Biomimetic adhesives: a review of recent developments

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Abstract
Purpose – The purpose of this paper is to provide a review of recent progress into the development of biomimetic adhesives, particularly those that mimic the attachment mechanism of the gecko lizard’s foot.

Design/methodology/approach – This paper first discusses the discovery of the gecko’s adhesion mechanism. It then describes key “gecko glue” developments and summarises the properties of experimental adhesives that exploit this effect. It concludes with a consideration of anticipated applications.

Findings – This paper shows that, following the discovery of the gecko’s adhesion mechanism in 2002, which is based on van der Waals forces, biomimetic adhesives have become the topic of a major research effort. These developments are poised to yield families of novel adhesive materials with superior properties which are likely to find uses in industries ranging from defence and nanotechnology to healthcare and sport.

Originality/value – The paper provides a unique insight into the latest developments in biomimetic adhesive technology.

Keywords Adhesives, Nanotechnology, Polymers

Paper type Technical paper

In 1941, Swiss engineer George de Mestral became curious about the seeds of the burdock plant that had become attached so tenaciously to his clothes and dog’s fur. Examining them under a microscope, he saw that they consisted of hundreds of tiny but strong hooks (Figure 1) and realised that this type of structure could form the basis of simple, rugged and reversible jointing technology. He subsequently developed the idea and was granted a patent for his “hook and loop” fastener in 1955 which he named Velcro, after the French words velours, meaning velvet and crochet, or hook. This was probably the first example of a commercial biomimetics jointing technique. Far more recently, scientists have been studying the application of biomimetics to adhesives and this paper reviews recent developments in this technology.

Biomimetics is the creation of processes, devices or materials that imitate nature and one of the most recent and widely studied applications to adhesive technology is the so-called “Gecko glue”. Scientists had long wondered about the mechanism that allowed the gecko lizard (Figure 2) seemingly to defy gravity by clinging to vertical walls and hanging from ceilings. The problem was finally solved in 2000 by a research team led by biologists Kellar Autumn of Lewis & Clark College in Portland, Oregon, and Robert Full at the University of California at Berkeley (Autumn et al., 2000).

They showed that a gecko’s foot has around half a million microscopic hairs termed setae (Figure 3), which in turn bear perhaps a 1,000 smaller, mushroom-shaped, 200 nm wide fibres called spatulae (Figure 4). It was subsequently shown that the spatulae get so close to the substrate that molecules in both the foot and the surface generate a minute electrical charge that briefly draws one to the other (Autumn et al., 2002). Termed van der Waals forces, after the nineteenth century Dutch physicist who first described the effect, the forces occur when atoms or molecules come close to one another and, for a fleeting instant, display a weak electrical attraction:

Van der Waals forces
Van der Waals attractive forces are intermolecular forces that exist between atoms or non-polar molecules. They are extremely weak, typically less than 1 per cent of the average covalent bond strength. Van der Waals interactions are set up when the electronic distribution in a molecule becomes momentarily asymmetric, so that uneven charges are set up in the molecule. Hence, the molecule becomes transiently polar and is termed a “temporary dipole”. This can then disturb the electronic distribution in an adjacent molecule by inducing an opposite, or complementary, dipole. The two temporary dipoles attract each other and the two molecules are pulled close together. These forces operate only transiently because the electron densities in both the wall molecules and those of the gecko’s setae are constantly changing and so the forces are continuously being switched on and off. Prior to Autumn’s discovery, it was thought that van der Waals forces operated only at the sub-molecular level.

The combined effect of millions of spatulae provides an adhesive force many times greater than the gecko needs to hang from a ceiling by one foot and all 6.5 million or so setae on the toes of a single gecko attached simultaneously could support a weight of around 130 kg. These discoveries led to the idea that these structures and mechanisms might be exploited in a new family of adhesives and research groups from around the world are now investigating this concept. Indeed, interest in gecko-
Biomimetic adhesives is booming, as illustrated by the growing number of papers published on this topic (Figure 5).

One of the first developments was “gecko tape” which arose from a collaboration between the Centre for Mesoscience and Nanotechnology at the University of Manchester, UK, and the Institute for Microelectronics Technology in Russia. Work started in 2001 and 2 years later results were published in *Nature Materials* (Geim *et al.*, 2003). The group prepared flexible fibres of polyimide on the surface of a 5 μm thick film of the same material using electron beam lithography and dry etching in an oxygen plasma. The fibres were 2 μm long, with a diameter of around 500 nm and a periodicity of 1.6 μm, and covered an area of roughly 1 cm² (Figure 6). Initially, the team used a silicon wafer as a substrate but found that the tape’s adhesive power increased by almost 1,000 times if they used a soft bonding substrate such as Scotch tape. A sample of the tape was attached to the hand of a 15 cm high plastic Spiderman figure weighing 40 g, which enabled it to stick to a glass ceiling. The tape, which had a contact area of around 0.5 cm² with the glass, was able to carry a load of more than 100 g. Since, then, many groups have developed the concept further and in 2003 the University of California,
Berkeley group fabricated high-density arrays of spatular stalks which showed adhesion in shear in the order of 0.5 N cm\(^{-2}\) and in 2006 they demonstrated a novel high-friction array of 0.6 µm fibres (Figure 7) which showed shear resistance of 4 N cm\(^{-2}\). In 2007, they showed how the polypropylene fibre arrays can provide shear force without a normal load being present. The goal is to build arrays incorporating the necessary geometrical features which have a similar adhesive strength to geckos, about 10 N cm\(^{-2}\).

Several recent projects involve the application of nanotechnology, notably the use of carbon nanotubes (CNTs). In 2005, researchers from the University of Akron and Rensselaer Polytechnic Institute, USA, deposited multi-walled CNTs by chemical vapour deposition onto quartz and silicon substrates (Yurdumakan et al., 2005). The nanotubes were typically 10-20 nm in diameter and around 65 µm long. The group then encapsulated the vertically aligned nanotubes in PMMA polymer before exposing the top 25 µm of the tubes by etching away some of the polymer. The nanotubes tended to form entangled bundles about 50 nm in diameter because of the solvent drying process used after etching. Testing the tubes with a scanning probe microscope revealed their adhesion behaviour and force-distance curves showed weak repulsive forces as the probe approached the nanotubes and high adhesion as the probe was retracted. The team calculated the minimum force per unit area as 1.6 ± 0.5 × 10\(^{-7}\) nN nm\(^{-2}\), which is far larger than the figure the team estimated for the typical adhesive force of a gecko’s setae, which was 10\(^{-9}\) nN nm\(^{-2}\). Unlike conventional adhesive tape, which eventually loses its stickiness, this new material sticks like a permanent glue but can be removed and reused. It can also adhere to a wider variety of materials, including glass and Teflon. The team is now working on techniques to improve the tape’s strength. Presently, when pulled parallel to a surface, the tape releases, not because the CNTs lose adhesion from the surface but because they break. The researchers are currently working on a number of ways to strengthen the nanotubes and are also aiming to make the tape reusable thousands of times, rather than the dozens of times it can now be used. Other groups have also experimented with CNTs on silicon substrates as well as on Scotch tape. In the latter instance, the Akron/Rensselaer group found that this material could support a shear stress of 36 N cm\(^{-2}\), nearly four times higher than a gecko foot, and sticks to a variety of surfaces, including mica, glass and Teflon. It was also found that a 1 cm\(^2\) patch could support nearly 4 kg. Reported in the literature in 2007 (Ge et al., 2007), this was the first time that a macroscopic flexible patch that can be used repeatedly with peeling was shown to exhibit adhesive properties better than those of the natural gecko foot.

The structure of the feet a beetle from the family Chrysomelidae (Figure 8) has provided the inspiration for research by the Evolutionary Bimaterials Group at the Max Planck Institute for Metals Research in Stuttgart and colleagues at Gottlieb Binder GmbH, a specialist fastener systems company. This adhesive, based on a polymer mixture, is produced from a mould which has the required surface features – mushroom-shaped micro-hairs (Figure 9) – embossed as a negative image. The mould is filled with a polymerising mixture which is allowed to cure and then released. Whilst sounding deceptively easy, producing the material in this way has posed a significant challenge and details of the process remain secret. However, the material has
been shown to last for hundreds of applications, does not leave any visible surface marks and can be thoroughly cleaned with soap and water. It was found that 5 cm² of the material can hold objects weighing up to 100 g on walls and can also perform with higher weights: adhesive fibres on the soles of a 120 g robot helped it to climb a vertical glass wall (Daltorio et al., 2005).

A selection of results for macro-scale patches of gecko adhesive materials from a range of research groups, published over the period 2003-2007 is shown in Table I. For comparison, the final row shows natural gecko data. Adhesion coefficient is the ratio of pull-off normal stress to preload stress; a high value indicates that only light contact is needed to engage the adhesive.

Whilst all of these developments concern dry adhesion, researchers are also now studying how derivatives of naturally occurring compounds from molluscs can be combined with gecko-type structures to yield adhesives that will operate in either dry or wet conditions. In a recent paper in Nature (Lee et al., 2007), a group from Northwestern University described...
<table>
<thead>
<tr>
<th>Authors/date published</th>
<th>Material</th>
<th>Modulus</th>
<th>90° peel (N m$^{-1}$)</th>
<th>Pull-off (N)</th>
<th>Shear (N)</th>
<th>Area (mm²)</th>
<th>Normal preload (N cm$^{-2}$)</th>
<th>Adhesion coefficient</th>
<th>Effective modulus (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geim et al. (2003)</td>
<td>Polyimide on Scotch tape</td>
<td>3 GPa</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>100</td>
<td>50</td>
<td>0.06</td>
<td>3,000 (without buckling)</td>
</tr>
<tr>
<td>Sitti and Fearing (2003)</td>
<td>PDMS$^a$</td>
<td>0.5 MPa</td>
<td>–</td>
<td>0.003</td>
<td>–</td>
<td>100</td>
<td>0.025</td>
<td>0.1</td>
<td>~100</td>
</tr>
<tr>
<td>Shan et al. (2006)</td>
<td>PDMS$^a$</td>
<td>2.5 MPa</td>
<td>–</td>
<td>2.01</td>
<td>–</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>~240</td>
</tr>
<tr>
<td>Kim and Sitti (2006)</td>
<td>Polyurethane</td>
<td>3 MPa</td>
<td>0.07</td>
<td>0.07</td>
<td>–</td>
<td>0.4</td>
<td>12</td>
<td>1.5</td>
<td>~300</td>
</tr>
<tr>
<td>Gorb et al. (2006)</td>
<td>PVS$^b$</td>
<td>3 MPa</td>
<td>~1</td>
<td>0.4</td>
<td>–</td>
<td>7</td>
<td>2</td>
<td>2.9</td>
<td>~300</td>
</tr>
<tr>
<td>Zhao et al. (2006)</td>
<td>CNT on silicon</td>
<td>1,000 Gpa</td>
<td>0.08</td>
<td>0.5</td>
<td>0.6</td>
<td>8</td>
<td>&gt;500</td>
<td>&lt;0.01</td>
<td>~200</td>
</tr>
<tr>
<td>Schubert et al. (2007)</td>
<td>Polypropylene</td>
<td>1 Gpa</td>
<td>&lt;0.1 N cm$^{-1}$</td>
<td>~0</td>
<td>1</td>
<td>1,000</td>
<td>0.05</td>
<td>~2</td>
<td>~200</td>
</tr>
<tr>
<td>Ge et al. (2007)</td>
<td>CNT on Scotch tape</td>
<td>1,000 Gpa</td>
<td>2.5</td>
<td>0.8</td>
<td>36</td>
<td>16</td>
<td>25-50</td>
<td>&lt;0.1</td>
<td>~200</td>
</tr>
<tr>
<td>Qu and Dai (2007)</td>
<td>CNT on silicon</td>
<td>1,000 Gpa</td>
<td>–</td>
<td>~5</td>
<td>~2.5</td>
<td>16</td>
<td>125</td>
<td>&lt;0.2</td>
<td>~</td>
</tr>
<tr>
<td>Kustandi et al. (2007)</td>
<td>Parylene</td>
<td>2.8 Gpa</td>
<td>–</td>
<td>0.7</td>
<td>–</td>
<td>100</td>
<td>1</td>
<td>0.7</td>
<td>~</td>
</tr>
<tr>
<td>Autumn et al. (2000)</td>
<td>Beta keratin (natural gecko)</td>
<td>2 Gpa</td>
<td>~0</td>
<td>1</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>8.16</td>
<td>100</td>
</tr>
</tbody>
</table>

Notes: $^a$PDMS – polydimethylsiloxane; $^b$PVS – polyvinylsilane
an array of gecko-mimetic, 400 nm wide silicone pillars, fabricated by electron beam lithography and coated with a mussel-mimetic polymer poly(dopamine methacrylamide-co-methoxyethylacrylate) – p(DMA-co-MEA), a synthetic form of the catecholic amino acid 3,4-dihydroxy-l-phenylalanine which occurs naturally in mussels (Figure 10). Unlike true gecko glue, the new material does not depend on van der Waals forces for its adhesive properties; instead, it relies on the chemical interaction of the surface with the hydroxyl groups in the mussel protein. Nevertheless, the material improves wet adhesion 15-fold compared with uncoated pillar arrays and the so-called “geckel” tape adheres through 1,000 contact and release cycles, sticking strongly in both wet and dry environments. So far, the material has been tested on silicon nitride, titanium oxide and gold, all of which are used in the electronics industry. However, if it is to be used in bandages and medical tape, a key potential application, it will need to adhere to skin. The researchers have since tested other mussel-inspired synthetic proteins that have similar chemical groups and found that they are indeed adhesive to biological tissues. According to Phillip Messersmith, who led the team: “The challenge will be to scale up the technology and still have the geckel material exhibit adhesive behaviour”.

Automated, high-volume fabrication techniques will be necessary for these adhesives to be produced commercially and are being investigated by several research groups. A group led by Martin Sitti from Carnegie Mellon University is studying a range of different techniques which include deep reactive ion etching (DRIE), which has been used successfully to fabricate mushroom-shaped polymer fibre arrays (Figure 11), micro-moulding processes, direct self-assembly and photolithography. In 2006, researchers at BAE Systems Advanced Technology Centre at Bristol, UK, announced that they had produced samples of “synthetic gecko” – arrays of mushroom-shaped hairs of polyimide – by photolithography, with diameters up to 100 mm. These were shown to stick to almost any surface, including those covered in dirt, and a pull-off of 3,000 kg m\(^{-2}\) was measured. More recently, the company has used the same technique to create patterned silicon moulds to produce the material and has replaced the polyimide with polydimethylsiloxane (PDMS). This latest material exhibited a strength of 220 kPa. Photo-lithography has the benefit of being widely used, well understood and scalable up to very large areas cheaply and easily, which is not the case with some of the other methods used to fabricate prototype materials.

So much for the technology but what are the applications for these materials? Recent work (Autumn, 2007) has identified seven key functional properties of gecko-inspired adhesives, i.e.:

1. anisotropic attachment;
2. high pull-off to preload ratio;
3. low detachment force;
4. material independence/van der Waals adhesion;
5. self-cleaning;
6. non-sticky default state; and
7. anti-self matting.

These features have led to many applications being suggested, ranging from nanotechnology and military uses to healthcare and sport. In the former, these materials have been proposed as a means of picking up, moving and aligning delicate parts such as ultra-miniature circuits, nano-fibres and nanoparticles, microsensors and micro-motors. In the macro-scale environment, they could be applied directly to the surface of a product and replace joints based on screws, rivets, conventional glues and interlocking tabs in manufactured goods. In this way, both assembly and disassembly processes would be simplified; the latter leading to easier compliance with product recycling directives. Perhaps more whimsically, they might lead to fumble-free football gloves, high-grip vehicle tyres and training shoes and revolutionary rock climbing aids. Emergency service personnel may benefit from radically improved safety harnesses and even the much-touted
concept of a Spiderman suit now seems less like science fiction.

Several military applications are being considered by BAe. One is to use the material as instant repair patches for damaged or holed structures such as fuel tanks and aircraft skins and another is the rapid attachment of armour or stealth panels to military platforms. It has even been suggested that aircraft might be tethered to carrier decks with the material. Perhaps a shorter term possibility is used in crawler robots. These are used in the military context to examine the surfaces of aircraft for defects and are starting to replace manual inspection methods. Today’s crawlers use vacuum pumps and heavy-duty suction pads which could be replaced by this material. Other robotic uses are also being investigated, for example, climbing robots have been identified as a potential application by the group at Carnegie Mellon University, who have developed a prototype “Geckobot” (Figure 12) which has climbed at angles of up to 60°. These robots would have unprecedented freedom of movement and might be employed to search for survivors in fallen buildings as well as conducting test and inspection tasks on large components and structures. The wet Geckel material might be used to fabricate adhesive tapes that could replace sutures for wound closure and may also be useful as water-resistant adhesive for skin grafts, drug-delivery patches and bandages. Such a bandage would remain firmly attached to the skin during bathing but would permit easy post-healing removal.

Figure 12 Prototype “Geckobot” developed at Carnegie Mellon University, uses gecko adhesive to help it to climb walls (Sitti Group, Carnegie Mellon University, Pittsburgh, Pennsylvania, USA)

Biomimetic adhesive developments are progressing rapidly and it is anticipated that these materials will become available within the next few years. Their impact is likely to be dramatic and will open up a whole range of new uses, as well as replacing existing jointing techniques such as rivets, screws and conventional non-reversible adhesives in many applications.

References

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