

# The role of intermolecular forces in contact electrification on polymer surfaces and triboelectric nanogenerators†

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The contact electrification of polymer interfaces provides an energy harvesting function to triboelectric (nano)generators (TEG). The electron transfer between contacted-separated surfaces has been considered as the main electrification mechanism for polymers in TEG. The electron transfer mechanism widely proposed in literature requires a contact between chemically different polymer materials, as well as subsequent increase of the specific contact area, which is commonly accomplished via nanostructuring. Herein, we showed that contact electrification could be controlled by intramolecular forces in the polymer bulk and adhesive forces at the contact interface, and the chemical contact between different polymers was not needed for contact electrification. The results also confirm the breaking of the covalent bond as a mechanism of the contact electrification of polymer insulators.

TEG devices have the potential to satisfy the increasing energy needs in portable electronics and sensors, providing a clean alternative to conventional batteries.<sup>1</sup> The TEG devices are produced from cheap, lightweight, flexible, widely used polymer materials and offer promise to capture the neglected and unutilized forms of mechanical energy. These devices consist of two conductive electrodes, where at least one electrode is covered with a polymer insulator film.<sup>1</sup> The two electrodes in TEG are connected by an outer circuit, and upon electrode oscillation, a surface charge on polymer layers and an electric potential are created that drive the electrons to flow between two electrodes to balance this electric potential difference; the TEG devices can be operated in different modes: vertical separation, sliding, rotating, single electrode etc.;<sup>2</sup> however, the

## Broader context

Triboelectric nanogenerators (TEG) that harvest ambient mechanical energy through contact electrification can be used as a power source in autonomous devices. The same phenomenon could also be applied to create local electric fields in applications such as electroactive filters. The polymeric TEG devices are currently designed based on the understanding that charging occurs through electron transfer. However, several recent studies have demonstrated that triboelectrification is instead caused by a heterolytic covalent bond breakage. In the present study, we provided a substantial proof of the occurrence of covalent bond scission to further establish the understanding of its underlying role in polymer contact electrification. We also showed, by example, how the proposed new principles could be followed in the design of superior TEG devices.

key feature for high TEG efficiency is the generation of surface charge from contact electrification.<sup>3</sup>

Different mechanisms are responsible for contact electrification and depend on the material used. It is well demonstrated that upon metal–metal, metal–semiconductor or semiconductor–semiconductor contact, electron transfer occurs;<sup>4,5</sup> however, this is not very obvious for polymer insulators.<sup>6</sup> Moreover, three mechanisms for polymer insulator contact electrification are considered: electron transfer,<sup>7</sup> ionic transfer,<sup>6</sup> and covalent bond cleavage.<sup>8</sup> The electron transfer between polymers is doubtful because there are no available free electrons in insulators. The usage of the term “effective work function” in connection to the driving force for charge exchange between polymer insulators is also questionable even if the polymer is in contact with the metal.<sup>6</sup> Therefore, ion exchange between contacted polymer insulators has been considered because water under ambient conditions is adsorbed even on hydrophobic polymers.<sup>9</sup> The water layers on contacted surfaces fuse together upon contact, and as different polymer materials may have different affinities towards cations and anions in water, an imbalance between ions is formed during separation, thus creating the surface charge.<sup>6</sup> However, contact electrification is known to occur if the same polymer material is used on both sides.<sup>10</sup> The same material, however, should also exhibit the

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same affinity towards different ions in water, and should not lead to contact charging. In addition, it has been shown that contact electrification of polymer insulators occurs in the complete absence of water.<sup>11</sup>

Baytekin et al. have observed that nanoscopic mosaic-like structures carrying positive and negative charges are formed on polymer insulators after contacting-separating.<sup>8</sup> The non-equality between the positive and negative species adds up to the net surface charge. The fact that different charges may be observed on the same surface has not been reported earlier. The formation of charged species was attributed to heterolytic covalent bond cleavage. The covalent bond breaking on polymer surfaces is accompanied by reversible material transfer from one surface to another.<sup>12</sup>

If covalent bond cleavage is the mechanism for contact electrification, it must be higher for soft polymers with smaller cohesion energy or higher molecular weight between crosslinks because they are more prone to mechanical damage and bond breaking. In the present study, we investigated contact electrification of a large variety of polymer materials with different physicochemical properties.

Fig. 1(a) shows surface charge for various thermoplastic polymers with different elastic moduli. Polymer full names, surface charge and nanoindentation measurements are described in the (ESI†) and listed in the ESI† Table S1. Polymers with lower moduli exhibit higher surface charge values than those with higher moduli, and modulus is directly proportional to the cohesive energy of the material. The specific surface contact area-enhanced electrification can be excluded because all samples are flat (prepared with the same hot-pressing approach) and have similar surface roughness values, which have been measured by atomic force microscopy (ESI† Table S2). The average surface roughness for the polymers shown in Fig. 1(a) was 59.76 nm with the standard deviation of 21.78 nm. Moreover, we examined the influence of roughness on the surface charge for different polymers in contact with ITO, as shown in the ESI† Fig. S3 and Table S3. As expected, polymers with larger roughness produced over an order of magnitude higher surface charge values than their smooth counterparts. For example, upon increasing the surface roughness of polycarbonate (PC) from 70 nm to 654 nm, the surface charge value increases from 0.052 to 0.152 nC cm<sup>-2</sup>, whereas the soft styrene-ethylene-butylene-styrene copolymer (SEBS) with the surface roughness of 79.40 nm exhibits the surface charge value 0.92 nC cm<sup>-2</sup> after contacting ITO. SEBS, in accordance with nanoindentation measurements (Fig. 1(a) and ESI† Table S1), shows lowest modulus. Thus, the polymer cohesion energy has a significantly stronger influence on contact electrification than the surface roughness.

We also contacted and separated chemically different polymers with the same or different hardness values (Fig. 1(b)). Although chemically different, a hard polymer (PI, polyimide) in combination with other hard polymers (PS, polystyrene) produces a small surface charge. The same was observed for soft polymers by contacting-separating low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE), which have similar

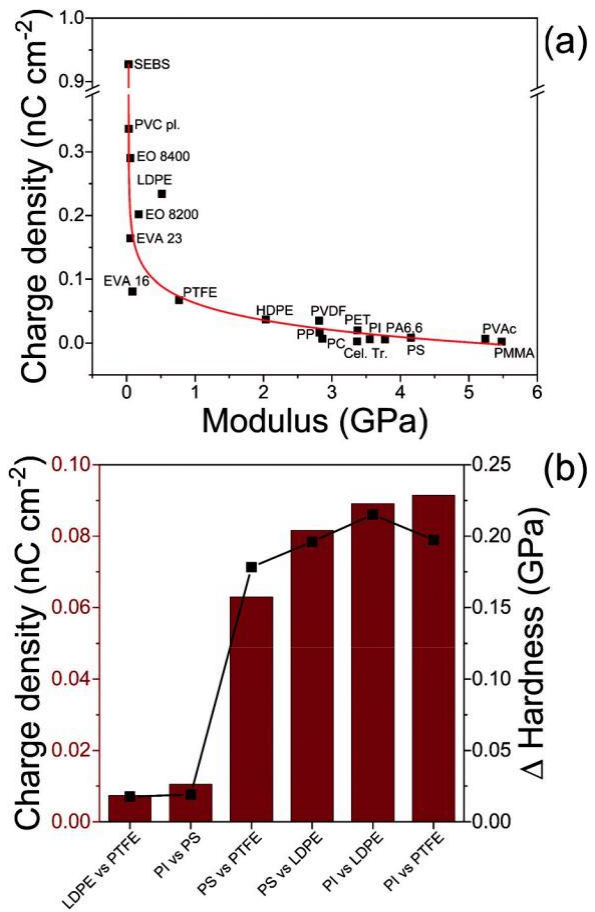


Fig. 1 Contact-electrification charge of thermoplastic polymers related to their mechanical properties. (a) Correlation between the modulus of polymer material and surface charge. (b) Contact-electrification charge density and hardness gap for different polymer combinations.

hardness values. When hard polymers were contacted with soft polymers, surface charges higher by an order of magnitude were obtained. Interestingly, the mutual contact of chemically different soft and hard polymers with the same difference between hardness produces very similar surface charge values. Open circuit voltage ( $V_{OC}$ ) and short circuit current ( $I_{SC}$ ) measurements for TEG devices based on polymers shown in Fig. 1 are presented in ESI† Fig. S4–S20.

To date, there is a general understanding that to observe surface charge, the contacted materials must have different chemical compositions;<sup>13</sup> polymers are even empirically ordered into a so-called “triboelectric series” based on their “electron affinity”—a tendency to acquire a positive or negative charge when in contact with a distinct material.<sup>13</sup> These electron affinity values are commonly used to select materials for TEG. Herein, we showed that there is no need to contact chemically different polymers for electrification to occur. Fig. 2 shows the current generated by the TEG device constructed from the same poly-propylene (PP) films. If the thermal history of the PP films was same, no current was observed; however, when PP films with different thermal histories were contacted-separated, the current of 35 nA and surface charge of 0.071 nC cm<sup>-2</sup> were generated.

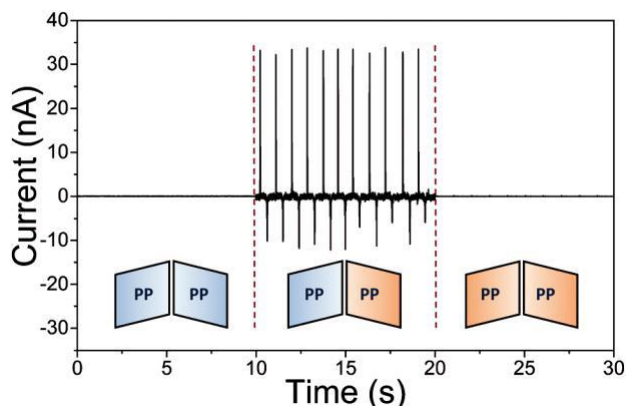


Fig. 2 Short-circuit current peaks generated by the contact-electrification of PP with similar and different thermal histories. Blue figures represent original polymer films and red figures represent polymer films subjected to thermal treatment (130 °C, 60 min).

Different thermal histories change macromolecular ordering and cohesion energy, as indicated by lower phase transition temperatures (ESI,† Fig. S21) and hardness change from 107.6 MPa to 96.2 MPa, respectively. This is in sharp contrast with the recently reported theory of contact electrification.<sup>7,13</sup>

Further, we studied contact electrification of polydimethylsiloxane (PDMS) with a different cross-linking degree, which was varied by changing the ratio between pre-polymer and the curing agent.<sup>14</sup> The surface charge increased from 0.31 to 3.39 nC cm<sup>-2</sup> with an increase in the molecular weight between crosslinks ( $M_C$ , g mol<sup>-1</sup>) (Fig. 3(a)). The method and measurements for the determination of  $M_C$  are described in ESI,† and the  $M_C$  values are shown in Table S4 (ESI,†). The TEG device constructed from flat PDMS with the curing agent to prepolymer ratio 1 : 30 in contact with ITO generate  $V_{OC}$  400 V (80 V cm<sup>-2</sup>) (voltage and current for all PDMS based TEG devices are shown in ESI,† Fig. S22 and S23).

Further, we contacted and separated chemically identical PDMS and studied contact electrification. When the cross-linking degree between contacting PDMS films was same, almost no

contact electrification was observed. The surface charge values for TEG when PDMS films in the ratio of 3 : 1 vs. 3 : 1 and 20 : 1 vs. 20 : 1 were contacted were 0.00143 nC cm<sup>-2</sup> and 0.00161 nC cm<sup>-2</sup>, respectively. When PDMS films with different cross-linking degrees were contacted (3 : 1 vs. 20 : 1), surface charge (0.0168 nC cm<sup>-2</sup>), voltage, and current higher by an order of magnitude were obtained (ESI,† Fig. S24 and S25), thus confirming the above-mentioned results obtained from TEG based on thermoplastic polymers.

The increased surface charge for PDMS with a smaller cross-linking degree can also be related to higher adhesion at the contact interface. The force necessary for the separation of the two contacted films increased when the cross-linking degree was reduced. Based on our understanding, to provide high net surface charge density on the polymer, the polymer should show strong surface adhesion and low cohesion energy in bulk, such that the energy of the adhesive (physical) bonds formed between contacting surfaces is larger than the energy of the chemical or/and physical bonds in bulk. This could potentially allow enhanced covalent bond scission and material transfer between two contacting surfaces.<sup>15</sup>

To observe higher adhesion, we increased the contacting force as described in ESI,† With the increasing contacting force, the adhesion between contacted surfaces and force to separate them increases, and as shown in Fig. 3(b), when separation stress between two films is larger, the surface charge increases drastically.

If the reason for contact electrification is a heterolytic covalent bond break, the mass transfer should occur alongside with surface charging.<sup>12</sup> The mass transfer was confirmed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) studies. As demonstrated in the ESI,† Fig. S26, the ITO surface viewed by AFM contains polymer pieces after being contacted with PDMS. The mass transfer of PDMS was also confirmed by the XPS studies, where the Si 2s (153.9 eV) and Si 2p (102.7 eV) signal peaks were observed in the photoelectron spectrum from the ITO surface after contact with PDMS (ESI,† Fig. S27).

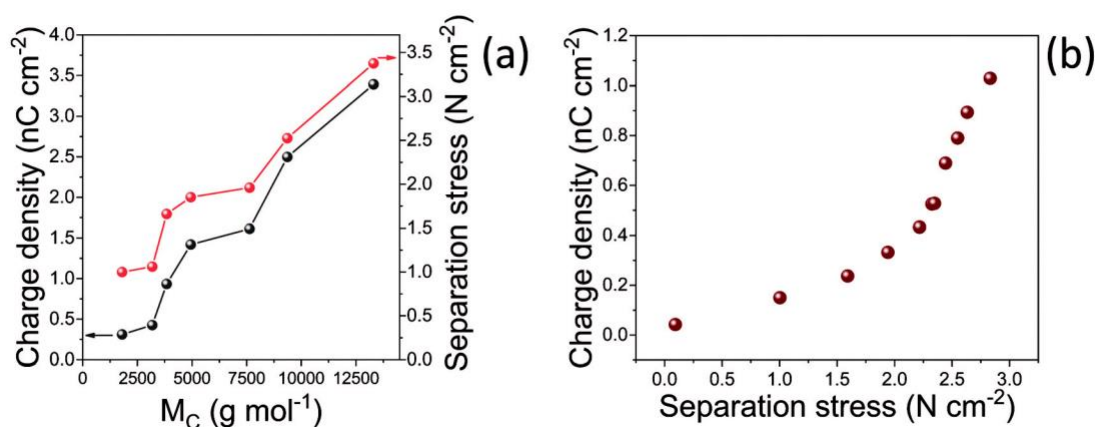


Fig. 3 Contact-electrification charge of PDMS: (a) surface charge density and adhesion force increase as we increase the molecular weight between PDMS crosslinking points. (b) Relationship between the charge and separation stress required when the contacting force before separation step is gradually increased for PDMS (10 : 1 ratio).

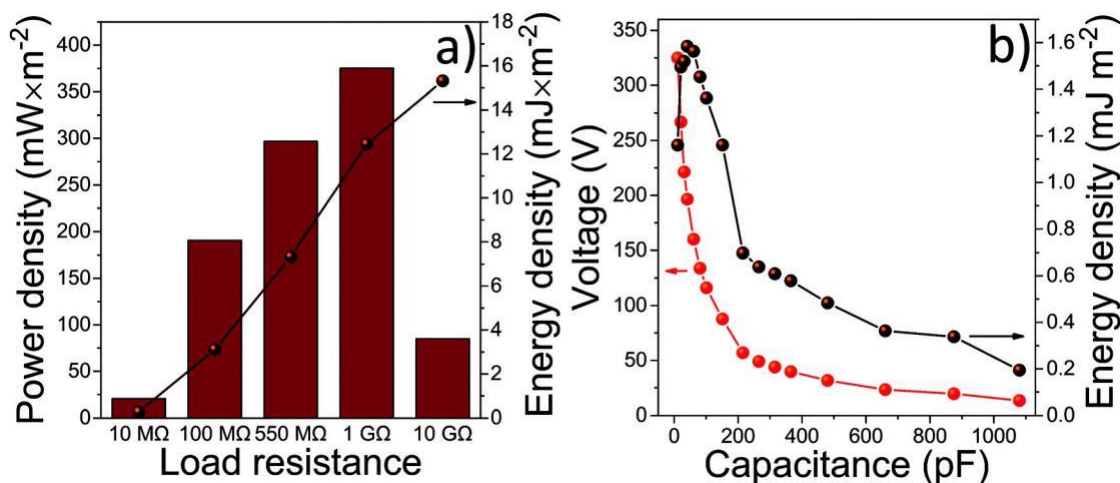


Fig. 4 Hydrogen peroxide-modified SEBS TEG energy density measurements. (a) Power and energy densities of hydrogen peroxide-treated SEBS-based TEG. (b) Energy density stored in the capacitor after contact-electrification of hydrogen peroxide-treated SEBS TEG. The corresponding voltages are shown besides the energy.

Although material transfer occurred, the TEG devices were stable because material transport could also occur in both ways. The covalent bonds could restore during contacting due to frictional heat,<sup>16</sup> and thus, the long-term performance had a relatively simple explanation. The long-term stability is demonstrated in the ESL† Fig. S28 for TEG devices from three different polymers: hard (PMMA), soft (SEBS) and soft-crosslinked (PDMS). In the beginning, all the TEG devices showed smaller voltage; however, it became saturated at about 2000 cycles and did not change in the further 10 000 cycles.

Finally, we produced a TEG device using the soft thermo-plastic SEBS block copolymer (ESL† Fig. S10), which showed highest surface charging, as depicted in Fig. 1(a). We modified the surface of SEBS to make it more adhesive by treatment with a hydrogen peroxide solution, as described in ESL† Via this, we observed an increase in the separation stress by 38% from 2.97 N cm<sup>-2</sup> to 4.11 N cm<sup>-2</sup>. The increased adhesion of the peroxide-treated SEBS surfaces can be attributed to the formation of quasi-free ends of macromolecular chains.<sup>17</sup> As expected, for modified SEBS, the surface charge increased 3.14 times from 0.92 nC cm<sup>-2</sup> to 2.89 nC cm<sup>-2</sup>, I<sub>SC</sub> increased 2.4 times from 0.14 mA cm<sup>-2</sup> to 0.33 mA cm<sup>-2</sup> and V<sub>OC</sub> increased from 60 V cm<sup>-2</sup> to 156 V cm<sup>-2</sup>. Further, our 5 cm<sup>2</sup> TEG device generated 780 V, as demonstrated in the ESL† Fig. S29. Moreover, the hydrogen peroxide-treated SEBS reached 375.27 mW m<sup>-2</sup> power density under the optimized load resistance of 1 10<sup>9</sup> Ω (Fig. 4(a)). The energy density was obtained by integral  $E \frac{1}{4} P dt$ , which yielded 15.32 mJ m<sup>-2</sup> under load resistance of 1 10<sup>10</sup> Ω (Fig. 4(a)). The hydrogen peroxide-treated SEBS was also used to charge a variable capacitor circuit. The energy density stored in the capacitor after one contact–separation cycle and the corresponding voltage are shown in Fig. 4(b) for each capacitor value. The highest energy stored in the capacitor (1.58 mJ m<sup>-2</sup>), calculated by  $E = 0.5CU^2$ , was reached when the capacitance of the capacitor circuit was set to approximately 40 pF. Note that the

TEG device based on SEBS was produced for simple readily industrializable hot pressing approach. Thus, the expensive and complex nanostructuring approaches that have been considered essential for high-performance TEG devices can be excluded.

## Conclusions

The surface charge for polymers can be controlled by varying their physicochemical properties, such as the strength of macromolecular interactions in bulk and the surface adhesion, and thus, our experiments confirm the covalent bond cleavage as the mechanism for the contact electrification. Higher surface charge can be expected from the polymers that show strong surface adhesion and low cohesion energy in bulk. Thus, our strategy enables the improvement in the performance of TEG, leaving aside the expensive and complex nanostructuring approaches.

## Author contributions

A. Sutka and K. Malnieks conceived the study. A. Sutka interpreted results and wrote the manuscript. K. Malnieks, A. Linarts, L. Lapcinskis and P. Kaufelde performed sample preparation and testing. A. Berzina executed AFM measurements. R. Zabels performed nanoindentation measurements. Vilnis Jurkans and Ilvars Gornevs conducted electrical measurements. J. Blums and M. Knite performed calculations and contributed to result interpretation.

## Conflicts of interest

There are no conflicts to declare.

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# References

- 1 Z. L. Wang, ACS Nano, 2013, 7, 9533.
- 2 R. Hinchet, W. Seung and S.-W. Kim, ChemSusChem, 2015, 8, 2327.
- 3 J. Wang, C. Wu, Y. Dai, Z. Zhao, A. Wang, T. Zhang and Z. L. Wang, Nat. Commun., 2017, 8, 88.
- 4 J. Lowell, J. Phys. D: Appl. Phys., 1975, 8, 53.
- 5 J. Liu, A. Goswami, K. Jiang, F. Khan, S. Kim, R. McGee, Z. Li, Z. Hu, J. Lee and T. Thundat, Nat. Nanotechnol., 2018, 13, 112.
- 6 L. S. McCarty and G. M. Whitesides, Angew. Chem., Int. Ed., 2008, 47, 2188.
- 7 M. Willatzen and Z. L. Wang, Nano Energy, 2018, 52, 517.
- 8 H. T. Baytekin, A. Z. Patashinski, M. Branicki, B. Baytekin, S. Soh and B. A. Grzybowski, Science, 2011, 333, 308.
- 9 A. L. Sumner, E. J. Menke, Y. Dubowski, J. T. Newberg, R. M. Penner, J. C. Hemminger, L. M. Wingen, T. Brauers and B. J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2004, 6, 604.
- 10 M. M. Apodaca, P. J. Wesson, K. J. M. Bishop, M. A. Ratner and B. A. Grzybowski, Angew. Chem., Int. Ed., 2011, 49, 946.
- 11 H. T. Baytekin, B. Baytekin, S. Soh and B. A. Grzybowski, Angew. Chem., Int. Ed., 2011, 50, 6766.
- 12 H. T. Baytekin, B. Baytekin, J. T. Incorvati and B. A. Grzybowski, Angew. Chem., Int. Ed., 2012, 124, 4927.
- 13 J. Chen and Z. L. Wang, Joule, 2017, 1, 480.
- 14 A. Lamberti, M. D. Donato, A. Chiappone, F. Giorgis and G. Canavese, Smart Mater. Struct., 2014, 23, 105001.
- 15 R. K. Pandey, H. Kakehashi, H. Nakanishi and S. Soh, J. Phys. Chem. C, 2018, 122, 16154.
- 16 M. K. Beyer and H. Clausen-Schaumann, Chem. Rev., 2005, 105, 2921.
- 17 N. Maeda, N. Chen, M. Tirrell and J. N. Israelachvili, Science, 2002, 297, 379.