Contact charging of solution-cast polymers by metals

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Abstract

The charge transfer between metals and some solution-cast polymers has been investigated by employing intermittent soft contact under a controlled condition. The result of our measurements reveals that the measured charge is unaffected by our attempt at purifying the polymer samples and so we conclude that the charge transfer is an intrinsic property of the polymers.

The histogram of the charge distribution for all the polymers studied is not Gaussian but skewed towards larger charges. The metal work function influences the charge transfer to the polymer except polyvinyl chloride, which behaves as Teflon, already reported in our earlier work.

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1. Introduction

In recent years, contact charging of polymers by metals has been extensively studied. Nevertheless, there are still conflicting results because of the problem of
irreproducibility associated with static electrification [1,2]. Synthetic textiles such as nylon, polyethylene terephthalate and polypropylene are normally produced under closely controlled conditions and so reproducible experiments in static charging are possible with these materials [3]. It was proposed by some workers that the charge transfer to a particular sample of polymer might be determined by the accidental impurities rather than by the material itself [1,4–6]. The discrepancies between the results from different investigators can be attributed to their having used different polymers from different sources or different methods of preparation. Indeed, many investigators have found that charge transfer is sensitive to the method of cleaning or preparing the sample surface [1,7–11]. Furthermore, much of the research cited had been concerned with commercial plastics, and it is not clear whether the charge transfer to such materials is influenced by the additives and impurities which are always present. In order to reduce this problem, Fabish and his colleagues [12–14] took steps to purify their polymer before measurement.

The purpose of this paper is to report investigation on the contact charging of purified and non-purified solution-cast polymers by metals.

2. Experimental method

2.1. Contact equipment

Any apparatus which is used to study the contact electrification between metals and insulator must be designed to minimize the amount of rubbing due to making and breaking contact. With this in mind, our contact equipment is designed such that the spherical metal contactor can be brought into contact with an insulator and then separated after a specific time with zero relative motion. The contact equipment is also designed to fit into a vacuum system (10⁻⁴–10⁻⁵ Torr), and it normally performs many mechanical operations during a run. The work function of the metals are measured without breaking the vacuum using a Kelvin vibrating capacitor. A detailed description of this apparatus is given in our earlier reports [4,15,16].

2.2. Sample preparation

2.2.1. Metals

The metal contactor used in this experiment covered a wide range of work functions. Some of the metals (e.g. Al, Mg, Cu) were machined and turned into a bullet shape (diameter ~6 mm), while others (Au, Pt, Sn) were made from soldering a molded metal foil onto a brass sphere. The cleaning of these metals was done periodically by polishing them with a slurry of gamma grade alumina powder and water after which they are cleaned in trichloroethylene and methanol (the methanol rinse was omitted in the case of Mg because of rapid chemical reaction between them) [15,16]. The same method was used by previous investigators [17].
2.2.2. Polymer samples

Our experiments were carried out on four different polymer films cast from solution onto thin glass squares (microscope cover slips). Solution-cast samples were made by lifting the glass plate from the solution at a constant rate or by pouring the solution onto the plates in a boat of clean aluminium foil and allowing the solution to evaporate at 30 °C.

Poly(vinyl alcohol) (PVOH): PVOH resin (granulated form) with molecular weight of about 14,000 was supplied by BDH Chemical Ltd., UK. We prepared the solution by dissolving about 5 g of PVOH in 100 g of deionised water heated with reflux.

Poly(vinyl acetate) (PVAC): PVAC resin (molecular weight approximately 160,000) was obtained from the same source as PVOH. We prepared the solution by dissolving 10 g of the resin into 100 ml of methanol and heated with reflux.

Poly(methyl methacrylate) (PMMA): The PMMA resin (in granular form) was obtained from Rubber and Plastic Research Association (RAPRA), UK. The solution was prepared by dissolving 5 g of PMMA in 100 ml of chloroform. The mixture was heated with reflux.

Poly(vinyl chloride) (PVC): The PVC resin was from the same source as PMMA. The solution was prepared by dissolving the resin in tetrahydrofuran heated by reflux.

The purified solution used in the other sets of polymer films was prepared by repeated precipitation of the resin (in benzene followed by methanol) before casting the solution on the glass plates. The same procedure had earlier been used by other researchers [12–14].

3. Results and discussion

3.1. Charge transfer from metal to the polymer samples

In this experiment, we measured the charge transferred to several samples of a particular polymer prepared in the same way to investigate the degree of reproducibility. The histograms of the measured charge are shown in Figs. 1–4. We see that the charge transfer to PVC (Fig. 1) is quite reproducible. The mean charge observed is constant to within 10%, and even the width and form of the histogram are strikingly reproducible. The histograms in Figs. 2–4 also indicate the place-to-place variability of charge transfer for the metals/polymer combination (PVOH, PMMA and PVAC). Unlike the case of PVC in Fig. 1, the mean charge observed varies by up to a factor of 2. Nevertheless, the width and the form of the histogram is fairly reproducible. In all cases, the width of the histogram for all the polymers studied is similar from one sample to another. Also, their standard errors of the mean are comparable. These results suggest that the large mean charge percentage variation in some polymers may not be caused by any difference in the polymer sample but by the fact that the measured charge is small.
3.2. The effect of purification

In Table 1, we compare the charge transfer from metals to both purified and non-purified samples of PMMA and PVC. We observe that the purification does not significantly influence the charge transfer to PMMA; we reached a similar conclusion for polystyrene [16]. In the case of PVC, there is a difference of about a factor of 2 between the charge measured on both purified and non-purified samples. However, the difference is entirely explicable from the different apparent contact areas measured on the two samples (purified and non-purified PVC) when contacted by Au. The different contact area may arise because one film is thicker than the other.
Fig. 3. Histogram showing the charge transfer distribution from Au to two samples of PMMA (prepared in the same way).

Fig. 4. Histogram showing the charge transfer distribution from Au to two samples of PVAC (prepared in the same way).

Table 1
Charge transfer from metals to purified and non-purified PMMA and PVC

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Au (pC)</th>
<th>Al (pC)</th>
<th>Pt (pC)</th>
<th>Zn (pC)</th>
<th>Mg (pC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA Purified</td>
<td>$1.261 \pm 0.140$</td>
<td>$0.750 \pm 0.061$</td>
<td>$2.111 \pm 0.193$</td>
<td>$1.899 \pm 0.173$</td>
<td>$-0.247 \pm 0.116$</td>
</tr>
<tr>
<td>PMMA Non-purified</td>
<td>$1.526 \pm 0.200$</td>
<td>$1.064 \pm 0.154$</td>
<td>$1.597 \pm 0.249$</td>
<td>$1.363 \pm 0.358$</td>
<td>$-0.140 \pm 0.233$</td>
</tr>
<tr>
<td>PVC Purified</td>
<td>$-1.419 \pm 0.196$</td>
<td>$-3.318 \pm 0.252$</td>
<td>$-5.582 \pm 0.453$</td>
<td>$-4.769 \pm 0.435$</td>
<td>$-5.585 \pm 0.525$</td>
</tr>
<tr>
<td>PVC Non-purified</td>
<td>$-8.064 \pm 0.507$</td>
<td>$-10.979 \pm 0.478$</td>
<td>$-12.572 \pm 0.723$</td>
<td>$-10.908 \pm 0.563$</td>
<td>$-10.187 \pm 0.410$</td>
</tr>
</tbody>
</table>
and of course we do not have control over the thickness when the sample is cast from the solution. The apparent contact area was obtained by measuring the imprint, which the spherical metal left on the polymer surface. To render the imprint visible, we coated the polymer with a thin layer of soot particle, and contacts were made to the coated surface under the same conditions as our charge transfer experiments (though not in vacuum). The diameter of the imprint was measured by a travelling microscope. Measurements of apparent contact area when both purified and non-purified PVC were contacted with Au gives $0.168 \pm 0.001 \text{ mm}^2$ for purified PVC and $0.347 \pm 0.001 \text{ mm}^2$ for non-purified PVC. The charge density calculated using the apparent contact area for Au contact gives $-20.3 \pm 1.3 \mu \text{C/mm}^2$ for purified PVC and $-23.2 \pm 1.9 \mu \text{C/mm}^2$ for non-purified PVC. We may then conclude that the two values are not much different and so purification had no influence on the contact charging of PVC.

3.3. Role of work function of the metal

The charge transfers to the polymers from metals of different work functions are shown in Figs. 5–8. Each point on the plot is the mean of 64 contacts made with each metal to nominally the same $8 \times 8$ array of points on the polymer surface. The work function of the metals is expressed as its contact potential relative to gold metal. The results from the plot suggest that the metal work function may influence the charge transfer to PVOH, PVAC and PMMA. There seems to be a tendency for the low work function metal to transfer low charge while the higher work function metal transfers large charge. Conversely, the transferred charge seems to be independent of the work function for PVC. A similar observation was earlier made for the case of

![Graph](image)

Fig. 5. Graph of charge versus work function for samples of PVOH (same preparation).
Tellon and poly(2-vinylpyridine) in our previous research [11,18]. We observe a large scatter in almost all the graphs shown and we note especially in Fig. 5 (one of the graphs) that Sn and Bi fall well away from the general trend. We do not think these exceptions are the result of mere chance because the charge transfer is reproducible.
Fig. 8. Graph of charge versus work function for two samples of PVC—(A) purified and (B) non-purified samples.

We obtained the same observation in our work on metal/nylon contact [15], hence we may conclude that charge transfer from polymer to these metals are anomalous.

4. Conclusion

Based on the evidence presented in this work, the following conclusions can be made for all the polymers studied:

- The sample-to-sample contact charging for different polymers by metals is fairly reproducible.
- Purification has no effect on the charge transfer to PMMA and PVC as observed earlier for polystyrene [16].
- The histogram of the charge distribution is not Gaussian in all the polymers but skews towards the larger charge. This result is common to all the polymers studied so far.
- The metal work function influences the charge transfer to PVOH, PVAC and PMMA; there is tendency for the charge to increase with work function. This conclusion agrees with the plastic polymer samples studied earlier [16]. Conversely, the metal work function plays little or no role in the charge transfer to PVC.

In summary, we can say that the influence of the metal work is very different for different polymers. It is evident that there is no justification for concluding that there
is a linear (or other functional) relationship between charge and the work function of the contacting metal.

References