s, on a reciprocating pin-on-disk tribometer. The counterface was a lapped 304 stainless steel plate. The average friction coefficient over the entire experiment is given in the graph legend.

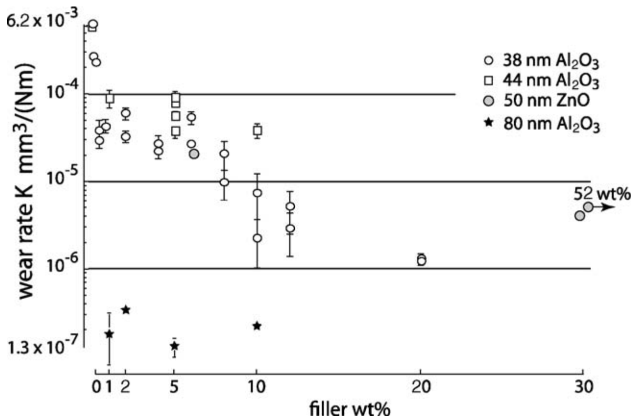

Fig. 3. Plot of wear rate vs. filler wt.% of alumina nanoparticles. The open circles and squares are both spherical alumina nanoparticles with reported crystal phases of 70% delta and 30% gamma. The solid stars are the irregular 80 nm alumina nanoparticles that are reported to be 99% alpha phase. The light gray circles are from Li et al. [3] and are uncharacterized ZnO nanoparticles with a reported particle size of 50 nm.

nanocomposite; the 1 wt.% ‘80 nm’ sample was an order of magnitude lower.

There have been several proposals on the governing mechanisms of wear reduction for filled PTFE. These include increased transfer film adhesion, preferential load support by the filler, prevention of crack propagation by the filler and control of debris size and shape to name a few. The transfer film of each sample was very thin and uniform after testing. Quantification of the thickness and uniformity of these films is difficult, but nano-indentation suggests an average thickness less than 1000 nm most likely around 200 nm. The literature of PTFE composites’ tribology almost universally documents the presence of thin uniform transfer films and small wear debris being indicative of wear resistant samples. It is our hypothesis that the thin transfer films that form with wear resistant PTFE materials are a result of the fine wear debris size and not on their own the source of wear resistance.

SEM observations of three PTFE-metal oxide systems revealed a compartmentalized microstructure, where regions of nominally unfilled PTFE are interconnected by PTFE fibrils and are encapsulated within particle rich reinforcing phases. The 5 wt.% sample in this study has an estimated compartment size of 5 μm; a sphere of this diameter contains approximately 6000 alumina nanoparticles. The reinforcing phases block the cracks that form in the unfilled regions, thus producing platelet debris approximately equal in size to the original compartment. The sizes of the domains, wear debris and wear rate are all reduced as filler content is increased. Debris size reduction is therefore believed to be the primary wear reduction mechanism for these systems. The effect of filler wt.% on wear can be seen by examining the initial wear transients for the 1–10 wt.% samples in Fig. 2. Initially, the surface area fraction is identical to the bulk volume fraction of filler, and the initial wear rate of the 1 wt.% sample is about an order of magnitude greater than for the 10 wt.% sample. As wear of the PTFE domains occurs, a surface rich in filler is left behind until a steady surface fraction of filler and matrix can be maintained. Since the 10 wt.% sample appears steady from the onset of sliding, it is assumed to be close the optimum surface fraction. It is speculated that an increase beyond 10 wt.% would produce increased wear due to induced brittleness at regions of very high filler concentration; to date this has not been quantified and remains a qualitative observation (the 20 wt.% sample broke under fixturing into the tribometer and thus could not be tested).

Filler accumulation at the sliding interface was previously observed for a PTFE microcomposite by Blanchet [6] and Han and Blanchet [7]. For microcomposite systems, the asperities are very small compared to the particle, and the volume of the particle held within the matrix is sufficient to withstand the force of the asperity contact. Filler accumulation is not typically observed in nanocomposite systems because the asperities are on a size scale much larger than the particle. With no chemical bond to attach the particle to the PTFE, the exposed filler at the surface is scraped off leaving only particles within the bulk to stop crack propagation. It is conjectured that the faceted nature of the 80 nm nanoparticles allow enough mechanical entanglement with the PTFE to enable filler accumulation at the tribological surface, which can result in high wear resistance at very low filler wt.%.

4. Conclusions

(1) The inclusion of irregular shaped filler particles was effective in reducing the wear of PTFE, but also leads to increased friction. The wear resistance of PTFE was increased 3000× with 1 wt.% filler.
(2) Steady values of friction and wear were not particularly sensitive to filler content in the range from 1–10 wt.%. The friction coefficient of the 5 wt.% sample was approximately 30% lower than for the other samples.
(3) The initial transient behavior of these nanocomposites is characterized by high wear and low friction, and was found to be sensitive to filler content becoming more pronounced and longer lasting as filler content is reduced.

Acknowledgements

This material is based upon work supported under NSF Grant No. #CMS-0219889, GOALI: Collaborative Research: Tribology of Nanocomposites and AFOSR-MURI grant FA9550-04-1-0367. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation or the Air Force Office of Sponsored Research.

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