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Friction, Tribochemistry and Triboelectricity: Recent Progress and Perpectives

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Production of electricity by friction is well known but poorly understood and it is the source of electrostatic discharge causing serious accidents. Recent results are in agreement with one of the conflicting views on this problem, according to which triboelectricity in polymers is triggered by mechanochemical and wear or mass transfer phenomena. These results also challenge the widely accepted paradigm of one-way charge transfer that is the basis of the triboelectric series. Experimental results from powerful analytical techniques coupled to surface charge mapping support the following hypothesis: charge-bearing species are ionic polymer fragments formed through mechanical action. Beyond, the atmosphere participates from tribocharge build-up and dissipation due to reactive plasma formation and to charge exchange at the gas-solid interface, mediated by adsorption of non-neutral water or to ion partition during water adsorption, as in hygroelectricity phenomena.

History

Triboelectric charging produced on contacting surfaces is a frequently observed phenomenon that was discovered 25 centuries ago: when two materials are rubbed or touched together, static electric charge is formed.[1] Its discovery is credited to Thales of Miletus, a pre-Socratic Greek philosopher, who observed that amber rubbed with fur attracts small pieces of straw, thread, hair and other solids. This was known as the 'amber effect'. However, there are no written reports supporting Thales' role in this discovery.[2]

By 1600, William Gilbert studied magnetism and the "amber effect", observing that many materials beyond amber attract others when rubbed and they were classified as *'electric'* (from *elektra*, the Greek word for amber)[3]. Later, Stephen Gray demonstrated experimentally the difference between insulators and conductors.

In the eighteenth century, Charles Dufay distinguished two kinds of electricity created by friction and called them *vitreous* (produced on glass, rock, crystals, precious stones, wool, etc) *or resinous* (formed on resinous materials, for example, rubber, copal, gum lack, silk, paper, etc). This classification was later abandoned in favor of the distinction between negative and positive charges introduced by Benjamin Franklin.[3] Faraday observed electricity created by friction of water and steam against other materials, when water and steam acquired positive charge, while the other materials became negative.[4]

Electrostatic phenomena attracted the attention of many scientists making important theoretical and experimental contribution, as Coulomb, Maxwell, Tesla, Volta, Faraday, Kelvin, Rutherford and Bohr. Earlier results are consolidated, for instance, in Maxwell's Treatise.[5]

Electrostatic charging is currently applied in many important technologies and processes such as photocopying,[6,7] laser printers,[8] electrostatic painting,[9] electrospinning,[10] electrets, which are found in a large range of equipment, including acoustic transducers[11,12] particle separators[13] and electrostatic filters.[14] Plastic residues separation based on triboelectricity[15] is increasingly useful in polymer recycling.

However, despite this long history, electrostatics is far from having reached the status of a mature scientific discipline since it still contains important unsolved problems and the literature is full of contradictory reports. For instance, Schein collected three conflicting reported results on the charge acquired by Teflon rubbed with gold: in one report it is positive, negative in another and neutral in the third.[8] Many other conflicts are well documented in the literature.[16]

Many open questions concern the nature and identity of electric charges in insulators as well as the mechanisms for their formation. For instance, how can charge-bearing species in insulators be detected, identified, and quantified? What are the mechanisms leading to solids contact electrification and/or triboelectric charging? The explanation of the production of electrostatic charge comes from a transfer of electrons, ions or both, which are presented in the literature?[16]

Poor knowledge on charge accumulation and dissipation mechanisms[17-19] is a root of large-scale personal and property losses, including serious industrial accidents and explosions that are described further in the next section. This is ultimately due to the lack of scientific understanding of the basic phenomena.

On the other hand, fundamental electrostatic concepts are well established for semiconductors and metals.[20] When two metals with different work functions are brought into contact, electrons migrate across the interface creating a potential difference between them.

Although knowledge on contact electrification progressed slowly during most of the last century, a surge of renewed interest can be observed recently.[21-25] Conflicting evidence supporting electrons, ions or material transfer mechanisms during contact electrification has been recently reported and debated by different groups but the level of understanding and consensus on some basic issues is growing. This will be discussed later in this review, including the triboelectric series, a concept widely used to assemble experimental information on triboelectrification.

Consequences of surface static charging

The complexity of contact electrification led Lacks to state that it could be unpredictable[26] and it has several important consequences, for technological and safety reasons. Fire and explosion hazards associated to electrification are associated to many production, storage and transportation activities[27] in process industries and manufacture, *e.g.* fluidized beds[28] and semiconductor chip manufacturing.[29]

Hazards triggered by electrostatic discharge (ESD)

Lightning and other natural discharges are acknowledged as dangerous even by primitive human beings and they have a prominent status in mythology. Electrotherapy used electrostatic machines in the 1800s[30] and some attempts to repeat Benjamin Franklin's experiment on atmospheric electricity were tragically unsuccessful. Dust explosions were first recorded in the 18th century, in an episode involving wheat flour in Turin, Italy but the risks of seemingly spontaneous charge build-up in handling dielectric materials were not recognized prior to the past century. Following Castle,[31] it was only in 1907, in the period when power transmission lines were being expanded, that a successful application of electrostatics was achieved, with the installation of the first commercial electrostatic precipitator. Thenceforth, many fires and explosions triggered by electrostatic discharges (ESD) were reported and great efforts were directed to create safer machines and processes.

Electrostatic charges are invisible and discrete. For this reason, materials that are apparently harmless and safe to naked eye can store large amounts of charge. Codes of practice for the avoidance of hazards due to static electricity and consequently the guidance for the use of Personal Protective Equipment (PPE) are thus very important and constantly updated in industrial environments.[32]

Since 1994, the U.S. Department of Transportation reported 1423 injuries, 370 fatalities and almost \$6 billion in property damage in pipeline transport (gas and hazardous liquids), where 13% of the cases had miscellaneous and unknown causes, possibly due to electrostatic discharges.[33] ESD are dangerous in many situations but obviously they are of great concern when flammable materials are present.

Accumulated electrostatic charges can explode entire industrial plants even without the participation of fuels. Incidents and explosions involving powder-processing plants are very well documented and dust explosions are known as main industrial hazards.[34] Small and large disasters are not rare in sugar, grain and other powder processing plants.[35-37] The most recent explosion in the US happened in January 2014 within a grain processing facility in Omaha NE killing two people and injuring ten. The Occupational Safety and Health Administration (OSHA) has a long list of powder materials including milk, soy, apple, tobacco blend, charcoal, dextrin, plastics that hold potential for a "combustible dust" explosion.[38] Also, OSHA constantly emits updated reports on prevention and safety conductions for processing or transportation of materials in powder forms.[39] Powder processing is a great problem in pharmaceutical industry, not only due to problems related to ESD but also because electrostatic charging can lead to non-homogeneous mixtures.[40] The dosage of the powders is based on the powder volume and reproducibility depends on the flow behavior during powder processing,[41] but this can be seriously affected by electrostatic charge.[42]

Undesirable adhesion and soiling

Another issue caused by electrification is unwanted adhesion, *e.g.* of dust particles in solar panels (SPs).[43] Huge efforts have been made to obtain better materials to increase solar energy conversion efficiency and each one-percent gain is celebrated by researchers and the media. However, one of the biggest limitations for the SP efficiency in the field is the shielding of light due to deposition of electrified dust. This is especially serious in deserts, the sites with higher levels of incident solar radiation on Earth but with abundant dust that easily adheres to the panel coatings. Water is not abundant in those areas and cleaning is always slow and costly. An even worse scenario is with SPs in space explorations of the Moon and missions to Mars, where SPs are essential to energy generation but cleaning is impracticable. One solution was reported by Calle *et al.*, who developed an electrodynamic display for SPs that repels dust particles from its surface by applying low frequency (usually 10 Hz) AC voltage.[44] Figure 1 shows the dramatic voltage drop due to dust deposition followed by its recovery when the electrodynamic cleaning is turned on.

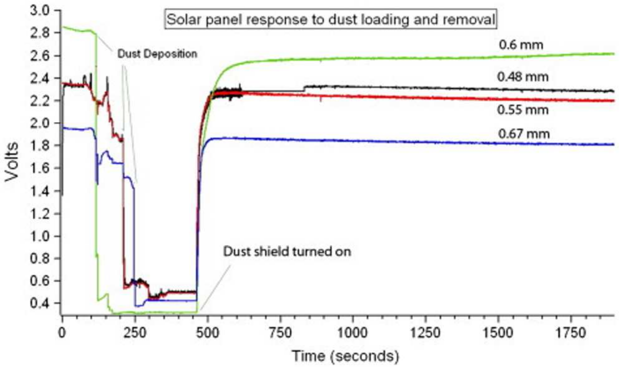

Fig. 1 Solar panel response to dust deposition and removal under high vacuum conditions. Removal was accomplished using dust shields with four different electrode distances. Reprinted with permission from Ref. [44].

ESD costs millions of dollars to electronics industry due to damaged components, non-functional circuit boards since it can destroy even the most robust semiconductor devices.[45] ESD can occur in the manufacturing and field handling of integrated circuits or computer boards leaving no visible signs of damage.[46] Besides, even the packaging for electronic components must be done using special non-static materials, which are made using expensive materials and processes.[47-49] Nevertheless, the advances in understanding the mechanisms for charge build-up and dissipation in dielectrics are allowing to design and build new materials capable to dissipate charge extremely fast, while still having a high bulk electrical resistance.

Flow electrification

Flowing dielectric liquids build-up electric charge as the result of friction against the walls in pipelines, eventually causing fires and explosions in apparent contradiction with the widespread concept of electroneutrality.[50] Electrification of liquids is a particular kind of contact electrification involving still poorly defined but probably different mechanisms for polar and non-polar liquids.[51-55] Initial interest was on insulating liquid fuels[56] that became important by the end of the nineteenth century, due to oil pipeline hazards but were later observed for many other liquids, including water.

Recently, it was discovered that ultrapure water used in the production process of semiconductor chips can electrify circuits causing serious breakdown of electronic components.[57] Four different groups[57-60,61] have shown that water flowing through hydrophobic materials like PTFE becomes positively charged creating a new possibility for energy harvesting that will be presented in the Perspectives section, in this paper. However, much additional work is needed on flow electrification of water in contact with hydrophilic surfaces.[62]

Last but not least, landing aircraft carry large amounts of electrostatic charge (hundreds of kV producing currents as large as 1000 μA).[63] This requires especial safety procedures and static discharge devices[64,65] are essential to prevent ESD causing fire and damage to electro-electronic aircraft components.[66]

The triboelectric series

As many others in the 18th century, the Swedish physicist J.C. Wilcke was using the so-called Leyden jar to investigate the *contrary electricities* (electrostatic attraction) during his doctoral dissertation. In 1757 he obtained the first list of materials empirically ordered according to their tendency to acquire positive or negative charges subsequent to mechanical contact.[67] Many other scientists also built their own lists of materials but the term **triboelectric series** (TS) was coined by Shaw in 1917.[68] Apparently simple, these empiric tables contain important contributions from solid surface properties and behavior that intrigue scientists since their inception and impair reproducibility.

Materials position

In the TS, different materials are vertically arranged within a single column as shown in Figure 2, where those closer to the bottom tend to acquire negative charge when contacting or rubbing the ones above them. Common hydrophilic solids such as glass and nylon cluster at the top whereas hydrophobic materials like polyethylene, polytetrafluoroethylene are found closer to the bottom of the TS. This simple observation and others like it lead to questions like: *what is the relationship between surface polarity and the amount of charge transfer between contacting surfaces?*

Some explanations have emerged to explain how and why materials are ordered in TS. One of the first (and most often quoted) theories was based on the work function of materials, where electron donor-receptor behavior should be responsible for the charge polarity acquired by the materials. In fact, in metal-metal or metal-semiconductor interfaces with zero or small band gaps, electrons flow from the material with lower work function until the Fermi levels are equilibrated[69] in an endothermic process but analogous events in dielectrics require large activation energies.[21]

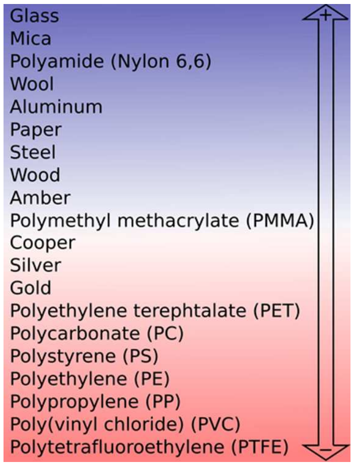

Fig. 2 Triboelectric series of common materials collected from Ref. [87].

The role of water

Observing thunderstorms, it seems obvious that water must be related to electricity formation and storage in the clouds. Electrostatic charge stored in the clouds has been described as the result of water crystals collision generating huge electric fields strong enough to initiate lightning.[20] Moreover, any solid surface in the environment contains some amount of adsorbed water that can accumulate charge. This and other observations pose the question: *what is the relationship between ambient water and electricity?*

In 1867, Lord Kelvin described a very simple but fascinating experiment, the *Kelvin water-dropper*, also known as Kelvin's thunderstorm.[70] The apparatus consists of two jets of water allowed to fall from separate nozzles, passing through metallic rings or cylinders and collected into separate metallic containers, electrically connected to the rings. Water becomes spontaneously charged during detachment from each nozzle due to the presence of external electric fields, always present in the environment (*the atmospheric potential gradient at the Earth surface is as high as 100V/m!*)[71] producing electric potential differences of many kV. The Kelvin dropper is constantly tested and revisited since achieving smooth operation is a big challenge. Recently, a microfluidic Kelvin dropper was built where small droplets of water charged and broke up due to electrohydrodynamic instabilities, converting pneumatic pressure into electrical energy.[72]

Ovchinnikova and Pollack[73] reported on water capacity to store charge for long periods of time and release substantial amounts of charge. This was questioned by Corti and Colussi[74] leading to a strong debate. The formation of water with excess charge was described later, including surface tension, electro-capillarity, density and viscosity data.[75] On the other hand, electrification phenomena can also be observed under careful exclusion of water, showing that different mechanisms may actually coexist, either competing or showing synergy.[76] The same authors found that water helps to stabilize the surface charges formed during contact in its absence.

Water is also responsible by another group of charging phenomena, the electrification by adsorption of water vapour or hygroelectricity. When exposed to variable humidity under shielded and grounded environment, many solids acquire charge due to the partitioning of OH^- and H^+ ions associated to water adsorption. Thus, the atmosphere is a source and sink of surface charge[24] that produces electric potential gradients along the surface, as high as 4 MV/m. Charging by this mechanism depends mostly on the Brønsted acid–base character of solid surfaces: hydronium ions adsorb on basic sites while hydroxide ions adsorb on acidic sites.[77] This suggests that the behavior of any material tested in a triboelectric series is dependent on the actual state of its surface and especially on the detailed surface chemical composition that is often ignored.

The effect of acid-base characteristics of solid surfaces on contact charging has been considered in the literature, independently of the participation of water sorption. Using the surface force apparatus, Horn *et al*.[78] demonstrated a correlation between acid-base interactions and contact electrification for two silica surfaces where one was coated with a compact positively charged monolayer. Also, the wettability was used as the approach to estimate the electron-donor surface tension parameter,[79] which was theoretically associated with the position of few solids in the TS.[80] Extension to other materials was limited and the applicability of this model is restricted to a few cases.

Recently, an MIT group showed that a set composed of water from various different sources and its container (*e.g.* polyallomer centrifuge tube) is always negatively charged and this is also function of temperature.[81] This apparent contradiction to Faraday's early results is mostly due to the experimental protocols. Although both were measuring the electrical charge of water, Faraday was conducting "*friction*" experiments, where water (or steam) was streamed through pipes whereas the MIT team was measuring the couple, water + recipient. It is remarkable that even playing such a key role in contact electrification (CE), water was never included in triboelectric series.

Building the triboelectric series

The beauty of the TS is that, even though CE experiments are acknowledged as hardly reproducible, TS described by different laboratories[82-84] are surprisingly similar and with few inconsistencies, albeit experiments, protocols and materials preparation are different. Experimental results are affected by surface variability, nature and intensity of contact and the effect of charge back flow across the interface as the surfaces are drawn apart, due to electron tunnelling or air breakdown. The precise nature of the surfaces is hardly known due to dust particles, atmospheric or exudate surface contaminants and adsorbed water layers. Besides, the real contact area is difficult to measure.[17]

The role of rubbing compared to simple touching or rolling is not clear. Some argue that rubbing just increases the contact area, while others assign some role to the energy associated with it.[20,69]

In general, there is a consensus that the electrification depends on the type of contact.[85] Besides, as pointed out by Shaw, most solids alter their positions if heated above a certain temperature, characteristic for each material.[68] For those reasons, most of the reliable TS are built using single or cumulative contacts between a planar sample of the sample and a metallic spherical probe, usually gold, with very well defined load and environmental conditions. Moreover, Whitesides and collaborators built an apparatus consisting of a ferromagnetic stainless steel sphere rolling on a flat dielectric where this rolling contact is used to achieve accurate contact charging measurements and consequently robust TS.[86]

Since there is no accepted theoretical basis to describe or predict TS neither a definite relationship to some parameter such as dielectric constant or conductivity, setting up and extending the tables relies on the critical analysis of accumulated information and on testing with well-controlled charge measurements using reliable Faraday cups. In fact, many semi-empirical TS (SETS) are found in the literature but often including non-significant data. On the other hand, Diaz and Felix-Navarro[87] built a robust SETS made only of polymers and were capable to relate, at least partially, the relative position of the materials with the chemical structure and some physical-chemical properties. According to these authors, nitrogen-containing polymers develop positive charge whereas hydrocarbon-based polymers acquire insignificant amounts of charge and halogenated polymers develop strong negative charge. They also show a reasonable correlation between the charge acquired and the pK_b equilibrium constant for the relevant acid-base dissociation reactions. Moreover, they also concluded that ion transfer is the decisive mechanism on CE of polymer-polymer contact.

Limitations of the triboelectric series concept

The usefulness of the triboelectric series derives from its contribution to predicting charge developed following friction or contact in a range of situations, including accident prevention. Unfortunately, this ambition is challenged in everyday situations. Asymmetry in mechanical contact, polymer processing history, disordered or contaminated surfaces including undisclosed antioxidant agents and many circumstantial factors contribute to make CE acknowledged as highly unrepeatable phenomena in the world real. Moreover, most of the charging measurements are done using Faraday cups connected to electrometers. Irrespective of the quality of the instrumentation, this is limited in an intrinsic way: the amount of charge measured is the algebraic sum of all charged species, positive and negative. This objection only appeared recently in the literature, when the coexistence of positive and negative charge patterns was first disclosed (see the section on "Charge patterns in polymer surfaces", ahead). Till then, contact or tribo-charged objects were considered either positive or negative. Thus, charge measurements made on Faraday cups tell only the balance of charge acquisition, omitting the separate contributions. Moreover, the TS concept implies that mutually rubbing two separate pieces of the same material should not produce a net charge but this has been observed under different circumstances (see the section on "Charge patterns)".

Current conflicting views

The nature of charge carriers in insulators has been a matter of disagreement among researchers and the authors believe that this is at least partly due to the emphasis in finding a single overarching solution to a complex problem with many factors. Its status was summed up by Harper: “A crucial question for the explanation of the production of static charge is whether the charging of insulators comes from a transfer of electrons, of ions, or of both. Montgomery would say that the carriers of charge are always electrons and Loeb that they are generally electrons: Henry feels that the question is still an open one. I am of the opinion that a definite answer can now be given which is that the carriers are never electrons - when the material being charged is strictly an insulator”.[1]

Three charging mechanisms[88] have been examined in recent years: ion partition between surfaces, electron transfer and mass transfer, represented in Figure 3.

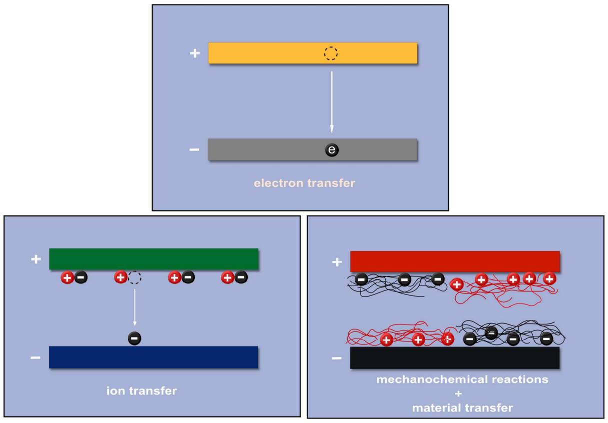

Fig. 3 Representation of three models for electrification of insulating surfaces.

Evidence in favour of ion partition was presented by Whitesides and coworkers who proposed a mechanism for transferring ions in the formation of electrets.[21,89,90] They showed that glass rendered positive or negative (with silanes containing quaternary ammonium salts and sulphonated silanes) acquired charge opposite to the mobile counter-ion of its surface, following contact with metal spheres.

The mechanism of ion transfer proposed by Diaz [91-93] relates the polarity and magnitude of the charge to the structure and concentration of ionic species. The model is based on Lee’s model for charge equilibration between two surfaces and it assumes that this is proportional to the relative contact areas. The model can explain the electrification of polymers containing ionic additives, except when they are hygroscopic salts.

Recent work from the authors’ group shows the participation of OH$^-$ and H$^+$ ions derived from atmospheric water on charge pattern formation and suppression, in many materials.[24,77,94-100] and its dependence on the acid-base characteristics of the solid surface was referred to in the previous section. Hogue *et al.*[101] considered that surfaces may have regions with more or less available sites for a given ionic species, causing charge imbalances and giving rise to differences in electric potential. Moreover, ion exchange at the surface and the amount of charge decrease with decreasing atmospheric pressure. Yu *et al.*[102] assign triboelectric charging of moving particles to the different mobility of H$^+$ and OH$^-$ between contacting particles, considering also the effect of temperature differences.

A completely different interpretation was given by the Bard group to PTFE charging by contact with PMMA. These authors obtained evidence for the formation of electrons on PTFE surface, since charged PTFE triggers some reactions assigned to the presence of free electrons.[22,103,104] Earlier, Gubanov[105] predicted electron emission following many-fold extension of polymer chain bonds. Also, Lowell and Truskott considered that contact between two surfaces provides a way to liberate high-energy electrons trapped in insulators. Contact brings together an occupied high-energy state with a vacant low-energy state on another surface, enabling electron transfer[106] of trapped high-energy electrons, in a situation analogous to phosphorescence observed following ultra-violet irradiation.[107] The theory was used to explain charge decrease by humidity, considering the formation of a water layer, through which trapped high energy electrons can escape to lower-energy states on the same surface, without electron exchange with the other surface[108] as well as the electrification of identical materials, where smaller particles became negatively charged.

One evidence in favor of electron transfer is the reduction of Pd^{2+} and Cu^{2+} ions on tribocharged PMMA. This was criticized by Piperno *et al.* [109] who observed the mutual transfer of material between PMMA and PTFE, increasing the capacity for cation adsorption on PTFE. Following these authors, "the static charge might be due to uncompensated ions rather than cryptoelectrons". On the other hand, the “single electrode electrochemistry” concept introduced by the Bard group was experimentally verified but using charge injection from Al into PMMA.[110] This will be further discussed under “Lithography”, in this review.

Mass transfer associated to surface contact and wear was first considered by Clark *et al.*[111] who observed polymer transfer in the contact of PTFE and PET films, using the then newly developed ESCA or XPS technique. Material transfer was observed on PET and PTFE surfaces, following contact. These two materials are well apart in the triboelectric series, and a large material transfer accompanied a large charge exchange, evidenced by F and C-F group detection in PET surface spectrum. Polymer transfer evidence was also obtained in tribocharged PTFE spectrum, where the characteristic Cls and Ols peaks of PET were observed. The double mass transfer occurred even when no external pressure was applied. An additional F1s line corresponding to fluoride ions was also detected, evidencing some complex chemistry. Clark *et al.* called the attention to the fact that to detect charge is easier than mass and stated: “Mass transfer, therefore, cannot be ruled out as the mechanism of charge transfer in triboelectric phenomena. On the contrary, mass transfer must be considered in models of contact charging, simply because of the great degree to which it occurs”

However, Lowell assigned a minor role for mass transfer in contact charging, being responsible only for minor effects such as dispersion of experimental values. He showed that charge transfer persists over many contacts steps, concluding that mass transfer cannot be the main mechanism in the whole process.[112]

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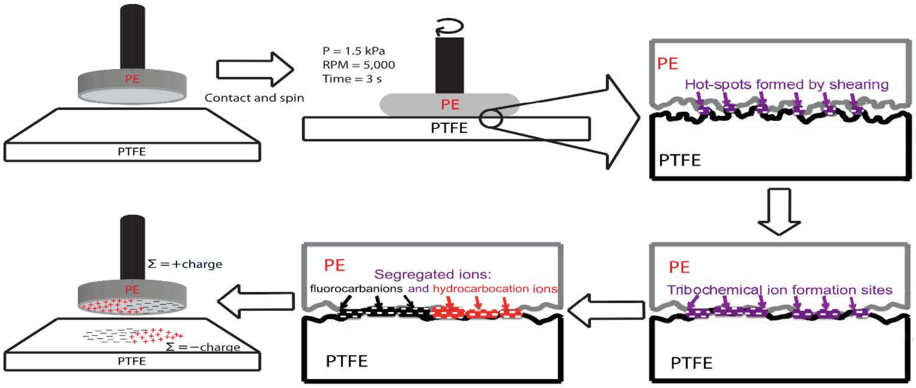

Fig. 4 Mechanism for contact triboelectrification of insulating polymers. Shearing the polymer interface forms reactive spots, due to forced contact on surface hills. Plasticization and melting also may take place, added to chain breakdown and protrusion fragmentation. Reprinted with permission from Ref. [116].

More recently, Grzybowski and his colleagues[113] added new support to the material transfer mechanism. They observed charge mosaic nanoscopic patterns consistent with material transfer concurrent to polymer charging. They also showed the existence of oxidized species using Raman spectra, justifying it as a result of homolytic or heterolytic chain rupture followed by reaction with atmospheric oxygen and/or water, a topic previously reviewed by Dubinskaya[114]. Caruso et al.[115] reported that polymer chain heterolytic and homolytic breakdown may coexist during tribocharging.

Grzybowski group[113] also considered intrinsic material heterogeneity or spatial variations in chemical composition. Any polymer properties show spatial fluctuations in viscoelasticity, topography, crystallinity degree, hardness, chemical composition and chemical potential, especially at the surface of the material.

Following results from the authors' laboratory, mutual triboelectrification of PTFE and LDPE is consistent with the mechanism represented in Figure 4.[116] Shearing the polymer interface causes breakdown of surface protrusions and it also heats contacting areas unevenly forming hot spots, due to forced contact on surface hills. Plasticization and melting take place, added to chain breakdown and fragmentation but cooler areas are more prone to brittle fracture. Homolytic scission produces free radicals with markedly differing electronegativity that may undergo electron transfer, according to the following equations:

$$– H_2CH_2CH_2\dot{C} \quad + \quad – F_2CF_2CF_2\,\dot{C}$$
$$\rightarrow \quad – H_2CH_2CH_2C^+ \quad + \quad – F_2CF_2CF_2\,C^-$$

Ions are segregated due to the chain size, following Flory–Huggins theory[117] and superseding electrostatic attraction between distant ions. Given the amphiphilic nature of the charged polymer fragments, the ionic terminals are occluded in subsurface layers that explains their impressive stability. The relative importance of the various events that can occur depends on the materials used, the history of their surfaces and subsurfaces, oxidation state, morphology, kind of intervening mechanical action and the environment. Evidence from IR, Raman, pyrolysis and EELS identify the negative domains as fluorocarbon fragments, whereas positive domains are hydrocarbon fragments. EELS spectra also revealed oxidized species which means that oxidation reactions are also triggered during the triboelectrization process.

Ions and free radicals formed by chain scission are high energy and short half-life species that can participate from various reactions, such as the well-known transformation of carbon radicals in peroxy radicals[118,119] under air, but these are not detected by charge measurements. Low polarity of the carbon-carbon bonds in both PTFE and LDPE chains suggests that the homolytic scission predominates as the initial mechanochemical event.

More recent results[120] show the presence of nitrogen on tribocharged HDPE surfaces. This is understood considering the participation of atmospheric nitrogen in a tribo-plasma formed during friction,[121,122] adding to what Ireland called "the mysterious and complex nature of the process".[123] In a tribo-plasma, the energy generated in a variable force field (under the action of shock waves or friction) determines not only strong local overheating, but also brings the polymer into a new state, composed of very unstable ions, free radicals and electrons, i.e., a plasma that decays rapidly towards unusual but more stable species.

These developments and complexity of electrostatic charging dielectrics led Williams to give a simple explanation for the slow progress of Electrostatics, during 20th century: it was only treated as a subject of physics, but important questions are now been answered by chemistry, tribology and other disciplines.[88]

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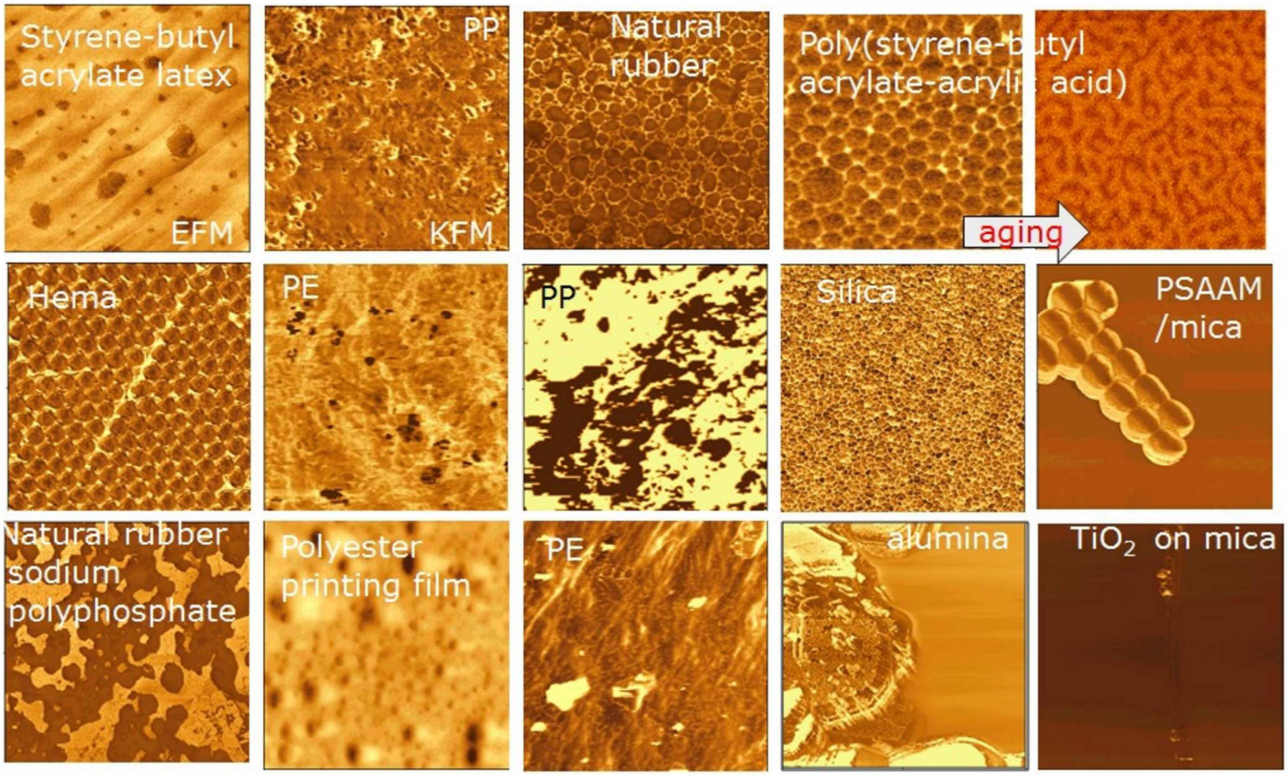

Fig. 5 Electric force (EFM) and Kelvin force (KFM) maps of some polymers and inorganic materials. Reprinted with permission from Ref. [97].

Charge patterns in polymer surfaces

The widespread concepts of contact charging and triboelectricity held a fundamental role in explaining many experimental observations and they were the basis for the now superseded theory of adhesion of Derjaguin[124] that had some impact, in the late 1950-80's. The uniformity of surface charge density that holds on metals[125] and to a lesser extent on some other materials was also presumed but was never verified on insulating surfaces.

Early evidence on surface charge non-uniformity came initially from the application of the then recent electrical scanning probe microscopy techniques, such as Kelvin force (KFM), Electric Force (EFM) and Scanning Electric Potential (SEPM) microscopies,[126] together with Lateral Force Microscopy (LFM) that measures friction at the nanoscale. These techniques show that surface charge distribution on polymer colloidal particles[127] is non-uniform as well as the electrostatic potential on dielectric solid surfaces[128] that forms various types of patterns, as shown in Figure 5. Latex films patterns are regular, especially in the case of macrocrystals but irregular patterns are observed in most cases, with fractal dimension 1.64-1.72.[129] This is higher than fractal dimension for surface roughness (1.53 ± 0.04), showing that charges are less mobile than mass, in these surfaces. They are thus associated to higher MW components, not to oligomers or any mobile contaminants.

When first observed, potential maps like those in Figure 5 were much unexpected. First, the molecules forming these materials are neutral. Second and perhaps more important, electroneutrality is often touted as a first principle of matter, an idea that has been challenged, recently. This led to an intensive effort to verify the significance of KFM images of dielectric materials. Fortunately, this produced fast progress in developing handling techniques and experimental methods, facilitating the identification of charge-bearing species.

The basic assumption in interpreting these images (Figure 5) is the validity of the superposition principle of electrostatics, according to which the potential measured in any point of space is the summation of contributions from surrounding charged objects. In insulator solids, charges are immobile or only slowly mobile, in a time scale much slower than the measurement time. This allows the calculation of potential patterns, given an assumed charge distribution. On the other hand, direct charge measurements are also possible from electric force microscopy (EFM), but these are not as often used, perhaps due to the more involved calculations.[130]

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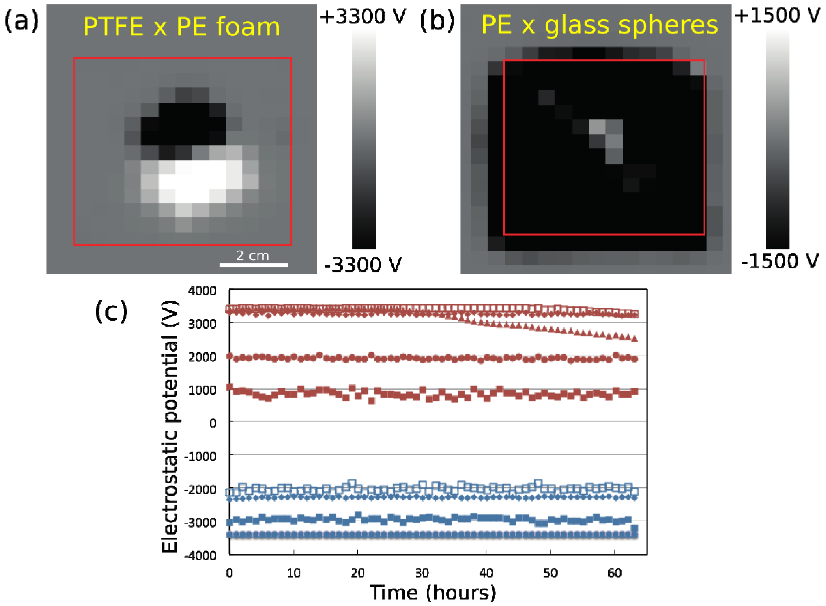

Fig. 6 (a,b) Representative macroscopic electrostatic potential maps in tribocharged polymer surfaces and (c) kinetics of potential decay on different pixels of PTFE tribocharged with PE foam under 60% RH. Adapted and reprinted with permission from Ref. [116].

Few years later, scanning Kelvin electrodes showed that surface charge non-uniformity is widespread on many macroscopic surfaces.[116] Indeed, it is difficult not to observe charge patterns on the surfaces of common thermoplastics. Figure 6 shows macroscopic patterns obtained on polytetrafluoroethylene (PTFE) rubbed with a spinning polyethylene (PE) foam and on polyethylene films under glass spheres shaken in a reciprocating table. Electrostatic patterns on polymer surfaces are very stable and decay only slowly if the relative humidity is in the 60% range or lower, as shown in Figure 6c.[116] Potential change is negligible for most pixels, especially the negative values. However, some spots show faster change assigned to surface chemical heterogeneity.

The interpretation of surface patterns on polyolefin surfaces and of their modification under various experimental conditions benefits from fundamental information on general properties of polymer surfaces:[131] polyolefin surfaces are chemically different from bulk polymer and they tend to accumulate oligomers and non-polar impurities, driven by surface tension.[132] They are dynamic and respond to environmental stimuli, for instance covering with water following a pattern that was discovered long ago by Adam,[133] while working with wax. Under air, they are always undergoing oxidation that is not spatially uniform, creating chemical patterns where different spots may contribute to local changes in charge acquisition and stability.[134] Moreover, different charge modification procedures are currently used for various industrial purposes, using common chemicals, plasma, flames and corona discharge.[135]

A striking feature of the potential and charge maps is the magnitude of the electric potential gradients observed that easily reach tens of megavolts per meter, just below the fields required to provoke ionization of atmospheric gases and non-polar solids and liquids.

Another surprising finding is the detection of electrostatic potential patterns[113,120] in the surface of a given polymer following contact with another piece of the same material, as shown in Figure 7. This is completely unexpected considering the triboelectric series and often-assumed charging factors like electron transfer driven by differences in work functions or ion transfer driven by specific adsorption.

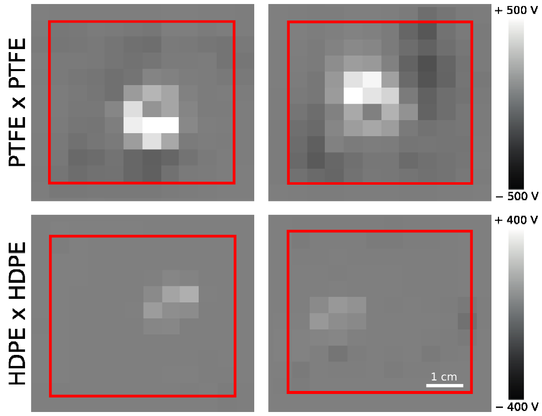

Fig. 7 (Top) Potential maps of PTFE films sheared with PTFE stubs and (bottom) of HDPE films sheared with HDPE stubs. Reproduced from Ref. [120] with permission from The Royal Society of Chemistry.

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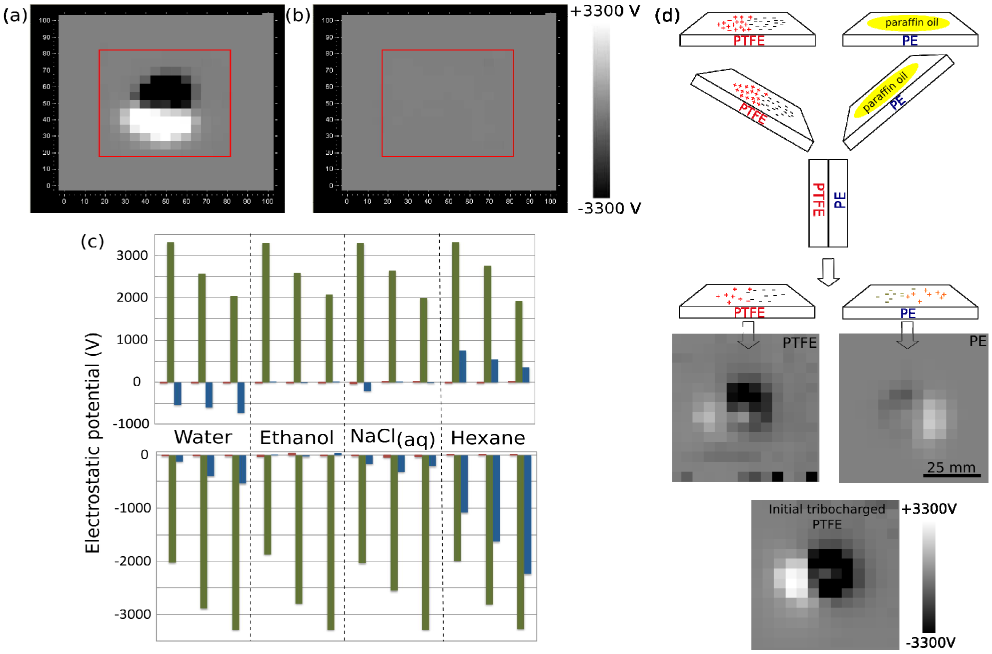

Fig. 8 Tribocharge extraction with various solvents: (a) maps from a tribocharged PTFE surface (b) and the same but following rinsing with ethanol. (c) electrostatic potential on different pixels of tribocharged PTFE following extraction with different solvents. (a, b and c) reprinted with permission from Ref. [116]. (d) Procedure used to extract charges from PTFE to LDPE using paraffin oil as transfer agent. Reprinted with permission from Ref. [136].

Atmospheric triboplasma formation during the tribocharging process can also contribute to the potential decay of charged surfaces, whenever distant charged surfaces are brought together.

Immersion in liquids is an effective way to remove tribocharge from a surface.[20, 136] Figure 8 shows the effect of some liquids on PTFE tribocharged with PE: ethanol is more effective than water, NaCl aqueous solution and n-hexane. The latter removes positive charges better than negative charges. This can be easily understood considering the chemical composition of both: cations derive from hexane-soluble PE fragments. On the other hand, the charge associated with the PTFE fragments can be considerably reduced when in contact with polar and nonpolar liquids, including water.

The removal of tribocharge by immersion in liquids may be due to different events: a) extraction of ionic polymer segments formed by the disruption of the macromolecule chains; b) tribo-ions of opposite charge migrate and they recombine forming block copolymer chains; c) in the case of water and other liquids with acid-base properties, $[H(H_2O)_n]^+$ or $[OH(H_2O)_n]^-$ bind to charge carrier fragments carrying opposite charge.

An interesting feature of the water effect on the positive areas of tribocharged PTFE is the residual negative charge left following immersion. Interspersion of a small amount of negative ions is expected in the positive domains, given the fractal nature of charge distribution. If negative ions are less soluble than positive ions, they will be extracted to a lesser extent.

The generality of charge removal by polar and non-polar liquids is not yet established but it can certainly greatly help experimenters and polymer users to get rid of unwanted charge, as shown in Figure 8. Besides, not only extraction but transferring charges to another surface keeping the same pattern its possible when an appropriate agent is chosen, as shown in Figure 8(d). In this case, charge patterns from tribocharged PTFE surface were transferred to a clean low-density polyethylene (LDPE) sheets using paraffin oil. The PE film shows weakened mirror image of the PTFE surface, while the PTFE surface also shows lower contrast after the transfer procedure.[136]

The observation of contiguous domains with opposite charge allowed a further development that is the identification of polymer ionic fragments as the tribocharge bearing species that will be described in the next section.

Actually, using the very first generation of the Kelvin force microscope, Terris and collaborators tapped a tip on a PMMA surface where subsequent electrostatic mapping revealed positive and negative domains in the same area of contact.[137] Many years later, Baitekyn *et al.*[113] and Knorr[138] also verified microscopic bipolar (*or multipolar*) electrostatic domains after tribocharging experiments. This bipolar electrostatic phenomenon was also observed in gas–solid fluidized beds where the polarity acquired by the materials depends on the size of the particles: smaller particles become predominantly positive and larger ones are negatively charged.[139]

Hydrocarbon based polymers are reportedly barely charged following contact, according to Faraday cup measurements. Mapping with Kelvin electrodes reveals that they are strongly charged but with separate positive and negative domains reaching potentials in the order of kV. Pattern formation is reproducible and hundreds of electrostatic maps as those in Figures 6 until 9 were obtained in the authors' laboratory. Individual patterns differ in the precise position of the charged domains but not in the appearance of domains or in the potential range achieved.

Intentional formation or self-assembled charge patterns was achieved by Grzybowski and colleagues[140] using a bottom-up approach: two different sets of polymer spheres of identical dimensions were mutually tribocharged forming well-defined macroscopic particle arrays that in some cases possess a net charge.

To sum up, a major new advancement is the recognition of the ubiquity of complex charge patterns that have been found in any insulator surface examined, so far.

Identification of charge-bearing species

Many-thousand volts electrostatic potentials are easily detected observing long-range interaction with surrounding objects, the formation of sparks and the associated light emission, formation of ozone or nitrogen oxides that are easily detected by smell. On the other hand, charging does not provoke detectable changes in colour, smell, taste, acid-base character, and other properties of the charged chemicals and materials, which could be associated with chemical reactions. This is easily understood, considering that the Faraday electrochemical equivalent is close to 10^5 C/mol and excess charges as low as 10^{-10} C are easily detected, in the laboratory. Thus, the charge of 10^{-15} mols of monovalent ions is detectable in a lab bench but detecting 10^{-15} mol of a component in a macroscopic solid sample is hardly accessible without resorting to specialized techniques. This explains the difficulty to associate electrostatic charging to chemical changes within the material under examination.[97]

The observation of potential patterns and identification of charge-bearing species with opposite charge in the same surface was obtained by coupling charge or potential mapping techniques - Kelvin force microscopy (KFM), scanning macroscopic Kelvin electrodes and electric force microscopy (EFM) - with highly sensitive analytical techniques: electron-energy loss spectroscopy (EELS), electron spectroscopy imaging in the transmission electron microscope (ESI-TEM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS), infrared reflectance microspectroscopy (ATR/IR) and Raman confocal microscopy (CRS).

For example, Kelvin force micrographs from poly(styrene-*co*-hydroxyethylmetacrylate), PS-HEMA latex shows that the particle outer layers have excess positive charge while the particle cores are negative. This result converges with the information gathered from ESI-TEM elemental maps showing that the sulphate initiator residues are distributed throughout the particles, while the potassium counter-ions are clustered in the outer particle shell, as shown in Figure 9. However, in many other cases the species responsible for excess charge could not be identified by this combination of techniques due either to the nature of the ionic species, to its low concentration or the technical difficulty to do TEM on polymer surface layers. Direct evidence for the participation of ions derived from water – $[H(H_2O)_n]^+$, $[OH(H_2O)_n]^-$ – was obtained from water vapour adsorption experiments, analogous to previous evidence for OH^- ion adsorption at hydrophobic/nonpolar water interfaces.[99,141]

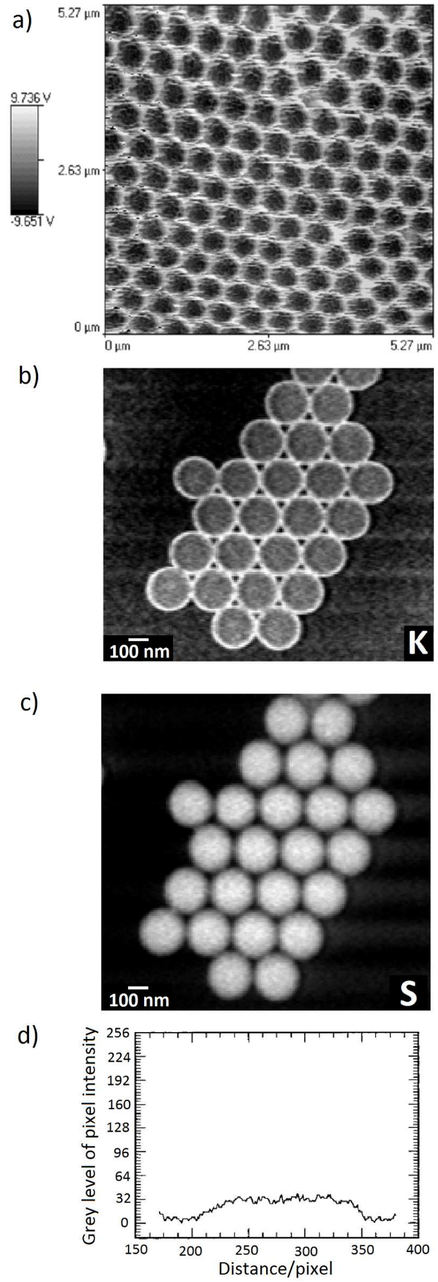

Fig. 9 (a) KFM image and elemental maps obtained by ESI-TEM for (b) potassium and (c) sulphur of a self-assembled macro crystal of PS-HEMA latex particles. The negative charge sites associated with the presence of sulphate groups (c) (from initiator residues) are distributed throughout the particles, but their counterions (b) accumulated at the particle periphery. The distribution of sulphur within PS-HEMA latex particles is not symmetrical and this could be evidenced by line-scan profile of pixel intensity across a sulphur elemental image of thin-sectioned PS-HEMA latex film (d). Reprinted with permission from Ref. [97].

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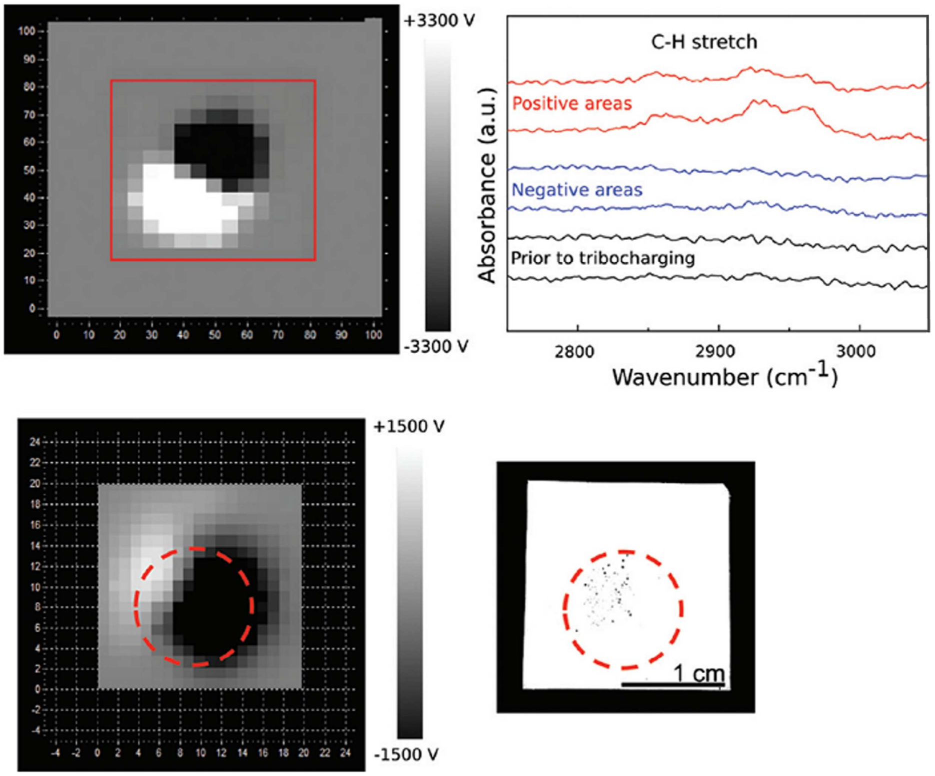

Fig. 10 Left: potential maps of two pieces of PTFE charged by shearing with PE disk. Right: (top) IR reflectance spectra of positive and negative areas from the PTFE piece at left; (bottom) picture (contrast enhanced) of the PTFE piece mapped at left. Reprinted with permission from Ref. [116].

Hydroxide ion adsorption is also consistent with the observation of only negative zeta potentials in many polymers examined in the presence of water: PTFE, PMMA, PVC, PC, PAc, PS, PE and PVA.[21]

Baytekin and colleagues[113] observed the formation of electrostatic potential random mosaic patterns on two contacting surfaces of identical chemical composition. KFM, Raman spectroscopy and XPS analyses were performed on polymers pairs with distinct elemental composition, verifying material transfer between the contacting surfaces.

The formation of separated but adjacent macroscopic domains with opposite charge on mutually rubbed PTFE and PE allowed the identification of charge-bearing species: ATR/IR spectra (Figure 10a) from positive domains cut out from tribocharged PTFE show the presence of compounds with carbon-hydrogen bonds and its absence in the negative areas, thus verifying that tribocations derive from PE.

Moreover, positive tribocharged domains on PTFE undergo discoloration upon heating, acquiring first a yellowish colour that is followed by the appearance of dark spots shown in Figure 10b (right) and finally disappear upon further heating. This behaviour is expected for PE charring and oxidation, but PTFE does not char, confirming that the positive macrodomains on PTFE are formed by species derived from PE. Negative domains on PTFE do not show any visible changes as expected considering that PTFE just depolymerizes upon heating, forming volatile species.

The authors presented further evidence on polymer fragment transfer[120] between rubbed PTFE and PE surfaces and their association with tribocharging, using SEM-EDX coupled to electrostatic potential mapping techniques and ATR/IR, confirming that material transfer between rubbed polymer surfaces produces wear and it is always concurrent with charge deposition and patterning. Backscattered-electron micrographs (SEM-BEI) as well as elemental maps (Figure 11) showed that the areas occuppied by tansferred material covers a range of sizes, including lumps of PTFE pulled out and transferred to the PE surface. This contributes to charge seggregation and the fractal distribution of charge. On the other hand, the larger lumps seen by SEM are not easily detected by other techniques such as Kelvin force microscopy (KFM), due their height which introduces imaging artifacts and also due to the amount of localized charge, which provokes strong deformation even on stiff KFM cantilevers.

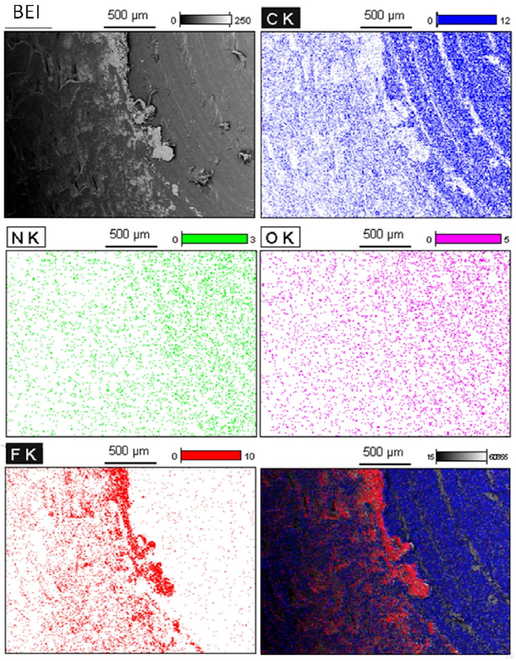

Fig. 11 Elemental maps of an area of the HDPE stub surface that sheared a PTFE film. Reproduced from Ref. [120] with permission from The Royal Society of Chemistry.

Charge dissipation mechanisms

Insulator surfaces have the ability to store charge on their surfaces for many months, at least. Charge elimination by surface conductance was the object of Schrödinger's Ph.D. thesis[142] who related it to the adsorbed water layer. This was further examined by Seaver,[143] but the reproducibility of surface conductivity measurements is poor and Seaver explained this considering that the number of molecules involved in the water layer could vary statistically. Besides, water layer thickness depends on polarization of the dispersed particles and hydrophobic properties of the surface.[144] Moreover, surface water films are hardly continuous due to the dewetting events.[145,146]

Another mechanism for charge dissipation is its coupling to water vapor adsorption and desorption events, under dynamic equilibrium conditions, considering the strong independent evidence on the role of atmosphere as a charge reservoir.[24,75,77,94-100] In this case, a surface carrying excess negative charge, for instance, desorbs $[OH(H_2O)_n]^-$ ions and/or adsorbs $[H(H_2O)_n]^+$ ions, exchanging them with the atmosphere and thus showing a net decrease in the negative charge.

The rate of charging increases with the humidity, in contact electrification experiments of polystyrene with gold or stainless steel.[147] When a chamber was saturated with 1 mol L^{-1} of ammonia or acetic acid, the charging of polystyrene increased under the basic atmosphere and decreased under acidic conditions. Moreover, charge decay of polyetherimide electrets is a consequence of water interaction with the surface and the bulk of the films.[148]

Atmospheric ions are charge carriers that migrate under electric fields according to Poisson-Boltzmann equation;[149] they adsorb on solid and liquid surfaces, and discharge electrochemically on metal and semiconductor surfaces. On the other hand, water at equilibrium under an electrostatic potential V shows excess $[H(H_2O)_n]^+$ ions concentration if V<0 and excess $[OH(H_2O)_n]^-$ ions concentration if V>0, following the electrochemical potential:

$$\mu_i = \mu_i^\circ + RT \ln a_i + z_i FV$$

Figure 12 shows the half-lives of electric potential decay in LDPE samples previously charged with positive and negative corona. Electrostatic potential dissipation rates are slower at lower relative humidity but negative potentials generally decay at a slower rate than positive ones, in agreement with Baum *et al.*[150]

A surprising finding was the negative equilibrium potential at LDPE (*ca.* -6V), which can be also be explained assuming that negative ions are partitioned between the polymer and the atmosphere, as observed or suggested in other situations[151,152]. Specific OH^- adsorption at water-oil and water-air interfaces is well established in the literature[153-155] and an analogous specific adsorption can also be considered in the LDPE-humid atmosphere interface thus accounting for the excess negative potential at equilibrium. As an application, Cao *et al.* used water transfer and printing to induce charge dissipation forming high-resolution patterns that could be useful in data storage, nanocomponent optoelectronics and self-assembly systems.[110]

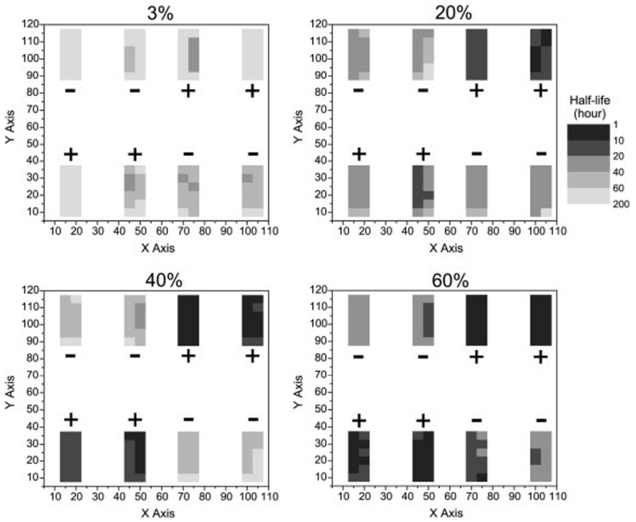

Fig. 12 Maps showing the half-lives of electric potential decay as a function of the position on LDPE pieces under variable relative humidity. Reprinted with permission from Ref. [99].

Friction dependence on tribocharge

Triboelectrification produced by friction should have an effect on friction itself, modifying friction coefficients between the intervening surfaces. The Johnson-Kendall-Roberts (JKR) and Derjaguin-Muller-Toporov (DMT) theories for contact mechanics consider the effect of adhesion forces on elastic deformations at contacting interfaces,[156,157] but electrostatic contributions arising from contact are not considered in these theories, probably due to the lack of knowledge on tribocharging and also to the complex nature of tribocharging events at insulator-insulator interfaces.[123]

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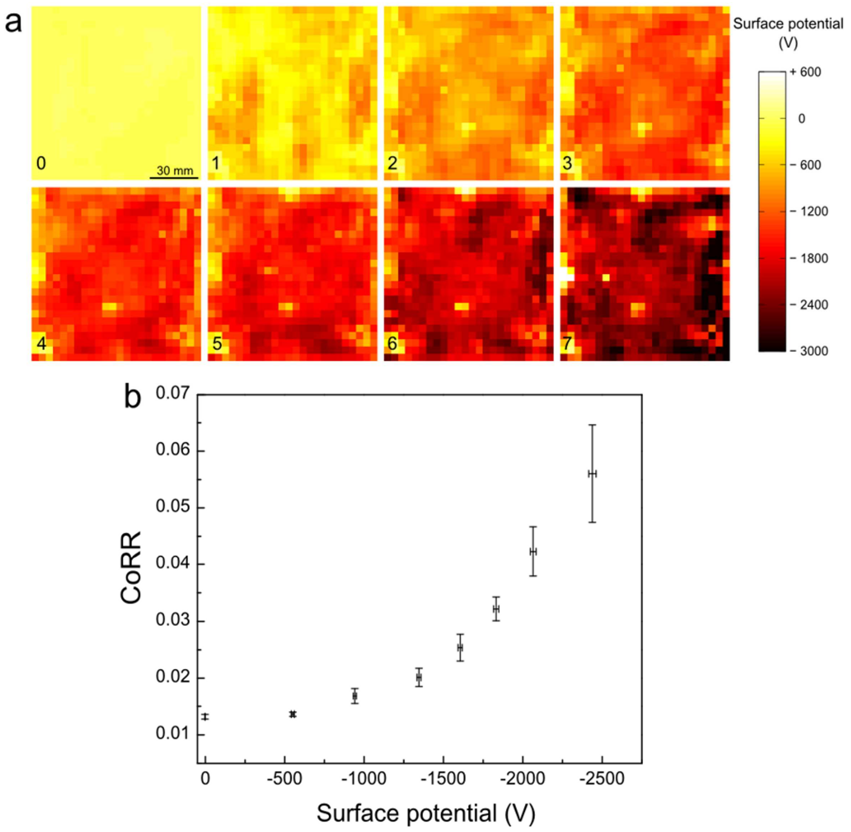

Fig. 13 (a) Potential maps for each PTFE sample and the (b) coefficient of rolling resistance versus the electrostatic potential on tribocharged PTFE. Reprinted with permission from Ref. [159].

A common origin was identified for the stick-slip phenomenon and Coulombic interactions at poly(methylmethacrylate) – gold sphere interfaces under relative motion, where strong electronic interactions arising from contact electrification at metal-insulator interfaces are large enough to affect macroscopic bodies.[158]

Recent progress in this direction was possible thanks to the preparation of samples and the acquisition of static potential maps showing macroscopic tribocharging domains, suitable for further use during friction experiments.[159] Friction coefficient measurements on tribocharged samples showed that tribocharge produced by friction has a large effect on the friction coefficients of dielectrics that may exceed all other factors for mechanical energy dissipation, as seen in Figure 13.

Very recently, friction force fluctuations (stick-slip) were found to be simultaneously accompanied by bipolar charging at metal-insulator interfaces (Figure 14), which means that during random events of force maxima, charges are exchanged in both directions, from metal to the insulator and in the opposite direction. The magnitude of charged species exchanged across the interface is highly dependent on the surrounding atmosphere. Besides, mechanical contact increases the pull-off force fifteen times, producing a resilient electrostatic adhesion.[160]

Some general lessons

Progress in understanding contact charging and triboelectricity speeded up in recent years, a lot was learned, new tools led to paradigm changes but the emerging picture includes perhaps too many important interacting elements challenging any attempts to create detailed, quantitative models, so far. Electricity produced by friction affects adhesion between the intervening surfaces that in turn feeds back on the friction force itself. Given this picture, it is not surprising that most basic scientists left aside friction and electrostatic charging, preferring to concentrate on other topics more amenable to deeper understanding, during the 20th century. Moreover, the dependence of electrostatic phenomena on chemical events adds to its complexity, since mechanochemistry largely implies the formation of high-energy species that can later follow many different reaction paths, with a great product diversity. Since real life takes place under the atmosphere, atmospheric tribo-plasma formation is also part of the picture, producing additional species.

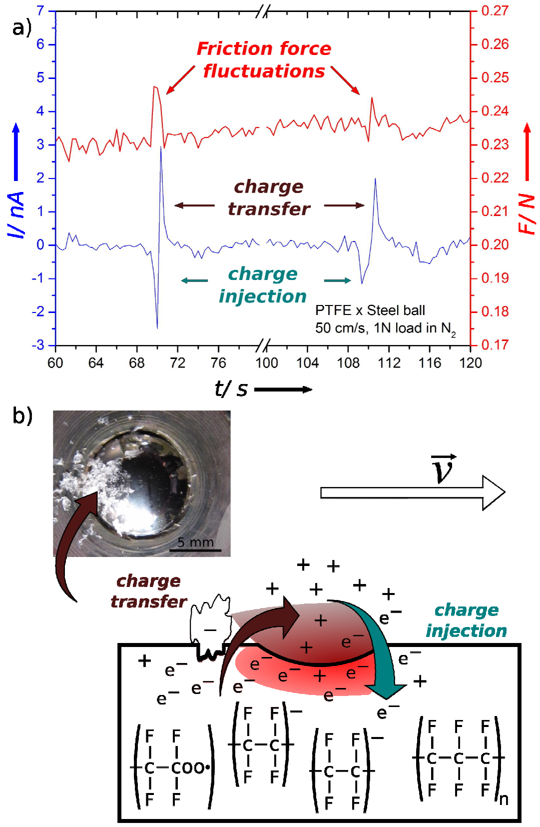

Fig. 14 Friction force fluctuations (stick-slip phenomena) are accompanied by complex tribocharging events at metal-insulator interfaces. Due to mechanochemical reactions, a microscopically high-energy non-equilibrium steady state is formed at the interface, with formation and exchanging of electrostatic charges, heat and phonon propagation and emission of electromagnetic radiation. Reprinted with permission from Ref. [160].

Tribology takes place at surfaces that are by themselves quite complex entities. This is true even in the case of metals like aluminium and steel that are usually covered with a dielectric layer showing wide variations of chemical composition, crystallinity and morphology. For this reason, discussing the "friction behaviour of aluminium" and many other common materials is meaningless if known features of theirs surfaces are not taken into account.

Tribocharging phenomena forming fractal patterns are chaotic-deterministic and they are thus sensitive to initial conditions. As a result, predictability and reproducibility of specific experimental results cannot be expected but the ensuing *patterns* are reproducible, as shown in this work. This is not to be taken as a misdemeanour, since it is also observed in many other current important scientific subjects, starting with climate.

Unfortunately, many researchers, engineers and lay persons believe that electrostatics and friction, separate or together, are old-fashioned topics that do not hold the same promise as many other currently fashionable scientific subjects. Or else: lack of interest is assigned to the maturity of the topics when it is indeed due to the unwillingness of many to face very complex subjects, even if these are with us every day and may be the source of significant life and property losses. At any rate, great care should be taken not to continue propagating disproven ideas on electrostatic phenomena.

Perspectives

Electrostatic phenomena are the basis for many important technologies that will probably benefit from the recent surge of new information and understanding. Some examples are discussed in the following sections, taken out of a large number of imaginable possibilities.

Toners

The global market for electrophotography industry was close to \$60 billion in 2009 and it is estimated that it will reach 90 billion dollars in 2015.[161] The technology of electrophotography is now dominated by several companies but, on the other hand, the electrification of particles still poses problems that are reflected in the strong patenting activity in this area. The number of patent applications to USPTO related to toner products numbered 1,824 in 2012, only. Toner, which is basically formed by a mixture of thermoplastic particles (styrene methacrylates or acrylates), with a size typically 5-25 μm and 5-10% weight pigment is used in laser printers and photocopiers to form images on paper.[162] The detailed understanding of how these particles become electrically charged and how the adhesive forces act becomes increasingly important (see Figure 15).[17] Improving this knowledge could dramatically improve the efficiency of printer machines and reduce printing costs, raising image technology to a new level.

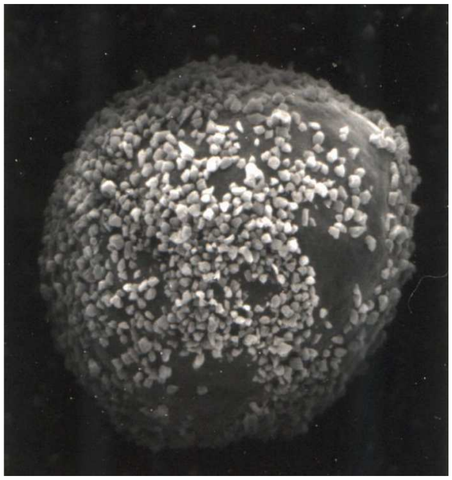

Fig. 15 Scanning electron micrograph of a toner particle. Reprinted with permission from Ref. [17].

Lithography

Many possibilities are currently being considered for electrostatic lithography and imaging, well beyond electrophotography. An interesting example uses the selective discharge of electrostatic charges on electrets using a patterned hydrogel stamp, producing metal (Ag, Ni, Cu) micro and nanostructures formed by reducing metal ions with patterns of charge. According to the authors, this is an evidence in favour of electrostatic or "single electrode" electrochemistry, since they used biased Al to charge the PMMA substrate.[110] The authors obtained designed patterns by rolling glass spheres on PTFE within masks, showing the possibility for new triboelectricity-based lithography procedures.[116] Using the techniques for charge build-up and dissipation that our group has been developing, macroscopic electrostatic lithography can be made on a previously tribocharged PTFE sheet (Figure 16). After rubbed with felt wool or glass, PTFE builds-up a high and relative homogeneous negative potential where a felt-tip pen filled with ethanol can be used to write on its surface by "erasing" (or extracting) negative charges.

Fig. 16 Electrostatic lithography on a previously tribocharged PTFE sheet.

Electrostatic adhesion

Electrostatic adhesion has been largely neglected for the past 30 years but it makes an important contribution to rubber-clay nanocomposite formation by the latex route,[163,164] stability and properties. It is now conceivable that controlled tribocharging will be used to achieve electrostatic adhesion in a range of practical situations.

Electrostatic levitation

Electrostatic levitation has been often overlooked considering the limitations posed by Earnshaw's theorem. However, it is useful for transportation without mechanical contact, within very well controlled environment in the production of equipment for information technology.[165] It is reasonable to expect that possessing better control and stability of electrostatic charging added to increased feasibility of patterning complex structures will introduce electrostatic levitation into many applications.

Energy harvesting

The Wang group recently described[166] triboelectric nanogenerators (TENGs) based on water-solid contact electrification. Successive improvements on triboelectric hydrophobic nanostructures are nanoarrays producing power sufficient to light hundreds of LEDs, simultaneously.[167] The authors consider that these systems will probably find application as self-powered pressure, chemical, biochemical, temperature and flow (water and wind)[168] sensors as well. Self-powered distress signal emitters for life saving, environmental monitoring and maritime search and rescue[169] are other prospective applications. Finally, a hybrid solar cell coupled to a water-drop TENG could be a new possibility for green energy harvesting.[170] A related development using similar experimental arrangements but under a different conceptual analysis framework are WMATs (water motion active transducers).[171]

Conclusions

Triboelectricity is now much better understood than it was twenty years ago but the emerging picture on its fundamental mechanisms is much more complex than what can be read in elementary and advanced textbooks or even reference books. It is now clear that every object, device, utensil, apparel, furniture, car part and whatever made with insulating materials displays electrostatic patterns that are more or less easily altered by contacting other materials of any type, including liquids and the atmosphere that exchanges charge with solids due to adsorption and desorption of non-electroneutral water. Humans are thus immersed in changing electrified microenvironments contained within the "Earth capacitor". Surface chemistry and mechanochemistry play a special role in this new picture and determine many phenomena observed.

Better understanding of electrostatic charging mechanisms should contribute to increased safety in handling flammable materials as well as seemingly harmless solids like wheat flour, sugar and polyethylene that respond for great life and property losses in many places around the world, every year. On the other hand, it will certainly contribute to create new technologies or to improve existing ones.

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Notes and references

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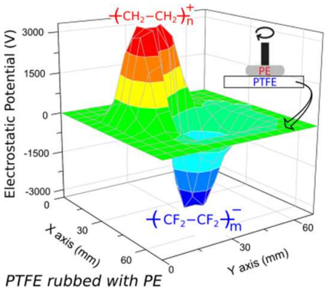

Mechanochemical reactions during polymer friction or contact produce ionic fragments distributed on positive and negative domains at both surfaces.

Fernando Galembeck FRSC obtained B.Sc. and Ph.D. degrees at the University of São Paulo and he was a postdoc in the Universities of Colorado and California, followed by a stay in Unilever Port Sunlight. He was in the faculty of USP and later became a Professor of Chemistry at the University of Campinas, working on colloids, surfaces, materials and nanotechnology while consulting with industry and advising funding agencies. He is the recipient of Álvaro Alberto and Anísio Teixeira Prizes, the two most important for Brazilian scientists and educators. He is the current Director of the National Nanotechnology Laboratory at Campinas.

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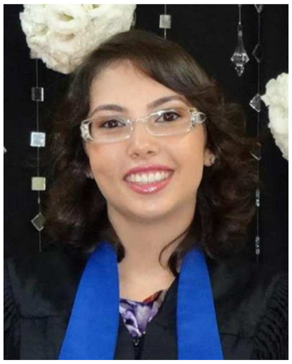

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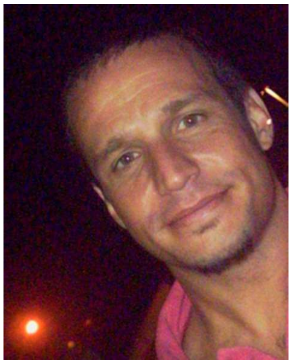

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