



Environmental dependence of ultra-low wear behavior of polytetrafluoroethylene (PTFE) and alumina composites suggests tribochemical mechanisms

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ABSTRACT

Composites of polytetrafluoroethylene (PTFE) and alpha phase alumina produce wear rates that can be nearly five orders of magnitude less than the wear rates of virgin PTFE. The mechanism for this reduction in wear cannot be explained solely by mechanical effects. The influences of oxygen and humidity on the tribological performance of both unfilled PTFE and PTFE/alumina composites were studied. The wear rate of PTFE/alumina composites is dependent on the humidity of the environment; this dependence suggests a tribochemical mechanism is responsible for the ultra-low wear behavior of these PTFE/alumina composites.

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1. Introduction

Polytetrafluoroethylene (PTFE) has been an important, widely studied tribological material since the discovery of its low friction coefficient in the 1940s [1–4]. In addition to having a low coefficient of friction, PTFE is chemically inert and capable of withstanding elevated temperatures making it a candidate for various extreme environments [1,5] including space applications in low earth orbit [6]. Despite these obvious benefits, PTFE has been excluded from many tribological applications due to its high wear rate under engineering sliding conditions [7–9].

Unfilled PTFE is known to suffer from subsurface crack propagation and subsequent delamination [8]. To abate this high wear mode, fillers have been added to a PTFE matrix to reduce the wear by typically one or two orders of magnitude by fracture toughening and load support mechanisms [8,10]. Fillers of all shapes and sizes have reduced the wear rates of PTFE by as little as a few percent to up to five orders of magnitude [7–23].

The subject of this paper is the ultra-low wear behavior of the PTFE/alumina nano composites previously reported [19,21–23]. Burris et al. have reported that the inclusion of less than one volume percent alpha phase alumina particles can reduce the

wear of PTFE by three to four orders of magnitude [22]; this suggests that the ultra-low wear nature of these systems cannot be explained by traditional fracture toughening mechanisms. On steel countersurfaces, ultra-low wear PTFE systems consistently develop a thin and bronze-colored transfer film; this transfer film is uniform in both color and thickness and appears to provide protection for both the composite and the countersurface [22,24]. This transfer film takes time to develop, which results in a run-in period of poorer wear resistance as compared to the ultra-low steady state wear rates that have been reported previously. The generation of a new chemical species within the transfer film is repeatedly observed in X-ray photoelectron spectroscopy (XPS) within the C1s spectrum [25]; this new species is often referred to as “degraded” PTFE. However, this XPS signature is also consistent with a number of potential tribochemical events, including defluorination, conjugation of the carbon backbone, chain scission, and/or the formation of new side-chains and end-groups.

The key to understanding such low wear systems will likely be found in the study of the tribochemical mechanisms; evaluating the environmental effects on the wear of these composites can direct us to the chemical species involved in the function of ultra-low wear PTFE/alumina composites. To do this we built a linear reciprocating tribometer within an environmental chamber. Friction coefficient and wear rates of PTFE and ultra-low wear PTFE/alumina composites were evaluated in a nitrogen environment with various concentrations of oxygen and water. It was

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hypothesized that the formation of the persistent, ultra-low wear transfer films required both oxygen and water in the ambient environment.

2. Materials and sample preparation

PTFE composites and control samples were made of DuPont Teflon® PTFE 7C resin (~30 µm particles). The filler used was an Alfa Aesar alpha phase alumina powder (Stock #44652) with supplier specified 80 nm average particle size [26] discussed further by Burriss and Sawyer [19]. Powders were massed and mixed at 5.0 wt% alumina filler for all PTFE/alumina composites in this paper. The alumina powder was first dispersed at 3.45 wt% into dry isopropanol with the assistance of an ultrasonic horn (Branson Digital Sonicator 450 with titanium tip, operating at about 40% amplitude (400 W)). The dispersion was poured onto the PTFE 7C powder and the solvent was removed *in vacuo* (55 °C, 26.7 kPa) on a rotary evaporator and further dried on a high vacuum line (50 °C, 4 h, 4 Pa). Portions of this powder (13 g at a time) were then compressed, free sintered above the PTFE melting point at 380 °C for 30 min, and cooled to ambient temperature [27]; PTFE control samples were compression molded from DuPont 7C powder resin using the same conditions. The sintered samples were then machined into 6.3 mm × 6.3 mm × 12.7 mm pins for tribological testing. One of the 6.3 mm × 6.3 mm ends of the pin was finished to an average roughness, $R_a \approx 100$ nm. All samples were sonicated in methanol for 30 min, and allowed to dry for 3 h in laboratory air.

Counterface samples were 304 stainless steel rectangular flat plates (38 mm × 25 mm × 3.7 mm) with an average roughness, $R_a \approx 150$ nm. The effects of countersurface roughness on the wear properties of this material have been studied previously [24]. The counterface samples were washed with soap and water, followed by acetone and finally methanol; new samples were used for each test.

3. Experimental methods

3.1. Tribometer

A linear reciprocating tribometer similar to those previously described by Sawyer and Schmitz [9,28,29] was designed and built inside of an environmentally controlled glove box. The glove box can be regulated to as low as 10 ppm of O₂ and 0.5% relative humidity under a nitrogen backfill at 23–28 °C. The polymer sample was mounted to a 6-channel load cell that measures the normal and tangential forces. The polymer sample was loaded against the steel counter sample with a normal load of 250 N; normal load was applied and controlled by a pneumatic cylinder. Utilizing reversals, reported friction coefficients have an uncertainty of less than 0.005 [29].

In this flat on flat configuration the nominal average contact pressure is approximately 6.3 MPa, which is 20–50% of the yield strength of PTFE. The steel counter sample was mounted directly to a linear ball-screw stage, which reciprocated with a stroke of 25.4 mm at a rate of 50.8 mm/s. Tribological sliding conditions were chosen to be the same as previous studies [9,19,22,24,30–32] to match engineering conditions and to be easily compared between studies.

3.2. Wear measurements

The mass of polymer samples was measured before and after sliding using a Mettler Toledo scale that has 10 µg precision.

Using the change in mass, m_{lost} , and the density of the composite, ρ , a wear volume, V_{lost} , was calculated. Wear rates are calculated by dividing the volume lost during sliding in mm³, by the normal force, F_N , times the sliding distance, d , in m resulting in a wear rate, k , in units of mm³/Nm shown in (1) [28,29,32].

$$k = \frac{V_{lost}}{F_N d} = \frac{m_{lost}}{\rho F_N d} \quad (1)$$

Traditionally, mass measurements are taken intermittently and steady state wear rates can be computed [28]. For experiments in this paper, reported wear rates are average wear rates over the duration of sliding in an effort to eliminate potential contamination of the samples. Uncertainty in wear rates are less than 1%.

3.3. Experiments

Tribological experiments of PTFE/alumina composites and PTFE control samples were performed in the glove box in environments containing primarily nitrogen and consisting of various concentrations of oxygen and water. Oxygen was controlled at either a trace level of less than 100 ppm using a nitrogen fill gas or at 20% using a premixed “dry air” gas consisting of 80% nitrogen and 20% oxygen. Trace levels of oxygen were measured using a DeltaF 300ε oxygen analyzer. Relative humidity was controlled at values of 0.5, 0.6, 0.8, 2.5, 2.7, 3.6, 10, 30, 35, 68, 69, 78, and 87% RH by doping the closed environment with water and allowing the system to reach equilibrium; humidity was monitored with a General Eastern Hydroguard 2650 and an Omega digital thermo-hygrometer, which also monitored temperature.

Each PTFE/alumina sample was slid for 50,000 reciprocation cycles, a distance of ~2.5 km. Each PTFE reference sample was slid for 10,000 reciprocating cycles, a distance of 508 m. Due to the poor wear rates, PTFE samples wear out more quickly than PTFE/alumina composites. At 50,000 cycles the mass lost for a typical PTFE/alumina sample is on the order of a few hundred µg, which is easily measured with the balance.

For submerged experiments, an aluminum wet cell was mounted on the linear reciprocating tribometer. The aluminum cell was filled with deionized water and all other experimental conditions were matched.

For vacuum experiments, a similar linear reciprocating tribometer [33] was used in a vacuum system to evaluate PTFE/alumina composites at 6×10^{-6} Torr. All other experimental conditions and methods were matched.

3.4. XPS

X-ray photoelectron spectroscopy experiments were performed on the transfer film on the steel surface, the tribofilm generated on the polymer wear surface and an unworn surface of the polymer for both PTFE and PTFE/alumina composites worn in the laboratory air environment. XPS experiments were carried out with a Physical Electronics Quantera Scanning ESCA Microprobe, using a focused (100 µm) monochromatic Al K-alpha X-ray (1486.6 eV) beam operated at 18 kV and 100 W. The X-ray beam is generated using an electron gun and scanned over ~1400 µm × ~200 µm to define the analysis area. The electron energy analyzer was operated in the constant energy mode with pass energy of 112 eV and 0.2 eV step size between points for high resolution spectra (typically 20–40 eV scan for each element). Charge compensation in the form of a dual electron and argon ion beam system was used. The photoelectron take-off angle was 45° relative to the sample normal. The energy resolution of the system was approximately 0.84 eV using the Ag3d5

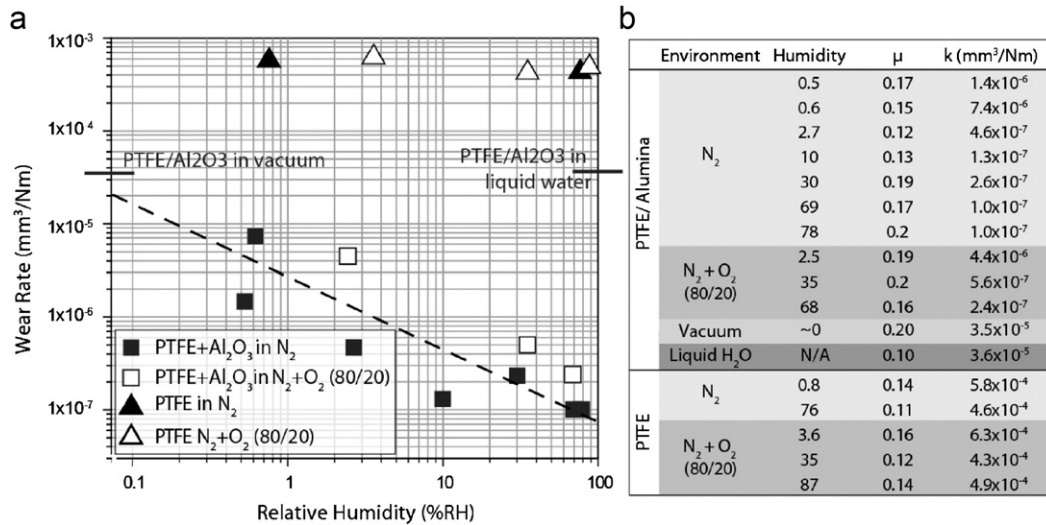


Fig. 1. (a) Average wear rate of PTFE/alumina composites and PTFE controls in various humidity and oxygen environments. Polymer samples were slid against 304 stainless steel, at 250 N normal load, 50.8 mm/s sliding speed and 25.4 mm stroke. PTFE samples were slid for 10,000 cycles while PTFE/alumina samples were slid for 50,000 cycles. (b) Summary of steady state friction coefficient and wear rate results for PTFE/alumina composite and PTFE samples in various humidity and oxygen environments.

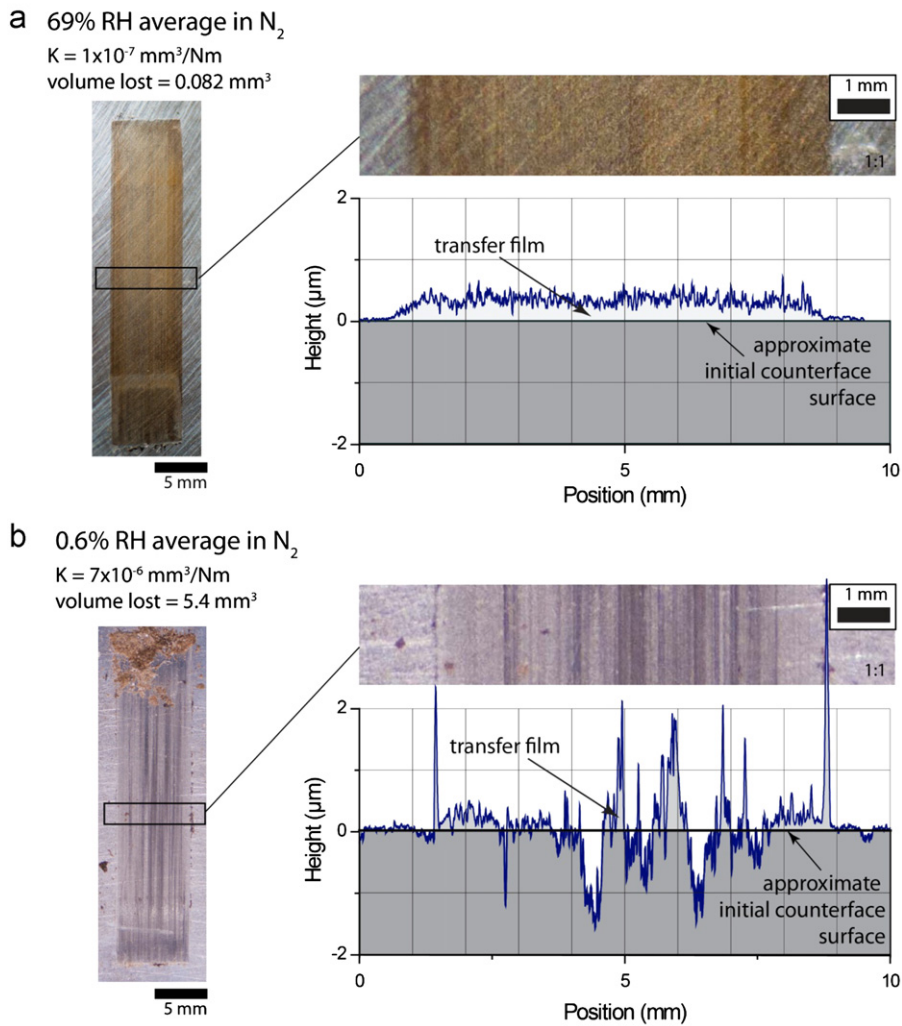


Fig. 2. Transfer film optical image and profile for PTFE and alumina composites slid against stainless steel in (a) 69% average relative humidity in nitrogen and (b) 0.6% average relative humidity in nitrogen.

peak. Quantification was based on peak areas calculated after Shirley background subtraction [34]; by multiplication with calculated atomic sensitivity factors corrected for the analyzer transmission function.

4. Results and discussion

4.1. Impact of environmental constituents on the wear of PTFE/alumina composites

The average wear rate for PTFE filled with 5 wt% alumina decreased with increasing relative humidity in both nitrogen and nitrogen/oxygen environments (Fig. 1). Wear rate varied more than two orders of magnitude by simply changing the content of gaseous water in the environment in which sliding occurs. For wear rates below 1×10^{-6} mm³/Nm (RH > 2.5%), a thin, bronze-colored, protective transfer film was formed (Fig. 2a). This transfer film was consistent with transfer films commonly observed in low wear PTFE composites.

For the lowest relative humidity experiments, a high wear rate was observed along with a patchy black transfer film. Fig. 2b shows a stylus profilometric scan across the wear track for the high-wear, low-humidity experiment; this profile reveals that the thin protective transfer film associated with ultra-low wear PTFE composites has not formed and there is actually some scratching observed on the steel counter sample.

At the limiting case for low relative humidity (vacuum at a pressure of 6×10^{-6} Torr) the wear rate was a maximum of 3.4×10^{-5} mm³/Nm; this wear rate is consistent with many of the traditional fracture toughened PTFE composites. There is an obvious link between wear rate of the PTFE/alumina composites and the presence of water in the environment.

This environmental dependence and the presence of a new tribochemical species in the transfer film suggest that there is a tribochemical reaction occurring during sliding that, in the presence of water, produces a thin, protective, low-wear transfer film. XPS studies of the transfer film generated on the 304 stainless steel by the PTFE/alumina composite are consistent with possible defluorination and chain scission of the polymer. The presence of a new peak of around 290 eV was observed in the carbon spectra for the wear surface of the polymer composite and the transfer film generated by the PTFE/alumina composite (Fig. 3a). This peak suggests a tribochemical degradation of the polymer and generation of a new species at the interface that may be responsible for the added wear resistance observed in PTFE and alumina composites. The species observed at 290 eV was observed in a much smaller quantity in transfer film generated by unfilled PTFE and was not observed on the wear surface of unfilled PTFE within the detection limit (Fig. 3b).

There is a small but significant difference in the wear rate at a given relative humidity with and without oxygen for the PTFE/alumina composites. However, oxygen is present in some quantity for all low-wear experiments (detected limit ~ 100 ppm). A definitive conclusion on the role of oxygen in the tribochemistry will require further exploration.

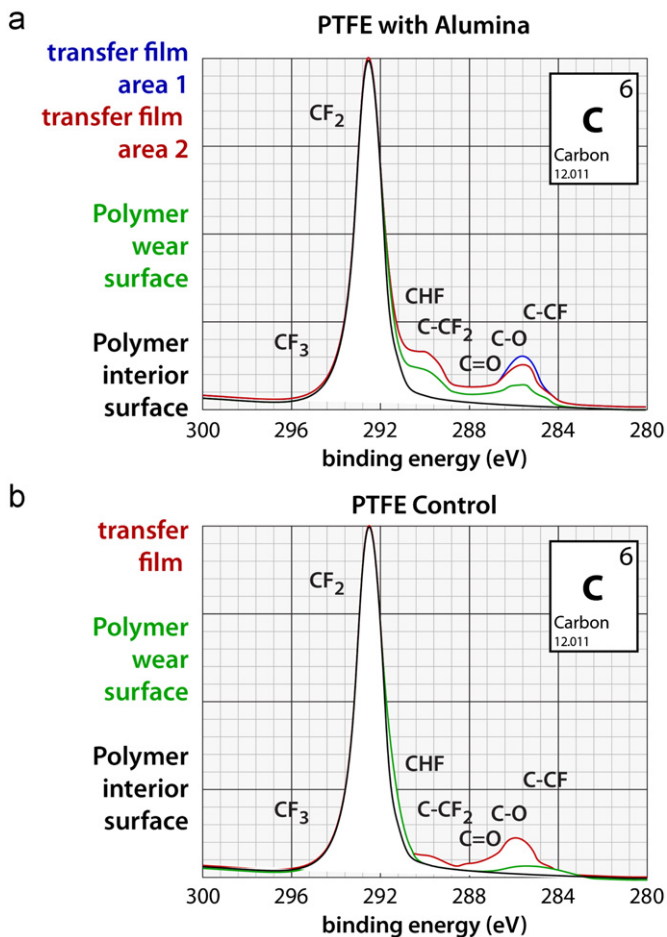


Fig. 3. C1(s) X-ray photoelectron spectrum for transfer films, wear surface of the polymer and non-worn surface of the polymer for (a) PTFE and 5 wt% alumina composite and (b) unfilled PTFE slid against stainless steel in environment of nitrogen ($\sim 80\%$), oxygen ($\sim 20\%$) with a relative humidity of 35%.

4.2. Impact of submersion in water on the wear of PTFE/alumina composites

The wear rate of the composites of PTFE filled with 5 wt% alumina was 3.6×10^{-5} mm³/Nm in the submerged water environment. This is significantly higher than the wear rate of the composite in the humid environment and comparable to the wear rate of the composite in vacuum. This suggests that the formation of the tribofilms responsible for the reduction of wear in these systems is inhibited in the submerged liquid water environment.

4.3. Impact of environmental constituents on the friction coefficient of PTFE/alumina composites

In a nitrogen environment, the friction coefficient of PTFE/alumina composites seemed to be lowest in the 2.7 and 10% RH experiments. There is no clear trend with the friction coefficient as a function of oxygen or water content. Friction coefficient in the submerged experiments was the lowest of all experiments.

4.4. Impact of environmental constituents on the friction coefficient and wear rate of PTFE control samples

There is no apparent trend in the wear rates or friction coefficients for PTFE as a function of oxygen or humidity in the environment. The presence of water may help to slightly reduce the wear over the dry conditions. There is a difference in the formation of a transfer film. The transfer film formed at low humidity is patchier with large islands while in the higher humidity environment the transfer film is slightly more uniform and is slightly discolored. The wear debris for the PTFE slid in the humid environment is generally smaller than that formed in the dry environment by optical observation.

5. Conclusions

Water is essential in the ultra-low wear behavior of PTFE/alumina composites. In the absence of gaseous water, PTFE/alumina composites behave like other fracture toughened filled PTFE systems by shutting down the subsurface crack propagation and delamination of PTFE during sliding. The further reduction in wear rate in the presence of water suggests that a secondary wear mechanism can be reduced or shut down by the formation of thin, protective tribofilms. The tribofilms associated with ultra-low wear rates do not form in the absence of water in our experiments, suggesting that a tribochemical reaction may be responsible for the formation of the transfer film and ultimately the ultra-low wear behavior of this material.

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