

Cryogenic friction behavior of PTFE based solid lubricant composites

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Solid lubricants used in aerospace applications must provide low friction and a predictable operation life over an extreme range of temperatures, environments and contact conditions. PTFE and PTFE composites have shown favorable tribological performance as solid lubricants. This study evaluates the effect of temperature on the friction coefficient of neat PTFE, a PTFE/PEEK composite and an expanded PTFE (ePTFE)/epoxy coating. These experiments evaluate friction coefficient over a temperature span which, to the investigators' knowledge, has not been previously examined. Results show a monotonic increase in friction coefficient as sample surface temperature was decreased from 317 to 173 K for all three samples. The frictional performance of these and other published solid lubricant polymers was modeled using an adjusted Arrhenius equation, which correlates the coefficient of friction of the polymer materials to their viscoelastic behavior. A model fit of all the polymer data from 173 to 450 K gives an activation energy of 3.7 kJ/mol. This value suggests that breaking of van der Waals bonds is the likely mechanism responsible for the frictional behavior over this temperature range.

KEY WORDS: cryotribology; polytetrafluoroethylene; PTFE; solid lubrication; space lubrication

1. Introduction

Solid lubricants are frequently used under operational conditions where the use of fluid lubricants is precluded. Such conditions are typically considered extreme, often existing at opposite ends of the temperature spectrum either high ($T > 200$ °C) or low ($T < 0$ °C). Other extreme conditions include vacuum and harsh chemical environments. Aerospace applications include both temperature extremes and vacuum. The desire is to operate moving mechanical assemblies in such environments for extended operational cycles. This objective can be met using solid lubricants and solid lubricant coatings [1,2].

For moving mechanical assemblies that require limited operational cycles, such as hinges and other single event assemblies, thin sacrificial solid lubricants such as burnished films of MoS₂ have been successfully used [3]. These thin films pose two main problems for the design engineer: (1) they wear during operation and thus have finite life, and (2) they are often poor performers in the Earth's environment where they are operated prior to launch and deployment. Bulk polymeric composites containing Polytetrafluoroethylene (PTFE) offer an attractive option to the design engineers because of their predictable operational life [4,5], ability to operate from cryogenic temperature (4 K) to 500 K, and their relative insensitivity to oxygen and humidity [3].

Despite the demonstrated successes of devices using PTFE bushings that operate at cryogenic temperatures, there is a paucity of data available for friction coeffi-

cients and wear rates of PTFE and PTFE composites at temperatures below 300 K. Further, the data that is available is often collected at cryogenic temperatures in baths of liquid nitrogen ($T_{LN_2} = 77$ K) or liquid helium ($T_{LHe} = 4.2$ K) and as a data set does not provide any clear or understandable trend in friction coefficient. As rather bluntly summarized by Gardos [3],

"...the review of the reference literature yields little fundamental information on the materials science-related aspects of cryogenic tribosystems. Mostly, one finds only empirical data generated by improperly instrumented bearing testers or friction and wear testers of limited test specimen configuration(s)."

There are a number of experimental challenges in performing cryotribology studies. Foremost is the difficulty in preventing sample contamination of condensed water and ice from the gaseous environment. This has been solved, in part, by submerging the contacts in liquid baths of nitrogen or helium. However, it is questionable whether or not the friction coefficient data collected from experiments that involve a liquid bath surrounding the contacts is relevant to the dry sliding cryogenic environment of space. Another challenge and potential problem is in the apparatus design for such submerged contacts, which typically involves the use of long flexible shafts for torque transmission and measurement. Finally, the hypotheses that attempt to define the mechanistic origins of the frictional behavior at cryogenic temperatures do not link up with the data and models for the frictional behavior at 300 K and above (i.e., the hypotheses often involve cryo specific explanations and the data has strong disconnects with other

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Table 1.

Various publications have provided hypotheses for cryogenic tribology of solid lubricants, particularly PTFE and PTFE composites.

Author	Trend	Theory
<i>Cryotribology</i>		
Gradt <i>et al.</i> [13]	$\mu \downarrow$ as $T \downarrow$; $K \downarrow$ as $T \downarrow$ until 8 K	$H \uparrow$ as $T \downarrow$; $A_{real} \downarrow$ as $T \downarrow$; $F_f \downarrow$ as $T \downarrow$; $H \uparrow$ as $T \downarrow$; $K \downarrow$ as $T \downarrow$
Hubner <i>et al.</i> [14]	$\mu \downarrow$ as $T \downarrow$ until 4.2 K	$H \uparrow$, $E \uparrow$, and $K \downarrow$ as $T \downarrow$; $\Delta T_{flash} \uparrow$ as $T \downarrow$
Michael <i>et al.</i> [15]	$\mu \downarrow$ as $T \downarrow$ until 77 K; $\mu \uparrow$ at 4.2 K	
Theiler <i>et al.</i> [16]	$\mu \downarrow$ as $T \downarrow$ until 77 K; $\mu \uparrow$ at 4.2 K	cryogen generates a gaseous film around the contact decreasing the cooling ability of the environment
Wisander <i>et al.</i> [17]	$\mu \downarrow$ as $T \downarrow$; $K \downarrow$ as $T \downarrow$	$H \uparrow$ as $T \downarrow$; $K \downarrow$ as $T \downarrow$
Yukhno <i>et al.</i> [12]	$\mu \uparrow$ as $T \downarrow$	$T < 77\text{K}$ physical and mechanical properties degrade causing increases in wear and friction
<i>Non-cryogenic temperatures</i>		
Friedrich <i>et al.</i> [18]	$K \uparrow$ as $T \uparrow$ $\mu \downarrow$ as $T \uparrow$ $T < T_g$ $\mu \uparrow$ as $T \uparrow$ $T > T_g$	$T < T_g$: $\tau_s \downarrow$ as $T \uparrow$ $F_f \downarrow$ as $T \uparrow$ $T > T_g$: $H \downarrow$ as $T \uparrow$ $A_{real} \uparrow$ as $T \uparrow$ $F_f \uparrow$ as $T \uparrow$
Lu <i>et al.</i> [19]	$\mu \downarrow$ as $T \uparrow$ for $T > 150^\circ\text{C}$	$T > 150^\circ\text{C}$: fiber fragments increased with increasing temperature causing stick-slip behavior
Makinson <i>et al.</i> [20]	$\mu \uparrow$ as $T \uparrow$ for $T > 150^\circ\text{C}$	T on the order of T_0 PTFE transfer films provide low $\mu \uparrow$ as $T \downarrow$ when $\tau_s > \tau_{critical}$ large PTFE debris is generated
Pleskachevsky <i>et al.</i> [21]	$\mu \downarrow$ as $T \uparrow$ for $T < 130^\circ\text{C}$	$F_f \downarrow$ as $T \uparrow$ due to easier chain extension
Speerschnieder <i>et al.</i> [22]	$\mu \uparrow$ as $T \uparrow$ for $T > 130^\circ\text{C}$	$T > 200\text{ K}$: non-crystalline deformation gives low τ_s which provides low μ

A partial table providing references, authors, friction coefficient trend, and an abbreviated description of their hypothesis is provided. Nomenclature: μ friction coefficient, T temperature, K wear rate, A_{real} real area of contact, F_f friction force, H hardness, E modulus of elasticity, k thermal conductivity, ΔT_{flash} asperity temperature rise, T_g glass transition temperature, and τ_s surface shear stress.

existing data at or 10 above 300 K). This is summarized in table 1.

There were two objectives for this research effort. This first objective was to collect data on PTFE, a PTFE/PEEK composite [6], and an expanded PTFE/epoxy coating (table 2) [7] from ambient temperatures to cryogenic temperatures in an inert gaseous environment of high purity nitrogen (< 5PPM O_2 and H_2O). The second objective was to link the frictional behavior at cryogenic temperature to the existing data and models for the frictional behavior at ambient temperatures and above.

2. Experimental setup

The experimental setup used in this study is shown in figure 1. The tribometer is a commercially available rotating pin-on-disk tribometer with a modified stainless steel disk holder that places the sample surface above cylindrical retaining walls. The entire apparatus is located inside a glove box that is continuously purged with extra-dry nitrogen. The ambient temperature of the glove box and the relative humidity are continuously monitored. For these experiments the relative humidity of the glove box was maintained at or below 1%.

A jet of extra dry nitrogen is positioned normal to the sample surface near the centerline. This nitrogen flow impinges the sample and splits into a nearly axi-symmetric flow that washes over the disk and around the pin contact creating a blanket of extra dry nitrogen across

the contact. A concentric tube configuration that has a stainless-steel cooling line of liquid nitrogen located inside a larger stainless-steel line of extra-dry nitrogen is used to direct a blanketed stream of liquid nitrogen into the impinging jet of extra dry nitrogen. The liquid nitrogen is evaporated and the cold nitrogen flow washes over the sample. The temperature of the sample can be regulated by varying the liquid nitrogen flowrate while holding the other flowrates constant. Any force that is exerted on the pin sample as a result of these gas flows is reacted along the radial direction of the tribometer sample arm and does not affect the friction force.

Two thermocouples are used to continuously monitor the surface temperature of the polymer disk sample and the temperature at the back-side of the stainless steel pin sample. All temperatures reported in this manuscript will be from the thermocouple positioned on the surface of the disk. Frost did not appear on any of the test surfaces during these experiments at temperatures above 150 K, although it did appear on some of the metal connections within the glove box. Another complication was that at disk surface temperatures below 150 K liquid nitrogen was found to flow across the sample and flood the pin contact. Only results from steady and dry cryogenic tests are reported here.

The samples were roughly 50 mm in diameter and 6.35 mm thick and were wet sanded with 600 grit SiC paper, washed in soap in water, cleaned with methanol, and stored in the inert gas chamber for over 24 h prior to testing. The PTFE sample was obtained from commercially available rod stock, the PTFE/PEEK

Table 2.

The average friction coefficient and measured surface temperature for 3 different PTFE containing solid lubricants the friction coefficient was average over 50–100 cycles at steady disk surface temperature.

Material	v (m/s)	μ_{ave}	T(K)
PTFE-PEEK	0.1	0.089	303
		0.155	236
		0.169	227
	0.4	0.193	218
		0.211	177
		0.130	313
PTFE	0.4	0.174	248
		0.215	273
ePTFE-epoxy	0.1	0.216	273
		0.099	301
		0.146	253
		0.177	233
		0.214	218
	0.4	0.231	209
		0.249	198
		0.254	173
		0.099	315
		0.148	248

The applied normal load was $F_n = 10$ N, and each combination of speed and material were run on a single wear track. A 6.35 mm diameter polished 304 stainless steel sphere was used as the pin sample.

composite was machined from a sample that was prepared via a powder blending and compression molding procedure described in [6], and the ePTFE/epoxy coatings were prepared as described in [7]. The PTFE/PEEK composite was 50 wt% PEEK and the ePTFE/epoxy composite was 46 wt% epoxy. All experiments were run for over 10,000 cycles in a dry nitrogen environment to develop transfer films on the pin and disk surfaces prior to cooling with the liquid nitrogen streams. Steady

friction coefficient data was recorded at various steady surface temperatures that were randomized during each experiment. The randomization of surface temperature occurred quite naturally as small changes in the manual adjustments of the liquid nitrogen flowrate greatly enhanced or retarded cooling. Efforts were made to cover the widest possible range of cryogenic temperatures, but the manual adjustments of liquid nitrogen flowrate prevented any orderly or monotonic temperature control. After an adjustment in liquid nitrogen flowrate the disk surface was allowed to come to an equilibrium temperature and once there a reported friction coefficient was calculated by averaging 50–100 cycles.

The applied normal load was $F_n = 10$ N, and the sliding speeds were $V = 0.1$ m/s and $V = 0.4$ m/s. All experiments were run on the same wear track diameter, resulting in the same angular speed of the disk (~ 300 RPM). A 6.35 mm diameter polished 304 stainless steel sphere was used as the pin sample. The maximum central Hertzian contact pressure at room temperature was calculated to be 40 MPa for the PTFE, 150 MPa for the PTFE/PEEK composite and the ePTFE/epoxy coating. New stainless steel pins were used for each experiment.

3. Results and discussion

The normalized friction coefficient results from these experiments are plotted in figure 2 for these experiments. Data from previously published work on PTFE and other polymers are also plotted as a function of temperature. The friction coefficient is normalized by taking the ratio of the measured friction coefficient at temperature $\mu_{(T)}$ to the friction coefficient measured at

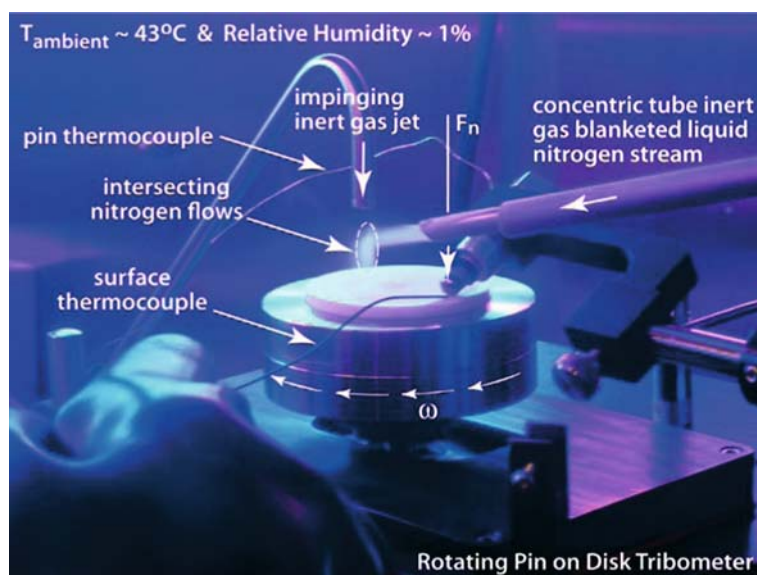


Figure 1. A photograph of the rotating pin-on-disk tribometer and nitrogen gas lines used in this study. The entire apparatus is located within a humidity controlled glove box containing high purity nitrogen. The white vertical ellipse above the disk sample is a mist of liquid nitrogen created when the liquid nitrogen stream intersects the impinging jet of dry nitrogen that is aimed normal to the disk surface.

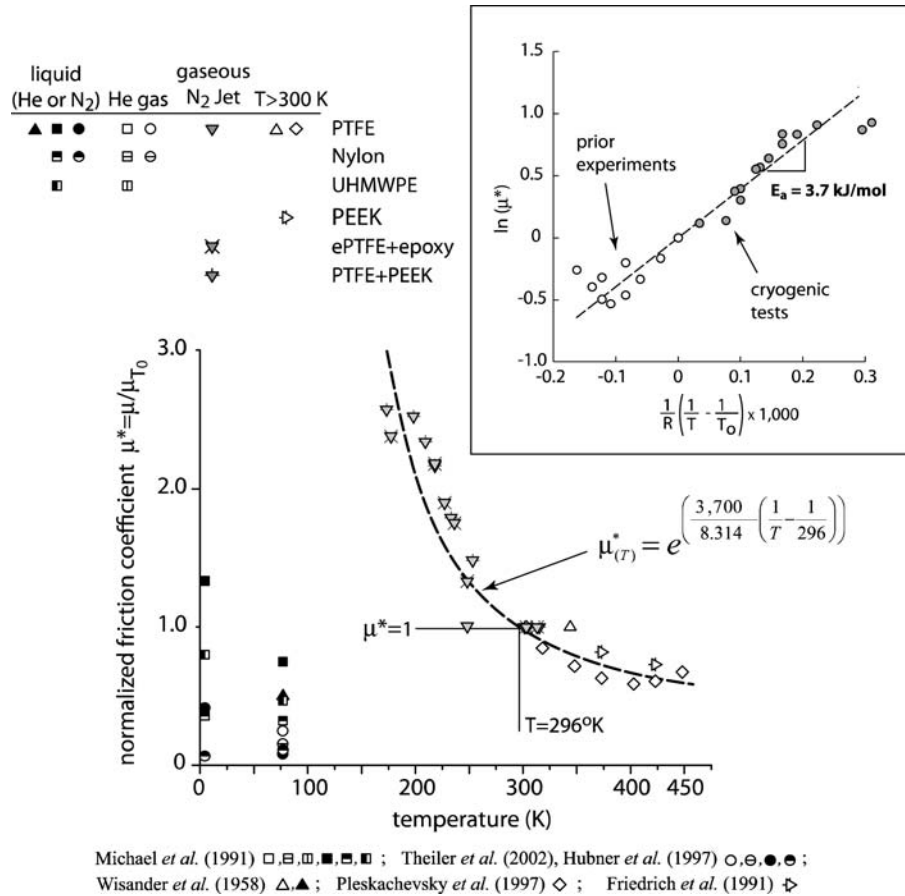


Figure 2. A plot of normalized friction coefficient versus sample temperature. All data collected from samples immersed in liquid nitrogen or helium are denoted by filled markers, data collected in this study have markers that are filled in gray. Data from: Michael *et al.* [15], Theiler *et al.* [16], Hubner *et al.* [14], Wisander *et al.* [17], Pleskachevsky *et al.* [21], and Friedrich *et al.* [18].

$T_0 = 296$ K (or the reported ambient temperature for many studies that did not have data at $T_0 = 296$ K). The friction coefficient prior to liquid nitrogen cooling was $\mu_{(T=317K)} = 0.188$ for neat PTFE, $\mu_{(T=315K)} = 0.123$ for the PTFE/PEEK composite, and $\mu_{(T=316K)} = 0.096$ for the ePTFE/epoxy coating.

There are a number of striking observations from the results presented in figure 2. First, there is essentially no published data between liquid nitrogen temperatures and ambient. Second, the normalized friction coefficient data collected using this experimental setup with PTFE, a PTFE/PEEK composite, and an ePTFE/epoxy coating all follow the trend of data collected on polymeric samples at temperatures above ambient (as the surface temperature decreases the friction coefficient increases). The large scatter in data collected at temperatures at or below liquid nitrogen temperature is clearly illustrated and the origin of this scatter is unknown; however, one can speculate that the multi-physics problem of fluid flow, heat transfer, and boiling under a Hertzian contact changes the contact conditions. For example Merriman and Kannel [8] evaluated elasto-hydrodynamic lubrication with cryogenic fluids, and measured film thickness that were between 500–1000 nm.

The effect of temperature on the friction coefficient of PTFE has been related to its viscoelastic behavior, which has strain rate and temperature dependent properties. As described in Blanchet *et al.* [9], the temperature dependence of the tribological behavior can be fit using an adjusted Arrhenius equation. This is given in Equation (1) where E_a is an activation energy with units of (J/mol), R is the universal gas constant (8.314 J/(mol K)), T is the surface temperature in K, and T_0 is a reference temperature about which the temperature effects are normalized ($T_0 = 296$ K). Equation (1) is a shift factor $a(T)$ and at $T = T_0$ this expression is unity.

$$a(T) = e^{\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (1)$$

The friction coefficient of PTFE has been shown to follow an empirical relationship given in Equation (2), where the product of the dimensionless shift factor $a(T)$, sliding velocity V in (m/s) and a constant C in (m/s)⁻¹ is raised to a sliding speed exponent (n).

$$\mu_{(T,V)} = (CV)^n e^{\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (2)$$

As previously described, the friction coefficient data plotted in figure 2 were normalized to the room temperature friction coefficient datum. Each data set from the literature had been collected at a single sliding velocity, although the sliding velocities were not constant between data sets. However, as shown in Equation (3) this normalization process yields an expression without sliding velocity dependence.

$$\mu_{(T)}^* = \frac{\mu_{(T,V)}}{\mu_{(T_0,V)}} = e^{\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (3)$$

A curve fit of Equation (3) to of all data from 173 to 450 K is shown in figure 2 along with the fit parameters. The activation energy from this fit is $E_a = 3.7$ kJ/mol, which is less than the value obtained by Tanaka *et al.* [10] ($E_a = 7.5$ kJ/mol). This low value of activation energy is consistent with a friction coefficient that is dominated by the breaking of van der Waals intermolecular bonds [11]. It is interesting to note that Equation (3) predicts nonsensical friction coefficients at very low temperatures (the function goes to infinity as $T \rightarrow 0$). The limited range of this expression is not altogether unexpected. As the temperature of the PTFE is further reduced the ability to shear PTFE films is further impaired. It is hypothesized that the friction will cease to be dominated by viscoelastic effects and another mechanism of operation, such as brittle fracture, will truncate the friction coefficient at some upper bound and provide velocity accommodation across the sliding interfaces through particle liberation rather than the shearing of running films.

4. Closure

The monotonic trend of increasing friction coefficient with decreasing surface temperature over the range of $173\text{K} < T < 317\text{K}$ followed previous observations of decreasing friction coefficient with increasing surface temperature above ambient for PTFE and PTFE composites. Fits of the activation energy and viscoelasticity dominated friction coefficient models appear to be acceptable quantitative descriptions of the friction coefficient behavior from $173\text{K} < T < 450\text{K}$. Finally, the experimental techniques reported here are believed to address many of the concerns associated

with cryotribology testing of solid lubricants, although modifications must be made for operation below $T = 77\text{K}$ (there is a study that has successfully utilized a cold finger in vacuum to perform tribological measurements on thin films [12]).

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