CARBON NANOTUBES BASED GECKO INSPIRED ADHESIVES

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Geckos have the ability to stick and peel their feet at rapid rates without expending significant energy, thus enabling them to climb smooth vertical surfaces at rapid rates\textsuperscript{1}. It was observed that despite repeated adhesion and peeling, geckos were able to maintain their stickiness for months\textsuperscript{2}. Adhesives used in our daily life are viscoelastic in nature and behave differently than gecko foot. The synthetic adhesives are not suitable for repeated adhesion and are soiled easily in dusty environments. A successful viscoelastic adhesive needs both liquid-like and solid-like characteristics\textsuperscript{3}. Liquid-like properties allow them to wet the bonding surface, thus allowing a very large area of contact. Solid-like properties allow them to sustain certain level of stress during de-bonding\textsuperscript{3-4}. Materials where this liquid-to-solid transition occurs with changes in temperature, or solvent evaporation, or some chemical reaction cannot be used in applications where continuous bonding and de-bonding is required. Pressure sensitive adhesives (PSA) can stick to different surfaces without involving any change of temperature or solvent evaporation. PSA could be used reversibly, but being viscoelastic they have some inherent shortcomings\textsuperscript{5}. The low modulus limits the maximum stress the PSA can hold. Additionally, the peeling of PSA is rate-dependent, they exhibit creep, and their tacky nature makes them susceptible to contamination. Synthetic adhesives based on the gecko mechanism could overcome the difficulties encountered with PSA. These materials can find applications in robotics, microelectronics, sports, and space applications.

The Gecko foot has a multi-dimensional hierarchical structure\textsuperscript{6}, which consists of macroscopic lamellas that are composed of thousands of microscopic hair called setae. Each setae further divides into hundreds of nanoscopic hair called spatula. When pressed against any surface these hair bend to conform to the surface allowing very large area of contact. Figures 1A and 1B show a comparison of how a liquid and a solid system can achieve large area of contact with the bonding surface. The high area of contact is important in maximizing the van der Waals interactions and translating that to high adhesive forces. Split contact mechanism\textsuperscript{7,8} (Figure 1C) suggests that small diameter are necessary to achieve larger area of contact. Besides the diameter of hair, the hierarchical structure also plays an important role in achieving high adhesion (Figure 2 shows the hierarchical structure found on gecko foot).

Inspired from the structure found on gecko feet, we have synthesized carbon nanotube-based hierarchical hairy structure. Carbon nanotubes were synthesized using chemical vapor deposition process\textsuperscript{9}. Figure 3 shows scanning electron microscope (SEM) image of carbon nanotube structures. Photolithography was used to create patterns of size ranging from 50-500 \(\mu\)m. The patterns act as setae and individual carbon nanotubes as spatula. These vertically aligned nanotubes were transferred onto a polymeric substrate (the geometry would be referred as gecko tape). Adhesion measurements were done in shear geometry as shown in Figure 4A. Gecko tape was pressed on various surfaces and force required to peel them off were measured.
In case of un-patterned carbon nanotubes, the shear forces for a 0.12 cm$^2$ area tape were 14 N/cm$^2$. This force is comparable to the shear forces measured for natural geckos (10 N/cm$^2$). However, we observed that shear forces did not scale up with increase in area (as shown in Figure 4B). The hierarchical structure on gecko feet plays an important role in high shear adhesion. Figure 4C shows shear forces for different pattern sizes. By optimizing the pattern size and the height of carbon nanotubes, very high shear forces can be achieved. The 50 μm pattern size with 200 μm carbon nanotube length showed four times higher adhesion than natural gecko foot$^9$.

Synthetic gecko tape is inherently non-tacky and sticks only when high area of contact is achieved on application of preload, indicating that it may have self cleaning abilities like gecko foot. When a sample of synthetic gecko tape was soiled using silica particles, it regained back its stickiness by touching it to mica for a few times. Applying small vibrations to these materials also made dust particles fall off, rendering them cleaner. Another mechanism of self-cleaning observed in nature are lotus leaves. In the case of lotus if the material is superhydrophobic, water can roll off the surface carrying the dust particles with it$^{10-11}$. We have observed that if suitable pattern size is chosen, the synthetic gecko tapes showed very high water contact angle in addition to high shear adhesion. Here, we have shown cleaning properties of carbon nanotubes of 250 μm pattern size with 100 μm length. These samples had a static contact angle of 155±3° (Figure 4D)$^{12}$. The carbon nano tube-based synthetic gecko tapes were extremely stable under water and exhibit high contact angle even after multiple exposures to water. The high hydrophobic stability of these carbon nanotubes as compare to other vertically aligned structures may arise from fact that synthetic gecko tapes are formed by transferring carbon nanotube structure onto a polymer matrix using a glue. This glue at the base of carbon nanotubes gives extra stability to the structure thus preventing it from collapsing.

Shear test were done on pristine samples and cleaned samples to measure how the shear adhesion strength is regained back (Figure 4E). Results showed that shear stress of cleaned samples was 60-90% of the values of the pristine samples. The slightly lower shear stress may be due to the small silica particles getting stuck in the spacing between carbon nanotubes. The recovery of shear stress is very promising in comparison to gecko. The gecko measurements regain only 50% of the original shear stress after eight steps$^2$.

To conclude, we synthesized gecko inspired synthetic adhesive tapes based on completely elastic system unlike conventional viscoelastic adhesives. These synthetic micro-patterned carbon nanotube-based gecko tapes show not only higher adhesive shear strength than natural gecko feet, but also mimic the remarkable self-cleaning abilities of the gecko and the lotus leaf. The properties could be further enhanced by studying and optimizing the patch size and spacing between nanotube bundles. The backing material and binding glue may also play an important role in the overall performance. Carbon nanotubes based synthetic gecko tape will not only form basis of a new class of adhesive but will also help in better understanding of elastic adhesive systems.

References


**Figure1.** Elastic and viscoelastic adhesives. (A) A sketch showing conventional adhesive forming a high area of contact with two bonding surfaces by flowing and filling in the gaps. (B) A sketch illustrating the mechanism of adhesion for elastic hair. The hairs could bend and conform to the topology of the surface thus allowing very high area of contact with the bonding surface (C) Split contact mechanism explains how a smaller diameter hair could have higher area of contact than a thicker fiber, thus leading to higher force of adhesion\(^7\),\(^8\).
Figure 2. Different levels of hierarchical found on gecko foot. (A) Optical image showing macroscopic structure of gecko feet. (B) Optical image showing lamella structures (scansor) on toes. (C) SEM image showing each scansor is composed of thousands of microscopic hair called setae. (D) Images of setae further divide into nanoscopic hair called spatulas.²

Figure 3. Scanning electron microscope images of carbon nanotube microstructure. (A) SEM image of 50 μm pillars of carbon nanotubes. (B) Higher magnification SEM image of these pillars. Each of these pillars is composed of millions of nanometer sized carbon nanotube hair.
Figure 4. High adhesion and self-cleaning behavior of carbon nanotube based synthetic gecko tapes. (A) The geometry used for shear measurement for gecko tape. (B) Force per unit area decreases as the sample area increases for a uniform sample of carbon nanotubes. (C) Force measurement for patterned carbon nanotube structure. By optimizing pattern size and height of carbon nanotubes we find four times higher adhesion than natural gecko feet. (D) A 10 μl water droplet on 250 μm pattern size synthetic gecko tape. (E) Measurements of shear stress of pristine sample with that of self-cleaned samples.
TECH 32 Technical Seminar Speaker

Carbon Nanotubes Based Gecko-Inspired Adhesives
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