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Singh, Shailendra Vikram; Kusano, Yukihiro; Morgen, P.; Michelsen, Poul

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Triboplasma: generation, characterization and application for surface modification

S. V. Singh¹, Y. Kusano¹, P. Morgen² and P. K. Michelsen¹

¹ Risø National Lab. for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

² University of Southern Denmark, Dept Chemistry & Physics, Faculty of Science, DK-5230 Odense, Denmark

Evidence of electrostatic charging, charge decay, and uniquely, gas breakdown-like incidences at a sliding contact using a simple non-contact electrical probe is presented. Measurements show that the ball track acquires non-uniform tribocharging because of preferential charging at some regions. Here not only the increase in charge density, but interestingly, increase in number of highly charged regions on the ball track was resolved. We are also able to comment on the behavior and the tribocharge decay time in the ambient air-like conditioned surrounding. Furthermore, triboplasma has been applied to study its influence for the surface modification on polyester.

1. Introduction

A sliding contact of dissimilar surfaces induces vivid tribophysical phenomena [1-3]. Among them tribocharging and triboplasma generation have attracted considerable technological interest in, e.g. the studies related to wear, lubricant decomposition, and surface modification [4-9]. The nature of tribological processes involving tribocharging and subsequent generation of triboplasma highly depend on the interacting materials and on the intensity of the contact, area and surrounding of the interaction. Here, the intensity of the contact involves the load at the contact and the sliding speed.

A physical mechanism behind tribocharging is still unknown, although an empirical classification scheme “triboelectric series” is available [10]. The triboelectric series classifies distinct materials in the order of their charge-acquisition tendency due to rubbing. The order of the triboelectric series can be affected by molecular level interaction at the contact. However, the ordering in the triboelectric series is different in different databases [11]. Triboelectrification may also occur even when the same materials with differing surface morphology are rubbed together. This can induce asymmetric heating, and consequently asymmetric charge supply. Other properties at the contact surfaces can also affect the order of the triboelectric series, including presence of water, oxides, hydrocarbons, and small particles, yield strengths of materials [12,13,14], and surface damage [15].

These tribological conditions directly affect triboelectrification and subsequent generation of a triboplasma. Interestingly, the cause of triboplasma generation has also been under discussion [2, 16, 17]. In this context, a plausible explanation for the ignition of a triboplasma is the generation of a high local electric field as a result of tribocharging by the

charge separation of opposite signs on the sliding surfaces [16]. This assumption of triboplasma generation has been supported by studying optical emissions at the sliding contacts [2, 5, 6, 18, 19]. The optical emissions are observed mostly in the ultraviolet region. As these measurements were performed in ambient air, the emissions were dominated by nitrogen emission lines. These measurements however, do not contribute to the understanding of the tribocharging. The tribocharging of such sliding contacts are often measured by using electrostatic probes [8, 20]. These probes are coupled to the circuits through non-contact arrangements to measure tribocharging on the rotating disks of pin- or ball-on-rotating-disk experimental setups.

Here generation, characterization and application of triboplasma are presented. A ball-on-rotating-disk setup was used to generate sliding contact and a non-contact electrical probe was installed above the rotating plate to study tribocharging and triboplasma. We have been able to resolve change in tribocharge level and its evolution on the ball track. A gas breakdown-like incidence has also been evidenced. Dedicated experiments to study tribocharge decay time in the ambient air were performed. In connection to the technological application of the triboplasma, we have been able to successfully demonstrate the effect of triboplasma for polyester surface treatment. The analysis of the samples using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) spectroscopy showed slight modification of the triboplasma treated surfaces.

2. Experimental setup

The ball-on-rotating-disk setup utilized here is discussed in details elsewhere [21]. Briefly, the

schematic diagram of ball-on-rotating-disk setup utilized is shown in Fig. 1 (a). Here the sliding contact is created between the (unidirectional) rotating plate and the steady spherical ball. The disk can rotate up-to $V = 1000$ rpm, and a normal force of up-to $F_N = 8$ N could be applied on the steady ball. One revolution corresponds to a length of around 6.25 cm (i.e., sliding speed of around 62.5 cm/s). Stainless steel, diamondlike carbon (DLC) coated stainless steel, and teflon (Polytetrafluoroethylene, PTFE) 10 mm spheres have been used as balls, whereas 2 to 3 mm thick glass, sapphire, teflon, and polyester has been used as a disk material.

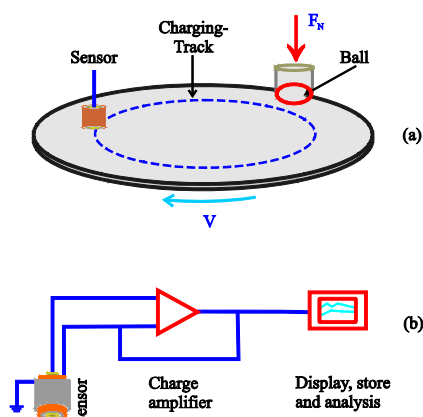


Figure 1. Schematic of (a) ball-on-rotating-disk setup (b) non-contact probe.

These sliding contact materials were chosen with the help of available triboelectric series with intent to achieve high opposite charges once brought in sliding contact. To study tribocharging and gas breakdown effect, a homebuilt capacitive non-contact electrostatic probe was used; see Fig. 1 (b) [21]. The probe was staged (depending on the conditions) 0.8 - 1.1 mm above the disk and 180° opposite to the scratching ball as shown in Fig. 1(a). These measurements were performed by monitoring the tribocharging on the disk. The probe is only sensitive to the change in the charge density. Hence once the disk was at rest, the signal was zero [8]. Whereas, the probe signal was non-zero above the rotating plate, even without sliding contact, due to minor surface irregularities. The probe contains a homebuilt sensor and a charge amplifier which is directly connected to an oscilloscope (Tektronix DPO7104). The probe is made up of 8 cm long bulk coaxial cable RG402/U. The 0.9 mm diameter inner conductor is used as the probe tip, separated by teflon from the 3.6 mm outer-diameter copper shield. The sensor circuit is similar to a capacitor divider, which is surrounded by a grounded shield. The probe is then connected via a charge amplifier

(frequency response up-to 300 MHz, sensitivity 0.45 V/pC, and rise-time < 30 ns) to the oscilloscope. Through this combination high sampling rates were achieved, and consequently, highly resolved measurements (up-to 500 ns at sample rates of 2 MSa/s) could be performed on the charging track.

These measurements were performed in a conditioned box (80% N₂, 20% O₂, 35 - 45% relative humidity at 20 °C). Moreover, in comparison to the conditioned box, no noticeable difference was observed in open air with relative humidity as large as 35 to 55 % and at temperature 20 - 22 °C. The signals strength was 7 to 10% lower at high humidity around 55% than at around 35%.

3 mm thick polyester plates were treated by triboplasma to study surface modifications, where DLC coated 10 mm steel balls were used for the treatment. They were cleaned before plasma treatment, see method in Ref. [22]. The treated surfaces were studied by XPS. Where data were collected using a double anode (Mg/Al) source, and for the present measurements the Mg K_α line with an energy of 1253.6 eV was used, with a lateral resolution of 2 mm to study the changes in elemental compositions and the functional groups on the polyester surfaces. Atomic concentrations of all elements were calculated by determining the relevant integral peak intensities subtracting a Shirley-type background. A high-resolution analysis was performed on the carbon 1s (C1s) peak (pass energy 40eV) acquired over 3 scans. The accuracy of the measurement is estimated to be better than 2 %. The binding energies were referred to the hydrocarbon component (C-C, C-H) at 285 eV. The spectra were de-convoluted through curve fitting, taking purely Gaussian components with linear background subtraction. The instrumental full-width at half-maximum for all peaks of C1s was 1.6 eV which is the resolution of the spectrometer as well as the X-ray source. The fitted components had larger widths than this. Some of the widening of the peaks is due to various energy-loss phenomena at the polymer surface [23].

3. Results and discussion

The measured probe signals were bipolar in nature. Principally, once a charged part passes the sensor face an opposite charge will be induced on the sensor active area. The current induced by the appearance of the opposite charge will be measured. The bipolar nature is attributed to nonuniform charging on the surface. The preferential charging at certain places on the disk depends on the surface morphology and impurities. For example, in case of sliding contact between glass plate and teflon ball,

the probed glass plate will accumulate positive charge. Resulting into in Fig.2, the positive currents (maxima) correspond to the accumulated positive charge on the plate, whereas the negative currents (minima) correspond to the adjacent uncharged or

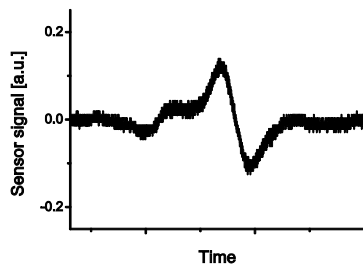


Figure 2. Bipolar signal from the electrostatic probe.

relatively less charged region. Hence, positive and negative currents indicate that the monitored location has higher and lower charge densities than the neighbouring location monitored just before, respectively. Furthermore a bipolar signal, a positive peak immediately following a negative peak, indicates an isolated highly positively charged region. Note that any comment on increase/decrease in tribocharge level in the present work is mainly based on relative increase/decrease in highly charged regions compared to the neighboring less charged regions.

Our results of long measurements could be divided into several regions on a broader scale, as was the case in the literature [4, 7, 8]. Among all, a noticeable region was the one immediately after the test started, dominated by running-in process [8]. The running-in (20 ± 3 s) had distinctive two segments however, time frame of the two regions was not reproducible [21].

Tribocharging and occasional discharge can be seen in the long (time/distance) measurements for teflon ball and glass plate combination, see Fig. 3. Note that Fig. 3 is recorded after ~ 20 s of running-in. However, before going into the detail of these experiments, here the charge decay time in the ambient air-like environment was also studied. We noticed that any abrupt discontinuity in sliding contact will not bring an instantaneous decrease in the bipolar signal (tribocharge level). For example, after discontinuing the sliding contact (with teflon ball), decay time was measured for the tribocharge on the glass and sapphire. The decay half life was around 1 second for glass and more than 10 seconds for sapphire. Note that there are several channels where tribocharge can neutralize or diffuse. This can be affected by the resistivity of the material, surface energy, water content, surface impurities, but most

essentially by the surrounding experimental conditions [24, 25].

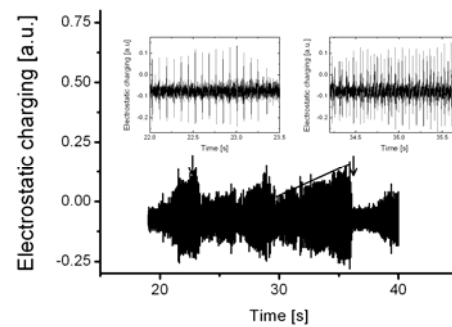


Figure 3. Measurements after running-in demonstrating electrostatics and slow as well as instantaneous discharge. Inset (left): shows increase in signal strength and with two noticeable fluctuations per cycle before the slow disappearance of charge. Inset (right): shows increase in signal as well as threefold increase in the fluctuations per cycle immediately before the instantaneous discharge.

Coming to Fig. 3, the increase in tribocharge level with time of interaction can be obviously noticed for the incidences starting at 20 s and at 30 s, respectively. The difference in the rate of charging is noticeable. No reproducibility on this could be obtained. However, the most striking events were where continuous increase in charging (starting at ~ 30 s) was abruptly followed by significant decrease in the signal (at ~ 35.6 s). Based on tribocharge decay experiments, any abrupt decrease in charging (charge level) could only be explained by the process where the accumulated charge is neutralized effectively and promptly. We believe that the observed abrupt decrease in charge level in Fig. 3 at ~ 35.6 s might be due to gas breakdown. The way of discharging after the peak at ~ 35.6 s is distinctively different from that of at ~ 23.3 s and ~ 28 s. As after ~ 23.3 s and ~ 28 s, the charge decay is relatively slow ($t_{1/2}$ of ~ 0.4 s to that of ~ 0.1 s after 35.6 s).

Though the strength of the bipolar signal has been comparable at around 23.3 s, 28 s, and 35.6 s; thorough study reveals contrasting evolution of tribocharge on the ball track in the vicinity of these time frames. The tribocharge evolution close to 23.3 s and 28 s is contrastingly different to that of close to 35.6 s, see Insert (left) and Insert (right). These inserts are zoom-in at ~ 23.3 s and ~ 35.6 s, respectively. Comparison of graphs in Insert (left) and (right) indicates that the number of bipolar current increased almost three-times per cycle before the abrupt breakdown at ~ 35.6 s. The number of bipolar current indicates two adjacent regions with distinct level of charging on the ball track, whereas the positive strength of the signal indicates the relative increase in charge density of the highly

charged regions [20, 21]. Almost threefold increase in the number of bipolar current per cycle demonstrates proportionate increase in the highly charged regions on the track. Based on this we tentatively propose that the charge density has significantly increased through the ball track before the breakdown situation (~35.6 s) as compared to other slow decays. Independent to that, the high charge density and the increase in highly charged regions followed by abrupt fall in signal due to gas breakdown corroborate each other.

To study surface modifications due to triboplasma diamond like carbon coated (DLC), 10 mm steel balls were used. The surface treatments were performed on polyester disk samples. The triboplasma effect was evidenced by XPS and EDX. XPS analysis shows the decreasing trend in oxygen to carbon (O/C) ratio with increase in treatment time (30 s, 60 s, 120 s and 240 s). Furthermore, deconvolution of C1s peak [23, 26] indicates decrease in assignment corresponding to C-H/C-C at 285 eV and carboxyl at 289.5 eV with increase in treatment time. Whereas, C-O-C/OH at 286.5 eV decreased with increasing treatment time.

4. Conclusions

Tribocharging, charge decay, and uniquely, gas breakdown-like incidences at a sliding contact using a non-contact electrical probe is evidenced. These measurements were performed by monitoring the charging/ball track on the disk surface of a ball-on-rotating-disk apparatus for several material contacts. For a glass disk and a teflon ball arrangement the increase in tribocharge density, but interestingly, increase in number of highly charged regions on the ball track was resolved. Threefold increase in the number of such highly charged regions per cycle was measured immediately before the gas breakdown-like incidences compared to that of other tribocharge/discharge incidences at a fixed disk rotation speed. Furthermore, we have been able to perform triboplasma treatment on the polyester surfaces, which were supported by XPS measurements.

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