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Original Research Paper

Effects of particle size on the triboelectrification phenomenon in pharmaceutical excipients: Experiments and multi-scale modeling

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ABSTRACT

Particle sizes play a major role to mediate charge transfer, both between identical and different material surfaces. The study probes into the probable mechanism that actuates opposite polarities between two different size fractions of the same material by analyzing the charge transfer patterns of two different sizes of microcrystalline cellulose (MCC). Quantum scale calculations confirmed alteration of charge transfer capacities due to variation of moisture content predicted by multiple surface and bulk analytical techniques. Discrete Element Method (DEM) based multi-scale computational models pertinent to predict charge transfer capacities were further implemented, and the results were in accordance to the experimental charge profiles.

1. Introduction

Tribocharging refers to the phenomenon of charging two solid surfaces when they are brought into contact and separated [1,2], acquiring positive or negative polarities based on the mechanisms of charge transfer. The hazards and problems related to tribocharging have been long known, and reports of related instances can be dated back to as early as 1745, when jets of water from an electrostatic machine led to the ignition of Spritius Frobenii (a sulfuric ether) [3,4]. Among multiple incidents reported in the past century include severe explosions

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Abbreviations: φ, Work Function; ε_o, permittivity of the free space; ε, Relative permittivity of the medium; eV, electron Volts; E_{gap}, Energy gap between HOMO and LUMO; F_c, Columbic Force; F_N, Normal Forces; F_{sc}, Screened Columbic Force; F_T, Tangential Forces; ΣF_i, Net force acting on a particle; IP, Ionization Potential; K_B, Boltzmann's constant; m_i, Mass of the particle; n_i, number of particles within the screening distance; q, Charge of particle; q_e, Charge of an electron; s, Contact area; T, Temperature in Kelvin; ΣT_i, Net torque acting on the particle; z, Cut off distance for charge transfer.

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in 1969 that took place when 200,000 ton oil tankers exploded while washing with high velocity water jets [5]. Repeated accidents during the period 1950–1970 in different industries including petroleum [6], defense, chemical [6] and powder handling triggered meticulous investigation of the underlying cause of these incidents (i.e. tribocharging). Since then more than several thousands of research articles have been published discussing tribocharging in various fields ranging from pharmaceuticals, explosives, xerography, food, polymers, nutraceuticals, catalysts, etc.

Tribocharging triggers multiple impediments in industrial storage and handling [7,8], including jamming [9], segregation [10], loss of material due to adhesion, reduced fill, change in dispersion or aggregation behavior in fluidized beds, pneumatic conveying [11], functional interruptions of equipment components, in drug delivery devices such as dry powder inhalers [12,13] and often personal discomforts due to electric shock. Tribocharging can also lead to potential hazards of fire explosions by the discharge of static charges (known as charge relaxation) from the tribocharged surfaces in the presence of low flash point solvents such as ethanol. Flash point of 70% ethanol is 16.6 °C, which means that even at a temperature as low as 16.6 °C, the 70% ethanol will have enough concentration of ethanol vapors in the air to cause explosion in the presence of an ignition source. This ignition source can be provided by the electric discharge from various surfaces. Considering the present wide spread use of several low flash point organic solvents and large quantity of dry powders (a major source of tribocharging) in pharmaceutical, food, defense and nutraceutical industries, tribocharging raises major safety concerns.

Tribocharging has been known mostly to take place between different materials and has been found to increase with increased surface contact area, suggesting increased accumulation of specific charge for particles with smaller dimensions. Among the various surface factors affecting the polarity and magnitude of tribocharging includes roughness, contact force, friction, co-efficient of restitution, hygroscopicity, crystallinity and shape. However, bipolar charging has also been observed between particles of the same material with different size fractions. Bipolar charging in similar materials has predominantly been observed to trigger tribocharging [14–22] in a way where smaller particles tend to acquire negative charge on coming in contact with bigger counterparts, which acquire positive charge. Tribocharging in identical materials has been observed in various fields ranging from i) pharmaceutical unit operations such as fluidized bed drying [15], and pneumatic conveying [14]; ii) natural phenomenon such as dust storms [18–20,22] and volcanic plumes [21]; iii) aerosols such as found in DPIs [16]; and iv) Mars regoliths [17] etc. This phenomenon has also been confirmed through various experimental set-ups, and the magnitude of charge is found to increase with a concomitant increase in particle size ranges [23,24]. Some of the earliest experimental evidence of bipolar charging in identical materials can be traced back to 1957, when Henry [25,26] reported different polarities of charge on two similar rods, and the polarity of charge was based on their position as a bow or string of a violin.

Conductor or metal contact electrification has been studied for many years and is well understood to be a process of the transfer of electrons between two metal surfaces, driven by the difference in chemical potential of the interacting materials to achieve thermodynamic equilibrium [27]. But a consensual theory to describe insulator–metal or insulator–insulator contact driven tribocharging is still missing, considering the insulator surfaces are not well characterized. The three most widely accepted hypotheses for the same are as follows: i) *Electron transfer*: advocating the procurement of positive or negative charges based on the lower or higher ionization potential values respectively [28–31]; ii) *Ion transfer*: advocating the transfer of charge to and from insulators with the help of mobile ions [32–35]; and iii) *Mass transfer*: advocating the transfer of mass from a soft material (polymer) to a rougher and harder material (metal) [36,37]. The effects of electron transfer have often been regarded as the main charging mechanisms in case of non-ionic polymers in absence of the mobile ions [2,28,29]. However, what is more intriguing is how to define the charge transfer mechanisms in identical materials. Since its first observation, many literature reports and hypotheses have been published to describe this phenomenon. In 1985, Lowell and Truscott [38] made an attempt to explain this phenomenon using various experimental procedures ranging from sliding a ball over a plane in both vacuum and atmosphere, and they came up with a mathematical model based on the non-equilibrium distribution of energy states to describe the same [39]. Recently in 2008, Lacks et al. have embarked on the same principle and have mathematically demonstrated the viability of this non-equilibrium state model [40]. However, it is necessary to explain the energy distribution of electron states at the surface of insulators [39], otherwise limiting its physical understanding and hence failing to provide ways to mitigate bipolar charging in real scenarios.

The fact that the insulators are not ideal insulators and there are trapped electrons in the band gap [40] available to be transferred to lower energy states, allows scope of metal-like work function treatment of the insulators to predict charge transfer and develop a triboelectric series. Similar treatments could also reveal surface work function differentials between different size fractions of identical materials. Recently Murata [41] and Zhao et al. [42] have discussed the effects on work function values in different polymers based on the depth of the surface electronic states, the trap densities and the distribution of the filled states. Zhao et al. [42] have discussed the effects of surface roughness on tribocharging, i.e. different amounts of surface roughness can lead to different amounts of adsorbed species and hence different extent of contact and charge transfer. Li and Li [43] observed a decrease in work function in metals with increase in physical properties like plastic strain. Brocks and Rusu [44] investigated the changes in work function due to atmospheric contamination or chemisorbed surface species, by altering the surface dipoles based on the intrinsic dipoles of the molecules of the absorbed species. Cartwright et al. [14] have also discussed the effects of surface moisture on bipolar charging of polyethylene powder and determined that the relative humidity (RH) plays a significant role in determining the polarity as well as the magnitude of the charges generated.

All the afore-mentioned theories and discussions have been around for some time, but they still lack a satisfactory explanation for tribocharging in identical insulator materials. In the