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Probing Contact Electrification: A Cohesively Sticky Problem

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Abstract

Contact electrification and the triboelectric effect are complex processes for mechanical-to-electrical energy conversion, particularly for highly deformable polymers. Contact electrification and the triboelectric effect are complex processes for mechanical-to-electrical energy conversion, particularly for highly deformable polymers. Whilst generating relatively low power density, contact electrification can occur at the contact-separation interface between nearly any two polymer surfaces. This ubiquitousness of surfaces enables contact electrification to be a important phenomena to understand for energy conversion and harvesting applications. The mechanism of charge generation between polymeric materials remains ambiguous, with electron transfer, material (also known as mass) transfer and adsorbed chemical species transfer (including induced ionisation of water and other molecules) all being proposed as the primary source of measured charge. Often, all sources of charge, except electron transfer, are dismissed in the case of triboelectric energy harvesters, leading to the generation of the ‘triboelectric series’, governed by the ability of a polymer to lose, or accept, an electron. Here, this focus solely on electron transfer is challenged through rigorous experiments measuring charge density in polymer - polymer (196 polymer combinations), polymer - glass (14 polymers), and polymer - liquid-metal (14 polymers) systems. Through the investigation of these interfaces, clear evidence of material transfer via heterolytic bond cleavage is provided. Based on these results, a generalised model considering the cohesive energy density of polymers as the critical parameter for polymer contact electrification is discussed. This discussion clearly shows that material transfer must be accounted for when discussing the source of charge generated by polymeric mechanical energy harvesters. Thus, a correlated physical property to understand the triboelectric series is provided.
1. Introduction

Contact electrification (CE), where opposing surfaces become strongly charged after contact with one another, is an intriguing and powerful phenomenon, attributed broadly to friction and subsequent charge transfer between two dissimilar materials. In the case of contact between metal-metal,\textsuperscript{1} metal-ceramic,\textsuperscript{2-5} and ceramic-ceramic\textsuperscript{6} interfaces, CE is well understood to arise from electron transfer. However, the source of charge remains ambiguous for organic interfaces (e.g., polymers) undergoing CE.\textsuperscript{7} Commonly, in the energy harvesting community CE between two polymers is rationalised through an electron transfer mechanism between the materials,\textsuperscript{7} leading to the establishment of the triboelectric series.\textsuperscript{8, 9} Due to the lack of free electrons in dielectric or ferroelectric polymer materials, it is unlikely that electron transfer alone can explain the large charges and voltages measured from CE.\textsuperscript{10}

In the case of metals, where electrons are delocalised, it is more energy efficient for an electron to be transferred between materials, than a metal atom to be transferred.\textsuperscript{1} However, in polymer systems, electrons are localised to a given covalent bond, and thus if this electron is transferred to another material the bond must break. Consequently, the occurrence of electron transfer between two polymeric materials would imply the presence of a remnant fragment of either a functional group or oligomeric backbone chain which is unbound from the bulk polymer.\textsuperscript{12} Depending on the cohesive energy of each respective contacted polymer,\textsuperscript{13, 14} these unbound moieties will either remain as charged species on the host surface, or be transferred (material transfer), along with any charge inherent to the moiety, to the opposing surface.\textsuperscript{15} Here, the cohesive energy is defined as the energy required to dissociate polymer fragments. In contrast, atoms in ceramics are supported by a 3D bonding network, and thus breaking a single bond leaves the atom or ion supported by other bonds and not available for material transfer.
The occurrence of this material transfer in polymers has been demonstrated by quantum mechanical calculations\textsuperscript{16} and mechanochemistry experiments\textsuperscript{17, 18} as either homolytic bond cleavage (leaving a radical on each fragment), or heterolytic bond cleavage (leaving an ionic charge on each fragment). In fact, the existence of material transfer during polymer contact has been documented for several decades.\textsuperscript{19, 20} Indeed, it has been proposed that such material transfer may be the dominant mechanism for charge generation from CE in a large range of polymeric materials.\textsuperscript{7, 10} However, to date, a systematic link between the generated surface charge from CE and material transfer has not been established. Thus, it is crucial to understand this mechanism in order to truly understand CE in polymeric materials. While there is strong discussion around both homolytic and heterolytic bond cleavage in chemistry-focused literature, this discussion has not typically crossed over into mechanical energy harvesting discussions.

Herein, the effect of cohesive energy on measured CE in polymers is discussed. Rigorous experiments involving contact between a polymer and 1) another polymer; 2) glass; and 3) liquid metal; demonstrates an equivocal trend where cohesive energy is broadly inversely proportional to the measured CE. This study provides a new way to consider triboelectrification from polymers, and provides guidelines to predict the magnitude and sign of the generated surface charge from contact electrification.

2. **Results & Discussion**

In considering how CE occurs in conventional mechanical energy harvesting devices, the interface and motion between materials needs to be understood. Triboelectric generators (TEGs) operate through four standard modes of motion in order to harvest energy by CE: 1) lateral sliding mode; 2) free-standing mode; 3) contact-separation mode; and 4) single electrode
However, within these four TEG operation modes, there are two main forces responsible for charge generation, namely, interfacial friction (for lateral sliding and free-standing modes, Figure 1a) and interfacial adhesion (in single electrode and contact-separation modes, Figure 1b). Thus, to understand the CE effect a thorough understanding of the factors affecting the magnitude of the friction and adhesive forces at the interface between materials is needed. Frictional forces at interfaces where one material is a polymer are highly dependent on the molecular weight of the polymer, as well as the type of intermolecular bonds formed at the interface. For example, crosslinked polymeric surfaces exhibit interfacial friction orders of magnitude lower than non-crosslinked polymeric surfaces (Figure 1c-d).

Figure 1. Schematic of the two basic types of contact forces that lead to contact electrification between two dissimilar polymers in triboelectric energy generators; a) the lateral sliding mode, where interfacial friction leads to separated surface charge on either electrode; b) the contact separation mode where interfacial adhesion leads to surface charges on opposing materials. In a
device structure these charges are measured through electrodes deposited on each material, which are not shown here for clarity, nor are they necessary for surface charge generation; c) schematic representation of a polymer | polymer interface during CE; and d) magnified surface structure showing chains available for entanglement dependent on the cross-linking of a polymer.

The presence of dangling bonds also increases the adhesive forces at polymer | polymer interfaces by promoting entanglement of the polymer chains during contact.\textsuperscript{25} Therefore, material interfaces of high molecular weight (long chain) polymers require significant energy to separate following extended or cyclical contact.\textsuperscript{26} Indeed, when polymer | polymer interfaces are repeatedly contact-separated, the energy to overcome either the interfacial friction or adhesion forces is often greater than the cohesive energy of the polymer itself and will thus lead to bond scission resulting in material transfer.\textsuperscript{12,27}

To quantify whether it is more energetically favourable for these friction and adhesion forces to lead to bond scission (resulting in material transfer) or electron transfer, the energy required for each process can be examined. The first ionisation energy (i.e., the minimum energy required for electron transfer to occur) for commonly studied TEG polymers is between 670 kJ mol\textsuperscript{-1} and 890 kJ mol\textsuperscript{-1} (Table S1).\textsuperscript{28-33} This first ionisation energy is notably higher than the homolytic bond dissociation energy (BDE) of the C-C bond (360-430 kJ mol\textsuperscript{-1}, depending on the functional moieties surrounding the bond).\textsuperscript{34} However, the first ionisation energy only accounts for the energy of the addition or removal of an electron from the polymer. For electron transfer to occur in CE of polymers, the electron must be 1) removed from the polymer, 2) tunnel to the surface of a dissimilar polymer, and 3) subsequently add to this dissimilar polymeric material. The multiple
steps in this process result in a summation of energies which have been estimated to be as large as 1 MJ mol\(^{-1}\), and thus not a practical argument for CE.\(^{35}\)

In contrast, if electron transfer is ignored as the dominant mechanism for CE, the energy required for charge to transfer between materials can be conceptualised and described more simply. If the intermolecular attractive forces formed at a polymer | polymer interface during contact have a higher net energy than a covalent bond, then the covalent bond will separate into organoionic species as the interface is broken. This bond cleavage then results in material transfer, and thus oppositely charged surfaces. While the strength of the intermolecular forces can vary widely depending on molecular weights, crosslinking, crystal phases and contact time, the force required to fragment a covalent bond into organoionic species still remains the same. The summation of the total energy to break all the bonds in a molecule is the cohesive energy, which in polymers is dominated by the repeating backbone units.

2.1. Cohesive Energy and Charge Density

To probe the influence of the cohesive energy of polymers on measured charge, films were produced (see experimental section) from 14 different polymer materials (allowing for 196 combinations) and experimentally studied in the contact-separation mode (Figure 1b) of a TEG. Experiments were designed to minimise the influence of environmental factors. Polymer films were allowed to equilibrate for at least 48 hours prior to testing, and care taken to ensure a near constant humidity (35% to 40% as measured by the lab hygrometer) during testing. The polymers studied were polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), polyvinylidene difluoride (PVDF), polypropylene (PP), high-density (HD), low density (LD), and linear low-density (LLD) polyethylene (PE), poly(ethylene-co-vinyl acetate) (EVA), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene carbonate) (EC),
polycarbonate (PC), polyethylene terephthalate (PET), and poly[imino(1,6-dioxohexamethylene) iminohexamethylene] (PA66). The surface charge was measured on both polymers concurrently and independently (Figure 2a). The mode average cohesive energy density (CED), and a range of reported CEDs were collated from literature and database values and are shown in Table S2. The polymers were then ordered from lowest CED (PTFE, 180 J cm$^{-3}$) to highest CED (PA66, 682 J cm$^{-3}$) to produce a matrix (Figure 2b). The measured surface charge from each pair of polymers was measured (Table S3) and overlayed onto this matrix as a colour scale (Figure 2b). This approach showed a general visual correlation, whereby if:

$CED_{(Polymer\ B)} > CED_{(Polymer\ A)}$ - a negative (green) surface charge was measured; and

$CED_{(Polymer\ B)} < CED_{(Polymer\ A)}$ – a positive (purple) surface charge was measured.
Figure 2. Comparison of cohesive energy and measured charge from contact electrification. a) Schematic of the experimental set-up for contact-separation testing; and b) the matrix of surface charge density of Polymer A (y-axis) after 3000 cycles of contact separation with Polymer B (x-axis). The polymers are ordered by CED (from Table S2), with the lowest value in the bottom left corner, increasing moving to the top or to the right. The dotted line represents squares where identical materials are contact-separated.

Further, it was clear that a lower CED resulted in a higher magnitude of measured charge density. Interestingly, contrary to many theories of triboelectric charging that predict a net-zero charge when two identical polymers were contacted (represented as the dotted line in Figure 2b), here surface charge was measured for many pairs of identical polymers. This is a clear indication of material transfer and heterolytic bond cleavage.

Statistical analysis using a Logistic Regression model (see methods for full details), revealed a strong correlation between the CED(Polymer A) and CED(Polymer B) with the sign (positive or negative) of the measured surface charge (Table S5). When this analysis was applied as a training set for simple machine learning, the test data was predicted with an ~77% accuracy (Table S6). This 77% prediction accuracy shows that by simply knowing the CED of each of the two contacted polymers, a confident prediction about which material will act as a positive or negative triboelectric material can be made. This accuracy is increased to 90% when excluding charge values approaching zero (defined as |Q| > 0.022 nC cm⁻²).

This analysis provides a simple tool to demonstrate the role of material transfer and heterolytic bond cleavage in the CE of polymers. The remnant 23% of data is explained by considering the complexity and diversity of the polymer-polymer interfaces. Indeed, CED is only half of the
equation – with the work of adhesion (which describes the energy required to separate two surfaces) being critical in defining if material transfer and charge generation can occur.\textsuperscript{24} This work of adhesion (the sum of adhesive forces, $\sum F_{\text{adh}}$) depends greatly on polymer chemistry (availability of hydrogen or van der Waals bonds, solubility, surface topography (roughness), and the force applied during contact).\textsuperscript{40} The variability of the work of adhesion for polymer interfaces produced experimentally, due to roughness, crosslinking, molecular weight and crystallinity variations, means the complete equation governing the ordering of triboelectric polymers cannot be compiled.

However, by understanding the relationship between CED and the work of adhesion, the following guidelines can be proposed:

If $\sum F_{\text{adh}} > \text{CED} \text{ (Polymer A)}$ and $\sum F_{\text{adh}} < \text{CED} \text{ (Polymer B)}$ heterolytic bond cleavage of polymer A will occur with charged mechnano-radicals and mechnano-ions transferred from polymer A to polymer B;

If $\sum F_{\text{adh}} < \text{CED} \text{ (Polymer A)}$ and $\sum F_{\text{adh}} < \text{CED} \text{ (Polymer B)}$ heterolytic bond cleavage will not occur for either polymer; and

If $\sum F_{\text{adh}} > \text{CED} \text{ (Polymer A)}$ and $\sum F_{\text{adh}} > \text{CED} \text{ (Polymer B)}$ heterolytic bond cleavage will occur for both polymers A and B, resulting in a complex mosaic of charged surfaces.\textsuperscript{41}

This complex source of adhesive forces between polymer interfaces explains the anomalies in Figure 2b. For example, PTFE, which has a very low CED presents a moderate surface charge upon contact with most materials which is attributed to the low work of adhesion for PTFE substrates (Table S4).\textsuperscript{40} This low work of adhesion is specifically linked to the lack of available hydrogen bonding from the PTFE backbone, and results in a friction coefficient which is an order of magnitude lower than other polymer materials.\textsuperscript{42} In contrast, the ‘sticky’ polymer PDMS
will typically have a significantly higher work of adhesion. This higher work of adhesion, when coupled to the low CED of PDMS, will results in a high degree of bond cleavage and subsequent mechano-radical and/or mechano-ion generation at the interface.43

2.2. Modelling Interfacial Behavior – A Case Study of the PA66 | PDMS interface

In order to understand the relationship between polymer CED, charge stability of the radical, and their relative desorption energies, in silico modelling (finite element analysis (FEA) and molecular dynamics (MD)) of the PA66 | PDMS interface was performed. This interface was selected as it demonstrated a high measured charge density and possessed a large difference in CED (CED\textsubscript{PA66} = 682 J cm\textsuperscript{-3}; CED\textsubscript{PDMS} = 230 J cm\textsuperscript{-3}; and charge density = ±0.330 nC cm\textsuperscript{-2}) (Figure 2b).
Figure 3. FEA modelling of the PA66 | PDMS interface during a vertical compression. The displacement a) and the x-direction strain and b) were calculated without considering interfacial friction (left), and with interfacial friction (right).

The FEA simulations were performed (using the Simulation add-in of the Solidworks software package) for a vertical compression contact mode TEG with the simulated contact stress corresponding to the experimental values (20 kPa). During the vertical compression modelling it was clearly observed that lateral deformation of the polymer interface occurred (highlighted by
red on the colour scale, Figure 3a). When interfacial friction was considered in the modelling, a clear visual deformation of the PDMS polymer was observed. The PDMS distortion was significantly greater than the PA66 distortion, which arises from their relative elastic modulus (experimentally measured as 3775.88 MPa for PA66 and 1.52 MPa for PDMS). The relative lateral strain experienced by the polymers was on the order of $10^{-6}$ (Figure 3b), well below the strain required for direct monomer chain cleavage (estimated here by steered MD at 0.19 and 0.16 for PA66 and PDMS, respectively).

This result implies that when adhesive forces and chain entanglement are not considered, heterolytic bond cleavage will not occur. This assumption was supported by the common theory of polymer physical chemistry, which predicts that the scission of a polymer backbone, as a result of the energy of intermolecular interactions, is higher than that of the weakest bond energy in a polymer backbone.\textsuperscript{44}

MD simulations allowed for the consideration of these adhesive forces at the PA66 | PDMS interface (Figure 4, Supplemental Movie 1, 2). Indeed, MD simulations showed dissociation of the silicon-oxygen (Si-O) bonds of PDMS under forces applied during perpendicular (Figure 4, bottom; see Figure 1b) and shear separation (Figure 4, top; see Figure 1a). It should be noted that dissociation of the C-Si bond was not observed in the simulations. The dissociation of PA66 fragments was not considered in view of the significantly higher stiffness and crystalline structure of the material. According to the FEA results, the PA66 demonstrates lower deformation, and hence does not undergo significant bond dissociation. This lack of bond dissociation correlates with the lack of measured charge density for PA66 when contacted with high CED polymers (Figure 2b).
Figure 4. Molecular dynamics simulations, left, snapshots of initial configuration of a PA66 | PDMS interface and, right, ruptured fragments of surface-bound PDMS fragments after being pulled, top, along the surface or, bottom, away from a (010) surface of PA66 (● – O, ● – H, ● – Si, ● – N, ● – C).

Finally, in a separate experiment, a dissociated di-dimethylsiloxane (DDMS) dimer was investigated to assess the relative stabilities of the generated mechano-radicals (Table 1, Figure S1). This experiment breaks a covalent bond in DDMS resulting in two fragments, one with a silicon termination and the other with an oxygen termination.

Table 1. Potential energies of charged dissociated di-dimethylsiloxane (DDMS) dimers.
During fragmentation, the bond scission can be either homolytic (where both terminations are uncharged) or heterolytic (generation of radicals on both silicon and oxygen terminations). The relative stability of either radical termination or uncharged termination is shown in Table 1. Homolytic (uncharged) mechano-fragments were observed to possess the most stable charge distribution (-330 kcal mol\(^{-1}\)), in agreement with prior experiments.\(^{16}\) However, the formation of mechano-radicals with a negative charge on the oxygen termination had a lower energy (-257 kcal mol\(^{-1}\)) than a neutral oxygen termination (-182 kcal mol\(^{-1}\)). Only charged fragments will contribute to contact charge density. Thus, the relative instability of the positively charged oxygen termination (-15 kcal mol\(^{-1}\)) to the negatively charged oxygen termination (-257 kcal mol\(^{-1}\)) supports the concept that PDMS will typically fragment with a (partial) negative charge on the oxygen and a (partial) positive charge on the silicon.

In a typical PA66 | PDMS contact-separation experiment, the desorption energies of mechano-fragments (Table 2) from either PA66 or PDMS will define which surface has the majority of charged species. Thus, the desorption energies of the most stable charge fragments (partial negative charge on the oxygen termination, and partial positive charge on the silicon termination) were probed for a PA66 | PDMS interface.

**Table 2.** Energies of desorption of PDMS fragments from the PA66 and the PDMS surfaces.
The oxygen terminated PDMS radical was found to significantly lower desorption energy (Table 2) from bulk PDMS compared to the silicon terminated radical. The higher energy of desorption of silicon terminated radicals (generated from heterolytic bond cleavage of PDMS) compared to oxygen terminated radicals will result in a greater degree of oxygen terminated radicals transferring to the PA66 surface. This transfer will result in PDMS having a net positive charge (from the silicon terminated fragment), and the PA66 surface having a negative charge (from the oxygen terminated fragment) which correlates to experimental results. This combined modelling which combines the CED of the polymers, charge stability of the formed radicals, and their relative desorption energies can now be broadly applied to identify other high charge density triboelectric polymer pairs.

2.3. Material Transfer in Polymer-Glass Systems

The role of chain entanglement and subsequent heterolytic bond cleavage is relatively simple to visualise at a polymer | polymer interface. However, in systems with a network of covalent (i.e., ceramics or glasses) or metallic bonds, bond scission of polymer chains is less intuitive.

To evaluate where this bond scission and subsequent material transfer occurs, even if one material has no dangling polymer chains for entanglement, polymer samples (PTFE, PDMS, PVDF, PP, LDPE, LLDPE, HDPE, EVA, PS, PMMA, EC, PC, PET, PA66) was repeatedly contacted with a soda-lime glass substrate for 3000 contact-separation cycles (Figure 5a, Step 1). Soda-lime glass was selected as a common glass substrate, and discussed as such to provide a clear distinction in use from conductive ITO/Glass.
Figure 5. a) Schematic of surface roughness and charge density measurement via repeated contact with glass; b) RMS surface roughness of soda-lime glass surface before (none) and after 3000 contact-separation cycles with different polymers, compared to the CED of a given polymer; c) charge density of transferred polymer material between ITO and soda-lime glass, contacted against plasma cleaned ITO (corresponding to the bottom left of a)); and d), left the measured charge when a soda-lime glass | PDMS material transfer electrified surface is oscillated with respect to an ITO substrate, right, the remnant charge after the soda-lime glass | PDMS is grounded with a metal rod showing there is only a small loss of induced current flow.
This polymer-contacted piece of soda-lime glass was then contact-separated a single time with a plasma cleaned indium tin oxide (ITO)-coated glass to measure the charge density in a polymer-glass system (Figure 5a, Step 2, Step 3). The polymer contacted soda-lime glasses produced a surface charge that was 5 to 30 times greater (between 0.05 and 0.3 nC cm\(^{-2}\)) than native soda-lime glass (0.01 nC cm\(^{-2}\)) when contacted with conductive ITO-coated glass slides (Figure 5c).

If the PDMS-coated soda-lime glass (Figure 5a, Step 3) is grounded with a metal rod and oscillated in non-contact mode with respect to the ITO the measured density decreases by 0.08 pC cm\(^{-2}\), around 4% of the total charge (Figure 5d, grounding occurs during Figure 5a, Step 3). This decrease occurs as mobile charge, i.e. electrons, leave the polymer-contacted surface and only bound surface charge, i.e. mechano-radicals and mechano-ions, is measured upon contact with the ITO glass (Figure 5d). This conclusively showed that material transfer dominates the measured surface charge at the soda-lime glass | PDMS interface.

Following 3000 contact-separation cycles (Figure 5a, Step 3) the root-mean-square (RMS) surface roughness of the soda-lime glass slides was measured via atomic force microscopy (AFM, Figure S2), with the RMS surface roughness shown in Figure 5b. From this experiment, there was no clear correlation between CED and the RMS surface roughness (Figure 5b) or between CED and generated charge density (Figure 5c). It has been previously demonstrated that such an increase in RMS surface roughness of soda-lime glass slides can be directly attributed to material transfer of polymer fragments.\(^43\) Thus despite the lack of clear correlation between CED and RMS surface roughness, the general increase in RMS surface roughness is clear evidence of material transfer.
As described in section 2.2., the measured charge density is defined by a balance between the work of adhesion and the CED. In a polymer | glass system, the work of adhesion is presumed to be lower than in a polymer | polymer system, due to the lack of chain entanglement at the interfaces. Therefore, it is expected that the experimentally measured charge density will have a weaker correlation with the CED of a polymer.

From Figure 5c, glass | EC (0.3 nC cm$^{-2}$) and glass | PDMS (0.3 nC cm$^{-2}$) separately provide the highest charge density (after PVDF) when contacted with soda-lime glass, likely due to the polymer backbone bonding through an oxygen atom. The enhanced charge stabilisation on an oxygen terminated fragment, as highlighted in the FEA and MD data, is critical when considering a two-stage mechanism; 1) polymer material transfer; and 2) measured surface charge after a certain period of time in air.

It is noted that the PVDF is anomalous, generating approximately 10 times the charge density (3.4 nC cm$^{-2}$) of any other polymer (Figure 5c). This merits further investigation, and is hypothesised to arise due to the intrinsic electronic dipole in PVDF that can lead to a measured piezoelectric contribution.

2.4. Material Transfer in Polymer-Liquid Metal Systems

The dominant contact electrification mechanism in polymer | polymer systems and polymer | glass systems has been clearly demonstrated to be material transfer. However, both systems examined above are between non-conductive materials, where electrons are not readily available. To ascertain the role of material transfer, and the importance of CED, in systems with available electrons, polymer | liquid metal systems were studied in contact-separation experiments.

So far, in this work, the role of material transfer on CE in a range of polymer | polymer and polymer | glass systems has been demonstrated. More recently, a model approach to study
polymer | liquid metal interfaces has been developed by Wang et al.44 To follow on from this, here, a range of polymers was cyclically immersed into a liquid metal alloy, Galinstan, (Figure 6a-c). Galinstan consists of gallium (Ga), indium (In) and tin (Sn). In contrast to older methods that have used liquid mercury, which has an ultrastable electronic configuration and will not wet a polymer surface,9 liquid Galinstan will adhere to most polymer surfaces. This adhesion between a polymer surface and liquid metal enables material transfer of polymer fragments, as the polymer is removed from the liquid metal bath (shown in Figure 6a and b). Each polymer sample was immersed in Galinstan for 10 cycles, and the generated charge density was measured and correlated to the CED of the polymer36 (Table S2 and Figure 6c).

Figure 6. Determination of generated charge density from contact between a Galinstan (liquid metal) and a polymer; a) photograph demonstrating the immersion of a PTFE film into Galinstan; b) photos of the PTFE film; i) prior to immersion in Galinstan; ii) after one dip cycle in Galinstan; iii) after five dip cycles in Galinstan; and iv) after ten dip cycles in Galinstan; and c) correlation between the absolute value of charge density (bar graph, left y-axis) measured during contact-separation and the cohesive energy density (CED) (data points, right y-axis) of a given polymer.
These results conclusively demonstrated that PDMS and PTFE, with the lowest CED (Figure 6c, purple circles, right y-axis, Table S2), had by far the highest absolute measured charge densities of ~35 pC cm\(^{-2}\) and ~17 pC cm\(^{-2}\), respectively (Figure 6c bar graph, left y-axis). Similarly, the PA66 exhibited the lowest charge density due to the largest CED. For the polymers with moderate CEDs, several other factors beyond cohesive energy play a role in the fragmentation; 1) surface roughness; and 2) surface energy match between the liquid metal and the polymer. While surface roughness was controlled by identical polymer film preparation methods, the surface energy matching between Galinstan is difficult to quantify due to oxidative effects over time.\(^\text{47}\) Further, Galinstan is able to donate or accept an electron during the CE processes, so the contribution of electron transfer cannot be ruled out.

This result highlights that polymers with similar cohesive energy densities, between 300 J cm\(^{-3}\) to 425 J cm\(^{-3}\), have very similar measured charge densities when contact-separated with a liquid metal. However, in the case where there is very high CED (PA66; CED\(_{\text{PA66}}\) = 682 J cm\(^{-3}\); Q\(_{\text{PA66|Galistan}}\) = 0 pC cm\(^{-2}\)) or very low CED (PTFE; CED\(_{\text{PTFE}}\) = 166 J cm\(^{-3}\); Q\(_{\text{PTFE|Galistan}}\) = 17.5 pC cm\(^{-2}\) or PDMS; CED\(_{\text{PDMS}}\) = 230 J cm\(^{-3}\); Q\(_{\text{PDMS|Galistan}}\) = 35 pC cm\(^{-2}\)) there is a clear relationship between charge density and CED. The lack of charge transferred during contact between PA66 and Galinstan provides strong support for the theories developed by Lacks \textit{et al.},\(^\text{10}\) specifically, that there is a strong interplay between transferred mechano-radicals and mechano-ions, and electron transfer. This concept, which revolves around the presence of localised charge on these fragments lowering the energy barrier to electron hopping from the metal to the polymer, helps explain the exceptionally high charge density measured on PDMS.
within any triboelectric system due to the ability of oxygen terminated oligomers to hold charge, and hence accept electrons after an initial material transfer process.

2.5. **Summary**

In summary, the experiments in this work (196 polymer | polymer interfaces; 14 polymer | glass interfaces; 14 polymer | liquid-metal interfaces) have demonstrated that cohesive energy can be used in place of the triboelectric series in polymer-based TEG systems, due to interfacial entanglement and the inability for low energy electron transfer. In polymer-glass systems, there are significantly lower interfacial forces, thus polymers with higher cohesive energies will not fragment and surface charge will not be proportional to cohesive energy. For polymer-liquid metal systems, electron transfer still plays a key role in conjunction with CED. In this case, fragmentation of the polymer backbone and the resulting localised charge can lead to enhanced electron transfer, thus leading to significantly higher charge densities during triboelectric charging.

Comparing the ordering of polymer by CED, with seminal reports of triboelectric series\(^3\), \(^4\)\(^8\)\(^-\)\(^5\)\(^1\), a strong correlation is observed (Table 3). Notably, PMMA does not appear to correlate with the ordering of CED used here. Whilst the accepted value of CED\(_{\text{PMMA}}\) is 359 J cm\(^{-3}\), PMMA has the largest variation in reported CED of all studied polymers (Table S2), ranging from 310 J cm\(^{-3}\) to 704 J cm\(^{-3}\). This CED\(_{\text{Max, PDMS}}\) of 704 J cm\(^{-3}\) is the second highest value (after PA66; CED\(_{\text{Max, PA66}}\) = 866 J cm\(^{-3}\)) of CED for any studied polymer, and justifies why PMMA and PET (CED\(_{\text{Max, PET}}\) = 616 J cm\(^{-3}\)) have switched positions in several reported triboelectric series. The high degree of correlation between triboelectric series and polymer CED is further evidence for the importance of material transfer in polymer containing triboelectric systems.
Table 3. Comparison for common triboelectric series reported in literature (Gooding and Kaufman;48 Coehn;49 Henniker;50 Adams;51 Diaz and Felix-Navarro37) with the order produced considering cohesive energy density. Blue text corresponds to polymers where their position correlates to the CED order, Red text is polymers where their position on the reported triboelectric series does not correlate to CED.

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<td>PP</td>
<td>PP</td>
<td>PS</td>
<td>PS</td>
</tr>
<tr>
<td>PE</td>
<td>PE</td>
<td>PE</td>
<td>PDMS</td>
<td>PTFE</td>
<td>PE</td>
<td>PE</td>
</tr>
<tr>
<td>PP</td>
<td>PP</td>
<td>PTFE</td>
<td>PTFE</td>
<td>PTFE</td>
<td>PP</td>
<td>PTFE</td>
</tr>
</tbody>
</table>

*ordered from highest to lowest CED (Table S2); †Correctly ordered if taking the maximum reported CED for PMMA

Contact electrification and the triboelectric effect and multi-faceted and complex system. Within this manuscript we have explored CED as a tool for taking a physical property of a polymer and predicting surface charge. However, it remains important to acknowledge the complexity and complementary nature of many charge transfer mechanisms, as highlighted separately by Li et al.21 and Lacks & Shinbrot.10 Critically, factors such as transfer of ions,
ionisation of gas molecules, absorption of water molecules, and secondary charge transfer from ionised surface moieties cannot be accounted for by a single physical property such as CED. The explosion of the hygroelectric research field, generating energy from water absorption, motion, and ionisation, has probed these effects in great detail – and such factors should be considered when accounting for experimental results.\textsuperscript{52,53}

However, for contact electrification and the triboelectric effect, it is the \textit{interplay} between each of these mechanisms that leads to the total measured charge. The CED, enables a prediction of the first charge species transfer, which occurs in polymers by the transfer of mechanoradicals and mechanoions. A lower CED, \textit{generally} resulting in more bond fragmentation will lead to enhanced secondary charge transfer mechanisms from adsorption, ionisation, and even electron transfer between ionised species as well.

The magnitude of the role of each of these contributions to contact electrification will also depend on factors such as hydrophillicity, surface roughness, and sample age or storage conditions.\textsuperscript{21} Gaining a holistic picture of contact electrification remains a work in progress, building on advanced understanding each individual contribution, and their complex interplay.

Thus, whilst CED is not an perfect predictor, and surface and interfacial forces still need to be considered, the 77\% accuracy of CED for predicting the sign of the charge between any two contacted polymers is a considerable advance on the current empirically derived triboelectric series.
3. Conclusions

Material transfer has been demonstrated to play a critical role in polymer-polymer; polymer-glass and polymer-liquid metal triboelectric pairings by correlating the CED of a given polymer with its measured charge density. It is evident that in polymer-polymer systems, due to chain entanglement and greater stresses at the contact-separation interface, CED is a key fundamental factor driving triboelectric charge generation. This is represented as an extremely strong inverse relationship between the CED of a given polymer, and the magnitude and sign of the measured surface charge. Extrapolating these results to polymer-glass and polymer-liquid metal systems presents a more complicated picture. However, in cases of polymers with cohesive energies above 500 J cm\(^{-3}\) or below 250 J cm\(^{-3}\), the CED can be a key factor to consider as to whether CE will occur or not. Finally, it is proposed that the charge that is stabilised on any oligomers transferred can enable secondary electron transfer in polymer-liquid metal systems, and the absence of material transfer (notably in PA66) results in the inability of liquid metals to transfer charge to certain polymers. This interplay between electron and material transfer is crucial to understand for the design of more complex triboelectric energy generators.

4. Experimental

*Polymer Film Preparation:* A range of polymers, namely, polyvinylidene difluoride (PVDF), poly(ethylene-co-vinyl acetate) (EVA), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene carbonate) (EC), polycarbonate (PC), polyethylene terephthalate (PET), and poly[imino(1,6-dioxohexamethylene) iminohexamethylene] (PA66) were dissolved in the appropriate solvents to obtain solutions, as shown in the Table 4.
**Table 4.** Selected polymer solution preparation parameters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent system</th>
<th>Polymer concentration, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylidene fluoride (PVDF)</td>
<td>Dimethylformamide</td>
<td>15</td>
</tr>
<tr>
<td>Ethylene-vinyl acetate copolymer (EVA)</td>
<td>Toluene</td>
<td>20</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>Dimethylformamide</td>
<td>20</td>
</tr>
<tr>
<td>Polymethyl methacrylate (PMMA)</td>
<td>Dimethylformamide</td>
<td>15</td>
</tr>
<tr>
<td>Ethyl cellulose (EC)</td>
<td>Ethanol/toluene, 20:80 (w/w)</td>
<td>10</td>
</tr>
<tr>
<td>Polycarbonate (PC)</td>
<td>Dimethylformamide</td>
<td>15</td>
</tr>
<tr>
<td>Polyethylene terephthalate (PET)</td>
<td>Trifluoroacetic acid</td>
<td>15</td>
</tr>
<tr>
<td>Polyamide 6,6 (PA66)</td>
<td>Trifluoroacetic acid/acetone, 50:50 (w/w)</td>
<td>10</td>
</tr>
</tbody>
</table>

For the fabrication of the polymer, polydimethylsiloxane (PDMS), Sylgard 184 (Dow) base prepolymer was mixed with the curing agent in a ratio of 10:1 and degassed under vacuum prior use. All prepared polymer solutions and the uncured PDMS mix were spin-coated onto an ITO-coated polyethylene terephthalate (PET) substrate (ITO/PET, Sigma Aldrich). The thickness of each of spin-coated film was in the range 20-50 μm as measured by electronic micrometer (Yato, YT-72305, range 0-25 mm, step 0.001 mm). After spin-coating the PDMS samples were subjected to curing at 100 °C for 35 min in laboratory drying oven.

Hot pressing (details shown in Table 5) was used to produce films of polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). The thickness of each film was set as 500 μm by a separator. The hot-pressed polymers and the commercially obtained polytetrafluoroethylene (PTFE) (Sigma Aldrich, 300 μm) films were then adhered to ITO/PET slides by a conductive double adhesive tape. The size of all prepared polymer films was 2.5 × 2.5 cm.
Table 5. Polymer film preparation details.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylidene fluoride (PTFE)</td>
<td>Commercially obtained</td>
</tr>
<tr>
<td>Polydimethylsiloxane (PDMS)</td>
<td>Base prepolymer / curing agent in a ratio of 10:1</td>
</tr>
<tr>
<td>Low density polyethylene (LDPE)</td>
<td>Hot pressing at 120 °C under 5 MPa for 5 min.</td>
</tr>
<tr>
<td>High density polyethylene (LLDPE)</td>
<td>Hot pressing at 135 °C under 5 Mpa for 5 min.</td>
</tr>
<tr>
<td>Linear low density polyethylene (LDPE)</td>
<td>Hot pressing at 125 °C under 5 Mpa for 5 min.</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>Hot pressing at 175 °C under 5 Mpa for 5 min.</td>
</tr>
</tbody>
</table>

Charge Measurement: The surface charge was measured under controlled conditions, namely, a separation distance of 5 mm, a pressing force of 10 N and a contact-separation frequency of 1 Hz. The generated current signals were measured using a Keithley 6514 electrometer connected to a Picoscope 5444B PC oscilloscope system in a Faraday cup circuit. Surface charges, Q (nC), were calculated from the measured current peaks using the equation \( Q = \int i \, dt \), where \( i \) is the instantaneous current (nA) and \( dt \) is differential of time (s). Contact-separation was carried out using an Instron E1000 material testing machine to ensure repeatability.

Logistic Regression Model: Logistic regression is a statistical classification model that can be used to solve binary problems.\(^3^9\) This is carried out using a logistic function to estimate the probability of a variable fitting into one of two classifications. The function generates a curve for each independent variable, \( x \), where in this work \( x \) is the CED, with a dependent variable, thus producing a slope (\( m \)). The equation utilised is as follows (Equation 1):

\[
\text{logistic}(y) = \frac{1}{1 + e^{-(m_1 x_1 + m_2 x_2)}} \quad \text{Equation 1.}
\]

A table (referred to as elec.data) of Accepted Cohesive Energy density A and B (CED.A and CED.B, respectively) and the sign of output charge was generated for each polymer-polymer pair, where polymer B was lowered down onto polymer A. The table was imported into Rstudio.
(Ver: 1.4.1106) and a logistic model (function: glm) applied to determine the sign using CED.A and CED.B. The results are shown in Table S5.

For machine learning Table S5 was randomly split into two tables: 1) a train table and 2) a test table. The train set was used to train the model to predict the sign of charge based from CED.A and CED.B. The test set was used to determine the accuracy of the model generated (Table S6).

Polymer-Glass Testing: To evaluate material transfer in polymer-glass systems each polymer (PTFE, PDMS, PVDF, PP, LDPE, LLDPE, HDPE, EVA, PS, PMMA, EC, PC, PET, PA66) was repeatedly contacted with a soda-lime glass substrate for 3000 contact-separation cycles in the same manner as in the previously described charge measurements. After contacting the soda lime glass with each polymer, the soda lime glass was then contacted-separated against a plasma cleaned (Harrick Plasma PDC-002-CE) ITO-coated glass substrate. The charge was calculated from current measured between ITO and ground. For comparison, ITO/glass was also contacted against pristine soda-lime glass substrate after plasma cleaning. In separate experiment the mobile charge carriers were extracted from the polymer-contacted soda-lime glass by taping with a simple copper rod. In this case, after the mobile charge carriers were removed, the glass was oscillated against the grounded ITO in non-contact regime moving back and forth in separation distance from 0.5 to 5 mm.

Polymer-Liquid Metal Testing: For evaluation of material transfer in polymer-liquid metal systems polymer films of LLDPE, LDPE, HDPE, PP, PS, PMMA, PC, EVA, PA66; 10 × 30 mm were hot pressed to a thickness of 500 μm. A PTFE film, 300 μm thick; 10 × 30 mm, was cut from commercial film and PDMS (prepolymer/curing agent, 10:1) was drop-cast into a Petri dish to obtain a 500 μm thick film. For testing, each film was secured in a clamp and then vertically submerged into liquid Galinstan for 2 s to a depth of 10 mm. Subsequently, the polymer film was
rapidly removed (10 ms duration). Charge was measured by the liquid Galinstan electrode connected in a Faraday cup circuit.54,55

Simulations: The FEA simulations were performed using the Simulation add-in of the SolidWorks CAD software.56 For the simulations, non-proportionally sized layered elements of the contact surfaces were employed. A normal pressure load of 2 N/cm² was employed, according to a corresponding experimental value. No-penetration contact setting was employed for interface modelling. The starting positions are shown in Figure S3. For simulation involving sliding friction, a friction coefficient of 0.25 was employed. A large deformation setting was employed for consideration of geometric nonlinearities. Materials were modelled as isotropic and elastic, with an elastic moduli of 1.52 MPa and 3775.88 MPa (experimental values) and a Poisson’s ratios of 0.48257 and 0.4258. The applicability of Hooke’s law was verified by comparison of the maximum principal strains, which did not exceed 2 %, and the conservative estimates of linear response range of about 30 % according to the tensile response of PDMS (Figure S4).

For the MD simulations, the NAMD/MOPAC implementation59 of PM7 parameterisation60 of Dew’r and Thiel’s NDDO approximation61 was employed. Particular settings include an integration time step of 0.25, 0.5 or 1.0 fs due to energy conservation considerations, Langevin thermostat damping constant of 50 ps⁻¹, and equilibration at room temperature (300 K). Except for energy calculations for the dimers, the Localized Molecular Orbital method, MOZYME,62 was employed for calculation speed improvement. For simulations involving external forces, the steered molecular dynamics (SMD) approach was employed. This was performed by harmonic potentials with force constants of 10000 kcal/mol/Å and linearly changed (4 or 2 Å/ps) centres, defined with respect to projected-axis-distance based collective variables.63 The simulated
PDMS chain segment lengths were chosen as 50 monomer units for pristine polymer fragments according to experimental estimates of mean chain length between consecutive crosslinking sites and 25 monomer units for the charged or radical type fragments of the chains. For PA66 modeling, 4 monomer units per segment were included for compatibility with contact state with a 25-unit PDMS fragment. For minimal representation of a chain-axis-aligned crystallite surface (010) of a PA66, 2 layers of 4 fragments per layer were included. The distance between terminal atoms of the fragments was fixed by means of harmonic constraints, mentioned above. For preparation of the molecular structures, the software tools of OVITO\textsuperscript{64} and Maestro\textsuperscript{65} were used. For visualization, both OVITO and VMD\textsuperscript{66} tools were applied.

For the estimates of Gibb’s reaction energies of desorption of the polymer chain fragments, or DDMS dimers, a simplified approach was followed. The approach was based on the assumption that the entropy of an isolated chain is solely dependent on the end-to-end distance of the chain\textsuperscript{44} and, hence, may be considered constant if the end-to-end distance of the chain does not change. Consequently, the change in Gibb’s energy at constant temperature can be approximated by the respective change in potential energy. For estimates of the potential energy values, averaging was applied over at least the last 500 time integration steps of the production runs. For estimation of the free energy change during steered molecular dynamics (SMD) simulations in terms of potential of mean force (PMF), the thermodynamic integration approach was followed.
ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supporting information file containing; MD snapshots of DDMS; Selected AFM images showing surface roughness post-contact with glass (Glass, EC-Glass, EVA-Glass, PDMS-Glass, PMMA-Glass, PS-Glass); FEA starting conditions for modelling; Modelled tensile response and linear range approximation of PDMS samples; Tables of collated and measured polymer properties (ionization energy, cohesive energy density, output charge density, work of adhesion); logistical regression code. (PDF)

Videos of MD simulation in perpendicular mode (mpg)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. §These authors contributed equally.


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SYNOPSIS

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