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VIP Triboelectrification Very Important Paper

Bipolar Tribocharging Signal During Friction Force Fluctuations at Metal–Insulator Interfaces**

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***Abstract:** Friction and triboelectrification of materials show a strong correlation during sliding contacts. Friction force fluctuations are always accompanied by two tribocharging events at metal–insulator [e.g., polytetrafluoroethylene (PTFE)] interfaces: injection of charged species from the metal into PTFE followed by the flow of charges from PTFE to the metal surface. Adhesion maps that were obtained by atomic force microscopy (AFM) show that the region of contact increases the pull-off force from 10 to 150 nN, reflecting on a resilient electrostatic adhesion between PTFE and the metallic surface. The reported results suggest that friction and triboelectrification have a common origin that must be associated with the occurrence of strong electrostatic interactions at the interface.*

Friction and triboelectrification of materials are well-known phenomena and have been thoroughly studied for many years.[1,2] Despite the great technological advances, their mechanisms at the atomic/molecular level are not fully understood and still a subject of debate.[3] Specifically, the macroscopic friction force is rarely correlated with the electronic properties of materials,[4a] and triboelectrification, which occurs whenever two solids rub or touch each other, remains among the most poorly understood concepts of solid-state physics.[4b,c]

During recent years, great efforts have been focused on the triboelectrification of materials to improve or create new technologies, to control electrostatic discharges, and to explore this complex phenomenon at the atomic/molecular scale.[5] As a result of these efforts, significant progress has recently been made, and although some controversy exists on the nature of the charge carriers,[6] it is now clear that water, atmospheric pressure, and the asymmetric charge partitioning of ions at interfaces play key roles in triboelectrification.[7] Furthermore, materials can build up static electricity with positive and negative charges at the same contact area, which contradicts the widespread concept of the triboelectric series.[5e,8]

Similar to triboelectrification, understanding of friction also faces important technological and scientific obstacles.[9] Nevertheless, great progress has been made in understanding the contact mechanics phenomena, first with the prodigious work of Hertz and later with the elastic contact theory of asperities and the concept of the real area of contact.[10] The Johnson–Kendall–Roberts (JKR) and Derjaguin–Muller–Toporov (DMT) theories, which added adhesion forces to elastic deformations at contact interfaces, also significantly contributed to our understanding of this phenomenon.[11]

Much more recently, advances were made using atomic force microscopy (AFM) techniques to understand the contact at a microscopic level where friction was strongly correlated with the electronic properties in silicon pn junctions and GaAs surfaces.[12] Altfeder and Krim studied the nanotribology behavior of yttrium barium copper oxide (YBCO) compounds, and they concluded that phononic dissipation, electron conduction, and triboelectrification play important roles in the friction mechanisms at the nanoscale. Fractal geometry[13] was also applied to better understand the true nature of the contacts considering the roughness of interfaces, and as fractals have symmetry of scale, these concepts should be extendable to any scale. Unfortunately, extrapolations to the macroscopic scale are not always straightforward, and reproducible experiments are difficult

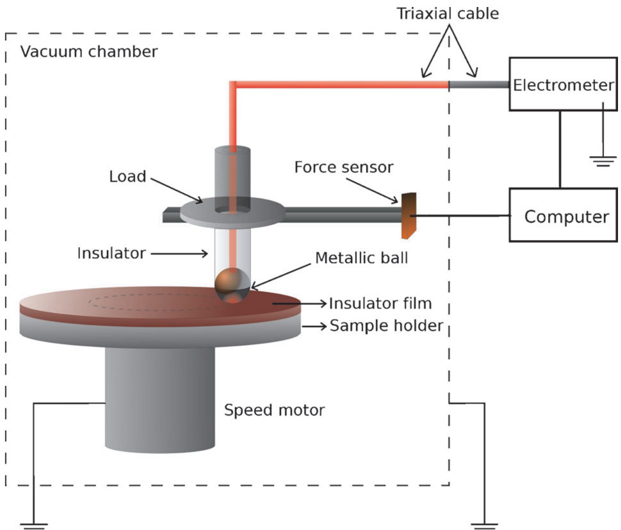

Figure 1. Setup to measure the tribocurrent and macroscopic friction force using the ball-on-disc geometry. PTFE sheets that were sold for general use and previously immersed in ethanol were used as the discs, and a steel ball was used as an electrode connected to the input of an electrometer. The system allows the recording of in situ information on the electric charges that are transferred at the interface while measuring the friction force response.

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to setup and perform. Furthermore, for macroscopic objects, forces such as gravity tend to be more significant than forces, such as van der Waals or Coulombic forces, that arise from intermolecular interactions,[14] and only a few studies deal with the correlation between the macroscopic friction force and the electronic properties of the material.

Nakayama and co-workers[15] have published extensively on the mechanochemistry of sliding contacts, and in summary, when two surfaces are brought into contact and rubbed, a very high energy state is formed at the interface with the generation of electromagnetic radiation, including X-rays,[4,16] phonons,[12c] cryptoelectrons,[6b,17] free radicals,[8b] and heat, causing the interface to attain a non-equilibrium state and triggering a triboplasma.[18]

A direct result from tribological experiments, but rarely used to investigate the triboelectrification of materials, is the flow of charged species at the interface, also called tribocurrent.[19] This small electric current essentially consists of the flow of charges between two surfaces under relative motion as the result of the different electron work function for metal–metal interfaces and a set of mechanisms for metal–insulator and insulator–insulator interfaces.[6]

Important new results for metal–insulator and insulator–insulator interfaces under relative motion point towards a strong correlation between friction and triboelectrification, which can be large enough to affect the friction behavior of macroscopic bodies.[20] Putterman and co-workers[19a,21] have shown that macroscopic friction originates from and scales to the intrinsic electronic interactions and modifications of the electronic properties of surfaces (e.g., anodic oxidation), stimulating changes in macroscopic friction force. Burgo et al. have shown that tribocharges previously deposited on polytetrafluoroethylene (PTFE) surfaces affected friction forces from the macro- to the nanoscale and can exceed all other factors for mechanical energy dissipation.[20b] As electrostatic forces[22] have a strong influence on the friction parameters, and sliding motion always induces contact electrification at interfaces, a very simple and common, but rigorous test in tribology, the ball-on-disk geometry, was used to record the macroscopic friction force and simultaneously measure the current generated at the metal–insulator interface, which is strongly correlated with the friction force. Figure 1 shows the experimental design. Friction/tribocurrent experiments were conducted in a vacuum tribometer with an electrometer

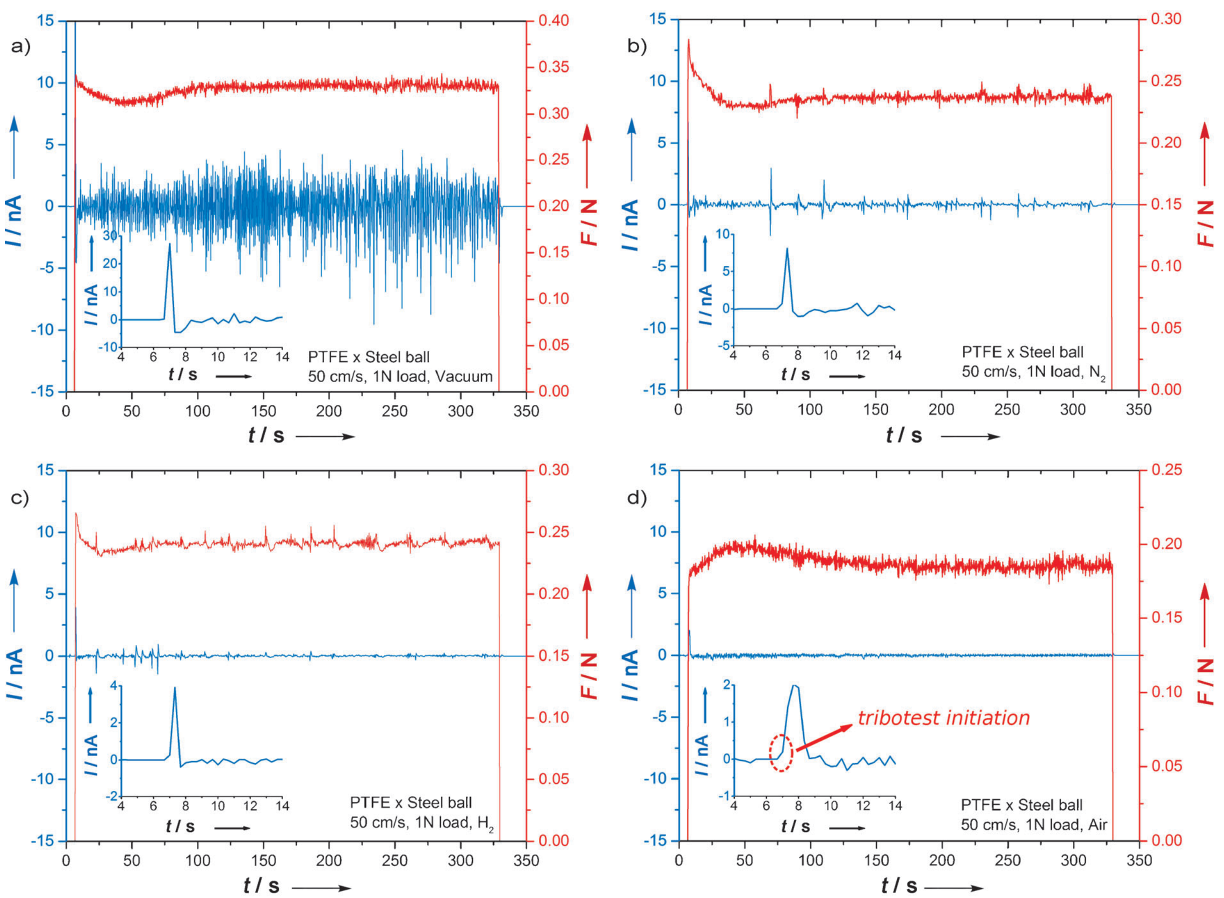

Figure 2. Tribocurrent (blue) and friction force (red) measurements for a PTFE surface and a steel ball under a) high vacuum (10^{-7} bar), b) nitrogen or c) hydrogen atmosphere, and d) in open air. Tribocurrent curves are shown at the center with a zero reference on the left-hand side, and friction forces are shown at the top with reference scales on the right-hand side. Under non-vacuum conditions, the electric current is dramatically reduced, as the triboplasma generated by mechanical stress at the interface is consumed by mechanochemical reactions, triboluminescence, corona charging reactions, phonons, and heating propagation. The inset graphs show the current signal for the very first cycle (see also the Supporting Information).

attached, where a metallic ball was connected to the electrometer through a low-noise triaxial cable.

The friction forces and tribocurrents that were recorded simultaneously by sliding a steel ball on a PTFE surface under various gas atmospheres are shown in Figure 2. Initially, the electric current response occurred immediately when the ball touches the disc surface, and it was highly dependent on the atmosphere. The highest currents were measured under vacuum, but the tribocurrent signal is dramatically reduced under nitrogen atmosphere, and it is even more attenuated under reactive atmospheres, such as hydrogen or air. In vacuum, a great amount of the high-energy species that had been formed by mechanical stress were turned into electrical current. Nevertheless, when reactive atmospheres were introduced, some of the triboplasma generated could be consumed by redox reactions,[8b] triboluminescence,[23] and corona reactions with gaseous species.[24] All of these extra factors are energy consumers, which lead to a decrease in the amount of charged species that are exchanged between PTFE and the steel ball, but refine the tribocurrent signal.

The inset graphs in Figure 2 show the electric current generated during the very first rubbing cycle, when the metallic ball is sliding on a pristine PTFE surface. The first cycle registers the highest tribocurrent values with sharp peaks that reach 30 nA in vacuum, 8 nA in N_2, 4 nA in H_2, and 2 nA in open air. The electric current measured during the first cycle is important because it helps to understand how much the atmosphere influences the tribological experiments. Coincidentally, the friction force also usually reaches the highest values during the first cycle of the tribological tests. The tribocurrent generated varies intermittently between positive and negative values (see Figure 2b–d and Figure 3a); this means that the direction of the flow of charges is constantly altered. On the other hand, this bipolar electric signal is only observed when there is an oscillation of the friction force at the same time. Although the tribocurrent signal depends on speed and load, the charged species per force ratio does not appear to change significantly (10 μC/N under N_2 atmosphere). In other words, this means that tribocharging is highly correlated to the friction force fluctuation events, and for each unit of force, approximately 6.24×10^{13} charged species are exchanged at the interface (see the Supporting Information).

Friction force fluctuations occur with a certain regularity in tribological tests, and Singer et al. have shown that this effect is generally caused by the presence of third bodies (material transfer).[25] As seen in Figure 3b, after the tribological tests, macroscopic flakes or residues of PTFE were strongly adhered to the metallic surface, but only on the “tail” of the sphere, which means that the PTFE seems to stick only after the ball slipped on the surface. In fact, material transfer has also been pointed out to be playing a key role in triboelectrification,[5e,6c] and herein, we show that friction force fluctuations are always followed by two tribocharging steps: first, an extra flow of electric charges from the ball to the PTFE and then a second flow in the opposite direction. We speculate that during mechanical stress of metallic bodies, electrons flow from compressed regions to extended ones, so that the Fermi level remains the same.[26] Consequently, extended regions feature a high density of negative charges; these excessive electrons should be injected into the PTFE surface, as confirmed by the negative sign of the electrical current. Also, PTFE (which has a tendency to acquire negative potentials during contact electrification because of mechanochemical reactions)[8b] must re-transfer negative charges to the metallic ball (mostly by material transfer), resulting in the positive current signal measured by the electrometer. Van der Waals interactions, Coulombic forces and chemical bonds must be formed at the interface when the metallic ball is sliding on the PTFE surface,[8b,27] which instantly increases the contact area, directly reflecting on the macroscopic friction force. Coulombic forces that arise from triboelectrification must play an important role in contact mechanics, but neither the JKR nor the DMT theories are capable to describe this contribution because of the complexity of the triboelectrification phenomenon.

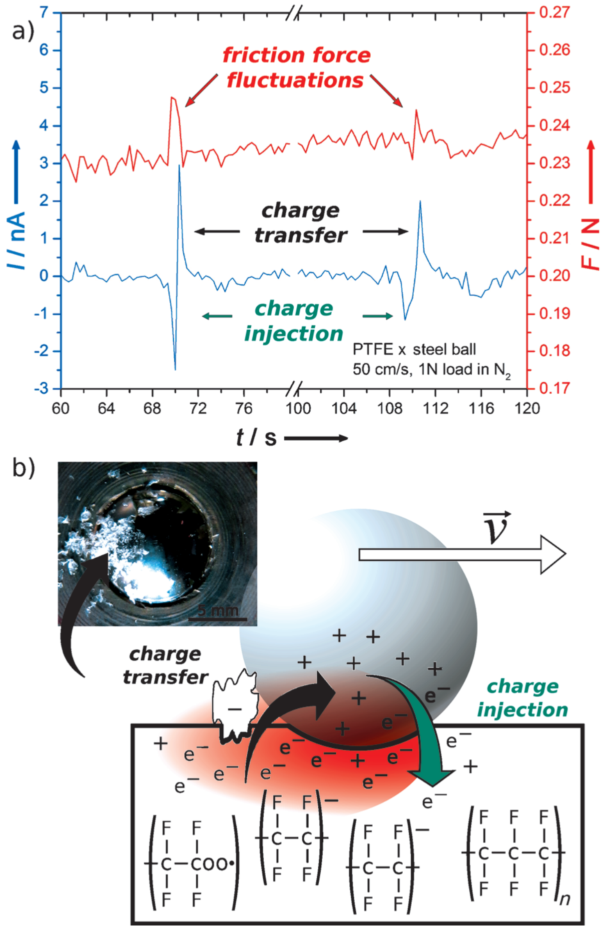

Figure 3. a) Friction force fluctuations and tribocurrent generation at the metal–PTFE interface and b) schematic representation of the underlying mechanism. Initially, electrons are injected into the pristine PTFE, where the mechanical stress leads to rupture of PTFE bonds, thus forming free-radical species and triggering mechanochemical reactions. A part of the charge build-up on PTFE is transferred (by material transfer) to the steel ball resulting in a positive current, so that this bipolar tribocurrent signal is always accompanied by a transient increase in the friction force signal.

The adhesive component of the force–distance curves is not larger than 10 nN on clean PTFE,[20b] and this is one of the reasons why PTFE has such a low-energy surface and does not easily stick to other materials. On the other hand, as can be seen in Figure 4 (see also the Supporting Information), the

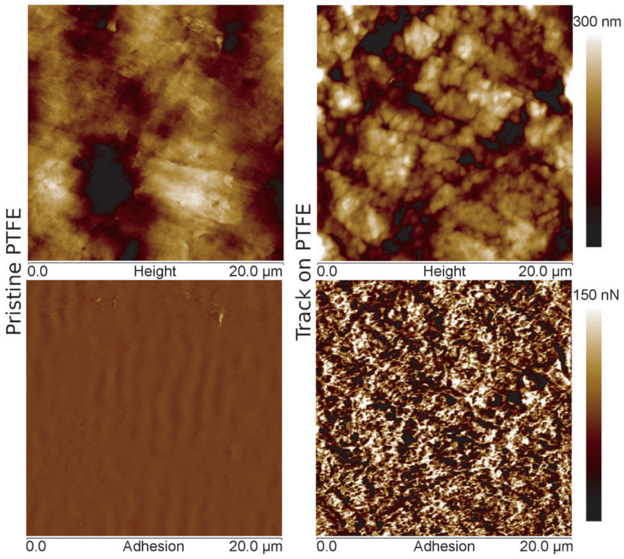

Figure 4. Topography (top) and adhesion (bottom) maps of pristine and tribotested (N_2, 2N load, and 50 cm s^{-1}) PTFE obtained using the PeakForce Quantitative Nanomechanical mode (PKQNM). Force–distance curves can be found in the Supporting Information.

groove on tribotested PTFE has adhesion values that reach 150 nN, which is characteristic of tribocharged surfaces.[20b] This range of adhesion forces is comparable to those observed for geckos: Each little hair in their paws leads to an adhesion of 100 nN because of van der Waals and capillary forces.[28] As most of the pixels along the tested PTFE surface have attractive forces greater than 150 nN, strong electrostatic adhesion occurs through the interface, which explains how PTFE flakes stick to the metallic ball (Figure 3 b). Moreover, strong electrical fields created at the interface as a result of charged domains are used for energy dissipation.[29] The electrical fields are also responsible for triboemission processes, where charged particles can be accelerated thus exciting gas atoms (producing luminescence) and emitting bremsstrahlung radiation[4a] (see the Supporting Information).

Other tribocurrent measurements have recently been reported,[19,30] but for the very first time, such a strong and clear signal was correlated to the friction force, allowing us to show in situ how tribocharges, an extremely challenging phenomenon, are built up and exchanged at the interface by mechanochemical reactions. The overall picture that emerges from this study suggests that friction force and tribocharges have a common microscopic origin as they vary concurrently and with similar rates, depending on the test conditions.

Finally, as metal–insulator interfaces undergo triboelectrification and subsequent charge transfer to a passing AFM tip, which results in large electrostatic forces,[31] the use of contact modes, such as friction force microscopy (FFM), could be combined with techniques for monitoring the triboelectrification of surfaces, for example by measuring the tribocurrent, which would result in a powerful complementary method to AFM.

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