Mechanisms of Triboelectric Charging of Insulators, a Coherent Scenario

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Abstract: Whether electrons or ions are involved in triboelectric charging of insulators remains elusive. In keeping with the multidisciplinary nature of the problem, we designed polymers whose surface compositions (determined by XPS) differed from the bulk. Charging against insulators related to their topmost surface compositions, but against metals related to their bulk compositions. We propose the hypothesis that the former involves ion exchange between the topmost surfaces and the latter involves electron tunneling into the bulk, thus postulating a relationship between charging mechanism and charge penetration depth, which is supported by the fact that ions are known to adsorb to polymer surfaces and electrons are considered to penetrate into the bulk.

Integration of this with the frequently conflicting evidence and hypotheses of others has, for the first time, led to a coherent overall understanding of brief contact charging mechanisms: ion exchange for insulator-insulator contacts, both electron and ion exchange for metal-insulator contacts, and electron exchange for metal-metal contacts, consistent with successively increasing ‘electron availability’ at these interfaces. We suggest that this concept of relative surface ‘availability’ of charge exchange agent also accounts for the predominance of mobile ion exchange over hydroxide ion and electron exchange when mobile ion containing organic salts or polymers are involved.

Application of current surface analysis techniques to our polymer surface enrichment approach provides a clear opportunity for quantification of charge penetration depths which, according to our hypothesis, would result in definitive determination of charging mechanisms as a function of material composition, nature of the contacts, ambient conditions, etc.

INTRODUCTION

There is convincing evidence for both electron and ion exchange mechanisms for the triboelectric charging of insulators but the evidence is limited and contradictory, and there is no overall understanding. “Electrostatics is at the same time both a well-defined subject and a very ill defined area of research and technology. This is mainly due to the inter- or perhaps the better term, multi-disciplinary nature of the subject”, a recent quote from the British Institute of Physics. Analysis of the recent literature indicates that the use of physics concepts such as effective work function and density of states have not been useful for distinguishing between electron and ion exchange mechanisms. On the other hand most, if not all, advances have resulted from the use of chemistry concepts such as polymers containing mobile counterions, adsorption of ions to surfaces, chemical analysis of surfaces (XPS, SIMS, etc.), electrochemistry (redox) and electrokinetics (zeta potential). Similarly, it was variation of developer material compositions that led to the greatest single advance which transformed electrophotographic copy quality, namely the use of positive toners containing quaternary ammonium salts with conductive developers, technology introduced in the Kodak Ektaprint copiers in the 1970s (1) and later in Xerox copiers.

In this paper we will describe an hypothesis which resulted from a chemistry approach. It was based on the concepts that ions are known to adsorb to polymer surfaces whereas electrons are considered to penetrate beneath the surfaces of polymers. We designed polymer systems such that their surface compositions differed from those of the bulk, determined if the charging related to the surface or bulk compositions and deduced whether ions or electrons were involved. It appears that the connection between charge penetration depth (CPD) and charging mechanism has not previously been made. For some systems we made the assumption that surface compositions differed from those of the bulk on the basis that the high surface energy of ionic components led to their avoidance of surfaces during the solution based film fabrication process.
process; and fluorinated components are known to enrich polymer surfaces on account of their low surface energies. In one system we confirmed the compositional differences between surface and bulk using XPS analysis.

The experimental part was presented at the 1975 IEEE IAS meeting in Atlanta, GA (2). Here it is expanded and integrated with recent evidence and hypotheses of others to present the current level of understanding of the triboelectric charging of insulators and to suggest how we believe it should be continued.

EXPERIMENTAL

Polymer films were cast from solution onto polished aluminum sheets (4” x 10”), dried in air and finally in a vacuum at 50° C, a process that allows for the thermodynamic equilibration of the film components. The polymers were commercially available and used without further purification. Triboelectric charge values were determined by cascading 100µm or 250µm beads over the inclined films and determining the charge on the beads, as previously described by Gibson (3), a method that allows for precise and reproducible measurements (Fig. 1). Our finding that charging varied systematically with film composition argued strongly against the charges being determined by surface impurities. Ambient laboratory conditions were used. It is important to note that contacts between beads and film are few, light and brief, so charges on the beads are considered to be non-equilibrium charges, reported as nanocoulombs/gram of beads; and they are typically less than equilibrium charges on carrier beads in xerographic developers by a factor of $10^{-2}$.

RESULTS

A. The first system consisted of films of carbon black (Vulcan 3) ultrasonically distributed in a solution of polyvinyl chloride (PVC) in tetrahydrofuran solvent. Charging was determined by cascading 100µm beads of bare nickel, bare steel and steel coated with styrene/methyl methacrylate (65/35 mole ratio) copolymer. This initial experiment was conducted with an objective that was different from investigating charging mechanisms, but its results were so surprising that this became the objective of subsequent experiments. Results are shown in Fig. 2. Surprisingly, the charge values were totally unchanged by adding up to 22% of the carbon black. In order to interpret this result we introduced the term ‘charge penetration depth’ (CPD), which is the depth below the surface of a film which affects the magnitude of the charge; in this case the idea being that all of the carbon black particles were covered by polymer to a depth greater than the CPD. This appeared to be logical in view of the known fact that carbon black usually affects the triboelectric charging of polymers, as is the case with toners but we also know that toners are prepared by mechanical pulverization so that carbon black is present at the toner surface.

B. The second system consisted of styrene/methyl methacrylate (65/35 mole ratio) copolymer containing dispersed Black Pearls L carbon black. We made the even more surprising observation (Fig. 3) that charging against insulating beads (100µm and 250µm beads coated with styrene/methyl methacrylate copolymer, 65/35 mole ratio) was unaffected by the level of carbon black up to 22%, but charging values against bare nickel and steel beads increased systematically with carbon black loading. Continuing our CPD hypothesis, it would follow that the CPD into the films is significantly greater in charging against a metal than against another insulator.

C. It was now incumbent on us to design experiments to test our CPD hypothesis using entirely different materials. Our approach was to design polymer systems in which the surfaces have different compositions from those of the bulk.

   C1. We cast films of n-butyl methacrylate/dimethylaminoethyl methacrylate copolymer neutralized in solution by addition of increasing amounts of benzoic acid; the concept being that the high surface energy ionic or polar component will avoid the topmost surface layer of the films. We determined the charging with metal (bare nickel) and insulating (steel coated with styrene/methyl methacrylate copolymer, and steel coated with polyvinyl pyridine) beads. We found (Fig. 4) that charging of the insulating beads was totally independent of the level of benzoic acid loading up to 2.4 mole equivalents, but charging of the bare nickel beads was highly dependent on the benzoic acid loading and even changed sign. This result supports our CPD hypothesis on the basis that the topmost layers of the films are expected to remain unchanged by addition of benzoic acid.
C2. In the next test of our hypothesis we analyzed the surface compositions of the films using XPS (x-ray photoelectron spectroscopy), also known as ESCA (Electron Spectroscopy for Chemical Analysis). We selected a blend of two polymers, one of which is known to exhibit selective surface enrichment during processing of films cast from a solution of the mixture. Soluble fluoropolymers are known to exhibit surface migration of this kind on account of their low surface energies. We selected mixtures of polyhexafluoroisopropyl methacrylate (HFIPMA) with polydimethylaminoethyl methacrylate (DMAEMA). Films containing up to 20% of the fluoropolymer were cast from acetone solution and dried in a vacuum oven at 50° C. The fluorine content of the top 14A (1.4nm) of the films was determined. We found that addition of as little as 2% of the fluoropolymer HFIPMA was sufficient to saturate the top 1.4nm with fluorine (Fig. 5).

Triboelectric charging of insulating beads - steel coated with styrene/methyl methacrylate copolymer (65/35 mole ratio) and with polyhexafluoroisopropyl methacrylate (HFIPMA) is shown in Fig. 6. We found that the charging profile as a function of composition is identical to that of the fluorine content of the top 1.4nm layer. On the other hand, Fig. 7 shows that charging of metal (bare nickel or steel) beads related to the bulk composition of the films. (But charging of glass beads, being insulating, related to the surface compositions). These results again support our CPD hypothesis of substantially greater CPD in contact with a metal than with an insulator. In order to show the two patterns more clearly we normalized all of the curves to a value of -1.0 nanoCoulombs/g of beads for the 0% HFIPMA polymer (Fig. 8).

DISCUSSION

The fact that there are two distinctly different patterns showing that the CPD into the polymer films is significantly greater for metal contacts than with insulator contacts demonstrates that different charging mechanisms must be involved. It is reasonable to believe that these mechanisms must be electron and ion exchange if we discount the possibility of material transfer. The only logical interpretation is that the former involves tunneling of electrons from the metals into the polymer films, and the latter involves exchange of the much more bulky ions between the topmost layers of the two insulators.

<table>
<thead>
<tr>
<th>Model for the triboelectric charging of insulators</th>
<th>Rev. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPD</td>
<td></td>
</tr>
<tr>
<td>Against insulators</td>
<td>Against metal</td>
</tr>
<tr>
<td>Topmost layer (1.4nm)</td>
<td>Relates to ‘bulk’ composition</td>
</tr>
<tr>
<td>Mechanism</td>
<td>Ions</td>
</tr>
<tr>
<td>Electrons</td>
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Charging of insulating beads

We have shown that the charging of insulating beads against our film series is related to the composition of the top 1.4nm of the films but we currently have no information on the detailed composition of this layer. The experience of others may be useful. Takahagi et al. (4) have found that when polytetrafluoroethylene is subjected to ion sputtering, fluorine atoms are removed preferentially leaving carbon atoms behind, clearly indicating that the fluorine atoms are at the topmost atomic layer. Yu et al. (5) used XPS to analyze the surface of fluorinated polymethacrylate polymers and found that fluorinated alkyl side chains were found to orient towards the surface. Others (6, 7) have studied solution cast films of perfluoroalkyl polymethacrylates and found that the C-C bonds of the perfluoroalkyl side chains are preferentially oriented perpendicular to the surface, a clear indication that the fluorine atoms are at the topmost layer of the films. Our fluoropolymer also has fluorinated side chains and the way we cast the films from solution would provide the maximum opportunity for these to migrate to the topmost surface layers. We believe that fluorine atoms reside at the topmost layers of our films and that charging of these films with insulators is determined by these topmost fluorine atomic layers. More refined surface analysis is required to confirm that fluorine atoms do indeed reside at the topmost atomic layers of our films, and this will be discussed below.
**Charging of metal beads**

How can we determine the penetration levels of electrons into our films? We know that the driving force for surface enrichment in our films is the low surface energy of the fluorine component which is an integral part of the polymer molecules. From this we deduce that, at 2% loading, the topmost molecular layer is saturated with the fluoropolymer, there being no surface energy driving force for further surface enrichment beyond this. If this is the case, compositions below the topmost molecular layer are those of the bulk for all of the films. And since we found that charging with metals related to the bulk composition, we deduce that charging with metals is determined by a depth significantly greater than a monomolecular layer, which we estimate to be approximately 0.3nm.

**Model for the triboelectric charging of insulators  Rev. 2**

<table>
<thead>
<tr>
<th>Against insulators</th>
<th>Against metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPD</td>
<td>&gt;&gt; Monomolecular layer</td>
</tr>
<tr>
<td>Mechanism</td>
<td>Ions</td>
</tr>
</tbody>
</table>

**INTEGRATION WITH RECENT WORK OF OTHERS**

**CHARGE PENETRATION DEPTH**

There is very little agreement in experimental results for charge penetration depth. This can be summarized as follows for metal-insulator contacts. No experimental information appears to be available for insulator-insulator contacts.

<table>
<thead>
<tr>
<th>Date</th>
<th>Authors</th>
<th>Experimental results (CPD into insulator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1976-1984</td>
<td>Numerous</td>
<td>&lt;1.0nm – 10 microns</td>
</tr>
<tr>
<td>1991</td>
<td>Labadz &amp; Lowell (8)</td>
<td>30nm or less for magnesium/silica films</td>
</tr>
<tr>
<td>1992</td>
<td>Brennan, Lowell et al. (9)</td>
<td>3nm or less for metal/fluoropolymers</td>
</tr>
<tr>
<td>1996</td>
<td>Burkett et al. (10)</td>
<td>37-40nm metals/plasma polymerized methane</td>
</tr>
<tr>
<td>1997</td>
<td>Watson et al. (11)</td>
<td>30nm or less for mercury/polystyrene</td>
</tr>
</tbody>
</table>

Brennan et al. (9) deposited layers of a fluoropolymer onto a nylon tape from a plasma of hexafluoropropylene. They determined that (single and repeated) contact charging with gold and platinum was determined by a depth of 3.0nm or less, and “perhaps as little as a monolayer”. Our conclusion that charging of films with metals is determined by a depth significantly greater than a monomolecular layer is consistent with that of Brennan et al. that the CPD in contact with metals is less than 3.0nm, but contradicts their speculation that charging may be determined by a monolayer.

**ELECTRONS VERSUS IONS**

Evidence has been provided which both supports and contradicts our CPD/charging mechanism hypothesis. It is not our intention here to provide details of all relevant experiments; we have selected a few definitive examples of each.

**Supporting evidence. Metal-insulator electron exchange.** Both Davies (12) and Lowell (13) reported a linear relationship between charge density of polymer charging and metal work functions, providing evidence for electron exchange.

**Supporting evidence. Insulator-insulator ion exchange.** Law et al. (14) have provided strong evidence for ion exchange in a xerographic developer between toner coated with a cesium salt (mobile ions available at the toner surface) and an insulating carrier. The negative sign of the toner charge was consistent with cesium ion transfer to the carrier and there was linear correlation between the toner charge and the amount of cesium transferred as determined by the surface analysis techniques TOF SIMS and XPS. We note,
however, the difference between polymers containing mobile surface ions (used in the above example) and the non-ionic polymers used in our experiments, a distinction that was clearly pointed out by McCarty and Whitesides (21).

**Contradictory evidence. Metal-insulator ion exchange.** Law et al. extended their studies to metal carriers (15) and found similar evidence for cesium ion exchange. Diaz (16,17) and McCarty et al.(18) have also reported evidence for ion exchange between metals and polymers having covalently bound ions and mobile counterions.

We respond to the contradictory evidence for metal-insulator charging by expanding our hypothesis to include both electron and ion exchange for metal-insulator contacts, again noting the distinction between polymers containing mobile surface ions and non-ionic polymers. Which mechanism predominates in any particular case would perhaps be determined by the specific circumstances of material composition and conditions of charge determination, etc.; but they would be competitive until the limiting charge (being simply additive for both mechanisms) is determined by the electric field created at the interface, which has been experimentally verified by Schein et al. (19) and Castle et al. (20).

<table>
<thead>
<tr>
<th>Model for the triboelectric charging of insulators  Rev. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Against insulators</td>
</tr>
<tr>
<td>CPD</td>
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<tr>
<td></td>
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<td></td>
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<tr>
<td>Mechanism</td>
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A strong hypothesis has been proposed by McCarty and Whitesides (21), based on their work and that of Diaz et al. (22) for hydroxide ion exchange between two non-ionic polymers, that is polymers with no obvious source of surface ions. Hydroxide ions generated from equilibration of hydroxide and hydronium ions within the thin water layer between the polymers are preferentially adsorbed to the polymer with the greater affinity for hydroxide, though it is not understood why some polymers have greater affinity for hydroxide ions than others. The presence of a few monolayers of water has been shown on the surfaces even of strongly hydrophobic fluoropolymers at 80% RH (23), which is of interest in connection with our work.

**Contradictory evidence. Insulator-insulator electron exchange.** Recent evidence has been provided for electron exchange for insulator-insulator contacts. Liu and Bard (24) reported electrochemical evidence for electron exchange when Lucite and Teflon were rubbed together vigorously, and Otero (25) reported the same finding. These results contradict our hypotheses and we account for this by proposing that charging mechanism can be determined by the nature of the contacts. Recall that our experiments involved a few brief light contacts. Our interpretation is that brief light contacts are sufficient for fast ion exchange between topmost surfaces of two insulators, but more prolonged contact is required for the slower process of electron tunneling beneath surfaces. Then why does our model propose electron exchange for brief metal-insulator contacts? We propose that this results from the more electron – rich interface for metal-insulator contacts relative to insulator-insulator contacts. And we postulate that the progression: ion exchange for insulator-insulator contacts, both ion and electron exchange for metal-insulator contacts, and the well understood electron exchange for metal-metal contacts is a consequence of the successively increasing ‘electron density’ or ‘electron availability’ at these different interfaces.

The picture that now emerges for fast non-equilibrium charging in a few light contacts (except for prolonged rubbing for insulator-insulator contacts) is shown below.
SUMMARY: ELECTRONS versus IONS  
CAPITALS INDICATE EVIDENCE   *Italic* indicates hypothesis

<table>
<thead>
<tr>
<th>Metal-Insulator</th>
<th>Electron Exchange</th>
<th>For Non-Ionic Polymers</th>
<th>For non-ionic polymers (Williams et al., 1975)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ION Exchange</td>
<td>Mobile Ions for Polymers Containing Mobile Ions</td>
<td>Insulator-Insulator</td>
<td>Ions for non-ionic polymers (Williams et al., 1975)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>OH⁻ ions for non-ionic polymers (McCarty et al., 2008)</td>
</tr>
</tbody>
</table>

The question of the relative predominance of mobile ion, hydroxide ion and electron transfer can be addressed by consideration of the evidence by Law et al. (14, 15). They concluded that, for polymers containing mobile ions, the fact that charge density related linearly to the amount of cesium ion transfer indicated that charging resulted predominantly from the mobile ion transfer. And this was the case for both insulator-insulator and metal-insulator contacts. This relationship existed as a function of mixing time, from which we infer that it is true for brief contact, non-equilibrium charging in addition to equilibrium charging. This indicates that, when surface mobile ions are present, transfer of these mobile ions takes place in preference to hydroxide ions and electrons for metal-insulator contacts; and in preference to hydroxide ions for insulator-insulator contacts, in which case electron exchange does not need to be considered for brief contacts because prolonged rubbing is required for this. We suggest that the preference for mobile ion transfer over hydroxide ion transfer results from the greater surface availability of the mobile ions relative to hydroxide ions.

In the absence of mobile ions (non-ionic polymers), the analysis presented above indicates that the relative predominance of electron versus hydroxide ion transfer depends on whether a metal is present in the contact. Electron exchange predominates in metal-insulator contacts, but hydroxide ion exchange will be the default mechanism in insulator-insulator contacts, that is in the absence of both mobile ions and the electron rich interface provided in contact with a metal.

**PROPOSED FURTHER WORK**

Modern surface analysis techniques have the capability to analyze topmost surface atomic and molecular layers and depth profiling below that. Application of these techniques to the polymer surface enrichment approach we have described here provides a clear opportunity to quantitatively determine CPDs and to lay to rest issues relating to monomolecular layer depths and the role of the surface atoms in charge exchange. Quantitative determination of polymer CPD values for contacts with metals and insulators should result in definitive resolution of electrons versus ions as the charging mechanism. Our design approach to materials having different surface-bulk compositions can be applied to a wide range of polymer and other material compositions, thus providing considerable latitude to approach the objective.

Modern techniques include TOF SIMS (Time of Flight Secondary Mass Spectrometry) (26), which is considered highly complementary to XPS (27), and LEIS (Low Energy Ion Scattering) (28), which is unique in its sensitivity to both structure and composition of surfaces. Additionally, LEIS is one of a very few surface-sensitive techniques capable of directly observing hydrogen atoms. It is now possible to analyze parts per billion which is highly relevant since it has been calculated by Schein (29) that “the number of surface molecules involved in the charging process is extremely small, on the order of one molecule in 10⁸ or 10⁹” so that contact electrification involves an extremely small fractional area of the material surfaces.

One of our results, described above, provides an opportunity to determine if simultaneous electron and ion
exchange mechanisms can occur for metal-insulating charging of polymers containing mobile ions. Here is a proposal for doing this. Fig. 4 shows the charging of a series of films n-butyl methacrylate/dimethylaminoethyl methacrylate copolymer neutralized in solution by addition of increasing amounts of benzoic acid. Charging of nickel beads was highly dependent on the benzoic acid content and even changed sign. The film containing 1.8 mole equivalents of benzoic acid gave zero charge against the amount of benzoic acid. Charging of nickel beads was highly dependent on the amount of benzoic acid and ion transfer occurs for the zero charging system, this would prove simultaneous electron and ion exchange for this zero charging system.

REFERENCES

[27] L-T Weng and C-M Chan, ECASIA 2007, ’07, Polymer Surface Characterization by XPS and ToF-SIMS, 12th European Conference on Applications of Surface and Interface Analysis, Brussels – Flagey
Fig. 1. Apparatus for determining triboelectric charge on beads after brief light contacts with polymer films.

Fig. 2. Triboelectric charging of metal and insulating beads against PVC containing dispersed carbon black (Vulcan 3).
Fig. 3. Triboelectric charging of metal and insulating beads against S/MMA copolymer containing carbon black (Black Pearls L)

Fig. 4. Triboelectric charging of metal and insulating beads against nBMA/DMAEMA copolymer neutralized with benzoic acid
Fig. 5. ESCA/XPS fluorine signal for polymer blends of HFIPMA with DMAEMA

Fig. 6. Triboelectric charging of insulating beads relates to composition of topmost 1.4nm layer of polymer blends of HFIPMA with DMAEMA
Fig. 7. Triboelectric charging of glass beads relates to top 1.4 nm of polymer blends of HFIPMA with DMAEMA but charging of metal beads relate more to bulk compositions.

Fig. 8. Triboelectric charging of metal and insulating beads against polymer blends of HFIPMA with DMAEMA. All curves normalized to $-1.0 \text{ nC/g}$ for 0% HFIPMA to clearly show two different patterns.