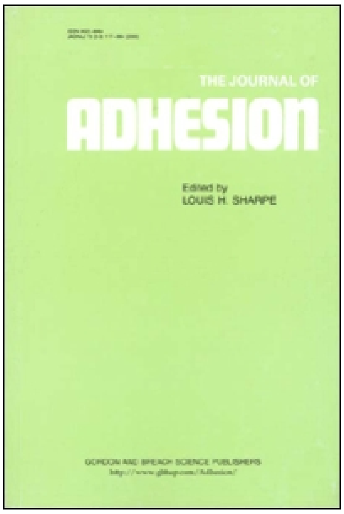

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Contact Electrification of Materials: The Chemistry of Ions on Polymer Surfaces

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Contact Electrification of Materials: The Chemistry of Ions on Polymer Surfaces*

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This report summarizes some recent studies aimed at determining the role of ion transfer in contact charging in polymers. The studies were carried out using blends of polymers and ionomers or polymers and organic salts. These blends were charged by contacting with a metal surface and the contact charge which developed was related to the amount and structure of the ions in the polymer blend. A Kelvin Probe and an atomic Force Microbalance were used to determine the charge. A ion transfer model for contact charging was developed which relates the charge to the ions which are on the surface and are mobile, i.e. not covalently bonded or ion pair associated.

Keywords: Contact charging; ion transfer; ionomers; *N*-methylpyridinium toluenesulfonate; Kelvin probe; Atomic Force Microbalance

1. INTRODUCTION

Contact electrification (contact charging), also known as static electricity, is a well known phenomenon often encountered in daily activities. It is the charge that develops when two dissimilar materials are contacted and separted. During this contact the two materials develop the same magnitude of charge but of opposite polarity. Contact electrification is a complicated process where both the magnitude and

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polarity of the developed charge is sensitive to the material composition. "Tribo" Series of the type shown in Figure 1 list materials in the order of the relative polarity/magnitude of the charge they acquired. In this series, the higher positioned materials will acquire a positive charge when contacted with a material at a lower position. The lists are qualitative because the charge is sensitive to the environmental conditions, especially the humidity.

Contact electrtification affects many different manufacturing environments. While it is quite prevalent at reduced levels, the build up of static electricity is known to produce electrical shocks, fires, explosions, mechanical jams and to damage sensitive electronic components. Not only is the charge developed between solids but also a nonconducting liquid flowing through a pipeline can generate a charge at a rate of 10^{-9} to 10^{-6} A, while a powder coming out of a grinding mill can generate a charge of 10^{-8} to 10^{-4} A. At these charging rates the potential of an insulator container can rise at a rate of 10 to 10,000 V/s. Charge can also be generated when a material is in the proximity of an electric field.

On the other hand, contact electrification is a key performance factor in certain technologies involving polymeric materials. For example, in electrophotography the toner is electrostatically charged before it enters the printing cycle of the printer/copier engine [1, 2]. The polarity and magnitude of the charge on the toner is carefully controlled to regulate the adhension and mobility of the toner particles and ultimately affect the print quality. Flocking and electrostatic

"TRIBO" SERIES	**Charge Polarity**
Nylon	(Positive)
Polymethyl Methacrylate	
Styrene Butylmethacrylate Copolymer	
Polyesters	
Polyacrylonitrile	
Polycarbonate	
Polystyrene	
Polyethylene	
Polypropylene	
Polyvinylchloride	
Polytetrafluoroethylene	
Halogenated Polymers	(Negative)

FIGURE 1 An example of a "Tribo" series for various polymers.

coaters also rely on having a controlled charge on the sprayed particles to produce good adherent coatings.

MECHANISM OF CHARGING

Basic studies on contact charging go back to the turn of the century. For reviews on this subject, see the reports by Harper [3,4], Davies [5,6], Duke [7], Seanor [8], Rose-Innes [9] and Krupp [10]. The mechanism of charging is well understood for metals and semiconductors and the charge results from the transfer of electrons between the contacting surfaces. The mechanism of charging with polymers (insulators) is less well inderstood, and has been described by transfer of electrons, ions and/or material between the two contacting surfaces. The electron transfer mechanism has been accepted by extension of the case with metals. Much of the data is interpreted using Lee's model, or extensions of it, which describe the process as the equilibration of charge between the two contacting surfaces [11]. The transfer of charge results from the population of surface states with approximate energy. These models consider the charge as a point charge, imply electron transfer, and make no connection between the charge and the chemical structure of the materials being considered. This model, plus charge–structure correlations using Hammett's substitutent parameters, have led to the interpretation that charging results from electron transfer [12, 13, 14].

Much of the recent literature on contact charging with polymers containing ions has been published by a few industrial laboratories and the studies are related to charge control in "toners" used in electrophotographic printers and copiers [12–26]. Because much of this work is published in trade journals, it often does not specify the details of the materials used in the study due to proprietary limitations. The mechanistic studies published in the last seven years which employ polymers with added salts provide good insight into the charging mechanism. Particularly informative are those studies with polymers blended with ionomers or with molecular salts which have large anion-cation size differences.

Ions have a big effect on the contact charge on polymers. The sign of the charge is dependent on the chemical structure of the ions in the salt and the magnitude usually responds monotonically to the amount of salt in the polymer. Salts are often used as additives to control the charge. The response is not linear with salt concentration, but instead reaches a maximum charge level then decreases. At high salt concentrations, charge run off is rapid and polymers do not retain a charge [27]. Results from two industrial laboratories demonstrated that ion transfer accompanies charging, and it accounts for the charging [22–24]. There is no need to invoke electron transfer. These reports have resulted in an open controversy on the mechanism of charging on polymers containing ions. Our study with polymers containing salts was based on the premise that if ion transfer is important, then the polarity can be manipulated by immobilizing one of the ions in the salt [24–26]. Salts which have only one mobile ion should produce a charge with a predictable polarity. For example, a blend containing an ionomer, $[P]\text{-}M^+X^-$ (immobile cation and mobile anion), should develop a positive charge upon contact since the anion can transfer to the contacted surface leaving behind an excess of cations. The contacted surface develops the negative charge. This is shown schematically in Figure 2 which shows the location of the ions on the two surfaces (only one surface contains ions initially). In the scheme, an ionomer with the covalently bonded cation, $[P]\text{-}M^+$, and the mobile anion, X^-, exists on the surface of the blend before contact. After contact and separation, only the mobile X^- can exist on the contacted second surface, and the ionomer surface will have an excess of cations. The two surfaces will have equal and opposite charges. The polarities arise from the inequality in number of cations and anions on a given surface. The schematic is qualitative and is not meant to imply all the mobile ions transfer between the surfaces.

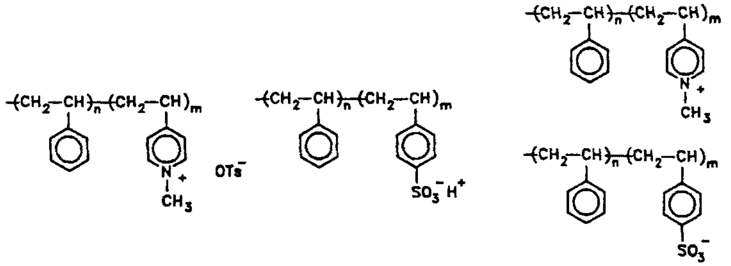
The validity of the premise was demonstrated using a blend containing the ionomer poly(styrene-co-methylvinylpyridinium toluenesulfonate), $[P]\text{-}PyMe^+\ OTs^-$, which induced the expected positive charge. Likewise, a blend containing an ionomer, $[P]\text{-}X^-M^+$,

	Surface-1	*Surface-2*
Before contact	$[P]\text{-}M^+X^-$	(no ions)
After contact	$[P]\text{-}M^+$	X^-

FIGURE 2 Schematic showing the possible locations of the ions of an inomer with bonded cations and mobile anions.

with an immobilized anion is expected to acquire a negative charge, and this was demonstrated with a partially sulfonated polystyrene, [P]-$PhSO_3^-H^+$, and the corresponding sodium salt, [P]-$PhSONa^+$. Finally, in the absence of mobile ions on either surface, little or no charge is expected. Accordingly, we observed a small charge on the blend. This was shown using the ionomer pair, [P]-$PyMe^+$ [P]-$PhSO_3^-$, the charge balanced mixture of the poly(styrene-co-methylvinylpyridinium toluenesulfonate) ionomer and the partially sulfonated polystrene. These results are shown graphically in Figure 3.

The structures of [P]-$PyMe^+$ OTs^-, [P]-$PhSO_3^-$ H^+ (or Na^+) and [P]-$PyMe^+$ [P]-$PhSO_3^-$ are given below.



[P]-$PyMe^+$ OTs^- [P]-$PhSO_3^-$ H^+ (or Na^+) [P]-$PyMe^+$ [P]-$PhSO_3^-$

STRUCTURE 1

All the ionomers are styrene polymers with 2–10% of a vinylpyridinium toluenesulfonate salt ([P]-M^+X^-) or a styrene-sulfonic acid ([P]-$SO_3^-H^+$) as the co-monomer. The selected ionomer was blended with a styrene butyl methacrylate copolymer and then either ground to a fine powder (10 micron mean particle diameter) or cast as films for measurements with a Kelvin Probe and Atomic Force Microbalance (Discussed below). The fine powder of the ionomer/polymer was charged against 100–200 micron size metal beads (sometimes coated with a resin). A mixture of the powder and the beads were gently rolled to develop the charge, separated, then the charge (q) and mass (m) of the powder or beads were measured. The resulting charges were reported as charge per unit mass, q/m (μC/g). This quantity is important in the evaluation of toners used in electrophotography. For those studies involving single contacts between

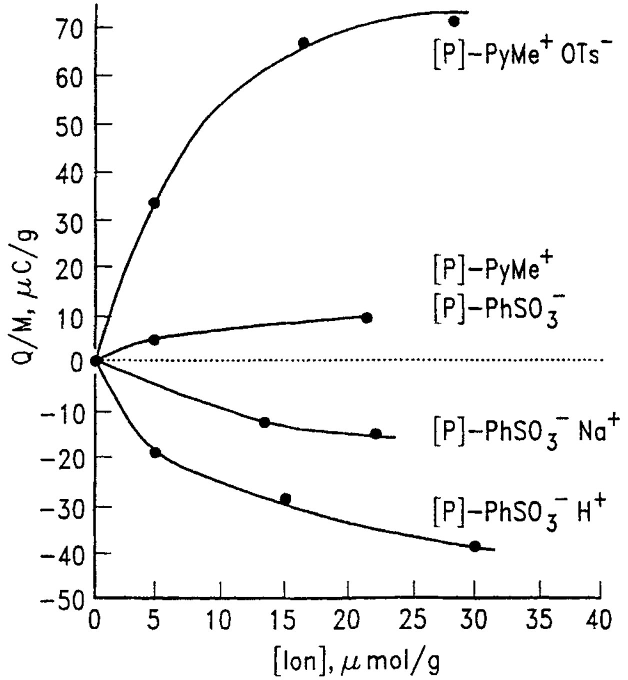


FIGURE 3 Plot *q/m versus* [ion] for 4 different ionomers (From Reference 26, with permission).

two surfaces, the charges are reported as charge per unit area, *q/a* (μC/cm^2).

Several studies involving the use of ionomers are found in the earlier patent and trade literature related to the printing technology. Examples of other ionomers with bonded cations and mobile anions which induce a positive charge in the resin are ionomers with arylphosphonium arylsulfonate ions, e.g., poly(styrene-co-methyldiphenylstyrylphosphonium OTs), [P]-PhPPh$_2$Me$^+$OTs$^-$, and an ionomer from a modified octene-maleic anhydride copolymer with pendent 3-aminopropylene-(trimethylammonium groups) [17, 18, 28]. With these ionomers, the contacting material developed the complementary negative charge. An example of an ionomer with bonded anions and mobile cations which induce a negative charge in the resin is the styrene-2-acrylamido-2-methylpropane-sulfonic acid copolymer [29]. This copolymer is called an "inner salt", and it is the proton that is mobile. With this ionomer, the contacting material developed the complementary positive charge.

The relationship between the developed charge and the mobile ion content was confirmed in a study using films of the same ionomer/polymer blends and a Kelvin Probe [30]. In this experiment, the metal tip of the Kelvin Probe first contacts the film, separates, then returns to measure the charge. As seen in Figure 4 a significant charge is observed with the films containing an ionomer with a mobile cation or anion. Films with no mobile ions did not develop a charge. This was the case with both the unblended styrene butylmethacrylate copolymer and the blends with the ionomer pair, [P]-PhMe$^+$ [P]-PhSO$_3^-$, where both ions are bonded. Thus, *contact charges of this magnitude develop if and only if mobile ions are present on the surface.* This result supports the ion transfer mechanism for charging. Parallel results were found with the Atomic Force Microbalance measurements [31].

Further evidence in support of the ion transfer mechanism is the observation by XPS of the transferred ion on the contacted surface [22]. Analysis of the contacted surface after contact and separation revealed the presence of an S signal appropriate for presence of OTs$^-$ anions and no N signal indicating no pyridinium cation. A similar result was reported for the contact charging experiments using stearylpyridinium bromide salts. In this case, the contacting surface developed a negative charge and a signal for the bromide anion was detected by SIMS [24].

ION TRANSFER MODEL

The ion transfer mechanism consistently explains our charging results and those from other laboratories. We developed a model which relates the polarity and magnitude of the charge to the structure and concentration of the ionic species in the polymer [25, 26]. This model is also based on the equilibration of charges between the two surfaces (Lee's model) and assumes that ions transfer across the contact interface and equilibrate between the two surfaces in proportion to their relative surface areas. However, unlike the previous models, our model considers the chemical structure of the ions [25, 26], instead of treating the charges as point sources [11, 32].

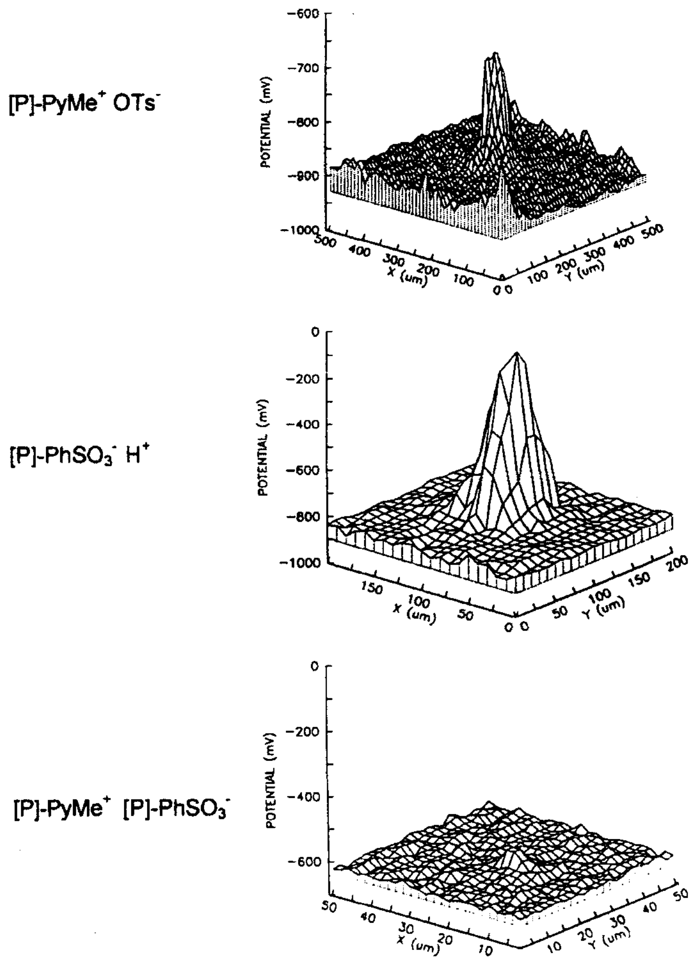


FIGURE 4 Charge profiles measured using a Kelvin probe (From Reference 30, with permission).

In addition, we proposed that the nonlinear dependence of charge on the ion concentration, [ion], is a linear dependence on $[\text{ion}]^{1/2}$, and is attributed to ion pairing of the salt on the surface of the polymer blends [25, 26, 27].

According to the model, only those ions that are *on the surface*, are *dissociated* and *not immobilized*, will transfer. Therefore, ions which are below the surface, ion-pair associated or immobilized by chemical bonding or adsorption, or simply too bulky, will not transfer.

The relationship between charge (q) and surface ion content (Γ) for the case where the ions equilibrate between the two available surfaces is shown in Eq. (1).

$$q/(n)a = F\ [(AK)/((n)a + AK)]\ [(z\,\Gamma)_{M+} + (z\,\Gamma)_{X-}] \tag{1}$$

where $q/(n)a$ is the charge per unit area ($\mu C/\mathrm{cm}^2$), F is Faraday's constant, $(n)(a)$ and A are the areas of the first and second surfaces (cm^2), z is the number of charges on the ion, and K is equilibrium constant for the distribution of the ions between the two surfaces. The equilibrium constant K is a complicated term and is influenced by many chemical and environmental considerations, such as specific interations between the ions and the polymers, electrostatics, moisture, etc. The effect of these considerations on the distribution of the ions between two surfaces is beyond this summary.

The surface concentrations, Γ_{M+} and Γ_{X-} are related to Γ_{MX} by $[K_D \Gamma_{MX}]^{1/2}$ in line with the ionpair dissociation equilibrium, $MX \rightleftharpoons M^+ + X^-$, which has the equilibrium dissociation constant, K_D. Relating Γ_{MX} to $[MX]$ is difficult and is estimated using Eq. (2) which considers the ions in the outer "skin" of the surface to be "surface" ions. This "skin" has a volume, δV, and a thickness, δr.

$$\Gamma = \rho(\delta V)/A[MX] = \rho(\delta r)[MX] = 10^{-7}[MX] \tag{2}$$

For (δr) equal to 1 nm and ρ (the density of the host resin) near 1 g/cm^3, Γ_{MX} equals 10^{-7} $[MX]$. The density enters into the equation because $[MX]$ is normally in moles/g of blend. This value is for the case where the ions have near-equal stability in the bulk and on the surface. In the case where there is a stability difference, as with surfactant ions, the value will vary accordingly. This has been reported [33].

The resulting equation for the equilibrium charge between two surfaces of areas a and A which takes into account ion-pair dissociation is,

$$q/(n)a = F\,[(AK)/((n)a + AK)]\,z\,(K_D(\delta r)\,\rho\,[MX])^{1/2} \tag{3}$$

where K^D is the ion-pair dissociation constant for the salt, δr is the surface thickness containing ions that can transfer (cm), ρ is the density of the film (g/cm^2), and $[MX]$ is the bulk concentration of the salt. The ion structure, ion pairing and surface moisture all have a big effect on the charge.

The more complete relationship which includes the relative mobilities and resulting distribution of the two ions in the MX salt on the surface of the polymer is as follows,

$$q/(n)a = F\ [[z_M(AK_M)/((n)a + AK_M)] \\ + [z_X(AK_X)/((n)a + AK_X)]]\,(K_D(\delta r)\rho\,[MX])^{1/2} \qquad (4)$$

With ionomers either K_M or K_X is equal to zero and the maximum charge is obtained. With molecular salts, where both ions transfer and the net charge can be very small. The equation corresponds to the intuitive feeling that for charging to occur not only must the ions be near the surface and mobile but there must be *selectivity of transfer*, otherwise there is no net charge. Simply put, charge will develop when there is an unequal transfer of anions and cations.

Data treated using an equation similar to Eq. (4) but adjusted for the case where powders are charged against beads provided the relative charging responses for various ionomers [25,26,27]. The charging response provided by the slope of the plots of charge *versus* $[MX]^{1/2}$ was the same for $[P]\text{-PhMe}^+X^-$, for (Where $X^- = OTs^-, I^-$), and $[P]\text{-PhSO}_3^-\ H^+$ and was twice as large as for the salts of $[P]\text{-PhSO}_3^-\ M^+$, where M^+ are pyridinium, ammonium and sodium cations [26]. In addition, the ion pair dissociation constant for $[P]\text{-PhSO}_3^-\ H^+$ was also determined and found equal to 6×10^{-14} mol/cm^2 for the surface environment. This corresponds to a value 6×10^{-4} mol/L for the bulk. This bulk value is 2–3 pK units higher than the value from direct bulk measurements and this difference was previously reported [35].

CONCLUSIONS

In conclusion, the model we present here relates the charge to the chemical structure of the ions used to affect the contact charge. The model consistently explains the charging results with polymers containing ionic additives in the form of ionomers or as molecular salts where there is a large size difference between the anion and the cation. The model was applied to results from our laboratory and results published by others. One or two exceptions to the model exist and these are cases involving hydroscopic salts. This is not surprising since surface moisture has a strong influence on charging and its effect is not well understood [34].

This model is a powerful tool in the hands of organic chemists who can properly design ionomers for use in polymer blends. This is a viable approach to control successfully the contact charging (magnitude and polarity) and adhesive properties of the materials. However, it is important to recognize that the charge will vary widely with the purity of the materials and the environmental conditions. In particular, ionic impurities and humidity have a big effect on the level and the stability of the charge.

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