

# Correlating Material Transfer and Charge Transfer in Contact Electrification

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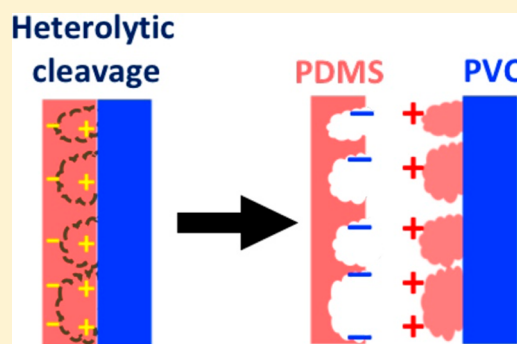
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## S Supporting Information

**ABSTRACT:** Static charge on surfaces of materials is generated when two solid surfaces come into contact and are then separated. It is important to understand the phenomenon because the influence of static charge on surfaces is widely felt in our daily lives and can have a wide range of applications or undesirable effects in industry. Although the phenomenon has been observed since antiquity, the fundamental mechanism that underlies the generation of charge on insulating surfaces is still not known. After many decades of research, different mechanisms have been proposed, including electron and ion transfer. One other possibility has been discussed to a lesser extent: material transfer (i.e., the transfer of quantities of charged materials). This study seeks to investigate the significance of material transfer by correlating the amount of charge transferred and the amount of material transferred from one surface to another after contact.

The investigation involved varying the degree of softness of a polymer (polydimethylsiloxane; PDMS), contact-charging it against another reference material, and analyzing the surfaces of the materials after contact. Results showed that when more material transferred, more charge was generated. An explanation for these results is that the surface of PDMS experienced heterolytic cleavage of bonds, which resulted in the generation of charge. When more cleavage of bonds occurred, more charge was generated, and more materials were transferred. Hence, material transfer seems to have an important contribution for the generation of charge by contact.



## INTRODUCTION

When two solid surfaces come into contact and are then separated, charge is usually transferred from one surface to another by contact electrification.<sup>1,2</sup> After contact, one surface charges positively, while the other surface charges negatively. Contact electrification is ubiquitous and has a wide range of consequences in our lives. For example, dust particles charged by contact electrification can adhere onto surfaces (e.g., glass or computer screens) easily. In many types of industries (e.g., petrochemical, chemical, pharmaceutical, semiconductor, and packaging), contact electrification can be problematic for different manufacturing processes. In the pharmaceutical industry, for example, charged drug particles can agglomerate or separate during processing, thus leading to nonuniform dosage of drugs.<sup>3,4</sup> In addition, excessive accumulation of charge by contact electrification may produce electrostatic discharge. This discharge can cause damage to electronic components and has been reported to cause the electronic industry billions of dollars per year.<sup>5,6</sup> Electrostatic discharge may also cause explosion of flammable materials (e.g., liquid and dust). In the petrochemical industry, for example, a static spark produced during loading and unloading of flammable liquids may potentially cause explosions. On the other hand,

the generation of charge by contact electrification is useful for many types of applications. Examples include the triboelectric generators for generating power (e.g., the triboelectric nanogenerators),<sup>7–10</sup> electrophotography,<sup>2</sup> electrostatic coating,<sup>11</sup> electrostatic filtration,<sup>11</sup> and manipulation of multiphase flow in microfluidic systems.<sup>12</sup>

Although the phenomenon has been known since antiquity,<sup>13</sup> the fundamental mechanisms that underlie contact electrification of insulating materials is still not completely understood. In general, the phenomenon is complex and many studies have observed unexpected results experimentally (e.g., contact de-electrification and the anomalous changes in the charge of materials).<sup>13–17</sup> In the past few decades, researchers have mainly been investigating two main mechanisms for the transfer of charge during contact electrification: electron transfer and ion transfer.<sup>18,19</sup> Relatively recently, Bard and co-workers have further provided experimental evidence that the species responsible for the transfer of charge between the surfaces is an electron.<sup>20,21</sup> On the other hand, other studies

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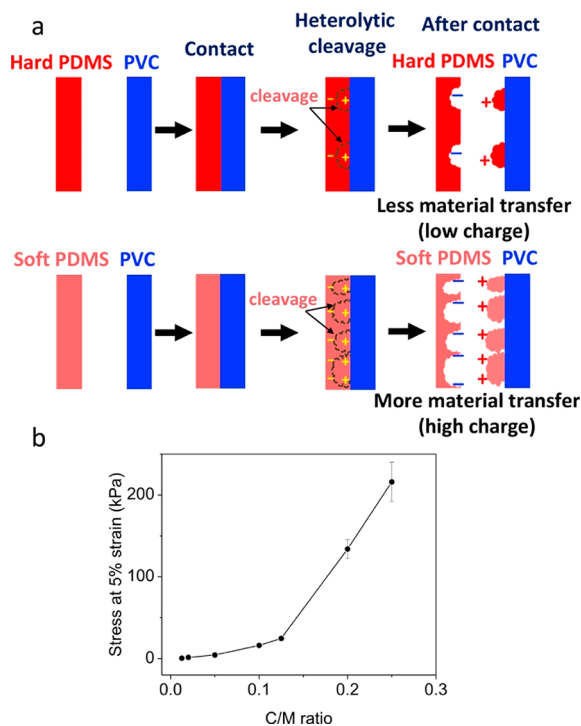
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proposed that ions, instead of electrons, are transferred during contact electrification.<sup>22–24</sup> Whitesides and co-workers have proposed that the charge transfer is due to the separation of aqueous ions (i.e.,  $H^+$  and  $OH^-$  ions) of the water adsorbed on the surfaces of materials during contact.<sup>2</sup>

One other possible mechanism that has been studied to a relatively lesser extent is material transfer. It is well-known that when two solid surfaces come into contact, small (e.g., nanoscopic) quantities of materials are transferred from one surface to another.<sup>25–28</sup> If the material is also charged (e.g., via heterolytic cleavage), charge can be transferred along with the small quantity of material from one surface to another (Figure 1a). Although this mechanism has received less attention in the



**Figure 1.** (a) Scheme illustrating material transfer and charge transfer occurring simultaneously during the contact electrification of two materials. (b) Plot of compressive stress measured at 5% compressive strain against the ratio of curing agent to monomer (C/M) of polydimethylsiloxane (PDMS).

past,<sup>27,28</sup> its significance has recently been discussed by various research groups.<sup>29–34</sup> For example, one study reported that material transfer is responsible for the reversal of the polarity of the materials after a prolonged period of contact between the materials.

In general, material transfer has not been recognized as an important mechanism in contact electrification of insulating materials due to one important reason: although it is known that small quantities of materials can transfer between solid surfaces during contact, it is not known whether a significant amount of charge is transferred along with the transfer of materials.<sup>27–30</sup> In this study, we seek to understand the significance of material transfer in contact electrification by investigating if there is a correlation between the amount of material transferred and the amount of charge transferred after contact. Specifically, we contact-charged a polymer of varying degrees of softness against a reference material. Our hypothesis is that, with an increasing softness of the polymer, there is an

increase in the amount of material transferred after contact. At the same time, we will also determine if the increase in material transfer can lead to a larger amount of charge transferred.

We chose polydimethylsiloxane (PDMS) as the polymer for investigating the mechanism of material transfer due to the following reasons. First, PDMS has many desirable properties (e.g., optically transparent, nontoxic, inert, and inexpensive), which allow it to be used in many types of applications (e.g., microfluidic and microelectromechanical systems).<sup>35–37</sup> In terms of contact electrification, PDMS usually charges highly upon contact; hence, it is often used for the investigation of the phenomenon.<sup>38–40</sup> PDMS charged by contact electrification may affect the performance of the polymer when it is used in its targeted applications (e.g., as a microfluidic chip); thus, it is important to study the fundamental mechanism of contact electrification of PDMS. In addition, the softness of PDMS can be varied easily. For example, the ratio of the curing agent to monomer can be changed (Figure 1b).<sup>35</sup> A difference in the time of curing at a high temperature can also lead to different softness of PDMS (Figure S1a,b, Supporting Information, SI). This ease and flexibility of preparation of PDMS make it a suitable candidate for our investigation.<sup>35–37</sup>

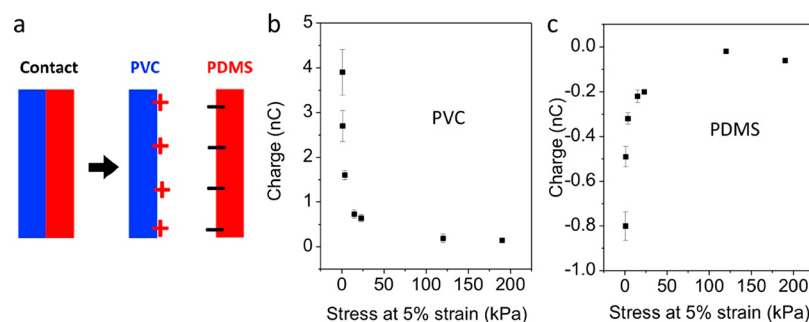
## EXPERIMENTAL SECTION

Thin flat pieces of PDMS ( $2.0 \times 1.5 \times 0.2$  cm) were fabricated for the contact-charging experiments (see the SI for more details on the methods and materials of the experiments). A typical process of fabrication involved mixing a certain ratio of curing agent and monomer (C/M ratio) at room temperature. Air bubbles were removed using a centrifuge (400 rpm). This mixture was kept at room temperature for at least 12 h, followed by heating it at 70 °C for 60 min. After polymerization, the pieces of PDMS of a certain softness against the reference material. Importantly, we only contacted the two materials once. The reason is because a previous study reported that multiple contacts between materials may lead to anomalous charging behaviors.<sup>29</sup> The experiments were conducted with the same amount of force for the contact (0.2 N) and under the same humidity (45%) and temperature (25 °C). Differences in experimental conditions can lead to different results (Figure S1c, SI).<sup>41</sup> After contact, we measured the charges of both of the contacting materials using a Faraday cup (ADCMT, 8031) connected to an electrometer (ADCMT, 8252 digital electrometer). The experiment was repeated for pieces of PDMS of different softness.

The contact-charging experiment involved bringing the pieces of PDMS into contact with another reference material. We chose polyvinyl chloride (PVC) as the reference material ( $2.0 \times 1.5 \times 0.1$  cm) because it tends to charge highly by contact electrification. Similarly, the pieces of reference materials were first washed and dried. After cleaning the pieces, we contacted a piece of PDMS of a certain softness against the reference material. Importantly, we only contacted the two materials once. The reason is because a previous study reported that multiple contacts between materials may lead to anomalous charging behaviors.<sup>29</sup> The experiments were conducted with the same amount of force for the contact (0.2 N) and under the same humidity (45%) and temperature (25 °C). Differences in experimental conditions can lead to different results (Figure S1c, SI).<sup>41</sup> After contact, we measured the charges of both of the contacting materials using a Faraday cup (ADCMT, 8031) connected to an electrometer (ADCMT, 8252 digital electrometer). The experiment was repeated for pieces of PDMS of different softness.

## RESULTS AND DISCUSSION

After preparing the pieces of PDMS of different softness by varying the C/M ratio, we quantified their softness using a mechanical tester. Specifically, we pressed a piece of PDMS



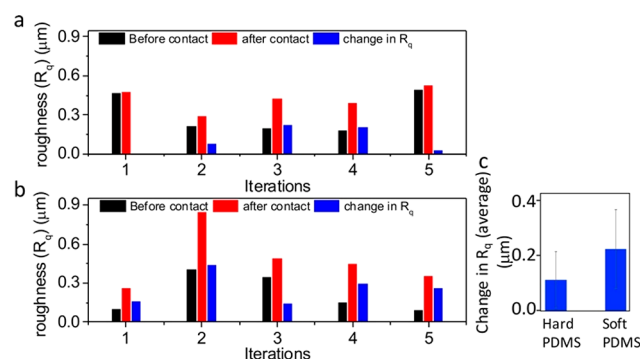
**Figure 2.** (a) Contact between PDMS of different softness (i.e., defined as the stress at 5% strain) and PVC. Charge generated on (b) PVC and (c) PDMS after contact.

with a measured amount of force up to a compressive strain of 5%. The stress applied at the compressive strain of 5% for all of the pieces of PDMS prepared with different C/M ratios is plotted in Figure 1b (see Figure S2 in the SI for the stress vs strain curves). Pieces of PDMS prepared with a higher C/M ratio required larger stress to be exerted in order to produce a compressive strain of 5%. The reason is because a higher ratio of C/M produces a more cross-linked and, thus, a harder piece of PDMS. Importantly, PDMS is usually prepared with a C/M ratio of 0.1 for most common applications (e.g., microfluidics); hence, our work involved the investigation of pieces of PDMS that are much harder or softer than the common type of PDMS.

After fabricating these pieces of PDMS, they were cleaned and contact-charged against the reference material, PVC. Results showed that the charge generated by contact electrification is higher for pieces of PDMS that are softer (Figure 2). Similar results were obtained when pieces of PDMS of different softness were prepared by using the same C/M ratio (i.e., 0.1) but with different curing times of the liquid monomers (Figure S1a-b, SI). We measured the contact angles of the pieces of PDMS of different softness and found that they were similar (see SI, section 7 and Figure S3); hence, surface wettability may not be important for the different amounts of charge generated by pieces of PDMS of different softness.

One possible explanation for the higher amount of charge generated by the softer pieces of PDMS is based on the mechanism of material transfer. When softer pieces of PDMS come into contact with the reference material, more material from the softer piece of PDMS is transferred to the reference material. If the material transferred is charged, then charge transfer takes place at the same time. In order to investigate if softer pieces of PDMS transfer more material to the reference material, we performed the analyses as follows. First, we analyzed the root-mean-square surface roughness ( $R_q$ ) of the surfaces of both the pieces of PDMS and PVC before and after contact electrification using a laser scanning confocal microscope for noncontact profilometry. In the first set of experiments, we contacted a piece of hard PDMS (C/M: 1/4; stress at 5% strain is 190 kPa) against a piece of PVC (Figure 3a).

The experiment was then repeated another four more times using new pieces of PDMS (of the same hardness) and PVC. In addition, we repeated the whole set of experiment using pieces of soft PDMS (C/M: 1/80; stress at 5% strain is 0.9 kPa) (Figure 3b). Results showed that there is consistently an increase in the surface roughness of PVC after contact with



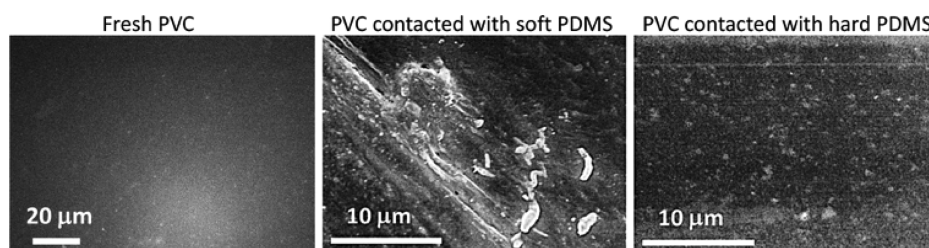
**Figure 3.** Changes in the root-mean-square surface roughness,  $R_q$ , of PVC after contacting with a piece of PDMS. A piece of PVC was contacted against a piece of (a) hard PDMS (i.e., C/M = 1/4; stress at 5% strain is 190 kPa) and (b) soft PDMS (i.e., C/M = 1/80; stress at 5% strain is 0.9 kPa). The black bars represent the  $R_q$  of PVC before contact. The red bars represent the  $R_q$  of PVC after contact. The blue bars show the difference of the  $R_q$  before and after contact. The plot shows the results of the contact-charging experiments for five pairs of PVC and PDMS. (c) Average change in  $R_q$  of PVC after contacting it with a piece of hard or soft PDMS.

PDMS for all of the contact charging experiments performed. Importantly, the increase in surface roughness is larger when PVC was contacted with a piece of soft PDMS than with a piece of hard PDMS (Figure 3c). One explanation for these results is that some quantity of materials was transferred from the surface of PDMS to the surface of PVC, and that softer pieces of PDMS transferred more materials over to PVC than harder pieces of PDMS.

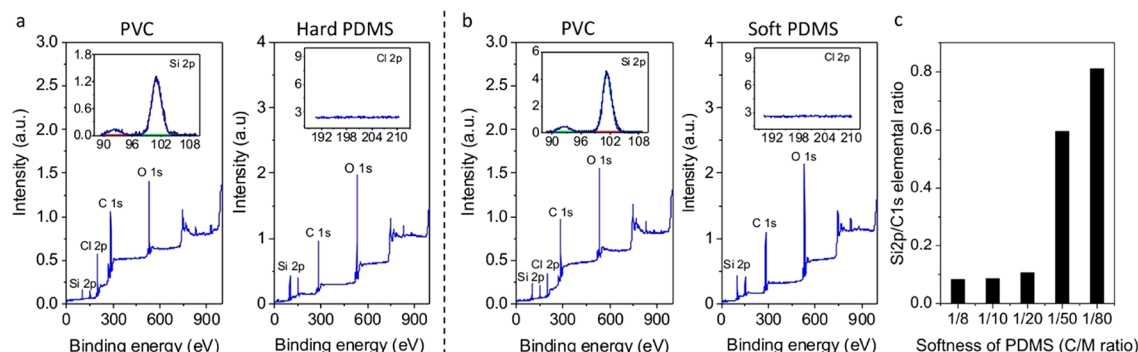
Besides analyzing surface roughness, we also observed the transfer of material visually by SEM (Figure 4). Specifically, we first analyzed the surface of a fresh piece of PVC by SEM, that is, a piece of PVC that was cleaned but not contacted with any other materials. The SEM image showed that the surface is fairly smooth. Subsequently, we contacted a piece of PVC with a piece of PDMS (either a soft piece of PDMS in which C/M = 1/80, or a hard piece of PDMS in which C/M = 1/4) and then analyzed the surface of the PVC by SEM and EDS.

Results showed that, for the piece of PVC that was contacted against the soft piece of PDMS, small fragments of materials (approximately a few μm) are present on the surface of PVC. The presence of these fragments indicates that material has been transferred from PDMS to PVC. We also observed the presence of smaller fragments of materials (e.g., ~1 μm or less) on the surface of the piece of PVC after it was contacted with a piece of hard PDMS. With respect to elemental mapping using EDS, we found that Si is present on the surfaces of PVC after





**Figure 4.** SEM images of a piece of fresh PVC (left), a piece of PVC contacted with a piece of soft PDMS (middle), and a piece of PVC contacted with a piece of hard PDMS (right).



**Figure 5.** Survey XPS spectra of the surfaces of the materials after contact electrification. A piece of PVC contacted against (a) a piece of hard PDMS or (b) a piece of soft PDMS. (c) The ratio of the Si 2p over C 1s for pieces of PVC after contacting them against pieces of PDMS of different softness.

contact (Figure S4, SI). These results again show that material has been transferred from PDMS to PVC.

In addition, we analyzed the chemical composition of the surfaces of the contact-charged materials by X-ray photoelectron spectroscopy (XPS; Figure 5). For a fresh piece of PVC that was cleaned but not contact-charged against other materials, the analysis showed only the peaks of C 1s, Cl 2p, and O 1s (Table 1 and Figure S5, SI); the presence of the O 1s peak is probably due to the small quantity of water adsorbed on the surface.<sup>2</sup> After contacting a piece of PVC with a piece of hard PDMS (C/M: 1/8; stress at 5% strain is 23 kPa) and analyzing the surface of the piece of PVC, an additional Si 2p peak was observed (Figure 5a). The presence of this Si 2p peak

indicated that material transferred from the piece of PDMS to PVC.

Subsequently, we contacted a piece of PVC against a piece of soft PDMS (C/M: 1/80; stress at 5% strain is 0.9 kPa) and analyzed the surface of PVC. Results showed that the Si 2p peak was larger for the contact between PVC with a piece of soft PDMS than that for PVC with a piece of hard PDMS (Figure 5a, b). We repeated the experiment for pieces of PDMS of different softness (i.e., different C/M ratios; Figure 5c). In general, the results indicated that softer pieces of PDMS transferred more materials over to PVC than harder pieces of PDMS.

In order to understand the nature of the transfer of materials better, we also performed the following two types of analyses. First, we analyzed the chemical composition of the surfaces of the pieces of PDMS after contacting them with the pieces of PVC. No Cl 2p peak was observed after analyzing the surfaces of both the hard and soft pieces of PDMS. This result indicated that the transfer of materials is unidirectional: materials transferred from PDMS to PVC but not from PVC to PDMS. In the second experiment, we washed the piece of PVC after it was contacted against the piece of soft PDMS. Specifically, we cleaned the piece of PVC by ultrasonication for 10 min in a solvent that was composed of a 1:1 mixture of ethanol and acetone. Analysis of the surface of this piece of PVC by XPS showed that there was still a significant amount of Si on the surface (Figure S6–S7, SI, and Table 1); hence, it seems that a significant proportion of the material that transferred from the piece of PDMS to PVC was strongly adhered onto the surface of PVC and was resistant to cleaning.

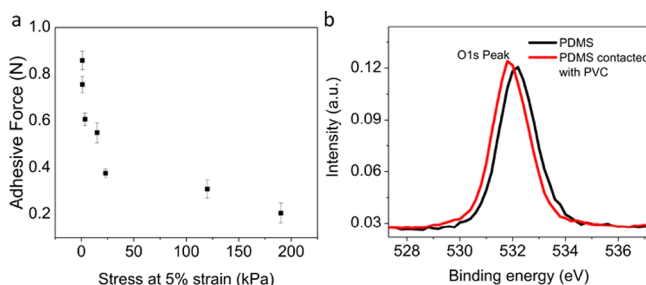
The results discussed above (i.e., from analyzing the surface topology and the chemical composition of the surfaces) showed that a piece of soft PDMS transfers more materials over to the piece of PVC than the piece of hard PDMS. One

**Table 1.** Percentages of the Elements of Different Pieces of PDMS and PVC as Analyzed by XPS

elements	% of elements			
	PVC (after contact with hard PDMS) <sup>a</sup>	PVC (after contact with soft PDMS) <sup>b</sup>	PVC (cleaned after contact with soft PDMS) <sup>c</sup>	fresh PVC <sup>d</sup>
C	48.44	44.3	58.5	66.4
O	16.28	19.3	11.7	10.9
Si	6.1	28.3	11.8	-
Cl	29.2	8.1	18.0	22.7

<sup>a</sup>Refers to the chemical composition of the surface of a piece of PVC after it was contact-charged against a piece of hard PDMS (C/M = 1/8). <sup>b</sup>Refers to the chemical composition of the surface of a piece of PVC after it was contact-charged against a piece of soft PDMS (C/M = 1/80). <sup>c</sup>Refers to the chemical composition of the surface of the piece of PVC represented by b that was subsequently cleaned by ultrasonication in a 1:1 mixture of ethanol and acetone. <sup>d</sup>Refers to the chemical composition of the surface of a fresh piece of PVC that was not contact-charged with any material.

possible explanation for this phenomenon is that the surface of the piece of soft PDMS may have a higher adhesive force when contacted with the reference material than the piece of hard PDMS. We investigated this possibility by bringing a piece of PDMS of a certain softness into contact with a piece of PVC and measured the adhesive force by a mechanical tester (MCT-2150, A&D company Ltd.). First, we adhered the pieces of PDMS and PVC onto the mechanical tester. The pieces of materials were then brought into contact with a force of 10 mN. Subsequently, the materials were gradually pulled apart while the maximum adhesive force between the materials was measured. We repeated the experiment using pieces of PDMS of different softness; the force of contact was the same at 10 mN for all of the experiments performed. Results showed that the surfaces of softer pieces of PDMS have larger maximum adhesive forces when contacted against the piece of PVC (Figure 6a). The adhesive force for the softest piece of PDMS was about five times more than that of the hardest piece of PDMS.



**Figure 6.** (a) Amount of adhesive force between two contacting pieces of PDMS and PVC depends on the degree of softness of the piece of PDMS (or, expressed as the amount of compressive stress at 5% of compressive strain) and (b) narrow range XPS spectra of O 1s of a fresh piece of PDMS (black) and a piece of PDMS contacted with PVC (red). A shift of about 0.27 eV to lower binding energy is observed.

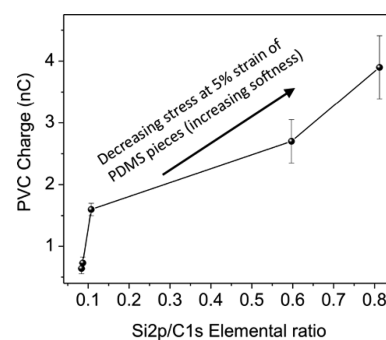
The adhesiveness of the surface of PDMS with the contacting surface may be due to intermolecular forces between the molecules at the surfaces, such as van der Waals forces (e.g., when the feet of a gecko adhere onto surfaces).<sup>42–45</sup> Alternatively, the attractive electrostatic force between the surfaces due to the presence of charges of opposite polarity on the contacting surfaces may contribute to the adhesive force. This attractive electrostatic force,  $F_E$ , between two charged flat plates of opposite polarity can be calculated by the equation,  $F_E = Q^2/(2A\epsilon)$ , where  $Q$  is the amount of charge on each surface,  $A$  is the area of contact, and  $\epsilon$  is the permittivity of air.  $Q$  is on the order of  $\sim 1$  nC in our experiments, and  $A$  is  $2.0 \times 1.5$  cm for the materials we used. Hence,  $F_E$  is calculated to be on the order of magnitude of  $\sim 10^{-4}$  N. This amount of force is negligible compared to the adhesive force that we measured (Figure 6a); hence, electrostatic force does not play a significant role in the adhesion. Because adhesiveness is a good measure of the amount of force involved and material transferred in contact electrification, we have replotted the amount of charge generated against the adhesive force in Figure S8, SI. The adhesion between PDMS and PVC may also be due to acid–base interactions.<sup>46</sup>

After pulling apart the surfaces that adhered onto each other, heterolytic cleavage of bonds may occur on the surface of the

materials. To investigate the heterolytic cleavage, we analyzed the surfaces of two pieces of PDMS by XPS: a piece of PDMS (C/M = 1/20) that was freshly prepared, and a piece of PDMS of the same C/M ratio that was contact-charged against a piece of PVC as the reference material. Results showed that the O 1s peak position for the freshly prepared piece of PDMS is 532.19 eV, whereas the O 1s peak position for the contact-charged piece of PDMS is 531.92 eV; hence, there is a shift of 0.27 eV to a lower binding energy after contact. A shift of the peak to a lower binding energy suggests the generation of an anionic oxygenated species on the surface.<sup>47</sup> Importantly, it has been reported in a previous study that a shift of  $\sim 0.2$  eV to a lower binding energy is due specifically to the heterolytic cleavage of bonds on the surface of PDMS.<sup>48</sup> The authors reported that mechanical modification of the surface of PDMS resulted in rupturing of bonds from the original unbroken polymeric chains ( $-\text{Si}(\text{CH}_3)_2\text{O}-$ ) of freshly prepared pieces of PDMS to the generation of anions ( $-(\text{CH}_3)_2\text{SiO}^-$ ) on the surface as a result of the heterolytic cleavage of the chains.

Based on all of the results described in this study, we propose an overall mechanism for the generation of charge on the surfaces of PDMS by contact electrification (i.e., the mechanism illustrated in Figure 1a) and the correlation of material transfer and charge transfer. When a piece of PDMS and a piece of reference material are brought into contact, the surfaces adhere onto each other due to the adhesiveness of the surfaces. Subsequently, the materials are pulled apart by an external force. This force may cause heterolytic cleavage of bonds of the molecules on the surface of PDMS;<sup>5,39</sup> heterolytic cleavage of bonds results in the generation of charged fragments of materials on the surface. After the heterolytic cleavage of bonds, a quantity of the charged material transferred from the surface of PDMS to the reference material (together with material that is not charged). In general, a softer piece of PDMS gives rise to a larger amount of adhesive force upon contact with the reference material. This larger amount of adhesive force may result in a larger amount of heterolytic cleavage of bonds on the surface of PDMS, a larger amount of charge generated, and a larger amount of material transferred to the reference material. When a larger amount of charged material transferred to the reference material, the softer piece of PDMS charges to a larger amount.

The correlation of material transfer and charge transfer can best be observed by replotting Figure 2a (for charge transfer) and Figure 5c (for material transfer). Figure 7 shows the amount of charge and material (i.e., Si 2p/C 1s ratio as analyzed by XPS) transferred onto the pieces of PVC after



**Figure 7.** Charge of PVC, after contact with pieces of PDMS of different softness (i.e., C/M ratio), with respect to Si 2p/C 1s.

contacting them with pieces of PDMS of different softness. This plot showed a positive correlation between charge transfer and material transfer. This empirically derived correlation strongly suggests that the material transferred during contact electrification is also charged in order for both charge and material to be transferred simultaneously.

## CONCLUSIONS

Despite many decades of research, the phenomenon of contact electrification of insulating materials is still not well understood. Several fundamental mechanisms have been proposed to explain the phenomenon; however, more studies have investigated electron transfer<sup>20,21</sup> and ion transfer<sup>22–24</sup> than other mechanisms, including material transfer.<sup>25–34</sup> This study showed that, by using pieces of PDMS of different softness for contact electrification, a general trend was observed: a larger amount of material transfer corresponded with a larger amount of charge transfer. Hence, it seems that a significant amount of charge transferred by material transfer. This relationship demonstrates the importance of material transfer as the fundamental mechanism that underlies contact electrification. In general, this importance likely applies to materials that are soft. Similar studies will be needed to investigate the relationship for hard materials. This study also showed that the softness of PDMS will need to be considered for applications that involve contact electrification of PDMS.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04357.

(1) Materials; (2) PDMS preparation method and contact electrification experiments; (3) instrumentation; (4) mechanical testing experiments: (i) stress versus strain measurements and (ii) adhesive force measurements; (5) roughness measurements; (6) XPS measurements; (7) influence of surface wettability. Figure S1: Factors affecting contact charging; effect of PDMS curing time and applied pressure during contact. Figure S2: Stress versus strain curves for PDMS prepared at different C/M ratio and PDMS prepared at different curing times. Figure S3: Contact angle of water droplet on different pieces of PDMS with different degree of softness. Figure S4: SEM and elemental imaging of fresh PVC, PVC contacted with a soft PDMS and hard PDMS. Figure S5: Survey XPS spectra of a fresh PVC piece. Figure S6: Survey XPS spectra of a cleaned PVC piece that was used to contact with a soft PDMS. Figure S7: Narrow range XPS spectra of a cleaned PVC piece that was used to contact with a soft PDMS. Figure S8. Charge of materials as a function of adhesiveness of PDMS (PDF)

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## Notes

The authors declare no competing financial interest.

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