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Macroscopic Evidence of Thermally Activated Friction with Polytetrafluoroethylene

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Abstract Under macroscopic pin-on-disk testing the sliding friction coefficient of Polytetrafluoroethylene (PTFE) was investigated over a temperature range of approximately 200–400 K. This study examines the nature of the temperature dependence by testing PTFE pins at varying temperature and humidity on a linear reciprocating pin-on-disk tribometer. The friction coefficient increased monotonically with decreasing temperature from $\mu = 0.075$ to $\mu = 0.210$ in a manner consistent with thermal activation; it deviated from this trend only during phase and glass transitions in the PTFE and temperatures below the frost-points for the respective environments.

Keywords Cryogenic tribology · Polytetrafluoroethylene · PTFE · Solid lubrication

Introduction

There are a number of applications where operation in a temperature range from 200 to 400 K or larger is required for device success [1–3]. These extreme conditions are often the motivation for variable temperature studies in tribology [4–7], but there is a paucity of relevant tribology data available for temperatures below 273 K. In the range from 300 to 400 K the friction coefficient of PTFE increases with decreased temperature and increased speed.

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This behavior has been interpreted as evidence for a viscoelastic friction dependence of PTFE since McLaren and Tabor [8] first proposed the hypothesis in 1963. It is well-known that PTFE films transfer and adhere strongly to the counterface, and a modern hypothesis is that both friction and wear of PTFE are dominated by the interactions of PTFE chains sliding past one another at weak self-mated interfaces, often within transfer films [9–15]. A recent paper by McCook et al. [4] found that friction of PTFE matrix composites continued to increase in the cryogenic regime down to 200 K, and the notion of a thermally activated friction coefficient for PTFE was proposed (analysis of an activation energy gave $E_a = 3.7$ kJ/mol).

A recent molecular scale study of graphite by Zhao et al. [16] provided evidence that the temperature dependent friction found for PTFE may be a general result of interfacial sliding. In these studies, an atomic force microscope was used to collect friction data on molecularly smooth terraces of graphite over a temperature range from 140 to 750 K at a vacuum level of 2×10^{-10} torr. The friction coefficient increased with decreasing temperature, and the data collected followed an Arrhenius dependence with an activation energy of $E_a = 9.6$ kJ/mol. The molecular scale experiments by Zhao et al. [16] addressed many of the uncertainties raised in the macroscopic experiments conducted by McCook et al. [4]; namely, the sliding interface was well-characterized, interfacial sliding was confirmed, and the experiments were run in ultra-high-vacuum at temperatures well above the temperature for equilibrium ice formation on the surfaces (*frost-point*).

It is difficult, if not truly impossible, to prescribe interfacial sliding and zero-wear in macroscopic tribological testing. Under conditions where wear, viscoelastic losses, and plastic deformation are negligible, interfacial sliding forces may be captured in the global force mea-

surements. Solid lubricant films and composites of materials such as MoS_2, PTFE, and graphite, operating in their lowest wear environments and preparation, provide the best opportunity to make fundamental measurements of interfacial sliding forces in macroscale tribology testing.

A molecular view of thermally activated friction is one where the thermal energy blurs the potential surfaces giving rise to a reduction in the effective barriers for sliding with increased temperature and vice versa. In systems with wear, athermal behavior of friction is often reported; this may result from a cancellation of thermally sensitive material properties that govern both the deformation resulting in wear and friction or temperature independent mechanics. In the schematic shown in Fig. 1, the steep curve from low to high friction is indicative of thermally activated behavior. At elevated temperatures, thermodynamic, chemical, and physical properties of materials will dictate changes in the friction behavior from that predicted by the Arrhenius relationship. Suggested transitions from Arrhenius behavior in the realm of rapidly increasing friction at low temperature may exist due to interfacial forces that reach such a high level that alternative athermal mechanisms of motion become more favorable. In macroscopic testing, the solid lubricant systems appear to transition into a mode of fine wear debris generation at the lowest temperatures examined, which is coincident with the greatest deviation from an activated trend.

The goal of this study was to improve our understanding of thermally activated friction of PTFE. In the experiments by McCook et al. [4], the role of ice could not be quantified, and the effectiveness of the liquid nitrogen boil off to prevent ice deposition at cryogenic temperatures was uncertain. Data were collected here at elevated humidities over a similar temperature range to study the potential role of ice on cryogenic PTFE sliding interfaces. The results demonstrate that the experiments by McCook et al. were likely free of ice contamination at the tribological interface, and provide further evidence that interfacial sliding is a thermally activated process.

Results and Discussion

The reciprocating tribology experiments described here (6.3 MPa contact pressure, 50 mm/s sliding speed) were run in an open gaseous environment of nitrogen and water vapor with the temperatures of the steel counterface being prescribed by a copper heating and cooling block. The experimental details are described in the methods section and are fundamentally different than the experiments published in McCook et al. [4], which used liquid nitrogen gas boil-off in an impinging jet configuration to cool and inert the tribological surfaces. The results of friction experiments run at 2% and 6% relative humidity are given in Tables 1 and 2 respectively. In this experiment no effort to inert the environment below the ambient water vapor content was attempted, and the cooling of the sample did not rely on an impinging jet of volatilized liquid nitrogen (i.e., the temperature and environmental control are decoupled). These data are also plotted in Fig. 2, where the lines and arrows denote the order in which the data has been collected (the sequential data is given in Tables 1 and 2). For cryogenic experiments, temperatures were ramped from ambient to sub-ambient and back.

For the case of 2% RH, the friction coefficient climbs as the temperature is reduced to 225 K, which corresponded to visible ice formation on the counterface (initially shiny but becoming hazy); deviations from this trend were
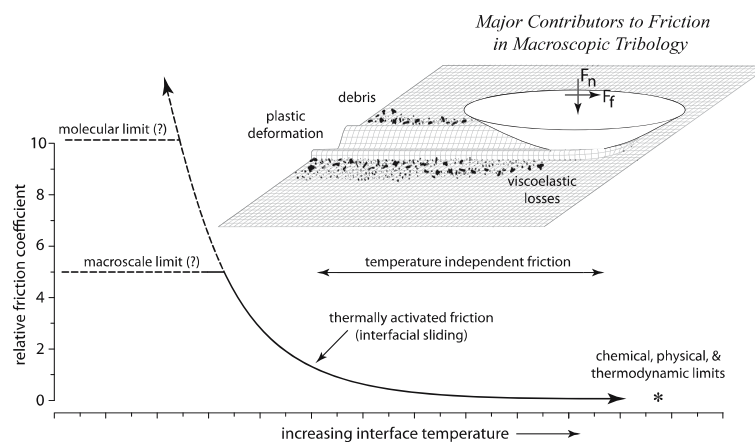
Fig. 1 A schematic for the thermally activated hypothesis of friction coefficient as applied to macroscopic tribology experiments for materials that accommodate slip through interfacial sliding. The temperature independent friction coefficient and macroscale limits are likely the results of opportunistic modes of accommodating slip in tribological systems, which prevent direct assessment of interfacial sliding forces. Upper temperature limits and theoretical molecular scale postulated limits are noted.

Table 1 Results of 2% relative humidity variable temperature experiments

Test	T (K)	$\sigma(T)$	Friction coefficient	$\sigma(\mu)$
1	299.8	0.15	0.145	0.0010
2	309.5	0.08	0.135	0.0001
3	342	0.08	0.102	0.0007
4	390.5	0.12	0.075	0.0016
5	399.1	0.20	0.077	0.0010
6	408	0.14	0.076	0.0009
7	416.3	0.13	0.075	0.0008
8	406.8	0.26	0.080	0.0006
9	395	0.44	0.083	0.0008
10	391	0.20	0.085	0.0008
11	341.1	0.67	0.102	0.0008
12	307.8	0.12	0.141	0.0016
13	299.3	0.66	0.149	0.0016
14	289	0.12	0.152	0.0016
15	279.9	0.10	0.155	0.0009
16	252	0.48	0.207	0.0011
17	224.7	0.09	0.210	0.0009
18	204.2	0.16	0.180	0.0010
19	188.1	0.46	0.152	0.0015
20	197.7	0.24	0.160	0.0007
21	219.5	0.12	0.143	0.0041
22	248.9	0.09	0.209	0.0013
23	281.7	0.72	0.156	0.0012
24	291.3	0.55	0.163	0.0012
25	298.8	0.23	0.162	0.0009

Listed are the average and standard deviation of the friction coefficient 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 ± 2 N and 1.85 ± 0.13%, respectively. The background temperature inside the glove box was held constant at 296 ± 1 K.

Table 2 Results of 6% relative humidity variable temperature experiments

Test	T (K)	$\sigma(T)$	Friction coefficient	$\sigma(\mu)$
1	301.1	0.46	0.167	0.0008
2	287.8	0.34	0.164	0.0009
3	281.4	0.08	0.156	0.0008
4	270.6	0.93	0.174	0.0030
5	261.5	0.11	0.203	0.0038
6	249.7	0.20	0.094	0.0017
7	239.0	0.08	0.118	0.0007
8	217.7	0.12	0.143	0.0060
9	234.9	0.09	0.124	0.0027
10	247.1	0.10	0.113	0.0010
11	259.9	0.08	0.101	0.0028
12	268.9	0.09	0.039	0.0018
13	280.5	0.09	0.148	0.0028
14	289.9	0.10	0.157	0.0014
15	297.1	1.60	0.157	0.0033

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 ± 2 N and 5.5 ± 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 ± 1 K.

observed during the room temperature phase transitions [17–19] and during a hypothesized glass transition near 400 K [17, 20–22]. At 2% RH with a background temperature of 296 K, the frost-point is approximately 243 K. As the temperature was further reduced below 225 K, the friction coefficient continues to fall, which is presumably due to a more contiguous film of ice on the surface. Upon heating from 188 K, the friction coefficient exhibits significant hysteresis, presumably because the ice film is intact and the trend is that of PTFE on ice—*at a temperature above the frost-point (250 K) the friction coefficient rejoins the original trend*.

For measurements at 6% RH, values of friction coefficient followed the previous experiments conducted at 2% RH until crossing the 6% RH frost-point at 255 K, where a
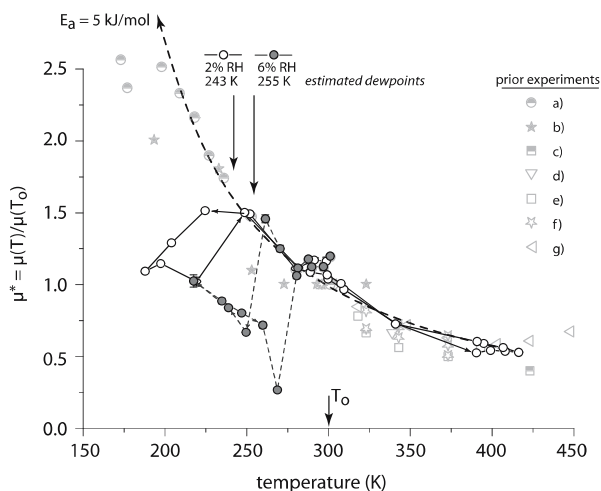
sharp drop in the friction coefficient was observed. Upon further cooling, the friction coefficient resumed a monotonic increase, eventually overlapping the heating data (thought to be PTFE/ice) collected at 2% RH. During heating from 225 K the friction coefficient showed little hysteresis (a deviation thought to be associated with ice melting was observed just below 273 K). Collectively these results suggest that below the frost-points ice formed on the wear tracks—perhaps in a competitive rates fashion [23, 24]—and that the presence of ice provides a weaker pathway to interfacial slip.

The relative change in friction coefficient, μ^*, is computed by normalization with the ambient temperature datum. The relative change in friction coefficient from the variable temperature experiments of PTFE presented above and those of previous studies have been calculated and plotted versus temperature in Fig. 3. It should be mentioned that a recent study by Burton et al. [26] completely spanned the range from 4 to 450 K, but due to transients in setting up transfer films and the velocity dependence of PTFE, this data is not included as the single pass experiments were done under variable speed.

The effect of ice formation on the frictional behavior in macroscopic PTFE sliding experiments is clear—*devi-*
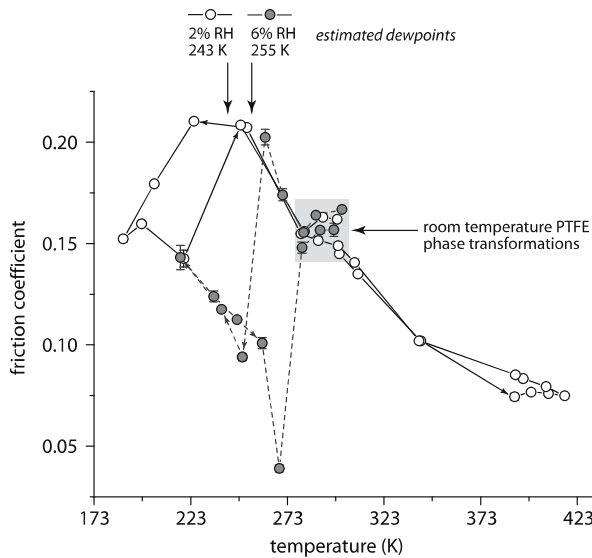
Fig. 2 Friction coefficient plotted versus interface temperature for unfilled PTFE in tests varying interface temperature. Tests were conducted on a 304 stainless steel counterfaces in a nitrogen environment at two humidity levels. Sliding speed was 50 mm/s over a 25.4 mm reciprocation length. The normal load and humidity were held constant at 275 ± 2 N and $1.85 \pm 0.13\%$ at the low humidity condition and 273 ± 2 N and $5.5 \pm 1.1\%$ at the high humidity condition. The background temperature inside the glove box was held constant at 296 ± 1 K. The dew points of the 2% and 6% relative humidity experiments were calculated to be 243 K and 255 K, respectively.

ations from Arrhenius behavior are observed when the surface temperature is decreased below the temperature for ice formation. The temperature at which such deviations occur is related to the kinetics of equilibrium ice formation. Based upon these observations, the data of McCook et al. [4] can be seen to be free of ice contamination down to 200 K. A subtle deviation from the more global trend is observed at 173 K. Any future macroscopic studies designed to interrogate this regime will likely require cryogenic vacuum instrumentation. This combined data set is well fit to a thermally activated process with an activation energy of 5 kJ/mol, as shown in Fig. 3.

Conclusions

(1) In the absence of ice, the friction coefficient of PTFE increases monotonically with decreasing temperature.

(2) The friction results collected here are in excellent agreement with data collected during previous investigations of PTFE under different experimental setups. A fit of activation energy $E_a = 5$ kJ/mol over the collective dataset suggests thermally activated friction.

(3) The presence of ice at a nascent PTFE interface provides a lower energy pathway to interfacial sliding. The friction coefficient of this interface also tended to increase with decreasing temperature.

Methods Appendix

Materials

The solid lubricant tested in this study was virgin polytetrafluoroethylene (Teflon[TM] 7 C from DuPont). The sample powders were first jet-milled to break up agglomerates and then compression molded at 633 K according to the procedure described in Sawyer et al. [27]. After molding, the final $6.3 \times 6.3 \times 12.7$ mm^3 tribology specimen was machined from the $\varphi 12.7$ mm $\times$ 38 mm molded puck. The counterface used in this study was a 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 [28].

Fig. 3 Normalized friction coefficient plotted versus interface temperature for variable temperature studies of PTFE in the literature: (a) McCook et al. [4] (b) Bowden [25] (c) Pooley and Tabor [10] (d) Blanchet and Kennedy [13] (e) McLaren and Tabor [8] (f) Tanaka and Uchiyama [12] (g) Pleskachevsky and Smurugov [14]. This dataset 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 425 K. The results collected in the current study are connected by lines.

Tribometry

Experiments were conducted on a linear reciprocating tribometer. The details of the tribometer design and a detailed uncertainty analysis of friction coefficient can be found in Schmitz et al. [29]. Briefly, a polymer specimen was mounted directly to a 6-channel load cell. A feedback controlled electro-pneumatic valve pressurized the pneumatic cylinder/linear thruster assembly that presses the load cell/sample assembly against the reciprocating counterface. Tests were conducted on a 25.4 mm track with a normal pressure of 6.3 MPa and a sliding speed of 50 mm/s. The total sliding distance at each temperature condition was 50 m. Post test analysis revealed that the first 10 m of sliding contained the tribological transients of every test and the averages and standard deviations of temperature and friction coefficient were calculated using the data from the remaining 40 m.

These tests are unique for several reasons: (1) The experimental setup allowed excellent variability and stability of temperature over the range of 190 to 420 K. This enabled a sufficient number of discrete temperatures to be tested such that trends and transitions in the data could be more effectively interrogated. Most prior cryogenic experiments included a room temperature control and only one or two cryogenic temperature conditions; as a result, interpretation of a general temperature behavior is impossible. (2) Tests were conducted for dry sliding under fixed atmospheric conditions to enable investigation of thermal effects on friction in the absence of other environmental effects. Generally, this has not been the case in prior studies as liquid and gaseous cryogens have been employed at cryogenic conditions and ambient air for the control measurements. (3) The environmental control was implemented without negatively affecting the experimental uncertainties of the tribometer. In most previous cryogenic tribology studies, the cryostats and vacuum chambers place serious design limitations on the tribometers, introducing high uncertainties and low 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. (4) The uniform and constant contact pressure distribution generated by the elastic square on rigid flat geometry simplifies the interpretation of friction coefficient from the typical pin-on-disk type experiments that have a non-constant, semi-elliptic pressure distribution.

Environment

The tribometer was completely contained within a commercial environmental glove box (manufactured by Vacuum Atmospheres Company, VAC). The glove box was purged of oxygen and water using liquid nitrogen boil-off at a high flow rate. A GE HygroGuard 2650 trace moisture analyzer was used to measure the relative humidity within the glove box. The measurement was continuously collected using custom data acquisition software. Once the humidity dropped below 2%RH, the nitrogen flow was stopped and the environment was sealed for the studies. The glove box was left to reach thermal equilibrium with the laboratory at 296 ± 1 K (this value was maintained for the duration of the experiments). The relative humidity was RH = 1.85 ± 0.13% (average ± standard deviation) during the first series of tests. Following the low humidity experiments, nitrogen was bubbled through water, and the moist gas was fed into the chamber until the relative humidity reached 6%. For the duration of the second set of experiments, the relative humidity was RH = 5.5 ± 1.1% (average ± standard deviation).

The condensation and growth of water/ice layers on a surface will depend on a number of factors including the composition and structure of the surface, the temperature of the surface, the ambient temperature of the environment and the relative humidity of the environment, which is related to the equilibrium vapor pressure of water. In the present study, the surface temperature at which ice films will exist in equilibrium with the ambient environment is of interest. This temperature has been estimated using the Goff-Gratch equation in which ice formation from the ambient vapor is considered [30]. While the nature of the sliding tribological interface will likely modify the exact equilibrium relationship, the predicted surface temperatures correspond closely to the observed deviations from an Arrhenius behavior and strongly implicate the role of ice under these conditions.

Thermal 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, which kept the stage near ambient temperatures. The block was drilled and tapped, and 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 before sliding commenced. The part of the load cell closest to the interface never exceeded 2 K above or below 296 K because the PTFE sample provided insulation.

Temperature control feedback was provided by a thermocouple that was permanently mounted to the surface of the copper block near the counterface. This temperature was also continuously recorded. A handheld thermocouple

was used to determine thermal equilibrium of the counterface/sample interface region as well as the temperature gradient from the copper block to the wear track. The temperature differential was negligible at 300 K, but was as high as 40 K at a block temperature of 148 K. This differential was used to adjust the collected temperature data from the copper block.

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