

Triboelectrification – why is it variable?

A. R. AKANDE

Department of Physics, University of Botswana, Private Bag 0022, Gaborone, Botswana.

Abstract-A major problem in the static electrification research is irreproducibility which is often encountered. Charge transfer by contact of a metal to an insulator for example may vary widely from one contact to another even on the surface of a single polymer sample. The variation may in principle be a result of a place-to-place variation in the properties of the polymer or it might be changes in the properties of the metal (e.g. work function); or variation in the process of charge transfer (e.g. variation in the amount of back tunneling or material transfer). In the present study, we made a detailed study of the variation in the charge transfer for a variety of metals and polymer samples in order to decide among the possibilities. Our analysis shows the evidence that charge transfer is associated with variation in the properties of polymer surfaces. There are strong correlations between the fluctuations in the charge transfer from different metals, and between the neighboring places on the polymer surface. However, the variability of charge transfer is not a consequence of contamination as often suggested. We observed that the variation has little influence on the surface treatment before measurement is made. We conclude that the fluctuations in the charge transfer must be more closely connected with basic mechanisms of the transfer than has hitherto been supposed.

I. INTRODUCTION

The electrification of insulators by contact or friction is a familiar effect which has been the subject of much research. Nevertheless, there is no generally accepted explanation of the phenomenon. One major obstacle towards making progress in the explanation of static electrification is the well known problem of irreproducibility. We have observed (and many other authors) large differences between samples of the same nominally the same material and even a single piece of insulator may show place-to-place variation over its surface, or its charging characteristics may change with time [1] – [6]. Consequently, it is difficult to decide experimentally between alternative theories e.g. theory of insulator/insulator charging credited to Davies [7]; Duke and Fabish [8] bearing in mind the uncertainty set by the large scatter. Furthermore, even the straightforward empirical question can be difficult to resolve e.g. whether and in what way charge transfer from a metal depends on the work function [9].

Many attempts had been made to reduce the problem of irreproducibility, e.g. carrying out the experiment in the vacuum, using chemically well-defined synthetic

material/polymer such as nylon, polyethylene, polyvinyl chloride and some composite materials. Nevertheless, charge transfer remains ill-defined, showing considerable variation from sample to sample [7], [9], and [10]. The problem may be avoided to some extent by averaging the charge measured over a large area of insulator surface; either explicitly, by calculating the average of large number of measurements [9] or implicitly; by using other form of contacts (e.g. rolling or sliding) to cover a relatively large area [7], [11]. However this does not entirely eliminate the difficulties because the variations are large and unaccounted for.

It is not known why charge transfer is so unpredictable. It is commonly supposed that surface contamination is responsible [3], [12]; this is certainly plausible because it has been reported that the triboelectric properties of some polymers are sensitive ozone which is a common laboratory pollutant [13]. There is still yet no experimental evidence that the variation of charge observed is a consequence of accidental contamination.

In this study, we have investigated the place-to-place variation in charge transfer which may be a consequence of variation in the properties of the polymer surface, including for example contamination and variation in hardness. We investigated whether there is a correlation between the charge transferred by contact to different points and different metals. The correlation coefficient may possibly provide a clue to the various possible causes of charge transfer variation.

II. EXPERIMENTAL TECHNIQUES

All our experiments were carried out in a vacuum of better than 10^{-4} Torr, most importantly to avoid loss of charge by gas break down. The vacuum chamber is enclosed in a glove box so that the sample mounting and other operations can be carried out in an atmosphere of pure dry nitrogen; exposure of contacting metals to the laboratory atmosphere can thus be avoided for a long time. Our contact apparatus and measurement techniques were automated similar in many ways to that described in our previous work [9]. However, it was necessary to make contacts to precisely located positions on the surface of the insulator and the design of our apparatus was improved to achieve this. The essential features of the equipment are shown in simplified form in Figure 1.

To study the variation of charge transfer over the sample surface we made 400 contacts with each of the four metals; the contact with each metal are arranged in a 20 x 20 array whose spacing is about 1mm in each of the principal directions X and Y (Figure 1). The number of contacts with a particular metal must be large if the standard deviation and the shape of

distribution of charge transfer are to be meaningful. Our previous report on contact charge measurement were based on the average of 64 contacts [9] but were insufficient to determine properly the spread about the mean. The array of contact position for a particular metal is slightly displaced with respect to the contacts for other metals (see figure 1), so that all contacts were to previously uncontacted regions.

The details of sample preparation were essentially the same as described in our reported work [9]. Most of our experiments were on solution-cast polymers film (polyvinyl acetate, polyvinyl alcohol, polystyrene, polycarbonate, polymethyl methacrylate and polyvinyl-2-pyridine) and few of the samples are commercial materials in the form of

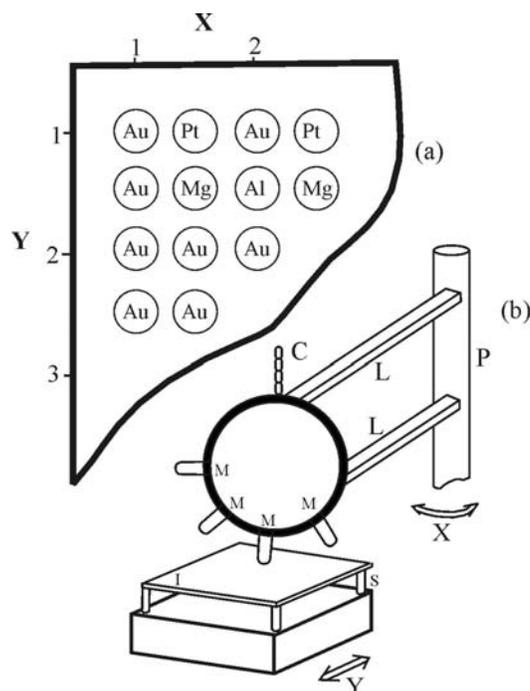


Fig.1. (a) A diagram of the contact position on a polymer surface, (b) part of contact equipment redesigned for accurate location of contact position on the surface of an insulator sample.

sheet of typically ~ 4 mm thickness (i.e. Teflon, polyvinyl chloride and polymethyl methacrylate). Such samples were prepared by lapping them to create a fresh surface [9], [11] or by 'cleaning' them by exposure to solvents.

A. Data analysis

The main focus of the work is to determine the whether variation in charge transfer are spatially correlated; for example if the charge transfer from a given metal is large at a particular position we want to know whether the charge at the neighboring positions is also and , if so, over what distance the correlation extends. To provide a quantitative answer to these questions we define correlation coefficients for points

separated by ΔX and ΔY in X and Y directions (Figure 1), and for a particular metal, as follows:

$$C_X(\Delta X) = \frac{\sum [q(X, Y) q(X + \Delta X, Y)]}{(\sum q(X, Y))^2} \quad (1)$$

$$C_Y(\Delta Y) = \frac{\sum [q(X, Y) q(X, Y + \Delta Y)]}{(\sum q(X, Y))^2} \quad (2)$$

where $q(X, Y) = Q(X, Y) - \langle Q \rangle$

$Q(X, Y)$ is the charge transfer at the grid position X, Y (Figure 1) and $\langle Q \rangle$ is the mean charge for 400 measurements. The sum is taken over the range $6 \text{ mm} < X < 15 \text{ mm}$ and $6 \text{ mm} < Y < 15 \text{ mm}$ so that ΔX and ΔY can range from -5 to 5 mm. Evidently, $C_X(\Delta X)$ is a measure of correlation between the fluctuation in the charge transfer at contact position ΔX mm apart in the X direction (grid spacing is ~ 1 mm). $C_X(\Delta X) = 0$ indicates no correlation and $C_X(\Delta X) = 1$ indicates perfect correlation.

We also want to know whether there is correlation between the fluctuations in the charge transfer from different metals; i.e. if a given place is strongly charge by a metal say gold, is it still also strongly charged by other metal? To provide a quantitative answer we define correlation coefficient for a given pair of metals A and B by

$$C_{AB} = (1/S) \sum q_A(n) q_B(n) \quad (3)$$

$Q_A(n) - \langle Q_A \rangle = q_A(n)$, which is deviation from the mean $\langle Q_A \rangle$, and

$Q_B(n) - \langle Q_B \rangle = q_B(n)$ which is a deviation from the mean charge $\langle Q_B \rangle$ and the normalizing constant is define by

$$S = [(q_A(n))^2 \times (q_B(n))^2]^{1/2} \quad (4)$$

Using a small computer program to do this calculation, each summation is carried over 400 contact positions. C_{AB} can vary from 1 (indicating perfect correlation) through 0 (indicating anti-correlation). It should be noted that a given grid position X, Y corresponds to slightly different position on the sample surface for the two metals A and B as we pointed out earlier (Figure 1a).

III. OBSERVATIONS

A. Charge distribution

Table 1 shows the mean charge transfer (400 contacts) and its standard deviation for Au, Pt, Al and Mg contacts to a range of polymers samples. We include measurements on nominally identical polymers samples so that sample-to-sample reproducibility can be assessed. As usual, the charge transferred is widely scattered about its mean value, i.e. the standard deviation is quite large compared to the mean. But this variation does not seem to be entirely a matter of chance because for many of the polymers there is strong correlation between the mean charge and the standard deviation.

More detailed information on the spread of the charge transfer from the mean value could be obtained from the histogram distribution. From our previous report [9] polymers which are

in sensitive to work function (e.g. PTFE, PVC) showed rather less spread than the others. We observed that the characteristic form of the charge distribution is the same for samples of quite different origin and treatment as can be seen solution-cast sample of PMMA, with commercial sheet prepared by lapping and washing in hot detergent followed by prolonged rinsing in water and drying.

Table1. Charge transfer from four metals to a number of polymers

	Charge transfer in (pC)			
	Au	Pt	Al	Mg
PTFE (lapped)	-2.3 (0.4)	-2.6 (0.4)	-3.1 (0.7)	-3.6 (0.7)
	-3.3 (0.3)	-3.8 (0.4)	-4.6 (0.4)	-5.0 (0.6)
PVC	-1.3 (0.4)	-1.3 (0.3)	-1.1 (0.3)	-1.5 (0.4)
	-1.8 (0.4)	-1.5 (0.4)	-1.2 (0.6)	-1.2 (0.3)
pvAc	0.20 (0.3)	0.24 (0.4)	0.09 (0.1)	0.08 (0.2)
	0.19 (0.4)	0.19 (0.3)	0.16 (0.2)	0.08 (0.1)
pvOH	0.39 (0.4)	0.56 (0.2)	0.11 (0.1)	0.45 (0.3)
	0.28 (0.3)	0.53 (0.2)	0.12 (0.1)	0.30 (0.2)
PS	-0.04 (0.1)	-0.01 (0.02)	-0.03 (0.05)	-0.04 (0.05)
	-0.01 (0.07)	-0.01 (0.02)	-0.03 (0.05)	-0.04 (0.05)
PS (oxidised)	-0.73 (0.6)	-1.5 (0.4)	-1.9 (0.8)	-2.0 (1.6)
PC	0.09 (0.08)	0.07 (0.07)	-0.03 (0.07)	-0.02 (0.1)
	0.05 (0.05)	0.09 (0.1)	-0.01 (0.2)	0.02 (0.06)
PV2P	1.4 (0.7)	2.1 (0.5)	0.33 (0.1)	1.1 (0.4)
	1.6 (0.9)	2.0 (0.6)	0.47 (0.3)	0.7 (0.5)
PMMA	0.11 (0.1)	0.26 (0.3)	0.07 (0.07)	0.08 (0.2)
PMMA (methanol)	0.39 (0.3)	0.55 (0.4)	0.24 (0.2)	0.28 (0.6)
PMMA (detergent)	0.39 (0.2)	0.27 (0.3)	0.21 (0.2)	-0.39 (0.7)
PMMA (lapped)	0.22 (0.2)	0.46 (0.3)	0.24 (0.2)	0.03 (0.2)

B. Spatial correlation

The place-to-place fluctuations in the charge transfer are not entirely random, table 2 shows that the fluctuations at neighboring points are nearly always correlated in the case of Au contacts (the same is true for other metals). The correlation coefficient calculated from equations (1) and (2) for 100 contact positions are nearly always positive and well in excess of the levels expected from chance (estimate to be about ± 0.1). The correlation sometimes persists to quite large distance. This was demonstrated in our work on nylon, polystyrene and polyvinyl chloride [6].

Table 2. Spatial and Inter-metal correlation

	Correlation				
	Spatial		Inter-metal		
	X	Y	Pt	Al	Mg
PTFE (lapped)	0.23	0.53	0.56	0.56	0.32
	0.05	0.32	0.13	0.37	0.12
PVC	0.03	0.13	0.14	0.65	0.20
	0.42	0.21	0.28	0.06	0.38
pvAc	0.48	0.46	0.47	0.34	0.24
	0.05	0.49	0.84	0.79	0.06
PS	0.02	0.01	0.06	0.13	0.03
	0.05	0.47	0.13	0.01	0.01
PS (oxidised)	0.35	0.55	0.46	0.62	0.54
pvOH	0.72	0.53	0.46	0.56	0.02
	0.74	0.67	0.57	0.58	0.38
PC	0.29	0.36	0.14	0.13	0.07
	-0.15	0.33	-0.06	-0.13	-0.10
PV2P	0.67	0.88	0.12	-0.04	-0.26
	0.76	0.69	0.39	0.28	0.08
PMMA	0.33	0.24	0.19	0.04	0.02
PMMA(methanol)	0.30	0.21	0.56	0.55	0.34
PMMA(detergent)	0.72	0.11	0.65	0.45	0.16
PMMA(lapped)	0.51	0.60	0.58	0.60	0.11

C. Correlation between different metals

Table 2 shows the fluctuations in the charge transfer from Pt (which has a similar work function to Au) is generally quite strongly correlated with the fluctuations observed with Au. The correlation coefficients (calculated from equation (3)) are almost always positive and well above chance level (0.05). The correlation coefficient between Au and the lower work function metals Al and Mg are also well above the chance level, but tend to be smaller, as a rule, than for Au/Pt. It is especially interesting to examine those polymers which acquire charge of opposite sign from different metals. They include polycarbonate and sometimes polystyrene, but the correlations are small and no reliable conclusion can be reached. We conclude from the above observations that the fluctuations in the charge transfer from different metals are not independent; if a particular region of polymer surface is strongly charged by gold, it will be also strongly charged by contacts with other metals.

IV. SUMMARY AND CONCLUSION

In almost all of the polymers we have studied the charge transfer varies widely from place-to-place on the sample surface. It seems that this variation is not entirely a matter of chance, however, because it exhibits the following distinctive features: (i) the distribution of charge about the mean is similar for different polymers if the charge is scaled with respect to the mean charge; the similarity hold even though the mean charge is very different for different metal/polymer combination; (ii) for most polymers the standard deviation is roughly equal to the mean charge; (iii) widely different surface treatment leave the width and shape of the distribution almost unchanged, indicating that

adventitious contamination is not responsible for charge variation in our samples.

The most striking similarity between most of the histograms (not shown in the present report) strongly suggests that the variation must have a common cause. Whatever the cause might be, it is obvious that it must involve some variation in the properties of polymer itself, because it is not otherwise possible to account for the correlations between the charge transfers for different metals.

We have assumed in our analysis that there is no backflow of charge from metal to the insulator during separation. Charge can, in principle, *tunnel* between metal and polymer during the early stages of separation, but probably not the low levels of charge commonly observed [14].

In conclusion, we have observed striking similarity in the charge transfer variations between one polymer and another. The evidence assembled above strongly indicates that the variation in charge transfer cannot be explained by deficiencies in experimental techniques nor the usual assumption that variation in charge transfer are associated with adventitious contamination of the surface. We therefore proposed that the variation may be as a result of the properties of the insulator itself and unavoidable feature of charge transfer mechanism.

REFERENCES

- [1]. P. E. Shaw, Proc. R. Society, (94) 16
- [2]. W. R. Harper, Proc. R. Soc. A. 218, 111-, 1953
- [3]. W. R. Harper, "Contact and frictional electrification" (Oxford: OUP) 1967
- [4]. A. H. Bowles, Proc. Phys. Soc. 78, 958-, 1971
- [5]. A. R. Akande and J. Lowell, "Contact Electrification of polymers by metals" J. Electrostat., vol. 16, no.2/3, pp 147-156, May 1985.
- [6]. A. R. Akande, "Charge correlation in metal/polymer contact", Composite structures, 54, 143-147, 2001.
- [7]. D. K. Davies, Advanced Static Electric, 1, 10, 1970
- [8]. C. B. Duke and T. J. Fabish, J. Appl. Phys., 47, 940-, 1978.
- [9]. A. R. Akande and J. Lowell, "Charge transfer in metal/polymer contacts", J. Phys. D: Appl. Phys., 20, 565- 578, 1987.
- [10]. R. Elsdon and F.R.G. Mitchell, J. Phys. D: Appl. Phys., 9, 1445-, 1976.
- [11]. A. Wahlin and G. Backstrom, "Sliding electrification of Teflon by metals", Journal of Applied Physics, vol. 45, no. 5, 2058-2064, 1974
- [12]. M. I. Kornfeld, Sov. Phys. Solid State, 11, 1306-, 1969
- [13]. D. A. Hays, Dechema Monographs, vol. 72, 1974
- [14]. J. Lowell, "The relationship between contact charging and the concentration of donor impurities in polymers", J. Phys. D: Appl. Phys., vol 12, 2217-2222, 1079.