

Contact Electrification of Some Organic Powders With Fused Aromatic Ring Structures

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Contact Electrification of Some Organic Powders With Fused Aromatic Ring Structures

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We certify that we have read this thesis and that, in our opinion, it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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The mechanism of static charge accumulation on the insulating surfaces via contact and the following charge dissipation has remained poorly understood since ancient times. Since many industries suffer from static electrification during product production, handling, and usage, scientists are trying to decipher the charging mechanisms, charge transfer modes, and any contributing factors. However, quantifying materials based on their tendency to accept or donate electrons upon contact has often proved challenging. The result is contradictory, irreproducible findings, especially with insulating powders. In this study, our objective was to provide a more comprehensive perspective on determining whether the chemical structure is a deciding factor in the triboelectrification of insulating powders. In this regard, we focus on common aromatic powders to see how variations in the number and spatial arrangement of aromatic rings affect the charging behavior. In addition, we study the impact of the type, number, and positioning of functional groups (FG) on the triboelectrification of these powders.

Powders were charged by grinding in an agate mortar with steel and agate pestles. The electric potential developed in the powder was then measured by an electrostatic voltmeter. Some consistent trends then emerged: the sign and magnitude of the electrostatic potential seemed to be related to the number of fused aromatic rings. Also, compounds having a nitro or carboxyl functional group were charged negatively, while a methyl FG resulted in the accumulation of positive electrostatic potential. Positional isomers demonstrated different electrification behavior as well. The effect of particle morphology was also investigated by analyzing the powders by SEM and XRD. Our results contribute to the fundamental physical and chemical understanding of powder charging. Finally, this work presents an initiative for a general approach based on these fundamentals to prevent powder charging and related problems in the industry.

Keywords: Static electricity, powder electrification, triboelectrification, fused ring aromatic compounds, grinding.

ÖZET

Bileşik Halkalı Bazı Organik Tozların Statik Elektriklenmesi

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Yalıtkan yüzeylerde temas yoluyla oluşan statik yük birikiminin ve bunu izleyen yük boşalmasının mekanizması antik dönemlerden bu yana yeterince anlaşılamamıştır. Birçok endüstride ürünlerin üretim, taşıma ve kullanım süreçlerinde statik elektriklenmeden olumsuz etkilendiği için, bilim insanları yüklenme mekanizmalarını, yük transfer modlarını ve bunlara etki eden tüm faktörleri çözmeye çalışmaktadır. Ancak, malzemeleri temas esnasında elektron alma veya verme eğilimlerine göre nicelendirmek çoğu zaman güç olmaktadır. Bunun sonucu olarak, özellikle yalıtkan tozlarda çelişkili ve tekrarlanabilirliği düşük bulgular ortaya çıkmaktadır. Bu çalışmada amacımız, yalıtkan aromatik tozların triboelektriklenmesinde kimyasal yapının belirleyici bir faktör olup olmadığını daha kapsamlı bir bakış açısıyla ortaya koymaktır. Bu bağlamda, aromatik halkaların sayısı ve uzaysal düzenlenişlerindeki farklılıkların yüklenme davranışını nasıl etkilediğini inceledik. Ayrıca, fonksiyonel grupların (FG) tipi, sayısı ve konumunun da bu tozların triboelektriklenmesi üzerindeki etkisini araştırdık.

Tozlar, çelik ve agat havaneleri kullanılarak agat havanda öğütülerek yüklenmiştir. Tozlarda gelişen elektrik potansiyeli elektrostatik voltmetre ile ölçülmüştür. Ölçümler sonucunda bazı tutarlı eğilimler gözlenmiştir: elektrostatik potansiyelin işareti ve büyüklüğü kaynaşmış aromatik halkaların sayısı ile ilişkili görünmektedir. Ayrıca, nitro veya karboksil fonksiyonel grubuna sahip bileşikler negatif yüklenirken, metil fonksiyonel grubu pozitif elektrostatik potansiyel birikimine yol açmıştır. Konumsal izomerler de farklı elektriklenme davranışları sergilemiştir. Parçacık morfolojisinin etkisi, tozların SEM ve XRD analizleri ile araştırılmıştır. Bu çalışma, toz yüklenmesinin fiziksel ve kimyasal temellerine ilişkin anlayışa katkıda bulunmaktadır. Son olarak, elde edilen bulgular endüstride toz yüklenmesi ve ilişkili sorunların önlenmesine yönelik bu temellere dayalı genel bir yaklaşım için bir ilk adım

niteliğindedir.

Anahtar sözcükler: Statik elektriklenme, toz elektriklenmesi, triboelektriklenme, bileşik halkalı aromatik bileşikler, öğütme.



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Contents

1	Introduction	1
1.1	Triboelectrification	1
1.1.1	Charging Mechanisms	3
1.1.2	Material's Chemistry	7
1.1.3	Mechanical Aspects of TE	9
1.1.4	Powders Characteristics.....	10
1.1.5	Environmental Factors.....	12
1.2	Triboelectric Series	14
1.3	Aim of the Thesis.....	16
2	Materials and Experimental Methods	17
2.1	Materials.....	17
2.2	Experimental Methods.....	17
2.2.1	Native Voltage Measurements.....	17
2.2.2	Triboelectrification.....	18
2.2.3	Effect of Relative Humidity	20

2.2.4	Binary Powder Mixing Experiments.....	20
2.2.5	Powders Characterization.....	21
3	Results and Discussion	23
3.1	Native Voltage Measurement.....	23
3.2	Triboelectrification via Grinding.....	24
3.2.1	Choosing the Appropriate Grinding System.....	24
3.2.2	Triboelectric Behavior in Agate/Agate System.....	26
3.2.3	Triboelectric Behavior in Agate/Steel system	34
3.2.4	Effect of Relative Humidity	36
3.3	Powders Characterization	38
3.3.1	Powders Morphology: Fresh vs. Ground.....	38
3.3.2	Ground Powders Morphology: Agate Pestle vs. Steel Pestle.....	45
3.3.3	X-ray Diffraction Analysis of Fresh and Ground Powders	47
3.4	Binary Powder Mixtures	52
3.4.1	Electrostatic Potential Measurements of Binary Powders.....	52
3.4.2	ATR data	55
4	Conclusion and Future Work	56

List of Figures

1.1	Course of an unconfined dust explosion (6 kg of maize starch), Reproduced from M. Glor, Powder Technology, 2003.....	2
1.2	Schematic illustration of electron transfer as the dominant mechanism in contact electrification between (a) two conductors, (b) a conductor and an insulator, and (c) two insulators at three stages of (1) rest, (2) contact, and (3) separation.....	4
1.3	Schematic illustration of ion transfer as the dominant mechanism in triboelectrification at three stages: (1) rest, (2) contact, and (3) separation. In this mechanism, charge transfer occurs through the redistribution of ions within water molecules adsorbed on the material surfaces.....	5
1.4	Schematic illustration of material transfer as the dominant mechanism in triboelectrification at three stages of two insulators (1) before contact, (2) d at asperities (black arrows), leading to localized deformation (red spots), interfacial bond scission, and material transfer through surface adhesion during contact. After separation, the material transferred results in a net positive charge on one surface and a net negative charge on the other.. . . .	6
1.5	Structure of phthalocyaninatecopper (a) with 16 hydrogen substituents, which are interchangeable with chlorine/bromine substituents. b) Potential difference between powder and a gold reference vs. the number of chlorine or bromine substituents. Reproduced from Tanoue et. al., AiChE Journal, 2001	8
1.6	Calculated effective WF of selected surfaces of aspirin and paracetamol. The effective WF difference between facets and the effective WF shift induced by the fractional coverage of water onto the surface is also shown—Reproduced from Middleton et al, Crystal Growth & Design, 2003.....	12
1.7	Triboelectric series of common polymers—Reproduced from J. Henniker, Nature, 1962.....	15

- 2.1 Schematic of setup used for measurement of voltage:) shows the commercial powder layer on top of an agate surface, and b) shows the mortar and pestle used for grinding the powders..... 19
- 3.1 The native electric potential series of organic powders studied. The potential difference is measured between each powder and the gold electrode attached to the electrostatic voltmeter. Organic powders (0.200 g each) stored in identical plastic vials for several days were placed on an agate surface and the electrostatic potential on the powders were measured by an electrostatic voltmeter equipped with a probe hanging down on the samples at a distance of 2 cm. (For details of the measurements, see Ex- perimental section, 2.2.1) The colored dots refer to the individual electric potential readings and the black dashed represent the average values of the electric potential values..... 24
- 3.2 Measured voltage as a function of time for naphthalene powder (0.200 g) ground using different mortar/pestle combinations; from left to right: agate mortar/agate pestle, agate mortar/steel pestle, and brass mortar/brass pestle systems. Each was studied in three independent trials (colored lines). Ground naphthalene powder was let in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements..... 25
- 3.3 Measured voltage as a function of time for 0.200 g of various powders ground using an agate mortar with an agate pestle. Each was studied in three independent trials (colored lines). Ground powders were left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2..... 27
- 3.4 Measured voltage as a function of time for 0.200 g of various powders ground using an agate mortar with an agate pestle. Each was studied in three independent trials (colored lines). Ground powders were left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2..... 28

- 3.5 Voltage versus grinding time curves for naphthalene, perylene, anthracene, and pyrene (each 0.200 g) powders ground using an agate pestle in an agate mortar. (Error bars depict the standard deviation obtained in three independent experiments). Ground powders were let in the mortar and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2)..... 29
- 3.6 The potential difference between each ground powder and a gold electrode after grinding the powder in an agate mortar with an **agate** pestle. Ground powders were let in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2). The outcome of all the experimental trials (colored dots) is included with an average value (the black dashed lines) for each powder.....30
- 3.7 The data in Figure 3.6 are sorted into the groups of the results for a) unsubstituted fused aromatic ring compounds, b) the functional group derivatives of pyrene and unsubstituted pyrene, c) the bromo derivative of anthracene and unsubstituted anthracene, and d) functionalized naphthalenes.....32
- 3.8 The data in Figure 3.6 shows the results for the isomer sets: naphthols (blue bars), dihydroxynaphthalenes (orange bars), and naphthalene carboxylic acids (green bars)..... 33
- 3.9 The rate of electrostatic potential change (charge decay) in the electrostatic potential of the powders charged (as depicted in Figure 3.6) by grinding and left to stay in the mortar for the given time. 34
- 3.10 The potential difference between each ground powder and a gold electrode after grinding the powder in an agate mortar with a **steel** pestle. Ground powders were placed in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2). The outcome of all the experimental trials (colored dots) is included with an average value (the black dashed lines) for each powder..... 35

3.11	The potential difference between each ground powder and a gold electrode after grinding the powders in an agate mortar using an agate pestle at relative humidity of 15-20 % and 30-40% (For details of the measurements, see Experimental section, 2.2.2). The outcome of all the experimental trials (colored dots) is included with an average value (the black dashed lines) for each powder.....	36
3.12	The dissipation rate of electrostatic potential of powders ground in agate mortar using an agate pestle over time at relative humidity of 15-20 % and 30-40%....	37
3.13	SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: naphthalene, c, d: 1-naphthoic acid, e, f: 2-naphthoic acid, g, h: 1-naphthol, i, j: 2-naphthol, k, l: 2-naphthaldehyde.....	39
3.14	SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: 1,5-dihydroxynaphthalene, c, d: 2,3-dihydroxynaphthalene, e, f: 2,6-dihydroxynaphthalene, g, h: 2-iodonaphthalene, i, j: 2,3-dimethylnaphthalene, k, l: phenanthrene	40
3.15	SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: anthracene, c,d: 9,10-dibromoanthracene, e, f: pyrene, g,h: 1-aminopyrene, i, j: 1-nitropyrene, k, l: perylene.....	41
3.16	Particle size distribution histograms for as-received powders obtained via SEM imaging and ImageJ analyses	42
3.17	Particle size distribution histograms for ground powders obtained via SEM imaging and ImageJ analyses.....	43
3.18	SEM micrographs of naphthalene powders: a) as-received, b) ground via agate pestle, and c) ground via steel pestle. Red circles show fine spherical particles.....	45
3.19	SEM micrographs of 1,5-dihydroxynaphthalene (a–c) and anthracene (d–f) in their fresh form (a, d), after grinding with an agate pestle (b, e), and after grinding with a steel pestle (c, f). The corresponding histograms show the PSDs for each condition.....	46
3.20	XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns.....	49
3.21	XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns (if available).....	50

3.22	XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns (if available).....	51
3.23	Mean electrostatic potential generated during grinding in an agate mortar using an agate pestle, plotted against the percentage change in crystallinity degree between the fresh and ground powder.....	52
3.24	Voltage vs. Time plots for pyrene (P), naphthalene (N), and naphthalene/pyrene mixtures (N.P) at different mass ratios (1:1, 1:3, 3:1). The letter t in the legends indicates the number of successive grinding trials using agate/agate mortar and pestle.....	53
3.25	Voltage vs. Time plots for 1-nitropyrene (N), 1-aminopyrene (A), and their 1:1 molar mixture. The letter t in the legends indicates the number of successive grinding trials using agate/agate mortar and pestle.....	54
3.26	ATR.IR spectra of 1-aminopyrene, 1-nitropyrene and their 1:1 molar mixture.	55

List of Tables

2.1	Selected organic powders and their structural characteristics	18
3.1	Crystallinity degree of powders before and after grinding in an agate mortar with an agate pestle.....	48

Chapter 1

Introduction

1.1 Triboelectrification

It is well-known that when two insulator surfaces come into contact and are separated, the surface's charge balance is disrupted. As a result, one of the surfaces acquires a negative charge, while the other becomes positively charged. This process is called contact or triboelectric charging. The type of charge (or electric potential) acquired on the surfaces is termed static charge [1, 2].

Static electricity is a phenomenon that is encountered in daily life, as well as in significant scientific contexts. For example, charge separation followed by sudden discharge, such as lightning, has been hypothesized to play a role in the synthesis of organic molecules such as amino acids in the Earth's early atmosphere, as demonstrated in the Miller–Urey experiment [3, 4]. In daily life, the attraction of hair to a plastic comb after brushing, or the small shocks felt when touching someone after walking across a carpet (usually with socks), are common experiences. However, not all instances of static electricity are harmless. Similar electrostatic discharges can cause hazardous sparks, equipment failures, explosions, or fires in industrial environments [5–7]. Figure 1.1 shows the course of an unconfined dust explosion with 6 kg of maize starch homogeneously dispersed in air [8].

Historically, the first known scientific observation of static electrification is attributed to Plato [9]. A significant milestone followed much later, when materials were categorized into those that become electrically charged through rubbing and those that do not [10]. Subsequent discoveries revealed the existence of two types of electrical charge [11] and demonstrated that the sign of the charge acquired by a material depends on the nature of the material it is rubbed against [12]. These insights eventually led to the creation of the first triboelectric series; a one-dimensional empirical ordering of materials based on how they exchange charge through contact and separation [2].

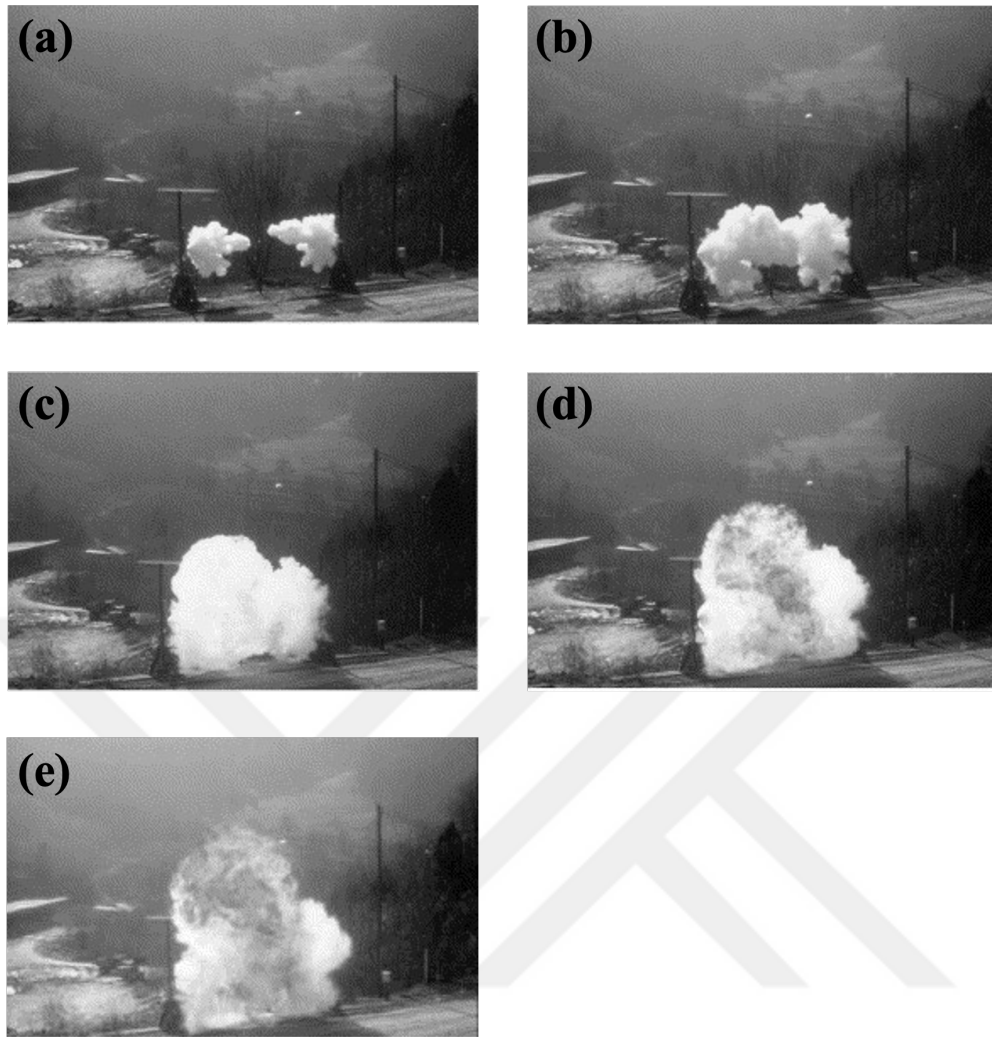


Figure 1.1: Course of an unconfined dust explosion (6 kg of maize starch), Reproduced from M. Glor, Powder Technology, 2003.

Since then, many researchers have attempted to reproduce and expand the triboelectric series to predict how different materials interact, harness the resulting charges for practical use, or mitigate problems caused by static electrification. This task has proven far more complex than initially expected, as tribocharging depends on various variables [2, 13, 14]. A striking observation highlighting this complexity is that even identical surfaces can accumulate significant static charge upon contact and separation. The tribocharging, therefore, cannot be fully explained by a material's inherent tendency to gain or lose electrons. The varying position of a material in the triboelectric series of different studies further proves this. For instance, Shaw reported that surface and environmental conditions can shift the relative order of materials in the series [15]. Factors such as surface texture and roughness, applied pressure, humidity, temperature, mechanical force, and type of contact have all been shown to influence the magnitude and polarity of the charges generated [14, 16–19].

1.1.1 Charging Mechanisms

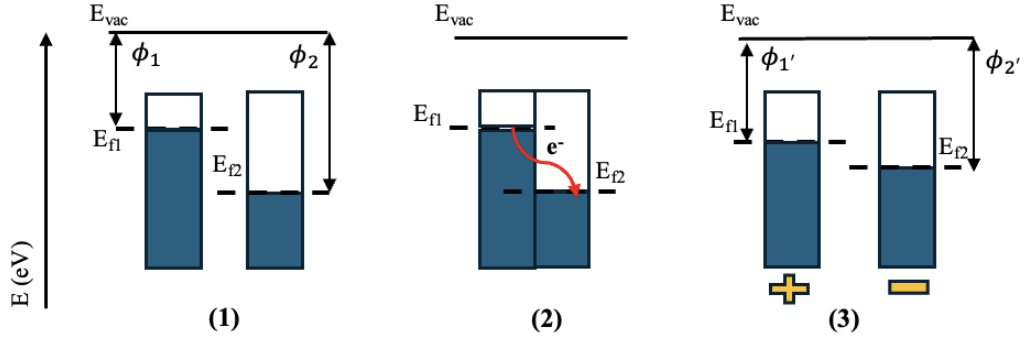
1.1.1.1 Electron Transfer Mechanism

It is intuitive to expect that when two surfaces come into contact, electrons flow from the one with a higher Fermi level to the one with a lower Fermi level, until equilibrium is reached, Figure 1.2 [2, 14]. As a result, in the case of conductive surfaces, the transferred charge can be explained by the contact potential difference between the surfaces (V_c) and the capacitance between them at the separation distance (C_0) [20]:

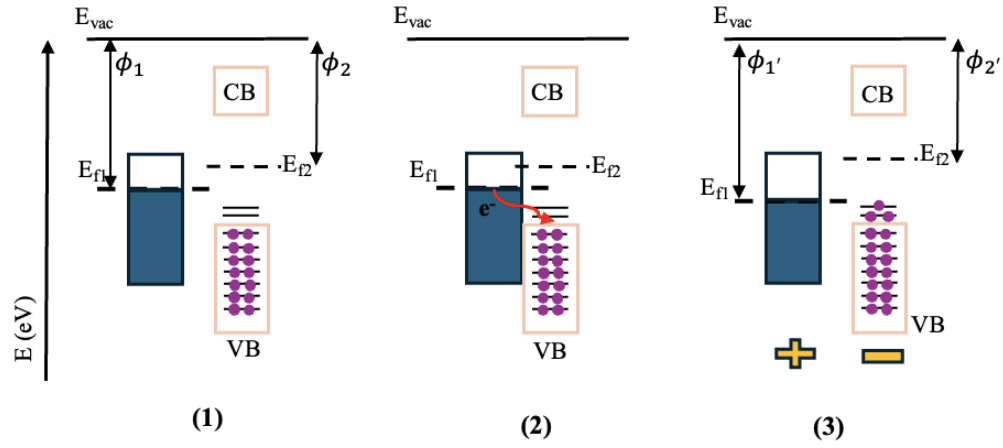
$$\Delta q_c = C_0 V_c$$

A similar approach can be extended to the contact between an insulating surface and a conductive one by introducing the concept of an effective work function for the insulator (1.2-b). However, when two insulators come into contact and charge builds up, the lack of free electrons on either surface challenges the theory based solely on Fermi level differences. To address this, some scholars have proposed that the surfaces possess accessible electron energy levels distinct from those of the bulk, as seen in Figure 1.2-c. According to this view, electron transfer between insulators is possible since one material has filled surface states while the other has empty ones; this makes effective work functions different [21, 22]. However, attempts to predict triboelectric behavior based solely on work function values often fail to align with empirical observations since various physical, chemical, and environmental factors beyond the material type influence the work function in powder systems [23].

(a) Charge Transfer Between Two Conductors



(b) Charge Transfer Between Conductor/Dielectric (having trap states)



(c) Charge Transfer Between Two Dielectrics (having trap states)

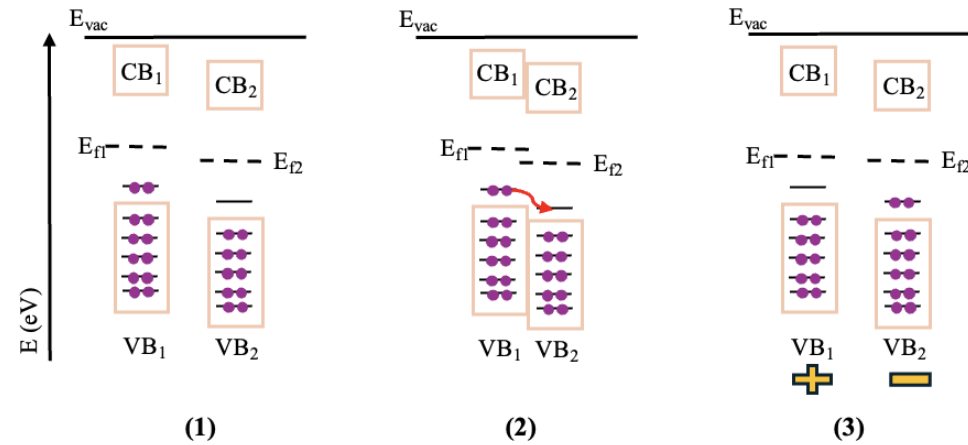


Figure 1.2: Schematic illustration of electron transfer as the dominant mechanism in contact electrification between (a) two conductors, (b) a conductor and an insulator, and (c) two insulators at three stages of (1) rest, (2) contact, and (3) separation.

Lowell suggested that defects, likely arising from highly strained bonds, provide intermediate states that allow electron flow [24]. However, others argue that such states are too few to explain the magnitude of charge usually observed in triboelectrification [25]. More recently, it has been proposed that when the interatomic distance between materials becomes shorter than the bonding length, electron cloud overlap occurs, making charge transfer possible [26]. This model also considers mechanical influences: friction, applied pressure during sliding or rubbing, and repeated contact can all bring surfaces closer together. That reduced separation increases the likelihood of charge exchange.

1.1.1.2 Ion Transfer Mechanism

It has been argued that TE between identical insulators cannot be explained solely by surface asymmetry or trapped electrons [25]. For a long time, ion mobility was also considered a contributing factor in contact electrification [20, 24]. Additionally, there is growing evidence that ion transfer, particularly involving hydroxide ions (OH^-), plays a significant role in surface charging upon contact. Figure 1.3 presents a schematic of the ion transfer model. According to Kornfeld [27], a thin layer of adsorbed ions on virtually any surface can promote generating and migrating of (OH^-) ions. Also, Diaz et. al [28] claimed that polymer's TE mostly depends on acid/base interaction rather than electron transfer since a correlation between polymers' charging and pK_b values was obtained. Consequently, water and relative humidity are now recognized as key contributors to TE, even under arid conditions, due to their influence on electrical conductivity [29], surface resistivity [30, 31], and even the work function differences between materials [32].

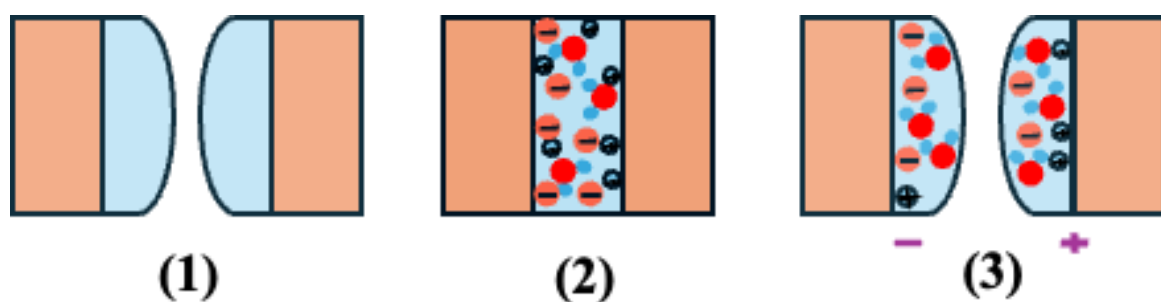


Figure 1.3: Schematic illustration of ion transfer as the dominant mechanism in triboelectrification at three stages: (1) rest, (2) contact, and (3) separation. In this mechanism, charge transfer occurs through the redistribution of ions within water molecules adsorbed on the material surfaces.

Nevertheless, most studies indicate that the highest charge accumulation occurs at RH levels between 25–40% [33, 34]. In the case of powder electrification, the situation becomes more complex. Elajnaf et al. demonstrated that the magnitude of charge reduction with increasing RH varies depending on whether a given powder is brought into contact with a metal surface or a plastic one. [35]

1.1.1.3 Material Transfer Mechanism

Bond cleavage and material transfer resulting from mechanical interactions at the interfaces are widely considered plausible mechanisms of TE, particularly in systems without mobile ions (see Figure 1.4) [36]. In such cases, charge carriers may be generated through the formation of ions and free radicals, or shifts in charge polarity [2,37,38]. For example, the dissociation of covalent bonds has been shown to produce pairs of identical radicals or cation/anion species by homolysis or heterolysis [39].

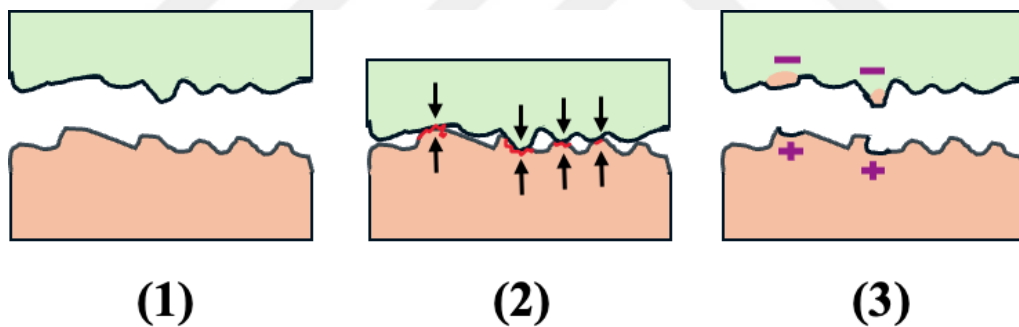


Figure 1.4: Schematic illustration of material transfer as the dominant mechanism in triboelectrification at three stages of two insulators (1) before contact, (2) during contact, and (3) after separation. High localized stress is applied at asperities (black arrows), leading to localized deformation (red spots), interfacial bond scission, and material transfer through surface adhesion during contact. After separation, the material transferred results in a net positive charge on one surface and a net negative charge on the other.

In addition, charge reversal upon contact may also be explained by material transfer between surfaces. For example, Baytekin et al. [40] indicated that increased material transfer between polymer beads and contact surfaces can lead to changes in polarity over time. Pandey et al. [41] similarly showed that charge transfer increases with enhanced

material transfer. Other studies have demonstrated that mechanical interactions, such as rubbing, can generate free radicals [42] and that applied strain influences the magnitude and direction of charge transfer [43]. Surface deformations have been proposed as a thermodynamic driver for TE, since surface asperities can generate strain gradients that produce electric fields and lead to charge accumulation [44]. Strain gradients may be important in powders, as the high surface-to-volume ratio and the frequent collision of particles with their adjacent particles and/or container walls can locally deform them and increase their surface roughness.

1.1.2 Material's Chemistry

Over the years, it has been proposed that a material's chemical structure contributes to its triboelectric behavior. Studies on polymer contact electrification showed that hydrocarbons do not acquire significant charge. Positive charging was observed in functional groups containing oxygen or nitrogen, while halogenated polymers typically acquired negative charges [28]. In another study, polymeric particles were functionalized with carboxyl, sulfonate, and dimethylamino ester groups. After being rubbed on oxidized iron powders, the particles modified with carboxyl and sulfonate groups developed negative charges, and those with dimethylamino groups acquired a positive charge [45]. Tanoue et al. also showed that halogen substitution in phthalocyaninacopper powders significantly increased the work function and shifted the CPD to more negative values. As Figure 1.5 represents how CPD varies systematically with the number and type of substituents, with bromine inducing a stronger effect than chlorine [46].

Surface modification techniques have been widely used to control and standardize functional end-groups and to adjust the charging behavior by controlling the material's structure and surface chemistry [47–49]. For example, silanization of glass beads or plates by applying a thin layer of terminal functional end groups has been used to create homogeneous surfaces or to isolate the effects of specific surface functionalities. Even a 1-nm-thick monolayer of such end-groups could affect the material's chargeability in triboelectrification [48]. Similarly, functionalizing the surfaces of coal or silica has successfully altered their work function values [50].

Conversely, in some studies, the influence of functional groups has been reported to be minimal. For example, organic lipids from leaves and animal skin were found to acquire positive charges during triboelectrification. Also, when synthetic lipids were examined, their triboelectric behavior was governed more by the electron-donating characteristics of the supporting lipid structure than by the specific functional groups present. This suggests that, in certain systems, the properties of the molecular backbone or underlying structure can play a more dominant role in charge generation [51].

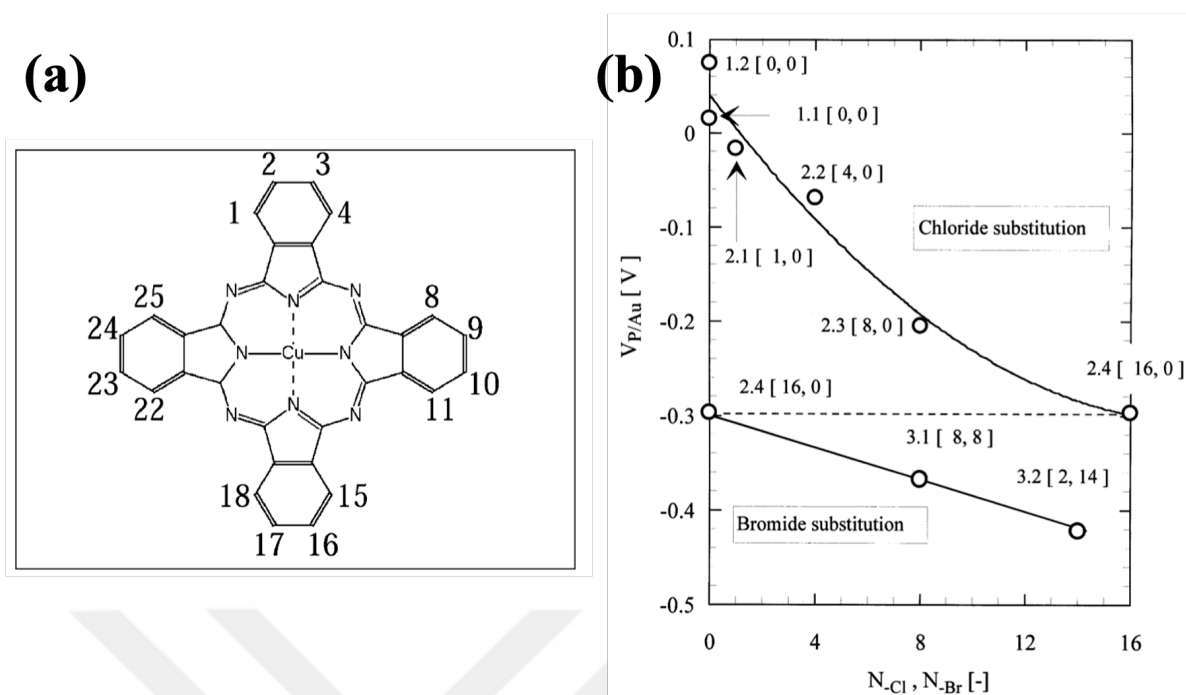


Figure 1.5: Structure of phthalocyaninecopper (a) with 16 hydrogen substituents, which are interchangeable with chlorine/bromine substituents, b) Potential difference between powder and a gold reference vs. number of chlorine or bromine substituents. Reproduced from Tanoue et. al., *AiChE Journal*, 2001

Research on the charging tendencies of active pharmaceutical ingredients (APIs) and excipients has provided valuable insights into powders' triboelectrification. Since TE can significantly alter the homogeneity or API-to-excipient ratio, potentially affecting drug formulation, understanding the underlying mechanisms, contributing factors, and mitigation methods is of great importance in pharmaceutical applications [52]. It has been observed that chemical structure does influence TE behavior, with APIs acquiring higher charges than excipients. [30, 52]. APIs with similar chemical structures have even been shown to exhibit comparable triboelectric behavior [30].

The ratio of API to excipient also affects triboelectric charging [29, 53]. In a binary mixture of ibuprofen and microcrystalline cellulose, intermediate concentrations exhibited lower charge magnitudes than the pure components. The researchers posit that the system's net charge was reduced due to electrostatic interactions between oppositely charged API and excipient particles. Theoretical studies further suggested that when particle-particle collisions dominate, the API tends to become positively charged, while the excipient acquires a negative charge [29].

The existing literature on how a material's chemical structure and functional groups influence TE covers only a limited range of substances [54]. In powder systems, isolating

the effect of a single functional group, specific chemical structure, or spatial arrangement is especially challenging. Hence, the contribution of materials chemistry remains mainly unclear, particularly in experimental studies.

1.1.3 Mechanical Aspects of TE

As the name implies, a fundamental aspect of triboelectrification is the “tribo” component, referring to mechanical interactions between surfaces. While tribo originates from the Greek word for “rubbing,” the modern understanding of TE encompasses a broader range of contact types, including impact, sliding, and pressing. Accordingly, the influence of applied forces and contact area must be recognized.

For instance, the charge generated while sliding a rough surface against a flat one is proportional to the normal pressure applied [55]. Based on TE studies, repeated contacts can significantly increase the transferred charge [24,56,57] and elevate the charge saturation limit [58]. Similarly, in friction-based systems, the accumulated surface charge on flat polymer materials rises with friction cycles [59]. The impact charge, defined as the charge transferred in a single collision to a previously uncharged particle, has been found to depend on the maximum contact area achieved during impact with a metal surface [60]. In single-contact experiments, charge density can be confidently used to quantify TE behavior [61]. When particles undergo a high-friction motion, though, the contact area continuously changes, and the charge density becomes less reliable. Finally, the mode of contact, sliding, bouncing, or rolling, also affects TE to a significant degree [62].

1.1.4 Powders Characteristics

1.1.4.1 Powder Morphology

Particle morphology (i.e., particle shape, size, size distribution, and surface roughness) strongly affects powder electrification. Particle shape is uncontrollable mainly during the production of powders, as different manufacturing methods, handling conditions, and mechanical degradation can result in a wide range of morphologies. Common commercial particle shapes include spherical, cubic, needle-like, flake-like, elongated planar, homogeneous planar particles, or a mixture of shapes. Additionally, auto-agglomeration and particle breakage throughout production, handling, transport, and storage stages continuously alter the effective shape distribution within a powder sample [63, 64].

The saturation charge has been shown to depend on particle geometry, with studies reporting differences between cubic and spherical particles [65]. Irregularly shaped particles have sometimes been associated with enhanced charge accumulation [66], and in some cases, even changes in charge polarity were observed [67]. However, there are reports of spherical particles having a higher charging tendency than irregular particles, challenging the above claim [68, 69].

It is important to note that particle shape also influences the mode of contact during motion: an increase in sphericity index of particles accompanies a larger, more uniform contact area. Therefore, particles can roll, slide, and bounce off surfaces. In contrast, irregularly shaped particles primarily experience sliding during movement [70]. This difference in contact behavior is believed to explain why spherical particles acquire higher charges than irregular ones, at least when turbulent flow is absent.

Extensive studies focused on the dependency of TE on particle size, yet the results remain contradictory. Sarkar et al. [69], and Mukherjee et. al. [71] show that smaller particles are more prone to charging than larger ones, since they would interact more with other particles and the walls. However, other research reports little to no correlation between particle size and charge accumulation [72, 73]. In some cases, larger particles were even found to acquire more charge than smaller ones, as fine particles may induce less surface deformation during collisions, resulting in reduced charge transfer [74].

Since the energy required to transfer an electron between two insulating particles depends on their size, it is widely believed that electrons tend to flow from larger particles to smaller ones of the same material [75, 76]. Consequently, large and small particles are expected to acquire opposite charges, with coarse particles losing electrons upon contact with finer ones and becoming positively charged [2,77]. Assuming an equal surface density of

charge-generating species, larger particles can trap more high-energy species. Upon contact, this asymmetry leads to a directional transfer of electrons or anions from coarse to fine particles, resulting in negatively charged fine particles and positively charged coarse particles [78].

1.1.4.2 Surface Roughness

Surface roughness of particles affects the true contact area during TE and the degree of friction involved [34]. Higher surface roughness is generally reported to cause higher contact charging [79]; charge accumulation at surface asperities is often cited as the reason for the inhomogeneous charge distribution observed on the surface of insulating materials [80]. Surface roughness and the spatial distribution of asperities can even influence moisture absorption; as a result, they affect both the charging and discharging behavior of powders [71, 81]. Recent studies have also shown that surface curvature plays a role in polarity: convex regions tend to gain negative charges, while concave regions often acquire positive charges [82].

1.1.4.3 Crystal Structure

The effect of crystallinity on triboelectric charging also remains inconclusive, as in some studies crystalline powders exhibit higher charging levels than their amorphous counterparts [83, 84], while in others increasing the degree of amorphicity correlates with higher charge magnitudes and greater variability in both the sign and magnitude of the charge [67, 85–87].

Inconsistent data could stem from overlapping variables such as particle size, shape distribution, and moisture content. Amorphous particles have broader size distributions, more irregular morphologies [67], and a higher porosity than crystalline ones [88]. Charge distribution also depends on crystallinity: amorphous particles tend to support more homogeneous charge dispersion due to their higher molecular mobility. Crystalline particles, on the other hand, exhibit charge localization at the tips and edges [89]. Variations in crystallinity affect specific surface area, mechanical hardness, and crystal packing, factors known to influence triboelectrification.

In recent computational studies, the crystal structure and the specific crystal facets exposed at the surface were also shown to influence the triboelectric behavior. Middleton et al. used density functional theory to demonstrate that effective WF varies by up to 1 eV in different crystallographic planes of aspirin and paracetamol crystals [90]. These variations, shown in Figure 1.6, arise from differences in the orientation of the surface dipole and the molecular packing. As a result, the crystal structure and the facet-dependent electrostatics should be considered along with the degree of crystallinity when evaluating the triboelectric performance of a material.

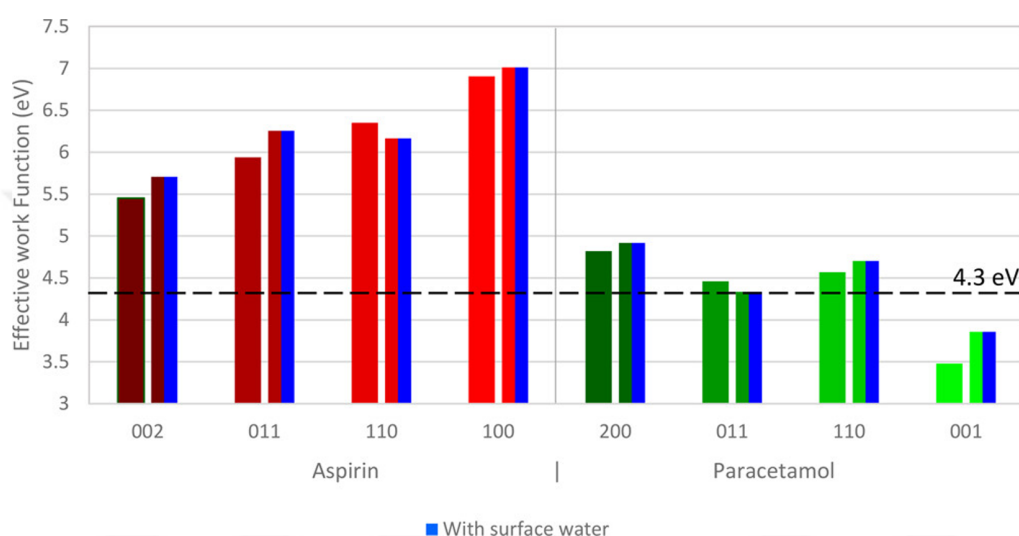


Figure 1.6: Calculated effective WF of selected surfaces of aspirin and paracetamol. The effective WF difference between facets and the effective WF shift induced by the fractional coverage of water onto the surface is also shown—Reproduced from Middleton et al, *Crystal Growth & Design*, 2003

1.1.5 Environmental Factors

1.1.5.1 Relative Humidity

Relative humidity (RH) plays a key role in triboelectric charging, especially when powders are involved. Increased RH generally leads to decreased surface resistivity due to the adsorption of water molecules, which promote charge dissipation and reduce the total accumulated charge [35,91,92]. Depending on the surface area, polarity, or hygroscopicity of powders, contradictory trends may emerge. For instance, the charge density of pharmaceutical powders was shown to remain stable up to 40% RH. However, it dropped sharply beyond that, likely due to condensed water lowering surface resistivity to a significant degree [93].

It is suggested that the dominant charge transfer mechanism shifts from electron transfer at low RH to ion-based processes at higher RH [17, 94]. Additionally, Kolehmainen et al. observed that for polyethylene-glass systems, effective WF differences vary with humidity, highlighting that both electron and ion transfer mechanisms may coexist and be material-specific [32].

1.1.5.2 Temperature

Another environmental factor influencing triboelectrification is temperature. Generally, elevated temperatures reduce charge accumulation by decreasing the electrical resistance, enhancing the charge mobility, and facilitating charge dissipation [19, 95]. Although temperature is less studied than RH, its impact is often intertwined with other variables like surface conductivity and humidity.

In a recent study, Nimvari et al. indicated that increasing temperature suppresses electrostatic charge accumulation during insulator–insulator contact [96]. They observed that the volume resistivity of the insulating materials decreased with rising temperature, which in turn enhanced charge carrier mobility and promoted charge dissipation to the ground.

1.1.5.3 Material of Contact Surface

The nature of the surface in contact with powders affects the magnitude and polarity of triboelectric charging to a significant degree. Since charge transfer occurs between particles and between particles and their container, changing the contact material alters the surface's effective WF, hence the charge outcome. Studies have demonstrated that the same powder mixture can exhibit different charging profiles when mixed in containers made of stainless steel, polypropylene, or acetal [35].

1.2 Triboelectric Series

As discussed in this chapter, the triboelectric series is a commonly used framework for ranking insulating materials based on their tendency to acquire charge through triboelectricity. A representative triboelectric series is shown in Figure 1.7.

Usually, materials more likely to lose electrons and become positively charged are placed higher in the series, while those prone to gaining electrons and becoming negatively charged are placed lower. This ranking can be based on the material's behavior in contact with a reference surface or through direct interaction with other materials. The primary goal of such a series is to predict how different insulators will behave when brought into contact, minimize unwanted static buildup, or to exploit the charging tendencies, namely in triboelectric nanogenerators (TENGs). However, these series are usually developed under significantly varying experimental conditions. Researchers often cite this as the main reason for the poor reproducibility of triboelectric series. Yet, some efforts have been made to identify polymers that consistently fall into the same position within various series [28], even at the expense of introducing materials triboelectric charging as a largely qualitative property.

Among the most notable attempts to quantify the triboelectric series, Wang et al. used a liquid metal under highly controlled conditions, developing a more standardized method and a quantitative ranking [15]. The downside of their approach is that it relies on flat surfaces; therefore, it cannot be readily applied to powder systems with a fundamentally different nature of contact. Since the charging behavior of powders often differs from that of their bulk counterparts, it remains uncertain whether the same triboelectric ranking would hold for powdered materials.

Although the development of such series aims to determine whether an inherent material property governs the tribocharging or if such a property can even be consistently defined, experimental results remain contradictory. These inconsistencies suggest that the triboelectric series, while a useful conceptual tool, still requires a deeper understanding of the underlying mechanisms of triboelectrification before it can be reliably applied in practical scenarios.

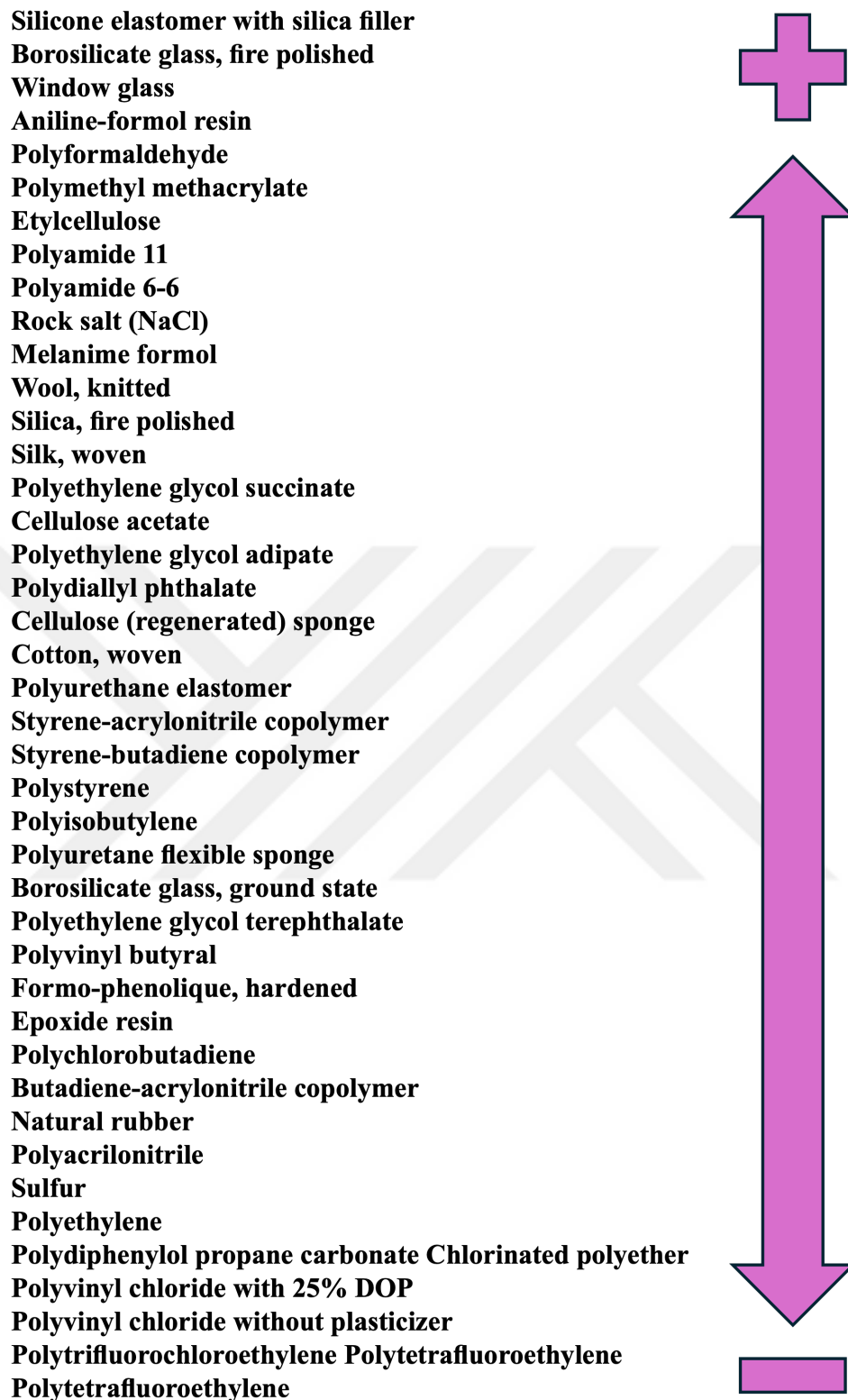


Figure 1.7: Triboelectric series of common polymers—Reproduced from J. Henniker, Nature, 1962.

1.3 Aim of the Thesis

Triboelectric charging in powders poses challenges and risks across many industries, affecting product quality, process reliability, material loss, and safety. This thesis investigates whether material chemistry at the molecular level, such as chemical structure, type, number, and position of functional groups, can influence triboelectric behavior at the macroscopic scale. The goal is to assess if such molecular features can meaningfully predict or explain tribocharging tendencies, even within complex and dynamic powder systems.

A particular focus is given to whether these chemical factors are strong enough to override or remain consistent despite other influential variables, including particle morphology, powder flow, environmental humidity, and the degree of mechanical agitation. Additionally, this study explores the possibility of ranking materials into a meaningful triboelectric series based on their powder behavior and whether such a series could offer predictive value despite the variability typically observed in powder systems.

Chapter 2

Materials and Experimental Methods

2.1 Materials

In order to explore how molecular structure influences triboelectric behavior, a set of common organic powders was selected. As listed in Table 2.1, the compounds studied differ in the number of fused rings, spatial arrangement, type, and position of functional groups. This allows a closer look at the roles of conjugation and chemical functionality in shaping triboelectric properties in Table 2.1.

2.2 Experimental Methods

2.2.1 Native Voltage Measurements

Since powders can acquire an electrostatic charge during storage, even in sealed containers, this study first aimed to determine whether such charging could be measured reproducibly and interpreted systematically. Commercial powders are typically stored in a variety of container types, which can influence the degree and nature of the charging. Therefore, we transferred 0.200 g of each powder to identical plastic vials and stored them for several days to minimize this variability and ensure uniform conditions. Before each experiment, we placed the powder samples on an agate surface thoroughly cleaned and discharged using acetone and isopropyl alcohol (IPA). A high-precision electrostatic voltmeter (TREK High Speed Electrostatic Voltmeter, Model 370) recorded the voltage between a gold probe and the powder layer on the agate. We took the difference between this reading and the baseline voltage of the clean agate surface as the native (initial) voltage of the commercial powders upon removal from their containers.

We repeated each measurement at least three times on different days for each powder, at

room temperature ($24\pm1^\circ\text{C}$) and a relative humidity of 38–42%.

Table 2.1: Selected organic powders and their structural characteristics

Compound	Functional Groups	Fused Rings	Group Count
Naphthalene	None	2	0
1-Naphthoic acid	Carboxylic acid	2	1
2-Naphthoic acid	Carboxylic acid	2	1
1-Naphthol	Hydroxyl	2	1
2-Naphthol	Hydroxyl	2	1
1,5-Dihydroxynaphthalene	Hydroxyl	2	2
2,3-Dihydroxynaphthalene	Hydroxyl	2	2
2,6-Dihydroxynaphthalene	Hydroxyl	2	2
2-Naphthaldehyde	Aldehyde	2	1
2-Iodonaphthalene	Iodo	2	1
2,3-Dimethylnaphthalene	Methyl	2	2
Pyrene	None	4	0
1-Nitropyrene	Nitro	4	1
1-Aminopyrene	Amino	4	1
Anthracene	None	3	0
9,10-Dibromoanthracene	Bromo	3	2
Phenanthrene	None	3	0
Perylene	None	5	0
TCNQ	Cyano	3	4

2.2.2 Triboelectrification

To electrify the powders, we ground the powders using a mortar and a pestle, with a consistent hand pressure. This deliberately simple setup ensures accessibility and reproducibility in various environments while avoiding the need for complex or isolated systems commonly used in triboelectric studies. Unlike conventional approaches that aim to eliminate external influences, the present method reflects a more realistic open system, closer to how triboelectric phenomena occur in everyday conditions.

The grinding served two distinct purposes. First, it provided sustained and intimate frictional contact between the powder particles and between the powders and the container surfaces, conditions not always guaranteed by simply rubbing a flat surface on top of the powders. The dynamic motion and confinement of the grinding process significantly enhance both the powder-powder and the powder-surface interactions, promoting more effective charge transfer through increased contact events.

Second, grinding incrementally reduced the size of the particles, thereby increasing the available surface area. Although not the primary goal, this size reduction may influence the triboelectric response by enabling finer particles to participate more actively in electrification. Since the powders were processed in three successive trials, this also allowed for the observation of whether progressively finer particles exhibited increased susceptibility to charge accumulation under continued grinding, or if a charge saturation limit existed. To identify the most suitable combination for this purpose, we evaluated three different mortar–pestle pairings: **(i)** agate mortar with agate pestle, **(ii)** agate mortar with steel pestle, and **(iii)** brass mortar with brass pestle. The inner volumes of agate and brass mortars were 55 ml and 100 ml, respectively. The goal was to determine an optimized pair that provides consistent and representative electrification behavior for the materials under study and assess the grinding medium’s effect on the tribocharging outcome.

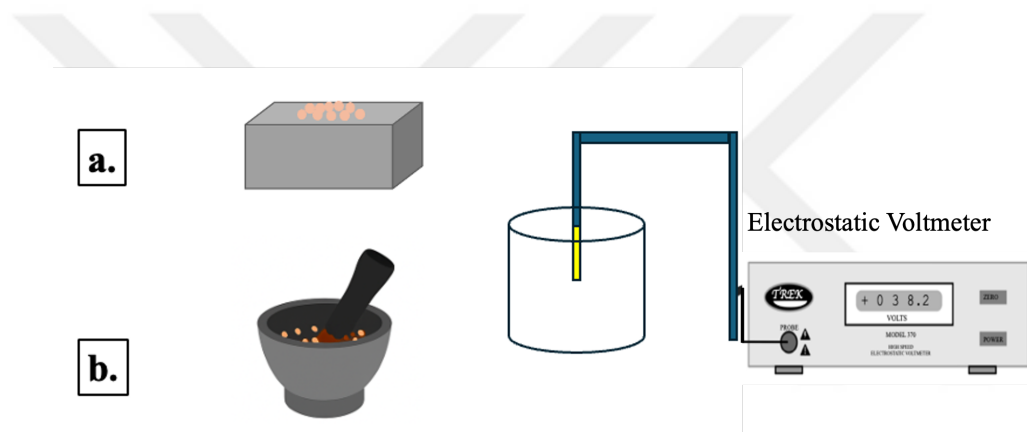


Figure 2.1: Schematic of setup used for measurement of voltage: (a) shows the commercial powder layer on top of an agate surface, and b) shows the mortar and pestle used for grinding the powders

Figure 2.1 shows a schematic of the setup. We ground 0.200 g of each powder for two minutes and placed the mortar inside a Faraday cage to eliminate interference from external electric fields during the measurements. The operator manually controlled the applied force during grinding, and between each cycle, discharged themselves by touching a copper plate. A gold probe, connected to a TREK high-precision electrostatic voltmeter, model 370, was positioned at a fixed height of 2 cm above the bottom of the mortar. Previous studies claim that non-contact voltage measurements employing an electrostatic voltmeter are a common, reliable approach to studying triboelectrification since it avoids disturbing the charge distribution on the sample’s surface [97]. Voltage measurements began 30 seconds after the mortar was placed inside the cage, allowing the system to stabilize. Then, we recorded the data over five minutes and repeated the procedure for at least two additional trials. Although the exact charge accumulation could not be

quantitatively determined due to geometric constraints, the measured voltage was used to assess the sign and relative magnitude of the accumulated charge in each trial.

2.2.3 Effect of Relative Humidity

As explained in **Section 1.1.5.1**, the material's tendency to gain or lose electrons during contact or friction with another surface is strongly influenced by humidity. Therefore, selected powders were examined under two relative humidity conditions: 'low', 15–20 % and 'medium', 30–40%. To reflect the natural conditions, we chose relative humidity ranges that typically occur in Ankara. The highest humidity levels typically occurred during the peak of summer (July and August), and the lowest throughout the dry winter months (January and February). It should be noted that the study remained within the bounds of naturally occurring humidity and did not artificially extend the range beyond what is locally observed.

2.2.4 Binary Powder Mixing Experiments

One of the central questions in triboelectrification is how charge transfer occurs between dissimilar materials in powder form. A key question is: What happens when powders with different charging tendencies are ground together? For instance, how might a powder bearing electron-accepting functional groups interact with one containing electron-donating groups? Do individual powder particles recognize such chemical differences and undergo directional charge transfer? Or does static electrification become increasingly random and less dependent on intrinsic material properties?

We studied two binary systems to investigate these questions:

- 1) Naphthalene and pyrene, two neutral polycyclic aromatic hydrocarbons, were mixed in three different mass ratios (1:1, 1:3, and 3:1).
- 2) 1-Aminopyrene and 1-nitropyrene, a pair selected for their contrasting electron-donating and electron-withdrawing substituents, were mixed in a fixed 1:1 molar ratio to probe the effect of functional group chemistry.

In all cases, the grinding procedure, powder mass, and voltage measurement method were consistent with those described in **Section 2.2.2**.

2.2.5 Powders Characterization

Various attributes of powders can affect their contact electrification, such as particle size, shape, surface roughness, and agglomeration tendency. Particle size distribution (PSD) and size range also influence how a material acquires static charge. Therefore, we characterized the as-received commercial powders and those subjected to three consecutive two-minute grinding steps using scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The binary mixtures were also analyzed by attenuated total reflectance (ATR) spectroscopy.

2.2.5.1 Morphological Characterization via SEM

For SEM, we first placed a small amount of powder on carbon tape, then coated it with a thin layer of Au–Pd using a Precision Etching Coating System (PECS™), and finally transferred it to an FEI Quanta 200 FEG SEM for imaging. Particle size distribution (PSD) plots were generated using ImageJ analysis.

2.2.5.2 Crystallinity Assessment via XRD

An X'Pert PRO X-ray diffractometer (PANalytical) equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) was used to evaluate the crystal structure's preservation after grinding. The measurements were performed at 45 kV accelerating voltage and 40 mA current.

We calculated the degree of crystallinity by taking the ratio of the integrated area of all crystalline peaks to the total integrated area under the XRD pattern for each powder.

2.2.5.3 ATR-IR Spectroscopy

We analyzed the binary powder mixtures before and after grinding using ATR-IR spectroscopy to examine whether grinding induced any spectral shifts indicative of chemical interactions. We acquired the spectra using a Bruker Alpha spectrometer over the range of 4000–400 cm^{-1} , with 256 scans per sample and a resolution of 4 cm^{-1} .



Chapter 3

Results and Discussion

3.1 Native Voltage Measurement

We arranged the received powders in a triboelectric series based on the results of the electrostatic potential measurements of native samples (See Experimental section **2.2.1**), as shown in Figure 3.1. If we consider the data purely from a chemical structure perspective, powders containing hydroxyl functional groups consistently acquired a negative charge. Functional groups like aldehyde, iodine, bromine, and cyano were associated with minimal native voltage. Powders with amino and methyl groups exhibited medium to high positive voltages (above +10 V), ranking third and second, respectively. Perylene produced the highest positive voltage ($+53.5 \pm 21.2$ V), while 1-nitropyrene and 2-naphthoic acid showed the strongest negative voltages (-71.5 ± 36.9 V and -112.0 ± 82.4 V, respectively). However, it should be noted that both 1-nitropyrene and 2-naphthoic acid exhibited a high standard deviation value, suggesting that electron gain or loss during storage is not equally reproducible. On the other hand, TCNQ is a well-known strong electron acceptor, which makes its powder's observed low electrostatic potential an unexpected result. One possible explanation is its symmetrical molecular structure combined with four cyano groups. This arrangement may stabilize accumulated charges on the powder surface by creating both electron-rich and electron-deficient regions, reducing the net electrostatic potential. Kelvin Probe Force Microscopy (KFM) analysis could provide further insights into this phenomenon.

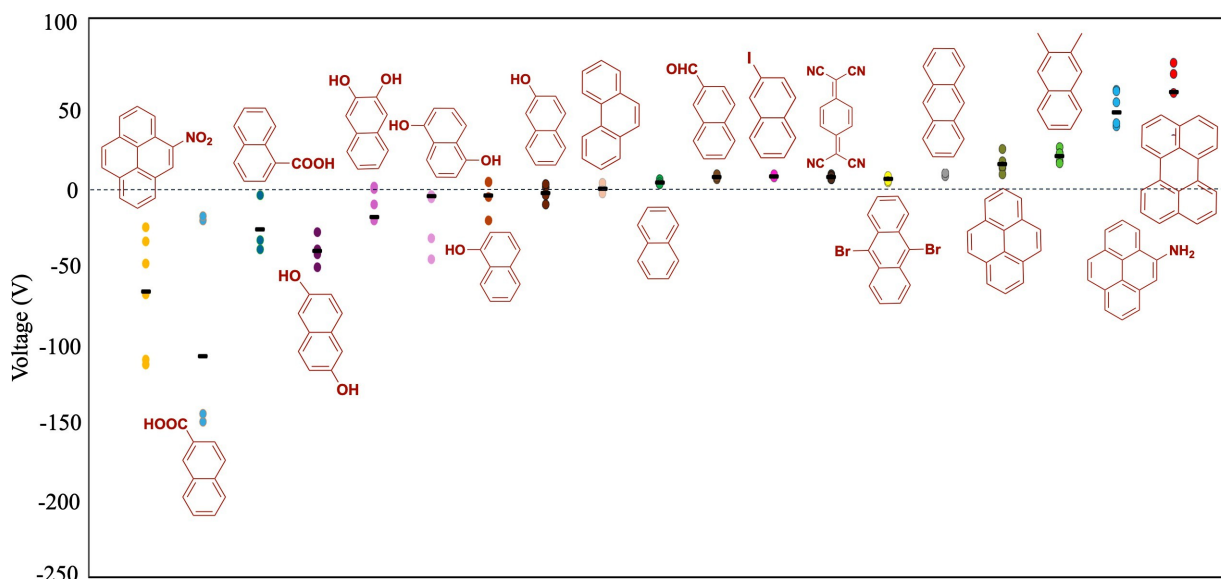


Figure 3.1: The native electric potential series of organic powders studied. The potential difference is measured between each powder and the gold electrode attached to the electrostatic voltmeter. Organic powders (0.200 g each) stored in identical plastic vials for several days were placed on an agate surface and the electrostatic potential on the powders were measured by an electrostatic voltmeter equipped with a probe hanging down on the samples at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.1) The colored dots refer to the individual electric potential readings and the black dashed represent the average values of the electric potential values.

3.2 Triboelectrification via Grinding

3.2.1 Choosing the Appropriate Grinding System

In the preliminary experiments of tribocharging powders in a mortar/pestle setup, naphthalene powders acquired a charge well enough to assess the differences between the grinding materials. Therefore, we ground naphthalene using three different mortar/pestle combinations: (i) agate mortar with agate pestle, (ii) agate mortar with steel pestle, and (iii) brass mortar with brass pestle. As shown in Figure 3.2, naphthalene consistently acquired a negative charge in all three combinations. The voltage measured in the brass/brass system was the lowest, compared to the agate/agate and agate/steel setups. Using a brass mortar also led to material loss, as the powder was difficult to collect from its surface. Based on these results, subsequent experiments with other powders were conducted using an agate mortar, paired with either an agate or a steel pestle. This approach also allowed us to study the effect of introducing a conductive (steel) or insulator (agate) pestle while keeping the mortar material (agate, insulator) constant.

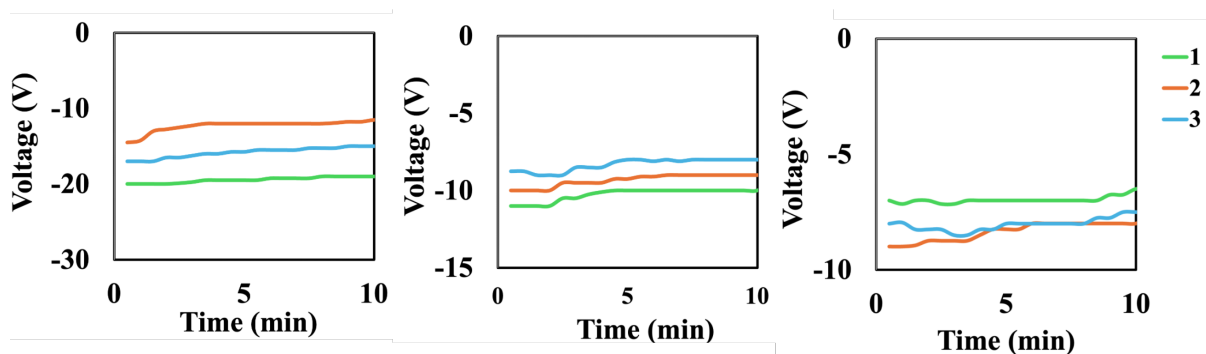


Figure 3.2: Measured voltage as a function of time for naphthalene powder (0.200 g) ground using different mortar/pestle combinations; from left to right: agate mortar/agate pestle, agate mortar/steel pestle, and brass mortar/brass pestle systems. Each was studied in three independent trials (colored lines). Ground naphthalene powder was left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2.

On another note, when comparing the different trials using the same mortar and pestle, we observed that although the exact voltage values varied, they remained within a comparable range. This suggests that the experiments are reproducible. Another critical point is that in each new trial, the ground material that decayed to zero is ground again. Nevertheless, the potential measured in this new trial did not display a consistent increase or decrease compared to the previous one.

Since these voltage readings correspond to subsequent grinding stages (e.g., in trial one, the powder is ground for two minutes, and by trial three, it has undergone six minutes of grinding in total), we can already see that changes induced by grinding, such as particle refinement, auto-agglomeration or de-agglomeration, or a more uniform PSD (see also below), do not always lead to predictable or consistently changing triboelectric behavior.

3.2.2 Triboelectric Behavior in Agate/Agate System

3.2.2.1 Variability of charge values in grinding experiments

In contact electrification studies, charge saturation is often discussed as a material property, where additional contacts or collisions no longer increase the accumulated charge [98, 99]. In our experiments, while some powders produced similar voltage magnitudes across different trials, others exhibited increased or decreased charging as we moved through successive grinding trials. This variability likely results from two key factors. First, most charge saturation studies are conducted under frictionless or low-friction contact conditions [60, 98, 99]. At the same time, our setup involves high-friction grinding, which can introduce additional mechanisms such as localized heating, surface modification, or tribochemical effects. Second, charge plateau behavior depends on particle size and PSD [99]. Because grinding continuously alters both parameters, comparisons across trials become inherently uncertain.

In the preliminary experiments, we charged all powders in consecutive grindings and recorded the electric potential (V) created on the powders with the increasing grinding time. Figures 3.3 and 3.4 show these $V-t$ plots in the 1st, 2nd, and 3rd grinding for the powders examined. Comparing them shows that most powders underwent gradual charging (i.e., with each grinding trial, a higher voltage was obtained); see naphthalene, 1-naphthol, 2-naphthoic acid, and pyrene. However, some powders reached higher voltages in earlier trials, such as 2,3-dihydroxynaphthalene, 1-naphthoic acid, and 1-nitropyrene (set 1). There are also cases where the voltage remained constant across all successive grindings (for example, 1-aminopyrene).

Because of these inherent variabilities in powder charging by grinding, we ground the samples carefully, taking extreme care of the environmental factors, and performing the experiments numerous times. The results below are statistically reproducible, ‘typical charging’ obtained through such data collection over months.

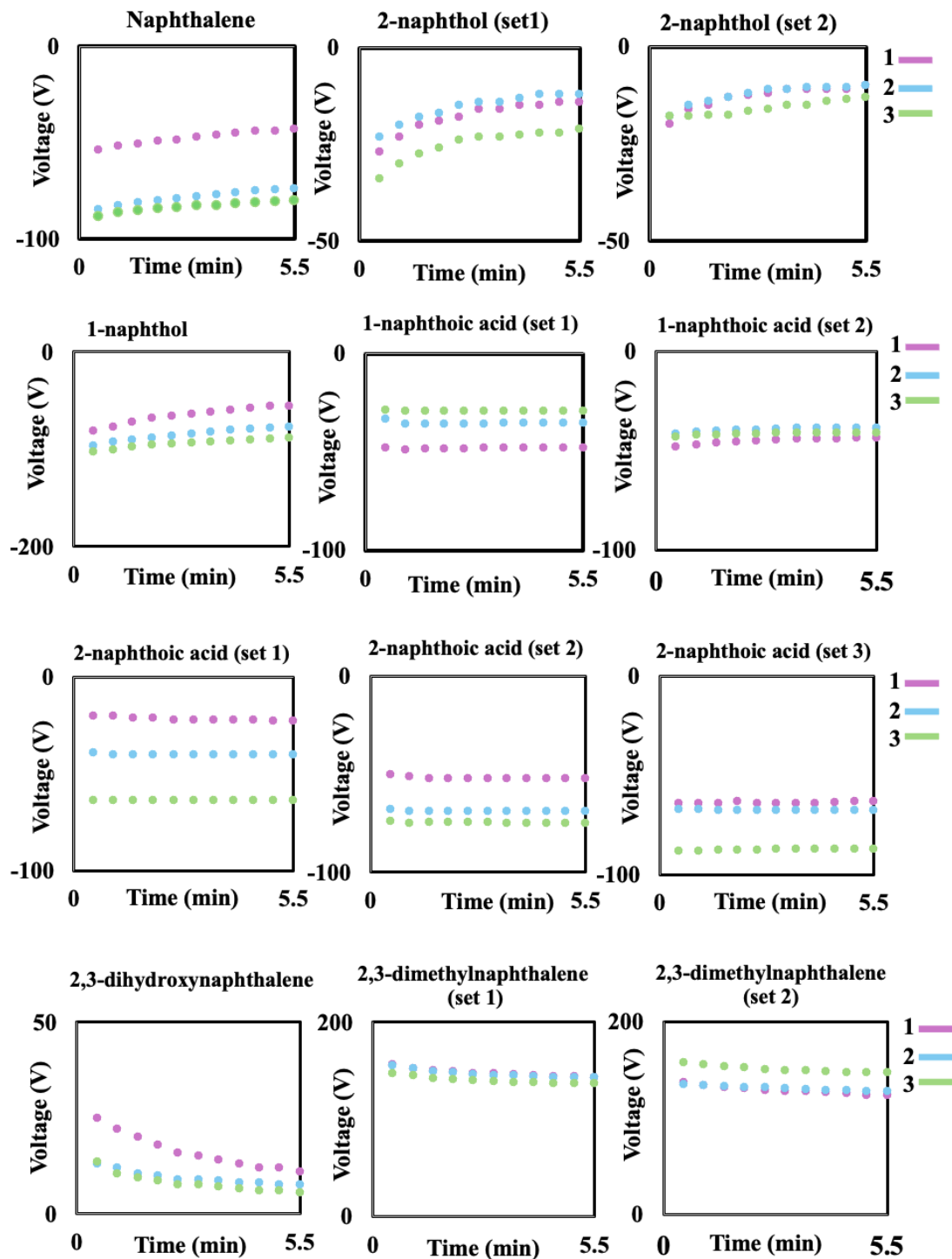


Figure 3.3: Measured voltage as a function of time for 0.200 g of various powders ground using an agate mortar with an agate pestle. Each was studied in three independent trials (colored lines). Ground powders were left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2.

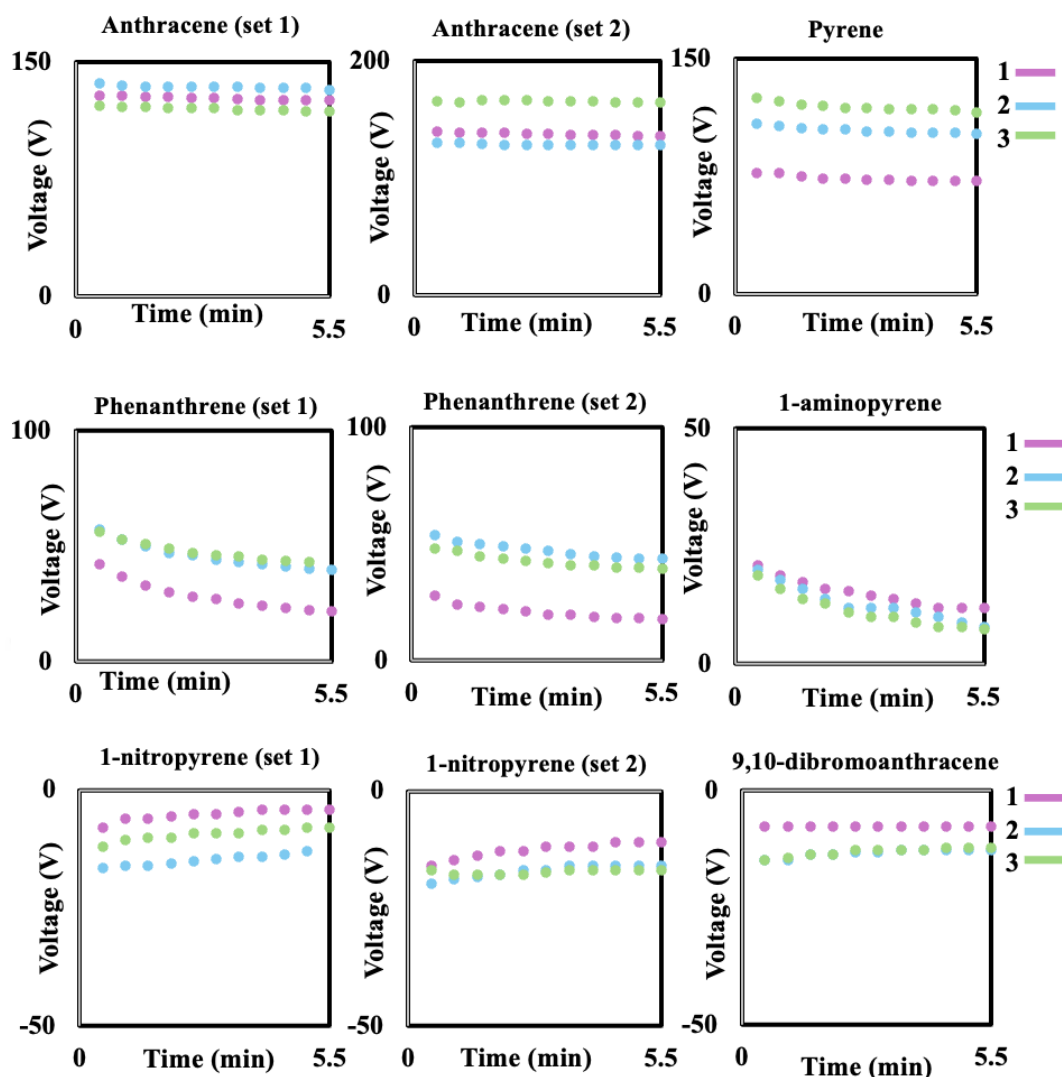


Figure 3.4: Measured voltage as a function of time for 0.200 g of various powders ground using an agate mortar with an agate pestle. Each was studied in three independent trials (colored lines). Ground powders were left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see Experimental section, 2.2.2.

3.2.2.2 Charge Generation and V-T Plots

The preliminary work for this thesis included grinding the unsubstituted fused aromatic ring compounds. We ground each powder following the procedure described in **Section 2.2.2**. In Figure 3.5, we show that aromatic compounds with different numbers of fused rings acquire different charges when ground using the agate/agate system, naphthalene being the only one to become negatively charged. Increasing the number of aromatic rings leads to more positive charges on the powder, i.e., anthracene and pyrene exhibit significantly high positive voltages.

When pyrene and anthracene are compared, pyrene acquires a higher positive charge, presumably affected by the higher resonance stabilization energy that makes the pyrene cation more stable than that of anthracene [100, 101]. On the other hand, perylene acquired a less positive charge compared to both anthracene and pyrene.

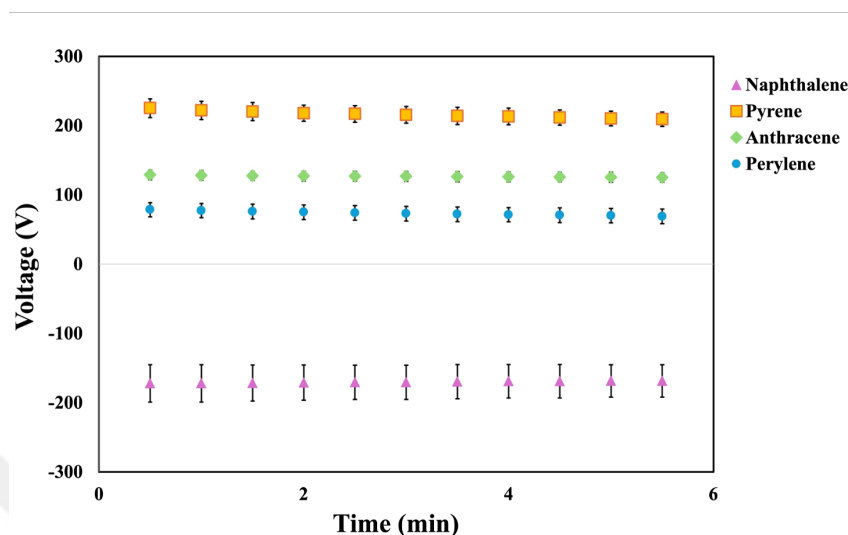


Figure 3.5: Voltage versus grinding time curves for naphthalene, perylene, anthracene, and pyrene (each 0.200 g) powders ground using an agate pestle in an agate mortar. (Error bars depict the standard deviation obtained in three independent experiments). Ground powders were left in the mortar, and the electrostatic potential of the powder was measured by an electrostatic voltmeter equipped with a probe hanging down on the sample at a distance of 2 cm. (For details of the measurements, see **Experimental Section 2.2.2**).

3.2.2.3 Triboelectric Series

Encouraged by the reproducible and interesting outcome of the fused aromatic rings grinding/charging results, we decided to probe the other aromatic compounds with different functional groups. Figure 3.6 presents the powders (0.200 g) ground for 2 mins using the agate mortar and agate pestle. (The ordering follows the arrangement shown in Figure 3.1 for better comparison.) We observed that applying mechanical force altered the triboelectric ranking of several powders. For instance, in this case, 1-naphthol exhibited the most negative voltage (-93.7 ± 11.4 V), while pyrene showed the highest voltage ($+164.5 \pm 68.9$ V). Compared to the native voltage measurements, some trends remained consistent: powders containing nitro and carboxyl functional groups continued to acquire negative charges. In contrast, those with amino and methyl groups tended to charge positively. Powders with aldehyde, iodo, and bromo functional groups also showed low charging, similar to their behavior when stored in vials.

Another example of this controversial result is with the positive charging of the dihydroxy derivatives. These compounds, because of their low pK_a s, would be expected to lose a proton upon grinding, forming phenolate (negatively charged) and acquiring a negative charge. However, these powders were found to be slightly positively charged. The stabilization of the positive charge, therefore, might be an indication that the charging is not through a proton transfer (leading to formation of a phenolate) but through an electron transfer from the neutral compound; i.e., to the surface of the pestle or the surrounding atmosphere.

The trends in tribocharging of the respective functional group sets were also analyzed separately, as shown in Figure 3.7 below. The fused aromatic rings without any substituents were found to display high electrostatic potential in almost all cases. Except for the smallest set member, naphthalene, the rest of the fused aromatic molecule powders charged positively. However, the magnitude of the generated charge did not follow the ring number in the series, Figure 3.7-a. Also, anthracene and phenanthrene, having the same number of rings and the same closed formula, were charged with different amounts in the grinding experiments. As mentioned above, the fused aromatic rings without substituents were found to charge more than the functionalized ones in almost all cases. This difference is clearly displayed in the set of pyrenes with unsubstituted, amino (electron-donating), and nitro (electron-withdrawing) substituted pyrenes (Figure 3.7-b). Pyrene significantly charged more than the functionalized ones. The same charging trend was repeated also with the bromo and unsubstituted anthracenes (Figure 3.7-c). Although charging was less in the electron-donating/accepting group decorated ring systems, they generally followed a trend of charging according to their electron-donating/withdrawing abilities (Figure 3.7-d) – except the dihydroxy naphthalenes discussed above.

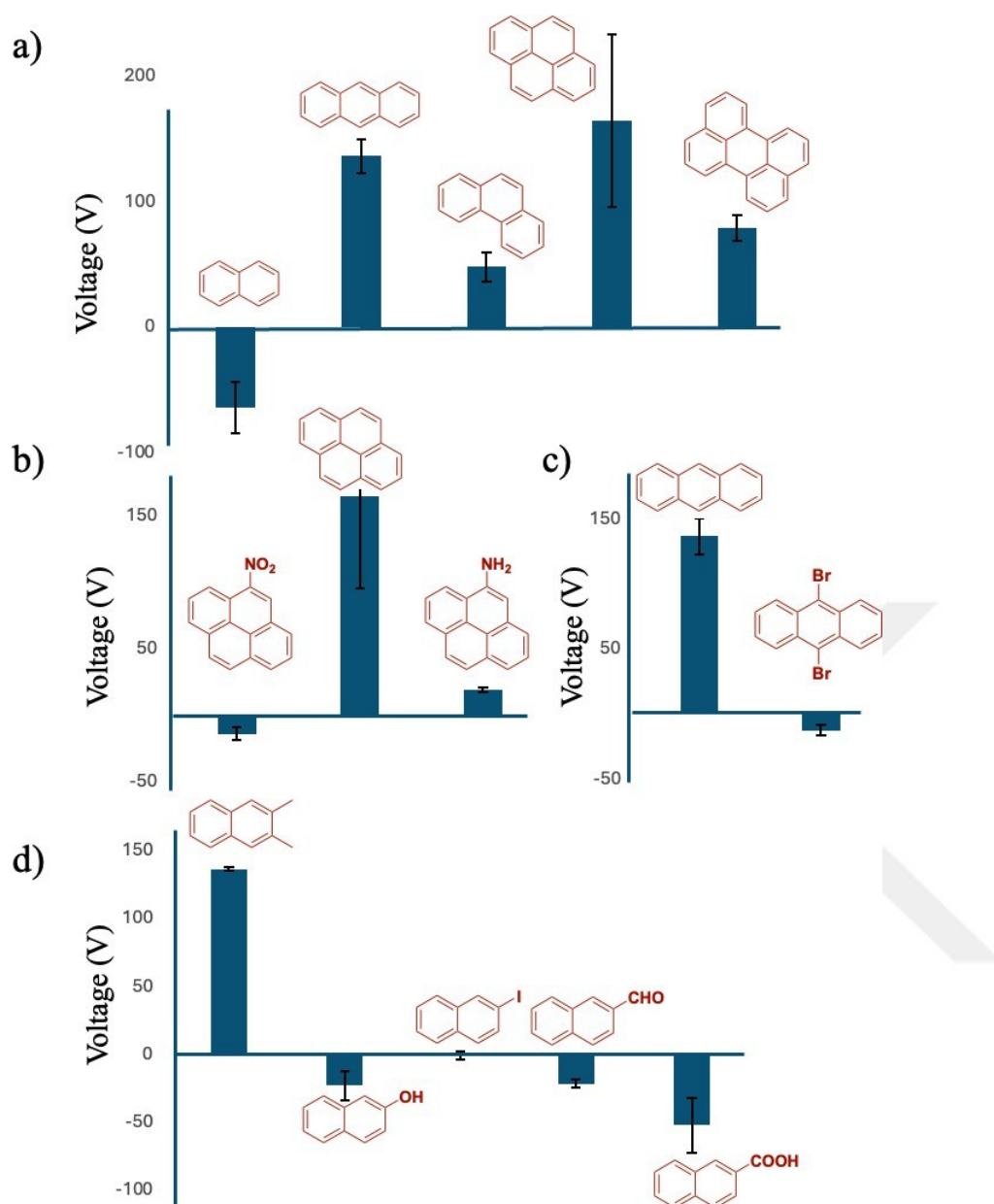


Figure 3.7: The data in Figure 3.6 are sorted into the groups of the results for a) unsubstituted fused aromatic ring compounds, b) the functional group derivatives of pyrene and unsubstituted pyrene, c) the bromo derivative of anthracene and unsubstituted anthracene, and d) functionalized naphthalenes.

Among all the studied sets, probably the most interesting tribocharging results appeared for the isomers of the same compound (Figure 3.8). If the powder materials were charged solely according to the chemical groups they possess, the isomers' charging behaviors would be the same. However, our results show that isomers can charge very differently under the same conditions. As depicted above in Figure 3.7-a, anthracene and phenanthrene charge to different extents.

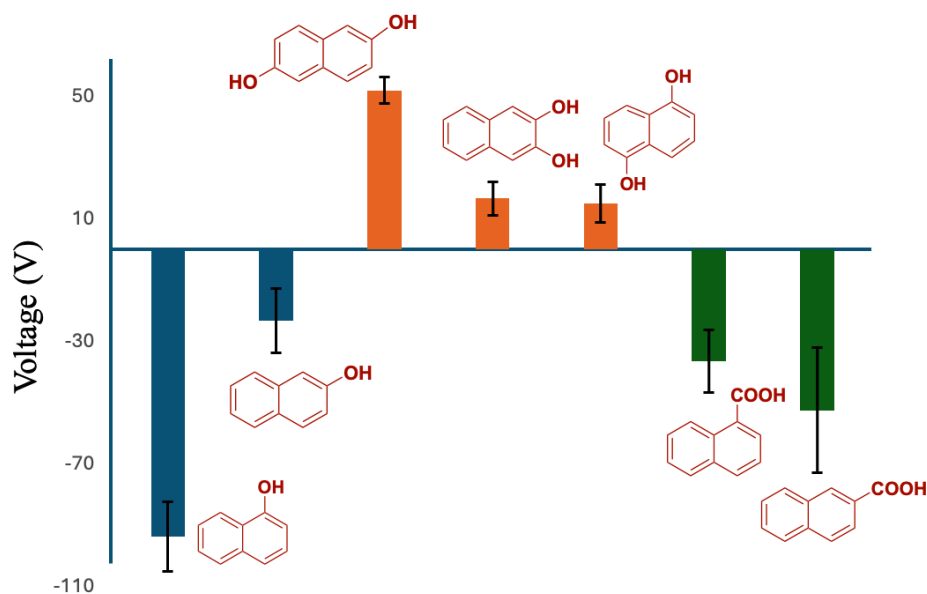


Figure 3.8: The data in Figure 3.6 shows the results for the isomer sets: naphthols (blue bars), dihydroxynaphthalenes (orange bars), and naphthalene carboxylic acids (green bars).

To compare the substituted ring systems, look at naphthols as examples: 1-naphthol acquires charge significantly more than its isomer, 2-naphthol. Among the three dihydroxynaphthalene isomers we investigated, 2,6-dihydroxynaphthalene charged more than the other two. The position of the functional group not only affects the charging propensity but also the charge variability; e.g., the position of the carboxyl group on the aromatic ring appears to affect charge stability since 2-naphthoic acid resulted in a broader range of voltages (ranging from -20 to -74 V) compared to 1-naphthoic acid with a standard deviation of only ± 10.2 V.

3.2.2.4 Charge Dissipation

The charge measured on the powders decayed after waiting for some time. The decay rates may also hint at the mechanisms by which the powders are charged and how the charge decays on these powders. Figure 3.9 presents the decrease in the electrostatic potential of the powders left in the mortar for the given time. The results generally indicate that powders with hydroxyl groups exhibit the fastest decay of accumulated charge compared to other powders. Naphthoic acids, naphthaldehyde, 2-iodonaphthalene, 9,10-dibromanthracene, and generally, the negatively charged powders show low decay rates. The powders of the positively charging unsubstituted fused aromatic molecules, pyrene, perylene, anthracene, and phenanthrene, showed the greatest variability in the charge decay. We surmise that there should be a couple of decay pathways for these compounds, acting at different rates, hence the high variability in the decay rates.

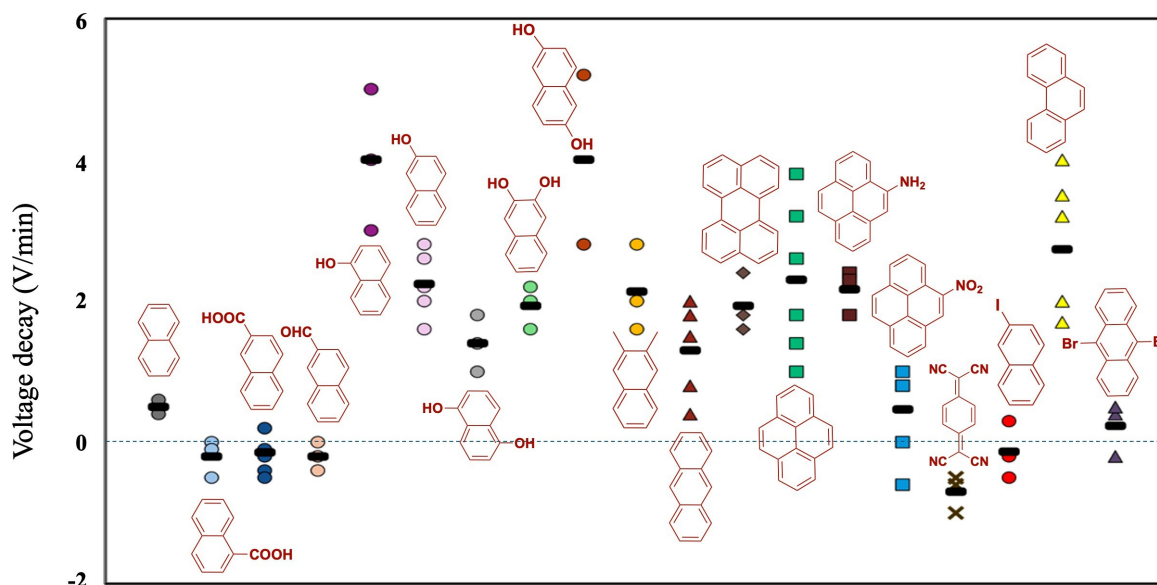


Figure 3.9: The rate of electrostatic potential change (charge decay) in the electrostatic potential of the powders charged (as depicted in Figure 3.6) by grinding and left to stay in the mortar for the given time.

3.2.3 Triboelectric Behavior in the Agate/Steel System

After grinding the powders using the steel pestle, the acquired voltages were recorded and are shown in Figure 3.10, arranged in the same order as the previous two series for comparison (Figures 3.1 and 3.6). By comparing these results with those from the agate/agate setup, we observed that most powders exhibited similar charging behavior in magnitude and polarity. For example, anthracene, pyrene, 2,3-dimethylnaphthalene, and perylene again showed high positive voltages, while 2-naphthaldehyde, 2-iodonaphthalene, and TCNQ remained in the low to moderate charging range. Naphthoic acids still acquired negative voltages in trials, often with relatively high magnitude and larger standard deviation than other powders. 1-Naphthol continued to show the highest average negative voltage of all powders studied (-137.3 ± 10.1 V).

These findings suggest that while the conductivity of the pestle may influence triboelectric behavior [35], it cannot alone account for the observed material-dependent changes. The variability across powders indicates that other factors, such as ease of flow, surface adhesion, and material properties, may have influenced the triboelectrification in these two grinding systems. Further analysis is needed to isolate these contributions before the effect of the pestle's material and conductivity can be reliably interpreted.

3.2.4 Effect of Relative Humidity

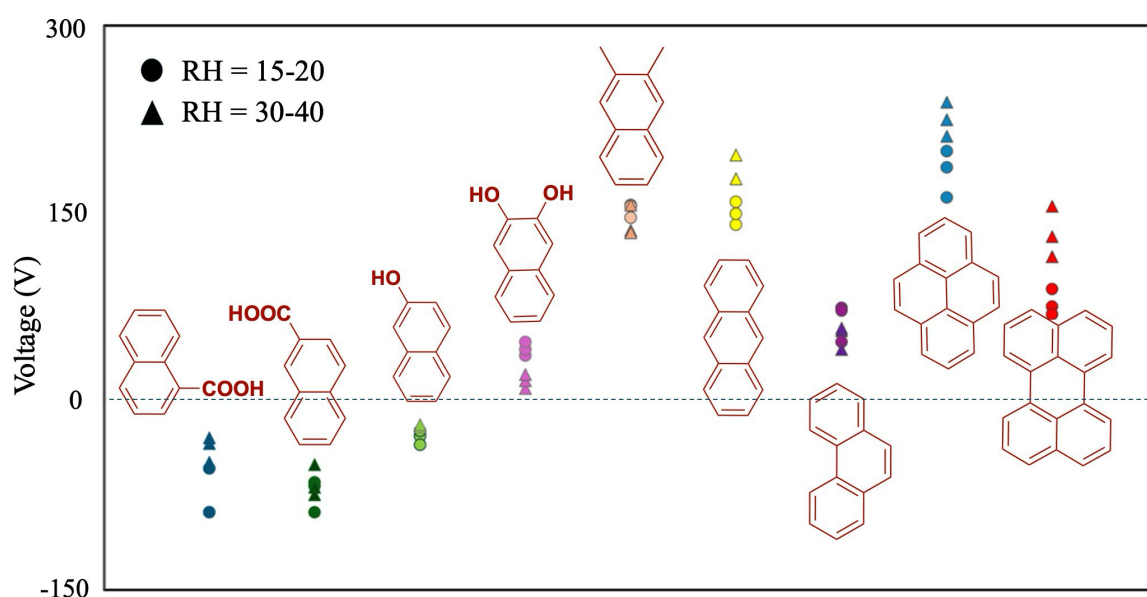


Figure 3.11: The potential difference between each ground powder and a gold electrode after grinding the powders in an agate mortar using an agate pestle at relative humidity of 15-20 % and 30-40% (For details of the measurements, see Experimental section, 2.2.2). The outcome of all the experimental trials (colored dots) is included with an average value (the black dashed lines) for each powder.

As mentioned in the previous chapter, humidity plays a major role in triboelectrification; water can act both as a charge stabilizer and as a charge dissipator. Therefore, we recorded the electric potentials acquired on the powders upon grinding and the decay rates of these values at two different humidities. The electrostatic potential of the powders ground in agate mortar using agate pestle under these two humidity conditions, 15–20 % and 30–40%, is presented in Figure 3.11. Among the tested compounds, 2-naphthoic acid, 2-naphthol, 2,3-dimethylnaphthalene, and phenanthrene exhibited comparable triboelectric voltages across these RH ranges. 2,3-dihydroxynaphthalene obtained a

61.9% lower mean electrostatic potential at higher humidity; In contrast, anthracene, pyrene, and perylene showed notable increases in mean potential at higher humidity, with 23%, 23%, and 72% TE increase, respectively.

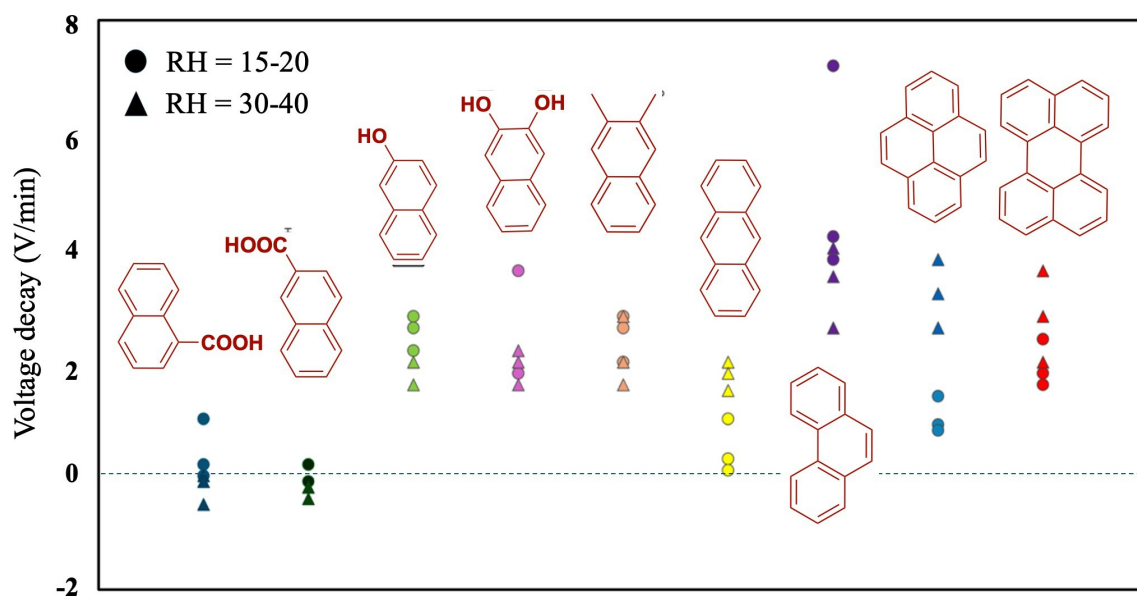


Figure 3.12: The dissipation rate of electrostatic potential of powders ground in agate mortar using an agate pestle over time at relative humidity of 15-20 % and 30-40%

Figure 3.12 shows that the electrostatic potential decays over time with overlapping rates at both humidity ranges for most powders. However, naphthalene derivatives and phenanthrene generally displayed higher decay rates at lower relative humidity. In contrast, anthracene, pyrene, and perylene showed substantially higher mean decay rates at 30–40% RH, with increases of 282.6%, 209.8%, and 45.1%, respectively.

Notably, powders containing carboxyl groups exhibited negligible decay rates, or in some cases, an increase in charge over time in both RH ranges studied. Naphthoic acids' electrostatic charge dissipation, therefore, may not strongly depend on RH in this range. We hypothesize that formation of surface carboxylates (--COO^-) and adsorption of counterions could have led to such slow charge dissipation. Further analysis by in situ XPS and/or ATR-FTIR is required to detect --COO^- formation. Also, performing the experiment under an inert, dry atmosphere can rule out the interactions with water molecules during the time that the powders are left inside the Faraday cage.

3.3 Powders Characterization

3.3.1 Powders Morphology: Fresh vs. Ground

SEM micrographs of powders before and after six minutes of grinding using an agate mortar and agate pestle (in three subsequent two-minute grinding sessions) are shown in 3.13, 3.14, and 3.15. Various shapes, such as spherical, planar, needle-like, and irregular aggregates with different sizes and surface characteristics (ranging from smooth to rough), are observed before grinding. As a result, no single, uniform shape or size can be assumed during the handling and storage of commercial powders, either. This observation further supports the framework of our study, which avoids using artificially uniform or isolated conditions in the experiments. The powders also exhibited varying tendencies for auto-agglomeration [63]. In cases such as naphthalene or 2,3-dimethylnaphthalene, the morphologies predominantly reflected the aggregates formed during production, handling, and storage. If these powders were de-agglomerated before native voltage measurement, their initial charge would change, no longer representing real-life conditions.

Attempts to correlate the native voltage readings with morphology revealed that charging behavior could not be predicted solely based on shape or surface roughness. Considering the particle's shape, planar powders such as 2-naphthoic acid, 2,3-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, pyrene, anthracene, and phenanthrene were charged to various degrees during storage. Needle-like particles such as 1-nitropyrene, 9,10 9,10-dibromoanthracene, and 1-aminopyrene also exhibited significantly different native voltages of -71.5, -1, and +40.7 V, respectively. Surface characteristics also failed to provide a consistent explanation: smooth particles such as anthracene, pyrene, and 9,10-dibromoanthracene displayed low to moderate voltages, while rough-surfaced powders exhibited voltages spanning the full observed range.

Using ImageJ software to analyze the particle size distribution histograms (Figures 3.16 and 3.17, we observed that neither the size ranges nor the size distributions were comparable across all the powders studied. Figure 3.16 indicates that 1,5-dihydroxynaphthalene consisted of very fine, non-agglomerated particles, while pyrene included particles as large as 1400 μm . Even powders with overlapping size ranges exhibited distinct distributions. For example, 1-naphthol and 2-naphthol both contained particles approximately ranging from 10 μm to 250 μm , yet their distributions differed significantly: 81% of the particles in 1-naphthol were below 50 μm , compared to only 21.35% in 2-naphthol.

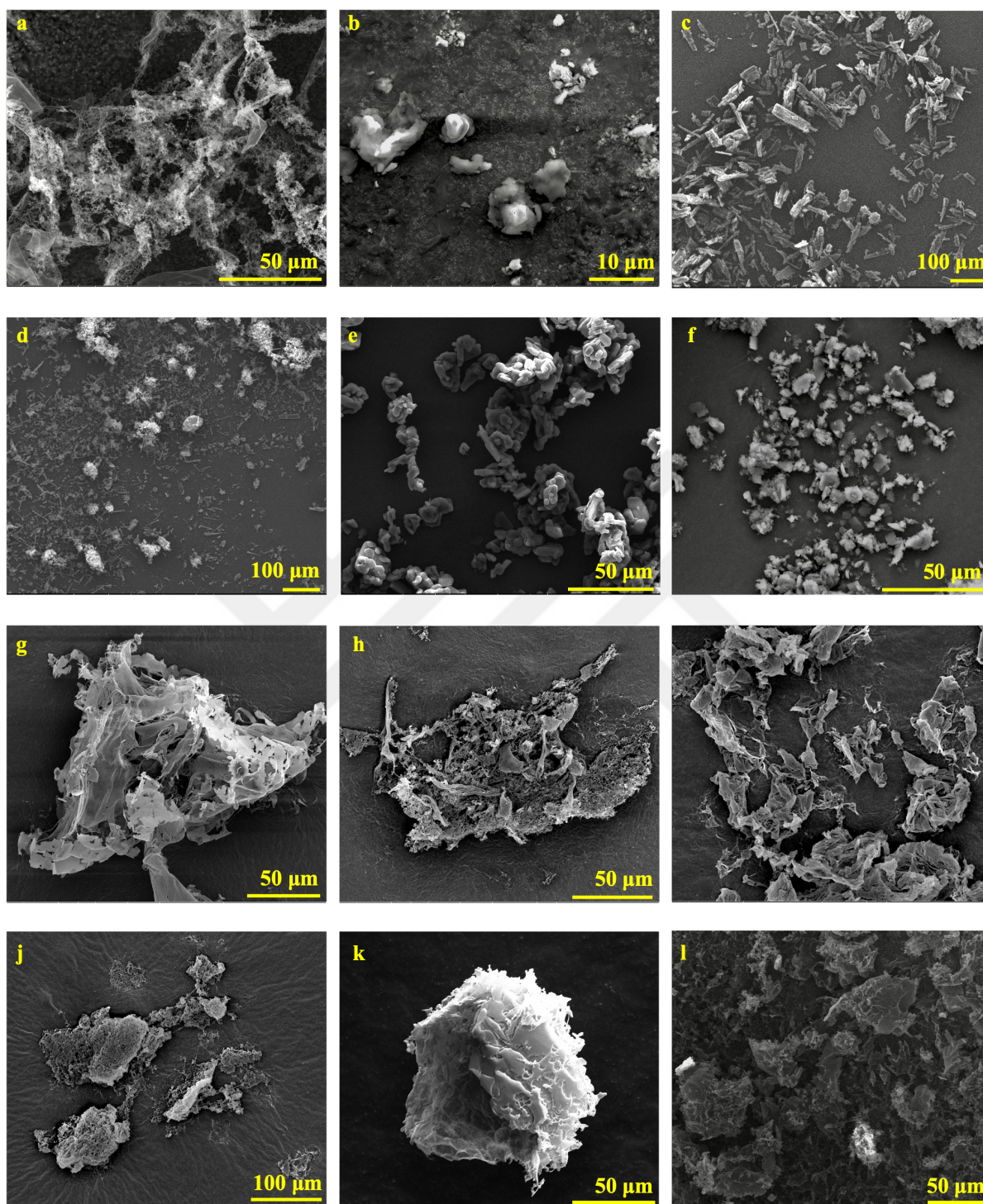


Figure 3.13: SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: naphthalene, c, d: 1-naphthoic acid, e, f: 2-naphthoic acid, g, h: 1-naphthol, i, j: 2-naphthol, k, l: 2-naphthaldehyde.

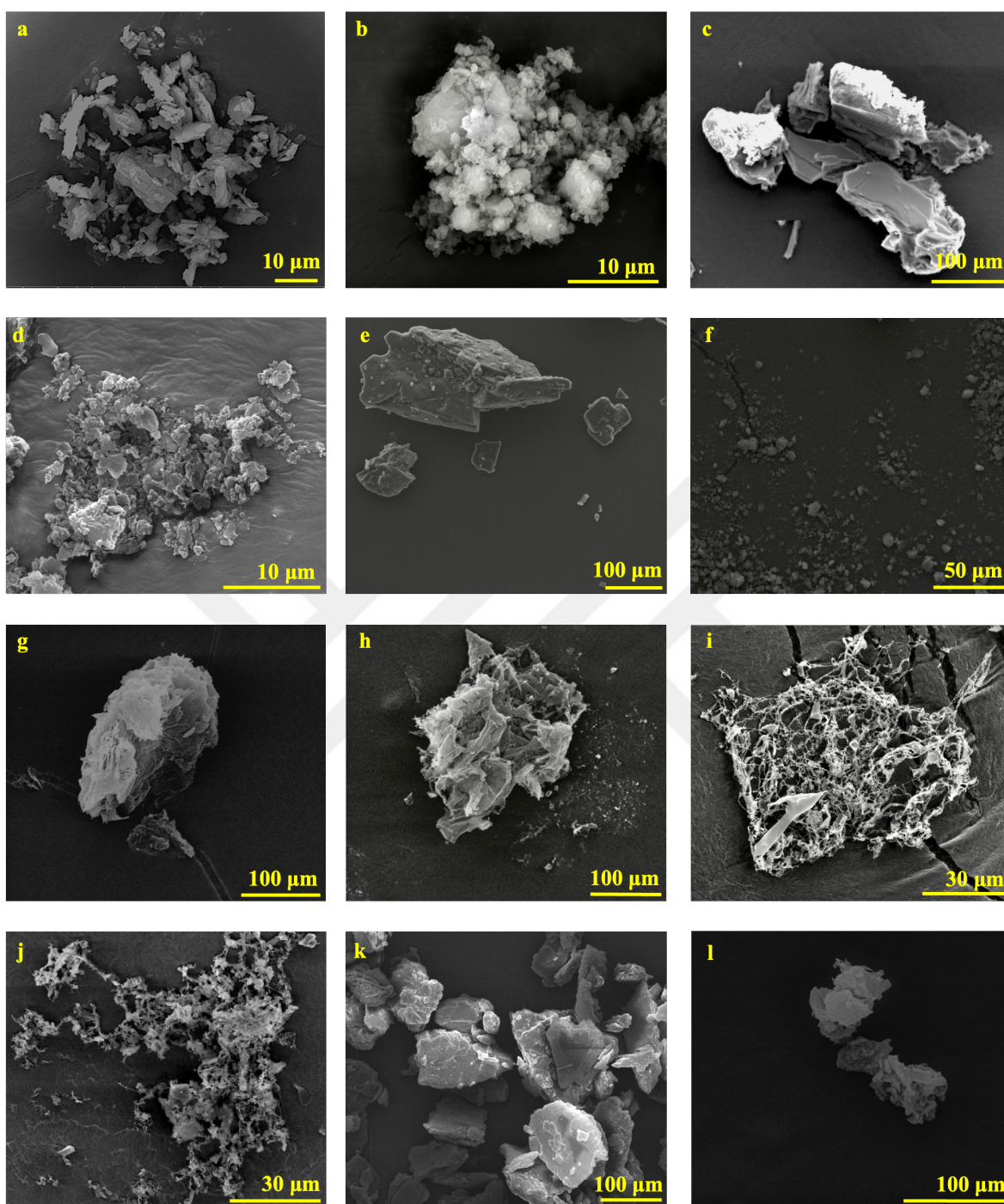


Figure 3.14: SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: 1,5-dihydroxynaphthalene, c, d: 2,3-dihydroxynaphthalene, e, f: 2,6-dihydroxynaphthalene, g, h: 2-iodonaphthalene, i, j: 2,3-dimethylnaphthalene, k, l: phenanthrene.

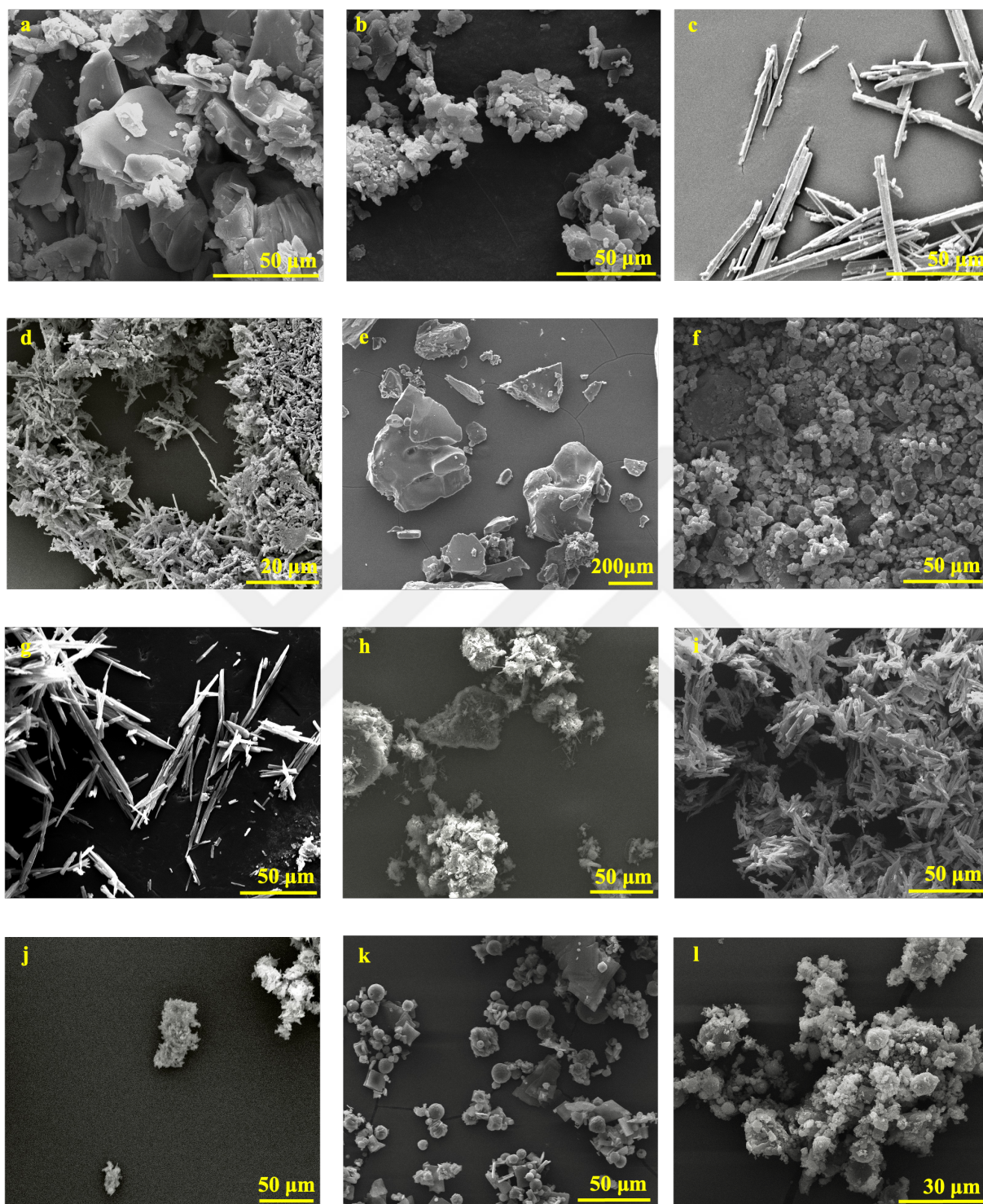


Figure 3.15: SEM micrographs of powders before and after grinding in the agate mortar with the agate pestle, respectively: a, b: anthracene, c,d: 9,10-dibromoanthracene, e, f: pyrene, g,h: 1-aminopyrene, i, j: 1-nitropyrene, k, l: perylene.

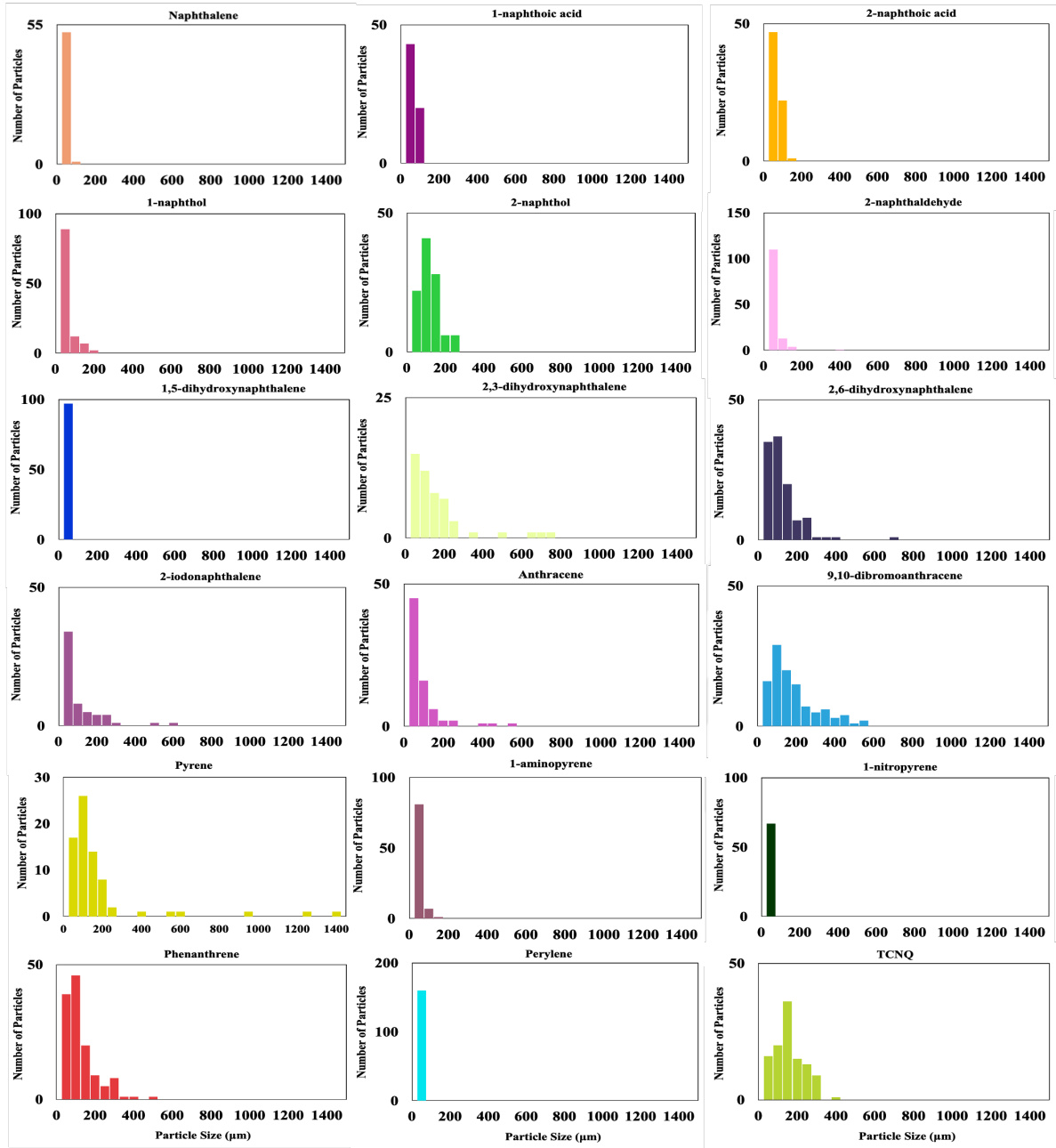


Figure 3.16: Particle size distribution histograms for as-received powders obtained via SEM imaging and ImageJ analyses.

PSD affects interparticle contacts in static powder assemblies, yet it alone cannot account for observed native triboelectric voltages. We observed the largest absolute voltages for 1-nitropyrene, 2-naphthoic acid, and perylene. Although 1-nitropyrene and perylene contain substantial fractions below 50 μm and 2-naphthoic acid exhibits a predominantly medium-sized distribution, other powders with similar PSDs (e.g., 1-aminopyrene and naphthalene) acquired only negligible net charge.

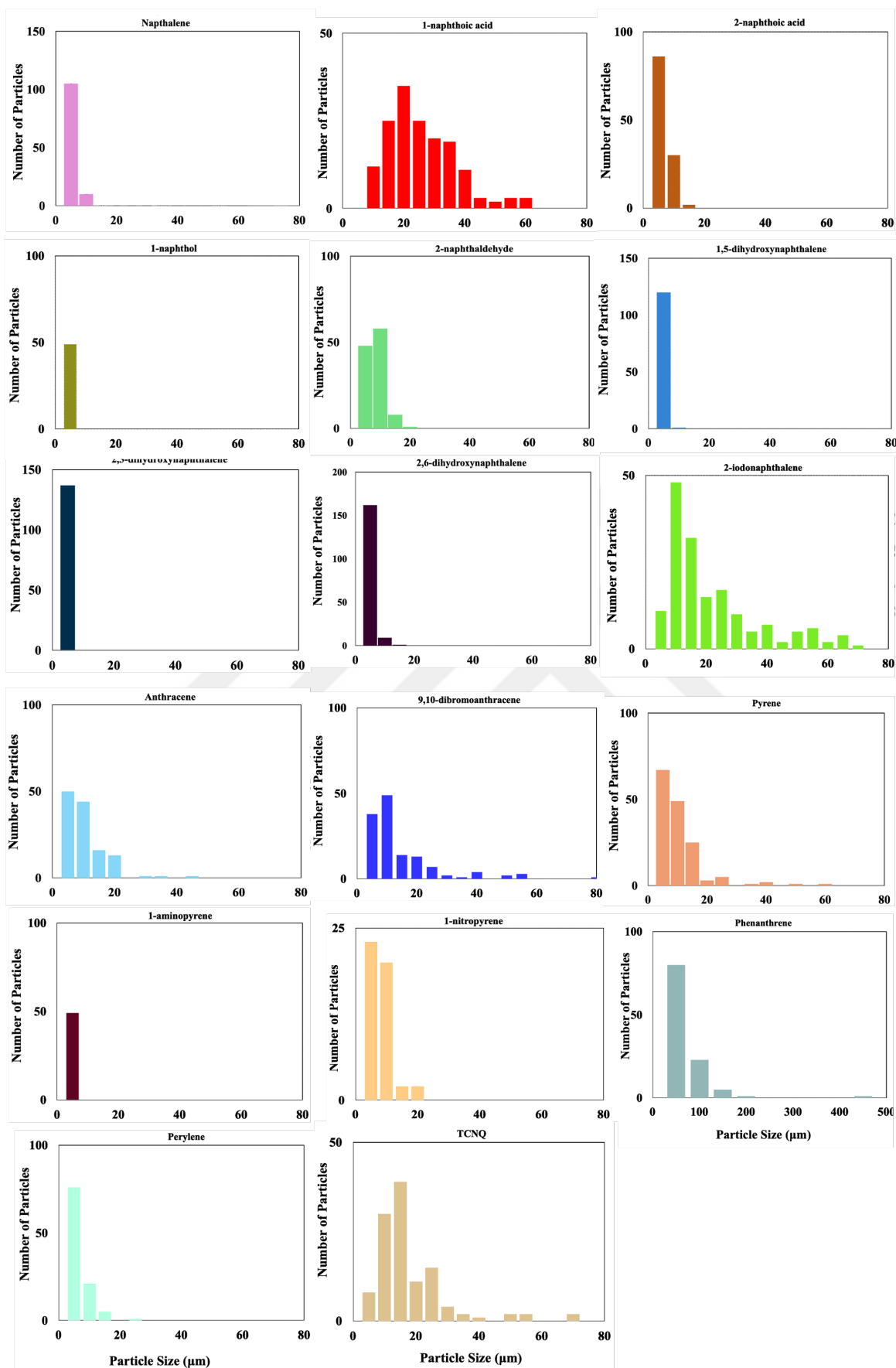


Figure 3.17: Particle size distribution histograms for ground powders obtained via SEM imaging and ImageJ analyses.

Likewise, materials having a broad PSD (2-naphthaldehyde, 2-iodonaphthalene, phenanthrene, anthracene, pyrene, TCNQ, and 9,10-dibromoanthracene) clustered near zero voltage. This is consistent with prior studies that report coarse particles tend to charge positively and fine ones negatively; as a result, a broad PSD may accompany an overall neutrality in powder systems. However, 2,3- and 2,6-dihydroxynaphthalene defied this pattern: despite broad size distributions, they developed medium to high negative voltages (-11.4 ± 8.8 V and -45.7 ± 9.1 V, respectively).

After grinding, most powders retained their overall shape, as seen in Figures 3.13, 3.14, and 3.15. However, all underwent a significant reduction in particle size. As a result, the PSDs became narrower and more uniform (compare Figure 3.16 to Figure 3.17. Most ground powders show a peak PSD within the 10–40 μm range. Even materials with a broader post-grinding PSD, such as pyrene, 9,10-dibromoanthracene, and 2-iodonaphthalene, show a significant reduction compared with their fresh form. The sole exception is 1-naphthoic acid, which retains a comparable PSD before and after grinding; this might be due to having lower grindability than the other powders studied. Also, while many powders remained agglomerated after grinding, naphthalene and 2,3-dimethylnaphthalene became noticeably de-agglomerated under the frictional work applied during grinding.

Although anthracene, pyrene, and perylene acquired high charges during grinding, this does not imply a general correlation between greater particle breakage or deformation and increased triboelectric voltage, as the trend does not hold across all powders. For example, 2,3-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 9,10 9,10-dibromoanthracene, and TCNQ also significantly reduced particle size. However, 2,6-dihydroxynaphthalene obtained a medium-to-high voltage (around 50 V), while the others acquired a low voltage (below 20 V, regardless of sign).

On the other hand, the behavior of 1-naphthoic acid and 2-naphthoic acid may be partially explained by differences in their size reduction upon grinding. 2-Naphthoic acid experienced a greater decrease in particle size and correspondingly exhibited a higher triboelectric potential than 1-naphthoic acid. However, whether this increased charging arises solely from morphological changes remains unclear, as both compounds already showed comparably high (or even higher) negative voltages in their as-received forms.

Interestingly, 1-nitropyrene and 1-aminopyrene displayed lower triboelectric voltages after grinding than their native values. This further suggests that mechanical work and friction do not universally enhance charge accumulation for powders. However, a meaningful comparison between the charging behavior of as-received and ground powders would require that the ground samples be stored in sealed vials for several days, under the

same conditions as those used in the native voltage measurement, and measured while resting on the agate surface in a similar geometry. A quantitative comparison between these two experiments may be problematic without this storage period and measurement setup.

3.3.2 Ground Powders Morphology: Agate Pestle vs. Steel Pestle

Figures 1.7 and 3.10 show that the triboelectric voltage acquired by naphthalene differed significantly depending on the pestle material, with average values of -64.2 V for the agate system and -8.7 V for the steel system. To better understand this contrast, the morphologies of the ground powders were studied using SEM. Very fine white particles were observed (examples shown by red circles in micrographs b and c). However, the sample ground with the agate pestle also contained larger, nearly spherical particles with diameters around 5 μm , which were absent in the steel-ground sample. Instead, the latter showed the formation of fragmented but continuous films, possibly resulting from the smashed-down and elongated bigger particles or even the physical adhesion of smaller particles.

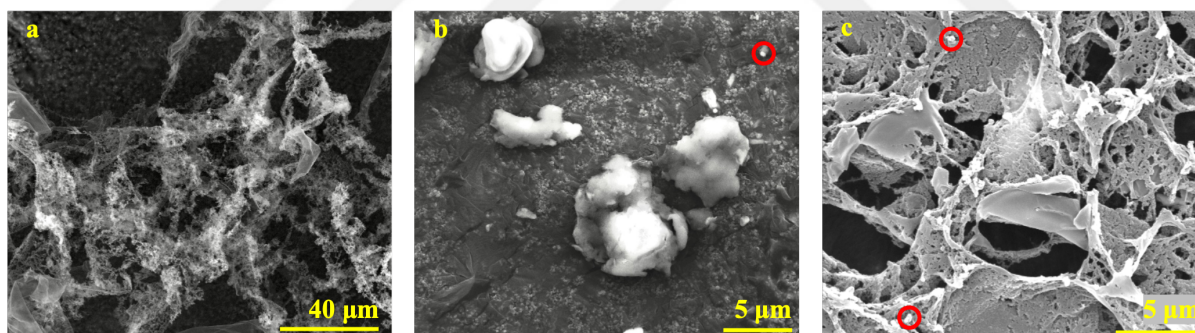


Figure 3.18: SEM micrographs of naphthalene powders: a) as-received, b) ground via agate pestle, and c) ground via steel pestle. Red circles show fine spherical particles.

It was mentioned earlier that naphthalene powders moved more freely under the steel pestle than the agate one. This smoother flow could have enhanced powder mobility, reduced auto-agglomeration, and resulted in a more efficient size reduction. The consequent increase in surface-to-volume ratio may have promoted stronger physical adhesion among the nanoparticles, contributing to the observed film-like morphology.

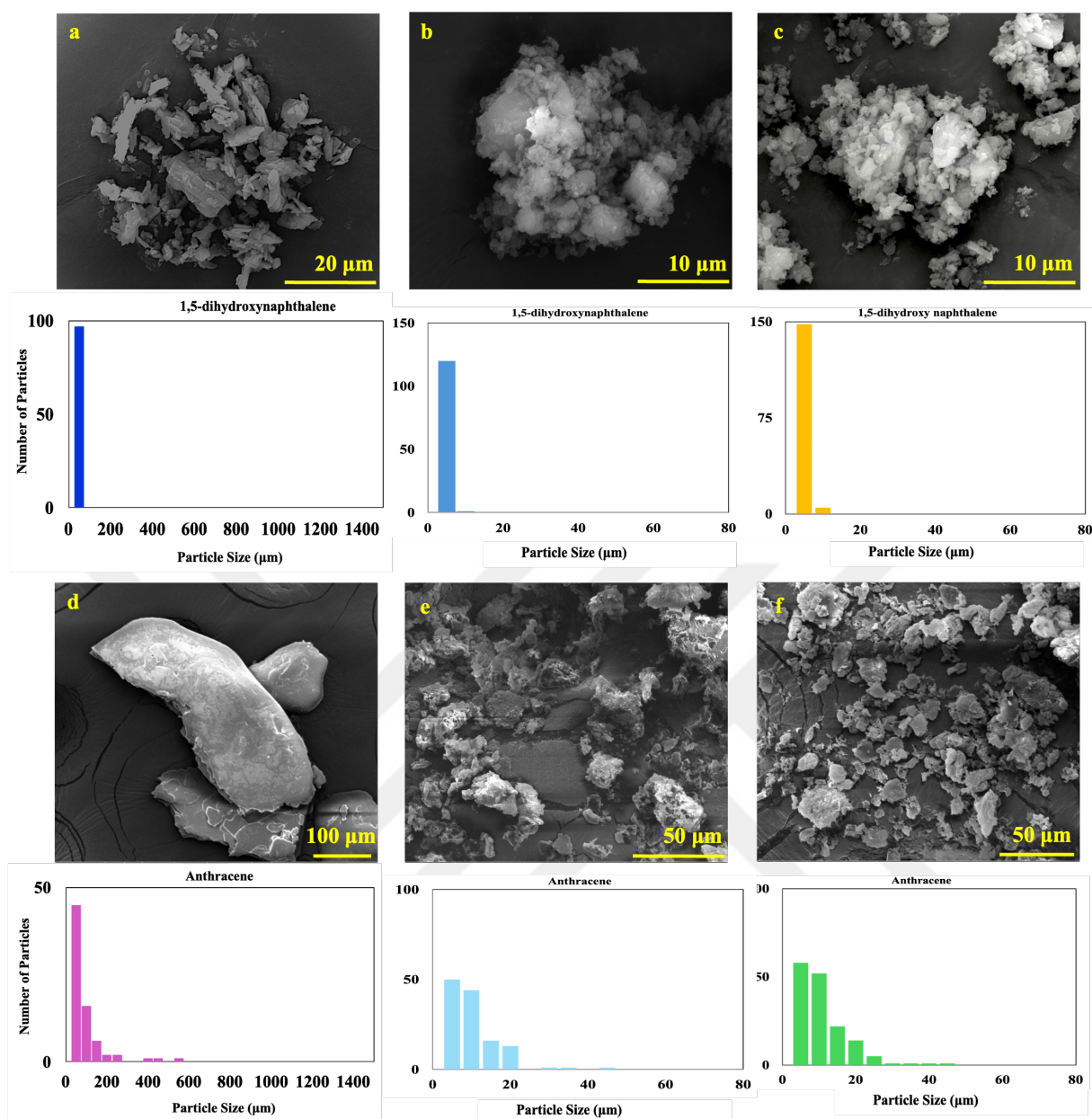


Figure 3.19: SEM micrographs of 1,5-dihydroxynaphthalene (a–c) and anthracene (d–f) in their fresh form (a, d), after grinding with an agate pestle (b, e), and after grinding with a steel pestle (c, f). The corresponding histograms show the PSDs for each condition.

The exact reason for the markedly lower voltage observed after grinding the naphthalene powder with the steel pestle may not be clear. Still, we hypothesize that forming a film-like morphology during the process probably played a key role. As grinding progresses, this adhered layer may suppress particle–particle and particle–wall interactions, which are essential for triboelectric charging. Consequently, the frequency and intensity of contact-separation events likely diminish, leading to reduced charge accumulation.

Apart from naphthalene, several other powders ground using the steel pestle were analyzed by SEM. Figure 3.19 presents representative examples: 1,5-dihydroxynaphthalene, which exhibited similar average voltages when ground with agate (+15 V) and steel (+5 V), and anthracene, which showed a higher voltage when ground with steel (+197 V) compared to agate (+143 V). The SEM micrographs and corresponding PSD histograms suggest that the magnitude of triboelectric potential generated during grinding cannot be explained solely by morphological changes such as particle size reduction. The size range and PSD peaks remained comparable for both powders, whether they were ground using an agate pestle or a steel one. In addition, no significant differences in particle shape were observed (compare Figure 3.15 b to c, and e to f). Despite undergoing similar morphological changes, one compound exhibited similar voltages with both pestles, while the other generated a significantly higher voltage when ground with steel.

This suggests that even when the choice of pestle material does not result in notable morphological changes or affect the grindability of powders, it can still significantly influence charge transfer at the powder–pestle interface. However, the extent of this influence remains highly material-dependent. Therefore, rather than considering only the pestle material's electronic properties (e.g., conductivity) or its mechanical geometry, the triboelectric behavior should be evaluated based on the specific powder–pestle material pairing [60, 71].

3.3.3 X-ray Diffraction Analysis of Fresh and Ground Powders

Grinding can induce various structural changes in crystalline powders, including phase transitions, polymorphic transformations, alterations in crystal structure, and changes in the degree of crystallinity [102–105]. Therefore, XRD analysis is essential to identify possible structural modifications that may influence charge transfer. Figures 3.20, 3.21, and 3.22 display the XRD diffractograms of each powder in its as-received form, after grinding with an agate pestle, and as simulated references.

Most powders' main diffraction peaks remain at approximately the same 2θ positions before and after grinding, suggesting that their overall crystalline phase is preserved after six minutes of hand grinding. However, changes in peak intensities are commonly observed, which may indicate disruption of preferred orientation due to mechanical stress [106].

Some powders, despite having the same main XRD peaks before and after grinding, still show minor alterations in their patterns. In the case of anthracene, a new peak emerges at $2\theta = 38^\circ$ after grinding, and for 2-naphthoic acid, new peaks appear at $2\theta = 11^\circ$ and $2\theta = 15^\circ$. In contrast, some diffraction peaks disappear after grinding; for instance, the peaks at $2\theta = 35^\circ$ and $2\theta = 51^\circ$ in pyrene. This may reflect partial amorphization or loss of certain crystal planes. Therefore, we calculated the degree of crystallinity from the ratio of the integrated area of all crystalline peaks to the total integrated area under the XRD peaks [107] and reported them in + Table 3.1. It should be noted that the results in Table 1 may have up to 3% calculation error, which could explain the increase in the crystallinity degree of some powders, like phenanthrene, after grinding. However, pyrene's 19% increase in its degree of crystallinity after six minutes of hand grinding needs further analysis to determine whether changes in preferred orientation caused an apparent increase in crystallinity degree.

Table 3.1: Crystallinity degree of powders before and after grinding in an agate mortar with an agate pestle.

Compound	Fresh	Ground
Pyrene	66	85
1-Naphthol	80	77
Phenanthrene	72	75
2-Naphthoic acid	80	73
1-Nitropyrene	81	72
TCNQ	81	69
2,3-Dihydroxynaphthalene	78	69
Anthracene	63	65
2-Naphthaldehyde	71	64
2-Naphthol	76	62
Perylene	74	62
1-Naphthoic acid	67	61
1-Aminopyrene	75	61
2,6-Dihydroxynaphthalene	69	60
2,3-Dimethylnaphthalene	60	59
Naphthalene	74	58
1,5-Dihydroxynaphthalene	65	57
2-Iodonaphthalene	48	53

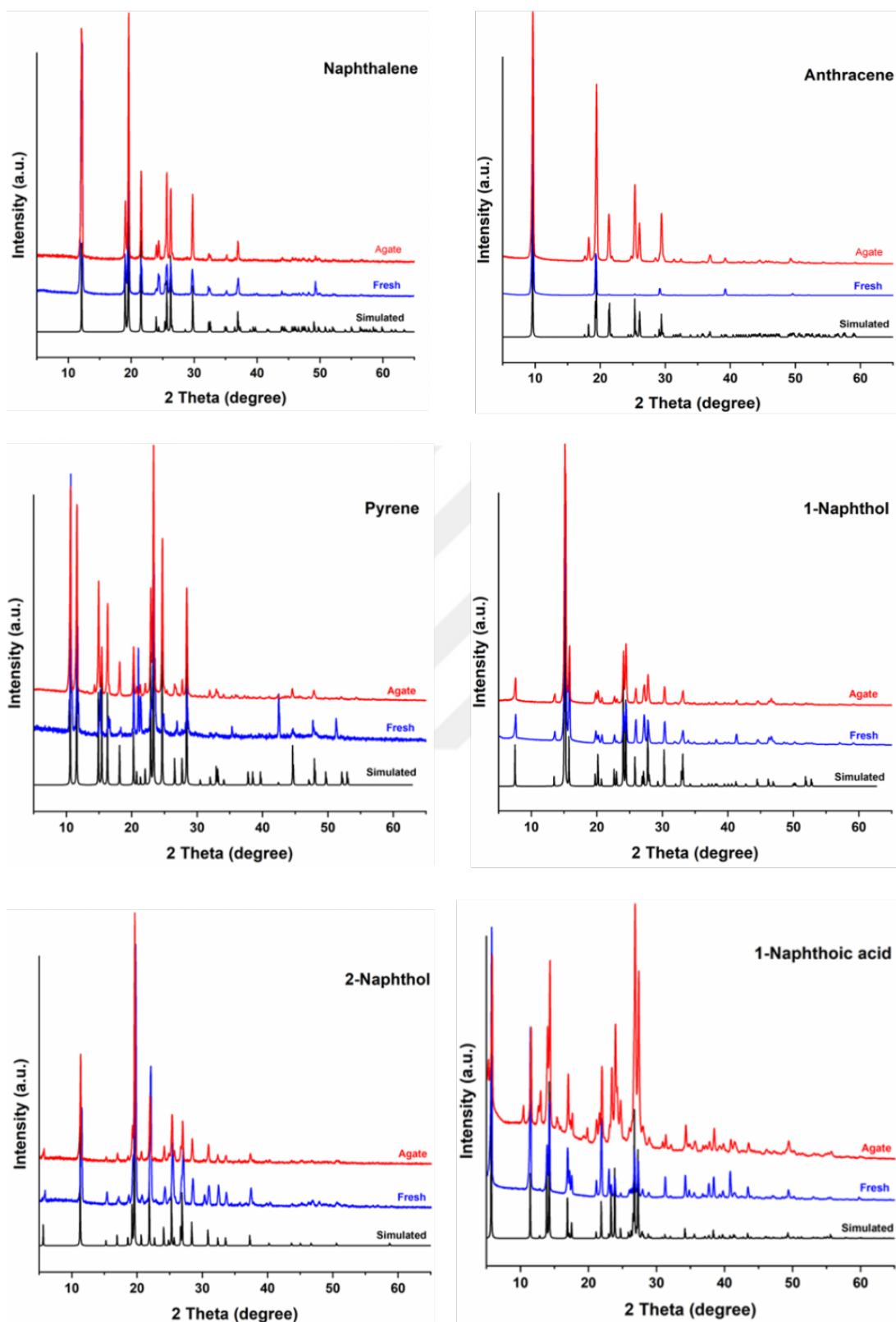


Figure 3.20: XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns.

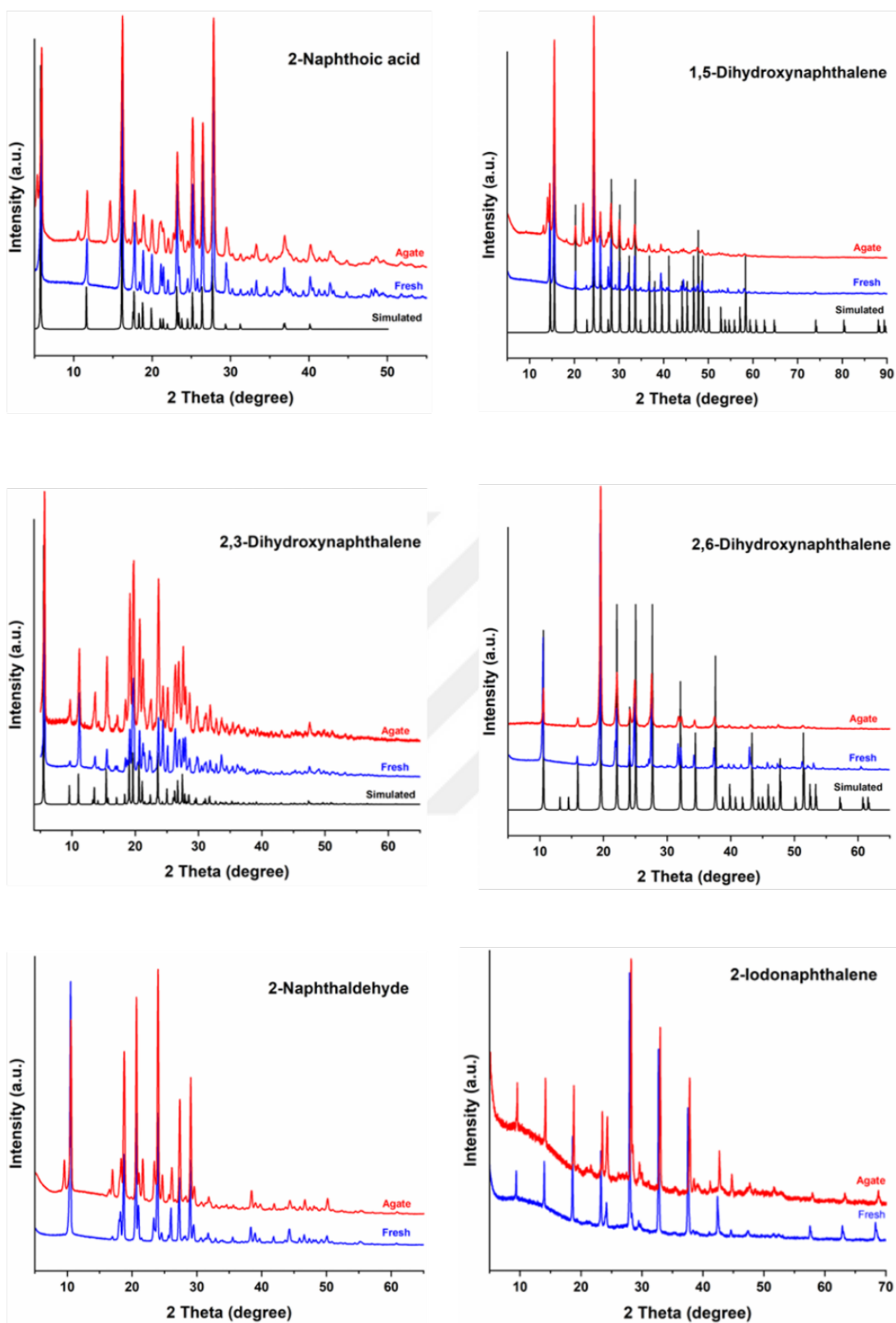


Figure 3.21: XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns (if available).

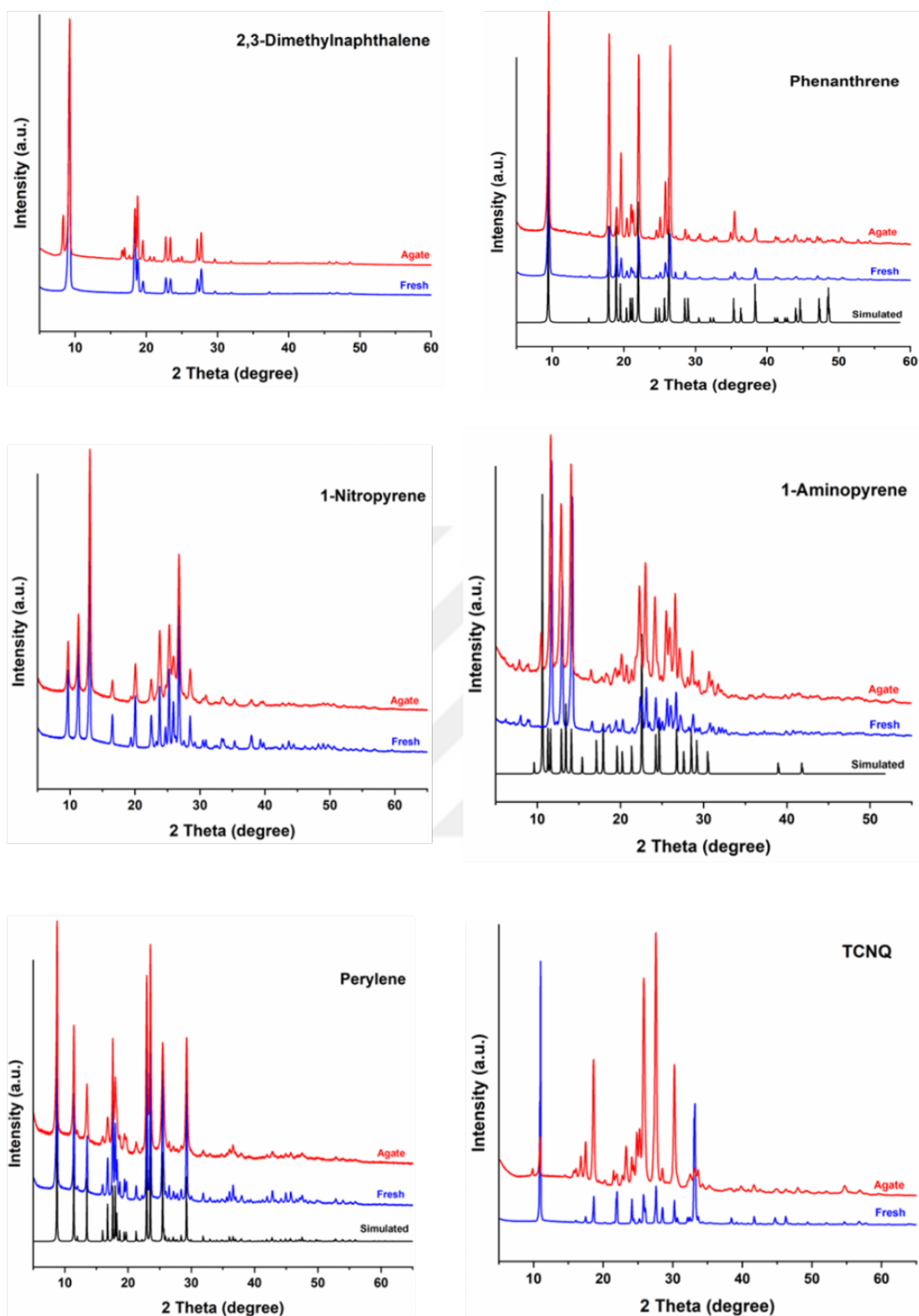


Figure 3.22: XRD diffractograms of powders in their fresh form, after grinding with an agate pestle, and simulated reference patterns (if available).

No straightforward correlation is observed when we plot the change in crystallinity degree of powders caused by grinding against the mean electrostatic potential measured

(Figure 3.23). Powders with small crystallinity degree change (below 5%) can exhibit high average electrostatic potentials, such as -100 V or $+150$ V. Powders with a small crystallinity degree change (below 5%) can exhibit high average electrostatic potentials, such as -100 V or $+150$ V. Similar high electrostatic potentials, including values up to $+150$ V, were also observed in powders that experienced more substantial changes in crystallinity degree (above 15%). Comparably, powders that generate low electrostatic potentials span a wide range of crystallinity changes. This indicates that a high electrostatic potential is linked to neither a slight nor a high shift in crystallinity degree (at least up to 20% seen in our experiments). These findings reinforce that TE is a multi-faceted phenomenon with no single parameter as the primary driver—particularly under real-world or non-isolated laboratory conditions.

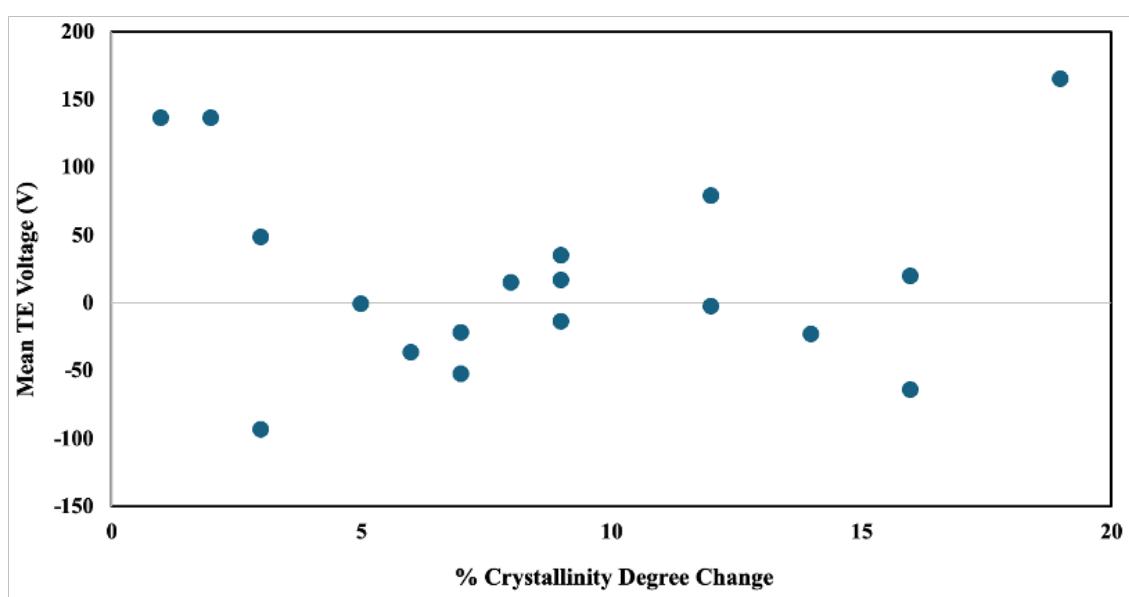


Figure 3.23: Mean electrostatic potential generated during grinding in an agate mortar using an agate pestle, plotted against the percentage change in crystallinity degree between the fresh and ground powder.

3.4 Binary Powder Mixtures

3.4.1 Electrostatic Potential Measurements of Binary Powders

According to the experimental framework of **Section 2.2.4**, we ground mixtures of pyrene and naphthalene at different mass ratios using an agate mortar and agate pestle. The voltage–time plots shown in Figure 3.24 display high positive voltages (above $+50$ V) for pure pyrene powders and moderately negative voltages (between -20 V and -40 V) for pure naphthalene powders. When mixed, the voltage generated for all mass ratios appears to lie between the individual voltages of pyrene and naphthalene. Notice that the

magnitude does not follow a linear trend concerning the mass ratio. Instead, the mixture with a 3:1 mass ratio of naphthalene to pyrene (N3.P1) exhibits the highest positive voltage among the mixtures (+80 V) in its second and third grinding trials, even though one might expect that the high naphthalene content (being the more negative component) would shift the voltage closer to that of pure naphthalene.

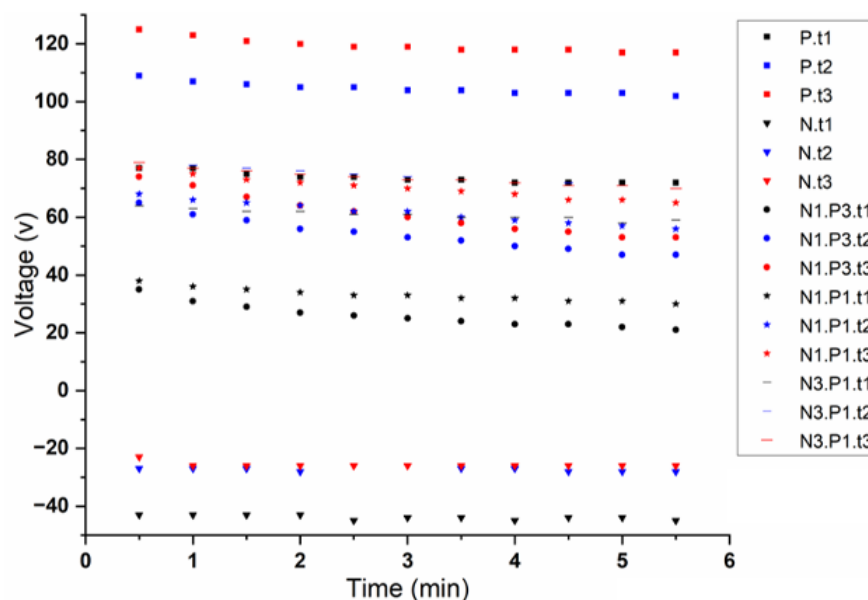


Figure 3.24: Voltage vs. Time plots for pyrene (P), naphthalene (N), and naphthalene/pyrene mixtures (N.P) at different mass ratios (1:1, 1:3, 3:1). The letter t in the legends indicates the number of successive grinding trials using agate/agate mortar and pestle.

This suggests that while the electrification in our system is governed by surface charge transfer, it does not scale proportionally with mass ratio. This outcome is reasonable, given that naphthalene and pyrene differ in chemical structure, π -stacking ability, and conjugation, which likely influence their respective roles in contact electrification. Their differing molar masses and surface interactions mean they cannot be treated as simple oppositely charged ions whose contribution to tribocharging is strictly additive or symmetrical.

We studied the TE behavior of 1-nitropyrene and 1-aminopyrene mixtures to further explore the charge transfer mechanism at a 1:1 molar ratio. The idea here was to use compounds with more clearly defined electron-donating and electron-withdrawing characteristics. As shown in Figure 3.25, pure 1-aminopyrene acquired a low positive voltage ($+8\pm3\text{V}$), while 1-nitropyrene exhibited a medium to high negative voltage ($-42\pm7\text{V}$). In their mixture, however, no or minimal charging was observed ($0\pm2\text{V}$).

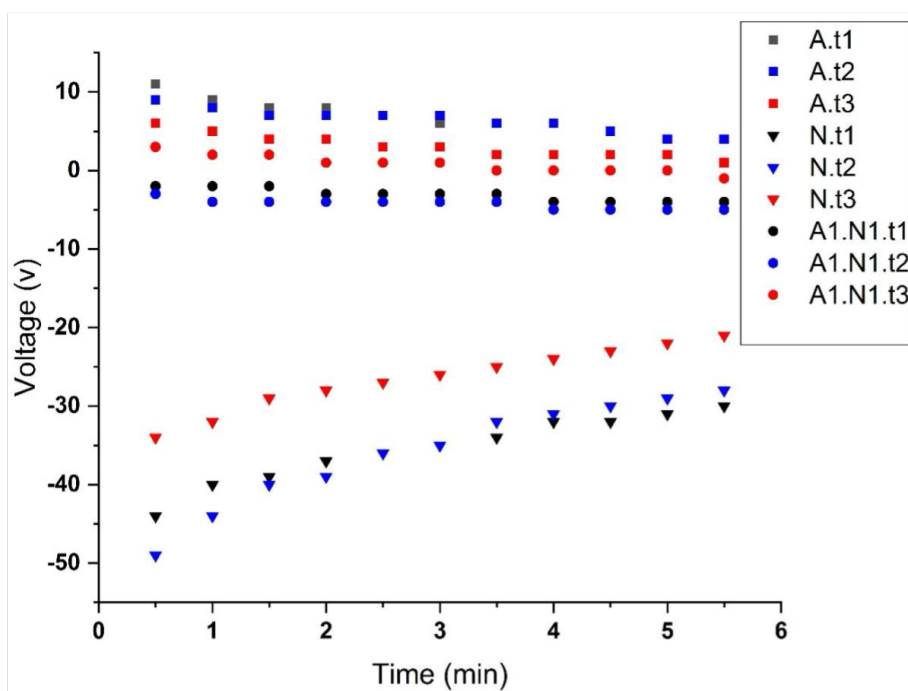


Figure 3.25: Voltage vs. Time plots for 1-nitropyrene (N), 1-aminopyrene (A) and their 1:1 molar mixture. The letter t in the legends indicates the number of successive grinding trials using agate/agate mortar and pestle.

While 1-nitropyrene accumulates a significant negative charge in isolation, even in a storage vial, likely due to its electron-withdrawing character and lack of relaxation paths, one might initially expect that adding an electron-donating compound like 1-aminopyrene would intensify this effect by pushing more electrons toward the acceptor. However, in triboelectric systems, where charge builds up due to limited conductivity and asymmetric contact events [13], chemically defined donor–acceptor species offer a route for charge equilibration. Rather than enhancing charge separation, the system shifts toward neutralization. The triboelectric charging in such mixtures is possibly not governed purely by molecular electron donor–acceptor behavior, but also by the interfacial dynamics of contact electrification.

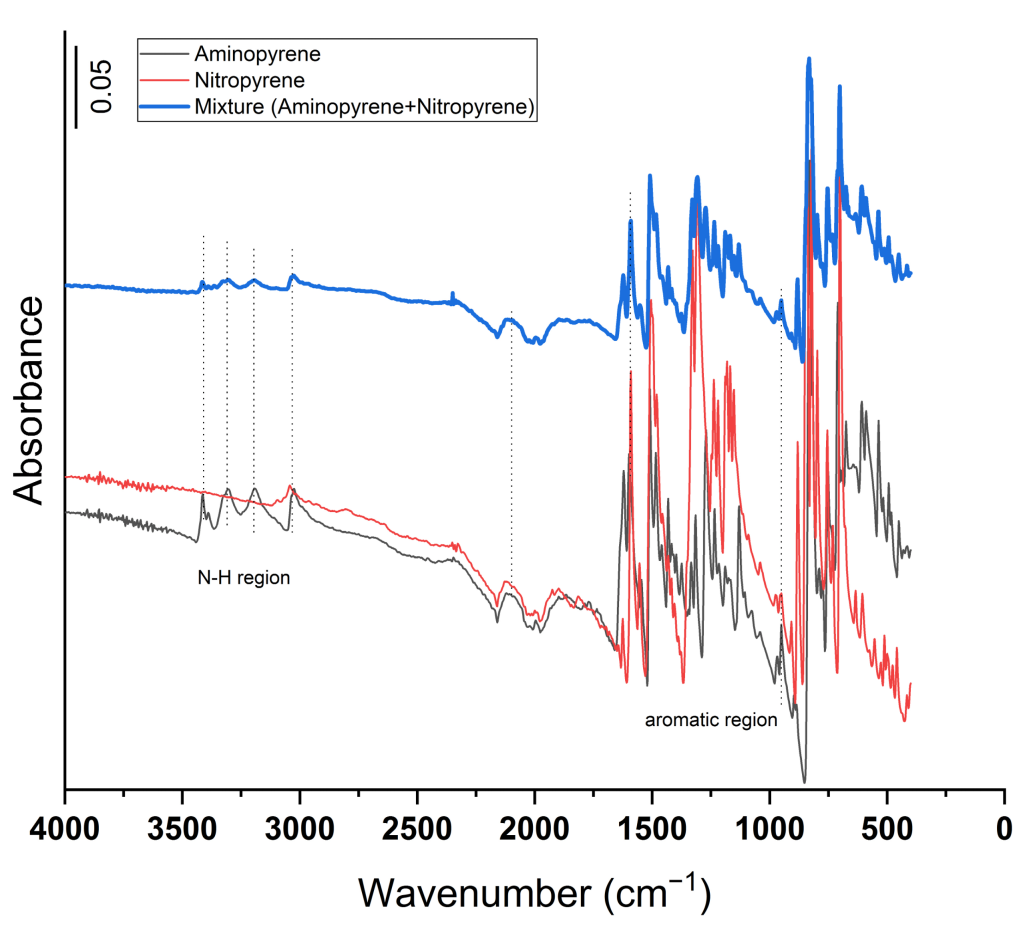


Figure 3.26: ATR-IR spectra of 1-aminopyrene, 1-nitropyrene and their 1:1 molar mixture

3.4.2 ATR Data

We performed ATR spectroscopy as a surface-sensitive technique to detect vibrational peak shifts in the mixture compared to the pure samples, which would indicate the formation of a permanent charge transfer complex due to interactions between the donor and acceptor in the system [108]. However, Figure 3.26 shows that the absorption peaks in the range of 800 to 1700 cm^{-1} , belonging to the aromatic groups of aminopyrene and nitropyrene [109], are present in the mixture without noticeable shifts. This aligns with our binary powder mixture's observed neutral triboelectric behavior, indicating that while no stable charge transfer complex forms at rest, the mechanical action of grinding and contact between particles enables transient charge redistribution and interfacial charge compensation.

Chapter 4

Conclusion and Future Work

In this work, we studied the native and mechanically induced electrification (through hand grinding) of aromatic powders. Though the triboelectrification, in essence, is a highly challenging phenomenon where obtaining reproducible data can sometimes be impossible, several consistent trends were seen in our experiments.

Our results indicate that the material's chemical structure indeed matters in how the bulk powder behaves in complex settings where numerous particle/particle and particle/wall interactions exist. The sign and magnitude of the electrostatic potential seem to depend on the number of fused rings, the types of substituents, and their position, at least to a significant degree.

Native voltage measurements indicated that hydroxyl- and carboxyl-bearing naphthalene derivatives typically acquire negative voltages, while amino- and methyl-substituted systems tend to charge positively. By applying mechanical force and enhancing the frictional interactions through grinding, unsubstituted fused aromatics generally produced significantly large positive voltages. Different functional groups may have changed the electric paths available in the system since some, like bromine, iodine, and cyano, prevented the high charging of powders. Isomerism also mattered: positional changes on the ring produced distinct charging trends and variabilities (e.g., 1- vs 2-naphthol; dihydroxynaphthalene isomers), showing that local electronic structure and adsorption geometry influence charge transfer.

As with all powder systems, the powder's characteristics and environmental conditions should not be overlooked. Since we aimed to design the experiments comparable with powder electrification in open systems of everyday encounters or industrial settings, we deliberately did not isolate any contributing factors. However, the interplay of powder's characteristics, materials properties, and environmental conditions was observable in our

results, each affecting the triboelectric charging to a degree.

Binary mixtures of pyrene/naphthalene and 1-aminopyrene/1-nitropyrene showed that the electrostatic voltage of such systems is significantly governed by the electron-donating and electron-withdrawing nature of the pair rather than through a ‘summation’ of individual powder characteristics, as the static voltage obtained in either studied pair was somewhere between the static voltages of their pure components. The mixture of 1-nitropyrene and 1-aminopyrene ATR-IR analysis did not show a significant shift compared to the pure 1-nitro- and 1-aminopyrene, proving that the powders do not form a significant amount of the charge transfer complex. Nevertheless, we hypothesize that even a minute amount of donor–acceptor pairs forming through grinding helps the fast dissipation of charge in these mixtures. As future work, we plan to study more pairs to understand the underlying mechanisms better.



Bibliography

- [1] D. Halliday, R. Resnick, and J. Walker, *Fundamentals of Physics*. John Wiley & Sons, 2013.
- [2] D. J. Lacks and T. Shinbrot, “Long-standing and unresolved issues in triboelectric charging,” *Nature Reviews Chemistry*, vol. 3, no. 8, pp. 465–476, 2019.
- [3] S. L. Miller, “A production of amino acids under possible primitive earth conditions,” *Science*, vol. 117, no. 3046, pp. 528–529, 1953.
- [4] S. L. Miller and H. C. Urey, “Organic compound synthesis on the primitive earth: Several questions about the origin of life have been answered, but much remains to be studied,” *Science*, vol. 130, no. 3370, pp. 245–251, 1959.
- [5] A. Ohsawa, “Brush and propagating brush discharges on insulating sheets in contact with a grounded conductor,” *Journal of Electrostatics*, vol. 88, pp. 171–176, 2017.
- [6] P. Tamminen, L. Ukkonen, and L. Sydänheimo “Correlation of component human body model and charged device model qualification levels with electrical failures in electronics assembly,” *Journal of Electrostatics*, vol. 79, pp. 38–44, 2016.
- [7] F. A. J. L. James and M. Ray, “Science in the pits: Michael Faraday, Charles Lyell and the home office enquiry into the explosion at Haswell Colliery, county Durham, in 1844,” *History and Technology*, vol. 15, no. 3, pp. 213–231, 1999.
- [8] M. Glor, “Ignition hazard due to static electricity in particulate processes,” *Powder Technology*, vol. 135, pp. 223–233, 2003.
- [9] P. Iversen and D. J. Lacks, “A life of its own: The tenuous connection between Thales of Miletus and the study of electrostatic charging,” *Journal of Electrostatics*, vol. 70, no. 3, pp. 309–311, 2012.

- [10] W. Gilbert, *De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure: Physiologia nova, plurimis & argumentis, & experimentis demonstrata*. London: Peter Short, 1600.
- [11] A. K. T. Assis, *The experimental and historical foundations of electricity*. Apeiron Montreal, 2010.
- [12] J. Canton, “Xciii. A letter to the right honourable the earl of Macclesfield, president of the Royal Society, concerning some new electrical experiments, by John Canton, M.A. and F.R.S.,” *Philosophical Transactions of the Royal Society of London*, no. 48, pp. 780–785, 1753.
- [13] H. T. Baytekin, A. Z. Patashinski, M. Branicki, B. Baytekin, S. Soh, and B. A. Grzybowski, “The mosaic of surface charge in contact electrification,” *Science*, vol. 333, no. 6040, pp. 308–312, 2011.
- [14] S. Matsusaka, H. Maruyama, T. Matsuyama, and M. Ghadiri, “Triboelectric charging of powders: A review,” *Chemical Engineering Science*, vol. 65, no. 22, pp. 5781–5807, 2010.
- [15] H. Zou, Y. Zhang, L. Guo, P. Wang, X. He, G. Dai, H. Zheng, C. Chen, A. C. Wang, C. Xu, *et al.*, “Quantifying the triboelectric series,” *Nature Communications*, vol. 10, no. 1, p. 1427, 2019.
- [16] F.-R. Fan, L. Lin, G. Zhu, W. Wu, R. Zhang, and Z. L. Wang, “Transparent triboelectric nanogenerators and self-powered pressure sensors based on micropatterned plastic films,” *Nano Letters*, vol. 12, no. 6, pp. 3109–3114, 2012.
- [17] X. Zheng, R. Zhang, and H. Huang, “Theoretical modeling of relative humidity on contact electrification of sand particles,” *Scientific Reports*, vol. 4, no. 1, p. 4399, 2014.
- [18] J. Hu, P. Gu, Q. Zhou, C. Liang, D. Liu, and X. Chen, “Experimental and modeling study on sliding and rolling electrification mechanisms,” *Powder Technology*, vol. 340, pp. 484–494, 2018.
- [19] C. Xu, Y. Zi, A. C. Wang, H. Zou, Y. Dai, X. He, P. Wang, Y.-C. Wang, P. Feng, D. Li, *et al.*, “On the electron-transfer mechanism in the contact-electrification effect,” *Advanced materials*, vol. 30, no. 15, p. 1706790, 2018.
- [20] W. Harper, “The volta effect as a cause of static electrification,” *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 205, no. 1080, pp. 83–103, 1951.

- [21] G. Castle and L. Schein, “General model of sphere-sphere insulator contact electrification,” *Journal of Electrostatics*, vol. 36, no. 2, pp. 165–173, 1995.
- [22] E. Gutman and G. Hartmann, “Triboelectric properties of two-component developers for xerography,” *Journal of Imaging Science and Technology*, vol. 36, no. 4, pp. 335–349, 1992.
- [23] U. Zafar, F. Alfano, and M. Ghadiri, “Evaluation of a new dispersion technique for assessing triboelectric charging of powders,” *International Journal of Pharmaceutics*, vol. 543, no. 1-2, pp. 151–159, 2018.
- [24] J. Lowell and A. Rose-Innes, “Contact electrification,” *Advances in Physics*, vol. 29, no. 6, pp. 947–1023, 1980.
- [25] S. R. Waitukaitis, V. Lee, J. M. Pierson, S. L. Forman, and H. M. Jaeger, “Size-dependent same-material tribocharging in insulating grains,” *Physical Review Letters*, vol. 112, no. 21, p. 218001, 2014.
- [26] Z. L. Wang and A. C. Wang, “On the origin of contact-electrification,” *Materials Today*, vol. 30, pp. 34–51, 2019.
- [27] M. Kornfeld, “Frictional electrification,” *Journal of Physics D: Applied Physics*, vol. 9, no. 8, p. 1183, 1976.
- [28] A. F. Diaz and R. M. Felix-Navarro, “A semi-quantitative tribo-electric series for polymeric materials: The influence of chemical structure and properties,” *Journal of Electrostatics*, vol. 62, pp. 277–290, 11 2004.
- [29] S. Naik, R. Mukherjee, and B. Chaudhuri, “Triboelectrification: A review of experimental and mechanistic modeling approaches with a special focus on pharmaceutical powders,” *International Journal of Pharmaceutics*, vol. 510, no. 1, pp. 375–385, 2016.
- [30] A. Rescaglio, F. De Smet, L. Aerts, and G. Lumay, “Tribo-electrification of pharmaceutical powder blends,” *Particulate Science and Technology*, vol. 37, pp. 1020–1027, 11 2019.
- [31] C. Rezende, R. Gouveia, M. Da Silva, and F. Galembeck, “Detection of charge distributions in insulator surfaces,” *Journal of Physics: Condensed Matter*, vol. 21, no. 26, p. 263002, 2009.
- [32] J. Kolehmainen, P. Sippola, O. Raitanen, A. Ozel, C. M. Boyce, P. Saarenrinne, and S. Sundaresan, “Effect of humidity on triboelectric charging in a vertically vibrated granular

- bed: Experiments and modeling,” *Chemical Engineering Science*, vol. 173, pp. 363–373, 2017.
- [33] J. A. Wiles, M. Fialkowski, M. R. Radowski, G. M. Whitesides, and B. A. Grzybowski, “Effects of surface modification and moisture on the rates of charge transfer between metals and organic materials,” *The Journal of Physical Chemistry B*, vol. 108, no. 52, pp. 20296–20302, 2004.
- [34] B. R. Conway and M. U. Ghorji, “Triboelectrification of Pharmaceutical powders: A critical review,” *British Journal of Pharmacy*, vol. 3, 12 2018.
- [35] A. Elajnaif, P. Carter, and G. Rowley, “Electrostatic characterisation of inhaled powders: effect of contact surface and relative humidity,” *European journal of pharmaceutical sciences*, vol. 29, no. 5, pp. 375–384, 2006.
- [36] O. Verners, L. Lapčinskis, P. C. Sherrell, and A. Šutka, “Contact electrification at dielectric polymer interfaces: on bond scission, material transfer, and electron transfer,” *Advanced Materials Interfaces*, vol. 10, no. 36, p. 2300562, 2023.
- [37] B. Baytekin, H. T. Baytekin, and B. A. Grzybowski, “What really drives chemical reactions on contact charged surfaces?” *Journal of the American Chemical Society*, vol. 134, pp. 7223–7226, 5 2012.
- [38] T. Siu, J. Cotton, G. Mattson, and T. Shinbrot, “Self-sustaining charging of identical colliding particles,” *Physical Review E*, vol. 89, no. 5, p. 052208, 2014.
- [39] A. Šutka, L. Lapčinskis, D. He, H. Kim, J. D. Berry, J. Bai, M. Knite, A. V. Ellis, C. K. Jeong, and P. C. Sherrell, “Engineering polymer interfaces: a review toward controlling triboelectric surface charge,” *Advanced Materials Interfaces*, vol. 10, no. 26, p. 2300323, 2023.
- [40] H. T. Baytekin, B. Baytekin, J. T. Incorvati, and B. A. Grzybowski, “Material transfer and polarity reversal in contact charging,” *Angewandte Chemie- International Edition*, vol. 51, no. 20, p. 4843, 2012.
- [41] R. K. Pandey, H. Kakehashi, H. Nakanishi, and S. Soh, “Correlating material transfer and charge transfer in contact electrification,” *The Journal of Physical Chemistry C*, vol. 122, no. 28, pp. 16154–16160, 2018.
- [42] S. Piperno, H. Cohen, T. Bendikov, M. Lahav, and I. Lubomirsky, “Absorption vs. redox reduction of Pd^{2+} and Cu^{2+} on triboelectrically and naturally charged dielectric polymers,” *Physical Chemistry Chemical Physics*, vol. 14, no. 16, pp. 5551–5557, 2012.

- [43] M. Sow, R. Widenor, A. Kumar, S. W. Lee, D. J. Lacks, and R. M. Sankaran, "Strain-induced reversal of charge transfer in contact electrification," *Angewandte Chemie International Edition*, vol. 51, no 11, pp. 2695–2697, 2012.
- [44] C. A. Mizzi, A. Y. Lin, and L. D. Marks, "Does flexoelectricity drive triboelectricity?" *Physical Review Letters*, vol. 123, 9 2019.
- [45] M. Kamiyama, M. Maeda, H. Okutani, K. Koyama, H. Matsuda, Y. Sano, "Effect of Functional Groups on the Triboelectric Charging Property of Polymer Particles" *Applied Polymer Science*, vol 51, 1667-1671, 1994.
- [46] K.-i. Tanoue, K. Morita, H. Maruyama, and H. Masuda, "Influence of functional group on the electrification of organic pigments," *AIChE Journal*, vol. 47, no. 11, pp. 2419–2424, 2001.
- [47] K. W. Biegaj, M. G. Rowland, T. M. Lukas, and J. Y. Heng, "Surface chemistry and humidity in powder electrostatics: A comparative study between tribocharging and corona discharge," *Acs Omega*, vol. 2, no. 4, pp. 1576–1582, 2017.
- [48] K.-E. Byun, Y. Cho, M. Seol, S. Kim, S.-W. Kim, H.-J. Shin, S. Park, and S. Hwang, "Control of triboelectrification by engineering surface dipole and surface electronic state," *ACS applied materials & interfaces*, vol. 8, no. 28, pp. 18519–18525, 2016.
- [49] J. Landauer, F. Aigner, M. Kuhn, and P. Foerst, "Effect of particle-wall interaction on triboelectric separation of fine particles in a turbulent flow," *Advanced Powder Technology*, vol. 30, no. 5, pp. 1099–1107, 2019.
- [50] S. Mohanta, S. Rath, and R. Dwari, "Surface functionalization of coal and quartz with aniline: A study on work function and frictional charge," *Powder Technology*, vol. 338, pp. 233–242, 2018.
- [51] D. W. Kim, S.-W. Kim, and U. Jeong, "Lipids: source of static electricity of regenerative natural substances and nondestructive energy harvesting," *Advanced Materials*, vol. 30, no. 52, p. 1804949, 2018.
- [52] E. Šupuk, A. Zarrebini, J. P. Reddy, H. Hughes, M. M. Leane, M. J. Tobyn, P. Timmins, and M. Ghadiri, "Tribo-electrification of active pharmaceutical ingredients and excipients," *Powder Technology*, vol. 217, pp. 427–434, 2 2012.
- [53] M. U. Ghorji, E. Šupuk, and B. R. Conway, "Tribo-electric charging and adhesion of cellulose ethers and their mixtures with flurbiprofen," *European Journal of Pharmaceutical Sciences*, vol. 65, pp. 1–8, 12 2014.

- [54] J. R. Middleton, A. J. Scott, and M. Ghadiri, "Triboelectric charging properties of the functional groups of common pharmaceutical materials using density functional theory calculations," *Pharmaceutics*, vol. 16, no. 3, p. 433, 2024.
- [55] J. Hu, P. Gu, X. Zeng, Q. Zhou, C. Liang, D. Liu, and X. Chen, "Triboelectric charging behavior of a rough surface sliding on a flat plane," *Journal of Electrostatics*, vol. 97, pp. 85–94, 2019.
- [56] W. Harper, "The generation of static charge," *Advances in Physics*, vol. 6, pp. 365–417, 10 1957.
- [57] W. R. Harper, "Contact and Frictional Electrification," Oxford University Press, New York, 1967.
- [58] D. 'Tabor and F. P. 'Bowden, *The Friction and Lubrication of Solids*. Oxford University Press, 2001.
- [59] K. Ohara, I. Nakamura, and M. Kinoshita, "Frictional electrification between flat surfaces of polymers and of Langmuir–Blodgett layers," *Journal of Electrostatics*, vol. 51–52, pp. 351–358, 2001.
- [60] H. Watanabe, M. Ghadiri, T. Matsuyama, Y. L. Ding, K. G. Pitt, H. Maruyama, S. Matsusaka, and H. Masuda, "Triboelectrification of pharmaceutical powders by particle impact," *International Journal of Pharmaceutics*, vol. 334, pp. 149–155, 4 2007.
- [61] P. M. Ireland, "The role of changing contact in sliding triboelectrification," *Journal of Physics D: Applied Physics*, vol. 41, 1 2008.
- [62] P. M. Ireland, "Triboelectrification of particulate flows on surfaces: Part I—experiments," *Powder Technology*, vol. 198, no. 2, pp. 189–198, 2010.
- [63] S. Bibiceva, S. L. Schroeder, and A. Hassanpour, "Auto-agglomeration of dry ibuprofen powder under mechanical vibration: Effect of particle morphology and surface properties," *Powder Technology*, vol. 433, p. 119172, 2024.
- [64] T. Bonakdar, M. Ali, and M. Ghadiri, "Particle breakability assessment using an aerosol-disperser," *International Journal of Pharmaceutics*, vol. 597, p. 120365, 2021.
- [65] L. Unger, D. Boulaud, and J. Borra, "Unipolar field charging of particles by electrical discharge: effect of particle shape," *Journal of Aerosol Science*, vol. 35, no. 8, pp. 965–979, 2004.

- [66] J. Yao and C.-H. Wang, "Granular size and shape effect on electrostatics in pneumatic conveying systems," *Chemical Engineering Science*, vol. 61, no. 12, pp. 3858–3874, 2006.
- [67] M. Murtomaa, V. Mellin, P. Harjunen, T. Lankinen, E. Laine, and V.-P. Lehto, "Effect of particle morphology on the triboelectrification in dry powder inhalers," *International Journal of Pharmaceutics*, vol. 282, no. 1-2, pp. 107–114, 2004.
- [68] S. Karner, E. M. Littringer, and N. A. Urbanetz, "Triboelectrics: The influence of particle surface roughness and shape on charge acquisition during aerosolization and the dpi performance," *Powder Technology*, vol. 262, pp. 22–29, 2014.
- [69] S. Sarkar, J. Cho, and B. Chaudhuri, "Mechanisms of electrostatic charge reduction of granular media with additives on different surfaces," *Chemical Engineering and Processing: Process Intensification*, vol. 62, pp. 168–175, 2012.
- [70] P. M. Ireland, "Dynamic particle-surface tribocharging: The role of shape and contact mode," *Journal of Electrostatics*, vol. 70, pp. 524–531, 12 2012.
- [71] R. Mukherjee, V. Gupta, S. Naik, S. Sarkar, V. Sharma, P. Peri, and B. Chaudhuri, "Effects of particle size on the triboelectrification phenomenon in pharmaceutical excipients: Experiments and multi-scale modeling," *Asian Journal of Pharmaceutical Sciences*, vol. 11, pp. 603–617, 10 2016.
- [72] W. D. Marra Jr, M. V. Rodrigues, R. G. Miranda, M. A. Barrozo, and J. R. Coury, "The effect of the generation and handling of the acquired electrostatic charge in airborne particles," *Powder Technology*, vol. 191, no. 3, pp. 299–308, 2009.
- [73] D. Armour-Chelu and S. Woodhead, "Comparison of the electric charging properties of particulate materials in gas–solids flows in pipelines," *Journal of electrostatics*, vol. 56, no. 1, pp. 87–101, 2002.
- [74] A. T. Ndama, P. Guigon, and K. Saleh, "A reproducible test to characterise the triboelectric charging of powders during their pneumatic transport," *Journal of Electrostatics*, vol. 69, no. 3, pp. 146–156, 2011.
- [75] C. Gallo and W. Lama, "Classical electrostatic description of the work function and ionization energy of insulators," *IEEE Transactions on Industry Applications*, no. 1, pp. 7–11, 2007.
- [76] A.G.Bailey, "Electrostatic phenomena during powder handling" *Powder Technology*, vol. 37, pp 71-85, 1984.

- [77] D. A. Engers, M. N. Fricke, R. P. Storey, A. W. Newman, and K. R. Morris, "Triboelectrification of pharmaceutically relevant powders during low-shear tumble blending," *Journal of Electrostatics*, vol. 64, no. 12, pp. 826–835, 2006.
- [78] D. J. Lacks and R. Mohan Sankaran, "Contact electrification of insulating materials," *Journal of Physics D: Applied Physics*, vol. 44, 453001, 2011.
- [79] A. Šutka, K. Mālnieks, L. Lapčinskis, M. Timusk, K. Kalniņš, A. Kovalovs, J. Bite-nieks, M. Knite, D. Stevens, and J. Grunlan, "Contact electrification between identical polymers as the basis for triboelectric/flexoelectric materials," *Physical Chemistry Chemical Physics*, vol. 22, no. 23, pp. 13299–13305, 2020.
- [80] B. O. Alan, M. Barisik, and H. G. Ozcelik, "Roughness effects on the surface charge properties of silica nanoparticles," *The Journal of Physical Chemistry C*, vol. 124, no. 13, pp. 7274–7286, 2020.
- [81] J. Kwek, D. Heng, S. Lee, W. Ng, H.-K. Chan, S. Adi, J. Heng, and R. B. Tan, "High speed imaging with electrostatic charge monitoring to track powder deagglomeration upon impact," *Journal of aerosol science*, vol. 65, pp. 77–87, 2013.
- [82] C. Xu, B. Zhang, A. C. Wang, H. Zou, G. Liu, W. Ding, C. Wu, M. Ma, P. Feng, Z. Lin, *et al.*, "Contact-electrification between two identical materials: curvature effect," *ACS nano*, vol. 13, no. 2, pp. 2034–2041, 2019.
- [83] P. Carter, O. Cassidy, G. Rowley, and D. Merrifield, "Triboelectrification of fractionated crystalline and spray-dried lactose," *Pharmacy and Pharmacology Communications*, vol. 4, no. 2, pp. 111–115, 1998.
- [84] J. Wong, P. C. L. Kwok, T. Noakes, A. Fathi, F. Dehghani, and H.-K. Chan, "Effect of crystallinity on electrostatic charging in dry powder inhaler formulations," *Pharmaceutical Research*, vol. 31, no. 7, pp. 1656–1664, 2014.
- [85] M. Murtomaa, P. Harjunen, V. Mellin, V.-P. Lehto, and E. Laine, "Effect of amorphicity on the triboelectrification of lactose powder," *Journal of electrostatics*, vol. 56, no. 1, pp. 103–110, 2002.
- [86] B. Y. Shekunov, J. C. Feeley, A. H. Chow, H. H. Tong, and P. York, "Physical properties of supercritically-processed and micronised powders for respiratory drug delivery," *KONA Powder and Particle Journal*, vol. 20, pp. 178–187, 2002.
- [87] S. Zellnitz, J. Pinto, M. Brunsteiner, H. Schröttner, J. Khinast, and A. Paudel, "Tribo-charging behaviour of inhalable mannitol blends with salbutamol sulphate," *Pharmaceutical research*, vol. 36, no. 6, p. 80, 2019.

- [88] C. Ahlneck and G. Zografi, "The molecular basis of moisture effects on the physical and chemical stability of drugs in the solid state," *International Journal of Pharmaceutics*, vol. 62, no. 2-3, pp. 87–95, 1990.
- [89] W. Kaialy, "A review of factors affecting electrostatic charging of pharmaceuticals and adhesive mixtures for inhalation," *International Journal of Pharmaceutics*, vol. 503, no. 1-2, pp. 262–276, 2016.
- [90] J. R. Middleton, A. J. Scott, R. Storey, M. Marucci, and M. Ghadiri, "Prediction of the Effective Work Function of Aspirin and Paracetamol Crystals by Density Functional Theory-A First-Principles Study," *Crystal Growth and Design*, vol. 23, pp. 6308–6317, 9 2023.
- [91] S. Karner and N. A. Urbanetz, "The impact of electrostatic charge in pharmaceutical powders with specific focus on inhalation-powders," *Journal of Aerosol Science*, vol. 42, no. 6, pp. 428–445, 2011.
- [92] K. Zhu, R. B. Tan, F. Chen, K. H. Ong, and P. W. Heng, "Influence of particle wall adhesion on particle electrification in mixers," *International Journal of Pharmaceutics*, vol. 328, no. 1, pp. 22–34, 2007.
- [93] M. Beretta, T. Hörmann, P. Hainz, W. Hsiao, and A. Paudel, "Investigation into powder tribo-charging of pharmaceuticals. Part II: Sensitivity to relative humidity," *International Journal of Pharmaceutics*, vol. 591, p. 120015, 2020.
- [94] E. Németh, V. Albrecht, G. Schubert, and F. Simon, "Polymer tribo-electric charging: dependence on thermodynamic surface properties and relative humidity," *Journal of Electrostatics*, vol. 58, no. 1-2, pp. 3–16, 2003.
- [95] W. D. Greason, "Investigation of a test methodology for triboelectrification," *Journal of Electrostatics*, vol. 49, no. 3-4, pp. 245–256, 2000.
- [96] M. I. Nimvari, A. Sowinski, and P. Mehrani, "Investigation of the role of temperature on contact electrification of polyethylene particles," *Powder Technology*, vol. 433, p. 119236, 2024.
- [97] M. Noras, "Monitoring of flowing charges with an electrostatic voltmeter," *IEEE Transactions on Industry Applications*, vol. 42, no. 1, pp. 2–6, 2006.
- [98] S. D. Ekim, G. E. Kaya, M. Dastemir, E. Yildirim, H. T. Baytekin, and B. Baytekin, "Organic charge transfer cocrystals as additives for dissipation of contact charges on polymers," *ACS Applied Materials & Interfaces*, vol. 14, no. 50, pp. 56018–56026, 2022.

- [99] F. Chowdhury, A. Sowinski, M. Ray, A. Passalacqua, and P. Mehrani, "Charge generation and saturation on polymer particles due to single and repeated particle-metal contacts," *Journal of Electrostatics*, vol. 91, pp. 9–15, 2018.
- [100] D. R. Klein, *Organic Chemistry*. Wiley, 3rd ed., 2017.
- [101] E. M. Arnett and T. C. Hofelich, "Stabilities of carbocations in solution. 14. An extended thermochemical scale of carbocation stabilities in a common superacid," *Journal of the American Chemical Society*, vol. 105, no. 9, pp. 2889–2895, 1983.
- [102] O. Makoto and K. Nobuyoshi, "Effect of grinding on the crystallinity and chemical stability in the solid state of cephalothin sodium," *International Journal of Pharmaceutics*, vol. 62, no. 1, pp. 65–73, 1990.
- [103] M. Otsuka, T. Matsumoto, and N. Kaneniwa, "Effect of environmental temperature on polymorphic solid-state transformation of indomethacin during grinding," *Chemical and Pharmaceutical Bulletin*, vol. 34, no. 4, pp. 1784–1793, 1986.
- [104] J. Kang, J. Kim, and W.-S. Kim, "Grinding method for phase transformation of glycine," *ACS Omega*, vol. 8, no. 19, pp. 17116–17121, 2023.
- [105] J. Pirttimäki, E. Laine, J. Ketolainen, and P. Paronen, "Effects of grinding and compression on crystal structure of anhydrous caffeine," *International Journal of Pharmaceutics*, vol. 95, no. 1-3, pp. 93–99, 1993.
- [106] J. R. Connolly, "Sample preparation and systematic diffractometer errors." Introduction to X-Ray Powder Diffraction, EPS400-002 course notes, 2005.
- [107] S.-H. Park, J. O. Baker, M. E. Himmel, and D. K. Johnson, "Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance," *Biotechnology for Biofuels*, vol. 3, p. 10, 2010.
- [108] V. Nampally, M. K. Palnati, N. Baindla, M. Varukolu, S. Gangadhari, and P. Tigulla, "Charge transfer complex between o-phenylenediamine and 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone: synthesis, spectrophotometric characterization, computational analysis, and its biological applications," *ACS Omega*, vol. 7, no. 19, pp. 16689–16704, 2022.
- [109] M. Khan, M. R. Shaik, S. F. Adil, M. Kuniyil, M. Ashraf, H. Frerichs, M. A. Sarif, M. R. H. Siddiqui, A. Al-Warthan, J. P. Labis, *et al.*, "Facile synthesis of Pd@graphene nanocomposites with enhanced catalytic activity towards Suzuki coupling reaction," *Scientific Reports*, vol. 10, no. 1, p. 11728, 2020.