Contact Electrification

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Is Water Necessary for Contact Electrification?**

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Contact electrification (CE)[1] is a phenomenon whereby charge develops on two surfaces that are brought into contact and then separated. CE has long been applied in several useful technologies including photocopying,[2] laser printing,[3] and electrostatic separations,[4] but its mechanism, despite history of research dating back to Thales of Miletus, remains poorly understood. Numerous studies focused on the molecular aspects of CE. An ion transfer mechanism was proven for contact electrification of ionic polymers[6] while an electron transfer mechanism was proposed[5] for nonionic polymers based on a method involving a reaction of a contact-electrified polymer with an electron receptor in the surrounding solution. Recently, we[7a] and others[7b–f] have also considered the effects of the atmosphere and relative humidity (RH) on CE. To date, the results of these studies have proven inconclusive suggesting that depending on RH and the properties of contacting materials, water contained in air can either promote or inhibit CE.[7a,8] These studies have been summarized by Whitesides and co-workers,[9] who proposed that CE is based on the transfer of physisorbed OH^- ions and is therefore dependent on—or at least promoted by—the presence of water. While interesting in concept, this scenario requires further verification since experimental techniques used so far do not completely eliminate water from the atmosphere around the contacting materials. In other words, to assess the role of water in CE, water-free conditions should be realized: if charge separation is then not observed, CE could indeed be attributed to the presence of water. In such experiments, the water-free environment should be maintained at all steps of the procedure including material preparation, contact, and subsequent handling and measurement of the developed charges. Since performing these operations in ultra-high vacuum chamber is impractical and since lower vacuum compatible with the glove-box environment does not ensure complete absence of water, we have developed a system in which CE can be studied in a water-free environment under a highly non-polar liquid (paraffin oil dried with molecular sieves and sodium, and maintained under dry, inert atmosphere) (Figure 1 a). As we show here, under these conditions, CE between non-elemental insulators is still observed, indicating that the presence of water is not critical for charge separation to occur. On the other hand, since the magnitudes of the developed charges are slightly smaller than those observed in air, we surmise that water, due to its high dielectric constant, helps stabilize these charges.

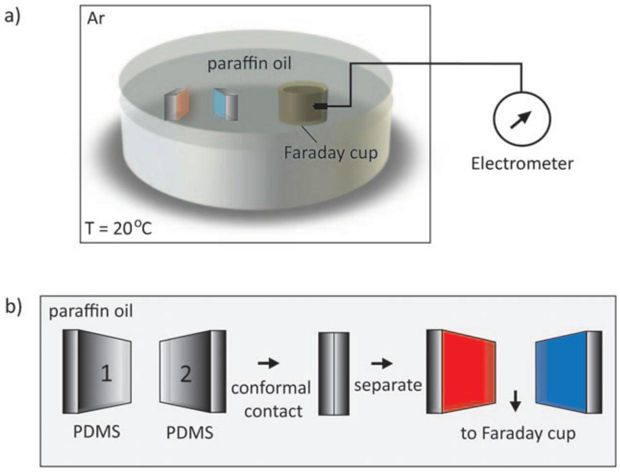

Figure 1. a) Illustration of an experimental setup in which the contacting pieces as well as the Faraday cup used for charge measurements are immersed in dry paraffin oil. The entire assembly is housed in a glove-box under inert atmosphere. b) When polymer pieces (here, PDMS) are touched and separated under paraffin oil, they still develop charges of opposite polarities.

The experimental arrangement is illustrated in Figure 1 a. A large oil bath (2 L) was filled with paraffin oil (puriss., Sigma–Aldrich), which was dried with molecular sieves for several days and then filtered (all procedures were performed under Ar). Although Karl Fischer[18] analysis showed that already at this stage the content of trace water was below the detection limit (few ppm), the oil was further dried using finely dispersed sodium ($3.75\,g\,L^{-1}$ of oil) at 100 °C under argon (*Warning: Sodium is extremely explosive in the presence of water!*). Drying with sodium continued for a week and its progress was monitored by the amount of hydrogen evolved (using a Crowcon Triple Plus, hydrogen detector, 0–2000 ppm H_2). After this time, no evolved hydrogen could be detected. Dried oil was kept in a glove-box maintained under a flow of high-purity, dry Ar at all times. A house-made Faraday cage (connected to a Keithley 6517B high-precision electrometer) and tweezers for manipulating the polymeric pieces were dried at 80–100 °C for at least 48 h, and were then completely immersed in the hot, dried oil bath. The entire system was kept at 80 °C and under Ar flow for another 48 h and was then allowed to cool down to the ambient temperature (20–25 °C), all the time under inert atmosphere in a glove box.

The polymers used in our experiments were polytetrafluoroethylene (PTFE, McMaster-Carr, CAT# 8545K26), polycarbonate (PC, McMaster-Carr, CAT# 8574K172), and polydimethylsiloxane (PDMS, Dow Corning, Sylgard 184).[19] While all combinations of these materials gave similar results (i.e., they separated charge under paraffin oil), the degree of CE was most readily quantified for pairs in which at least one piece was made of PDMS, which during CE comes into conformal contact with other materials (including PDMS itself). We verified that the charges developed by contact electrification did not depend on 1) the time of contact (for times 2 s to 1.5 h); 2) the pressure applied during contact (0.01–4.5 MPa); 3) the elastic properties of the PDMS (varied by changing the curing times from 24 to 96 h, range of Young's

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moduli 360–2000 kPa); and 4) the way in which the surfaces were separated (i.e., rapidly or slowly peeled off one another).[10]

PDMS pieces were prepared by casting the prepolymer/crosslinker mixture against atomically flat silicon wafers and curing under vacuum overnight at 65 °C.[11] After further heating at 120 °C for 24 h, the wafers supporting the PDMS were placed into the warm, dried paraffin oil (again, all operations were performed in a glove-box under argon). Afterwards, PDMS was cut into ca. 1 × 1 × 0.5 cm blocks (under oil) that were then peeled off the wafer, and were brought into contact with one another and then separated. During contact, the dewetting of paraffin oil from between PDMS pieces was clearly visible and these pieces readily "snapped" into conformal contact (also see Ref. [12]). The pieces were touched $n = 1$–250 times and were then transferred—still under oil—into the oil-immersed Faraday cup, which measured the magnitude of the accumulated charges on the pieces. The reliability of measurements in the Faraday cup filled with paraffin oil was confirmed by measuring the charges of objects previously placed in a "regular" Faraday cup in air. Also, for all materials described here, we performed additional, control experiments in which CE was performed under ambient atmosphere (i.e., in air, typical RH ca. 40 %). In air, the measured charge densities, ca. 0.5–4.0 nC cm^{-2}, were in general agreement with the previously reported values.[1bc,20]

The open markers in Figure 2 illustrate charging—that is, the magnitudes and polarities of the accumulated charges, Q, as a function of the number of touches, n—for different materials touched against PDMS under paraffin oil immersion. Clearly, all materials exhibit contact electrification. For comparison, solid markers give the charging curves recorded in air, in the presence of atmospheric water (RH ≈ 40 %). As seen, the degree of CE under water-free conditions is commensurate with but typically smaller than that observed in the presence of water. Thus, we conclude that water is not necessary for CE although it has effect on the magnitude of the measured charges.

We hypothesized that the differences in charge magnitudes observed under oil and in the presence of atmospheric water could be due to the different abilities of these media to stabilize charge. Stabilization and dissipation of surface charge by atmospheric water is an old problem[13–15] dating back to Schrödinger's doctoral thesis.[13] In a recent study by Cao et al.,[16] rapid (i.e., faster than in the air) decay of charge in the presence of water was used for selective patterning of PMMA surfaces. In at least two other fundamental studies on the effects of RH on the degree of contact charging, it was observed that atmospheric water can promote CE[7c] and cause a reorganization of a charged polymeric surface[7a] (provided that the water layer is not continuous/percolated allowing for "lateral" charge dissipation, see[7a]). On the other hand, these experimental observations did not resolve whether water is per se necessary for CE to occur or whether its role is to stabilize the developed charges. (e.g., by virtue of charge solvation).[17] In an attempt to resolve this issue, we monitored the decay of surface charge developed by CE under oil and in air as a function of time. Curves for PDMS/PDMS pair in Figure 3 a confirm that although immediately after charging the magnitudes of either positive or negative charges are commensurate for oil-immersed and air-exposed surfaces, the former dissipate charge much more rapidly. The linearity of the semi-log plots in Figure 3 b indicates that while in both cases the decay kinetics is first-order, the characteristic rate constant in air is approximately 0.001 s^{-1} vs. 0.01 s^{-1}

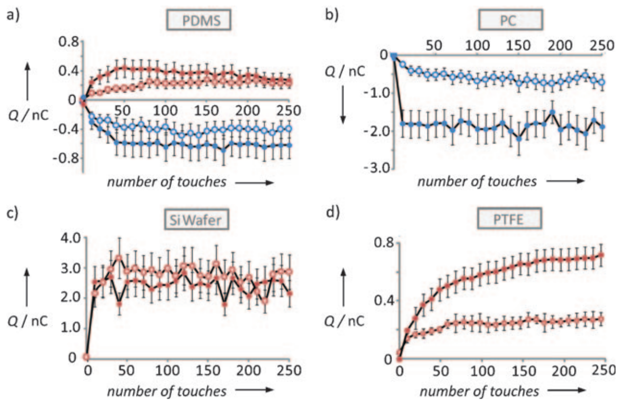

Figure 2. Typical charging curves recorded when PDMS is contacted against the materials indicated in the insets. In (a) charging curves for both contacting PDMS pieces (i.e., one charging positively and one negatively; see ref. [10]) are shown. In all cases, the area of contact was 1 cm × 1 cm. Open markers correspond to experiments conducted under oil; solid markers give results of control experiments performed in air. Red = positive charges; blue = negative charges. Error bars give standard deviations from at least five independent experiments for every condition. Times from CE to charge measurement in a Faraday cup were 1–2 s each.

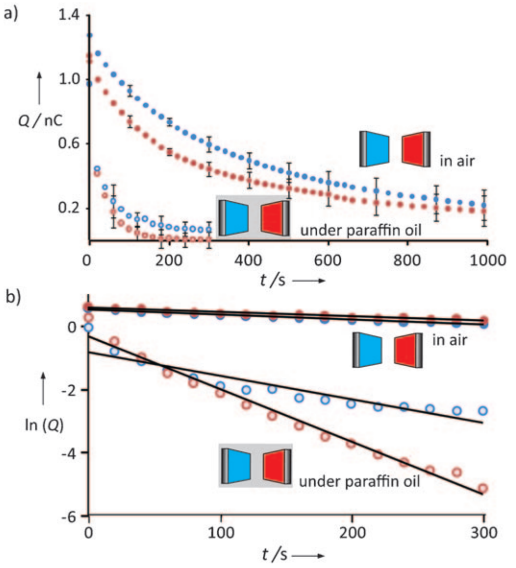

Figure 3. a) The magnitudes of charges on the negatively (blue) or the positively (red) charged PDMS pieces decay faster in paraffin oil (open markers) than in air. The decay rate constants are determined from the slopes of the semi-logarithmic plots in (b). In paraffin oil, these rate constants are 0.016 s^{-1} for a "+" piece and 0.007 s^{-1} for a "−" piece. In air, they are, respectively, 0.0016 s^{-1} and 0.0014 s^{-1}. Error bars correspond to standard deviations determined from at least six independent experiments for every condition.

under oil. We note that even more pronounced differences are observed for other polymers tested (see Supporting Information, Figure S1), where the rates of charge dissipation under paraffin oil are typically on the order of 0.01 s^{-1} vs. 0.00001 s^{-1} under humid atmosphere.[22,23c] These results suggest that charge stabilization by water is largely independent of the nature of the contact-electrified polymeric surface.

We suggest that the difference in the charge decay rates can be attributed to the different abilities of water and the paraffin oil to stabilize surface charges developed by CE. Under ambient conditions, polymers are known to harbor surface water layers, in which charges can be stabilized/solvated in polaronic states.[23a,b] While these charges can, potentially, be dissipated "laterally"[23c] through surface conductance, previous studies suggest that for dielectrics, this conductance—and concomitant discharge—become important only at significantly higher RHs,[7a] likely when the water layer percolates and becomes continuous. The other potentially important mode of charge dissipation is by the collisions with the surrounding molecules ("external decay")—this effect, however, gives rise to only slow discharging, unless there is a systematic flow of gas above the polymer surface.[23c] In contrast, under dry non-polar oil, polaronic stabilization of surface charge is not operative. In the absence of such stabilization, charge can transfer more readily to the surrounding liquid (especially that the collisions with the oil molecules are more frequent than with the "sparse" molecules/ions contained air; ca. 3×10^{21} molecules cm^{-3} in paraffin oil vs. 2×10^{19} in air). This mode of charge dissipation is consistent with the observation that when a charged polymer piece is moved under paraffin, discharge rate increases dramatically (full discharge occurs in roughly in 1 s). By moving the piece, one effectively increases the flux of the paraffin molecules at the polymer's surface (overcoming diffusional limitations), and thus facilitates the transfer of surface charge to the oil.

The conclusions of the present work are therefore twofold—on one hand, contact electrification does not require the presence of water to occur. On the other, water helps stabilize the surface charges developed during CE. In the context of the effort to control static electricity in many industrial applications, it becomes evident that the presence of air humidity does not necessarily guarantee rapid charge dissipation and that—contrary to common belief dating back to Thales' amber-against-wool experiments—low-humidity conditions might indeed limit CE charging more efficiently than humid ones.

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