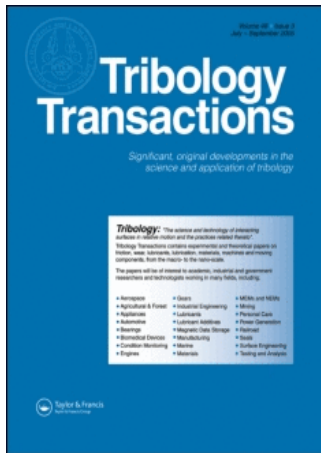


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Investigation of the Tribological Behavior of Polytetrafluoroethylene at Cryogenic Temperatures

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Investigation of the Tribological Behavior of Polytetrafluoroethylene at Cryogenic Temperatures

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Space applications are very demanding and require that lubricants provide low friction and predictable operation over a wide range of temperatures, environments, and contact conditions. Polytetrafluoroethylene (PTFE) is an attractive candidate solid lubricant due to its notably low friction coefficient, wide thermal range, and chemical inertness, but its tribology at space-relevant conditions has not been adequately investigated. This study seeks to gain insight into the cryogenic tribological behavior of PTFE using a well-studied linear reciprocating tribometer. The tribometer was contained within a nitrogen backfilled glove-box and tests were conducted at a constant background temperature of 296 K. Sliding experiments were conducted at a sliding speed of 50 mm/s and a normal pressure of 6.9 MPa, and the temperature of the lapped 304 stainless steel counterface was varied at 2% and 6% RH. Wear rate decreased monotonically with decreased interface temperature below 273 K in the absence and in the presence of ice, presumably due to improved mechanical properties at lower temperatures. The friction coefficient increased monotonically with decreased temperature in a manner consistent with thermal activation over van der Waals-type barriers; it deviated from this trend only during the phase and the glass transitions in the PTFE and after ice deposition occurred at temperatures below the estimated frost point. The data collected here are strikingly consistent with the general PTFE tribology literature and suggest that the friction coefficient of PTFE can be expected to increase by a factor of five as the temperature is reduced from 400 K to 200 K in a space environment.

KEY WORDS

Cryogenic; Friction; Thermal Activation; Seals; PTFE; Space; Solid Lubrication

INTRODUCTION

Achieving reliable and predictable lubrication is one of the primary challenges in the design of satellites and other space operated machinery. The extreme space environment includes

near perfect vacuum, a large operational temperature range (200 K to 400 K, typically), atomic oxygen, and radiation (Gardos (1); Miyoshi (2); Zhao, et al. (3)) and precludes the use of traditional fluid and grease lubricants. In addition, solid lubricant coatings that thrive in ultra-high-vacuum environments (e.g., MoS₂) are susceptible to oxidation and failure during terrestrial testing and transportation and have relatively short wear lives during operation (Miyoshi (A2)). Bulk polymers can address some of the shortcomings of thin coatings by providing additional wear material for the improved life and chemical inertness for environmental insensitivity, but these materials often lack the necessary friction performance. Polytetrafluoroethylene (PTFE) is a promising candidate polymer for space lubrication due to its unique combination of environmental insensitivity, thermal stability, and low friction, but its tribology at space-relevant thermal conditions has not been adequately studied.

The mechanisms of friction of PTFE near ambient conditions have been well studied for over 50 years. Pooley and Tabor (5) concluded that the unusually low friction coefficient of PTFE was due to the smooth molecular profile enabling low shear sliding along aligned chains within transfer films. McLaren and Tabor (6) found that elevated interface temperatures led to reduced friction coefficients and concluded that the trend of an increased friction coefficient with increased sliding speed was a result of viscoelastic effects rather than thermal softening. Since this pioneering work, a strong foundation of data has been collected that confirms this general relationship and supports the notion that, at conditions relevant to these studies (~273–373 K), the friction and wear of PTFE are dominated by the interactions of PTFE chains as they slide past one another at weak interfaces in the running films (Pooley and Tabor (5); Blanchet and Kennedy (7); Makinson and Tabor (8); Pleskachevsky and Smurugov (9); Smurugov, et al. (10); Steijn (11); Tanaka, et al. (12)).

Despite the breadth of existing fundamental work on PTFE friction at temperatures above 273 K, its friction response in cryogenic conditions remains unclear. The room-temperature models (Pooley and Tabor (5); McLaren and Tabor (6); Blanchet and Kennedy (7); Makinson and Tabor (8); Tanaka, et al. (12)) suggest higher friction coefficients at lower temperatures, but a number of cryogenic studies report comparable or reduced friction and substantially lower wear at temperatures below 77 K (Gradt, et al. (13); Hubner, et al. (14); Michael, et al. (14); Ostrovskaya, et al. (16); Theiler, et al. (17)). Studies by Bowden

(18) and McCook, et al. (19) report on the friction of PTFE at more space-relevant cryogenic temperatures ($170\text{ K} < T < 270\text{ K}$), but because the role of water could not be quantified, questions surrounding potential ice contamination remain. The goals of this study were to collect space relevant friction data for PTFE below 273 K in high confidence, to further probe the mechanisms of its tribological temperature dependence, and to help clarify the role of ice in the experiments of McCook, et al. (19).

EXPERIMENTAL METHODS

Materials

The solid lubricant tested in this study is virgin polytetrafluoroethylene (Teflon 7 C from DuPont). The sample powders were compression molded at 633 K according to the procedure described in Sawyer, et al. (20). After molding, the final $6.3 \times 6.3 \times 12.7\text{ mm}^3$ tribology specimen was machined from the $\phi 12.7\text{ mm} \times 38\text{ mm}$ molded puck such that the compression direction during molding is coincidental with the compression direction during testing. This orientation should influence the bulk properties, but the results are not believed to be orientation specific based on the hypothesis that the tribological interface is dominated by the shearing of molecular scale films drawn during sliding and oriented in the sliding direction. The counterface used in this study is a $38.25\text{ mm} (\times 3\text{ mm thick})$ grade 304 stainless steel flat with a lapped surface finish of 150 nm average roughness. Additional details of this surface can be found in Burris and Sawyer (21).

Tribometry

Tribological experiments were conducted on a linear reciprocating tribometer with 25.4 mm of unidirectional sliding (50.8 mm per cycle). The tribological conditions include a nominal sliding speed of 50 mm/s and a normal pressure of 6.9 MPa (275 N normal force, $6.3\text{ mm} \times 6.3\text{ mm}$ test area). These conditions are common in practice and result in severe wear of PTFE at room temperature

but do not lead to appreciable frictional heating of the interface (see the calculation in the Appendix).

The details of the tribometer design and the associated uncertainties in friction coefficient measurements can be found in Schmitz, et al. (22). Briefly, a pneumatic cylinder is used to normally load the sample against the reciprocating counterface via a feedback controlled electro-pneumatic valve. The PTFE sample is mounted to a 6-channel load cell that directly measures all forces and moments on the sample. The environmental control in these experiments precluded interrupted mass loss measurements, so the deflection measurements from a linear variable differential transformer (LVDT) were used to estimate wear rates in situ; this method of wear measurement is described in more detail in Burris and Sawyer (23). Ordinarily, this wear quantification technique is avoided for polymeric solid lubricants because creep and thermal expansion confound the measurement, but because the wear rates of PTFE are high compared to the creep rates, this technique provides a suitable measure of relative changes in the wear rate for the purpose of these experiments. At each test condition, a regression of the wear volume versus the sliding distance was calculated. The average wear rate is the result of this regression divided by the time-averaged normal load. The unknown contributions from the confounding factors such as the thermal and the plastic deformations precluded an uncertainty analysis of the wear rate.

The total sliding distance at each temperature condition was 50 m . The first 10 m of sliding contained the transient or run-in period of each test, and the averages and standard deviations of the temperature, the friction coefficient, and the wear rate were calculated using data from the remaining 40 m . The standard deviations in wear rate were much smaller than the wear rate in every case and therefore are not given. Figure 1 illustrates the run-in behavior (in this case, following the temperature reduction from 252 K to 225), the collection of data and the calculations of averages, regressions, and wear rates in these experiments.

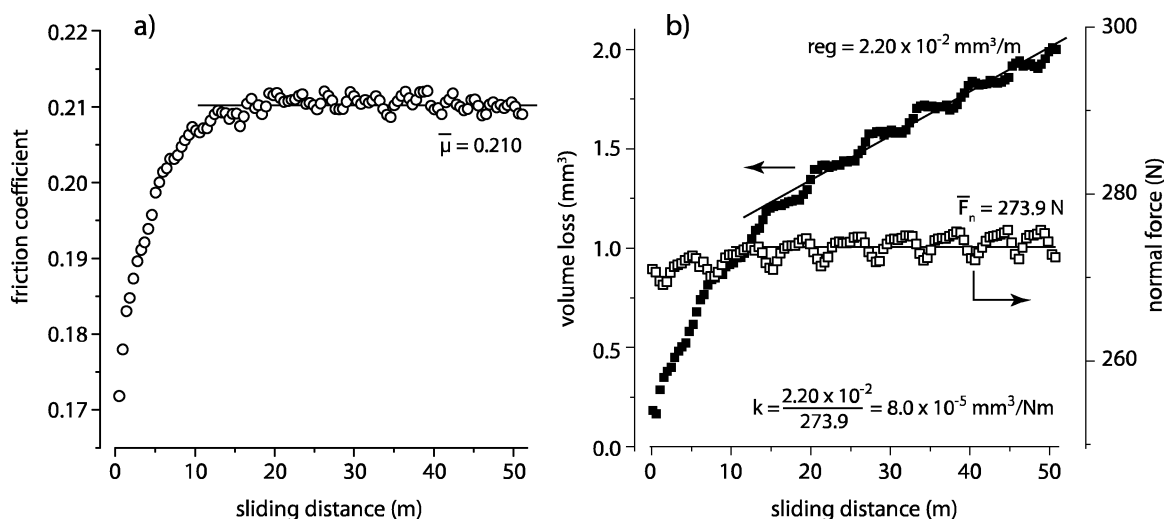


Fig. 1—Averaged data collected for PTFE on a lapped 304 stainless steel counterface following a temperature decrease from 252 K to 225 K in a 2% relative humidity environment: a) friction coefficient and b) volume loss and normal force plotted versus sliding distance. At a given temperature (in this case 225 K), data from the last 40 m of sliding are used to calculate the average temperature, the friction coefficient, the normal force, and the wear rate. The wear rate is calculated by dividing the result from the regression of volume loss versus the sliding distance by the average normal force.

Environmental Control

The maximum pressure of the water vapor that is thermodynamically stable over a surface (such as steel or ice) is a function of temperature and is referred to as the equilibrium vapor pressure. As the temperature of the surface drops, the equilibrium vapor pressure drops. Below the dew point temperature, the equilibrium vapor pressure falls below the original ambient vapor pressure, and the water vapor condenses on the surface until equilibrium is reached. If the dew point is below the freezing point of water, it is referred to as the frost point, and water vapor is deposited as ice onto the surface. Quantification of the frost point is critical to the interpretation of the results since the bulk ice deposition alters the nature of the tribological interface. The Goff-Gratch equation (Goff and Gratch (24)) is used here to estimate the relationship between temperature and the equilibrium vapor pressure of water over the counterface. Frost points are calculated using this relationship with the definition of relative humidity (the ratio of the ambient vapor pressure to the equilibrium vapor pressure). While the details of the tribological contact likely preclude an equilibrium condition, the frictional deviations observed here closely agree with frost point estimates and suggest that this method provides a reasonable approach to determining the frost points under these conditions.

The tribometer was contained within a commercial environmental glove box (manufactured by Vacuum Atmospheres Company, VAC). The glove-box was cleaned of oxygen and water using a liquid nitrogen boil-off at a high flow rate. The measurements of the environmental water content from a GE HygroGuard 2650 trace moisture analyzer were continuously recorded. The oxygen content was not measured, but it is thought to be much easier to remove than the water, and therefore much less abundant in the chamber. At 2% relative humidity (RH), the nitrogen flow was stopped and the environment was sealed for the studies. The glove box was left to reach equilibrium at a temperature of $296\text{ K} \pm 1\text{ K}$ (mean \pm standard deviation throughout testing) and a relative humidity of $\text{RH} = 1.85\% \pm 0.13\%$. In a second series of tests, the humidity and frost point temperature were increased to investigate the effects of water and ice. Following the low-humidity experiments, humidified nitrogen was fed into the chamber until the relative humidity reached 6%. After the chamber reached equilibrium, the relative humidity throughout the testing was $\text{RH} = 5.5\% \pm 1.1\%$. The relatively large variation in humidity in this case was the result of significant ice deposition onto chilled surfaces (such as the liquid nitrogen carrier lines) at temperatures below the frost point. The frost points for the 2% and 6% relative humidity experiments were 243 K and 255 K, respectively.

Temperature Control

Thermal control was achieved using a copper thermal block to which the 3.4-mm-thick counterface was mounted. The thermal block was mounted to the reciprocating stage; these components were separated by a PID controlled thin film resistive heater and a layer of thermal insulation that kept the stage near ambient temperatures. A controlled flow of liquid nitrogen through the copper block provided cooling. Before each test, the target temperature was set, the sample was loaded, and the interface was left

to reach thermal equilibrium. The measurements from a thermocouple mounted to the surface of the copper block near the counterface were continuously recorded and provided feedback for the controller. A handheld thermocouple was used to determine thermal equilibrium of the contact interface as well as the temperature differential from the feedback thermocouple to the wear track. The difference was negligible at 300 K but was as high as 40 K at a block temperature of 148 K. The collected feedback data were adjusted by this differential during post-processing and only these estimated interface temperatures were used for analysis. The temperature rise from frictional heating was neglected here. The calculation given in the Appendix estimates a nominal temperature rise of less than 3 K; previous unpublished measurements with imbedded thermocouples confirmed the reasonableness of this approximate calculation. As Kennedy, et al. (25) demonstrated, flash temperatures at asperity contacts may be substantially higher.

No part of the insulated load cell ever exceeded 2 K above or below 296 K, and the load cell was zeroed before each nominally isothermal experiment. It should also be noted that while the interface temperature was very stable throughout each experiment, the thermal stability of the bulk of the sample was not measured, and the poor thermal diffusivity of the PTFE likely led to a varying temperature distribution within the sample that may have further confounded the wear measurements. This effect would lead to artificially high measured wear rates during cooling and artificially low measured wear rates during heating.

EXPERIMENTAL DESIGN

The 2% RH experiments had a normal load of $275\text{ N} \pm 2\text{ N}$. The temperature profile included an increase from 298 K to 433 K, a decrease from 433 K to 148 K, and an increase back to 298 K. This cyclic profile was employed to capture hysteretic effects that come from the thermal and mechanical history dependences of PTFE. The 6% RH experiments had a normal load of $273\text{ N} \pm 2\text{ N}$. A new counterface was used for these experiments but the same PTFE sample was used in all cases to reduce material variability. The sample lacked sufficient volume to complete the temperature profile of the 2% RH condition and, as a result, only temperatures below 300 K were studied.

This study has a unique combination of experimental attributes: 1) the experimental setup allowed excellent variability and stability of temperature in the range from 148 K to 433 K. Data were collected at a sufficient number of constant temperature conditions to enable the interrogation of trends in this range. Most cryogenic tribology studies examine a room temperature control and one or two cryogenic temperature conditions (typically 4.2 and 77 K), and trends between these temperature extremes are not analyzed. 2) Tests were conducted in dry sliding with constant environmental conditions to enable investigation of thermal effects on friction in the absence of other environmental effects. Often, liquid and gaseous cryogens are used for cryogenic testing and lab air for ambient testing. 3) The environmental control was implemented without affecting the experimental uncertainty of friction coefficient. In most cryogenic tribology studies, the cryostats and vacuum chambers place serious design limitations on the tribometers, which often end up having large

uncertainties and poor sensitivities. In this study, the experimental uncertainty of a friction coefficient measurement is on the order of 1% of the nominal value over the entire range of temperatures tested (it was 2% of the nominal value during ice melting, and much lower elsewhere). It should be noted that only the relative changes in wear rates are significant here, as creep and thermal transients within the bulk precluded an uncertainty analysis of the absolute value of wear rate, and during cooling, the reported wear rate is always greater than the actual wear rate. 4) The uniform and constant pressure distribution generated by the elastic square on rigid flat contact geometry simplifies the interpretation of the friction coefficient from the more typical pin-on-disk type experiments that have non-constant, semi-elliptic pressure distributions and evolving contact geometries. 5) Custom acquisition software enables the collection of the traditional “averaged” data, which provide trends of global friction and wear behavior during the test, as well as “positionally resolved” data collected at 1 kHz along the wear track which enable the post test interrogation of sliding characteristics.

RESULTS

Friction Coefficient

The friction data collected in this study were previously published in Burris, et al. (26). Summaries of the experimental results for the 2% and 6% RH data sets are given in Tables 1 and 2, respectively. The friction coefficient is plotted versus interface temperature in Fig. 2 and four distinct regions of behavior are labeled: region (A) denotes a friction response from the self-mated PTFE interfaces alone (due to preferential PTFE transfer to the counterface), (B) denotes contributions from both self-mated PTFE and ice interfaces, (C) denotes friction dominated by ice-related interfaces alone, and (D) denotes the region dominated by ice melting.

During the first heating period from 300 K to 391 K in (A), the friction coefficient at 2% RH monotonically decreased from $\mu = 0.145$ to $\mu = 0.075$ in accordance with the known viscoelastic-like response of PTFE. The deviation from this trend at temperatures above 391 K is consistent with prior findings (Pleskachevsky and Smurugov (9); Tanaka, et al. (12)) and is thought to be associated with softening at a glass or phase transition that has been found near this temperature (Breiby, et al. (27); Brown, et al. (28); Clark (29); Yamamoto and Hara (30)). According to Clark (29), this transition is highly sensitive to the thermal and mechanical history of the sample, which makes the assignment of any specific transition difficult without characterization.

With the exception to the initial hysteresis that occurred (presumably due to lower quality running films that may have developed during wear at temperatures above the friction transition at 391 K), the cooling cycle followed the same trend (A) of increased friction at decreased temperature until a disruption occurred between the PTFE phase transformation temperatures of 292 K (phase IV to phase II) and 303 K (phase I to phase IV); Steijn (11) found the same global friction behavior with a similar disruption from 292 K to 303 K. For additional details of these phase transformations, see Clark (29); Bunn, et al. (31); Bunn and Howells (32); Clark (33); Farmer and Eby (34); Kimmig, et al. (35); Weeks, et al. (36); and Weeks, et al. (37) for molecular and struc-

TABLE 1—RESULTS OF 2% RELATIVE HUMIDITY VARIABLE TEMPERATURE EXPERIMENTS. LISTED ARE THE AVERAGE AND STANDARD DEVIATION OF THE FRICTION COEFFICIENT, WEAR RATE AND INTERFACE TEMPERATURE FOR 25 CONSTANT TEMPERATURE EXPERIMENTS CONDUCTED AT VARYING INTERFACE TEMPERATURE. THE NORMAL LOAD AND HUMIDITY WAS HELD CONSTANT FOR THE SET OF EXPERIMENTS WITH AVERAGE VALUES AND STANDARD DEVIATIONS OF $275 \text{ N} \pm 2 \text{ N}$ AND $1.85\% \pm 0.13\%$, RESPECTIVELY. THE BACKGROUND TEMPERATURE INSIDE THE GLOVE-BOX WAS HELD CONSTANT AT $296 \text{ K} \pm 1 \text{ K}$. THE FRICTION DATA CAN ALSO BE FOUND IN BURRIS, ET AL. (26).

Test	μ	$\sigma (\mu)$	$k (\times 10^{-5} \text{ mm}^3/\text{Nm})$	T (K)	$\sigma (T)$
1	0.1450	0.0010	110.0	299.8	0.15
2	0.1350	0.0001	83.0	309.5	0.08
3	0.1020	0.0007	41.0	342.0	0.08
4	0.0745	0.0016	33.0	390.5	0.12
5	0.0768	0.0010	26.0	399.1	0.20
6	0.0760	0.0009	30.0	408.0	0.14
7	0.0749	0.0008	34.0	416.3	0.13
8	0.0795	0.0006	27.0	406.8	0.26
9	0.0834	0.0008	20.0	395.0	0.44
10	0.0853	0.0008	15.0	391.0	0.20
11	0.1020	0.0008	11.0	341.1	0.67
12	0.1410	0.0016	19.0	307.8	0.12
13	0.1490	0.0016	14.0	299.3	0.66
14	0.1520	0.0016	31.0	289.0	0.12
15	0.1550	0.0009	38.0	279.9	0.10
16	0.2070	0.0011	14.0	252.0	0.48
17	0.2100	0.0009	8.0	224.7	0.09
18	0.1800	0.0010	3.3	204.2	0.16
19	0.1520	0.0015	2.6	188.1	0.46
20	0.1600	0.0007	2.1	197.7	0.24
21	0.1430	0.0041	3.2	219.5	0.12
22	0.2090	0.0013	20.0	248.9	0.09
23	0.1560	0.0012	43.0	281.7	0.72
24	0.1630	0.0012	55.0	291.3	0.55
25	0.1620	0.0009	52.0	298.8	0.23

tural changes, Brown, et al. (38) for mechanical behaviors, and Flom and Porile (39) and Steijn (11) for tribological behaviors.

At temperatures just below the phase transitions, the friction coefficient continued to follow trend (A), increasing with decreasing temperature for both 2% and 6% RH conditions. Adsorbed water plays a significant role in tribology and, in general, the amount of adsorbed water on a surface varies with the temperature and the humidity. Conceivably, the observed trend of increased friction with decreased temperature could be an effect of increased water contamination at lower temperatures rather than the temperature itself. However, despite the counterface having a greater amount of adsorbed water at 6% RH than at 2% RH at any given temperature, the friction characteristics of PTFE at 2% and 6% RH were quite similar above the respective frost points. This similarity suggests that the frictional behavior of PTFE is significantly more sensitive to temperature than to adsorbed water and ice. On the contrary, as temperature decreases to values below the frost point, bulk ice deposition led to a transition of the primary sliding interface. In addition, very different transition characteristics were observed for 2% and 6% RH conditions. At 2% RH, the friction coefficient transitioned to (B), deviating only slightly from

TABLE 2—RESULTS OF 6% RELATIVE HUMIDITY VARIABLE TEMPERATURE EXPERIMENTS. LISTED ARE THE AVERAGE AND STANDARD DEVIATION OF THE FRICTION COEFFICIENT, WEAR RATE AND INTERFACE TEMPERATURE FOR 15 CONSTANT TEMPERATURE EXPERIMENTS CONDUCTED AT VARYING INTERFACE TEMPERATURE. THE NORMAL LOAD AND HUMIDITY WAS HELD CONSTANT FOR THE SET OF EXPERIMENTS WITH AVERAGE VALUES AND STANDARD DEVIATIONS OF $273 \text{ N} \pm 2 \text{ N}$ AND $5.5\% \pm 1.1\%$, RESPECTIVELY. THE HIGHER VARIATION IN HUMIDITY IS DUE TO WATER FREEZING OUT OF THE SYSTEM TO A GREATER EXTENT. THE BACKGROUND TEMPERATURE INSIDE THE GLOVE-BOX WAS HELD CONSTANT AT $296 \text{ K} \pm 1 \text{ K}$. THE FRICTION DATA CAN ALSO BE FOUND IN BURRIS, ET AL. (26).

Test	μ	$\sigma(\mu)$	$k (\times 10^{-5} \text{ mm}^3/\text{Nm})$	T (K)	$\sigma(T)$
1	0.1670	0.0008	64.0	301.1	0.46
2	0.1640	0.0009	51.0	287.8	0.34
3	0.1560	0.0008	37.0	281.4	0.08
4	0.1740	0.0030	30.0	270.6	0.93
5	0.2030	0.0038	27.0	261.5	0.11
6	0.0940	0.0017	2.8	249.7	0.20
7	0.1180	0.0007	1.6	239.0	0.08
8	0.1430	0.0060	2.2	217.7	0.12
9	0.1240	0.0027	0.9	234.9	0.09
10	0.1130	0.0010	1.3	247.1	0.10
11	0.1010	0.0028	2.9	259.9	0.08
12	0.0391	0.0018	2.9	268.9	0.09
13	0.1480	0.0028	40.0	280.5	0.09
14	0.1570	0.0014	54.0	289.9	0.10
15	0.1570	0.0033	64.0	297.1	1.60

(A), while a dramatic transition to (C) occurred immediately at 6% RH. The difference in the transition behavior is attributed to differing deposition kinetics and the competitive rates of ice deposition and the removal by the passing pin (Blanchet and Sawyer (40); Dickrell, et al. (41)).

Additional evidence of the influence of ice during the transition from (A) to (C) at 2% RH is provided by the positionally resolved friction data collected at 1 kHz. The friction coefficient during deceleration (5 m/s^2 with no static contributions) near the reversal is plotted versus the sliding speed in Fig. 3 for several temperatures. The viscoelastic frictional characteristics (increased friction at increase speed) at 390 K, 340 K, and 290 K reflect self-mated PTFE and appear very similar to those published previously by McLaren and Tabor (6). At 220 K, the slope appears similar to the higher temperature tests, but the relative increase in the friction coefficient with speed is lower and suggests that both PTFE and ice interfaces are contributing to the total friction force. Insight into this result is provided by the transient behavior in Fig. 1. The initial friction coefficient for this test is lower than the steady-state value, and an examination of the positional data for the first few passes (not shown) reveals that velocity dependence of friction during the low friction transient is even lower. This suggests that the more coherent initial ice film was progressively removed by the passing pin until a steady fractional area could be maintained. The development of the ice film at lower temperatures and the subsequent transition to (C) at 190 K led to a complete and robust ice film, and a lower, velocity insensitive friction coefficient at 220 K during the heating cycle.

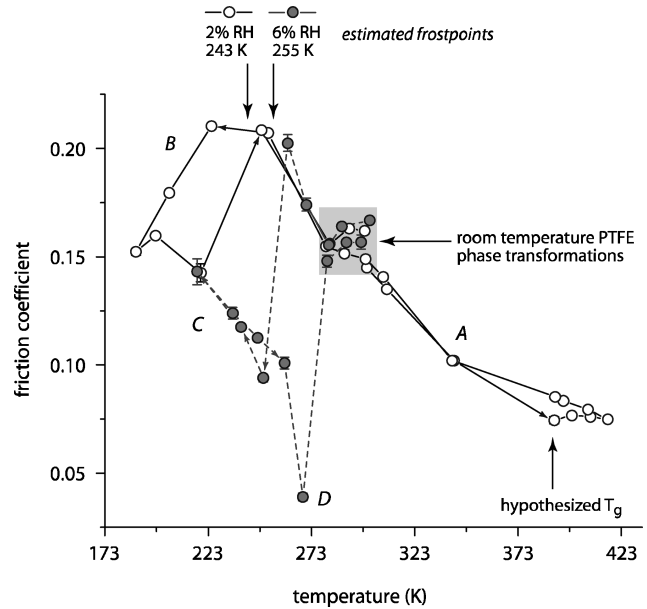


Fig. 2—Friction coefficient plotted versus the interface temperature for unfilled PTFE in tests varying interface temperature. Region (A) extends from 423 K down to the frost point temperature and represents the region where only PTFE-PTFE interfaces are involved in sliding. Contributions from both ice-PTFE and PTFE-PTFE interfaces are present in region (B), which extends from 250 K down to 190 K at 2% RH. The ice contribution increases with decreasing temperature in this region. Only ice-PTFE interfaces are involved in sliding in region (C), which extends from 190 K to 260 K. Frictional heating led to melting of ice and a low friction coefficient in region (D). Transitions in the sliding characteristics of self-mated PTFE interfaces were observed during the room-temperature phase transformations and at a hypothesized glass transition. The frost points of the 2% and 6% relative humidity experiments were calculated to be 243 K and 255 K, respectively. Error bars represent the standard deviation throughout the test. Experimental uncertainties were less than 2% the nominal value in all cases. These data can also be found in Burris, et al. (26).

Upon reheating past the frostpoints, behavioral differences between the 2% and 6% RH conditions were again observed (Fig. 2). At 2% RH, the friction coefficient immediately transitioned to trend (A) as a result of the low environmental water concentration and the high driving force for sublimation. At 6% RH, the lower driving force and thicker (due to the longer duration of development) ice film delayed complete sublimation to a temperature well above the frost point. In fact, another transition to very low friction at (D) was observed at 269 K as the surface of the remaining ice film melted from frictional heating. This behavior is in stark contrast to the much higher values of friction coefficient found for water lubricated conditions in the absence of ice. A follow-up experiment at 275 K in 50% RH ($\sim 282 \text{ K}$ dew point) revealed that the friction coefficient of PTFE against wet steel was comparable to that against dry steel (data not shown).

In the study by Bowden (18), the friction coefficient of ice was substantially lower against PTFE than against a number of other materials, which suggests that PTFE is involved at the interface of ice-PTFE tribo-systems. The present study has shown a transition from self-mated PTFE to ice containing interfaces after ice deposition occurs. The sliding interface of ice-PTFE tribo-systems must

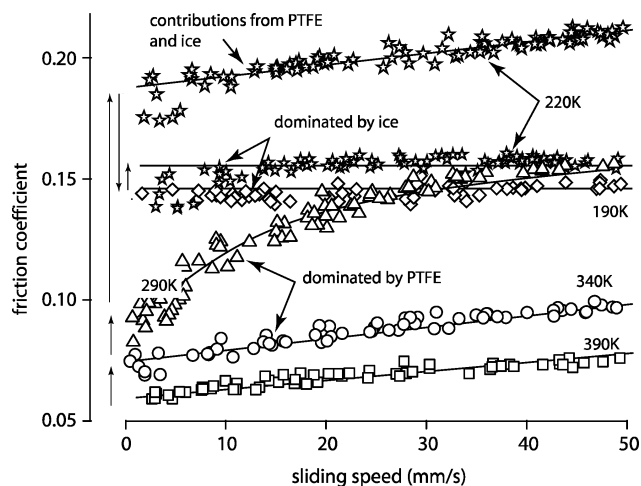


Fig. 3—Friction coefficient at 2% RH plotted versus sliding speed during deceleration near the first reversal. Deceleration (5 m/s^2) was used to eliminate the static contributions during acceleration. The arrows indicate the order in which the tests were conducted. The velocity dependence of the friction of PTFE is clearly present at temperatures above the frost point. As the temperature was reduced below the frost point to 220 K, the relative change in friction is lower as ice begins contributing to the total friction force. After the development of a robust ice film and a transition to region (C) at 190 K, the friction coefficients are characteristically low and insensitive to speed.

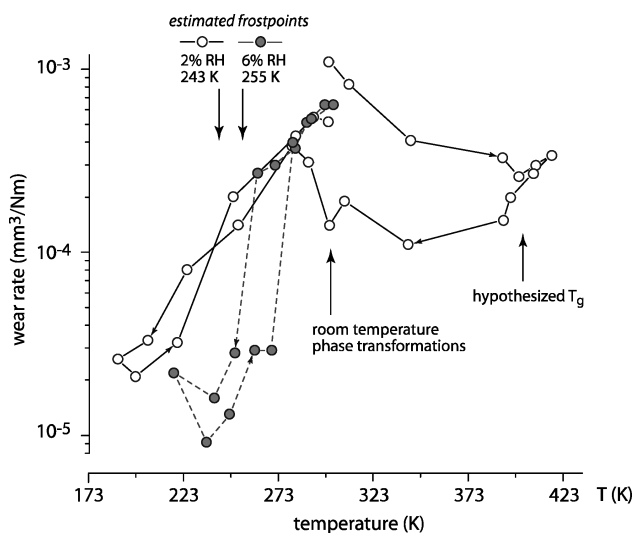


Fig. 4—Wear rate plotted versus interface temperature for unfilled PTFE in tests varying interface temperature. The frost points of the 2% and 6% relative humidity experiments were calculated to be 243 K and 255 K, respectively. The uncertainty in the wear rate could not be quantified and the absolute value of the wear rate at any given point is always lower than the reported value during cooling. Although it is impossible to ascribe uncertainty intervals to the data, the experimental setup is sensitive to relative changes in the wear rate, and the trends with temperature are thought to represent the temperature dependent behavior.

therefore be the ice-PTFE interface; although a seemingly intuitive result, this is not usually the case. Typically, PTFE preferentially transfers to the counterface and self-mated PTFE interfaces dominate sliding. The unusually low friction at the ice-PTFE interface is likely due to the poor intermolecular compatibility that makes PTFE unusually hydrophobic (Bowden (18)).

These results illustrate several key points: 1) self-mated PTFE interfaces continued to dominate friction below 273 K and above the frost point; 2) ice was deposited in the wear track at temperatures below the frost point, and although the passing pin prevented full ice coverage under certain conditions, fractional ice coverage led to fractional contributions of self-mated PTFE and ice-PTFE interfaces; 3) the ice provided a weaker slip interface when formed; and 4) the frictional transitions observed here at cryogenic temperatures were caused by ice deposition and were not indicative of a transition in the PTFE.

Wear

Wear rates were calculated here via continuous linear pin displacement measurements rather than more typical interrupted mass loss measurements (see methods). These wear rate data are plotted versus interface temperature in Fig. 4. The first 2% relative humidity experiment conducted at 299 K had a resulting wear rate of $1 \times 10^{-3} \text{ mm}^3/\text{Nm}$. As the temperature increased to 399 K, the wear rate dropped monotonically. On further heating, the wear rate increased, presumably due to the suspected thermal softening near 400 K (Breiby, et al. (27); Brown, et al. (28); Clark (29); Yamamoto and Hara (30)). As the temperature decreased, a hysteric effect was observed, which may have been due to the facilitated orientation of the near surface region during sliding at high

temperature conditions. Creep cannot account for the hysteresis as the last heating cycle followed the same general trend, and effects from thermal expansion would have produced the opposite trend (higher wear during cooling). A discontinuity in the trend of increasing wear rate with decreasing temperature was observed at 299 K after a transition from phase I to phase IV; neither the source nor significance of this discontinuity are known. At temperatures below 280 K (above and below the frost point), a transition occurred and the wear rate decreased rapidly with the decreased temperature. An abrupt decrease in the wear rate was observed below the frost point temperature at 6% RH, and the wear rate remained lower than at 2% RH, likely due to the lower friction coefficients. This trend is in agreement with previous cryogenic tribology studies of PTFE, which consistently report substantially reduced wear at temperatures below 77 K (compared to room temperature; Hubner, et al. (14); Ostrovskaya, et al. (16); Theiler (17)). Upon heating, a hysteric effect is again observed in both cases. This is likely due to the low wear transfer film morphology that may have developed during sliding at cryogenic temperatures, but wear and thermal expansion effects cannot be separated in this case. At 6% RH, a discontinuity in the wear trend accompanied the transition to ice melting.

There are far fewer fundamental studies of wear than there are of friction for PTFE. Smurugov, et al. (10) studied the wear of PTFE as a function of temperature from 273 to 373 K and found a trend similar to that found here with increased wear at decreased temperature. Following studies of the mechanisms of wear in PTFE, Blanchet and Kennedy (7) concluded that the transition from mild to severe wear in PTFE, in general, is due to the friction coefficient exceeding a critical value needed to

propagate cracks within the subsurface. Although no abrupt transition was observed here, the results above 280 K are in general agreement with this model as wear rate generally decreased with decreased friction coefficient and improved transfer film quality. Below 280 K, the wear rate decreased with decreasing temperature despite increased values of friction coefficient. A number of independent studies have shown that the various mechanical properties of PTFE, including hardness (Bowden (18)), modulus of elasticity (Bowden, et al. (28)), and yield strength (Bowden, et al. (28); Joyce (42)), increase rapidly with decreasing temperature. The improvements in mechanical properties at cryogenic temperatures may have been sufficient to arrest crack growth in the subsurface. While Smurugov, et al. (10) did not publish the data, the authors indicated that the wear rate was observed to decrease below 273 K. To the author's knowledge, this is the first quantification of wear for PTFE from 200 K to 273 K and the observed behavior is generally consistent with the findings for wear of PTFE at temperatures below 77 K (Hubner, et al. (14); Theiler, et al. (17)).

DISCUSSION

This study has quantitatively demonstrated that the friction behavior of PTFE at moderate cryogenic temperatures is consistent with the more fundamental models of friction coefficient and requires no cryogenic-specific adjustment. In addition, the effect of ice has been quantified and the results are applicable to previous studies. The experimental setup in McCook, et al. (19) was specifically designed to discourage ice deposition, but precluded any quantification of the relevant environmental conditions needed to evaluate the effect of ice contamination. The current investigation provides quantitative evidence that the experiments of McCook, et al. were ice-free down to 200 K.

A normalization of the friction coefficient to its room temperature value [$\mu^* = \mu(T)/\mu(T_0)$] eliminates the effects of other experimental variables (such as speed, load, etc.) and facilitates multi-data-set comparison. Normalized friction coefficients from the variable-temperature PTFE-tribology literature are plotted versus temperature in Fig. 5. Results that were potentially confounded by environmental effects such as ice, liquid cryogenics, etc., are denoted by semi-transparent labels. At temperatures above 200 K, these results form a very convincing trend of increased friction coefficient with decreased temperature and suggest strongly that the interfacial sliding of self-mated PTFE interfaces continues to dominate friction over a range no smaller than from 200 K to 400 K when other overpowering environmental effects are absent. Above 400 K, a transition to increased friction is believed to be the result of a hypothesized glass transition of PTFE (Pleskachevsky and Smurugov (9); Tanaka, et al. (12)).

An empirical formula (1) has been used (McLaren and Tabor (6); Blanchet and Kennedy (7); Tanaka, et al. (12); McCook, et al. (19)) to describe the temperature and velocity dependent friction coefficients of semi-crystalline polymers,

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

where C is a material constant, V is the velocity, n is a sliding speed exponent, E_a is the activation energy, T_0 is the reference temperature in Kelvin, and R is the universal gas constant. The quantity μ^* can therefore be described by a simple, velocity-independent

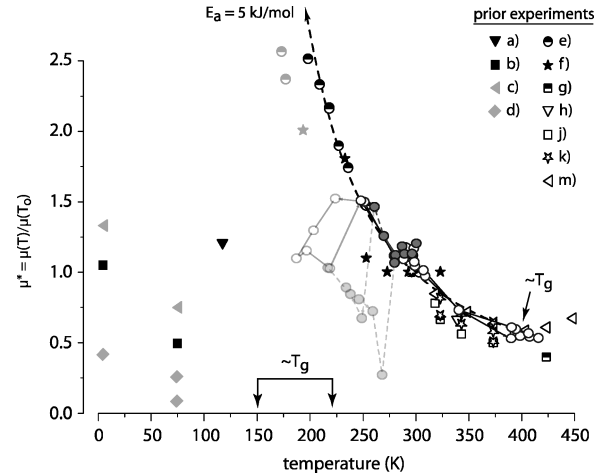


Fig. 5—Normalized friction coefficient plotted versus interface temperature for variable temperature studies of PTFE in the literature: a) Ostrovskaia, et al. (16), b) Gradt, et al. (13), c) Michael, et al. (15), d) Theiler, et al. (17), e) McCook, et al. (19), f) Bowden (18), g) Pooley and Tabor (5), h) Blanchet and Kennedy (7), j) McLaren and Tabor (6), k) Tanaka and Uchiyama (12), m) Pleskachevsky and Smurugov (9). Results that were potentially contaminated by environmental effects are partially transparent. This data set suggests that the friction of PTFE is a thermally activated process with an activation energy near 5 kJ/mol over the temperature range from 200 to 400 K. The data set above 150 K can also be found in Burris, et al. (26).

Eq. [2] that depends only on the temperature and the effective activation energy of the dominant intermolecular processes involved in sliding.

$$\mu^*(T) = \frac{\mu(T, V)}{\mu(T_0, V)} = e^{\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad [2]$$

The 5 kJ/mol activation energy that was used to fit this data set is indicative of van der Waals intermolecular forces and suggests that such interactions between PTFE chains dominate the friction during interfacial sliding of PTFE. Over the range from 8 K to 120 K, there are insufficient data to interpret a trend, but the data do suggest that a fundamentally different sliding mechanism begins to dominate the friction of PTFE at these temperatures. A low-temperature transition may occur as thermal barriers to interfacial sliding become sufficiently high to activate a more energetically favorable sliding mechanism, such as brittle fracture of surface asperities. It is unclear if the transition observed between 170 K and 200 K by McCook, et al. (19) was caused by a transition of the sliding mechanism or by ice contamination, but it is interesting that Durrell, et al. (43) cite a glass transition temperature at 223 K, both Lau, et al. (44) and Dlubek, et al. (45) cite a mean glass transition temperature of 195 K, and Brown, et al. (28) cite a similar transition at 178 K. A glass transition in PTFE may induce a transition in the primary sliding mechanism, but future investigations using high-vacuum cryogenic tribometry will likely be required to explore this temperature range.

CONCLUSIONS

1. In the absence of ice, the friction coefficient of PTFE increased monotonically with decreased temperature well below 273 K.

Wear rates decreased with increasing temperature between 280 K and 400 K and decreased with decreasing temperature below 280 K. Wear rate was also markedly dependent on the tribological history of the sample. The temperature dependence of wear observed here appears to be due to a competitive relationship between increased stresses at internal defects and increased mechanical properties at reduced temperatures.

2. The friction results collected here are in excellent agreement with data collected during a variety of previous investigations of PTFE. An activation energy of 5 kJ/mol fit the data set well and indicates that thermally activated van der Waals forces provide the primary resistance to interfacial sliding of PTFE over a range no smaller than 200 K–400 K. At temperatures above 400 K, a glass transition is thought to provide a transition in this mechanism. Future cryogenic studies in high-vacuum will likely be required to elucidate the behavior of PTFE below 200 K.
3. The deposition of ice at the interface provided a lower shear sliding pathway between ice and PTFE. The friction coefficient of this interface also tended to increase with decreased temperature.

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REFERENCES

- (1) Gardos, M.N. (1982), "Self-Lubricating Composites for Extreme Environment Applications," *Tribology International*, **15**, 5, pp 273-283.
- (2) Miyoshi, K. (1999), "Considerations in Vacuum Tribology (Adhesion, Friction, Wear, and Solid Lubrication in Vacuum)," *Tribology International*, **32**, 11, pp 605-616.
- (3) Zhao, X., et al. (2005), "An Experimental Study of Low Earth Orbit Atomic Oxygen and Ultraviolet Radiation Effects on a Spacecraft Material—Polytetrafluoroethylene," *Polymer Degradation and Stability*, **88**, 2, pp 275-285.
- (4) Miyoshi, K. (1999), "Aerospace Mechanisms and Tribology Technology—Case Study," *Tribology International*, **32**, 11, pp 673-685.
- (5) Pooley, C.M. and Tabor, D. (1972), "Friction and Molecular Structure—Behavior of Some Thermoplastics," *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences*, **329**, 1578, pp 251-&.
- (6) McLaren, K. and Tabor, D. (1963), "Visco-Elastic Properties and Friction of Solids—Friction of Polymers—Influence of Speed and Temperature," *Nature*, **197**, 487, pp 856-&.
- (7) Blanchet, T. and Kennedy, F. (1992), "Sliding Wear Mechanism of Polytetrafluoroethylene (PTFE) and PTFE Composites," *Wear*, **153**, 1, pp 229-243.
- (8) Makinson, K. and Tabor, D. (1964), "Friction and Transfer of Polytetrafluoroethylene," *Nature*, **201**, 491, pp 464-&.
- (9) Pleskachevsky, Y.M. and Smurugov, V.A. (1997), "Thermal Fluctuations of PTFE Friction and Transfer," *Wear*, **209**, 1-2, pp 123-127.
- (10) Smurugov, V., et al. (1992), "On PTFE Transfer and Thermoactivation Mechanism of Wear," *Wear*, **158**, 1-2, pp 61-69.
- (11) Steijn, R. (1968), "Sliding Experiments with Polytetrafluoroethylene," *ASLE Transactions*, **11**, 3, pp 235-&.
- (12) Tanaka, K., Uchiyama, Y. and Toyooka, S. (1973), "Mechanism of Wear of Polytetrafluoroethylene," *Wear*, **23**, 2, pp 153-172.
- (13) Gradt, T., et al. (1998), "Friction and Wear at Low Temperatures," *International Journal of Hydrogen Energy*, **23**, 5, pp 397-403.
- (14) Hubner, W., et al. (1998), "Tribological Behaviour of Materials at Cryogenic Temperatures," *Wear*, **216**, 2, pp 150-159.
- (15) Michael, P., Rabinowicz, E. and Iwasa, Y. (1991), "Friction and Wear of Polymeric Materials at 293-K, 77-K and 4.2-K," *Cryogenics*, **31**, 8, pp 695-704.
- (16) Ostrovskaya, Y., et al. (2001), "Low Temperature Tribology at the B. Verkin Institute for Low Temperature Physics and Engineering (Historical Review)," *Tribology International*, **34**, 4, pp 265-276.
- (17) Theiler, G., et al. (2002), "Friction and Wear of PTFE Composites at Cryogenic Temperatures," *Tribology International*, **35**, 7, pp 449-458.
- (18) Bowden, F.P. (1953), "Friction on Snow and Ice," *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences*, **217**, 1131, pp 462-478.
- (19) McCook, N.L., et al. (2005), "Cryogenic Friction Behavior of PTFE Based Solid Lubricant Composites," *Tribology Letters*, **20**, 2, pp 109-113.
- (20) Sawyer, W.G., et al. (2003), "A Study on the Friction and Wear Behavior of PTFE Filled with Alumina Nanoparticles," *Wear*, **254**, 5-6, pp 573-580.
- (21) Burris, D.L. and Sawyer, W.G. (2005), "Tribological Sensitivity of PTFE/Alumina Nanocomposites to a Range of Traditional Surface Finishes," *Tribology Transactions*, **48**, 2, pp 147-153.
- (22) Schmitz, T., et al. (2005), "The Difficulty of Measuring Low Friction: Uncertainty Analysis for Friction Coefficient Measurements," *Tribology Transactions*, **127**, 3, pp 673-678.
- (23) Burris, D. and Sawyer, W. (2007), "Tribological Behavior of PEEK Components with Compositionally Graded PEEK/PTFE Surfaces," *Wear*, **262**, 1-2, pp 220-224.
- (24) Goff, J.A. and Gratch, S. (1946), "Low-Pressure Properties of Water from -160 to 212°F," *Transactions of the American Society of Heating and Ventilation Engineers*, **52**, 95-122.
- (25) Kennedy, F.E., Frusescu, D. and Li, J.Y. (1997), "Thin Film Thermocouple Arrays for Sliding Surface Temperature Measurement," *Wear*, **207**, 1-2, pp 46-54.
- (26) Burris, D.L., Perry, S.S. and Sawyer, W.G. (2007), "Macroscopic Evidence of Thermally Activated Friction with Polytetrafluoroethylene" *Tribology Letters*, **27**, pp 323-328.
- (27) Breiby, D., et al. (2005), "Structural Surprises in Friction-Deposited Films of Poly(tetrafluoroethylene)," *Macromolecules*, **38**, 6, pp 2383-2390.
- (28) Brown, E., et al. (2006), "The Effect of Crystallinity on the Fracture of Polytetrafluoroethylene (PTFE)," *Material Science and Engineering C-Biomimetic and Supramolecular Systems*, **26**, 8, pp 1338-1343.
- (29) Clark, E. (2006), "The Crystal Structure of Polytetrafluoroethylene, Forms I and IV," *Journal of Macromolecular Science Part B-Physics*, **45**, 2, pp 201-213.
- (30) Yamamoto, T. and Hara, T. (1982), "X-Ray-Diffraction Study of Crystal Transformation and Molecular Disorder in Poly(tetrafluoroethylene)," *Polymer*, **23**, 4, pp 521-528.
- (31) Bunn, C., Cobbold, A. and Palmer, R. (1958), "The Fine Structure of Polytetrafluoroethylene," *Journal of Polymer Science*, **28**, 117, pp 365-376.
- (32) Bunn, C. and Howells, E. (1954), "Structures of Molecules and Crystals of Fluorocarbons," *Nature*, **174**, 4429, pp 549-551.
- (33) Clark, E. (1999), "The Molecular Conformations of Polytetrafluoroethylene: Forms II and IV," *Polymer*, **40**, 16, pp 4659-4665.
- (34) Farmer, B. and Eby, R. (1981), "Energy Calculations of the Crystal-Structure of the Low-Temperature Phase (II) of Polytetrafluoroethylene," *Polymer*, **22**, 11, pp 1487-1495.
- (35) Kimmig, M., Strobl, G. and Stuhn, B. (1994), "Chain Reorientation in Poly(tetrafluoroethylene) by Mobile Twin-Helix Reversal Defects," *Macromolecules*, **27**, 9, pp 2481-2495.
- (36) Weeks, J., Clark, E. and Eby, R. (1981), "Crystal-Structure of the Low-Temperature Phase(II) of Polytetrafluoroethylene," *Polymer*, **22**, 11, pp 1480-1486.
- (37) Weeks, J., Eby, R. and Clark, E. (1981), "Disorder in the Crystal-Structures of Phase-1 and Phase-2 of Copolymers of Tetrafluoroethylene and Hexafluoropropylene," *Polymer*, **22**, 11, pp 1496-1499.
- (38) Brown, E.N. and Dattelbaum, D.M. (2005), "The Role of Crystalline Phase on Fracture and Microstructure Evolution of Polytetrafluoroethylene (PTFE)," *Polymer*, **46**, 9, pp 3056-3068.
- (39) Flom, D. and Porile, N. (1955), "Friction of Teflon Sliding on Teflon," *Journal of Applied Physics*, **26**, 9, pp 1088-1092.
- (40) Blanchet, T.A. and Sawyer, W.G. (2001), "Differential Application of Wear Models to Fractional Thin Films," *Wear*, **250**, pp 1003-1008.
- (41) Dickrell, P.L., Sawyer, W.G. and Erdemir, A. (2004), "Fractional Coverage Model for the Adsorption and Removal of Gas Species and

- Application to Superlow Friction Diamond-Like Carbon," *Journal of Tribology-Transactions of the Asme*, **126**, 3, pp 615-619.
- (42) Joyce, J. (2003), "Fracture Toughness Evaluation of Polytetrafluoroethylene," *Polymer Engineering and Science*, **43**, 10, pp 1702-1714.
- (43) Durrell, W.S., Stump, E.C. and Schuman, P.D. (1965), "Glass Transition Temperature of Polytetrafluoroethylene," *Journal of Polymer Science Part B-Polymer Letters*, **3**, 10PB, pp 831-&.
- (44) Lau, S.F., Wesson, J.P. and Wunderlich, B. (1984), "Glass-Transition of Poly(Tetrafluoroethylene)," *Macromolecules*, **17**, 5, pp 1102-1104.
- (45) Dlubek, G., Saarinen, K. and Fretwell, H.M. (1998), "The Temperature Dependence of the Local Free Volume in Polyethylene and Polytetrafluoroethylene: A Positron Lifetime Study," *Journal of Polymer Science Part B-Polymer Physics*, **36**, 9, pp 1513-1528.

APPENDIX

Calculation of the Nominal Temperature Rise

In this experiment, a square pin reciprocates against a flat steel counterface. The frictional power developed at the tribological interface is partitioned between the two bodies, and at steady state, an elevated interface temperature is required to conduct the frictional power out of the contact. The thermal resistance of the pin is much larger than that of the counterface. A conservative approach (resulting in a negligibly higher predicted temperature rise) is to assume that all of the frictional power is conducted by the counterface. Every point on the counterface is subject to the heat source only for a fraction of each cycle. The Peclet number, $Pe = Va/\alpha$, is a dimensionless parameter that describes the relative contribution

of convection to conduction where a is the half length of the pin, α is the thermal diffusivity, and V is its velocity. In this case, Pe is greater than 10 and the convection effects are significant. Another conservative approach is to neglect the convection and consider a square stationary heat source of $2a \times 2a$ dimensions on a steel half-space. In this case, the maximum temperature rise is given by the approximate stationary heat source solution,

$$\theta = 1.12 \frac{\mu P V a}{K} \quad [A1]$$

Using constants of $K = 40 \text{ W/mK}$, $\mu = 0.2$, $P = 7 \times 10^6 \text{ N/m}^2$, $V = 0.05 \text{ m/s}$ and $a = 0.003 \text{ m}$ gives a maximum possible temperature rise is less than $\theta = 6 \text{ K}$. Now if convection is considered while still neglecting to partition power to the pin, the formula for the maximum temperature rise is

$$\theta_0 = 1.6 \frac{q'' a}{K} (Pe)^{-1/2} \quad [A2]$$

Using a thermal diffusivity of $3 \times 10^{-6} \text{ m}^2/\text{s}$ gives a temperature rise of just over $\theta = 1 \text{ K}$. This is likely an underestimate because the pin reciprocates over previously heated portions of the counterface. Considering the effects of convection, the reciprocating sliding path and the fact that the thin steel counterface is mounted to a copper block, the actual temperature rise is likely in the range from 2 to 3 K.