Contact Self-Cleaning of Synthetic Gecko Adhesive from Polymer Microfibers

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Natural gecko toes covered by nanomicro structures can repeatedly adhere to surfaces without collecting dirt. Inspired by geckos, we fabricated a high-aspect-ratio fibrillar adhesive from a stiff polymer and demonstrated self-cleaning of the adhesive during contact with a surface. In contrast to a conventional pressure-sensitive adhesive (PSA), the contaminated synthetic fibrillar adhesive recovered about 33% of the shear adhesion of clean samples after multiple contacts with a clean, dry surface.

Conventional pressure-sensitive adhesives (PSA) use soft viscoelastic polymers (Young’s modulus \(\leq 100 \text{kPa} \text{ measured at } 1 \text{ Hz}^{1–3} \)) to make intimate contact with surfaces to achieve high adhesion. However, soft polymers tend to collect dirt and lose adhesion with repeated use. In contrast, a gecko uses millions of keratinous nano and microhairs (Young’s modulus \(E \approx 1.5 \text{ GPa}^{4–6} \)) to cling to and walk on virtually any surface. These hairs shed dirt particles during contact with a surface, keeping its natural adhesive sufficiently clean to support the gecko’s body weight.\(^5\)

A key factor in the self-cleaning ability of gecko structures is the nonadhesive default state exhibited by the gecko fibers.\(^6\) To adhere, the fibers need to be dragged to expose the spatula tips, increasing the contact fraction by approximately 7.5-fold.\(^6\) In contrast to the well-known lotus effect\(^7\) in which particles are removed from a nonadhesive and highly hydrophobic surface by water droplets, gecko setae self-clean particles during use, even on dry surfaces. We restrict our discussion here to the self-cleaning of adhesives on dry surfaces during use. Natural gecko setae are the only previously reported self-cleaning adhesive on dry surfaces.

Recently, gecko-inspired synthetic adhesives (GSAs)\(^8\) have been fabricated using soft polymers (Young’s modulus \(\leq 10 \text{ MPa}^{9–14} \)) or hard polymers\(^15–18\) (Young’s modulus \(\geq 1.5 \text{ GPa} \)). Also, arrays of carbon nanotubes (CNT) have been used to achieve cleaning of the adhesive during contact with a surface. In contrast to a conventional pressure-sensitive adhesive (PSA), inspired by geckos, we fabricated a high-aspect-ratio fibrillar adhesive from a stiff polymer and demonstrated self-cleaning on dry surfaces during use, one of the important advantages of a gecko-inspired adhesive over conventional pressure-sensitive adhesives. Autumn\(^24\) has identified seven benchmark properties that are characteristic of geckolike adhesives, which are (1) anisotropic attachment, (2) a high adhesion coefficient, (3) a low detachment force, (4) material-independent adhesion, (5) self-cleaning, (6) anti-self-adhesion, and (7) a nonsticky default state. Although properties 1–4 and 7 have been previously demonstrated\(^25,26\) in a single material, in this letter we report the first geckolike microfibrillar material that also demonstrates self-cleaning during contact.

To create a self-cleanable adhesive, we fabricated high-aspect-ratio fibrillar arrays from polypropylene (Young’s modulus \(E \approx 1.5 \text{ GPa}, \text{ measured with Sintech tensile tester } 2/S, \text{ MTS Systems} \)). In previous work, these hard-polymer-based fibrillar materials have shown unique adhesion properties, similar to those of gecko setae, including sliding enhanced shear adhesion\(^19\) with low peeling force and frictional adhesion\(^21\) with a spherical indenter.\(^28\) In this letter, we use a contact “step” protocol similar to that used for natural gecko setal arrays\(^7\) to demonstrate self-cleaning of the synthetic fibrillar adhesive. The self-cleaning synthetic adhesive has been demonstrated using water\(^16,22\) and mechanical vibration.\(^22\) Superhydrophobicity may lead to the cleaning of fibrillar adhesive by water.\(^24\) However, no synthetic adhesive has demonstrated self-cleaning on dry surfaces during use, one of the important advantages of a gecko-inspired adhesive over conventional pressure-sensitive adhesives.

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adhesive should be useful in a variety of applications where conventional adhesives can be easily contaminated.

The fibrillar adhesives were fabricated by casting a single layer of a 25-µm-thick polypropylene (PP) film (TF-225-4, Premier Laboratory Supply Inc.) in a vacuum oven at 200 °C into a 20-µm-thick polycarbonate (PC) track-etched membrane filter (ISOPORE, Millipore Inc.) containing 300-nm-radius pores as illustrated in Figure 1A. Using a fixed fiber length, this fiber radius was selected to provide bending compliance while preventing fibers from clumping. The polycarbonate filter was etched completely for 10 min in a first bath and 5 min in a second bath of methylene chloride (MC) to release the polypropylene fibrillar surface and film. The resulting samples were rinsed in isopropyl alcohol and air dried (Figure 1D). The polypropylene film contains approximately 42 million fibers per square centimeter with the average length and radius of the fibers being 18 µm and 300 nm, respectively. The microstructured polypropylene film was cut into 2 cm × 2.5 cm rectangles using a razor blade, and a 2 cm × 0.5 cm × 0.05 cm load bar with a small hole in which a string goes through was attached to distribute the pulling force uniformly.

To simulate contamination with dirt particles, microspheres with a mean radius of 1.15 µm (gold powder, spherical, radius ≤2.5 µm, Alfa Aesar) were applied to cover the whole area of fibrillar adhesives and conventional pressure-sensitive adhesives by freely dropping microspheres from about 5 cm above the adhesives. (Au microspheres were supplied in dry powder form with only weak clumping. Au microspheres were applied uniformly with similar density on the PSA and fibrillar surfaces by gravity, without applying any contact force.) After application, the adhesives were gently shaken to remove excess microsphere particles. As shown in Figure 2A,C, microspheres initially covered most of the area.

The samples were tested using a “simulated step” protocol shown in Figure 3 similar to a gecko’s walking step. The samples were first compressively loaded (<1 N/cm²) onto a clean glass substrate manually with a gloved finger (Figure 3A). (It has been shown previously that the shear strength is independent of the initial normal preload.25) The samples were next loaded parallel to the glass substrate by a weight attached to the load bar through a string (Figure 3B), and then the normal load was removed while maintaining the parallel load (Figure 3C). If the sample could hold the weight, then we removed the sample from the substrate manually (Figure 3D) and increased the weight for the next step. If the sample could not hold the weight, then the sample fell and was caught by a gloved hand just below the weight. In case of failure to support the weight, we used the same weight for the next simulated step. Before each simulated step, the glass substrate was cleaned with isopropyl alcohol to remove residual particles. After 30 simulated steps, the fibrillar adhesive shed about 60% of the microspheres onto the glass substrate as shown in Figure 2B. Some microspheres remained embedded between fibers and were not self-cleaned. As a control, we used a 0.2 cm × 0.5 cm conventional pressure-sensitive adhesive (PSA) (Scotch Magic Tape, 3M). After the simulated steps, the soft polymer of the conventional PSA was almost completely covered by microspheres, as shown in Figure 2D. This is possibly because microspheres not in direct contact with the soft polymer are taken off and recaptured in the exposed area of the soft polymer during simulated steps.
To quantify the self-cleaning capability of the adhesives, the shear adhesion strength was measured by applying a load parallel to the glass substrate during every simulated step as shown in Figure 3C. (The normal compressive load is zero during this phase of the testing cycle; this is not a friction test.) With no contamination, both fibrillar adhesives and PSAs could sustain a 4 N load parallel to a glass substrate (precleaned microscope slides, Fisher Scientific). (We limited the shear force to 4 N to prevent plastic deformation or tearing of the samples’ thin backing.) After the samples were contaminated, the initial shear load tried was 0.2 N. This shear load was tested at every simulated step until the sample could sustain it (eight simulated steps for fibrillar adhesive sample 1). Once the sample could sustain this load, the shear load was increased by 0.1 N for the next simulated step. Following 30 successive simulated steps, fibrillar adhesive sample 1 could sustain a shear load of 1.0 N but did not show further improvement with five more simulated steps. This saturation is consistent with the quantity of microspheres deposited on the glass substrate after each step, as shown in the bottom three images in Figure 4. Initial contact steps left many microspheres on the clean glass substrate, with diminishing particle removal after further steps. As expected, the PSA contaminated by microspheres did not recover any shear adhesion and could not sustain 0.05 N, even after 35 steps.

The synthetic fibrillar adhesives did not self-clean larger particles during contact. To observe the self-cleaning dependence on particle size, four differently sized polystyrene microspheres, 1.5, 2, 3 (also containing 12% 5 µm), and 5 µm in radius (Corpuscular Inc.), were used as dirt particles. Unlike gold microspheres, dry polystyrene microspheres contained lumps of microspheres. To obtain single-sized microspheres, we mixed dry polystyrene microspheres in isopropanol in about a 1:30 ratio. The mixture was ultrasonically agitated (2510 Branson) for 10 min to separate lumps. Then, several drops of microspheres in an isopropanol suspension were deposited on a clean glass slide and air dried. Air-dried polystyrene microspheres became approximately single-layered. The polystyrene microspheres were transferred to fibrillar adhesives by dragging adhesive samples on the glass slide covered with the single-layer microspheres. The shear adhesion strength of clean samples before being contaminated with polystyrene microspheres was 4 N. Prior to reuse, fibrillar samples were cleaned by removing clogged microspheres in an isopropanol bath with an ultrasonic cleaner (2510 Branson) for 2 min after ultrasonic cleaning, samples could again hold 4 N of shear.

Contaminated samples with uniformly sized polystyrene microspheres were tested with the same methods for gold particles as described in Figure 4. After typically 20–25 simulated steps, samples contaminated with 1.5-µm-radius microspheres recovered about 34% (SD = 13%, three arrays, six measurements) of the shear force of uncontaminated samples, as shown in Figure 5. Samples contaminated with 2-µm-radius microspheres recovered about 29% of the shear force of uncontaminated samples (SD = 9%, three arrays, six measurements) after 20–25 steps. However, samples contaminated with 3- and 5-µm-radius particles could not sustain 0.2 N in shear (5% of the shear force of uncontaminated samples, three samples, six measurements) even after 25 steps. The contact self-cleaning of the fibrillar adhesives demonstrated above is consistent with a greater affinity of the microspheres for the glass substrate than for the fibers as described for natural gecko setae. The self-cleaning of natural gecko setae was explained by comparing attraction forces and energies acting on a microsphere in contact with spatulae and a glass substrate. Hansen and Autumn argue that the small number of spatulae
contacting a spherical particle have less net adhesive force than particle adhesion to a flat substrate. We use a similar argument as with Hansen and Autumn\(^5\) for self-cleaning using the Johnson–Kendall–Roberts (JKR) contact model\(^30,31\) and reported surface energies.\(^30\) Neglecting surface roughness, we can estimate the adhesion forces from the JKR model.\(^29\) The sphere–glass pull-off force is

\[
F_{\text{sg}} = \frac{3}{2\pi} R_s W_{\text{sg}}
\]

and the sphere–fiber pull-off force is

\[
F_{\text{sf}} = \frac{3}{2\pi} R_s R_f W_{\text{sf}}
\]

with mean radius \(R_s = 1.15 \mu m\) for gold microspheres (Alfa Aesar) and fiber radius \(R_f = 0.3 \mu m\). The work of adhesion is estimated with

\[
W_{\text{sg}} = 2\sqrt{\gamma_s \gamma_g}
\]

and

\[
W_{\text{sf}} = 2\sqrt{\gamma_s \gamma_f}
\]

(ref 32) where the surface energy is \(\gamma_g = 115–200 \text{ mJ/m}^2\) for \(\text{SiO}_2\)\(^30\) and \(\gamma_f = 30 \text{ mJ/m}^2\) for polypropylene.\(^31\) The ratio of pull-off forces is

\[
N = \frac{F_{\text{sg}}}{F_{\text{sf}}} = \left(1 + \frac{R_s}{R_f}\right) \frac{\sqrt{\gamma_g}}{\sqrt{\gamma_f}}
\]

and contact with \(N > 9\) fibers would be required to balance the microsphere–substrate contact. Considering an average fiber spacing of \(1.5 \mu m\), the typical microsphere (mean radius \(R_s = 1.15 \mu m\)) will be in contact with one to four fibers (Figure 2B). Thus, the microspheres are preferentially attracted to the glass substrate instead of the fibrillar adhesive. Note that the ratio of pull-off forces is independent of \(\gamma_s\). Although we have not tested other substrates, we predict contact self-cleaning for materials with small \(\gamma_f\) compared to \(\gamma_g\).

Because the sphere–glass pull-off force \(F_{\text{sg}}\) is proportional to \(R_s\) whereas the total sphere–fiber pull-off force \(N F_{\text{sf}}\) is approximately proportional to \(R_s^2\) (\(N_f\) is the number of fibers in the projected area of a microsphere), larger particles will not self-clean. The SEM images in Figure 6 show that 1.5- \(\mu m\) and 5-\(\mu m\)-radius (Figure 6B) polystyrene microspheres (Corpuscular Inc.) remain in contact with fibers after 25 simulated steps. From Figure 6, a 1.5 \(\mu m\) polystyrene particle is in contact with one to four fibers whereas 5 \(\mu m\) particles are embedded among fibers, many of which are also in side contact with the microspheres. Note that side contact has much more contact area than tip contact, which makes large radius particle self-cleaning less likely.\(^33\) From geometry, a 1.5-\(\mu m\)-radius microsphere comes into contact with an average of 3 fibers whereas a 5-\(\mu m\)-radius microsphere comes into contact with an average of 33 fibers. Hence, it is less energetically favorable to self-clean 5-\(\mu m\)-radius particles than smaller particles. The results of self-cleaning smaller particles and not self-cleaning larger particles support the model that fibrillar adhesives self-clean by unbalanced pull-off forces.

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microsphere for the glass substrate than for the fibers. Thus, more fiber tips are exposed to the substrate in the next step, increasing adhesion.

Surface roughness may help self-cleaning\(^{36}\) by catching particles during sliding, but under our experimental conditions (rms surface roughness of the glass slide scanned with an atomic force microscope (Metrology AFM, Molecular Imaging Inc.) is 3.3 nm) the surface roughness is about 1/1000 of the particle size.

The dry self-cleaning of the natural gecko setae\(^{5}\) and the synthetic fibrillar adhesive do not use water droplets, which are required for the wet self-cleaning (lotus effect) of nonadhesive surfaces. Although we report only the dry self-cleaning of the fibrillar adhesive in this letter, the superhydrophobic surface (water contact angles of \(150-160^\circ\)) of the fibrillar adhesive also shows almost complete wet self-cleaning with water droplets.

In conclusion, stiff polymer fibrillar adhesives showed self-cleaning properties with microspheres (radius \(\leq 2.5 \, \mu m\)), as samples recovered 25–33% of the original shear adhesion force after 30 simulated steps. In contrast, shear adhesion in gecko toes recovered 36% of the clean value after only eight steps using a larger particle size (radius \(\leq 6 \, \mu m\)).\(^{5}\) even though the contamination method and the simulated step protocol were not exactly the same. The higher efficiency of the natural gecko setae may be from the hierarchical structure of the gecko setae. The natural gecko’s spatula tips may push off particles efficiently while switching back and forth between adhesive and nonadhesive states. Also, longer natural setae provide more space between them, thus there may be a higher probability for larger particles to be removed from spatula tips. Experiments with different sized polystyrene microspheres showed that the synthetic fibrillar adhesives did not self-clean larger particles, which is consistent with a JKR pull-off force model. In addition, the large embedded microspheres protrude above the fiber tips, preventing fibers from making contacting with the substrate and thus preventing adhesion. We expect that as fabrication technology develops further, future hierarchical structured fibrillar adhesives will have thin, flat spatula tips and more space between fibers and hence will be able to self-clean a wider range of particle sizes with fewer steps as natural gecko setae do.

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