Review Article

# THE INCREASING ROLE OF CHEMISTRY IN UNDERSTANDING TRIBOELECTRIC CHARGING OF INSULATING MATERIALS


## ABSTRACT

Triboelectric charging of insulating materials has traditionally been considered a physics problem, but chemistry is playing a rapidly increasing role. Several important advances have been made since the last reviews. These developments, together with description of the role of chemistry are reported here.



## KEY WORDS

Triboelectricity; Contact charging


## INTRODUCTION

Contact and separation of two materials *of different compositions* usually results in the generation of electrical charges at the contacting surfaces. This is known as triboelectric or contact charging. Repeated contacts result in potential buildup which may result in an electrical discharge, and this is referred to as static electricity. How and why such charge generation occurs is still largely unsolved, though considerable progress has been made in addressing several unconnected pieces of the puzzle. Mechanisms have been experimentally established for contact between *specific materials* under *specific experimental conditions*: exchange of **ions** (when a polymer contains mobile ions), exchange of **material** involving a mechanochemical mechanism (between two polymers); and the exchange of **electrons** (in metal-polymer contacts). It appears evident that more than one of these mechanisms can occur simultaneously, depending on the compositions of materials involved and the precise nature of the contacts.

The shift away from physics and towards chemistry and other sciences was pointed out in 2012 [1]. Since recent reviews [2,3], several significant developments have occurred. These developments, together with the increasing role of chemistry, are reported here.

## DISCUSSION

**Demise of the (*physics-based*) electron exchange theory for insulator-insulator contacts, and the emergence of a new (*chemistry-based*) theory.**

Triboelectric charging is one of the basic phenomena upon which the electrophotographic process and copying technology is based, and it was at one time reasonable to assume that its mechanistic understanding would contribute to improvement of this process. At the Xerox Corporation Webster research laboratories in the 1970s, it was assumed that such understanding would result from the physics approach that charging resulted from the exchange of mobile electrons trapped at the contacting polymer surfaces (the Surface State theory). It has long been disputed. Fabish at Xerox in

1979 pointed out, as a result of reviewing models for the electronic structure of organic polymers with focus on those having highly ordered groups with rigid periodic arrays of atoms, some having nearly metallic properties, that “the description of the electronic structures of these materials requires the introduction of concepts more familiar in the field of electrochemistry and physical chemistry than solid state physics.” [4]. Diaz reported in 1993 that “theoretical considerations argue against an electron exchange mechanism for insulators [5]. And Whitesides et al pointed out in 2010 that “in the early physics literature, many discussions concerning charging of insulating materials have assumed without (as far as we can see) any compelling experimental evidence that electron transfer is involved.” [6].

This theory, in modified form, was later applied by Lacks et al to account for triboelectric charging in asymmetric contacts between particulate materials of identical composition [7]. **But it has recently (2014) been disproved by Jaeger et al** [8], so another theory is now required. Such a theory had already been proposed by Williams in 2012 [1,3]. Its basis was that polymers and other materials are typically not compositionally homogeneous as a function of depth beneath the surface. Since contact between particles of different sizes are asymmetric, differences of degree or type of mechanical forces in such contacts would expose different layers, and therefore **different compositions**, at the points of contact. Alternatively, it was proposed that the different stresses would result in differences in the mechanochemistry at the surfaces which would also result in different chemical compositions.

Lacks et al have now (2014) followed up by proposing a similar mechanism for charging in asymmetric contacts between identical glass plates [9]. They report a correlation between charging and the degree of deformation of the glass surfaces. Their interpretation is that, since deformation of a surface changes its chemical properties, asymmetric deformations change the chemical properties of the glass surfaces in different ways, so that the contacts are actually between materials having **different chemical properties**. It is suggested that, since glass, in common with polymers, is typically not compositionally homogeneous as a function of depth beneath the surface, application of asymmetric stresses between glass slides simply exposes different compositions at the points of contact, as earlier proposed by Williams.

**A chemistry-based discovery of major business significance**

In 2011, it was demonstrated by Grzybowski and his group that pressing together and separation of two different polymers resulted in material and charge transfer, both of which were totally different from that previously reported [10]. They demonstrated using Kelvin Force Microscopy (KFM) that each surface consists of irregular mosaic patterns, each domain supporting large numbers of either positive or negative charges, resulting in a net charge of one sign on both surfaces. Following up on this landmark discovery, they reported in 2013 [11] that the surface charges in the domains are stabilized by association with surface radicals, which are formed by polymer bond scission. And doping the polymers with free radical scavengers removes the radicals, resulting in destabilization of the domains and rapid discharge. The business significance of this is immense, because it allows the design of antistatic coatings to protect semiconductor devices from failure caused by buildup of static electricity, a matter of increasing concern in view of the continued miniaturization of such devices, with increasing sensitivity to such discharges.

**The role of mechanochemistry**

Galembeck et al have recently published [12] further support for the mechanochemical mechanism for triboelectric charge exchange which was previously published in 2012 [13]. Mechanochemical reactions, triggered by friction, produce ionic polymer chain fragments that are transferred between the surfaces, even when the two surfaces have identical compositions.

**Understanding metal-insulator contacts**

Contact between a metal and an insulator presents a different scenario than between two insulators. Since triboelectric charging between two metals has long been established to result from electron exchange, it was reasonable to suggest that electron exchange may be at least a contributory mechanism to metal-polymer charging. And, indeed, some experimenters have reported that charge exchange is linearly related to the work functions of the metals, which supports an electron exchange mechanism [14,15,16]. But others have found that this correlation does not always apply [17]. This strongly suggests that additional mechanisms can apply simultaneously. The finding that some materials form a cyclic triboelectric series [18] strongly supports more than one simultaneous mechanism. Based on current knowledge, it is reasonable to suggest that the additional mechanism would be material transfer.

The application of polymer chemistry has recently been proposed for determining the relative contributions of *material* and *electron* transfer to metal-polymer charging [19]. Polymers were designed such that the compositions of their topmost molecular layers were totally different from those of the bulk. There are two ways to achieve the surface-bulk compositional differences. Fluorinated molecules and polymers have low surface energies and, when added to polymers, will migrate to the topmost molecular layers when the films are solution cast to allow for thermodynamic equilibrium [20,21,22]. Alternatively, ionic components, on account of their high surface energies, will avoid the topmost layers. The availability of several extremely sensitive methods for analyzing surfaces at a molecular level adds to the appeal of this approach to determining the depth of a polymer surface that affects charging, a concept referred to as the “charge penetration depth”. These include XPS (x-ray photoelectron spectroscopy) [23], TOF SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) [24] and LEIS (Low Energy Ion Scattering) [25].

A series of polymer films was prepared such that their surface molecular compositions were identical, but they differed systematically in their bulk compositions. Bare metal and polymer coated beads were cascaded over these films, and the charge on the beads determined. It was found that charging of the polymer coated beads was constant for the film series, implying that charging was determined by the topmost surface layers of the films. But charging of the metal beads varied systematically according to the bulk compositions of the films, indicating that charging was determined by deeper levels of the films. It was suggested that the rougher metal beads may gouge out deeper layers of the films than the smoother polymer coated beads. Whether charging of the metal beads results from material or electron transfer depends on whether it is the surface roughness or the metallic nature of the beads that results in the charging to be related to the bulk compositions of the films. This can be determined by systematically varying the surface roughness of the metal beads.

## CONCLUSIONS

Triboectricity is of considerable importance in industry, in solving problems such as damage to electronic equipment and tanker explosions, and also for the design of industrial processes such as the separation of materials in the recycling industry. It is of major significance to NASA in connection with space exploration, and to the pharmaceutical industry on account of unwanted charges created in the handling of powders. And it is the basis for useful products, the best known being copiers and laser printers. Phone sized portable x-ray machines are currently being developed by California start-up Tribogenics, representing yet another major application of triboelectricity, and a revolution in the industrial and medical application of x-rays. The widespread importance of triboelectricity is such that research is currently being conducted on its various aspects by engineers (electrical and aeronautical), physicists, chemists, medical practitioners and meteorologists, and yet its basic understanding remains elusive. Significant levels of understanding of the mechanisms of triboelectric charge generation have been accomplished for specific materials and experimental conditions. But expanding this to include a wider range of materials, contact types and experimental conditions in general, and integrating these into a coherent whole, will require continued efforts along multidisciplinary fronts, with various aspects of chemistry being of prime importance.

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