Role of Contact Electrification and Electrostatic Interactions in Gecko Adhesion

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Electronic Supplementary Material

1. Materials and Methods

Teflon AF 1600, a tetrafluoroethylene (TFE) (35 mol%) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) (65 mol%) copolymer, was purchased from DuPont. One should note that "Teflon AF" is a different polymer from polytetrafluoroethylene (PTFE, Teflon). Polydimethylsiloxane (PDMS), received as a two-part Sylgard 184 Silicone Elastomer Kit with base to catalyst mix ratio of 10:1, was acquired from Dow Corning. Fluorinert Electronic Liquid FC-40 for dissolving Teflon AF was obtained from 3M and ethanol (ACS reagent, ≥99.5%) was purchased from Sigma. Ultra-smooth, mirror-finished copper sheets (99%, 28 gauge, 15×15 cm^2), which came coated with a plastic layer to protect them against scratches and possible surface oxidation, were obtained from Fire Mountain Gems and Beads. After cutting the copper sheets into smaller (~5×5 cm^2) pieces, and in preparation for spin-coating the polymer thin films over them, the protective plastic layers on the copper sheets were removed. Then, each sheet was cleaned individually using a commercial metal cleaner (Autosol Metal Polish from Autosol LLC.), followed by sonication in pure ethanol for 40 min using B1500A-MT Ultrasonic Cleaner (VWR International, LLC.). The sheets were finally rinsed with ethanol and, to prevent their oxidation in air, they were kept in ethanol prior to coating them with the polymers.

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The polymer thin films were spin-coated onto the ultra-polished copper sheets (~5×5 cm^2) using polymer precursor solutions and a G3–8 Spin Coater (Specialty Coating Systems, Inc.). The corresponding polymer precursor solution, spin speed (ω), and spin time (t) at which the polymer thin films were deposited, are detailed in table S1. After spin-coating, the polymer substrates were annealed for 2 h at 92 °C under vacuum. Annealing under these conditions ensures complete drying of Teflon AF thin films. The polymer substrates were then stored in ambient conditions for a week prior to conducting adhesion and charge measurement tests on them. The storage in ambient conditions was done to ensure that the PDMS was completely cured. The annealing under vacuum was followed by curing at ambient conditions. This was done to both polymer substrates so that the sample preparation was identical for both polymers.

Table S1. The corresponding solvent, concentration (C), spin speed (ω), and spin time (t) for fabrication of each polymer thin film as well as the ultimate thin film thickness (h_i), root mean squared (RMS) roughness, roughness average (R_a), and maximum height of the profile (R_t) of each thin film.

Polymer	**Solvent**	C (wt%)	ω (rpm)	t (s)	h_i (μm)	***RMS*** (nm)	R_a (nm)	R_t (nm)
Teflon AF	FC-40	4	1500	30	1.2±0.1	0.2±0.2	0.1±0.2	3.6±1.3
PDMS	—	—	6000	60	7.0±0.1	0.6±0.2	0.5±0.2	9.3±1.3

The thicknesses of the polymer thin films (see table S1) were measured by thin film step height measurements from ~1 cm off the edge of the copper sheets using a P-6 Stylus Profiler (KLA-Tencor Corporation). Roughness of the backing copper sheet, as well as of the polymer thin films (see table S1), were determined by atomic force microscopy (AFM) from a 5×5 μm^2 area from the substrate (see figure S1) using a Dimension Icon Atomic Force Microscope (Bruker Corporation). The tip used for AFM imaging was a silicon tip on a nitride lever (ScanAsyst; thickness: 650 nm; length: 115 μm; width: 25 μm), obtained from Bruker Corporation. Analysis of AFM images to obtain the roughness values of the substrates was carried out using WSxM software (Nanotec Electronica S.L.). Each roughness value cited in table S1 is the average value determined from three independently replicated tests, with the deviations corresponding to the standard deviation. The measured roughness values for the polymer thin films are comparable and are in the range of roughness at which gecko adhesion is fully functional [1,2]. Polarity characteristics (hydrophobicity and hydrophilicity) of the polymer thin films were determined by measuring the static contact angle of water on them using a home-built set-up. For the water contact angle measurement test, a water droplet (~30 µL in volume) was placed on the polymer thin film at a rate of 15 mL/min. An image of the water droplet was taken from the side, ~20 s after the water droplet was completely deposited onto the sample. The static contact angle of each water droplet was then measured by analyzing the captured image using a MATLAB code. Each reported water contact angle result represents the average from six individual and independently replicated experiments along with the standard deviation.

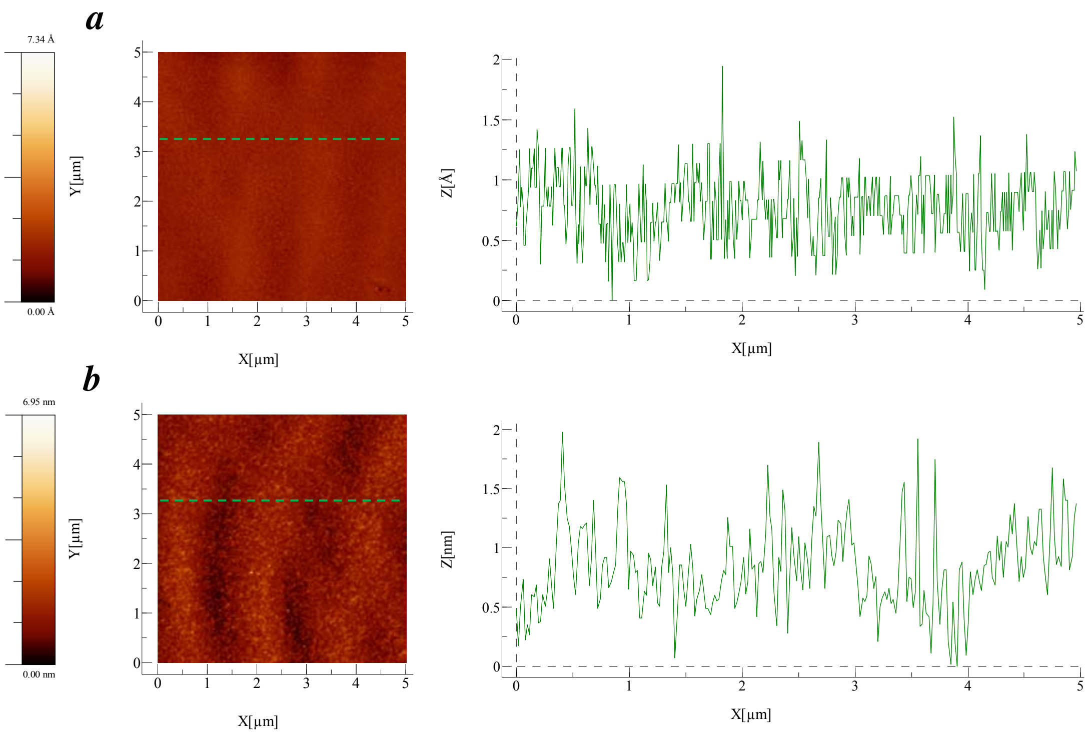

Figure S1. Characteristic AFM images taken from a 5×5 µm^2 area from (*a*) Teflon AF and (*b*) PDMS thin films coated on copper sheets. The cross-sectional profiles of the surface along the green dashed lines are shown on the right side diagrams.

Details on the length, weight, and size of the foot pads of all the five Tokay geckos employed in this research are outlined in table S2. The area of the gecko toe pads was measured by scanning the animal toe pads on a HP Deskjet F4480 All-in-One Scanner/Printer (Hewlett-Packard Development Company) and subsequently measuring the contact area using ImageJ software from National Institutes of Health. All adhesion/charge experiments on animals in this research were conducted in compliance with Animals for Research Act of Ontario (Revised Statutes of Ontario), the Guide to the Care and Use of Experimental Animals from Canadian Council on

Animal Care, and the University of Waterloo's Guidelines for the Care and Use of Animals in Research and Teaching.

Table S2. Weight, length, and toe pad area of the geckos employed. The pad areas were estimated from analyzing three different scans of the animal toe pads while the deviations correspond to the standard deviations.

Animal number	**Weight** (g)	**Length** (cm)	**Front toe pad area** (mm^2)	**Back toe pad area** (mm^2)
1	55	25	84±4	109±5
2	36	25	83±4	102±5
3	27	23	70±2	85±5
4	48	25	105±5	142±3
5	50	26	121±3	149±3

2. Charge and Force Measurements

To electrically isolate the polymer-coated copper sheets from the surroundings, each sheet was glued to a thick polytetrafluoroethylene (PTFE, Teflon) sheet (6×3.5×0.6 cm^3, L×W×H) using an ethyl cyanoacrylate-based glue (Krazy Glue Corp.) and dried under vacuum at ambient temperature for two hours. The PTFE sheet under the copper sheet was fit into a PTFE plate to provide a frictionless platform for adhesion tests (see figure S2). The whole set-up was then mounted on a ~1 cm thick wood plate which was mounted vertically on a wall.

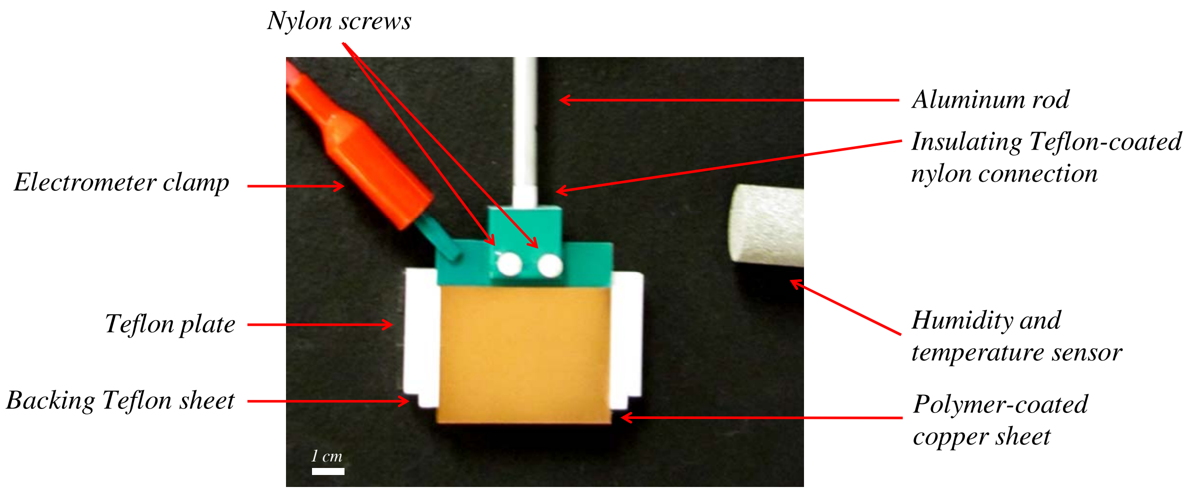

Figure S2. The image of the set-up used for *in-situ* adhesion/force measurements. The whole set-up was mounted on a black wood plate, fixed vertically on a wall.

Before performing adhesion and charge measurement tests, both of the polymer thin films, as well as the gecko foot pads, were grounded to remove any static charge which may have built up on them. Discharging the polymer thin films was carried out by using an Anti-Static Static-Away Brush (Ted Pella, Inc.) to obtain a completely clean and electrically neutral substrate. To remove any previously adsorbed water from the polymer thin films (*i.e.*, water that adsorbed after fabrication of the thin films and before performing the tests), they were rinsed with ethanol and allowed to air dry for a few minutes prior to discharging, before the tests were conducted. The gecko foot pads, on the other hand, were discharged by placing the foot pads on a large polished copper sheet that was grounded to a metal desk. Since the gecko's body is also electrically conductive, throughout both charge and adhesion measurements, the gecko's body itself was also grounded through one of its foot pads (opposite to the foot on which the test was being performed) using a grounded wire. For instance, when a test was carried out on the right-front leg, the left-back leg was grounded. Experiments were carried out on both front and back legs. The charge and force measurement results were processed and analyzed using Principal Component Analysis (PCA) on STATISTICA from StatSoft Inc.

2.1. Charge Measurements. During charge measurement tests, as a gecko foot pad was brought into contact with the polymer thin film, electric charges were separated at the contact interface, leading to induction of an image charge on the backing copper sheet. During contact of gecko foot pads with the polymer thin films, the sign and density of the induced image charges (σ_{image}) were concurrently recorded by an electrometer (Model 6517A Electrometer/High Resistance Meter from Keithley Instruments), which was connected to the back of the copper sheet (figure S2). Using σ_{image} and neglecting the effect of charge backflow via tunneling [3,4], the actual surface charge density over the polymer (σ_s) during contact was determined by [5]

$$\sigma_{image} = \sigma_s \left(\frac{D + d_i + d_g}{\frac{(h_i - d_i)}{\varepsilon_i} - \frac{d_g}{\varepsilon_g} + \frac{D}{\varepsilon_D}} \right) \tag{S1}$$

where D is the actual separation distance between the setae and the thin film; d_i and d_g are the charge penetration depths in the polymer and the nano-spatula at the tip of each seta, respectively. h_i is the thickness of the polymer thin film, and ε_i, ε_g, and ε_D are the dielectric constants of the polymer, the seta, and the separating medium, respectively.

In calculating the surface charge density during contact, since gecko toe pads come into intimate contact while both the nano-spatulas of gecko setae and polymer surfaces are perfectly smooth at a sub-nanometer scale (see table S1), the actual separation distance, D, was considered as that of the interatomic separation distance of ~0.3 nm [6,7]. The charge penetration depths, d_i and d_g, were considered equal and approximated by 3 nm [8]. The charge penetration depth of 3 nm was employed for all calculations because it is the upper limit of charge penetration reported for a single contact with an insulator (although lower charge penetration depths in the order of atomic dimensions, as small as 0.35±0.8 nm [9], have also been reported for a single contact with an insulator). It should be noted that using smaller charge penetration depth values for charge calculations does not affect any of the conclusions drawn herein. If, however, smaller penetration depths were used, the surface charge densities would be larger than those reported herein, which still completely supports our conclusions.

The dielectric constants (ε_i) of Teflon AF and PDMS were considered as 2.65 and 1.93, respectively [10,11]. Although the dielectric constants of the employed polymers are constant, the dielectric constant of β-keratin (ε_g), the main component of the fibrillar feature (setae) on the gecko toe pads [12,13], varies between ~4 and 20, depending on the water uptake of the material [14-18], which depends on the environmental conditions. In particular, keratinous materials absorb a specific amount of water depending on the humidity. Considering that absorbing water from air can dramatically alter both the dielectric constant and the conductivity of a keratinous material [14-19], and in order to reduce the influence of the humidity history on the uptake of water by gecko foot pads, the geckos were incubated in a plastic chamber (with relative humidity (RH) of ~100%) for ~2 h prior to both charge and adhesion tests. In addition, all tests were carried out at constant RH of 50±4 % (temperature, T=24±1 °C). Therefore, for the charge calculated using equation S1, the intermediate value of 16 was considered for ε_g, given that it is the approximate average value reported for keratinous materials in the range of relative humidity employed for our experiments [16,17,19]. It is also worthwhile mentioning that, for charge calculations, the effect of using the lower or upper values of ε_g (*i.e.*, 4 or 20, respectively) on the final results is negligible.

Although water uptake by gecko foot pads in humid conditions does not significantly affect the charge calculations, humidity variations have proven to have a significant (and complicated) effect on contact electrification, which differs from system to system [3,4]. Therefore, RH was kept constant – yet relatively high – in all experiments. The relatively high specific RH of 50±4 % was chosen for two reasons. First, Tokay geckos, employed in this research, inhabit tropical forests where humidity levels are normally high [20]. Secondly, formation of water layers over the polymer in humid conditions can help to stabilize their surface charging [4]. Therefore, to obtain more consistent results, all experiments were performed at the relatively high and consistent RH of 50±4 %. It should be noted that water is not necessary for contact electrification to occur [4] and effective surface charging does happen in even completely dry conditions [4,21,22]. Temperature and RH were monitored using a HI 93640N Thermohygrometer (HANNA Instruments Inc.) with resolution of ±0.5 °C for temperature measurements and ±4% for RH readings.

In calculations of charges densities by equation S1, the dielectric constant of the separating medium (ε_D) was considered equal to 1, the dielectric constant of air. However, it should be noted that at the RH of 50±4 % where the experiments were carried out, it is expected that small amounts of water adsorb over the polymer thin films. Since the employed polymers are hydrophobic, the thickness of the adsorbed layer of water is typically less than 0.2 nm – roughly a thickness of a monolayer of water [23]. Seeing that the dielectric constant of a monolayer of water (≈6) is not very high (as that of the bulk of water (≈80)), in charge calculations, the presence of water at the interface was ignored, since the effect of its incorporation in charge measurements was negligible.

2.2. Force Measurements. To investigate the influence of surface charging on the adhesion of gecko foot pads, the magnitude of the total generated adhesion force against each substrate was also recorded during all the experiments. In each test, the shear adhesion force was recorded using a dual-range force sensor (at the ±10 N range with ±0.01 N resolution; Vernier Software &

Technology, LLC.), which was connected to the vertically-aligned polymer-coated copper sheet – from the top – with an aluminum rod (see figure S2). Force data collection was conducted by Logger Lite software (Vernier Software & Technology, LLC.), connected to the force sensor.

During adhesion tests, the gecko foot pad was dragged across Teflon AF for 2–3 mm and across PDMS for about 10 mm. This was because dragging the toes further than few millimeters over Teflon AF led to a significant increase in surface forces that the fibrillar lamellae on the gecko toe pads were pulled off the toe. Therefore, to obtain consistent results without damaging the fibrillar feature of the toes, the foot pad was dragged for only few millimeters over Teflon AF to saturate the shear forces (up to 6–7 $\mathrm{N/cm^2}$). Over PDMS, on the other hand, since less adhesion occurred (maximum up to ~1.5 $\mathrm{N/cm^2}$), the foot pads could be dragged further. In order to reach the saturation shear adhesion forces, the foot pads were dragged about 10 mm over PDMS, which did not cause any damage to the fibrillar feature of the toes.

The magnitude of the van der Waals (vdW) interaction force between two smooth solid bodies, such as that between gecko toes and the polymer substrates, can be theoretically determined with the Hamaker method [24,25]. According to the Hamaker method, the vdW-driven force (F_{vdW}) interacting between phase 1 (a tip of a nano-spatula (considered as a curved segment of a sphere with radius, $R \approx 2$ μm) [6]) and phase 2 (polymer thin film) across medium 3 at the separation distance D (see figure 2 of the manuscript) can be calculated by $F_{vdW} = -A_{132}R/6D^2$, where A_{132} is the Hamaker constant between phase 1 and phase 2, interacting across medium 3 [6]. Since the geometry of contact on both Teflon AF and PDMS is the same, the difference between the vdW interactions of the employed polymers can be simply reduced to the difference between their Hamaker constants for contact with gecko foot pads. The corresponding Hamaker constant for each system can be determined according to the Lifshitz model [26], where multi-body interactions are considered in the presence of a continuous separating medium. According to the Lifshitz model,

$$A_{132} \approx \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3hv_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{\frac{1}{2}}(n_2^2 + n_3^2)^{\frac{1}{2}}\{(n_1^2 + n_3^2)^{\frac{1}{2}} + (n_2^2 + n_3^2)^{\frac{1}{2}}\}} \quad \text{S2}$$

where *k* is Boltzmann's constant, *T* is absolute temperature, *h* is Planck's constant, and v_e is the electron absorption frequency, which is typically around 3×10^{15} 1/s [25]. Here, ε_1, ε_2, and ε_3 are the corresponding dielectric constants of phase 1, phase 2, and medium 3, respectively, while n_1, n_2, and n_3 are the refractive indices of phase 1, phase 2, and medium 3, respectively. According to equation S2, and considering the dielectric constant of Teflon AF as 1.93 and its refractive index as 1.31 (which are the lowest dielectric constant and refractive index of all solid organic polymers) [10], the Hamaker constant for Teflon AF-seta contact would be 5.1×10^{-20} J. On the other hand, PDMS, which has a larger dielectric constant (2.65) and refractive index (1.41) than Teflon AF [11], has a Hamaker constant of 6.5×10^{-20} J (~1.3 times larger than that of Teflon AF) when in contact with a gecko seta. In contact with both substrates, the values of the dielectric constant and refractive index of a seta were considered as those of keratin and equal to 16 (as discussed earlier) and 1.55, respectively [27].

The magnitude of the electrostatic interaction force (F_{elc}) that was generated between the gecko toe pad and the substrate can be simply determined from [28]

$$F_{elc} = -\frac{a\sigma_s^2}{2\varepsilon_0\varepsilon_r} \quad \text{S3}$$

where *a* is the area of contact, σ_s is the contact surface charge density, ε_0 is the permittivity of free space, and ε_r is the effective dielectric constant of the contact interface; ε_r can be obtained from

$$\frac{D + d_i + d_g}{\varepsilon_r} = \frac{D}{\varepsilon_D} + \frac{d_i}{\varepsilon_i} + \frac{d_g}{\varepsilon_g} \quad \text{S4}$$

where *D* is the actual separation distance between the foot pad and the polymer thin film, while d_i and d_g are the charge penetration depths in the polymer and the nano-spatula at the tip of each individual seta, respectively (see figure 2*c* of the manuscript); ε_i, ε_g, and ε_D are the dielectric constants of the polymer, the gecko fibrils (setae), and the separating medium, respectively.

In calculations of contact electrification-driven adhesion forces by equations S3 and S4, the dielectric constant of the separating medium (ε_D) was again considered equal to the dielectric constant of air (*i.e.*, 1). However, it is worthwhile mentioning that by considering even a monolayer of water at the interface (which is doubtful to form on such hydrophobic materials as Teflon AF and PDMS at RH of 50±4 %), the force calculations would change by less than ~20%; in particular, the effective dielectric constant of the interface (ε_r) for Teflon AF would change from 3.1 to 3.5 while that of PDMS would go up from 3.9 to 4.6, leading to approximately 20% change in force calculations.

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