

Charging Characteristics of Polymer-Ionomer Blends

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Abstract

The results of recent charging experiments with the Kelvin probe shows that a surface charge can be developed on films of polymer-ionomer blends. On the other hand, films of the polymer alone or of the polymer blended an ionomer pair where all the ions are covalently bonded to the polymer backbone do not produce a charge. For these studies, ionomers containing a covalently bonded sulfonate anion and a mobile cation or a covalently bonded methylpyridinium cation and a mobile toluenesulfonate anion were used in the blends with a styrene butylmethacrylate random copolymer. These results are important because they are related to the charging process of toner materials and help understand the mechanism of charging. Correspondingly, powders of these same blends when charged by rolling with iron oxide beads show a similar charge response. However in this case, the sign of the charge is also determined and a correlation is observed between the sign of the covalently bonded ion (immobilized) and the sign of the charge acquired by the powder. The details of a model developed to describe these results will be presented and related to the mechanism of charging in toners.

Introduction

Many studies can now be found in the literature on the mechanism of contact charging with polymers. A quick survey of the literature reveals that the presence of ions in the polymers has a strong influence on the resulting charge. While there are many phenomenological studies, only in a few studies is close attention paid to the nature of the materials whereby the materials set is carefully selected to determine the relationship between the charging response and the molecular structures.¹⁻⁵ We feel that these are the studies which are particularly informative because the contact charging is a materials phenomenon and requires clear understanding of the nature of the materials involved. Our interest in the mechanism of contact charging is fairly recent compared to other laboratories. However, the design of our experiments has been guided by the premise that the charge observed with polymers containing ions results from the transfer of ions from one surface to the other. Many of our experiments have involved the use of blends of an ionomer and a styrene butyl methacrylate copolymer. In our earlier experiments,^{3,4} we studied the charge on these blends as fine powders. These powders were prepared in a process used for toners except they did not contain all the additives typically present in a fully formulated toner. These 'pseudo' toner powders were charge activated by gently rolling

against carrier beads and the charge was measured using the known total blow off technique. With these powders, we were able to produce well behaved monotonic increases in the charge with increasing ion concentration in the blend. This is often not the case for polymers containing organic salt additives. A correlation was observed between the charge acquired by the polymer blends and the sign of the ion bonded to the ionomer. In addition, the mobile ion could be detected by XPS on the surface of the carrier beads after rolling with and separation from the powder and a good correspondence was observed between the sign of the charge on the carrier beads and the ion type (anion or cation) detected on the surface of the beads. Similar charging results have been reported by Bugner and Anderson with arylphosphonium arylsulfonate ionomers.⁵ These results lead us to conclude that the ion transfer premise is appropriate for the charging mechanism which occurs with polymers containing ions. More recently, we have investigated the charging behavior of these blends using a Kelvin Probe and find corroborating evidence for the ion transfer mechanism for charging. The results of this study are described here.

Results

Thin films of polymer blends of an ionomer and a styrene butyl methacrylate copolymer were cast from powders of these blends. These blends were available from previous studies and were prepared by melt mixing the polymeric materials and milling the blend as previously described. The ionomers used were:

1. a styrene, N-methylvinylpyridium toluenesulfonate ionomer with pendent cations, [P] - Py⁺, and mobile anions, ArSO₃⁻.
2. a partially sulfonated polystyrene with pendent anions, [P] - SO₃⁻, and mobile cations, H⁺ or Na⁺.
3. a 'double ionomer' consisting of a styrene N-methylpyridinium and a partially sulfonated polystyrene ionomer with pendent cations, [P] - Py⁺, and pendent anions, [P] - SO₃⁻, and no mobile ions.

In these experiments,⁶ the films of the ionomer/polymer blends on a silicon wafer were contacted with a Pt/In tip and then the area of contact was scanned to measure the potential. It was observed that the blends with mobile ions (with ionomers 1 or 2) produce a large charge and the charge increased in size with repeated contacts. The films with no mobile ions produce no charge. This is the case with both the styrene butyl methacrylate copolymer (no ions) and

with the blend containing the double ionomer (ionomer 3) which has both the cation and the anion covalently bonded to the polymer backbone.

These results compare well with our previous results from the Electrostatic Force Microscope analysis of these materials.⁷ The EFM micrographs showed that charge is deposited by contacting the surface of the films with the EFM tip. The stability of the charge depended very much on the ion content in the films. The films with little or no ions could be charged and would hold the charge. Films with a higher ion content revealed a charge instability and the charge decay was found to scaled with the ion content. With the films containing a very high ion content, the charge decayed completely by the time the measurement was made. However, with the EFM the polarized tip revealed that the as-prepared films already had some charge on the surface and the charge could be enhanced by contacting with the tip even if no ions were present in the film.

These results in combination with our earlier results on charging with powders provide a consistent mechanism for charging with polymers containing ions. In every case, it

has been shown that a significant contact charge results with those materials having mobile ions and the sign of the charge can be anticipated from the relative mobilities of the ions.

References

1. P. J. Cressman, G. C. Hartmann, J. E. Kuder, F. D. Saevee and D. Wychick, *J. Chem. Phys.*, **61**, 2740 (1974).
2. H. W. Gibson, *J. Amer. Chem. Soc.*, **97**, 3832 (1975).
3. A. F. Diaz and D. Fenzel-Alexander, *Langmuir*, **9**, 1009 (1993), and references therein.
4. A. F. Diaz and J. Guay, *IBM J. Res. Develop.*, **37**, 249 (1993), and references therein.
5. D. E. Bugner and J. H. Anderson, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **29**, 463 (1988).
6. M. T. Nguyen, K. K. Kanazawa, P. Brock and A. F. Diaz, *Langmuir*, **10**, 597 (1994).
7. F. Saurenbach, D. Wollmann, B. D. Terris and A. F. Diaz, *Langmuir*, **8**, 1199 (1992).

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