EFFECT OF TRIBOELECTRIC CHARGES ON FRICTION AND WEAR OF POLYMERS AT MACRO SCALE

A THESIS

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We certify that we have read this thesis and that in our opinion it is fully adequate, in
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ABSTRACT

EFFECT OF TRIBOELECTRIC CHARGES ON FRICTION AND WEAR OF POLYMERS AT MACRO SCALE

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M.S. in Materials Science and Nanotechnology

Advisor: H. Tarik Baytekin

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The interest towards the study of underlying mechanism behind tribology has gained enormous attention recently since almost one-fourth of the total produced global energy is consumed by friction and wear. Dry sliding or rubbing two dielectric polymers on each other results in surface charging showing significant effects on friction coefficients and wear. Determination of the correlation between triboelectricity and tribologic events like friction and wear, the control of friction coefficient, and reducing wear by surface charging constitutes the main idea and research topic of this thesis. However, tribological events are very complicated considering the fact that diverse processes encompassing of physical and chemical changes occur at the counterface. Therefore, the fundamentals of friction is still controversial.

Owing to tribological actions that occur due to contact between different phases of the matter, interfaces generate tribocharges due to electron, ion, and material transfer mechanisms. Even though the fundamental mechanism is still vague and under debate, it is believed that static electrification due to tribological actions are utterly because of electron transfer. Current studies unveiled that physical based phenomena are not the only source of surface electrification but also chemical changes such as bond rupturing and following surface oxidation that can take place as a result of mechanical actions on an insulating polymer. Consequently, these two groups of surface events; surface electrification and friction are expected to demonstrate a mutual relation, and detailed

study concerning this relation needs to be investigated in order to solve e.g. energy loss and wear problems in tribology.

To achieve this goal, it is essential to understand the main mechanisms and processes involved, and reveal the connections between tribological events and establish a relationship between all the intrinsic and extrinsic properties of materials from molecular, nano to meso scale. Thus, in this study, we investigated the contribution of triboelectrification to friction by taking into account some factors - surface area, load, atmosphere - between common polymers and pure cellulose under dry friction conditions.

ÖZET

POLİMERLERDE TRİBOELEKTRİKLENMENİN SÜRTÜNME KATSAYISI VE AŞINMA ÜZERİNE MAKRO BOYUTTA ETKİLERİ

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Üretilen toplam küresel enerjinin yaklaşık dörtte biri sürtünme ve aşınma nedeniyle harcandığından, triboloji mekanizmasının incelenmesi hakkındaki çalışmalara olan ilgi yakın zamanlarda oldukça artmıştır. Kuru sürtünme şartları altında iki dielektrik polimerin birbiri üzerinde kayması veya sürtünmesi ile yüzeylerde elektriksel yük meydana gelmektedir. Bu olaya bağlı olarak sürtünme katsayısında ve yüzey aşınmasında önemli ölçüde değişimler olmaktadır. Sürtünme sonucunda oluşan elektriklenme ile sürtünme katsayısının değişmesi ve aşınma gibi tribolojik olaylar arasındaki ilişkileri saptamak, sürtünme katsayısının yüzey elektrik yükleri ile control edilmesi ve yüzey aşınmalarının azaltılması bu tezin ana fikrini ve çalışma konusunu oluşturmaktadır. Ancak, tribolojik olaylar, arayüzeylerde fiziksel ve kimyasal değişimlerin, ve bu değişimlerin birbirlerini de etkilemesi nedeniyle göz önüne alındığında oldukça karmaşık olaydır. Bu nedenlerden dolayı, sürtünmenin temel prensipleri hala tartışmalıdır.

Maddelerin farklı fazları arasındaki temaslarındaki tribolojik olaylardan dolayı arayüzlerlerde elektron, iyon ve malzeme transfer mekanizmaları nedeniyle triboelektriksel yükler üretilirler. Elektriklenmenin temel mekanizması hala belirsiz ve tartışmalı olsa da, tribolojik hareketlerden dolayı oluşan statik elektriklenmenin elektron

transferi yüzünden olduğuna inanılmaktadır. Şu an yapılan çalışmalar, fiziksel fenomenlerin yüzey elektrifikasyonunun tek kaynağı olmadığını, ayrıca yalıtkan polimerlerde mekanik etkilerin bir sonucu olarak gerçekleşebilecek kimyasal bağ kopması ve yüzey oksidasyonunu takip eden kimyasal değişiklikler olduğunu göstermektedir. Sonuç olarak, yüzey olaylarının bu iki grubu; yüzey elektriklenmesi ve sürtünmen karşılıklı bir ilişki sergilemesi ve enerji kayıpları ve aşınma problemleri üzerine ayrıntılı çalışmaların yapılması gerekmektedir.

Bu amacı gerçekleştirmek için, konu ile ilgili ve mekanizmaları ve ana noktaları ortaya çıkarmak tribolojik olaylar arasındaki ilişkileri moleküler, nano, ve mezo ölçekte malzemelerin tüm içsel ve dışsal özellikleri düşünülerek saptamak gerekmektedir. Bu nedenle, bu çalışmada, tribo elektriklenmenin sürtünme üzerine olan katkısı yaygın polimerler ve saf selüloz sürtünme sistemi için bazı faktörler - yüzey alanı, elektriksel yük, atmosfer - göz önünde bulundurarak kuru sürtünme şartları altında araştırılmıştır.

Anahtar sözcükleri: polimer, triboloji, triboelektrilenme, sürtünme katsayısı, aşınma

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To My Family

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CHAPTER 1

1 Motivation

The aim of this study was to investigate contribution of triboelectric charging to coefficient of friction (COF) of insulating materials in ambient and under various media and conditions. The history of tribology shows that the true mechanism of dielectric materials' triboelectrification and its effect on friction still remains ambiguous due to unclear and misunderstood mechanism of surface electrification. This makes the problem even more complicated and leaves the only choice for further and more detailed studies in the field of tribology. Here, on the contrary, we were able to investigate and elucidate the relation between friction and triboelectricity in a very simple and comprehensible way compared to the already available studies in the literature. Related studies, most of the times, solely demonstrated the formation of charges on the surface of dielectric materials and their behavior under various media and conditions without making any direct correlation with friction or coefficient of friction. However, after thoroughly studying, this study shows that the coefficient of friction (COF) is highly dependent on triboelectric charges.

The field of tribology is a very new concept and it has brought a lot of challenges with itself arrival. The literature results provide rich information about electronic [1-4] and phononic [5,6] contributions to the friction of metals and semiconductors but the dependence of friction coefficient on triboelectricity in insulators is yet poorly understood and not defined together with mechanism of triboelectricity. For better investigation and presenting this contribution to friction, experiments of this study were carried out under controlled mediums i.e. nitrogen and argon atmospheres, and Advanced Friction tester

instrument (AFT) was used throughout this study. Moreover, as well as different gaseous media, several other factors that effects both coefficient of friction and triboelectricity, namely, load, area, and various polymers of generating positive and negative charges on its surface were examined. For clarification of triboelectricity phenomenon, previous works merely concentrated on triboelectrification behavior of dielectrics inside these two (i.e. argon and nitrogen) and several other gaseous media [7, 8] the effect of these gaseous atmospheres on both triboelectricity and friction was shown. Nevertheless, the actual mechanism, behind triboelectrification and its effect on friction continues to be a poorly perceived concept contrary to many proposed in the literature. At nanoscale there have been a large number of researches on the mechanism of triboelectricity in metals and semiconductors [9, 10], thus, making it to remain an active research area for nanotribology. However, the mechanism of formation of triboelectricity in bulk or macro scale is not much focused owing to its complexity. In other words, it is difficult to make reproducible measurements the friction and triboelectrification at macroscale because of the effect of many uncontrollable factors such as surface roughness, humidity, temperature, load and other physical and chemical properties of a material. Hence, detailed study of the influence of some previously mentioned factors, in particular area, load, and gaseous medium on triboelectrification which alters static charging ability of material's surface which in return affects the coefficient of friction was studied for variety of polymers generating either positive or negative charges at their interfaces in hope to assist for better understanding the mechanism of triboelectrification and its contribution to friction coefficient in polymer materials at macroscale. More importantly, we demonstrated that through controlling triboelectricity and friction we can decrease wear of polymeric materials.

CHAPTER 2

2 Introduction

2.1. Tribology

Tribology is the study of relative moving surfaces, their friction, wear and lubrication properties and this phenomenon is very commonly observed in our daily lives. The word tribology comes from the Greek word of *tribos* meaning "rubbing". Although the term tribology was not used in the past, in 1964 this term was coined to education and research program as a result of the lack of knowledge of mechanical surface interaction phenomena and waste of resources [11]. Tribology is a natural occurring phenomenon and it is observed in day to day lives of people. Whenever two things come to physical contact and an act of sliding, rolling or sometimes even just contact takes place, it is regarded as tribology. Many mechanical surface phenomena (i.e. adhesion, frictional electricity, electric contacts) are included in this field; nevertheless, friction, wear and lubrication are mainly emphasized topics while dealing with tribological problems. Each of these topics has its own contribution to tribology and mechanism of approach is different for each of them. Friction, for instance, is a part of physics or sometimes classified as a branch of mechanical engineering which studies the resistance to relative motion, whereas wear shows how much material is lost due to surfaces moving parallel to each other. The third key topic is a lubrication and it is completely different from the other two. It is basically the use of fluid or sometimes solid to change (i.e. minimize the friction) the nature of two interacting surfaces. Depending on the application, the use of friction, wear and

lubrication can change. For example, most of the times friction is minimized in automotive, hydraulics and machinery due to minimization of energy loss, but in some cases increasing friction is very significant for prevention of life dangers such as in brakes or tires in order to make the vehicle to be able to stop. Wear is also used in several ways depending on the demands. In bearings, gears and tires, for instance, wear is minimized to prevent material loss, while in pencils and erasers, it is maximized. Sometimes both can be used interchangeably. To illustrate, in one case minimizing friction and maximizing wear is significant, while in another case maximizing friction and minimizing wear is needed, and sometimes maximizing both can be also helpful. However, in very rare cases minimizing both friction and wear tends to be a practical objective of tribology. Lubrication, contrary to friction and wear, is an act of lubricating between two surfaces with thin layer of low shear strength of gas, liquid and solid to improve smoothness between two surfaces and to prevent damage. The range of thin films is between 1 μm and 100 μm and the type of lubricating material can be of any type (i.e. gas, liquid or solid) depending on the effectiveness of the film to prevent the damage between the surfaces of solid materials. [11]

2.2. Friction

Friction is the study of two interacting surface moving relative to each other. The knowledge of friction has been known since the times of Leonardo da Vinci; however, Guillaume Amontons (1663-1705) refreshed the laws of friction by introducing them to the Academy [12]. The first law states that force of friction is proportional to the normal load. The second law which carried a lot of doubt even in past claims that the size or dimension does not affect the friction. Later, Coulomb (1736-1806) added another law as Coulomb's law of friction where mentioned that the sliding velocity does not influence the sliding (kinetic) friction [12]. These are all three laws governing friction force and some of past and present researchers still consider Amontons' second law of friction not fully accurate [46, 60]. Actually, it was Derjaguin who first proposed another relation for the friction force of two interacting materials under sliding motion [60]. Nonetheless, if we go back to classical way of formulating friction then we can conclude that friction force (F) for an object relatively moving on top of another object (plane or surface) is

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equal to the product of coefficient of friction (μ) and the normal force, L. For a surface with no inclination angle the formula stays the same as in (2.1) and (Fig. 2.1a).

$$F= \mu _*L \qquad (2.1)$$

While a surface with an inclined plane angle (θ) as shown in Fig. 2.1b is expressed in terms of frictional angle θ which is formulated in (2.4).

$$F= W_*\sin\theta \qquad (2.2)$$
$$L= W_*\cos\theta \qquad (2.3)$$
$$\tan\theta = \mu \qquad (2.4)$$

where W is weight, L is load, θ is an inclined angle of plane and μ is coefficient of friction of the object.
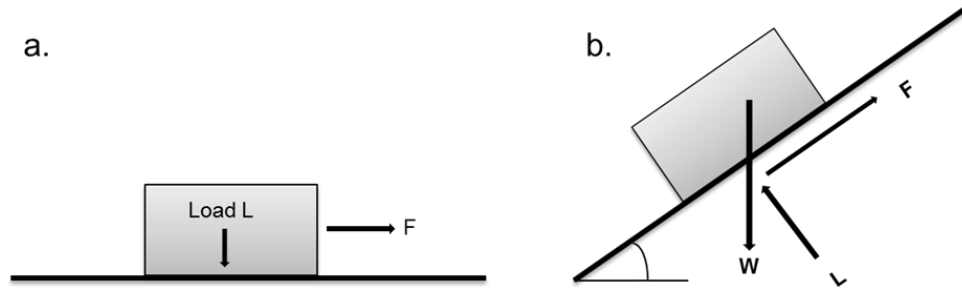
Figure 2.1 A schematic representation of friction force in (a) horizontal and (b) inclined planes [12].

Friction can be also of different depending on materials relatively moving on each other. Dry friction is the force of two solid materials sliding on one another. Lubricating friction illustrates the friction between materials where mostly viscous lubricant fluid separates two interfaces. Lastly, the friction concerning the interfaces of two fluids moving parallel to each other. However, in this work we will be discussing merely dry friction, therefore, it is significant to mention about static and dynamic or kinetic friction. When an object is at rest, the force needed to move is called static friction (FS) and corresponding friction coefficient is μS, but for an object to maintain its movement kinetic friction (FK or FD) supplies required force and corresponding friction coefficient is μk or μD [12]. In general,

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μS is greater than μD (Fig. 2.2), unfortunately the reasons for such difference will be discussed in the "Results and Discussions".

Lastly, Bowden and Tabor in their book discuss the solid contact between metals and non-metals separately because they believe that although in both cases the phenomena taking place at the real contact area are interfacial adhesion and deformation, each solid material, be it metal or non-metal, demonstrates different behaviors at these interfaces [12].
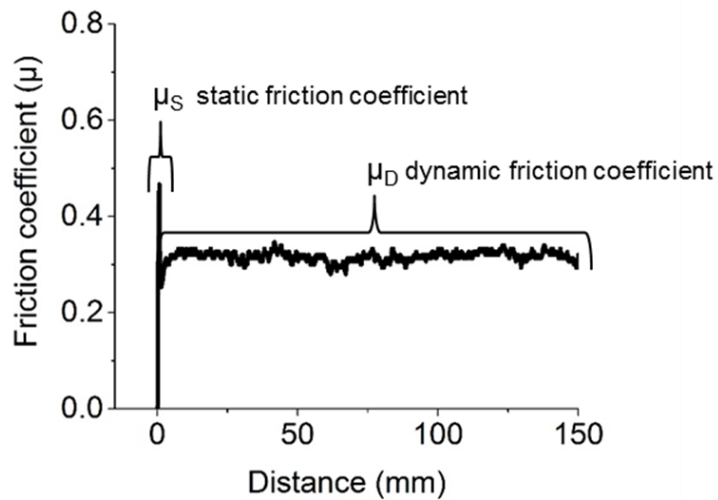
Figure 2.2 A schematic illustration of static and dynamic friction coefficient on friction coefficient versus distance graph taken from our data.

2.3. Wear

Wear is a response of two materials moving relative to each other. It mainly deforms or removes materials from the surface of interacting bodies consequent to mechanical action of dissimilar surfaces. When there is a strong interaction between asperities of the opposite surfaces, significant amount of materials is transferred or lost due to wear [13]. Increase in friction is sometimes related to simultaneous increase in wear, however, this may not be true in many cases. It is important to quantify wear since a material loss is of high importance. Wear rate, thus, is a term used to define a mass, volume or height loss of removed material per unit time or distance [13]. Also, wear debris quantifies and shows the type of wear happening at the interfaces. Mild wear debris takes place on the outer

surface layers with particle sizes ranging from 0.01 to 100nm and mostly they are from oxide particles on the sufaces. Whereas, severe wear debris particle size ranges from 100nm to 100 µm and takes place at deeper surfaces [13]. There are several mechanisms that governs wear process and classified depending on type of wear. Since wear is a part of tribology and has a complex nature, these mechanisms or processes of wear are among the mostly encountered mechanisms that exist in the literature [13].

Adhesive wear is a type of wear where two atomically clean surfaces have strong short-distance forces e.g. van der Waals, and these adhered interfaces are sheared when they are moved relative to each other. Consequently, material transfer occurs through shearing of soft surfaces adhered to hard surfaces [13]. This shearing might be of soft or strong wear depending on the type of sliding occurring at two interfaces. Sometimes, hard surfaces severely damage soft surface even at small friction leading to coverage of hard surface with thin film of soft material. Lastly, J.F. Archard came up with an equation that gives a theoretical representation of the adhesive rate (2.5) [13].

$$Q = K\frac{Wx}{3H} \qquad (2.5)$$

where W and H are load and hardness of the softer material. $K = \frac{k}{3}$ is the coefficient of wear.

Equation 2.5, hence, shows that wear volume is directly proportional to load and distance while being inversely proportional to hardness.

Abrasive is the other type of wear and it is one of the clearly comprehended wear types since it occurs in bulk. Indentation, grooving and lastly cutting the material out of the surface are the main processes occurring in abrasive wear [12]. One of the best example of such wear is emery papers that are used to abrade rough surfaces. It is basically a penetration of hard surface into softer and smoothing the softer surface to equal roughness.

Surface fatigue or *fatigue* wear is a type of wear that are observed in repeated rolling or sliding contacts. Surface and subsurface cracks are formed due to successive cycles of these contacts. Fatigue wear is an important event mainly in macro and micro scales since

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both happens at different surfaces [13]. Rolling and sliding fatigues are two types of fatigue wear each having different mechanisms. For instance, in dry rolling contact fatigue abrasive wear mechanism is more dominant while in sliding contact fatigue, wear takes place by both adhesive and abrasive wear mechanisms. Lastly, sliding contact fatigue has higher friction than rolling contact fatigue [13].

The other two types of wear are *fretting* and *corrosive/oxidative* wears. Fretting is mainly encountered in vibrating machines where low-amplitude oscillating motion occurs between contacting surfaces. In other words, fretting is sometimes an abrasive or adhesive type of wear where the surfaces are initially adhered to one another and then raptured due to vibration resulting in wear debris. While, corrosive wear is observed mainly in corrosive mediums e.g. air and this type of wear is sometimes named as oxidative wear since oxygen is the main corrosive medium [13]. In addition, it is significant to mention that oxidative layer is sometimes beneficial and behaves like solid lubricating surface. Therefore, it can decrease the rate of wear by several magnitudes [13].

2.4. Triboelectricity

When two materials physically contacted or rubbed on each other as in a typical friction event, or they are contacted, generation of charges occurs on the surface of these materials. This phenomenon in the field of tribology has several names. Contact electrification (CE) is used when contact is the primary cause of charge generation but triboelectricity or triboelectrification is the general name while explaining the charge generation due to relative motion of one surface to another. Each of these two materials can be of any two kinds such as metals [8], semiconductors [2, 3] or insulators [5, 17] or even two similar materials. However, insulators have shown more obvious accumulation of charges on their surface and retain electrostatic charges for longer period of time due to their poor charge conduction abilities. Triboelectricity or triboelectrification is experienced in daily life of a person who walks across carpet, floor or mat and feels a sudden shock or sometimes sparks from touching metal or doorknob. Also, triboelectricity can be encountered in many technological and natural phenomena or chemical processes because it is a well-known physical process. Electrophotography (i.e. laser printers and photocopiers) [14-16],

lithography [17], electrostatic separation and filtration and electrostatic coating in acoustic transducers [18-20] are some of the examples of technological phenomena. Naturally occurring phenomena can be listed as the behavior of sand storms, generation of lightning, volcanic plumes and etc. The third category can be in chemical systems, where generated charges take part into chemical process [20-22].
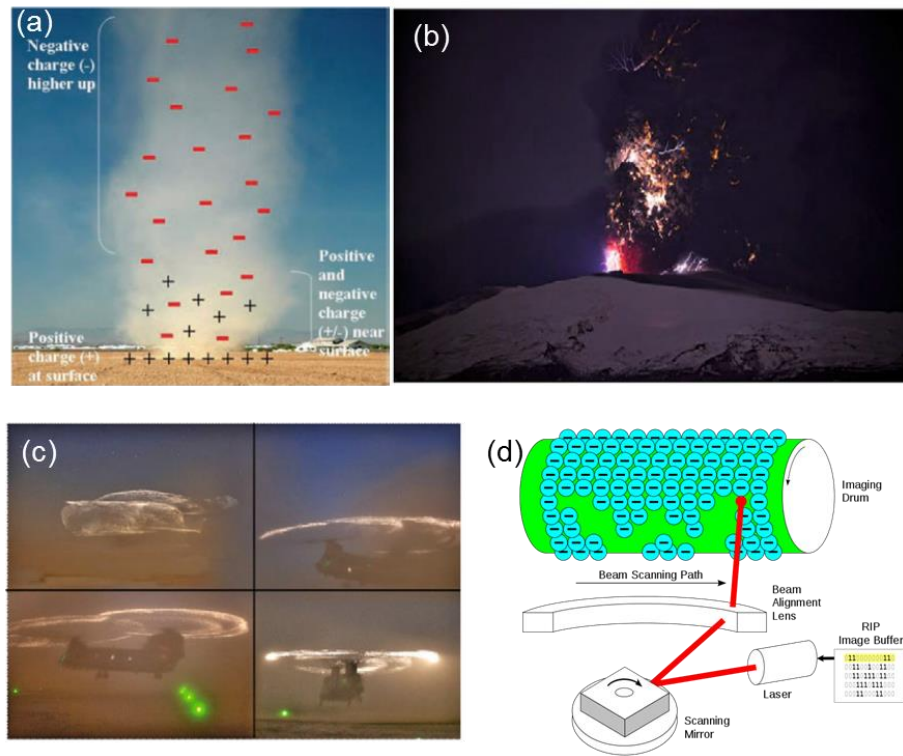
Figure 2.3 Triboelectricity encountered in nature and technology. a) A model for hypothetical charge distribution in a dust storm or dust devil [23, 24]. b) Volcanic Eruption producing lightning flashes. c) Sparks generated as a result of sand grains striking with helicopter's rotor blade whose other name is "corona effect" [25]. d) electrophotography or xerography taken from Wikipedia.

2.4.1. History of Triboelectric Effect

The knowledge of triboelectric charging has been known for 25 centuries' when Thales of Miletus, a pre-Socratic Greek philosopher, rubbed amber with a fur and attracted small

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pieces of straw, hair and other solids. He named it as "amber effect" which stands for today's 'triboelectric effect'.

William Gilbert in around 1600 was studying magnetism and "amber effect", and saw that the same kind of behavior can be observed for different types of materials that attracted other materials as a result of rubbing. Thus, these materials were classified as 'electric' that came from the word *elektra*, standing for the Greek word of 'amber'.

Stephen Gray, an English scientist and an active experimentalist of 18th century, categorized these materials under the title of insulators and conductors. However, these materials did not generate the same type of charges after friction. Later, the classification of materials that generated charges of either positive or negative after friction was studied by Charles Dufay. Materials that produced charges on glass, rock, crystals, wool, stones, etc. were named as vitreous, while charges formed on rubber, copal, gum lack, silk or paper (i.e. resinous materials) were called as resinous. Thus, after this classification, Benjamin Franklin demonstrated the difference between negative and positive charges created by friction substituting Dufay's definition of vitreous and resinous. Faraday generated electricity from friction of water and steam against other materials. These materials accumulated negative charges, while water and steam had positive charge [14].

Many experimental and theoretical studies had been carried out due to overwhelming attraction towards electrostatics phenomena and many scientists including Coulomb, Maxwell, Tesla, Volta, Faraday, Kelvin, Rutherford and Bohr had their contribution to this field; thus, all their results of experimental and theoretical works are collected in Maxwell's Treatise [14].

2.4.2. Triboelectric effect

Triboelectric effect is observed when two different materials are contacted or rubbed and consequently, triboelectric charges are generated with opposite charges of positive and negative. This phenomenon can be seen on many interfaces, namely, solid-solid, solid-liquid or liquid-liquid [26-28]. Specifically, for solid-solid combination which are of different nature and initially of zero-charge or at their ground potential [26], it is

commonly believed that the generation of opposite charge on interfaces is because of the electrical charge transfer from one solid materials to another [27, 29]. Nonetheless, it was shown that not only two similar pieces of PDMS resulted in one piece's net charge being (+) while other's (-). Moreover, the same study demonstrated that the charge generations after contact or rubbing of two materials resulted in mosaic-like structure of surface, comprising both negative and positive domains on the same surface rather than one surface becoming fully positive and the other negative [20]. Hence, this two oppositely charged materials formed electric field in between [26].

Taking a part and describing the fundamental reason of static electricity produced in our daily life, triboelectric effect has brought a lot of implications and applications of these tribocharges. Indeed, there have been a recent invention of the new field of triboelectric nanogenerators (i.e. TENG), where mechanically created static charges; in other words, tribocharges generated as result of consecutive contact, slide, roll or fluttering of two interacting materials is converted into electricity [30]. TENGs are simple, robust and relatively cheap for energy harvesting because this energy is simply obtained from periodic contact of two materials where one or sometimes both materials is the source for static electrification. For instance, single electrode triboelectric nanogenerators (S-TENG) and wind-energy TENG have only one dielectric material that produces energy from contact or fluttering of insulator with metal electrode [31, 32]. Moreover, these mechanically harvested energy is also transformed into electricity by using them for new and innovative energy applications, namely, chemical sensing [33], nanosensors [34], force sensors [31], charging devices [35], light sensing [36], magnetic sensing [37] and several other applications [38-40], rooting from triboelectricity and induction [39-42].

2.4.3. Harmful effects of triboelectricity

Although it has a lot of advantages as a new and unpolluting source of energy, triboelectrification sometimes brings serious hazards such as fire or explosion to mankind while production, storage and transportation events [43]. Home, workplace and industries are examples of such places where these kinds of risks are high. Therefore, for having a better knowledge or perception of triboelectrification, a brief discussion of some

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significant issues and threats happening after surface electrification will be reviewed in this section.

2.4.3.1. Hazards initiated due to electrostatic discharge (ESD)

Electrostatic discharge happens when a large amount of accumulated charge is neutralized through ionizing atmospheric molecules creating sparks that most of the times result in fire and explosions. Another unfortunate truth about ESD is that it mainly takes place as result of unrecognizable and discrete electrostatic charges. Hence, making materials which carry gigantic amount of static (SE) seem secure and unharmful [14]. Therefore, industries or even homes and offices where tens of kilovolts of charge exist, static electricity can generate flames and sparks due to gas failure. Between the years of 1950-1970, many chemical, defense and petroleum factories had the same type of issues of ESD which resulted in tragic way [44]. Moreover, in recent years many of these incidents took place in the powder-processing industries during processing of small powders of sugar, grain and other small powders; hence, resulting in explosions although no fuel was involved [14]. Personal Protective Equipment, standard measurements of static electricity, protective packaging for ESD-sensitive parts while being in environment are several ways to prevent or minimize Electrostatic Discharge (ESD) that can be very risky and life-threatening [45].

2.4.3.2. Other significant consequences of surface electrification

On top of what previously was mentioned, triboelectrification plays a significant role in many technological areas; however, it brings both positive and negative effects in terms of its use in electronic or technology; hence, causing some severe damages to these electronic devices. Electrophoretic and dielectrophoretic forces are among the majorly used applications in biotechnology for manipulating DNA [46]. Utilities for space applications, precipitation and coatings through static electricity [46], dispersal devices like dry-powder inhalers used in pharmaceutical applications [47, 48], electrostatic separation [49], charging of toner particles for digital printing [50] and xerography [51], self-powered biosensors [34] are all examples of electronic devices where technology takes advantage of triboelectrification.

2.4.3.3. Utilization of triboelectricity as an energy source

Despite the fact that the fundamental mechanism of triboelectrification remains unclear, its application as a new way of converting mechanical/vibrational motion into electricity has rapidly advanced. In 2012, Wang and coworkers for the first time introduced a novel path for converting mechanical energy into electrical energy [52], and they named it as triboelectric generators (TEG). Figure 2.2 represents a schematic illustration of TENGs working principle. Later, it become triboelectric nanogenerators when microscale types of triboelectric generators were invented. In fact, triboelectric effect has been known for thousands of years from the times of Thales of Miletus, but its application was negatively conceived due to some negative effects of electrostatic discharge (ESD) resulting in malefaction of electronics or even worse causing flame and explosions. Triboelectric nanogenerators (TENG) is a device made up of layers of insulators and conductive materials (i.e. mainly metals) that converts mechanical work/energy such as contact, slide, rolling, and so on, into electricity by using simple mechanism of triboelectrification and electrostatic induction [53]. Moreover, in recent years Wang has further developed TENG nanogenerators to self-powered and sensing nanosystems where these nano-generators harvest mechanical energy and then converting it to immediate force-sensing or self-powered nanosensors [31, 34]. Figure 2.3, thus, shows some of the already TENG technologies that has been developed by Wang's group [54].
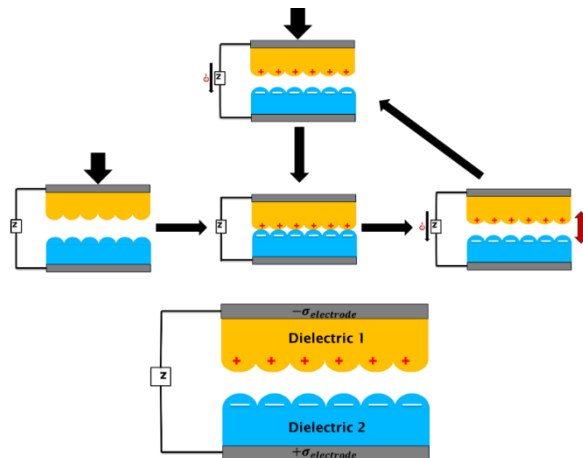
Figure 2.4 Schematic representation of TENGs contact-mode working principle. Adapted from [54].
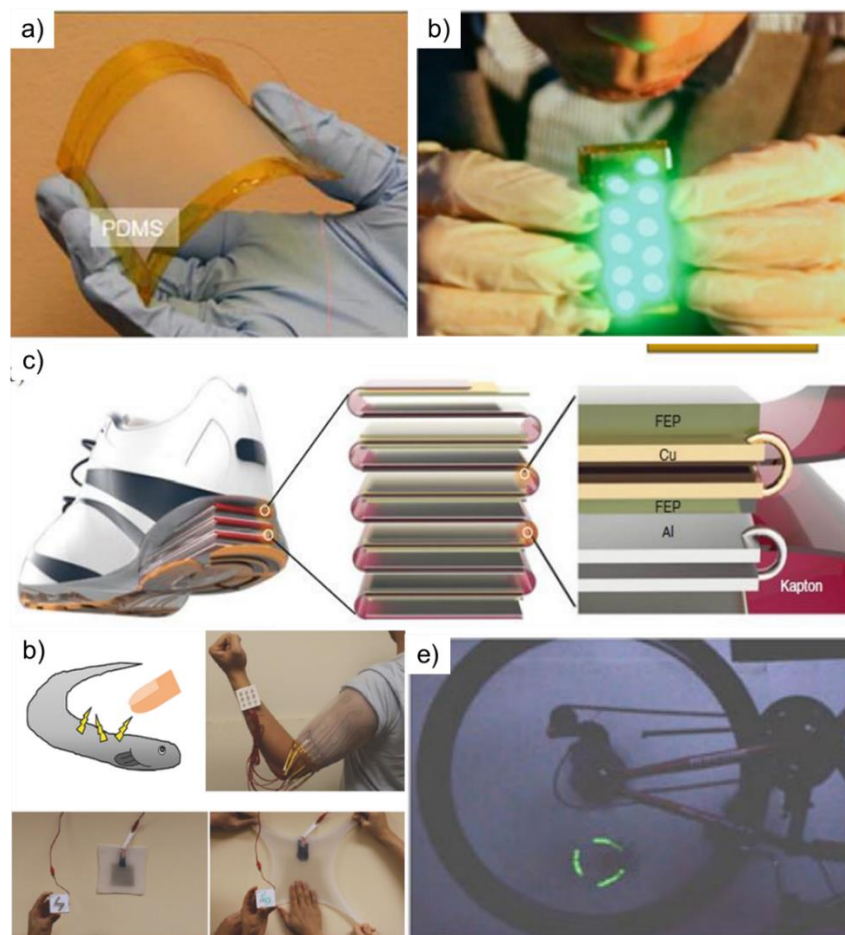
Figure 2.5 Examples of triboelectric nanogenerators used for various energy harvesting applications. a) Transparent TENG. b) Wind or air-flow energy. c) Walking energy in shoes. (d) Body motion energy harvesting using fabrics vibration. e) Cylindrical rotation energy in bicycle wheel. Reproduced from [54].

2.4.4. Triboelectric series (TES)

The arrangement of materials, having tendency to gain either positive or negative charge when contacted and separated afterwards, is clearly depicted in triboelectric series table (Fig. 2.3). This table is composed of both positively (top) and negatively (bottom) charging materials. Materials comprising the top of the list are mostly Lewis bases; hence, have high tendency to donate electrons and as well as being of hydrophilic nature [55]. For instance, poly (methyl methacrylate) (PMMA) has nitrogen atoms in its structure which is a Lewis base and has high tendency to donate electrons, therefore, it is on the

side of positively charging materials, while PTFE, the highest negatively charging material in TES, takes the lowest place in the table. However, it is not correct to generalize the order of these materials on triboelectric series since it was found heterogeneous for different groups [55-57]. Thus, it can be claimed that these inconsistencies in triboelectric series arise from various factors, namely, the way an experiment is performed (i.e. sliding, rolling, contact), surface roughness, humidity, temperature, area and so on. Moreover, Burgo et al, claimed that water locates on top of the TS, between air and glass [58]. Daniel Lacks also agreed with such inconsistency since the order of tribocharged materials alter for different investigations [59]. Finally, this series was directed towards triboelectrification of two non-identical materials; however, later it was revealed that two materials of similar nature could be charged through contact electrification [60]. Therefore, the mechanism of triboelectrification and the influence of various factors must be thoroughly studied for better understanding of these irregularities and in particular, the arrangement of materials in triboelectric series.
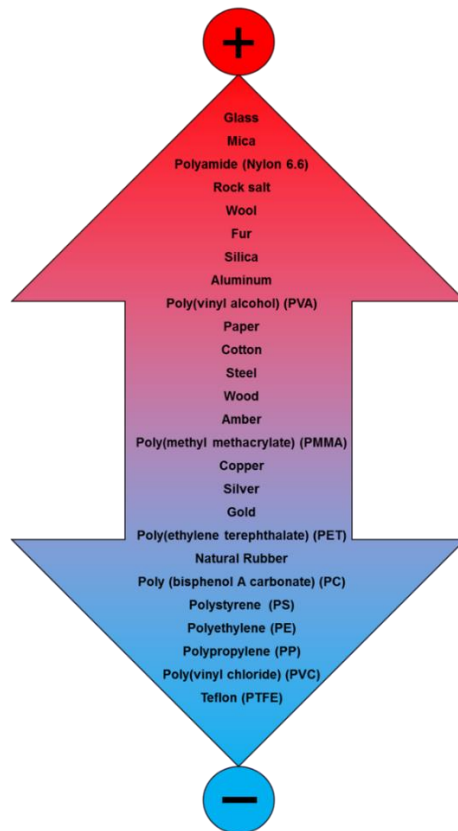
Figure 2.6 Triboelectric series (TS) of several inorganic and polymer materials, adapted from reference [57] and [61].

2.5. The underlying mechanism(s) behind triboelectricity

The resultant mechanism of ubiquitous contact electrification remains unequivocally poorly apprehended and controversial despite the technological advances and introduction of significant microscopy techniques of surface studies, in other words, AFM, KPFM, LFM, FFM. Many researchers and authors believe that this will remain an open discussion due to the complexities brought by factors influencing contact electrification. The mechanism of tribocharging between two materials or charge transfer from one material to another has been classified into three fundamental processes. Electron- transfer: when electron is a mean of charge exchange/transfer leaving one material positively charged and the other negative. The second process is through ion transfer where instead of electron bounded ion is transferred to another surface. The last one is through material transfer. In this process, a small part of materials is removed and adsorbed on other material's surface [14, 55, 57, 62, 63]. Later, other studies explored that bond formation, bond breakage and changes in their chemical nature were among the probable processes that gave rise to charge generation on the surfaces. [20, 55, 63-65].

These three underlying mechanisms of tribocharges are unique for different interactions and based on these interactions one, two or sometimes all three become dominating mechanism(s) in contact electrification. So, the following sections will be about all these three tribo-charge mechanisms on metal-metal, metal-insulator (or polymer) and insulator-insulator. Contact electrification between metal-metal and its underlying mechanism is a well-known fact [61]. Metals having difference in their work function, which is an energy required for removal of electron from the surface of metal, exchange electrons among themselves.

When two metals are brought into contact, the electron-tunnel occurs from the metal (A) having low work function φ_A to the metal (B) possessing higher work function φ_B till they reach a thermodynamic equilibrium and their Fermi level (EF) match, shown in the Fig. 2.7 [55, 66, 67]. In this figure, electron tunneling from Metal A (low work function,

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(φ_A) to Metal B (high work function, (φ_B) creates a potential difference of V_C, in other words, it is an energy required to remove and electron from the surface. However, it was found out that contact potential and the work function of some materials is not consistent. Therefore, although it is the most well-understood mechanism, there is possibility that both ion and electron transfer might occur due to hydroxide and hydronium ion participation form thin layer of water on metal surface [55, 61].

$$V_C = \frac{\varphi_A - \varphi_B}{e} \qquad (2.6)$$

where e is (e= 1.6 x10-19 C) the electronic charge [31, 66, 67].
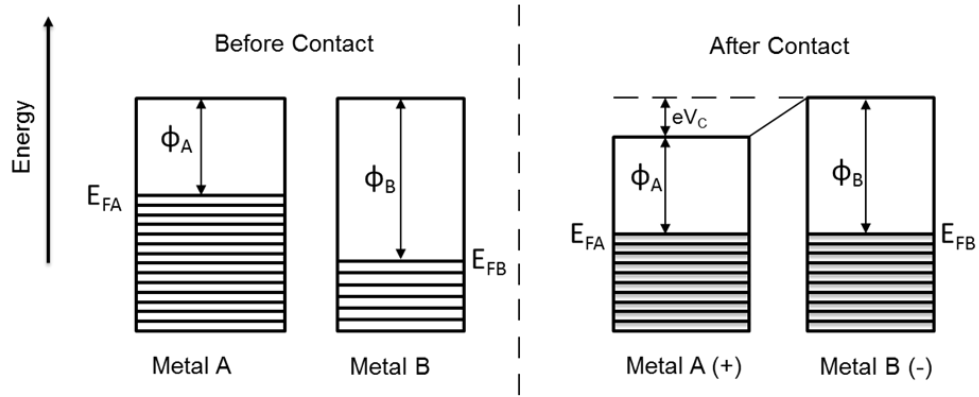
Figure 2.7 A charge transfer of two metals (A and B) after contact, while Metal A, lower work function, becomes (+) charged and Metal B (-) [67].

The effective capacitance is an important parameter to calculate the charge transfer between two metal surfaces. When two metals are set apart, electron tunneling occurs back to surface so that an equilibrium is maintained in difference between their potentials. Consequently, the product of effective capacitance (C) and potential difference gives net charge transferred among these metals [31].

$$Q = C * V_C \qquad (2.7)$$

Whereas, in insulating materials where the working concept is built upon tribocharging and electrostatic induction, their performance is compared by calculating open-circuit

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voltage (V_{OC}), short-circuit current (I_{SC}), charge transferred tribological event. In open-circuit cases, V_{OC} is defined by [68],

$$V_{OC} = \frac{\sigma_0 * x(t)}{\varepsilon_0} \qquad (2.8)$$

where ε_0, σ_0, and $x(t)$ are the vacuum permittivity, triboelectric charge density and interlayer distance respectively. Thus, formula 2.8 suggests that V_{OC} is independent of the composite films or thickness. σ_0, nonetheless, depends on capacitance of contact mode triboelectric generator. Maximum capacitance, C_{max} can be expressed by [68],

$$C_{max} = \varepsilon_0 S \frac{\varepsilon_r}{d} \qquad (2.9)$$

ε_r, ε_0, S, and d, are relative dielectric permittivity, vacuum permittivity, area of metal and thickness of insulating materials.

2.5.1. Electron transfer mechanism

A thorough study about contact electrification and the mechanism behind this phenomenon of contact and separation of two materials was carried out in the late of twentieth century [38]. In their study, Lowell and Rose-Innes [63] demonstrated the possible mechanism of charge transfer in metal-metal, metal-insulator and insulator-insulator. However, they also mentioned that static electrification of insulator surfaces is very complex because of deficiency in the knowledge of their electronic states. Therefore, when it concerns both being insulators, chemical characteristics such as the nature of functional groups need to be taken into account [55, 69]. Even very few charges exist on valence and conduction band of insulators, they become negligible when the surface of the bands possess some electrons that surpass or smaller than the Fermi level of a metal [63].

Thus, Matsusaka et al, proposed the probable electron transfer from metal to insulator with further explanation of energy "window" existence in insulator's lowest unoccupied molecular orbital (LUMO) whose range is close to the Fermi level of metal and electrons can tunnel from metal to insulator [67]. Figure 2.8 demonstrates probable representation of charge transfer of pre- and post- contact of metal-insulator. Highest occupied molecular

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orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are energy bands for insulators. Whereas, EF is the Fermi level for metal, and φ_M and φ_i are the work functions of metal and insulator respectively. The distance between two interfaces is denoted by z and the Fermi level (EF) coincides when metal and insulator is contacted and then separated [67]. In addition, due to the lack of explanation and not possessing Fermi level in insulating materials, the work function and charge transferred demonstrated a large discrepancy between theoretical and experimental results [61, 66].

The electron transfer in insulators is still unknown because of deficiency of electron in their electronic structure. Insulators possessing large band gap make electrons impossible to flow between conduction and valence bands [41]. There are several models for electron transfer in insulator-insulators system similar to metal-insulator model [63, 67]. As expected, the charge transfer in metal-insulator system occurs from metal to insulator; nonetheless, some insulators have tendency to charge negatively even after contact with a metal surface [63].

In insulator-insulator case, things become more complicated to explain because of electron deficiency and not having Fermi level, and it is commonly perceived that electrons reside on the surface of material rather than in bulk. Moreover, bulk electronic properties such as dielectric constant, or atomic properties, such as electronegativity, electron affinity, or ionization energy have no direct relation to triboelectrification of insulating materials [42, 44]. Figure 2.9, consequently, depicts this assumption and demonstrates the probable charge transfer in insulator-insulator (or polymer-polymer) tribocharging [67]. φ_{P1} and φ_{P2} are relative work functions of polymer (1) and polymer (2) respectively and the equilibrium state is reached when electrons from polymer (1) flow to polymer (2) after contact has taken place [67].
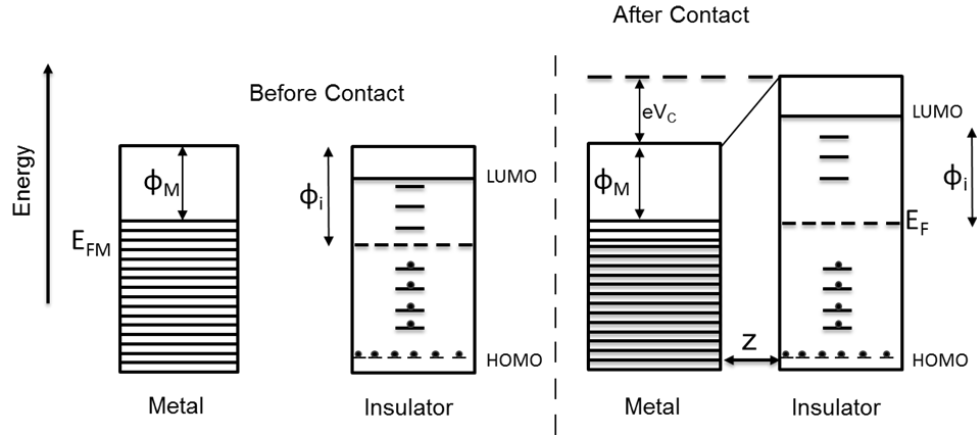
Figure 2.8 Pre- and post- contact electron transfer model of metal-insulator [67].

Many research believed that the tribocharging in insulators is the result of electron transfer [63,67]; nonetheless, experimental observations presents conflicting results. Harper, thus, brought several conflicting views about the possibility of insulators charging [14]. Liu and Bard, for instance, in their studies of application of triboelectric charges that were generated on the surface of PTFE, PMMA and PE polymers for reduction of some metals cations [22, 23, 70], argued that this happens due to electron transfer from tribocharged polymers to metal cations, hence reducing metal cations to metal particles. On the contrary, Baytekin et al [71], attributed this not only to electrons, ions or both but to the material transfer and mechanoradicals that become responsible for static electrification and the adsorption of ions on materials surface rather than reduction of metal cations.

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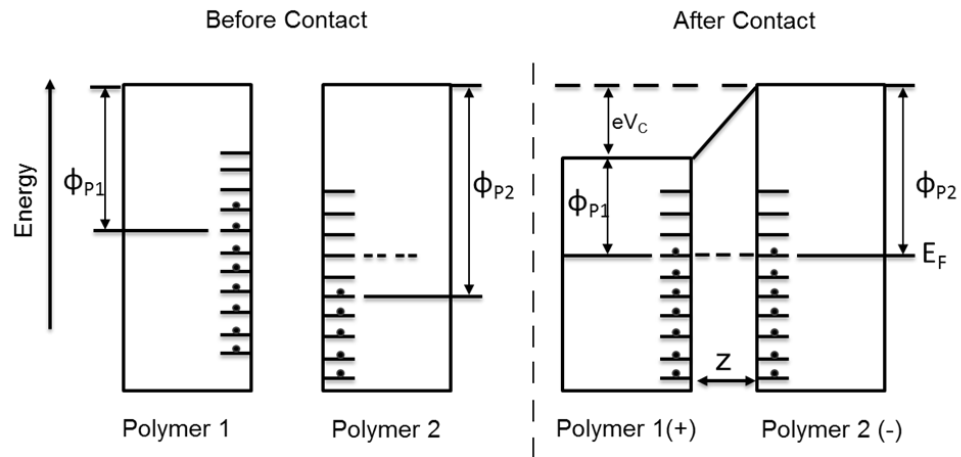
Figure 2.9 Charge transfer of two polymers (1 and 2) after contact, while Polymer 1 becomes (+) charged and Polymer 2 (-) [67].

2.5.2. Ion transfer mechanism

The clear evidence for ion transfer in contact electrification of insulating materials must be electrophotography where toner particles, an imaging powder, are charge carrying mobile ions [61, 66]. Hence, this shows that the mechanism for triboelectrification is the generation and transfer of ionic particles. McCarty et al [57], demonstrated other compelling mechanisms and evidence for ion transfer for polymers possessing covalently bound ions and mobile counterions where after contact some of these mobile ions are transported to another surface making the countersurface to be of equal charge of covalently bound ions [57]. He also proposed a mechanism of potential well regarding the contact electrification through transfer of mobile ions where it is overcome by mechanical work during separation of surfaces [57]. Several other researchers have found correlation between acidity/basicity and triboelectrification of insulators. Diaz et al [69], suggested the proton participation in triboelectrification of insulating materials might be a significant observation for explaining the triboelectrification of wider range of polymer materials. Hence, McCarthy and Whitesides believe that including both acidity/basicity and various ions such as hydroxide ions, alkali metal cations, protons, and halide anions are important for clearly observing the ion transfer from one Lewis acid/base surface to the other Lewis acid/base surface [57].

2.5.3. Material transfer and mechanochemical events

When two materials are contacted and then separated, this can lead to material transfer of one surface to another. The transferred material can be of any size as small as dust or some impurities on the surface [63]. Material transfer that could be regarded as a part of tribocharging was mentioned in the year of 1967 by Harper [61]. Later, Clark et al, with the help of recently developed ESCA and XPS techniques observed the material transfer between PTFE and PET polymers after contact [72]. In the same study, he also detected F peaks from C-F spectrum on PET surface whereas, C1s and O1s peaks on PTFE surface. Another important observation was reported that consecutive contacts of these materials

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led to decrease of material transfer and hence, Lowell concluded that for infinite numbers of contact, materials transfer would halt at some point [73]. Thus, this view brings a clear implication that material transfer cannot be the primary cause of tribocharging.

Recently, Baytekin et al, proposed that the static electrification of two materials has islands of both positive and negative charges than one polymer being fully positive and other fully negative [20]. They also claimed that both material and charge transfer as a result of hemolytic and heterolytic bond breakage are responsible contact electrification or static electrification at the interfaces. Moreover, in our study we will show that such occurrence is observable using X-ray Photoelectron Spectroscopy (XPS) after sliding electrification or triboelectrification of various polymers on cellulose surface (substrate). Thus, further conclusion regarding material transfer and its contribution to triboelectrification and coefficient of friction will be derived.

Another important concept elucidating the underlying mechanism of triboelectrification can be related to mechanochemical events. Since we already mentioned several works showing material transfer contribution to triboelectricity after contact or rubbing of two insulating materials, it is also worth to allude to mechanochemical events where ionic polymer fragments are produced due to hemolytic and heterolytic bond scission hence generating tribocharges [17]. These as formed ions and radicals act like a high-energy and short half-life species having tendency to form peroxy radicals and other diverse products e.g. triboplasma since they are produced in ambient conditions. Also, ions produced by mechanochemical reactions behave similarly even in materials with identical surface compositions. In 2012, Burgo et al, demonstrated that hemolytic bond cleavage is more favored in PTFE and LDPE as the commencing mechanochemical event [17]. Therefore, chemical reactions and mechanochemical events happening on the surfaces play significant role in understanding and explanation of surface events and surface charge generation. Figure 2.10 depicts mechanochemical events taking place at the surface of two insulating materials.
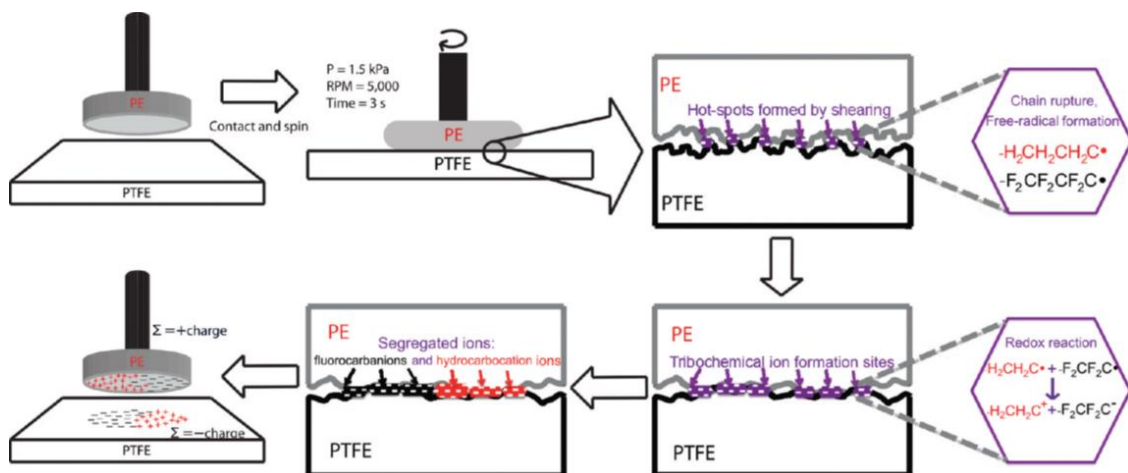
Figure 2.10 Mechanism of mechanochemical bond rapture and formation for contact electrification of insulating materials. Reprinted with permission from [17].

2.6. Friction and triboelectricity relationship

As previously mentioned, friction and tribocharging have attracted huge interest due to numerous applications and intense study of these phenomena has led to foundation of new technological field of TENG- conversion of mechanical energy to electricity via accumulated charges on the surface dielectric materials as a result of rubbing, rolling or contact. Triboelectrification is mainly the product of the friction and wear. However, even if great technological advances have been achieved, the underlying fundamental mechanism of these phenomena at nano- and macroscales has not been yet completely understood. For example, the dependence of friction on electronic properties of materials is overlooked for many years. Today, the effect of triboelectrification on friction has slightly changed with what Amontons' law that was mentioned in the past.

It is believed that friction is due to attractive forces between two surfaces and hence, it is very difficult to move one on top of the other. Contrary to Amontons' law regarding the independence of friction coefficient from contact area, Desaguliers was the first to demonstrate the effect of adhesive forces that increased the friction after polishing the metal surface [74]. Many years later in 1950, Bowden and Tabor shed light on this relation by introducing the concept of "real contact area" [74]. They illustrated the increase in frictional force due to rise in real contact area and load respectively.

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Following to Desaguliers' experimental inventions, other scientists proposed theories that governed the interactions of two interfaces during tribological experiments. Among all, Hertzian, JKR, and DMT are the most commonly used theories that explain elasto-plastic deformations at the interfaces due to attractive forces between elastic bodies. For instance, DTM theory is operated AFM instrument developed by Bruker for Young modulus calculation of materials [74].

Thanks to technological advancement, Surface Forces Apparatus (SFA) and Atomic Force Microscopy (AFM), the study of coulombic interactions at the interfaces of materials and friction become easy to investigate. Several works have been published on phononic and electronic contributions to the friction of metals and semiconductors surfaces. Using magnetic force microscopy, levitation and atomic-scale friction of Fe on YBCO semiconductor surface was studied, thus, revealing the significant influence of phononic dissipation to friction [75]. Furthermore, other groups confirmed that such phononic contribution gave rise to friction [14]. While, the electronic contributions to friction of silicon pn junction and GaAs were investigated at nanoscale [2-4]. Furthermore, recent studies suggested the significance of electronic contributions to friction via generating triboelectric charges that gave rise to friction by different modes of atomic force microscopy [76, 77]. Moreover, it was observed that friction continues to exist even at negative loads when attractive forces at the interface are majorly distributed forces across the surface [78]. Thus, these mentioned works have shown that phononic and electronic effects are of great importance at atomic-scale level in insulating materials. Unfortunately, all above mentioned studies on phononic and electronic contributions to fiction were either in metal-metal or metal-semiconductor pair.

Although numerous works in the field of nanotribology and tribocharging contributions to friction in metal-metal and metal-semiconductor at macro scale exist, there are very few studies on friction and tribocharging relation at insulator-insulator surface. Nakayama was one of the first who illustrated the formation of potential and triboplasma after scratching insulating materials such as Al_2O_3, Si_3N_4 and PTFE with diamond stylus [79]. Moreover, for the first time he claimed correlation between friction and tribocharging of

insulator-insulator at macro-scale. Nevertheless, it was more of scratching of insulating of ceramics and polymers by diamond stylus than just rubbing two materials. Recently published work on the effect of tribocharged polytetrafluoroethylene (PTFE) to friction coefficient by Burgo et al; suggested that controlling surface electrostatics or triboelectric charges can be useful for tuning friction of some important systems or equipment [14]. Nonetheless, these studies on friction to tribocharging dependence were more about nanotribology.

2.7. Wear and triboelectricity relationship

In addition to the relation between triboelectricity and friction, in this work we suggested that wear is also dependent on triboelectric charges and hence, it can be decreased to large extend if surface tribocharges are controlled. This relation has not been investigated in the literature and overlooked so far since surface charges have not been considered as a factor that affects friction. Therefore, we believe our results will be one of the first investigations regarding wear and triboelectricity relation. In this study, we demonstrated that wear behavior of polymer materials can be tuned through surface triboelectric charges.
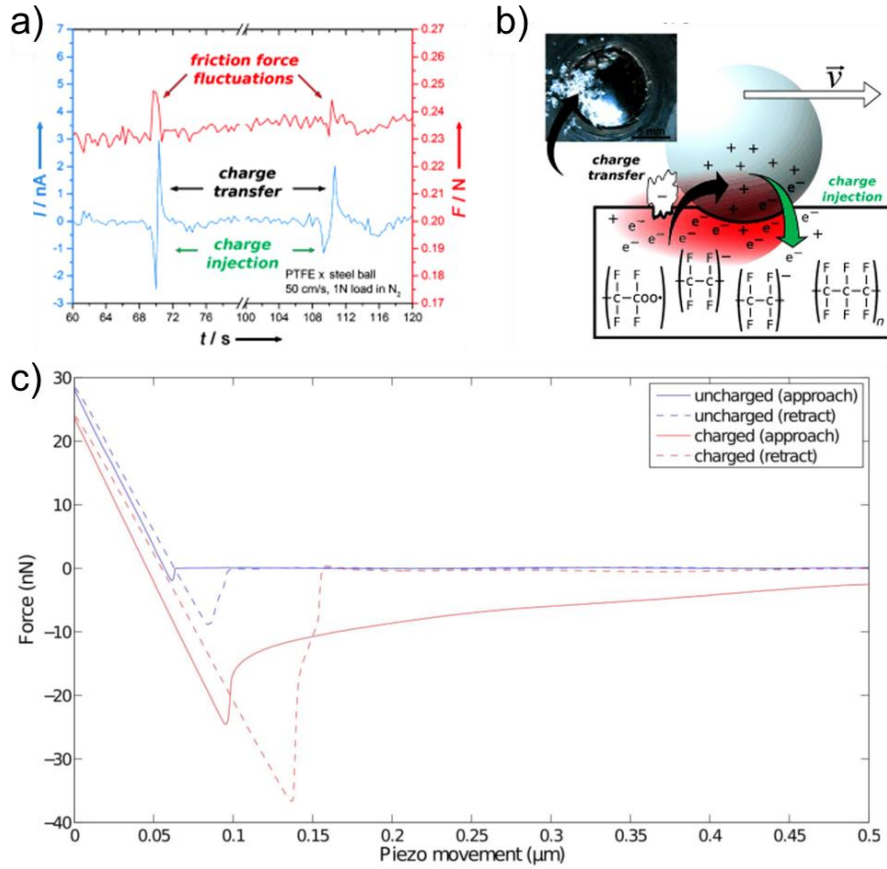
Figure 2.11 Some examples of triboelectrification contribution to friction. Formation of tribo-current at metal-insulator interfaces. (a) Tribo-current formation and fluctuations of friction at metal-PTFE interfaces. (b) A schematic illustration of the mechanism [80]. Force versus distance curve for uncharged and tribocharged PTFE by SiN tip [5]. Reprinted with permission from [5].

Our experiments were conducted in a controlled system of different gases such as nitrogen and argon. Argon and nitrogen were chosen for studying their effect on friction and tribocharging, despite the fact that previous works [80] mainly concentrated on tribocharging behavior inside these gases and several others. Secondly, although several factors like load, and area have their influence on triboelectricity, most of the studies have been mainly focused on humidity effect of triboelectrification in insulators. Another significant point is that the trend of charging in humid mediums may vary for each insulator. Therefore, we carried out separate humidity experiments for most polymers and

additionally we examined influence of the other factors like load and area on triboelectricity and friction simultaneously.

Briefly, this thesis consists of four major parts. First part covers the well-known phenomenon of triboelectricity and its contribution to coefficient of friction (COF). The second part investigates the friction and triboelectricity behavior under Nitrogen (N_2) and Argon (Ar) gases. The third part of this thesis studies other factors such as load and area affecting both triboelectricity and friction under ambient conditions in hope to assist for better understanding the underlying mechanism(s) behind triboelectrification and contribution of this phenomenon to coefficient of friction. The final part of this thesis provides information about possible control of wear through manipulation of triboelectricity and friction. Finally, relative conclusions are made regarding each section of the study.

CHAPTER 3

3 Methods & Materials

3.1. Experimental procedures

5 cm x 5 cm flat polymers of both negatively charging Polytetrafluoroethylene (PTFE), Poly (vinyl chloride) (PVC), Polyvinylidene fluoride (PVDF), Polypropylene (PP) and positively charging Polycarbonate (PC), Poly (ethylene terephthalate) (PET), Polyethylene glycol (PEG), Polysulfone (PSU), Polyester, Poly (4,4'-oxydiphenylene-pyromellitimide) (Kapton) with respective thicknesses as shown in the Table 3.1 were used in sliding experiments. The dimensions of PVC, on the contrary, were changed for contact area study and hence, it will be discussed in the relative section regarding effect of contact area on triboelectrification and coefficient of friction.

Before each set of experiment, for cleaning and at the same time for discharging purposes polymers were washed either by dipping into ethanol or wiping with ethanol sprayed Cleanroom Wipers (VWR North American Cat. No: 89065-956) and then drying with air gun via blowing air on polymer samples. Advanced Friction Tester (AFT) was used for sliding friction tests, Fig 3.1a-1. All friction tests including humidity, load, area and gas were performed by AFT and its experiment parameters were set to 1200 mm/min velocity, 150mm sliding distance and 15g load except for load experiments. Triboelectric charges were measured using home-made Faraday cup outside connected to high-precision electrometer (Keithley, model 6514). Moreover, several factors influencing triboelectricity, in particular load, area, gaseous medium and humid conditions were investigated. In the study of triboelectricity dependence on load, the series of loads

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ranging from 0.1N to 0.5N was studied, while the experimental parameters of AFT and polymers dimensions (5 cm x 5 cm) were kept the same as previously mentioned. For gas effect on triboelectricity study, nothing was altered, and the relative humidity of surrounding was measured using Hygrometer (Traceable, s/n: 150201304). Lastly, to investigate the effect of contact area on coefficient of friction and triboelectricity, PVC with dimensions of 10x10, 15x15, 20x20, 25x25, 30x30, 35x35, 40x40, 45x45 and 50x50 (in mm^2) were cut and AFT parameters were kept the same.

3.1.1. Friction measurements

A completely automated and high precision friction tester equipment Advanced Friction Tester (Hanatek Instruments, Serial Number: FT1506001, UK) was used for sliding friction tests, Fig 3.1a-4. This instrument provides an accurate friction vs. distance data and dynamic and static friction coefficients. All friction tests including humidity, load, area and atmospheres were performed by AFT and its experiment parameters were set to 1200 mm/min velocity, 150 mm sliding distance and 15g load except for load experiments.

3.1.2. Electrical measurements

Triboelectric charges were measured using home-made Faraday cup, Fig. 3.1d and e, with dimensions: 7.5x7.5x5.5 (cm^3) inside and 9.5x9.5x7.5 (cm^3) outside connected to high-precision electrometer (Keithley, model 6514), Fig. 3.1a-2. Also, for precise measurements of electrostatic charges, a small tip by the name of "ground" connected on top of Faraday cup, shown in Fig. 3.1e, was grounded for dissipating charges accumulated on dielectric materials holding the sample.
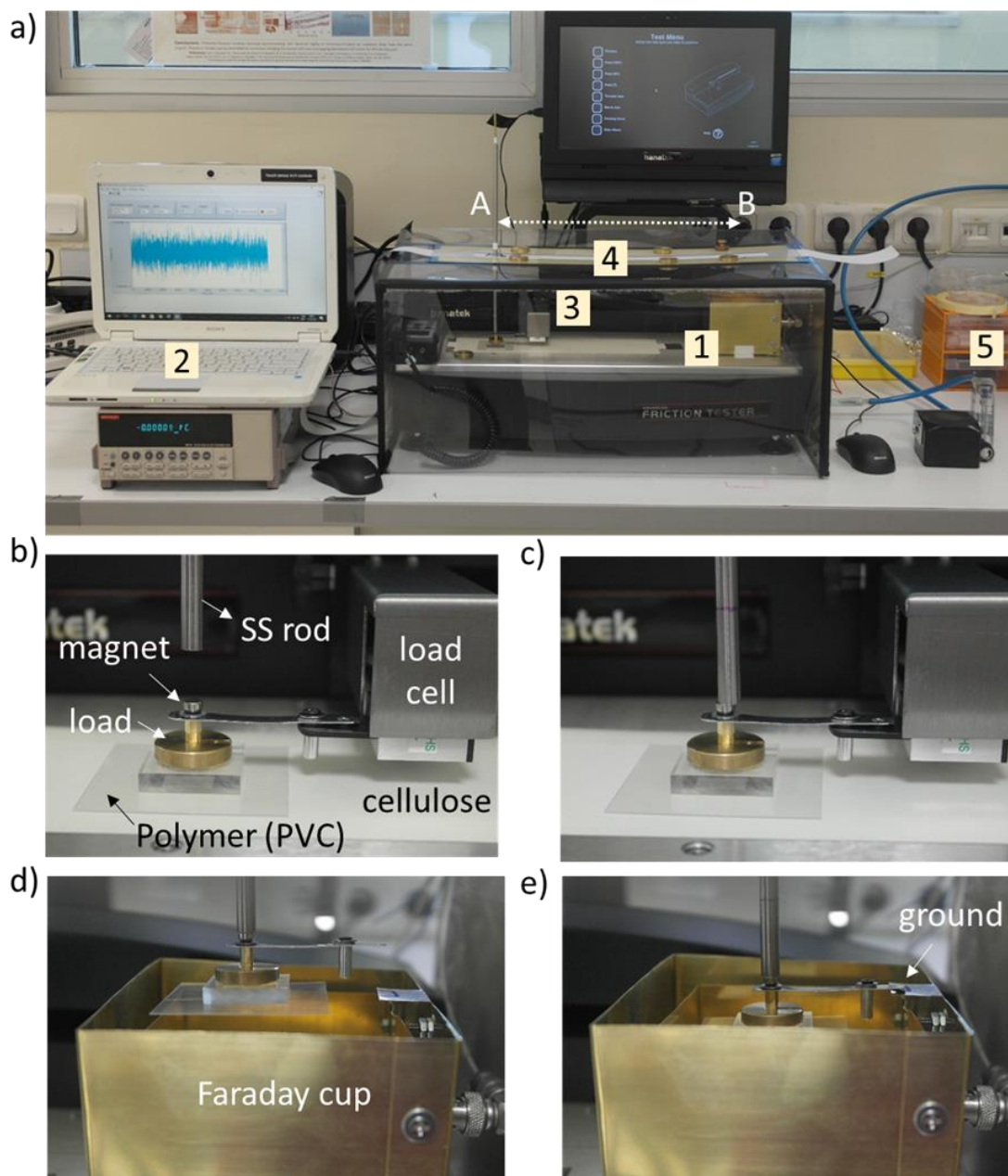
Figure 3.1 Measurement devices and experimental setup for the study of friction and triboelectricity under different atmospheres. (a) Faraday cup (1) for static electricity measurements, electrometer (2), load cell (3) and friction tester (AFT) (4). (b) and (c) placing polymer material in the load cell. (d) and (e) generated triboelectric charges are measured in the Faraday cup after sliding friction test.

3.1.3. Characterization techniques

In this thesis study, SEM, EDX, ATR and XPS characterization techniques were used for surface analysis of polymer materials (insulators). Related characterization techniques were performed before and after sliding friction tests to observe material transfer on cellulose surface. Since all these tests were about the study of surface triboelectrification between two solid interfaces of polymer materials, all three characterization techniques, namely Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Infrared Spectroscopy (IR), were operated to investigate morphological and compositional change occurring at the interface of cellulose paper pre- and post- sliding experiments. Following section will present a brief introduction of these characterization techniques.

3.1.4. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)

Scanning Electron Microscope, SEM, is an electron microscope that sends focused beam of electrons onto a surface of a sample and collects secondary electrons emitted by atoms. These electrons interact with sample's atoms producing a topographical image or it can also give information about the sample's composition (EDX) [81]. The resolution of SEM is highly dependent on vacuum condition, but it is mostly around 1 nm resolution; that is, it can give a topographical or surface image of 1 nm sized nanomaterials. As previously mentioned, SEM can also produce chemical composition characterization through collecting X-rays formed due to beam of electrons interacting with atoms. Thus, this technique is called with the most commonly used name among other names as Energy-dispersive X-ray Spectroscopy (EDS or EDX).

In this study, SEM images were obtained by utilizing FEI Quanta ESEM instrument. For sample preparation, cellulose papers were cut to as small as to 1 cm x 1 cm dimensions and placed on aluminum SEM sample holder. Due to the fact that the samples are insulator, 5 kV energy and between 2.5- 3 spot sizes were used for taking images and preventing ionization. For EDX analysis, the same energy (5 kV) was applied to acquire EDX survey spectrum. However, for better resolution SEM images cellulose sample were

coated with 50-100 Å Au/Pd alloy using Precision Etching Coating System and 15 kV energy were used instead of 5 kV prior to SEM imaging.

3.1.5. X- ray photoelectron spectroscopy (XPS)

X- ray Photoelectron Spectroscopy, XPS, is also a surface spectroscopic technique used for elemental analysis of material's surface. X- ray beams are send to the interface and data are collected from kinetic energies and the number of electrons (photoelectrons) escaped from the surface. XPS is a very significant instrument since the operation takes place in an ultra-high vacuum of approximately ~ 10-8 millibar (mbar) and provides precise quantitative information of sample's surface chemical composition. The detection limit for XPS is extremely high and it can go up to the limits of parts per million (ppm) which is very astonishing for quantitative spectroscopic technique of surface's elemental composition study. XPS replies to many question regarding the elements existing on top surface of a sample, the place of contamination in be it in bulk or the surface, empirical formula, the type of bonding of surface atoms, binding energies between atoms, the surface thickness of thin materials with around 1-8 nm thickness, electronic state density and so on. Another important operation that can be useful for specific applications, XPS enables to perform ion beam etching which in return provides information about elemental composition as a function of depth. Lastly, the spectrum of XPS gives information about number of electrons versus binding energy (BE). Specific elements bonded to another element have specific XPS binding energy which facilitates identification of an element and its corresponding bonded atom.

XPS can analyze almost any material such as inorganic, polymers, semiconductors, glasses, paints, papers and so on. In our study XPS technique were used to perform surface characterization of cellulose pre- and post- triboelectrification treatment in order to observe material transfer from polymer materials to cellulose surface.

Elemental composition and chemical bonding states of the transferred materials were determined by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific K-Alpha spectrometer (Thermo Fisher Scientific, Waltham, MA) with a monochromatized Al Kα X-ray source and spot size of 1 kV and 400 μm, respectively.

3.1.6. Polarizer optical microscopy

Zeiss Axio Imager.A2m Microscope was used to obtain optical and polarized optical imaging and studying wear on polymers' in surfaces pre- and post- sliding experiments. Also, the influence of triboelectricity to wear were studied by taking polarized images of tribocharged and discharged polymers (using Zerostat ion gun) after successive sliding experiments.

3.2. Materials

Mainly in textile, dye, printing, coating, packaging and automobile industries polymers are commonly utilized materials. Thus, in this study, different set of polymers and a substrate e.g. cellulose were used. To investigate both positively and negatively charging polymers, the highest positive or negative among these polymers (i.e. closer to the edge of TES chart), easy to detect triboelectric charges using home-made Faraday Cup, easy to handle and several others were the main reasons for choosing these polymer materials. These polymers were categorized into two groups of positive (+) and negative (-) charging materials. Whereas, cellulose paper is explained separately owing to its usage as a substrate material despite being among those positively charging in TES chart.

3.2.1. Cellulose paper

Cellulose is a fibrous polymeric compound of glucose molecules. In cellulose, D- glucose molecules (monomers) are linked through β (1→4) linkage which makes them different from starch where glucose molecules are bound via alpha- linkage, hence, Fig. 3.2 shows the chemical representation of cellulose with β (1→4) link and its SEM image. In Earth crust, it is one of the most abundant polymers and the main component of cotton and wood. Moreover, in cellulose industry, it is a significant material for printing, pharmaceuticals, fiber, textiles etc. Additionally, cellulose paper is on top part of TS chart meaning it has high tendency to become positive (+) after triboelectrification.

Cellulose as a substrate material

In the study of triboelectrification contribution to coefficient of friction, special cellulose papers (Southworth Resume Paper, 100% Cotton) were purchased. For each experiment

new paper with 7 cm x 28 cm dimensions were cut using paper cutter (KW-triO, 3925) and used as a substrate in all experiments. The reasons for choosing cellulose paper as the substrate material can be summarized as; i) cellulose generates triboelectric charges easily when rubbed to common synthetic polymers, and therefore electrification of cellulose and its products is highly important, ii) cellulose is a very common industrial product, produced in very large amounts annually worldwide, it is cheap and easily available material.
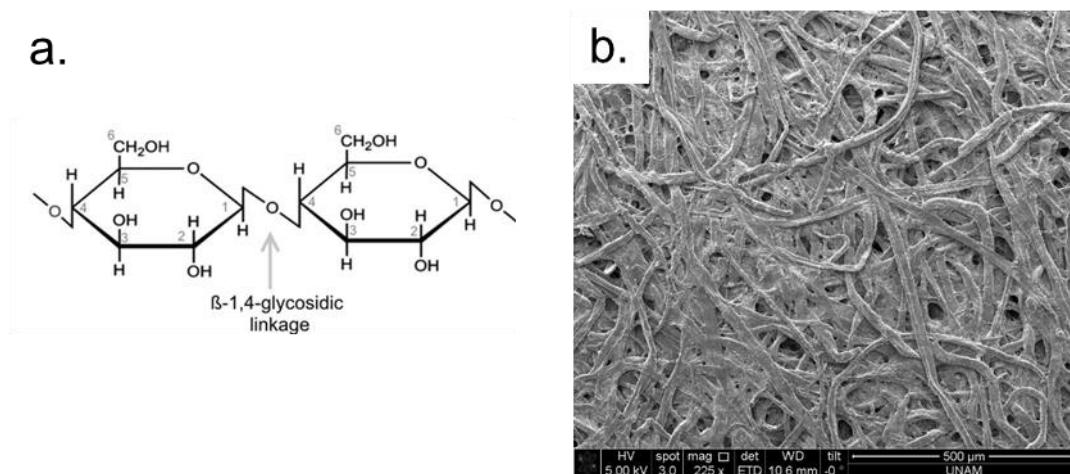
Figure 3.2 Cellulose (a) structure and (b) SEM image of fibrous cellulose paper that was used in this research.

3.2.2. Relatively positively charging polymers (PC, PET, PEG, PP)

Polycarbonate (PC), polysulfone (PSU) poly (ethylene terephthalate) (PET), poly (ethylene glycol) (PEG) and are materials that have tendency to possess positive (+) charge on their surfaces after sliding, contact, or rolling. In TS chart, there are a lot of inorganic materials that become positively charged subsequent to friction; however, only polymers were chosen in order to elucidate the underlying mechanism of triboelectricity at insulator-insulator interface.

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Poly (ethylene terephthalate) (PET)

Polysulfone (PSU)

Polycarbonate (PC)

Poly (ethylene glycol) (PEG)
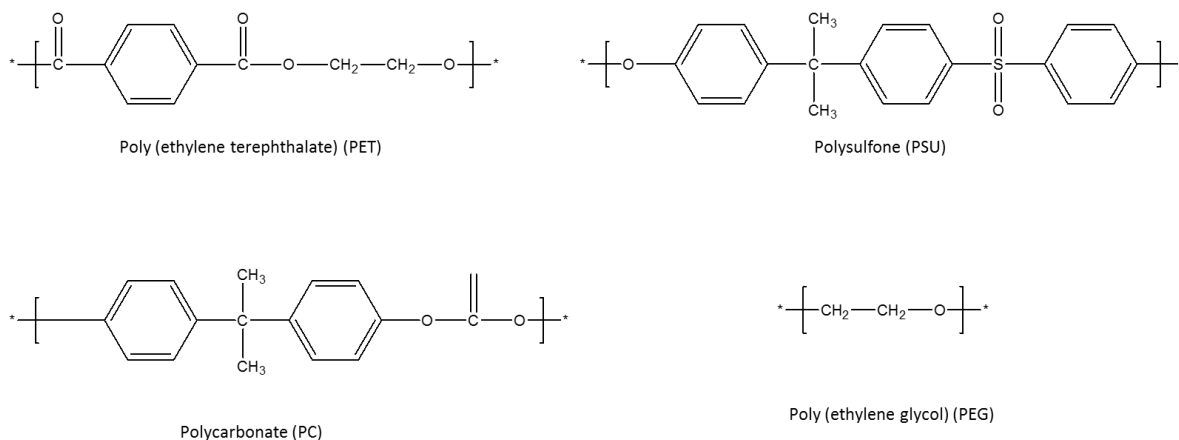
Figure 3.3 Polymeric structures of positively charging polymers.

3.2.3. Relatively negatively charging polymers (PTFE, PVC, PVDF, PP)

Poly (tetrafluoroethylene) (PTFE), poly (vinyl chloride), poly (vinylidene fluoride) and polypropylene (PP) are polymer materials that have tendency to obtain negative (-) charge on their surface after any type of friction phenomenon. They are on the lower part of TS chart. Similarly, these materials are selected for the sake of establishing the true mechanism of triboelectrification at insulator-insulator interface.

Poly(vinyl chloride)

Polypropylene (PP)

Poly(tetrafluoroethylene) (PTFE)

Poly (vinylidene fluoride)
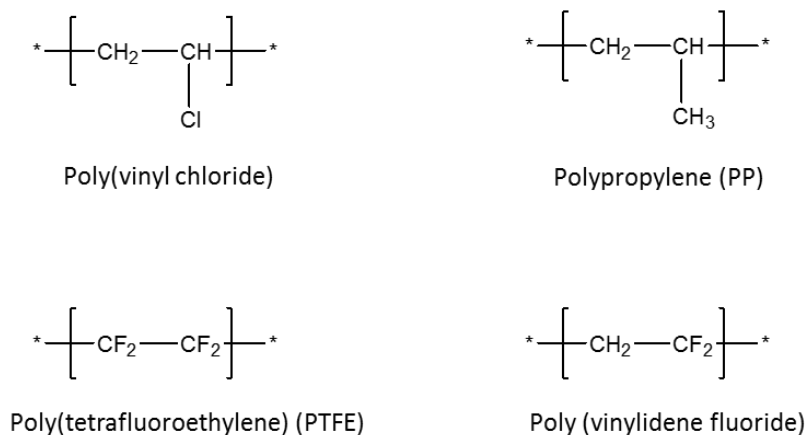
Figure 3.4 Polymeric structures of negatively charging polymers.

CHAPTER 4

4 Results & Discussion

4.1. Triboelectricity contribution to coefficient of friction (COF)

To perform friction experiments under dry conditions, polymers with dimensions of 5 cm x 5 cm were slid on a substrate (Fig. 4.1). Dynamic friction is normally considered to be constant along the sliding distance, Fig. 4.1a. However, COF goes up through the sliding distance for two contacting insulators after the first experiment and keeps on rising for the consecutive numbers of sliding experiments. Consequently, owing to common knowledge, the triboelectric charges are generated on the counter surface, Fig. 4.1b. Thus, these electrostatic charges give rise to development of a strong electrostatic potential which in return generates strong attractive forces between these surfaces and increases COF. When two insulating materials are slid on each other, the influence of triboelectricity on friction is expected, and these electrostatically charges could be discharged (or tuned) resulting in decline of COF to its initial value (Fig. 4.1c).
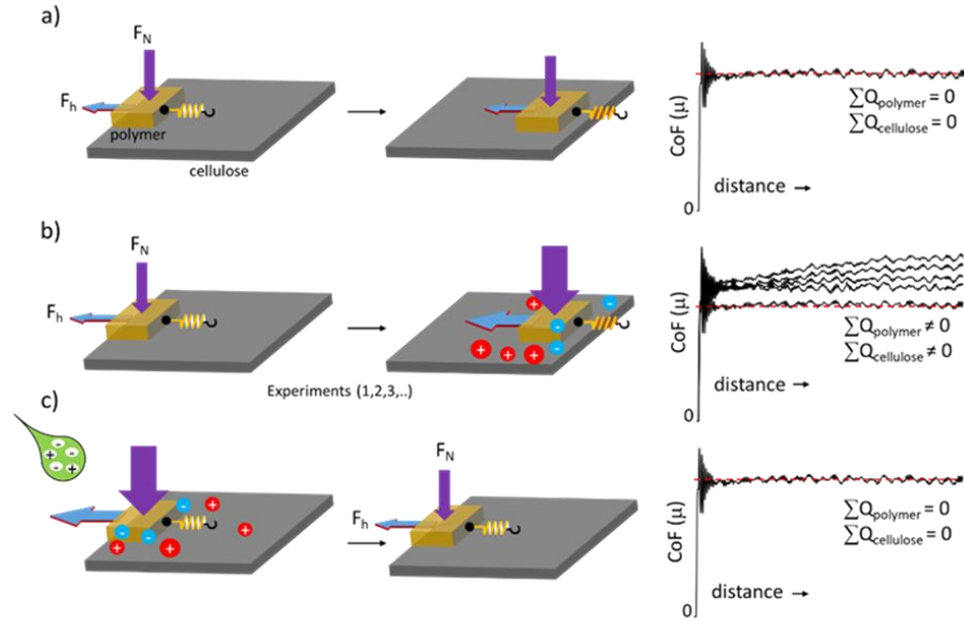
Figure 4.1 Triboelectricity contribution to friction and its control through surface charges. (a) A typical representation of friction between two objects and the resulting friction coefficients along a path (top, far right). (b) The increase in coefficient of friction of two insulators along a path because of surface triboelectricity (middle, far right). (c) Surface discharge can reduce friction coefficient to its initial value (bottom, far right). Surface triboelectricity elimination via bombardment of positively or negatively ionized air using ''zerostat'' ion gun.

The relation between COF and triboelectricity of PTFE on cellulose substrate was investigated in here (Fig. 4.2). Repeated sliding experiments with constant normal load of 0.15N were performed. Dynamic friction demonstrated an increasing trend consequent to repeated numbers of sliding experiments (Fig. 4.2b and 4.2c). At the same time, surface charge density increased and gave rise from sigma = 0.1 nC/cm2 to 0.75 nC/cm^2 (Fig. 4.2d) as the number of experiments raised. Static COF did not demonstrate any systematic order in its values, instead exhibited an alternating trend between COF(S) = 0.20 and 0.35, Fig. 4.2e. and Fig. 4.2f, nonetheless, shows a linear dependence of friction on surface charge density with an increasing trend. The line equation extrapolated from COF versus charge density provides information about the basic relation between dynamic friction

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coefficient and sigma (i.e. charge density plot for the PTFE polymer and cellulose system in this case). Succeeding 20th sliding experiments, coefficient of dynamic friction (COF(D)) raises from approximately 0.2 to 0.3 which is about 50% percent of its initial value. Thus, the "real" COF(D) for cellulose-PTFE sliding system can be extracted from the extrapolation of the best line when the PTFE surface charge reaches zero and this value is at around 0.15. Not only possible surface charges accumulation but also change in surface roughness might be one of the causes to increase the friction during sliding experiments (Fig. 4.2b and 4.2c). To analyze this hypothesis, surface charges were totally removed, and the experiment was repeated. Surface charge of PTFE polymer was discharged using ionized air following the last experiment (*) where coefficient of friction and charge density were the maximum. Afterwards, the same experiment was repeated and observed that total discharge of polymer surface resulted in significant decline in friction coefficient. Actually, it was demonstrated that the friction is like a binary device when the surface charge is fully eliminated and returned to its initial state. Ethanol treatment is an alternative way of removing charges from the polymer's surface; however, subsequent to such treatment, particle-sized materials (i.e. third bodies) could be also washed out resulting in and unwanted physical modification of polymer's surface.
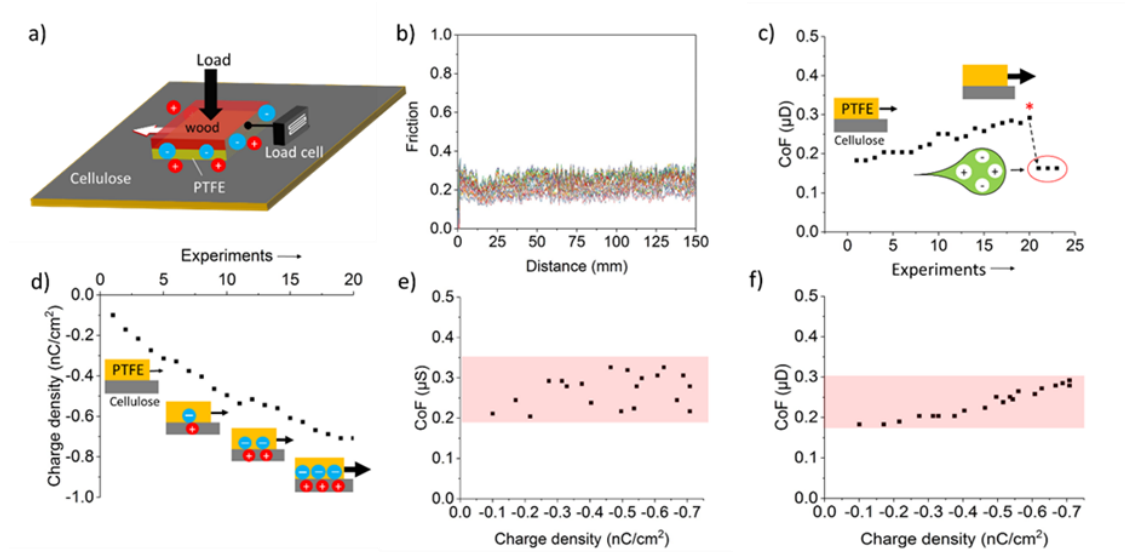

Figure 4.2 The relation between friction and triboelectrification in PTFE-cellulose sliding system. (a) A schematic representation of sliding experiment and friction in

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PTFE-cellulose system. (b) An increase in dynamic and static COF along the path after consecutive number of experiments. (c) Average dynamic friction coefficient increasing with the number of sliding experiments. (d) An increase in Charge density (nC/cm2) towards negative values consequent to consecutive sliding experiments. (e) The relation between static friction coefficients and sliding experiments. (f) Dynamic COF and the charge densities relation for the consecutive sliding experiments. Experimental conditions: RH~% 20, T: 20^0C, 5 cm x 5 cm, 0.15N, 1200 mm/min.

4.2. Triboelectricity contribution to coefficient of friction (COF) in various polymers

Polymers have an ability to accumulate either net positive or net negative charges at their interface consequent to contact or sliding electrification processes. As mentioned in previous sections about triboelectrification mechanisms, ion, electron and material transfer (or their combinations) are the reasons of charge generation on polymer surface. The influence of sign of triboelectric charges (+ and -) on friction of various polymers is investigated in this section. Positively charging polymers on cellulose substrate namely, PC, PMMA, PEG, and PSU caused a significant change on the dynamic coefficient of friction. Similar to PTFE-cellulose system (Fig. 2), a linear relation among COF and charge density was observed for these polymeric materials (Fig. 3a-d). Here the frictional alteration was very dramatic, and they exhibited almost 100% increase in their friction coefficient. On the other hand, polymers accumulating negative charges on their surface consequently to sliding process on cellulose substrate e.g. PTFE, PVC, PVDF, and PP showed a constant increasing relation between dynamic COF and charge density (Fig. 3e-h). Surprisingly, polymers accumulating positive charge had less influence on coefficient of friction compared to positively charged polymers. We believe that these might be due to two major factors that play an important role. The first major factor could be because of dissimilarity of positive and negative triboelectric charges stabilization ability. While the second major factor might be charging and discharging rates of positive and negative surface charges at the counter-surface.
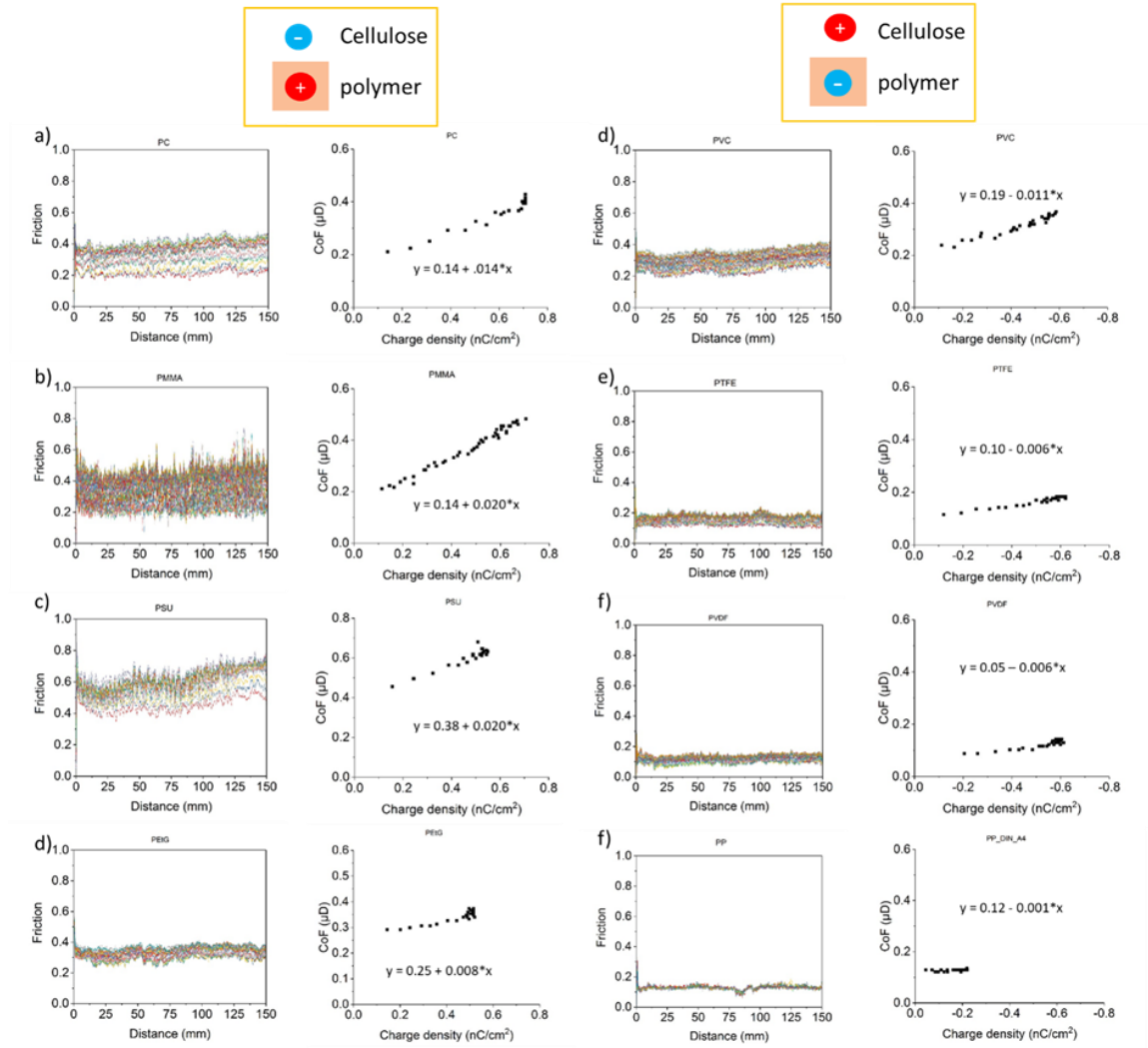
Figure 4.3 . Friction and triboelectrification relation of different polymer-cellulose sliding systems. (a) to (d) Friction experiments of positively charged polymers (PC, PMMA, PSU, PEO) slid on cellulose. (d) to (f) Friction experiments of negatively charged polymers (PVC, PTFE, PVDF, PP) slid on cellulose. Charge density (nC/cm2) vs. Friction (μD) are given for each polymer-cellulose sliding pair for positively and negatively charged polymers on right. Experimental conditions: RH~20-30%, T: 200C, 5 cm x 5 cm, 0.15N, 1200 mm/min.

4.3. Triboelectricity and coefficient of friction (COF) under various atmospheres

In this part of work, we investigated triboelectrification and friction correlation between flat PVC and cellulose system under air (i.e. ambient condition), nitrogen and argon

gaseous atmospheres (Fig. 4.4). Consequent to successive sliding experiments of PVC-cellulose system in these gaseous atmospheres demonstrated a large alteration both in coefficient of friction and triboelectricity. In air or ambient condition with relative humidity approximately 30% exhibited the highest triboelectric charging compared to other media (Fig. 4.4a). Whereas, in argon or nitrogen atmosphere triboelectrification resulted in much less charging than in air (Fig. 4.4b, c). The coefficient of dynamic friction in air increased linearly with tribocharging. Thus, a linear relation between COF and charge density (σ is charge density in nC/cm2) was obtained (COF(D)= COF0 – 0.026*σ) for PVC polymer in air. The offset for friction coefficient, COF0 (=0.29) when the charge on the surface is zero. However, in argon and nitrogen atmospheres even after fortieth sliding experiment the coefficient of dynamic friction turns out to be almost constant with a very little fluctuation which is negligible (Figs. 4.4f and 4.4j). Hence, Fig. 4.4c, f, i, shows the charge density and coefficient of dynamic friction relation for flat PVC slid on cellulose substrate under air, nitrogen and argon atmospheres. Coefficient of static friction (COF(μS)) of PVC polymer, nonetheless, depicted no direct correlation with charge density under these gases. Moreover, it was demonstrated that the charge generation and tribological behavior in nitrogen and argon atmospheres are different compared to air in sliding experiments [82]. Quenching of tribocharges are possible which happens due to localized surface charges that ionize N_2 and Ar under high electric field result in probable excitation transfer between triboplasma [83] and surrounding atmosphere.
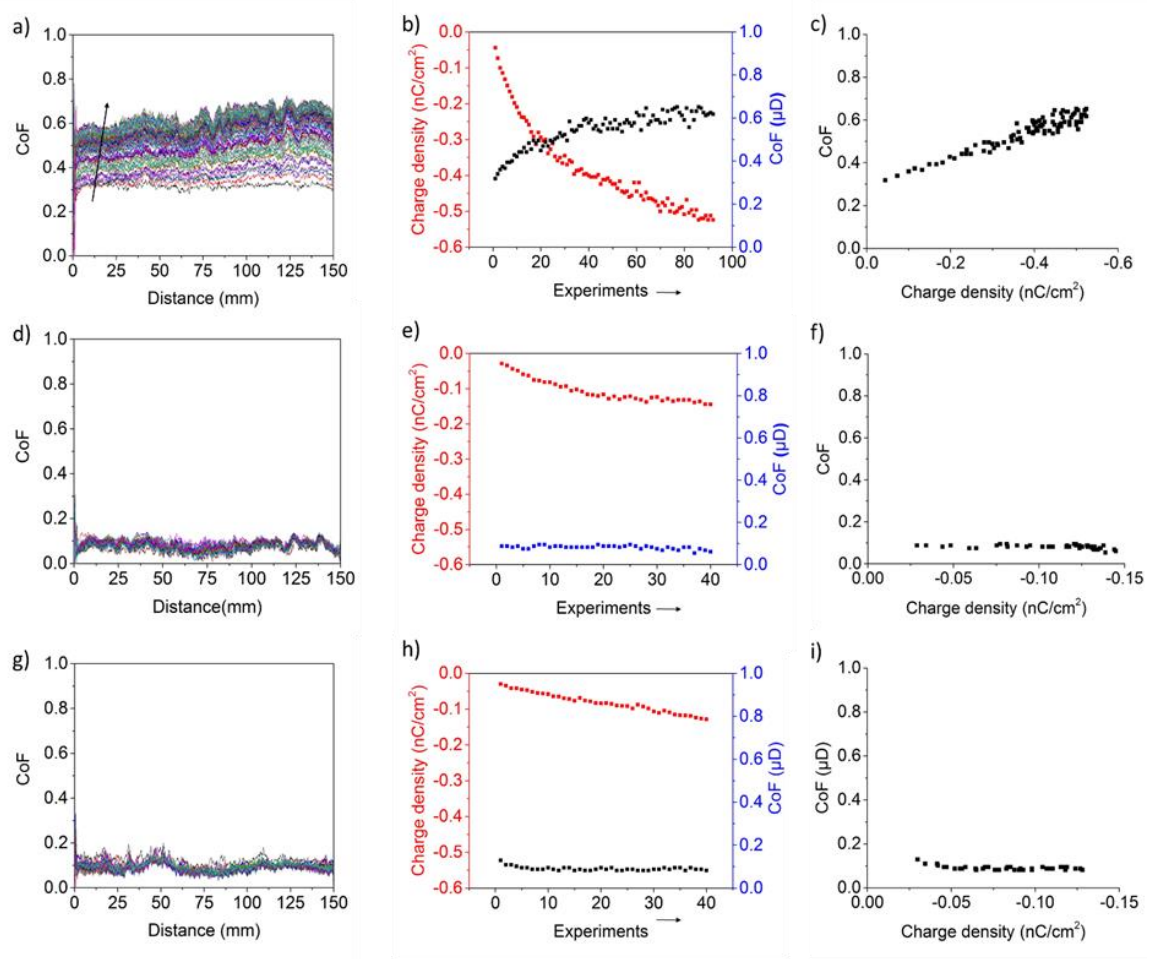
Figure 4.4 The relation between friction and triboelectrification under various gases. PVC-cellulose sliding experiments exhibited different dependency of triboelectric charge on dynamic friction in a) to c) air with the line equation: (y = 0.3-0.026x), d) to f) argon, and g) to i) nitrogen atmospheres. (T=200C and RH< 1% in Argon and Nitrogen, and 30% in air, 5 cm x 5 cm, 0.15N).

4.4. Other factors influencing triboelectricity and coefficient of friction (COF)

4.4.1. Effect of load

It is a well-known fact that the normal load is proportional to frictional force required to slide one body laterally over another. Several studies have shown that there exists inconsistency in this law and it is only valid for some specific polymers under specific conditions [84] (see Table 2). It was demonstrated that under relatively higher loads

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ranging from 2 to 100N many polymers such as PTFE, PMMA, PVC, and so on, show almost no change in their friction when a still ball is slid over polymer' surface [84, 85]. However, for lighter loads ranging 0.02-1N this proportionality differs. In lighter loads coefficient of friction (COF) experience a decline as load increases and it is explained by surface asperities' elastic deformation [84, 86]. Hence, in this study we investigate this relation and also demonstrated that it is not applicable to all polymers even the load is in the range of 0.02-1N since we believe that most of these studies neglected the knowledge of triboelectricity in their studies. Whereas, when the applied load is higher than 100N, the proportionality between friction and load becomes completely different. In other words, as the load increases, this time coefficient of friction also increases, and this phenomenon is explained by asperities' plastic deformation [84].
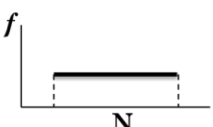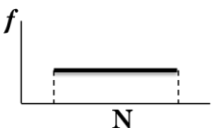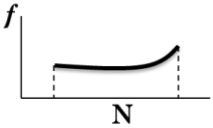
Materials and load	Graphical representation
2-15 N, steel-polymer (PTFE, PFCE, PVC, PVDC, PE)	
10-40 N, steel-polymer (PTFE, PMMA,PE, PC)	
10-100 N, steel-polymer (PTFE, PMMA,PE, PVC, nylon)	
Steel-polymer (PTFE, PE, nylon)	
Theory, steel-rubber	
Theory, steel-rubber	

Table 1 The load dependence of coefficient of friction (COF) (Adapted from [84]).

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Here, we investigated the dependency of triboelectricity on load hypotheses for tribocharged PVC-cellulose sliding system. Amontons' law states that as load increases, micro scale friction force increases too. Moreover, as previously discussed, for lighter loads it is expected that COF decreases with increasing load. Consequently, to interpret the relation between friction on normal load for tribocharged surfaces, here, firstly we analyzed this relation for a flat tirbocharged PTFE-cellulose sliding system. Hence, as the normal load increased, the linear decrease in charge density on PTFE surface was observed (Fig. 5a), concurrently, coefficient of dynamic friction COF (μD) decreased (Fig. 5b). Nevertheless, both in other positively and negatively tribocharged polymers, these relations (i.e. charge density vs. load and COF vs. load) showed a practically linear trend (Fig. 4.5c to 4.5f). Therefore, once again, it is hard to conclude that for lighter load ranges, coefficient of friction decreases with increasing load since we lack the knowledge of underlying mechanism of triboelectricity. In fact, Fig. 4.5a, b and c, illustrates that charge density or triboelectricity is dependent on load too.

In addition, we analyzed that coefficient of dynamic friction declined exponentially as the load went up. In the beginning dynamic friction was 0.31 and went down to 0.21 while the normal load raised from 0.12N to 0.41N (Fig. 4.5b) in the system. Clearly, a substantial decrease of roughly 30% in dynamic coefficient friction 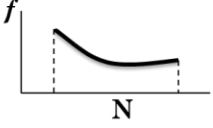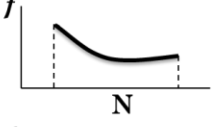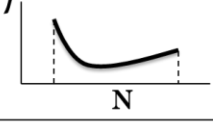took place due to the transfer of PTFE on cellulose substrate. Thus, we believe that mainly due to two main factors this decrease in dynamic COF was observed. Firstly, the decline happened due to self-lubrication between PTFE-PTFE sliding as a result of material transfer. Secondly, triboelectrification fell down to minimum since similarly charged surfaces decreased the friction because of repulsion among identical and identically charged materials' electrostatic charges.

Specifically, Fig. 4.5b provides information about the relation between friction force and load, and the exponential increase in friction as the load decreases. That being said, it can be concluded that the rise in friction is important both at micro and nano sized moving mechanical system where electrostatic forces are dominant compared to gravitational forces that turn to be of less importance at macroscopic level. Therefore, triboelectric

forces become of great importance over all the other factors with decrease in size and increase in surface area.
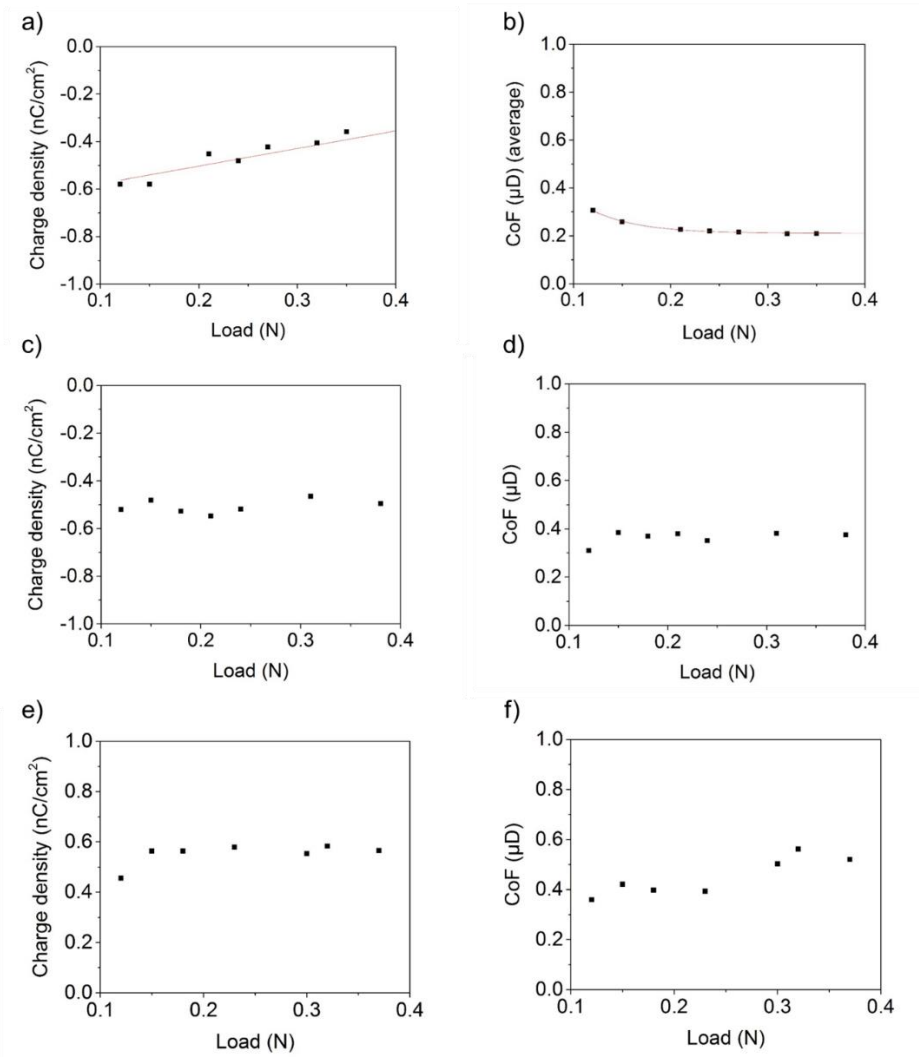
Figure 4.5 Graphs showing the effect of load on triboelectricity and coefficient of friction (COF) for various positively and negatively tribocharged polymers under relative humidity of 20-30% and 200C-250C temperature. a) and b) for PTFE. c) and d) for PVC. e) and f) for PC. Charge density vs. load, and friction coefficient vs. load relation for PTFE (a and b), PVC (c and d) and PC (e and f) under 0.15N load, 20% relative humidity and 20^{0}C in ambient condition.

4.4.2. Effect of area

However, Amontons' law of friction also states that friction force is independent of the macroscopic area of contact [86]. Hence, we examined the dependency of tribocarging on the contact area. In fact, the correlation between area of polymer and charge or friction showed quite poor dependency. PVC polymer's square root of the area (= length of an edge), however, exhibited a linear relation to the average charge accumulated on the surface of PVC after successive sliding experiments (Fig. 4.6a). Similar to average charge accumulated on PVC surface, average dynamic COF(D) also showed same correlation with the square root of the area (Fig. 4.6b).
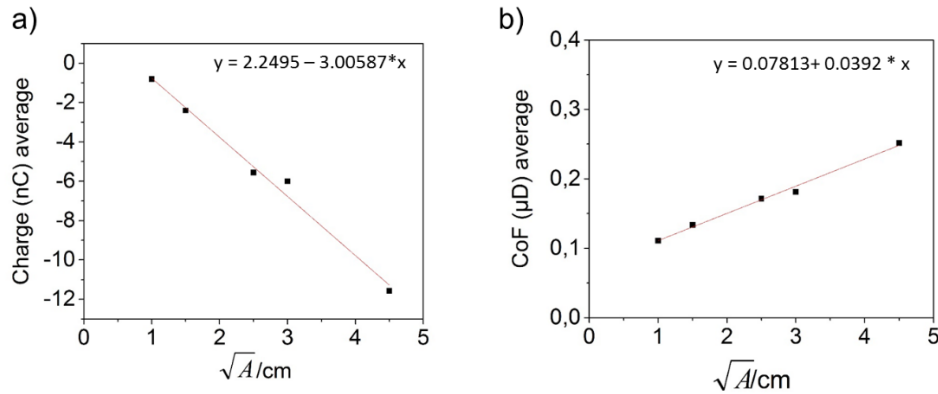
Figure 4.6 The relations between area vs. charge and friction coefficient. (a) The relation between the square root of the area under the sliding PVC and average charge accumulated on PVC, normal load= 0.11N. (b) Relation between dynamic coefficient of friction versus square root of the area for PVC-cellulose system.

To investigate the surface behavior of both cellulose and polymer materials, several characterization methods were carried out. Scanning electron microscopy (SEM) was performed to analyze surface morphology of cellulose substrates before and after sliding experiments. Unfortunately, SEM image of the fibrous cellulose demonstrates no change in morphology or cellulose's surface structure pre-and post-sliding experiments at the microscopic scale (Fig. 5a and 5b). This tells us that even though it is a common knowledge that tribocharge accumulation is due bond raptures taking place on material's

surface after contact or sliding, our study shows that it is hard to observe it in microscale using SEM electron microscopy.

4.4.3. Material transfer

Moreover, since the tribocharging is merely a surface event, potential material transfer during triboelectrification was suspected. In fact, using X-ray Spectroscopy (XPS) analysis the PTFE transfer onto cellulose' surface was verified. Fluorine of PTFE and Chorine of PVC characteristic elemental signals were detected on the cellulose surface after the sliding experiments (Fig. 4.7c and 4.7d). That is, a uniform coating of PTFE and PVC on cellulose' surface occurred during consecutive sliding experiments. Previously, it was described that indeed such material transfer on the counter surface is observed in PTFE giving rise to a variety of structures like lumps, ribbons or sheets and hence, resulting in decline in friction due to this reason. Until now, researchers overlooked the influence of triboelectricity on friction by taking into account the material transfer. However, recent studies revealed the occurrence of material transfer and its effects on triboelectricity. Accordingly, tribocharging is less observed during the sliding of two similar surfaces onto each other [87] as in the present case.

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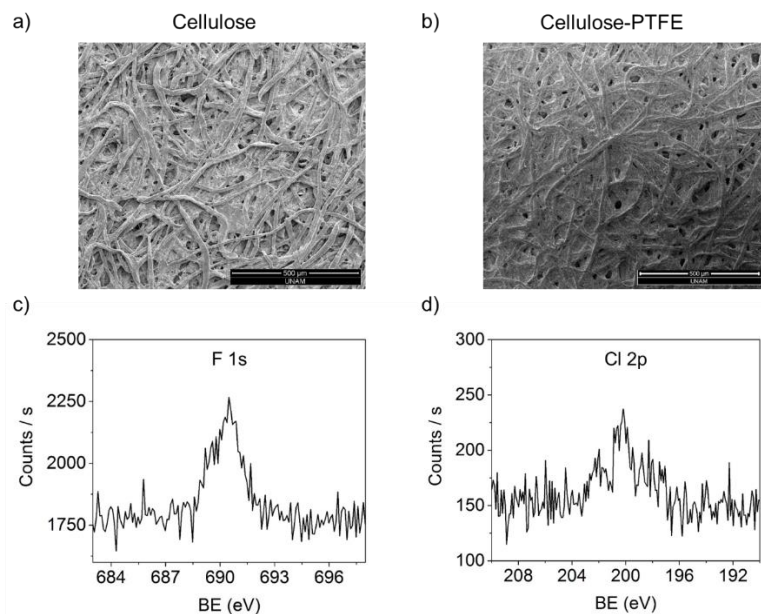
Figure 4.7 Cellulose surface characterization. (a) Typical SEM image of cellulose surface before sliding experiment. (b) SEM image of cellulose' surface after sliding experiment using PTFE. (c) XPS elemental analysis indicate PTFE transfer occurs onto cellulose surface. (d) XPS elemental analysis indicate PVC transfer occurs onto cellulose surface.

To further confirm material transfer on cellulose surface, Energy-dispersive X-ray (EDX) characterization was performed (Fig. 4.8). Prior to analysis, cellulose samples were coated with Au/Pd alloy of ~10nm thickness for better imaging. Fig 4.8a shows transferred fluorine (blue color encircled with red) once again approving our claim about material transfer during sliding experiments. Also, EDX spectra exhibits fluorine peak with 0.74 by weight percentage (Fig.4.8b).

a)

b)

Figure 4.8 EDX characterization of cellulose substrate after consecutive sliding experiments of PTFE-cellulose system. (a) EDX images of Au/Pd alloy coated cellulose surface. Scale bar is 100 μm. (b) EDX spectra of Au/Pd alloy coated cellulose surface.

Today, wear and minimization of materials' wear are one of the main challenges for current industries since vast amount of materials are wasted due to wear and millions of dollars used to compensate these losses [88]. It has been shown that about one-fourth of the total worldwide energy consumption is due to friction and wear. Therefore, apprehending the fundamental mechanisms of tribology has become a crucial weapon to tackle problems regarding friction and wear.

Consequently, in addition to common knowledge about friction and wear, latter being result of first one, we investigated the effect of triboelectricity on wear since we already demonstrated that friction and triboelectricity are dependent on one another. PVC polymer was used due to being transparent, easy to detect by eye and having higher tendency to charge negatively compared to other insulating materials. On one hand, PVC polymer surface charges were discharged after each consecutive sliding experiments using Zerostat ion gun. On th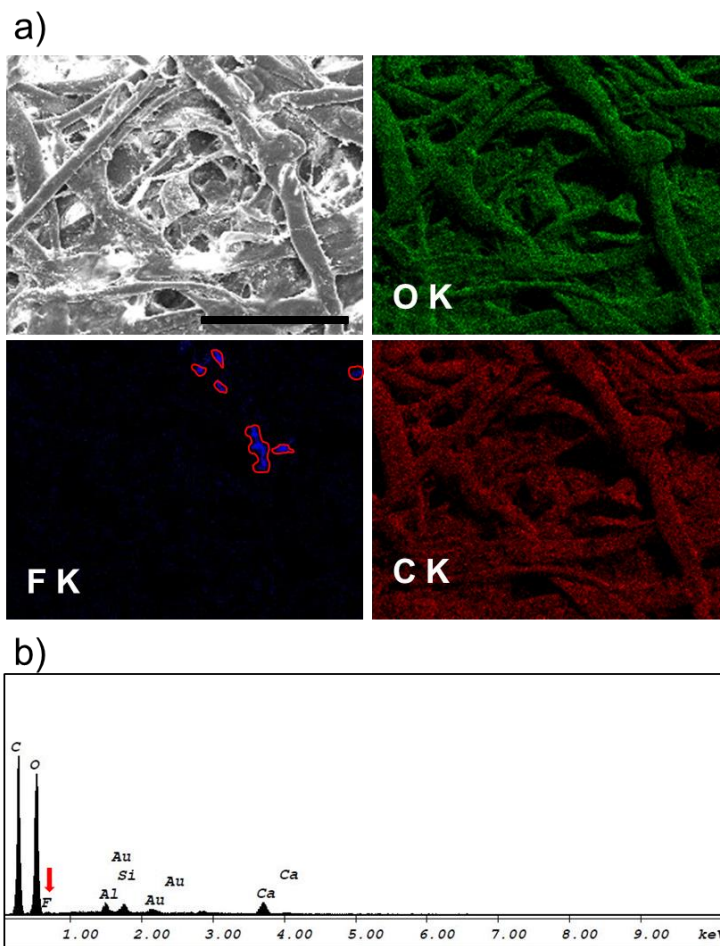e other hand, PVC-cellulose sliding experiments were carried like previous experiments without discharging surface charges e.g. tribocharges (Fig. 4.9). Dissipating charges from PVC polymer surface after successive sliding experiments resulted in a trivial increase of COF (Fig. 4.9a), while coefficient of friction of tribocharged PVC slid on cellulose showed a profound increase from approximately 0.18 to 0.4 (Fig4.9b). Fig. 4.9c and 4.9d demonstrate a detailed illustration of influence of tribocharged and discharged PVC polymer on COF. Since it is a well-known fact that increase in friction results in greater wear, here, our study once more confirmed that knowledge; however, by including a new factor to the common belief, which is surface charge or tribocharge. We actually showed that if tribocharges are eliminated from the surface of any material, increase in friction is diminished and consequently, wear is minimized. Figure 4.10, thus, approves our claim about wear control through elimination or dissipation of tribocharges on the surface of materials. Moreover, detailed investigation on control of friction and triboelectricity is discussed in coming section.

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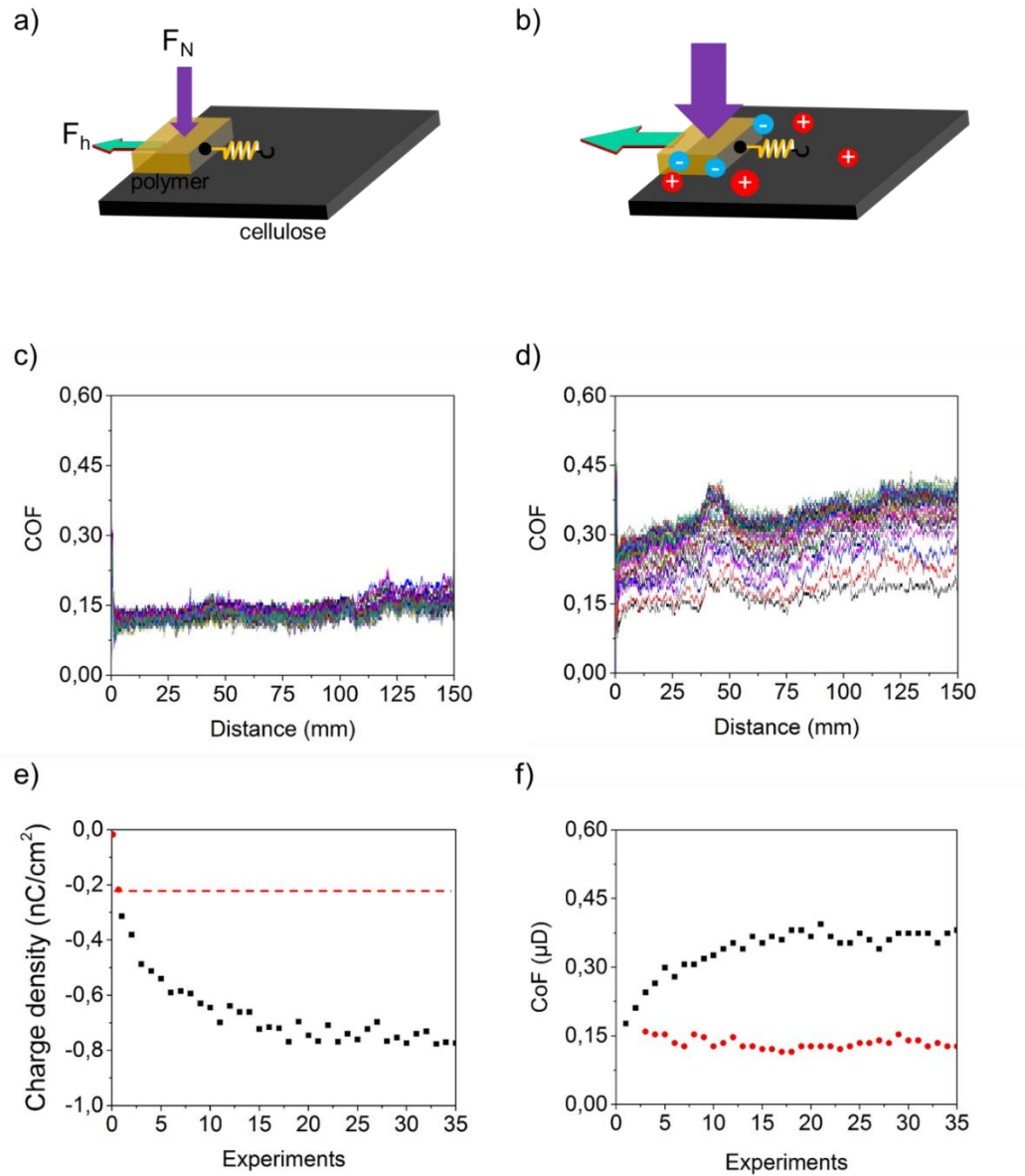
Figure 4.9 Graphs showing discharged and tribocharged PVC polymer. Schematic representation of a) discharged and b) charged PVC polymer. c) COF vs. distance graph of Zerostat ion gun discharged PVC polymer after each sliding experiment. d) Typical COF vs. distance graph for tribocharged PVC polymer. e) Charge density of Zerostat ion gun discharged (dashed lines) and tribocharged PVC polymer after successive sliding experiments. f) Dynamic friction coefficient versus sliding experiment for discharged (dashed lines) and tribocharged PVC polymer.
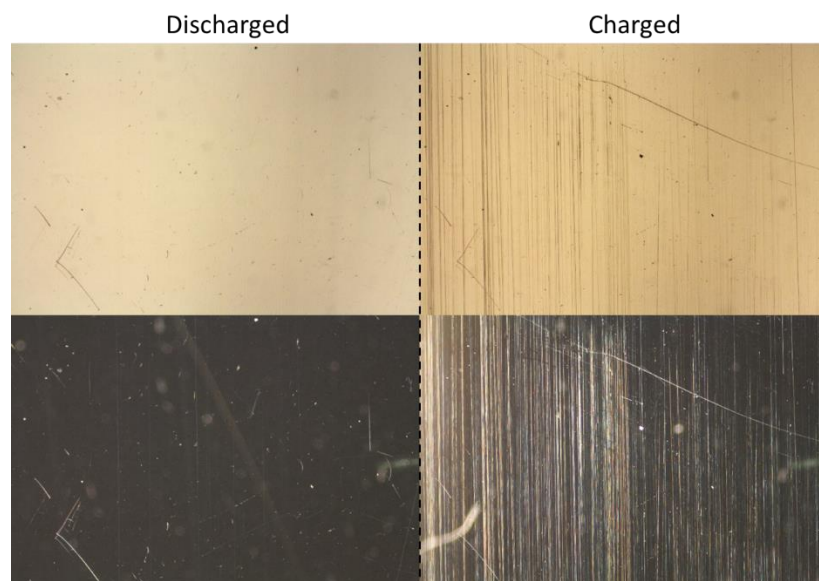
Figure 4.10 Polarizer Optical Microscope images of PVC surfaces pre- and post- sliding experiments.

4.5. Control of Triboelectricity and Friction

One of significant subjects in science and especially in the field of tribology is the control of friction and wear. Until now many researchers have provided rich amount of information regarding tribology, friction, triboelectrification and wear in separate context and making them completely independent from each other. Literature also shows that static electrification or triboelectrification of materials bring undesired consequences such as failures, ignition or even worst explosions. Thus, it is important for scientist, first to search for the origin or the source of these disasters and then control via elimination and manipulation of these phenomena. Consequently, in this part of the thesis, we demonstrate the ways to control triboelectricity and friction of tribocharged polymer materials which are correlated to each other, discussed in previous sections. Also, through manipulation of triboelectricity and friction, we will be first to show the control of wear. In other words, by getting rid of charges from the surface of the polymers, amount of scratches or wear is decreased to several orders. We believe that by using these methods it is possible to minimize the material loss which consequently saves a lot of money to industries. So, the methods provided for the discharge of polymer (i.e. insulating) materials can be

considered as the key or resulting purpose of this thesis since wear and its prevention are primary concerns of today's industries and also of our daily lives wherever friction is confronted. Therefore, the last part of this work will mainly focus on the methods for controlling triboelectricity and friction.

Three ways of controlling triboelectricity and friction are presented here. We believe that by applying on of these ways on polymer materials, triboelectricity and friction can be easily minimized and brought to its initial position. Actually, in this work we merely demonstrated methods to completely discharge tribocharged surface like binary systems (i.e. "on" or "off|) rather than partially discharging and showing ways to bring triboelectricity and friction to half or quarter of its final (saturation) value; in other words, tuning triboelectricity and friction of polymer materials between its initial (ground state) and final (maximum charged) value. However, we believe that it is possible but further detailed studies should be carried out.

As previously mentioned, by purging gases e.g. argon and nitrogen to tribocharged polymers, it is possible to minimize triboelectrification of polymer's surface resulting in decrease of friction and wear since these gases dissipate tribocharges through ionization and formation tripolasma, discussed in more details in "Triboelectricity and Coefficient of Friction (COF) under various atmospheres" section. Thus, Fig. 4.11a and 4.11b demonstrates this behavior by decreasing charge density to almost six-folds and coefficient of friction to almost zero change in its initial value compared to air where charge density is six times higher and almost 100% increase in coefficient of friction. The second method of dissipating charges from polymer surface which in return decreases COF simultaneously is through attaching metal or conducting material on top of polymer and further grounding metal (Fig. 4.11c and 4.11d). In fact, this result shows that when metal is attached to sliding material, triboelectricity is declined resulting in decrease of friction. Actually, attached metal is dissipating tribocharges by grounding them, while in TENGs this metal acts as electrode in converting tribocharges to electricity. Lastly, Zerostat ion gun and ethanol solvent were used for eliminating surface charges (Fig.4.11e and 4.11f). We observed that both these discharging methods are very efficient way to

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control both triboelectricity and friction since latter is dependent on the first. In brief, we investigate several methods for diminishing tribocharges from polymer surface, by this way we were able to control both friction and wear.
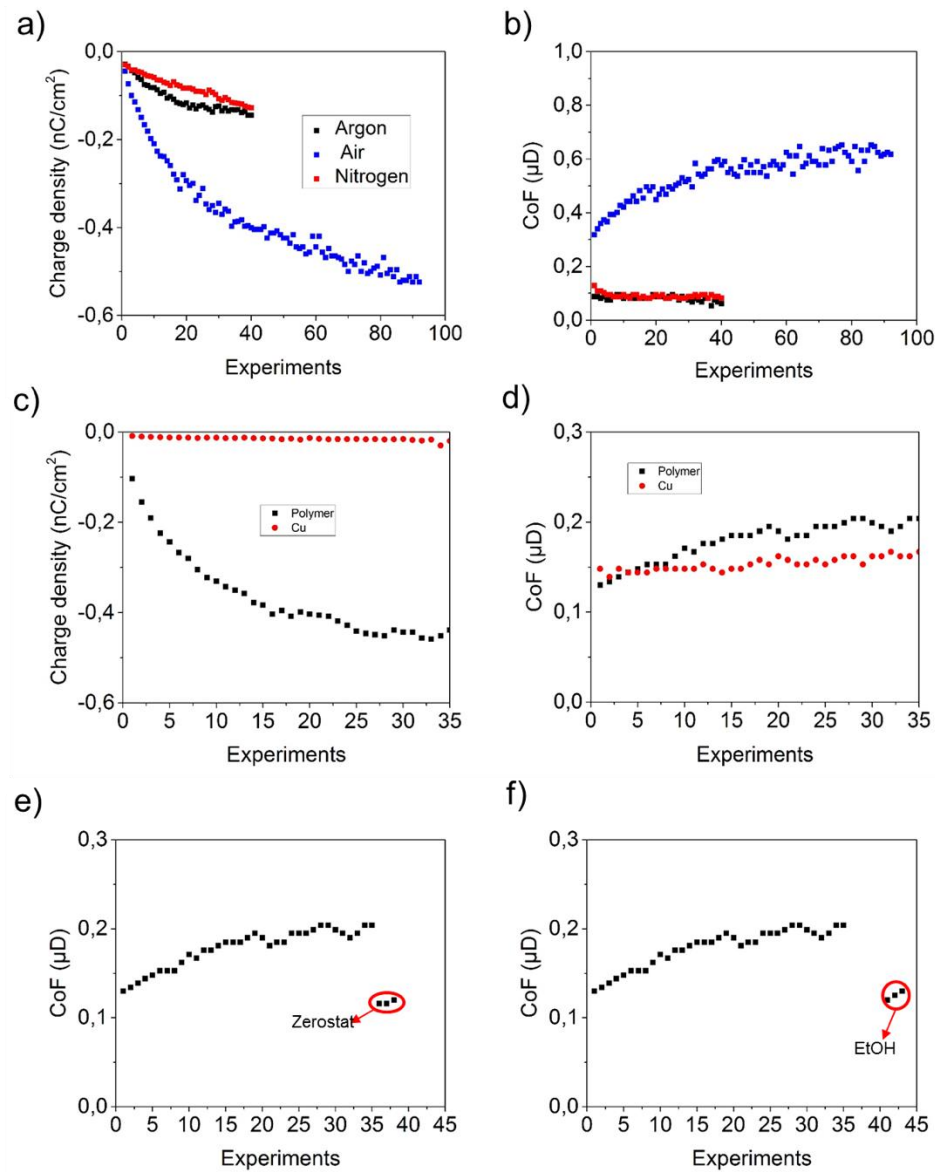
Figure 4.11 Methods for controlling triboelectricity and friction. a) Charging trend of PVC in air, nitrogen and argon atmospheres after consecutive sliding experiments. b) Dynamic coefficient of friction of PVC polymer under air, nitrogen and argon after

consecutive sliding experiments. c) Charge density after consecutive sliding experiments of PTFE with copper (Cu) metal plate (red dots) attached to it or polymer material (black dots). d) Dynamic coefficient of friction of PTFE attached to Cu (red dots) or polymer (black dots) slid on cellulose paper. e) Zerostat ion gun discharged PTFE. f) Ethanol discharged PTFE.

5 Conclusion

To conclude, this work presents significant results regarding friction, triboelectricity and wear. We showed a strong correlation between triboelectricity and friction, and both phenomena indicated their path dependency and hence, they are non-state functions. Another possible way to store energy as a result of friction, converting mechanical energy into static electricity on insulator surface, was revealed. A drastic alteration in frictional characteristics between two contacting interfaces are mainly due to electrostatic attractive and repulsive forces between sliding surfaces and material transfer. Material transfer is an evidence of plastic deformations occurrence during the friction of a polymer onto another. Most importantly, this transferred material is able to generate charges and act as 'electrostatic glue' between two sliding surfaces. Thus, it is quite complicate to quantify friction exhibiting surface charge dependency. Moreover, the decline in charge density and friction force while increase in load is explained by taking into account material transfer.

Our results regarding the relation between COF and charge density reveals different correlation of static COF with tribocharges than that of dynamic COF with surface charges for polymer – polymer friction. In the former, results showed an independent relation of static COF to charge density. Whereas, the latter case exhibited a linear correlation both with positively (net) charged and negatively (net) charged polymers. We believe that the heterogeneity in the surface charge is the main cause for these behaviors. The size of

surface charge heterogeneity is variable and ranges from nano to meso scale depending on insulating material, as pointed in previous studies.

Lastly, we showed that friction can be controlled by controlling surface triboelectric charges and thus, through manipulation of triboelectricity, friction and wear of polymer surface can be tuned. We believe that our results will help to take the attention of the energy and value losses due to increasing friction force and wear between charged insulators in applications.

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