

Effects of Surface Modification and Moisture on the Rates of Charge Transfer between Metals and Organic Materials

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This report is a study of the kinetics of contact charging resulting from the rolling of millimeter-sized metallic spheres on flat surfaces of polystyrene (PS). Charging was studied (i) for different values of the relative humidity (RH) of the air in contact with the system, (ii) in acidic and basic atmospheres, and (iii) for a series of PS surfaces oxidized to different degrees. The rates of charging *increased* with increasing RH; they were higher in basic atmospheres than in neutral or acidic ones and correlated with the numbers of hydrophilic groups on the surface of the polymer. These findings are consistent with a mechanism that implicates a thin film of water on the surface of PS as an important element of tribocharging in this system.

Introduction

The transfer of charge that occurs when two surfaces are brought into contact (with or without friction), and then separated, is known as contact electrification.^{1–4} Although contact electrification is central to many important processes, such as electrophotography⁵ and electrostatic separation technologies,⁶ the mechanism(s) of charge transfer is (are) not understood.^{7,8} The mechanism of contact charging of organic materials by metals at the level of molecules and molecular orbitals is especially ill-defined and has been variously postulated to be due to the transfer of electrons, or ions, or both.^{9,10} Even the origins of phenomena such as the influence of humidity on contact electrification of organic materials (generally, less charging is observed at high humidities) are not completely understood. Understanding how humidity affects contact charging would not only help to frame discussions of mechanisms but might also have practical ramifications (e.g., optimizing the design of toners used in electrophotography).¹¹

We have recently described a versatile and sensitive tool for the in situ noninvasive measurement of contact charge that develops on metallic spheres that roll on dielectric surfaces.¹² Using this tool, we quantified the contact charging of metallic spheres rolling on the surfaces of polymeric slabs and generated an internally consistent set of data. These data included the polarity and magnitude of charging for a homologous series of polymers that differed in the groups attached to an all-carbon (polyethylene) backbone. Quantification of the rate and extent of charging of different materials allowed us later to rationally design two systems in which contact electrification mediated the dynamic self-assembly of the components into extended structures.^{13,14}

A particularly attractive feature of our technique (and one that we have not exploited fully in previous work) is its ability

to monitor the *kinetics* of accumulation of charge on a sphere in contact with a dielectric surface. Here, we study the kinetics of charge transfer between rolling metallic spheres and flat surfaces of polystyrene (PS). We relate the rates of charge transfer to the relative humidity (RH) of the air in contact with the system and to the degree of surface modification of the polymer (including oxidation of PS that generated up to ~36 atom % oxygen¹⁵ at its surface). Although other workers have suggested that moisture adsorbed on the surface plays a role in contact electrification,^{11,16–18} our study is the first thorough investigation that allows a semiquantitative description of the influence of moisture and surface modification on the rates of contact charging. Specifically, we show that for the metal/PS system, these rates surprisingly *increase* linearly with RH and with the amount of water adsorbed on the surface of the polymer, and they increase with the time of oxidation t_{ox} of the PS surface (and, thus, with the surface density of hydrophilic groups). We suggest that these trends can be explained by the reorganization of the surface of PS in response to the adsorption of water. According to the proposed model, water pulls the oxygen-containing groups out of the bulk of the polymer, allowing them to make contact and exchange charge with the surface of the metallic sphere. This hypothesis is corroborated by experiments (i) in atmospheres of acidic and basic pH's and (ii) on polymeric surfaces on which surface reorganization is irrelevant to charging.

Results and Discussion

Measurement of the Rate of Charge Transfer. We measured the rate of charge transfer between a rolling steel sphere and a flat surface of PS (a petri dish) using the system¹² sketched in Figure 1. A ferromagnetic stainless steel sphere (or a stainless steel sphere with a thin gold coat in a core-and-shell geometry) 1 mm in diameter rolled on a surface of PS under the influence of the magnetic field produced by a bar magnet rotating in the plane of the surface at angular velocity $\omega \approx 1000$ rpm (Figure 1a). The sphere traced a circular path on the surface, and the rate of precession Ω of the sphere was ~20 rpm. The value of

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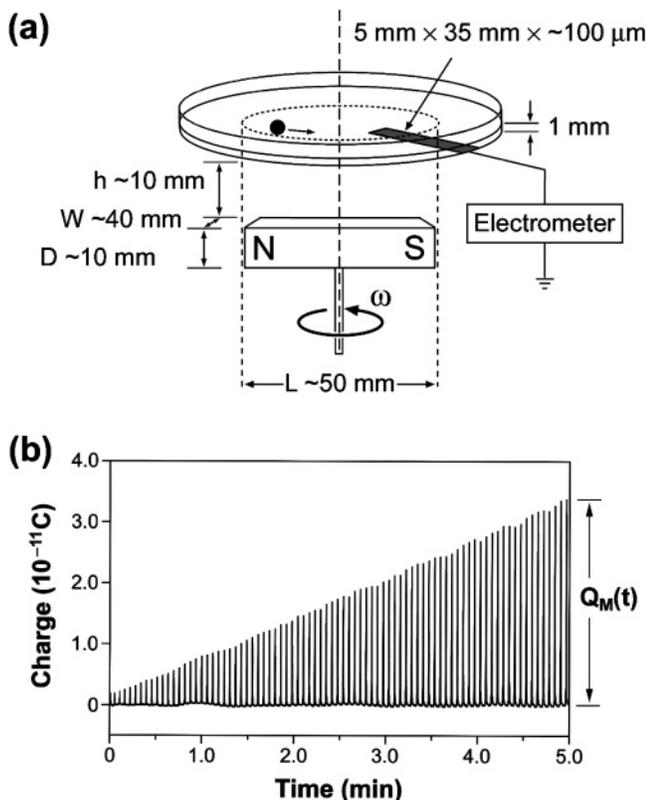


Figure 1. (a) Schematic illustration of the experimental arrangement for quantifying contact electrification. A stainless steel sphere (or gold-coated stainless steel sphere) rolled across the surface of a PS petri dish under the influence of the magnetic field produced by a bar magnet rotating in the plane of the surface at angular velocity $\omega \approx 1000$ rpm. The sphere and surface developed charges of opposite polarity and equal magnitude by contact electrification; the magnitude of the charges increased with time. The charge on the metallic sphere was measured inductively by the charging it induced by capacitive coupling in a thin electrode of aluminum ($5 \text{ mm} \times 35 \text{ mm} \times 100 \mu\text{m}$) placed ~ 1 mm below the surface of the PS petri dish. The charge was detected by an electrometer connected to this electrode and to ground. (b) Plot of the charge on a stainless steel sphere rolling on a surface of PS at 30% RH as a function of time. The upward signals in the plot designate instances when the positively charged sphere was above the aluminum electrode, registering induced charge. The periodic spacing of the signals in the plot corresponds to the time of precession of the sphere on the surface ($\Omega \approx 20$ rpm).

Ω was approximately a linear function of the rate of rotation of the external magnetic field with the constant of proportionality equal to the ratio of the circumference of the sphere (3.14 mm) to the circumference of the circular path the sphere traces on the surface ($\sim 157 \text{ mm}$).¹³ As the metallic sphere rolled across the surface of the PS petri dish, the sphere and the surface developed charges of equal magnitudes and opposite polarities by contact electrification. The magnitudes of these charges increased with time. Figure 1b shows the charge that accumulated on a stainless steel sphere rolling on the surface of PS at 30% RH as a function of time. The height of the signals in this plot is the magnitude of the time-dependent charge induced by capacitive coupling on the aluminum electrode ($5 \text{ mm} \times 35 \text{ mm} \times 100 \mu\text{m}$) on the bottom surface of the dish; the electrode was attached using electrically insulating adhesive tape and was separated from the sphere rolling on the top surface of the dish by ~ 1 mm. The upward signals in Figure 1b demonstrate that the stainless steel sphere was charged positively.

Before each measurement (with the external magnet static), a fresh sphere was placed gently on a fresh PS petri dish, and

any adventitious charge on the sphere and film was neutralized thoroughly by applying negative and positive ions from a corona discharge using a Zerostat piezoelectric antistatic device.¹⁹ The rotation of the magnet was started. Every time the charging sphere rolled (under the influence of the external magnet) across the surface of PS above the aluminum electrode, it induced charge Q_{Ind} on this electrode. The interval of time between each signal in Figure 1b corresponds to the time required for the sphere to make one circle around the PS surface. The charge Q_{Ind} on the electrode was measured (as Q_{M} , where $Q_{\text{M}} = -Q_{\text{Ind}}$) by a digital electrometer connected to the electrode and referenced to ground.²⁰ This procedure involved differential measurement (i.e., the charge Q_{Ind} on the electrode as a function of time was obtained from the height of the signals, Q_{M} , in Figure 1b). The charge Q_{M} measured by the instrument depicted in Figure 1 was $35 \pm 6\%$ of the actual charge, Q_{S} , on the sphere measured independently by a Faraday cup¹² (i.e., $0.35 \pm 0.06Q_{\text{S}} = Q_{\text{M}} = -Q_{\text{Ind}}$). The precision of the measurement was estimated to be ~ 5 – 10% by comparing the heights of the signals over a short period of time in a typical plot of $Q_{\text{M}}(t)$ (e.g., Figure 1b).

The kinetic data were acquired until the charge accumulated on a sphere was such (typically, $\geq 8 \times 10^{-11} \text{ C}$ or $5 \times 10^8 \text{ e}$) that the attractive electrostatic force between the sphere and the PS support exceeded the motive force exerted on the sphere by the rotating magnet. At that time, the sphere stopped rolling and adhered to the surface.

Using the rolling-sphere setup, we performed a series of experiments that allowed us to relate the rates of contact charging to the composition of the surrounding atmosphere and to the properties of the surface of the polymer. The results of these experiments are summarized in the following text.

The Initial Rate of Charging of a Stainless Steel Sphere Rolling on PS Increases Approximately Linearly with RH.

The entire setup, excluding the electrometer, was housed in a hermetic chamber surrounded by an electrically shielding Faraday cage. This arrangement permitted the rate of charging to be measured as a function of the RH of the atmosphere within the chamber. The RH within the chamber was adjusted to the desired level by introducing varying quantities of dry nitrogen gas (to obtain values of RH below ambient RH) or nitrogen gas saturated with water vapor (to obtain values of RH above ambient RH); the atmosphere was allowed to stabilize for 30 min before each measurement.

The curves in Figure 2a show the magnitude of charge that developed on a rolling stainless steel sphere as a function of time and for various values of RH. The largest values of charge in each of the curves represent its final magnitudes when the spheres adhered to the surface of PS. The initial rates of charge transfer as a function of RH are shown in Figure 2b and correspond to the slopes of the approximately linear regions of the plots in Figure 2a, ($t \leq \sim 5$ min).²¹ Remarkably, these rates increase linearly with the RH of the atmosphere in contact with the system over the entire range of humidities investigated (~ 10 – 60% RH, Figure 2b), $\dot{Q} \propto \text{RH}$ (where the dot stands for time derivative). The rate of contact charging is slow in the absence of water: extrapolation of the plot given in Figure 2b shows that the initial rate of contact charging is $\sim 0.07 \times 10^{-11} \text{ C/min}$ at 0% RH.²² We infer that water on the surface of the PS facilitates (or is necessary for) contact charging between stainless steel and PS. We note that this finding is in sharp contradistinction to the popular belief that contact electrification (CE) is more efficient in dry atmospheres. We also briefly mention that collecting reliable kinetic data for $\text{RH} > \sim 65\%$

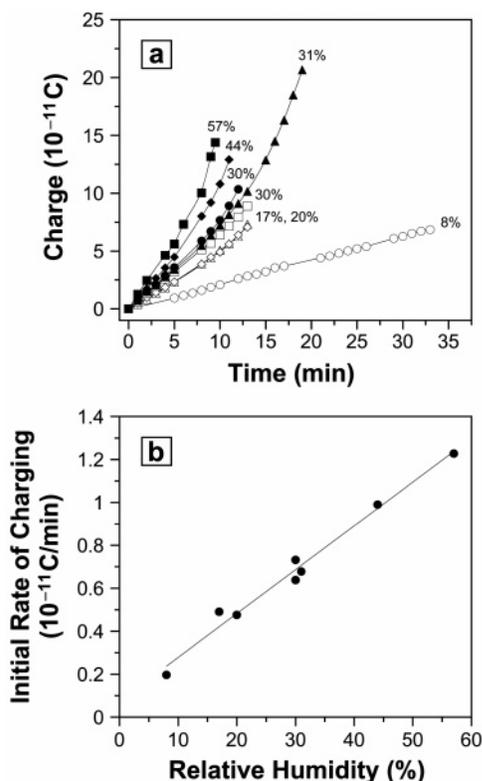


Figure 2. (a) Plots of the magnitude of charge on a stainless steel sphere that rolled on surfaces of PS as a function of time at various values of relative humidity (RH). The symbols used to represent the different values of RH are the following: \circ , 8% RH; \diamond , 17% RH; \triangle , 20% RH; \square , 30% RH; \bullet , 30% RH; \blacktriangle , 31% RH; \blacklozenge , 44% RH; \blacksquare , 57% RH. (b) Plot of the initial rates of charge transfer between rolling stainless steel spheres and surfaces of PS as a function of RH. The initial rate of charge transfer between the metallic sphere and the surface of PS corresponds to the slope of the initial linear region of the plots in (a) (i.e., where $t \leq 5$ min).

was problematic because condensation of water vapor on the charging surfaces gave rise to capillary forces between them; these forces hindered the rolling motion of the sphere.

The Amount of Water Adsorbed on PS Increases Approximately Linearly with RH. Workers¹⁷ who previously studied contact electrification between steel beads and powders of PS blends containing ionomers found that both the maximal magnitudes of charges accumulated on the spheres and the amounts of water on the PS particles increased as the humidity increased from 0 to 20–40% RH. Prompted by this observation, we investigated the influence of the water adsorbed on the surface of PS on the rates of contact charging. Using ellipsometry, we measured the thickness of the adsorbed water layer, W , for different values of RH of the atmosphere in contact with the PS surface. For unmodified surfaces, the differences in W over a range of RH from 10% to 90% were too small to establish a systematic trend. To overcome this experimental limitation, we increased the hydrophilicity of PS by exposing it to UV light and ozone (UVO oxidation); we expected that a more hydrophilic surface would adsorb more water. We chose mild UVO oxidation of PS because it may be applied with a high degree of control over the extent of oxidation, and because the identities and relative concentrations of newly formed surface species are well documented.^{15,23–27}

Most reproducible results over the widest range of RH's were obtained for a PS surface that was exposed to UV light and ozone for $t_{\text{ox}} = 75$ s (Figure 3a). The thickness of the water layer increased approximately linearly (i.e., $W \propto \text{RH}$) and

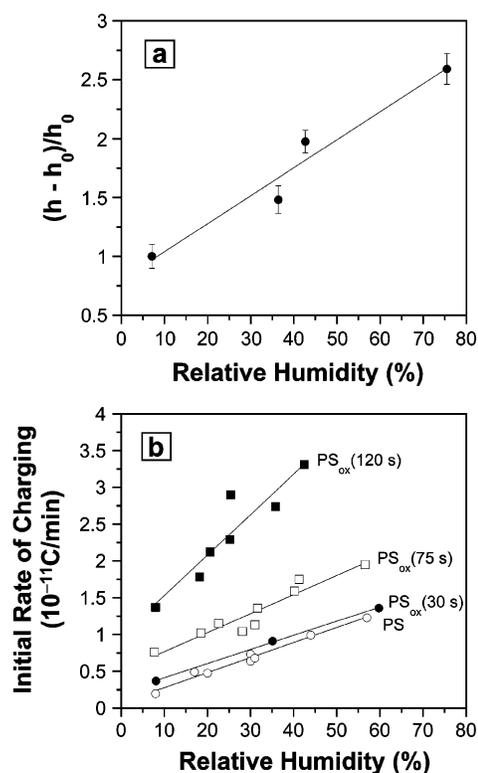


Figure 3. (a) Plot of the relative change in the average thickness of the layer of adsorbed water on a film of PS_{ox} (UVO oxidized for 75 s), measured by ellipsometry, as a function of RH. Here, h is the average thickness of the layer of adsorbed water at a given RH, and h_0 is the initial thickness at 7.1% RH. The reported values are the average of at least six measurements; the lengths of the error bars represent the standard deviations obtained from these values. (b) Plots of the initial rates of charge transfer between rolling stainless steel spheres and surfaces of PS and PS_{ox} as a function of RH. The symbols used to represent different experimental conditions are the following: \circ , PS; \bullet , PS_{ox} (UVO oxidized for 30 s); \square , PS_{ox} (UVO oxidized for 75 s); \blacksquare , PS_{ox} (UVO oxidized for 120 s).

by a factor of ~ 2.2 as the humidity increased from $\sim 10\%$ to $\sim 60\%$ RH.

The Rate of Charging Increases with t_{ox} . For a PS support oxidized for 75 s (PS_{ox75}), the increase in W with increasing RH was accompanied by a linear increase in the rate of charging, \dot{Q} (by a factor of ~ 2.4 from 10% to 60% RH; Figure 3b). This observation implies that $\dot{Q} \propto W$. Because the amount of water adsorbed onto a surface should correlate with the hydrophilicity of this surface, we expected that \dot{Q} should increase with increasing t_{ox} : the longer the time of oxidation, the more hydrophilic the surface, and the more water should adsorb onto it. This hypothesis was verified experimentally; the slopes of the rate-of-charging lines in Figure 3b increase with increasing t_{ox} .

Surface Groups are Responsible for Contact Electrification. The phenomenological rate laws described in the preceding section can be related to the concentration and nature of the chemical groups present on the surface of the PS supports. We and others have demonstrated previously¹² that surface groups have a dominant effect on the process of contact electrification. In a recent experiment, we transformed the surface of poly(acrylic acid) film to poly(methyl acrylate) (i.e., methylated poly(acrylic acid)) by reaction with diazomethane.¹² The polarity of the charge (negative) resulting from contact electrification of metallic spheres rolling on surfaces of methylated poly(acrylic acid) was the same as that observed for pure poly(methyl

acrylate); this polarity is the opposite of that observed for poly-(acrylic acid) (positive), demonstrating unambiguously that the modified surface groups are responsible for contact electrification. Another, elegant demonstration of the importance of surface groups comes from the work of Horn et al. who have shown that contact electrification between two surfaces of the same material occurs when one surface is coated with a single chemisorbed self-assembled monolayer.¹

On the basis of the observed correlations between \dot{Q} and RH and W , we hypothesized that contact electrification on PS and PS_{ox} should be predominantly due to oxygen-containing, acidic surface groups that impart surface hydrophilicity. We verified this hypothesis as follows:

(i) *The Numbers of Oxygen-Containing Groups Present on the Surface of PS Increases with the Times of Oxidation.* The chemical identities of the oxygen-containing species on the surface of PS_{ox} and their concentrations (determined by XPS and IR spectroscopy) as a function of the time of UVO oxidation are well-documented. The predominant species are alcohols or ethers, phenols (Ph-OR),²⁸ carboxylic acids or esters (RO-C=O), and aldehydes or ketones (R₂C=O).^{15,23,25–27} The total concentration of the oxygen-containing species increases monotonically with time of exposure to UV light and ozone until a level of saturation is reached (~36 atom %, determined by XPS, when $t > 150$ s).^{15,25,26} Oxygen-containing species are present even on native surfaces of “unoxidized” PS (not UVO oxidized) because surface oxidation occurs naturally for samples aging under ambient laboratory conditions;²⁹ native PS petri dishes have typically ~1 atom % oxygen on their surface.^{30,31} The oxidation of PS is restricted to its surface because the kinetics of oxidation of the surface of PS is much faster than that of the bulk as a consequence of the limited depth of penetration of UVO light and the limited diffusion of ozone into the bulk.²⁸

Using measurements of contact angles, we correlated the concentrations N_{ox} 's of oxygen-containing species on the surfaces of PS_{ox} to the times of oxidation t_{ox} 's (Figure 4a). The cosines of the contact angles (both receding, θ_r ; sessile, θ_s ; advancing, θ_a) depended linearly on t_{ox} and could also be related to the surface free energies through the Young's equation ($\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$, in which γ_{lv} , γ_{sv} , and γ_{sl} are the liquid-vapor, solid-vapor, and solid-liquid surface free energies, respectively). The changes in $\cos \theta$ were thus linearly proportional to the changes in interfacial free energies that, in turn, were proportional to the numbers of hydrophilic groups introduced onto the surface during oxidation.³² Overall, $N_{ox} \approx t_{ox}$. Our results are in accord with the work of others,¹⁵ who found that the magnitudes of the contact angles of a drop of water on the surface of PS_{ox} decrease with increasing time of exposure to UV light and ozone (for times where $0 \text{ s} \leq t_{ox} \leq 120 \text{ s}$) and with increasing concentration of oxygen-containing surface groups.

(ii) *The Initial Rate of Contact Charging Increases with t_{ox} .* This increase in the concentration of oxygen-containing surface groups correlates with the observed increase in \dot{Q} . The rate of charge transfer shown in Figure 3b at a given value of RH is approximately a quadratic function of the time of exposure of PS to UVO oxidation, $\dot{Q} \propto t_{ox}^2$.

(iii) *Rates of Charging Do Not Depend on the Nature of the Metal Surface.* Figure 4b shows plots of the initial rates of charge transfer between PS_{ox} surfaces of variable oxidation and gold-coated stainless steel spheres as a function of RH. As in the case of bare steel spheres rolling on PS_{ox}, the initial rates increase linearly with RH (over the range ~10–60%) and, for $t_{ox} \leq 30$ s, are virtually identical with those measured for the

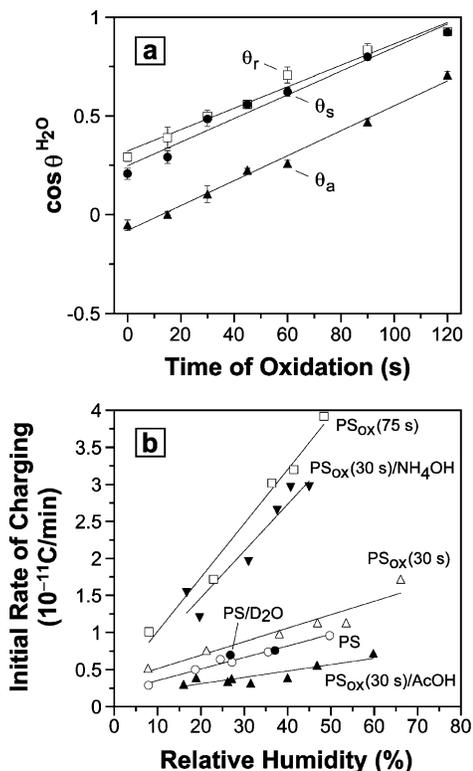


Figure 4. (a) Variation in the receding contact angle θ_r , sessile contact angle θ_s , and advancing contact angle θ_a of water on PS_{ox} as a function of time of UVO oxidation. The reported values are the average of at least three measurements taken at different locations on the surface of PS_{ox} under ambient laboratory conditions. The lengths of the error bars represent the standard deviations obtained from these values. (b) Plots of the initial rates of charge transfer between rolling gold-coated (300 nm) stainless steel spheres and surfaces of PS and PS_{ox} as a function of RH. The symbols used to represent different experimental conditions are the following: ○, PS; ●, PS under an atmosphere of deuterium oxide; △, PS_{ox} (UVO oxidized for 30 s); ▲, PS_{ox} (UVO oxidized for 30 s) under an atmosphere of 1 M acetic acid; ▼, PS_{ox} (UVO oxidized for 30 s) under an atmosphere of 1 M ammonium hydroxide; □, PS_{ox} (UVO oxidized for 75 s).

steel spheres (cf. Figure 3b). These results eliminate the possibility of iron ions being involved in contact charging.

(iv) *Charge Transfer Proceeds More Rapidly in Alkaline and More Slowly in Acidic Environments, as Compared with Neutral Environments.* We measured the rates of charge transfer between gold-coated stainless steel spheres (a surface more chemically inert than stainless steel) and PS_{ox} under atmospheres of acidic and basic media (vapors of 1 M aqueous solutions of acetic acid and ammonium hydroxide, respectively). The hermetic chamber was first purged with dry nitrogen gas for 30 min to remove atmospheric moisture before introducing vapors of the acidic or basic solutions. The RH within the hermetic chamber was raised to the desired level by introducing varying quantities of nitrogen gas saturated with vapors of acetic acid (1 M in water, pH ≈ 2.2) or ammonium hydroxide (1 M in water, pH ≈ 11.5); the resulting atmosphere was allowed to stabilize for 30 min before each measurement. Figure 4b shows that when PS_{ox}(30 s) was exposed to an acidic atmosphere, the rate of charge transfer decreased with respect to a neutral atmosphere, and when it was exposed to a basic atmosphere, the rate of charge transfer increased. This trend held over the entire range of humidities investigated.

(v) *Rates of Charging Are Low on Surfaces That Do Not Present Oxygen-Containing Surface Groups.* Additional charging experiments were performed on polyethylene (PE) surfaces,

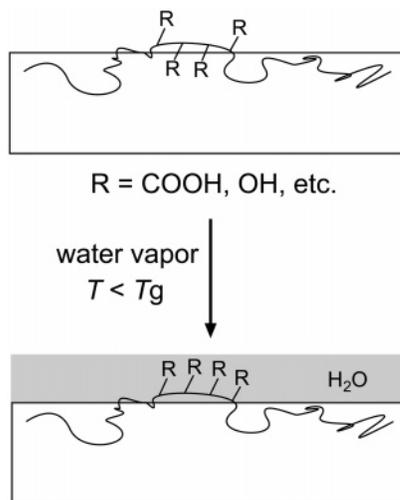


Figure 5. Schematic representation of reorganization of the polymer surface, at temperatures below the bulk glass-transition temperature (T_g), in response to adsorbed water.

which are more resistant to oxidation than PS,³³ and do not present hydrophilic, oxygen-containing groups. In contrast to PS, the initial rates of contact charging of metallic spheres rolling on PE varied little with RH and actually decreased with increasing RH ($\sim 0.03 \times 10^{-11}$ C/min at $\sim 10\%$ RH to $\sim 0.01 \times 10^{-11}$ C/min at $\sim 50\%$ RH). These experiments give additional evidence that the observed rate increase with increasing RH cannot be explained without accounting for the nature of the surface groups of the polymeric support (e.g., solely by the charge transfer between metal and water vapor).

Postulated Mechanism of Contact Electrification in the Metal/PS System. On the basis of the experiments in the preceding sections, we suggest that the charging kinetics observed in the metal/PS system is consistent with a mechanism that assumes reorganization of the polymer surface in response to the adsorbed water (Figure 5).

The wetting and restructuring behavior of surfaces of PS/PS_{ox} is well established.^{30,31,34} This dynamic behavior involves polar surface groups, that is, groups that play a dominant role in contact charging (cf. Sections ii, iii, v), migrating to and from the surface of PS in response to adsorbed water. For a given amount of water, the concentration of these surface groups is such as to minimize the free energy of the PS/water interface. When the RH increases, more water is adsorbed onto PS. The more water on the surface, the larger the degree of surface reorganization, the higher the concentration of polar groups that separate charge with the metal surface, and consequently, the higher the rate of charge transfer. The reconstruction of the surface of PS (occurring during the equilibration period of ≥ 30 min) is probably restricted to the reorientation of polar groups on polymeric chains near the surface because there is limited mobility of the chains at ambient temperature ($T_g(\text{PS}) \approx 100$ °C).

Furthermore, we suggest that the observed increase in the rate of charging with increasing atmospheric pH might be explained by different degrees of ionization of the acidic surface groups at different pH's of the adsorbed water. When the pH of the adsorbed water is higher than the pK_a of the acidic groups (e.g., carboxylic acids and phenols), these groups should ionize and thus increase the surface free energy and the hydrophilicity of the PS surface. Figure 6 shows plots of the advancing contact angles of drops of water on surfaces of PS_{ox} as a function of the pH of the drop. In accord with previous studies,³⁰ $\cos \theta_a$

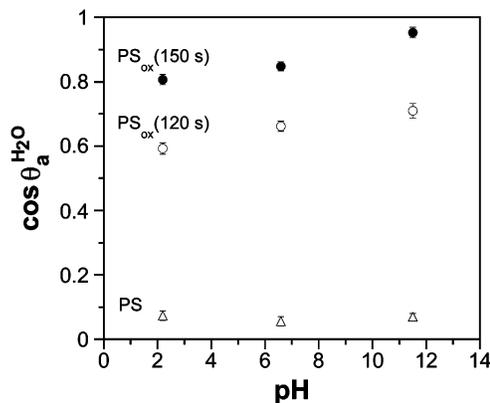


Figure 6. Variation in the advancing contact angle θ_a as a function of pH on surfaces of PS_{ox} of various extents of oxidation. The contact angles of the following three solutions were measured: aqueous acetic acid (1 M, pH \approx 2.2), water (Milli-Q, pH \approx 6.6), and aqueous ammonium hydroxide (1 M, pH \approx 11.5). The symbols used to represent the different times of exposure to UV light and ozone are the following: Δ , no exposure; \circ , 120 s; \bullet , 150 s. The reported values are the average of at least three measurements taken at different locations on the surface of PS_{ox} under ambient laboratory conditions. The lengths of the error bars represent the standard deviations obtained from these values.

increases with increasing pH for surfaces presenting appreciable concentrations of acidic oxygen-containing species (> 25 atom % oxygen; the concentration of acidic groups on the surface of “unoxidized” PS ($< 1\%$) was too low to detect using this method).

An increase in the hydrophilicity of the PS surface (with increasing pH) promotes adsorption of more surface water and, as has been shown by others,^{35,36} causes additional surface reorganization. More polar surface groups are “pulled out” of the bulk of the polymer and presented onto the surface to minimize its free energy. These groups can now participate in charge transfer with the metallic surface, and the rate of charge transfer increases.

Conclusions

We have shown that water adsorbed on the surface of PS increases the rate of contact charging between rolling metallic spheres and PS and related this effect to the concentration and ionization of oxygen-containing groups at the surface of the polymer. Our results are compatible with the postulated mechanism involving reorganization of the pH-sensitive surface to minimize the interfacial free energy between itself and the film of adsorbed water. This reconstruction allows the surface of PS to present increasing amounts of charge-exchanging groups, and thus to charge more rapidly.

Although our experiments give an accurate phenomenological description of contact electrification in the metal/PS system, they fall short of identifying the charge carriers (i.e., electrons, protons, or ions). The elucidation of the molecular aspects of charge transfer will likely require a physical organic approach involving testing of a series of structurally related materials and correlating their charging characteristics to the electronic properties of their chemical functionalities. This type of systematic study will be made easier with the device we have described here. The mechanistic knowledge of charge transfer by contact electrification would have implications for engineering materials of desired charging characteristics (e.g., noncharging polymeric thin films for packaging³⁷) and in mesoscale electrostatic self-assembly^{13,14,38} where it could be used to tailor

interactions (both their magnitude and time dependence) between the self-assembling components.

Experimental Section

Materials. (a) *General.* All materials were used as received unless stated otherwise. PS petri dishes (100 mm × 15 mm) were purchased from VWR. Acetic acid and ammonium hydroxide (28–30% ammonia in water) were purchased from Aldrich.

(b) *Spheres.* Stainless steel spheres (type 316, 1 mm in diameter) were purchased from Small Parts (Miami Lakes, FL). The spheres were washed successively with methylene chloride, hexanes, methanol, and acetone and were dried in an oven at 60 °C for 1 h. Spheres coated with gold were prepared by thermally evaporating (Edwards Auto 306) an adhesion-promoting layer of chromium (30 nm at a rate of 0.2 nm/s), followed by gold (300 nm at a rate of 0.2 nm/s), onto mechanically agitated stainless steel spheres. All spheres were stored under an atmosphere of dry nitrogen until use to prevent oxidation and/or contamination of the surfaces with adventitious organic materials.

Oxidation of PS. The surfaces of PS were oxidized by UV light and ozone (UVO oxidation) using a Boekel Model 135500 UV–ozone cleaner in which a mercury lamp emits UV light across a wide range of wavelengths that photosensitizes the surface of PS and excites molecular oxygen to form ozone. The surfaces of PS were UVO oxidized and then placed under a stream of nitrogen gas (~10 s, to remove excess ozone) immediately prior to use.

Thickness of the Layer of Adsorbed Water on PS. Films were prepared by spin-coating a 10 wt % solution of PS (from petri dishes) dissolved in toluene onto a silicon wafer (Silicon Sense) at 5000 rpm for 30 s. The films were dried in an oven at 100 °C for 12 h, followed by UVO oxidation of the surface of the film for 75 s just prior to use. The average thickness of the layer of water adsorbed on the surface of PS_{ox} (75 s) was determined using a Rudolph AutoEL-II ellipsometer; the thickness was calculated using a two-layer structure of films of water and polymer on silicon. The ellipsometer and the sample of PS were housed inside of a hermetic chamber, and the RH (monitored using a VWR Traceable model 35519-050 digital hygrometer/thermometer (±2% RH, 40–80% RH; otherwise, ±4% RH)) was adjusted to the desired value by purging with dry nitrogen gas (99.9%) or nitrogen gas saturated with water vapor. The atmosphere was allowed to stabilize for 30 min before each ellipsometric measurement. The reported values are the average of at least six measurements.

Contact Angles. Contact angles of drops (5 μL) of aqueous acetic acid (1 M, pH ≈ 2.2), water (purified by a Milli-Q filtering system, pH ≈ 6.6), and aqueous ammonium hydroxide (1 M, pH ≈ 11.5) delivered to the surfaces of PS and PS_{ox} by a Matrix Technologies microelectrode were measured using a Ramé-Hart model 100 contact angle goniometer. The surfaces of the PS and PS_{ox} samples were thoroughly rinsed with ethanol and dried under a stream of dry nitrogen gas prior to measurement of contact angles. The reported values are the average of at least three measurements taken at different locations of the surfaces under ambient laboratory conditions. All measurements were taken within ~15 s of the application of the drop.

Rates of Contact Charging. A description of the method of measuring the rate of contact charging is outlined in the Results and Discussion section. Further details of the instrument and protocol used for these measurements are described elsewhere.¹²

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- (19) A corona discharge occurs at the front of the antistatic instrument between two electrodes. Slowly squeezing the trigger (lasting 1–2 s) produces a stream of positive ions, and slowly releasing the trigger produces a stream of negative ions. The positive ions generated by corona discharge in air are composed of H⁺(H₂O)_n (n = 1, 2, 3, ...) and the negative ions of CO₃⁻(H₂O)_n, O₂⁻(H₂O)_n, NO₃⁻(H₂O)_n, NO₂⁻(H₂O)_n, O⁻(H₂O)_n, and O₃⁻(H₂O)_n (Sakata, S.; Okada, T. *J. Aerosol Sci.* **1994**, *25*, 879–893). Any adventitious charge was neutralized by squeezing and releasing the trigger of the gun (~10 times) that was positioned ~5 cm above the sphere and film.
- (20) The charge was detected as a potential difference across an accurately known capacitor in the electrometer. The voltage was scaled according to the equation $V = Q/C$ (where V is potential difference, Q is charge, and C is capacitance) and was displayed as charge on the digital readout of the electrometer. These data were transferred to a PC and analyzed using commercial graphing software.
- (21) We attribute the upward curvature in the plots in Figure 2a to an increasing area of contact between the sphere and the PS with increasing charge separation. The dependence of contact electrification on the area of contact is currently under study and will be described in a forthcoming communication.
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