

Triboelectric charging of a perfluoropolyether lubricant

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Perfluoropolyethers (PFPE) are used extensively to lubricate hard disks for high density information storage. Some PFPE lubricants have been shown to be vulnerable to dissociative electron attachment as well as electron bombardment. Triboelectric charges generated during sliding contact may generate quasi-free electrons capable of degrading the lubricant. We describe measurements of triboelectric charging in a model polymer-metal system with and without a PFPE lubricant and show that negative charge accumulates on the substrate polymer surface, both with and without the lubricant. In the presence of the lubricant, some of this charge moves through and becomes bound to the lubricant. Electron and positive ion emission from PTFE-lubricated surfaces during contact sliding again indicate motion of charge through the lubricant. Ion emission in particular suggests possible degradation of the lubricant. © 2003 American Institute of Physics.
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1. INTRODUCTION

Perfluoropolyethers (PFPE) are used extensively to lubricate hard disks for high density information storage. An extremely thin, 5–20 Å layer of lubricant can provide substantial protection against damage due to slider-disk contact. Because so little lubricant is actually on the hard disk, the chemical stability of the lubricant can be a major limiting factor in media stability and longevity. As pseudo and full contact recording become implemented, any contact induced degradation is of concern.¹ Several PFPE degradation mechanisms have been observed, including thermal decomposition,^{2,3} chemical degradation,^{4–8} electron impact dissociation (> 14 eV),^{9,10} and dissociative electron attachment following low energy (< 10 eV) electron bombardment^{3,11,12} or charge injection.¹³ Matuzunuma *et al.* have used molecular orbital calculations to show that PFPE oligomers have significant electron affinities (required for electron attachment); the resulting anions have low activation energies for dissociation at multiple bonds, consistent with unzipping.¹⁴ We propose that contact charging due to slider-disk contact is a potential source of low-energy electrons for dissociative electron attachment. In this work, we explore the generation of triboelectric charge and triboelectric currents due to contact charging between conducting and insulating sliders and a polytetrafluoroethylene (PTFE—a common perfluorinated polymer) substrate, with and without a protective layer of Fomblin-ZDOL. In previous work we showed that this same lubricant could act as an electrolyte in corrosive electrochemical reactions.^{15,16}

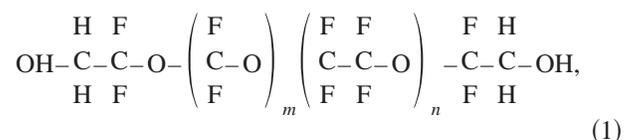
Triboelectric currents can be generated during the contact sliding between two materials. We have shown previously that such stimulation can lead to transfer of charge to a fluid phase (e.g., flowing gases).¹⁷ In polymers, charging can occur when metal–insulator or insulator–insulator contacts are broken by one of several mechanisms including interfa-

cial fracture,¹⁸ peeling,¹⁹ and abrasion.²⁰ Previous work has shown that a surface charge is created during such tribological loading on the order of 1 mC/m², and in the case of polymers such as high density polyethylene (HDPE) or PTFE, this charge is negative.²¹ This work also showed that electrons are spontaneously emitted from the surface at energies significantly less than 100 eV. Such energies are in a range similar to those found to cause the degradation of PFPE lubricants by both electron attachment and electron impact ionization, implying possible mechanisms for degradation of such lubricants under conditions found in the slider-disk contact of magnetic storage media.

This work describes a probe of the currents generated by stainless steel and glass styli on PTFE surfaces lubricated with Fomblin ZDOL PFPE lubricant. We show that both with and without the lubricant, negative charge (most likely electrons) leave the metal styli. We provide evidence that charge is flowing into the lubricant and that a fraction of the charge remains in the PFPE. Finally, single particle detection measurements performed in vacuum with lubricated PTFE indicate the ejection of both negatively charged (electrons/negative ions) and positively charged (positive ions) particles during tribological loading, strongly suggesting breakdown of the Fomblin.

II. EXPERIMENT

Commercial Teflon®, polytetrafluoroethylene (PTFE), with a density of 2.24 g/ml, was employed for the substrates in this work. Fomblin ZDOL lubricant, average molecular weight 4000 amu, was obtained from Ausimont, Morristown, NJ. ZDOL is a random copolymer of perfluorinated ethylene oxide and perfluorinated methylene oxide, with chemical formula:



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Apparatus for Transient Current Measurements

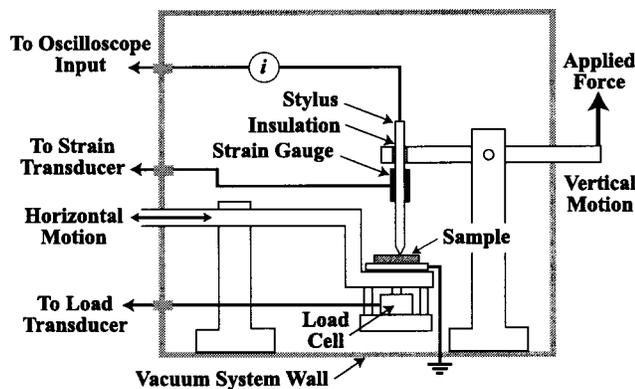


FIG. 1. Schematic of experimental apparatus for contact sliding of a stylus on a polymer surface and measurement of triboelectric current generation.

where $m/n \approx 2/3$.

The stainless steel stylus was machined to a rounded point with a radius of curvature $\sim 500 \mu\text{m}$. Prior to each experiment the PTFE substrate was cleaned with ethanol to remove surface contaminants and to neutralize any residual surface charge. Any ZDOL on the stylus (from a previous run) was removed with (nonafluorobutyl)methylether (Novec Engineered Fluid HFE-7100, 3M Corp.) and rinsed in acetone. The latter removed any adhering substrate material as well lubricant from the previous wear experiments. Most measurements employed a stainless steel stylus. Some experiments with a soda-lime glass stylus were performed to see if insulating contacts yielded similar effects. The glass stylus was constructed by melting a soda lime glass tube around a metal rod, which extended to within about 1 mm of the end of the stylus. Currents induced in the metal rod probed charge separation along the glass-polymer interface. The radius of curvature of the glass stylus was $\sim 1.6 \text{ mm}$.

Unless otherwise stated, all experiments were performed in room air at 1 atm. The experiment consisted of translating the PTFE sample relative to a stationary stylus while applying a fixed load, as shown in Fig. 1. The stylus was electrically isolated from the supporting cantilever, while the metal support beneath the PTFE sample was electrically grounded. The current delivered to the stylus was directed through a coaxial cable to the input of a LeCroy LC584AXL 1 GHz Digital Oscilloscope with an input resistance of $1 \text{ M}\Omega$. The time constant associated with the $1 \text{ M}\Omega$ input resistance and the internal capacitance of the oscilloscope limited the time response of the detection circuit to $\sim 40 \text{ ns}$. The normal force was measured using a Sensotek force transducer mounted beneath the polymer substrate platform. Throughout the experiments the normal force was kept constant at 5 N. We call the path of sliding contact the “wear track,” although little evidence of wear was seen at these normal forces due to the relatively large radii of curvature for the two styli. Sliding velocities were $\sim 20 \text{ cm/s}$.

Electron and positive ion emissions were detected with a Galileo 4800 Series Channeltron electron multiplier biased at $+2500 \text{ V}$ for electrons and -2500 V for positive ions. The signal output of the Channeltron was input to an Ortec

Current Generated by Drawing a Stainless Steel Stylus across a Teflon Substrate with and without Fomblin—Single Pass

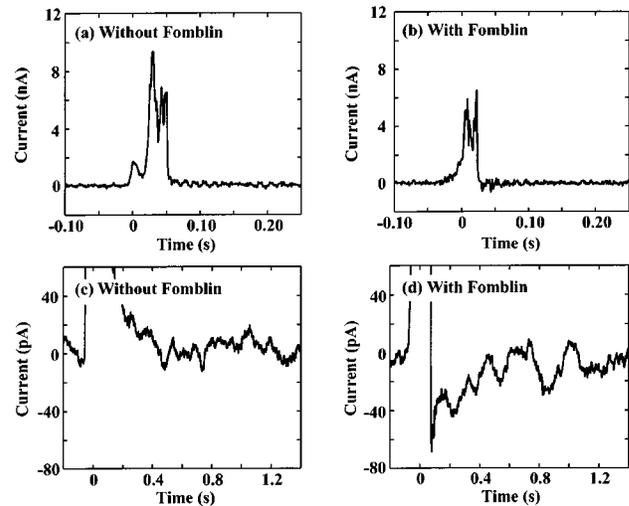


FIG. 2. (a) Overall current generated on a single pass by a stainless steel stylus without ZDOL lubrication and (b) with ZDOL lubrication. (c) An expanded view of the current in (a), along with (d) an expanded view of the current in (b). Note the presence of a negative decay current through the ZDOL in (d).

Model 9301 Fast Preamplifier ($10\times$ amplification) and then an Ortec 574 Timing Amplifier ($\sim 2\times$ amplification). The amplified signal was then directed to an EG&G Princeton Applied Research Model 914P Multi-Channel Scaler (MCS) with an associated computer. Placed in front of the Channeltron were two wire mesh grids to shield the rest of the vacuum system (and sample) from the high voltage on the Channeltron. The particle detection experiments were performed in vacuum at a pressure of 10^{-5} Pa .

III. RESULTS

A. Transient current to stainless steel stylus

Typical currents delivered to the stainless steel stylus during a single pass of the stylus across the PTFE substrate with and without Fomblin ZDOL are shown in Fig. 2. The presence of ZDOL has little effect on the magnitude of the resulting current. Positive currents with an average magnitude of 4–6 nA (delivered to the stylus) are observed in each case and correspond to negative charge leaving the stylus. However, the current signals during and immediately after the stylus slows to a stop show significant differences. On the expanded scales of Figs. 2(c) and 2(d), the current decays slowly from positive values over several hundred milliseconds in the absence of ZDOL, while in the presence of ZDOL, the current shows a sharp negative spike and a slow decay from these negative values. The slow decay from positive values in the absence of ZDOL is due to continued tribocharging as the stylus slows to a stop, i.e., negative charge continues to be deposited on the PTFE, resulting in a net positive charge delivered to the stylus. The negative current spike in the presence of ZDOL is due to the transport of negative charge formerly deposited on or near the PTFE surface back toward the stylus (a recombination current) as it slows to a stop. This negative signal suggests that the mag-

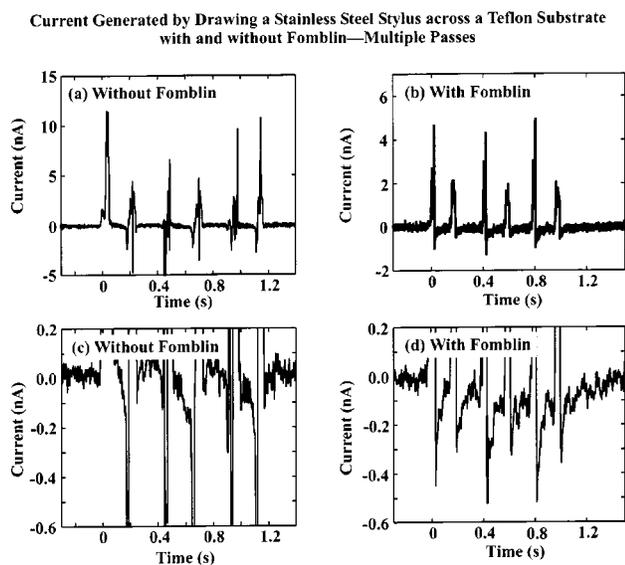


FIG. 3. (a) Current generated during multiple passes of a stainless steel stylus without ZDOL lubrication and (b) with ZDOL lubrication. The expanded current of (a) is in (c) while that of (b) is in (d). Notice the presence of negative current prior to each pass following the first in (c) and the presence of negative current after each pass in (d). Also notice the negative dip in the current in (d) that correlates with an increasing surface potential.

nitude of this recombination current is greater than the small positive triboelectric current generated as the stylus slows, resulting in a net negative current; importantly, all of this current travels through the ZDOL. The sharp drop off in the current when the bent stylus is stopped in ZDOL is attributed to the increase in lubrication which permits the stylus to come to equilibrium much more quickly. Conversely, in Fig. 2(c) the bent stylus does not have lubrication and therefore takes longer to reach equilibrium, thus the current does not die away as quickly.

The current signals of Fig. 2 can be integrated over the appropriate time intervals to determine the net charge transferred. The total charge transferred to the PTFE substrate during a single pass of the stylus is on the order of hundreds of pC. The decay current [Fig. 2(d)] constitutes tens of pC and requires the presence of ZDOL. Estimates of the thickness of the ZDOL layer based on elastohydrodynamic lubrication of the PTFE surface (assuming a geometry of edge-to-edge disk contact) yields a minimum lubricant thickness of 10 μm . Thus, charge transport intimately associated with the ZDOL has occurred either as charge moving through the fluid phase or with fluid displacement. In either case, during this transport negative charge has presumably attached to the lubricant molecules.

If the stylus is drawn across charged substrate material (e.g., charged negatively during a previous pass of the stylus across the substrate), negative charge is frequently delivered back to the stylus, either induced by bound negative charge on the substrate or transferred to the stylus in the form of free negative charge. A net positive charge may be delivered to the stylus if the stylus encounters fresh (or not fully charged) PTFE material along the sides of the wear track. Currents generated during six successive passes of the stylus along the same wear track, with and without ZDOL, appear in Fig. 3.

In the absence of ZDOL, every pass of the stylus (except the first) along the wear track begins with a negative transient current in coincidence with the beginning of sliding [Figs. 3(a) and 3(c)]. The data in Fig. 3(c) have been smoothed to show this negative current more clearly. In contrast, currents from the ZDOL coated surfaces rise toward the positive direction from the beginning of each pass along the wear track [Figs. 3(b) and 3(d)]. Between passes, negative recombination currents are observed. In the presence of ZDOL, the PTFE surface is not able to retain its full negative charge. The presence of ZDOL promotes discharge of the wear track as evidenced from the fact that stylus motion over the previously charged track yields positive current to the stylus. In contrast, without ZDOL, the wear track on the PTFE surface retains its full negative charge and induces strong negative currents in subsequent passes of the stylus.

The negative current due to negative charge returning to the stylus from ZDOL coated surfaces during the pauses in stylus motion is clearly seen in Fig. 3(d). The magnitude of this reverse current depends on the magnitude of the positive current of the preceding pass and hence depends on the total surface charge. This is evidenced by the magnitudes of the alternating peaks of the negative current in correlation with those of Fig. 3(b). Higher positive currents imply higher charge densities in the wear track which means a higher driving force for charge to return to the stylus. Transport of charge away from the wear track in either case means charge transport through the ZDOL and thus an opportunity for attachment of electrons onto PFPE molecules.

B. Charge uptake by lubricant

The total charge delivered to the ZDOL fluid during wear was estimated by machining a groove in the PTFE substrate which was then filled with ZDOL. After a wear experiment, the ZDOL was carefully removed with an insulated hypodermic needle; the total charge contained in the removed oil was then measured with an electrometer. In experiments involving many passes of the stylus through the trough, the charge associated with the ZDOL ranged from 2.4 to 8.5 pC, corresponding to a charge per unit volume of 14–50 pC/ml. Experiments in which the stylus passed only once along the trough yielded an average of 3 pC or approximately 18 pC/ml. By way of comparison, the total negative charge delivered to a ZDOL coated PTFE substrate in a single pass is typically 150 pC. Typical recombination charge transfer (estimated by integrating only the negative portions of the currents) are on the order of tens of pC, typically twice the total charge measured on ZDOL removed from the trough. These results show that for repeated passes of the stylus over the PTFE surface, a portion of the original charge is transported through the ZDOL and the ZDOL hangs on to a portion. In both cases, opportunity for attachment occurs. We point out that it was impossible to draw all of the oil from the PTFE and one would expect charged ZDOL to have high adhesion to the dielectric surface. We therefore doubt that we are collecting all of the charge transferred to the oil by this simple method.

Electron and Positive Ion Emission During Wear with a Stainless Steel Stylus

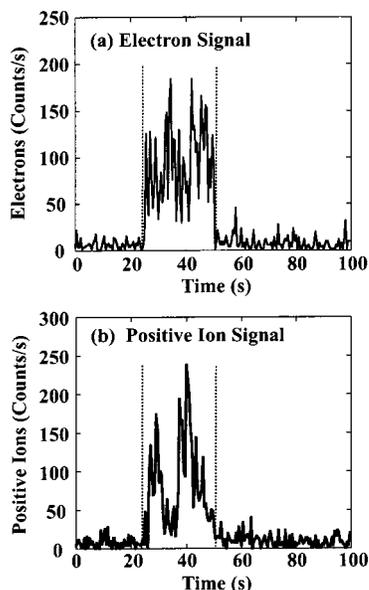


FIG. 4. Presence of (a) electrons and (b) positive ions during contact sliding of PTFE with ZDOL by a stainless steel stylus. The duration of sliding contact is indicated by the vertical dotted lines.

C. Electron and ion emission

Interfacial failure and polymer abrasion often yield significant electron and positive ion emission.^{22–25} Using a Channeltron electron multiplier (CEM) in vacuum we can detect charged particle emission accompanying contact sliding. Figure 4(a) shows the detection of electrons from lubricated PTFE with multicycle sliding occurring between 25 and 50 s. (The voltages applied to the grids in front of the CEM were +30 V on the front and +200 V on the back.) Once sliding is stopped the count rate drops almost immediately back to the noise level. In accompanying work, we have shown that emission accompanying triboinduced breakdown has a long tail of several seconds.²⁴ Thus, the negative charge emission (probably electron emission) does not appear to be due to breakdown but to direct emission from the surface.

With grid voltages of 0 V on the front and –30 V on the back, the electron count rate during contact sliding dropped to noise level and remained there during sliding. In the presence of this repelling electric field, this lack of signal indicates that the vast majority of the electrons emitted have energies below 30 eV. This energy range is on the same order as that which previous studies have shown is most likely to induce degradation of the ZDOL by electron attachment.^{3,12}

Figure 4(b) shows the detection of positive ions from sliding on the lubricated surface; the grid voltages used were –30 V on the front grid and –200 V on the back grid. Since the electrons have energies less than 30 eV, these grid voltages would repel any electrons. Thus, we can safely attribute this CEM signal to the emission of positive ions. Contact sliding occurred between the times of 25 and 50 s, in coincidence with the larger count rates well above the background noise level. The total ion emission is smaller than the

Current Generated by Drawing a Glass Stylus across a Teflon Surface with and without Fomblin—Single Pass

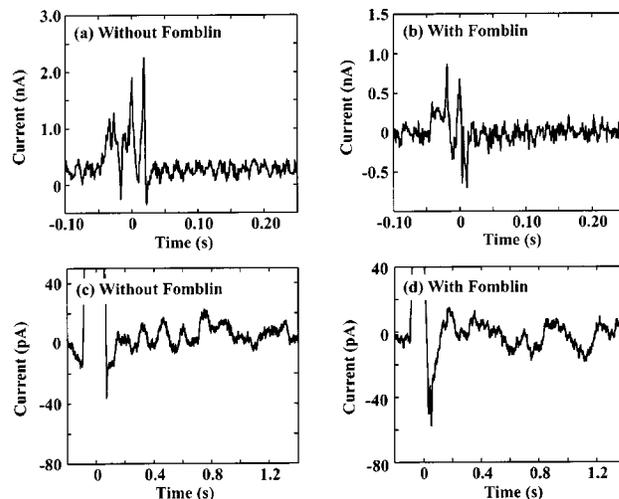


FIG. 5. Overall current with a glass stylus (a) with and (b) without ZDOL lubricant showing smaller magnitude current. Expanded view (c) with and (d) without ZDOL lubricant showing the presence of the negative decay current with a magnitude similar to that found with a stainless steel stylus.

electron emission by a factor of ~ 1.5 . Experiments were also conducted where the stylus was moved through a pool of ZDOL but was not touching or abrading the surface in any way. During these experiments no electrons or positive ions were detected above noise levels. Therefore the emission of electrons and positive ions is only associated with moving contact of the stylus along the PTFE substrate and the generation of charge on the surface.

Our estimate of oil thickness of $\sim 10 \mu\text{m}$ suggests a layer that is sufficient to prevent the direct escape of both low energy electrons and ions from the coated surface. Thus, these emissions require charge to be transported to the surface. (Compared to dry PTFE, the emissions from the lubricated surface are $\sim 20\%$ of the emissions from the dry substrate.) We envision that the charge carriers moving to the surface are in fact electrons pushed up by the remaining negative charge on the PTFE. A portion of these electrons escape into the vacuum to be detected. Some of the electrons near the free surface generate positive ions through collisions with the ZDOL; these + ions are also ejected which requires that the ionizing collisions are in regions of electric potential ~ 0 or positive, thus permitting the ions to escape. If the detected positive ions during contact sliding are indeed from the ZDOL, then they serve as a clear indication of the degradation of the ZDOL. Rather than electron attachment dissociation, this route to decomposition is due to electron impact ionization.

D. Glass stylus

To test if nonconductors would result in charge separation, we replaced the stainless steel stylus with nonconducting soda lime glass, sensing the charge by the induced current in a nearby electrode. Figure 5 shows this induced current generated by sliding the glass stylus on PTFE (a) without any ZDOL lubricant and (b) with ZDOL lubricant. In

both cases, the sign of the current corresponds to negative charge going to the PTFE from the glass stylus, similar to the metal. This also agrees with measurements of the charge remaining on the PTFE after the glass stylus is removed. The induced currents measured with the glass stylus were almost an order of magnitude lower than the currents observed with the stainless steel stylus. This is almost certainly due to using induced current versus direct current to the stainless steel. In the absence of a conducting path through the glass, the potential developed on the stylus relative to nearby grounds depends principally on the capacitance between the enclosed metal probe and the metal ground plate beneath the stylus. With capacitances on the order of tens of fF, we estimate the observed charge generated by a single pass is still tens of pC, perhaps an order of magnitude smaller than what we measured with the stainless steel stylus.

The glass stylus yielded somewhat smaller induced currents in the presence of the PFPE lubricant than without. Again, substantial recombination currents are observed in the presence of the PFPE lubricant, as shown in Fig. 5(d); i.e., a significant negative induced current is observed after the motion of the stylus ceases. The decay of this negative-going recombination current is significantly faster than that observed with the stainless steel stylus, possibly due to the reduced RC time constant (smaller C) for charge flow in the case of the glass stylus.

The similarity between the two styli regarding decay currents, despite having different magnitude overall currents, can be attributed to a limiting current at high voltages. Spada and Basov, showed that the current through ZDOL between two plates held at a given voltage difference levels off for voltages above ~ 10 V.¹³ In other work, we found that the potential along a polymer surface during sliding approached thousands of volts and was proportional to the overall average current.^{21,24} This would be well above the point where the current through the ZDOL would level off.

In addition to similar decay currents, the glass stylus also placed charge into the ZDOL in amounts similar to that placed by the stainless steel stylus. By removing the oil after sliding stimulation, the range of charges in the ZDOL went from 1.3 to 6.1 pC with an average of 3 pC. This corresponds to charge densities of 8–36 pC/ml with an average of 18 pC/ml. The similar charges placed by both the glass and the stainless steel styluses can be explained by the similar decay currents found with both types of stylus. The similar decay currents would push approximately the same amount of charge through the ZDOL during a given run with approximately the same probability to interact with and attach to the ZDOL. Hence, the amount of charge in the ZDOL would be approximately the same for each stylus.

Finally, we show in Fig. 6(a) the electron emission during contact sliding with a glass stylus and grid voltages of +30 V on the front and +200 V on the back. The average number of counts per second above background observed during sliding is comparable to those seen in Fig. 4(a) with the stainless steel stylus. Positive ions are also seen during contact sliding with the glass stylus [Fig. 6(b)], however the count rate is only $\sim 5\%$ of that observed with the stainless steel stylus.

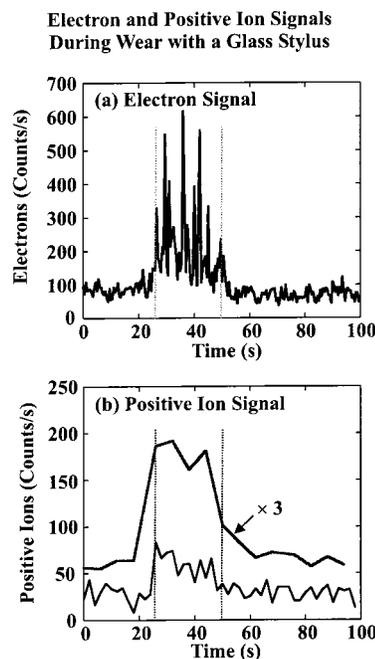


FIG. 6. (a) Electron and (b) positive ion emission during contact sliding of a glass stylus on PTFE with ZDOL lubrication. The duration of sliding contact is indicated by the vertical dotted lines. The upper line in (b) shows the smoothed positive ion signal vertically magnified by a factor of three.

IV. DISCUSSION AND CONCLUSIONS

During contact sliding with a stainless steel or glass stylus, a PTFE substrate develops a negative charge due to tribocharging. The negative charge is consistent with previous observations of contact charging on PTFE with a variety of clean metals.²⁶ A discussion of contact charging mechanisms involving polymers can be found in several publications.^{26–32} The basic concepts center on bringing electron free energies into equilibrium, and having simultaneously available charge carriers and unoccupied states.

We note that the fluid state itself is no barrier to contact charging and transport; i.e., charge transfer and transport involving fluids is responsible for serious electrostatic hazards in refueling and painting operations. Our measurements here indicate that the negative charge generated on the PTFE surface is relatively immobile in the absence of a lubricant, but displays significant mobility in the presence of a PFPE lubricant. This is in contrast to work by Oetelaar *et al.* who found that a silicon carbide-coated slider on carbon-coated hard disk media delivered a positive charge to the media, and that the decay of surface charge was reduced in the presence of monolayer lubricant coatings.³³ The contrasting charge is likely due to the different material couple in contact. Oetelaar *et al.* attributed the decay of surface charge to a reaction with atmospheric O_2 , perhaps accelerated by H_2O vapor.

In this study charge transfer to the lubricant from the charged interface and significant mobility are observed; these processes cannot be attributed to reactions with atmospheric species. In this context, the thickness of the lubricant layer and the negative sign of the surface charge are significant. This work shows through direct measurements that the oil is

in fact taking up negative charge and that negative charge moves through the oil both laterally and out into the vacuum. Once these electrons enter into the oil, they can potentially cause lubricant degradation by electron attachment. Both positive and negative charge is emitted from the surface, again implying that charge is transported through the oil. Finally, by measurements of electron energies *above* the surface we show that a portion of them have sufficient kinetic energies to cause ionization (> 14 eV) which is a second route to electron induced degradation; the observed positive ion emission suggests such ionization is occurring. Experiments are now underway to measure the mass(es) of the positive ions to determine if any C–F and C–O containing species related to ZDOL are emitted. We also plan to produce negative charge by multiple pass contact sliding in the presence of ZDOL and then analyze the lubricant by TOF-SIMS³⁴ in an attempt to detect degradation products accompanying this form of tribostimulation.

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¹International Disk Drive Equipment Manufacturers Association Report—Insight on Pseudo-Contact Recording IDEMA Insight **9**, (3) (1996).

²P. Basu, T. H. Ballinger, Jr., and J. T. Yates, *Langmuir* **5**, 502 (1989).

³J.-L. Lin, C. Singh Bhatia, and J. T. Yates, *J. Vac. Sci. Technol. A* **13**, 163 (1995).

⁴P. H. Kasai, W. T. Tang, and P. Wheeler, *Appl. Surf. Sci.* **51**, 201 (1991).

⁵K. J. L. Paciorek and R. H. Kratzer, *J. Fluorine Chem.* **67**, 169 (1994).

⁶R. Koka and F. Armatis, *Tribol. Trans.* **40**, 63 (1997).

⁷T. Fukuchi, *J. Tribol.* **121**, 348 (1999).

⁸C.-Y. Chen, D. B. Bogy, and C. Singh Bhatia, *J. Vac. Sci. Technol. A* **18**, 1809 (2000).

⁹L. Ng *et al.*, *Langmuir* **3**, 1161 (1987).

¹⁰J. Pacansky and R. J. Waltman, *Chem. Mater.* **5**, 486 (1993).

¹¹S. Mori and W. Morales, *Tribol. Trans.* **33**, 325 (1990).

¹²G. Vurens, R. Zehringer, and D. Saperstein, in *Surface Science in Tribology—Experimental Approaches*, edited by Y.-W. Chung, A. M. Homola, and G. B. Street (American Chemical Society, Washington, DC, 1992), Vol. 485, p. 169.

¹³F. E. Spada and D. Basov, *Tribol. Trans.* **8**, 179 (2000).

¹⁴S. Matsunuma, T. Miura, and H. Kataoka, *Tribol. Trans.* **39**, 380 (1996).

¹⁵J. T. Dickinson, S. C. Langford, W. Faultersack, and H. Yoshizaki, *Wear* **215**, 211 (1998).

¹⁶R. J. Greve, S. C. Langford, and J. T. Dickinson, *Wear* **249**, 727 (2001).

¹⁷L. Scudiero, J. T. Dickinson, and Y. Enomoto, *Phys. Chem. Miner.* **25**, 566 (1997).

¹⁸K. A. Zimmerman, S. C. Langford, and J. T. Dickinson, *J. Appl. Phys.* **70**, 4808 (1991).

¹⁹J. T. Dickinson *et al.*, *J. Adhes. Sci. Technol.* **8**, 1285 (1994).

²⁰J. T. Dickinson, S. C. Langford, S. Nakahara, L. Scudiero, M. -W. Kim, and N. -S. Park, in *Fractography of Glasses and Ceramics III*, edited by J. R. Varner, V. D. Fréchet, and G. D. Quinn (American Ceramic Society, Westerville, OH, 1996), Vol. 64, p. 193.

²¹J. V. Wasem, P. Upadhyaya, S. C. Langford, and J. T. Dickinson, *J. Appl. Phys.* (2003).

²²J. T. Dickinson, L. C. Jensen, and R. P. Dion, *J. Appl. Phys.* **73**, 3047 (1993).

²³J. T. Dickinson, L. Scudiero, and S. C. Langford, in *Structure and Properties of Glassy Polymers, ACS Symposium Series*, edited by M. Tant and A. Hill (American Chemical Society, Washington, DC, 1998), Vol. 710, p. 272.

²⁴J. V. Wasem, S. C. Langford, and J. T. Dickinson (unpublished).

²⁵J. T. Dickinson, in *Encyclopedia of Materials: Science and Technology*, edited by K. H. J. Buschow *et al.* (Elsevier, London, 2001).

²⁶A. Wählin and G. Bäckström, *J. Appl. Phys.* **45**, 2058 (1974).

²⁷T. J. Fabish, H. M. Saltsburg, and M. L. Hair, *J. Appl. Phys.* **47**, 930 (1976).

²⁸T. J. Fabish, H. M. Saltsburg, and M. L. Hair, *J. Appl. Phys.* **47**, 940 (1976).

²⁹J. Lowell and A. C. Rose-Innes, *Adv. Phys.* **29**, 947 (1980).

³⁰E. M. Charlson, E. J. Charlson, S. Burkett, and H. K. Yasuda, *IEEE Trans. Electr. Insul.* **27**, 1144 (1992).

³¹L.-H. Lee, *J. Electrostat.* **32**, 1 (1994).

³²M. Meunier and N. Quirke, *J. Chem. Phys.* **113**, 369 (2000).

³³R. J. A. van den Oetelaar, L. Xu, D. F. Ogletree, M. Salmeron, H. Tang, and J. Gui, *J. Appl. Phys.* **89**, 3993 (2001).

³⁴Y. Abe, M. Shibayama, and T. Matsuo, *Surf. Interface Anal.* **30**, 632 (2000).