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Bio-Inspired Adhesion

Paul Saville

Defence R&D Canada – Atlantic

Technical Memorandum

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Abstract

Examples of adhesive systems are found in the animal kingdom that have properties which man has been challenged to achieve. One of these properties is dynamic or reversible adhesion which is necessary for animals that move and inhabit environments where gravity or fluid flow (wind or water: oceans, rivers) is present. Another property is the ability of various species to achieve adhesion to surfaces in the presence of water. Three classes of adhesion are identified among biological systems: chemical, wet and dry adhesion. Chemical systems are found in marine species that use proteins, polysaccharides and carbohydrates to achieve a variety of chemical bonding. Tree frogs and some insects take advantage of wet adhesion which takes advantage of capillarity and Stefan forces as well as structural toe pad designs that increases liquid drainage and hence frictional contact. Species that employ dry adhesion such as insect and geckos have fibrous arrays which adhere to the surface through van der Waals forces, enabling these species to climb up vertical surfaces. This paper reviews recent research in these three areas of bio-inspired adhesion.

Résumé

Dans le royaume animal, on trouve des phénomènes d’adhésion difficilement imitables par l’homme. L’un d’eux est l’adhésion dynamique ou réversible nécessaire aux animaux qui se déplacent dans des milieux où la gravité ou un écoulement fluide (vent ou eau : océans, cours d’eau) est présent. Un autre est constitué par la capacité de certaines espèces d’adhérer à des surfaces en présence d’eau. On distingue trois types d’adhésion dans les systèmes biologiques : chimique, humide et sèche. On trouve l’adhésion chimique dans les espèces marines qui utilisent des protéines, des polysaccharides et des glucides pour établir diverses liaisons chimiques. Les rainettes et certains insectes utilisent l’adhésion humide, qui fait appel à la capillarité et aux forces de Stefan, et ont des extrémités palmées qui accroissent le drainage des liquides et, par conséquent, le frottement. Les espèces qui utilisent l’adhésion sèche, comme les insectes et les tokays, ont des réseaux fibreux qui adhèrent à la surface sous l’effet des forces de van der Waals, ce qui leur permet de grimper sur les surfaces verticales. Le présent mémoire passe en revue les recherches récentes sur ces trois types d’adhésion bio-inspirée.

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Executive summary

Bio-Inspired Adhesion:

P. Saville; DRDC Atlantic TM 2009-155; Defence R&D Canada – Atlantic; June 2009.

Introduction: Conventional adhesives typically afford one time use only, often leaving adhesive residue when removed from a surface and its surface energy has to be tailored for different bonding applications. Bio-inspired microfiber arrays potentially offer reversible adhesion to a variety of surfaces, with no residue through physical attractive van der Waal forces. These materials can remain firmly attached while being easy to release.

For defence these materials would find applications as reusable adhesive tape or appliqué. They would avoid wastage when tape repositioning is required and reduce surface preparation and cleaning requirements. These materials, as adhesive tapes, show promise in wet environments such as surgical bandages replacing sutures, and in robotic design for scaling vertical and inverted surfaces. Their physical structure lends these materials to being superhydrophobic and self cleaning.

The specific aims of the assignment are: a) to identify active research programs on, bio-inspired adhesion with potential defence applications, (b) identify research facilities and capabilities that could be applied in a collaborative program to bolster this research and broaden the relevance and outcomes of the research, and c) provide recommendations on collaborative programs and an operating assignment to achieve such outcomes.

Results: A literature review of recent work on bio-inspired adhesives has been undertaken. This review has been expanded beyond microfiber arrays employing van der Waals adhesion, to also include marine chemical adhesives and wet adhesion.

Dry adhesion or systems that employ van der Waals forces are employed by a number of insect species and lizards such as the gecko. These animals have the ability to walk up vertical surfaces through the action of microfiber arrays on their legs or feet. The size, shape, areal density and stiffness of the fibers play a role in the strength of adhesive forces obtained. Other unique properties include repeated reversible adhesive, self cleaning, and the ability to act on wet surfaces. Microfiber array materials have been developed to exploit this form of adhesion, with some demonstrating similar functionality to the biological systems, including high adhesion strength, reversibility and repeatability. Materials used range from carbon nanotube forests to structured polymeric arrays. Potential applications have been investigated for the fields of standard adhesive tapes, medicine, and robotics. In medicine an adjustable band-aid, or tape for wet regions is desirable. In robotics, wall climbing robots have been designed and demonstrated exploiting the functionality of these gecko inspired adhesives. AFRL, ARL and DARPA have had programs running to investigate these bio-inspired adhesive systems while most of the research resides mainly within academic laboratories.

Wet adhesion has been found for animals such as tree frogs, some insects and some mammals. This type of adhesion ensures the ability of the animal to make and maintain contact with surfaces

that may be wet or slippery. The forces involved in adhesion include friction, capillarity and Stefans adhesion forces which take advantage of the fine micro and nano structure of the foot or attachment pad, its soft nature and ability to conform to surface roughness, its ability to secrete a fluid film over the attachment pad, and its ability to make surface-surface contact when one or both surfaces are wet. The ability to exploit wet adhesion is limited due to the low adhesion forces, however, some of the lessons learned from the structural analysis of these animals may be applicable. For instance the channel design around the epithelial cells is thought to provide a mechanism for displacing excess water between a toe pad and the surface, increasing frictional contact and contact speed. This is seen in the design of some tire treads. Research in this area appears to be limited to academia.

Chemical adhesion is found in a large number of marine species, including mussels, barnacles, echinoderms and bacteria. Bacteria are often the first species to colonize a surface exposed to water and are capable of forming thick biofilms. The adhesion of these systems involves polysaccharides which can cause cell adhesion through hydrogen bonding. Other species such as barnacles may use the bacterial colonies to sense suitable attachment sites. Barnacles, mussels and echinoderms secrete chemical adhesives which contain protein sequences. DOPA features extensively in the adhesive proteins due to the ability of the hydroxyl groups to ionically coordinate with metal ions, or hydrogen bond with inorganic oxides. The oxidized quinone form of the DOPA species can react with thiol and amine groups to form covalent bonds, acting to crosslink the proteins. These marine bonding systems can be reversible (undergo a disbanding reaction) so that the animal can walk, they can be fast acting, have low biotoxicology and most importantly act in the presence of water, where man made adhesives are challenged. Synthetic marine bio-inspired adhesives have been made based on these systems and recombinant protein synthesis is being used as a method for producing larger quantities of mussel adhesive proteins than are practical to harvest from natural sources. Some model compounds have been developed and trialed including compounds to reduce biofouling. Practical applications include the development of new adhesive that are water tolerant and that may have low toxicity, such as would be needed for dental applications or as sutures for wet surgical areas, or for underwater adhesive applications. Another application of this research is in the field of antifouling coatings, where knowledge of the fouling mechanisms and chemistry can be used in coating design. ONR has funded extensive work in universities to understand the adhesive mechanism of marine species, and NSWC has an active program in studying antifouling coatings and barnacles. Antifouling coating investigations are fundamental to other laboratories such as DSTO and DRDC.

Significance: Bio-inspired adhesion has produced a wealth of new knowledge into adhesive systems that may provide new materials where current chemical systems are challenged: Reversible adhesives, repeated usage, stronger, faster bonding time, effective in wet environments and with low toxicity.

Development of dry, gecko-inspired adhesives has impacted the robotics field, permitting robots to scale vertical surfaces. These materials may also change the nature of adhesive tapes, permitting multiple attachment-detachment cycles, and may play a role in medicine.

Wet adhesion as seen in tree frogs will probably not result in revolutionary changes to adhesive systems, however their structural characteristics might be employed to increase the traction of boots or tires on wet surfaces.

Chemical adhesion systems and a knowledge of their adhesive mechanism will play an important roll in development of water compatible adhesives and in biofouling research.

Future plans: In terms of the original scope of this study, bio-inspired adhesion based on the gecko, has produced some interesting advances, in knowledge and capability. The work in this field appears to be limited to ARL, AFRL and DARPA. For this reason it is recommended that an assignment based on this field be reduced to a technology watch.

It is also recommended that some form of assignment or technology watch be established in the field of marine bio-adhesives and/or antifouling coatings based on marine adhesive systems.

Sommaire

Adhésion bio-inspirée

P. Saville; DRDC Atlantic TM 2009-155; R & D pour la défense Canada – Atlantique; Juin 2009.

Introduction ou contexte: En général, les adhésifs courants ne peuvent être utilisés qu'une seule fois et laissent souvent un résidu quand on les enlève, et leur tension superficielle doit être adaptée à l'usage. Les réseaux de microfibres bio-inspirés peuvent offrir une adhésion réversible à diverses surfaces, sans laisser de résidus résultant d'une attraction par les forces de van der Waals. Ces matières peuvent rester solidement fixées tout en étant faciles à libérer.

Pour les besoins de la défense, ces matières pourraient être utilisées comme rubans adhésifs réutilisables ou comme appliqués. Elles réduiraient le gaspillage quand il faut replacer le ruban et réduiraient également les besoins de préparation et de nettoyage des surfaces. Sous forme de rubans adhésifs, ces matières semblent promettrices dans les milieux humides, par exemple comme bandages chirurgicaux remplaçant les fils de suture, et dans la conception de robots pouvant escalader des surfaces verticales et se déplacer sur des surfaces inversées. En raison de leur structure physique, ces matières sont superhydrophobes et autonettoyantes.

Les buts spécifiques de la tâche sont les suivants : a) trouver des programmes de recherche en cours sur l'adhésion bio-inspirée qui pourraient avoir des applications pour la défense, b) identifier les installations et les capacités de recherche qui pourraient être utilisées dans un programme de collaboration pour simuler cette recherche et en élargir la portée et les résultats, et c) faire des recommandations sur des programmes de collaboration et sur une affectation opérationnelle pour obtenir ces résultats.

Résultats: On a entrepris un examen de la littérature sur les travaux récents en matière d'adhésifs bio-inspirés. La portée de cet examen ne se limite plus aux réseaux de microfibres utilisant les forces de van der Waals comme moyen d'adhésion, mais porte également sur les adhésifs chimiques marins et l'adhésion humide.

L'adhésion sèche ou l'adhésion sous l'effet des forces de van der Waals sont utilisées par un certain nombre d'insectes et de lézards comme le tokay. Ceux-ci peuvent monter sur des surfaces verticales grâce à des réseaux de microfibres sur ou sous leurs pattes. La force d'adhésion dépend de la taille, de la forme, de la densité surfacique et de la dureté de ces fibres. Celles-ci ont une adhésion réversible, sont autonettoyantes et restent efficaces sur les surfaces humides. Des matériaux microfibreux ont été mis au point pour exploiter cette forme d'adhésion, dont certains ont une fonctionnalité semblable à celle des systèmes biologiques, y compris une grande force d'adhésion, la réversibilité et la répétabilité. Les matériaux utilisés vont des forêts de nanotubes de carbone aux réseaux polymériques structurés. On a étudié des applications potentielles dans les domaines des rubans adhésifs, de la médecine et de la robotique. En médecine, un bandage ou un diachylon ajustable pour les régions humides serait désirable. En robotique, on a mis au point des robots pouvant grimper sur les murs exploitant la fonctionnalité de ces adhésifs inspirés du tokay et on en a fait la démonstration. L'AFRL, l'ARL et la DARPA ont eu des programmes pour

examiner ces systèmes d'adhésion bio-inspirée, mais la plus grande partie de la recherche se fait surtout dans les laboratoires universitaires.

On a observé l'adhésion liquide chez les animaux comme les rainettes, certains insectes et certains mammifères. Ce type d'adhésion est tel que l'animal peut conserver un bon contact avec des surfaces humides ou glissantes. Les forces en cause sont le frottement, la capillarité et les forces d'adhésion de Stefans, qui utilisent la micro- ou la nanostructure de la patte ou du coussinet plantaire, sa nature souple et sa capacité de s'adapter à la rugosité de la surface, sa capacité de sécréter un film fluide sur le coussinet plantaire et sa capacité d'établir un contact de surface à surface quand l'une ou les deux sont humides. La capacité d'exploiter l'adhésion humide est limitée parce que les forces d'adhésion sont faibles, mais certaines des leçons apprises de l'analyse structurale de ces animaux pourraient être utiles. Par exemple, la configuration des sillons parmi les cellules épithéliales offre une voie d'évacuation de l'eau excédentaire entre le coussinet plantaire et la surface, ce qui augmente le frottement et la vitesse de contact. Certains pneus ont des bandes de roulement conçues de la sorte. Dans ce domaine, la recherche semble limitée au monde universitaire.

On trouve l'adhésion chimique dans un grand nombre d'espèces marines, dont les moules, les cirripèdes, les échinodermes et les bactéries. Ces dernières sont souvent la première espèce à coloniser une surface exposée à l'eau et sont capables de former des biofilms épais. L'adhésion de ces systèmes fait appel à des polysaccharides qui peuvent causer l'adhésion des cellules par des liaisons hydrogène. D'autres espèces, comme les cirripèdes, peuvent utiliser des colonies bactériennes pour localiser des sites de fixation appropriés. Les cirripèdes, les moules et les échinodermes secrètent des adhésifs chimiques qui contiennent des séquences de protéines. La DOPA est fréquemment présente dans les protéines adhésives en raison de la capacité des groupes hydroxy à se coordonner avec les ions métalliques, ou à établir des liaisons hydrogène avec des oxydes inorganiques. La forme quinonique oxydée de l'espèce DOPA peut réagir avec des groupes thiol et amine pour former des liaisons covalentes, de façon à ponter les protéines. Les systèmes de liaison marins peuvent être réversibles (subir une réaction de séparation) de sorte que l'animal peut marcher; ils peuvent avoir un effet rapide, n'être que peu biologiquement toxiques et surtout être efficaces en présence d'eau, ce qui est une épreuve difficile pour les adhésifs de fabrication humaine. On a fabriqué des adhésifs bio-inspirés marins synthétiques basés sur ces systèmes et on utilise la synthèse de protéines recombinantes comme méthode de production de grandes quantités de protéines adhésives de moules faciles à récolter à partir de sources naturelles. On a mis au point certains composés modèles, y compris des composés visant à réduire l'encrassement biologique, et on les a soumis à des essais. Comme application pratique, entre autres on a mis au point un nouvel adhésif tolérant à l'eau qui pourrait être peu toxique, du type qui serait nécessaire pour les applications dentaires ou les sutures chirurgicales dans des zones humides, ou des applications sous-marines. Une autre application de cette recherche est dans le domaine des revêtements de protection contre l'encrassement, la connaissance des mécanismes et de la chimie de l'encrassement pouvant être utilisée dans la conception du revêtement. L'ONR a financé de grands travaux de recherche dans les universités afin que l'on parvienne à comprendre le mécanisme d'adhésion des espèces marines et le NSWC a un programme en cours pour étudier les revêtements de protection contre l'encrassement et les cirripèdes. Les recherches sur les revêtements de protection contre l'encrassement sont fondamentales pour d'autres laboratoires, comme le DSTO et RDDC.

Importance: L’adhésion bio-inspirée a produit une foule de nouvelles connaissances sur les systèmes adhésifs, qui pourraient mener à de nouveaux matériaux quand les systèmes chimiques actuels font face à des obstacles : adhésifs réversibles, utilisation répétée, plus grande adhésion, adhésion plus rapide, et efficacité dans les milieux humides avec une faible toxicité.

La mise au point d’adhésifs secs inspirés du tokay a eu des répercussions dans le domaine de la robotique et permis à des robots d’escalader des surfaces verticales. Ces matières peuvent également changer la nature des rubans adhésifs, permettant des opérations de fixation et de détachement répétées et pourraient être utiles en médecine.

L’adhésion humide, comme celle des rainettes, n’apportera probablement pas de changement révolutionnaire dans les systèmes adhésifs, mais ses caractéristiques structurales pourraient être utilisées pour accroître la traction des bottes ou des pneus sur les surfaces humides.

Les systèmes d’adhésion chimique et la connaissance de leur mécanisme d’adhésion joueront un rôle important dans l’élaboration d’adhésifs compatibles avec l’eau et dans la recherche sur l’encrassement biologique.

Perspectives: Concernant la portée initiale de la présente étude, l’adhésion bio-inspirée basée sur le tokay a mené à des progrès intéressants dans les connaissances et les capacités. Seuls l’ARL, l’AFRL et la DARPA semblent mener des travaux de recherche dans ce domaine. Pour cette raison, on recommande que toute affectation à ce domaine soit limitée à une veille technologique.

On recommande également d’établir une affectation ou une veille technologique dans le domaine des bio-adhésifs marins et/ou les revêtements de protection contre l’encrassement basés sur les systèmes adhésifs marins.

Table of contents

List of figures

1 Introduction

A feature of the animal kingdom is the ability to move which results in advantages such as being able to find food, hospitable environments, and partners. Animals are also faced with adhesive requirements to maintain position such as countering the effects of gravity, or pressure from fluid flow (water or wind). Mechanisms used by animals to maintain position, include: claws or spines that catch on surface irregularities or imbed in the surface. A second mechanism is friction, where intermolecular forces and surface contacts give rise to adhesion. Friction is proportional to the load and independent of the macroscopic area of contact. As a holding mechanism, experience shows that friction is most effective when both surfaces are rough. The third mechanism involves bonding. Bonding includes a number of mechanisms based on physical and chemical adhesion: capillarity or wet adhesion, van der Waals forces or dry adhesion, and chemical bonding, covalent, ionic and hydrogen bonding. Biological forms of adhesion have adapted to function in environments where man made adhesives function poorly, such as in the presence of water. There are also many examples of dynamic adhesion in biological systems where adhesive bonds are reversible or can be repeatedly applied. Thus natural adhesive systems may provide bio-inspired adhesives that can be used for: bio compatibility; underwater adhesion, reversible-reusable adhesives, antifouling, and climbing. This paper reviews some of the species that exhibit adhesion, elaborating on what is known about the mechanisms, bio-inspired adhesive research and military applications.

1.1 Species

For marine species, there exists mechanical, claw, spine, hooks and suckers, as well as chemical adhesion. Adhesion may be classified by function and permanency. Permanent adhesion, involves the cementing or fixing of an adult species to one location, examples being bacteria, adult barnacles, tube worms and bivalve mollusks. Transitory adhesion is observed for mainly soft bodied invertebrates that secrete a viscous film to glide along on. While temporary adhesion is found in those species such as echinoderms that attach temporarily to a location before moving on.[1]

A number of bacteria and animal species exhibit remarkable abilities to adhere to surfaces and in some cases this is a reversible process permitting movement and relocation. In dynamic marine environments, barnacles, tube worms, mussels,[2,3] and echinoderms[3,4] (sea stars and urchins) have adapted strategies that permit them to attach to surfaces and withstand tide induced shear forces. They also have the ability to adhere to a variety of materials with a range of surface energies, including perfluorinated surfaces.

Terrestrial examples of spies using adhesion include insects, (flies, grasshoppers, beetles), spiders, frogs and lizards,[5] permitting the animals to climb and grab surfaces after leaping to new locations. This list is not exhaustive but highlights some of the biological systems that employ adhesion and whose study has started to reveal the mechanisms they employed.

2 Mechanisms

Adhesive systems that have evolved in nature utilize chemical and physical processes in order to provide adhesion and in due to the mobile characteristic of animals these adhesive systems are often dynamic or reversible. Chemical mechanisms utilize covalent and ionic bonding as well as hydrogen bonding, where as biological examples exist that use van der Waals forces and capillarity.

2.1 Chemical Adhesion

There is a chemical component to all adhesive systems, whether it is in the formation of chemical bonds or the materials from which the adhesive system is formed. In the following sections those systems that provide ionic, covalent or hydrogen bonding are considered. Species exhibiting chemical adhesion include marine organisms such as barnacles, mussels, sea cucumbers, tubeworms and echinoderms.[3] These species demonstrate a remarkable ability to attach to a variety of materials with different surface energy (hydrophobic to hydrophilic). And the fact that they accomplish this underwater, an environment that is challenging for many synthetic adhesives, is impressive. Proteins often form an integral part of the adhesive systems and the amino acid 3,4-dihydroxy-L-phenylalanine, DOPA, has been found to participate in adhesive bonding from different species. The DOPA unit is capable of coordinating metal ions and hydrogen bonding with inorganic (metal oxide) surfaces, and upon oxidation to the quinone form it is reactive with amine or thiol groups forming covalent bonds. Other bonding examples exist, based on proteins and carbohydrates and polysaccharides.

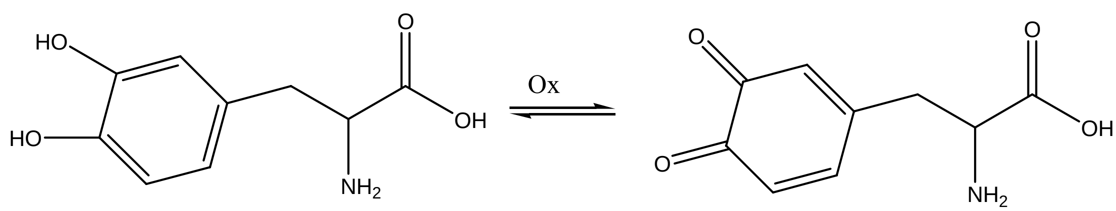


Figure 1: Oxidation of DOPA to the quinone.

2.1.1 Bacteria

Many bacterial colonies have been noted to form mats through bonding layers of cells together. *Caulobacter crescentus* is one of the first colonisers when a surface is placed in water and is difficult to remove once attached. Attachment of the bacterial cells is dependent on the life cycle and starts with swarmer cells that first find and start the colonization of the surface. These cells undergo a transformation to sessile stalk cells which form the biofouling.[6] After finding a surface the swarmer cells transform, producing a stalk which anchors the cells to the surface. The stalk is tipped with polysaccharides based on N-Acetylglucosamine that forms a gel-like structure bonding the cell to the surface.[7,8] Adhesion force measurements indicate detachment forces ranging from 0.11 to 2.26 μN, or an average areal detachment force of 68 N/mm^2.[7,9]

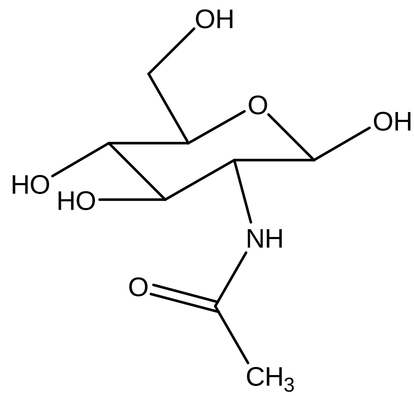


Figure 2: Structure N-acetylglucosamine

2.1.2 Tubeworms

Tubeworms (*Phragmatopoma californica*) have the ability to attach to surfaces, and form a protective coating that withstands wave and tidal action. Analysis of the tube worm's attachment and protective structures show a solid foam like structure.[10] The foam structure has several advantages such as increasing elasticity and toughness, and reducing crack propagation. They also can match the properties between the hard solid and elastic phases. Chemically, the structures are composed of soluble calcium and magnesium and proteins based on glycine, and lysine with high DOPA content. Another protein with high phosphorus content is also present: O-phosphoserine. A four stage mechanism has been proposed for foam formation. This involves the condensation of the oppositely charged polyelectrolyte proteins with divalent calcium and magnesium ions into a dehydrated granual. The condensation process causes a phase separation and formation of a foam structure. Rehydration of the condensed granules, after deposition onto mineral substrates, results in a displacement of water and facilitates underwater adhesion. Finally oxidation of dihydroxy phenylalanine (DOPA) to a quinone and reaction with the amine and thiol groups of glycine and lysine, crosslinks the continuous phase of the foam, locking in the structure.

2.1.3 Echinoderms

Three different adhesive systems are recognized including the tube feet involved in holding to animal to a surface, temporary attachment for larval stage organisms and cuvierinan tubules which are used as defensive mechanism.

2.1.3.1 Tube Feet

Sea stars, sea cucumbers and sea urchins are mobile in nature and have evolved a reversible adhesive mechanism in order to remain attached to surfaces and not be swept away by waves and tides. Adhesive secretions used by echinoderms originate from cells in the foot and the tenacity of adhesion (force/area) to glass surfaces has been measured for different species and is comparable to the tenacity of other marine organisms.[1] These range from 60 – 330 kPa. Two types of cells have been identified to be involved in the adhesive process secreting a thin porous adhesive film, and one that secretes a de-adhesive. Detachment of de-adhesion occurs at the outer layer of the cell and leaves behind an adhesive foot print. There are results that suggest that the de-adhesive cells are not incorporated in the foot print and may provide enzymes to detach the adhesive.[11] The adhesive composition has been determined to contain protein, (20%), carbohydrates (8%) inorganic residue (40%) and lipids (2.5%). It is thought that some of the material was not solubilised and therefore not recovered. This adhesive composition is closer to that of transitory adhesives such as those formed by limpets. Another feature of the soft foot of sea urchins and sea stars is its ability to conform to rough surfaces. By conforming to surface roughness, better adhesion is achieved. This is due to increased surface area of contact, the increased friction which causes shear forces and retardation of crack propagation.[4]

2.1.3.2 Larval Adhesion

Echinoderms undergo a larval to adult metamorphosis involving an adhesive settlement. Some of the adhesive mechanisms are similar to those found in tube feet.[1]

2.1.3.3 Sea Cucumber Cuvierian tubules

Sea cucumbers are part of the echinoderm family. When threatened, they discharge a protein-carbohydrate mixture in tubular form. These act to bond to and ensnare the threat in a matter of seconds. The protein is in a 3:2 ratio with the carbohydrate and is rich in small side chain amino acids with glycine featuring highly with charged and polar amino acids.[1] Although not very soluble, analysis of this material has revealed the presence of ten glycine and acidic amino acid-rich proteins with size ranging from 17 to 220 kD.[12,13] The polar small side chain feature may assist in hydrogen and ionic bonding to substrates and are also present in proteins that have an elastic nature.[1]

2.1.4 Barnacles

Barnacle adhesion depends on the developmental stage. Initial attachment of the barnacle cyprid larvae is via a mechanism resembling that found for mussels. The larvae walk using a reversible adhesive process until a suitable site is located.[14] Adult barnacle adhesive or cement is different with analysis indicating the presence of five proteins forming 90% of the adhesive. The proteins range in size from 7-58 kD and are different in composition and sequence from those found for the mussel, *Mytilus edulis*. The largest portion of these barnacle adhesive proteins is a 36 kD protein which has alternating regions of hydrophilic and hydrophobic sequences. It is suggested that these sequences play a role in assembly in seawater. The cross linking of these polymers is thought to involve disulfides. There is also some evidence for polymerization of small protein units to larger proteins.[15,16]

2.1.5 Mussels

Mussels[3] are known for their ready and tenacious attachment to nearly all surfaces including PTFE.[2,17,18] They secrete a series of byssal threads that adhere to surfaces by reaction of adhesive proteins. Research has shown the presence of nine proteins involved in mussel, *Mytilus edulis* adhesion with a tenth protein possibly involved.

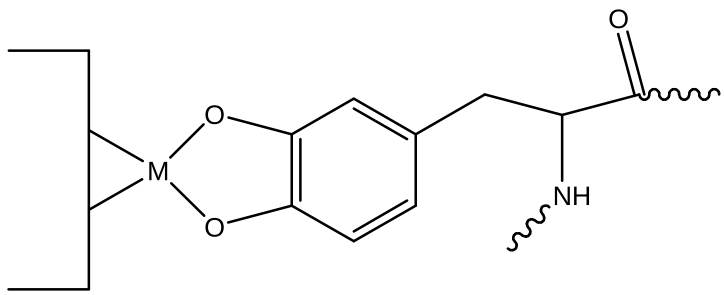
Two mechanisms are postulated to explain the wide range of surfaces that mussels are known to adhere to. And both result from the presence of 3,4-dihydroxy-L-phenylalanine, DOPA, in the proteins. DOPA is formed from hydroxylation of tyrosine residues by a polyphenoloxidase.[3] DOPA may form ionic bonds with cationic species and inorganic surfaces explaining the mussel's ability to adhere to rock and metal surfaces.[19] The catechol functionality of DOPA is readily oxidized in seawater conditions to a quinone.[2] The quinone is then reactive with amine and thiol groups forming strong cross linkages thus producing a coating suitable to lower surface energy material, Figure 3.[18]

AFM studies have been used to investigate DOPA-substrate interactions.[18] The AFM tip was derivatized with a single DOPA molecule and brought into contact with a titanium surface. At a pH of 9.7 (DOPA form) a pull off force of 740 pN was measured, compared to a force of 180 pN when the pH was adjusted to 8.3 and the quinone would be formed. Thus as would be expected the formation of quinone reduced the adhesion strength. Interaction of the quinone with an amine derivatized surface resulted in a pull off force of 2.2 nN, indicating the formation of covalent bonds (Si-C bond rupture force is about 2.0 nN). The chemical reactivity of the DOPA system was demonstrated by using dopamine as a simple model system. At a pH of 8.5, dopamine deposits in a uniform film on most surfaces.[2]

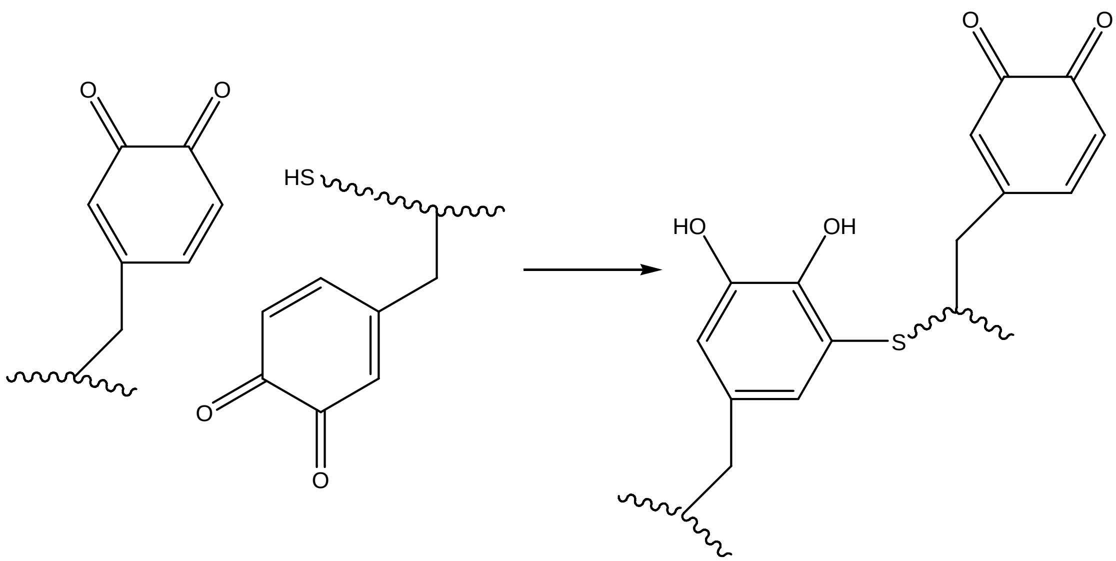
For covalent adhesion, it makes sense that there is high DOPA concentration in the mussel foot proteins. For *Mytilus californianus* foot proteins 3 and 5, Mcfp-3 and Mcfp-5 the DOPA content is 24 and 30%. Mcfp-6 however has only 4% DOPA but has lots of function side groups with eight amino and three thiol equivalents per mol.[20]

DOPA modified surfaces have been used to produce alkyl and PEG grafted surface and PEG-DOPA modified surfaces have been show to reduce biofouling and increase the ease of fouling removal.[2,21]

It is estimated that 10,000 Mussels are required to produce 1 gram of adhesive proteins. Recombinant mussel foot proteins have been expressed with varying degrees of success.[22]



Surface Adhesion



Quinone reaction with thiol

Figure 3: Reaction of DOPA with inorganic surface forming anchor point and oxidized quinine with thiol forming crosslink.

Synthetic adhesives based on mussel adhesion

Isolation has a high environmental cost (10000 mussels for 1 gram protein). Recombination methods.[22] Tend to be expensive and produced in small quantities. The mechanisms and requirements for adhesion and crosslinking are unknown. The adhesive mechanism (functionality present vs specific sequence) was tested, by randomly polymerising a few amino acids found in mussel adhesive proteins using α-amino acid N-carboxy anhydrides. Example polymers contained Lysine and DOPA were made with different ratios of lysine and DOPA. It was found that the gellation time of these polymer solutions could be varies from seconds to hours depending on pH and oxidizing agent.[23,24] The copolymers of lysine with 20% DOPA where capable of forming strong bonds with steel, aluminum and glass but failed to do so to non-polar plastics.[24-26]

2.1.6 Potential uses of bio-inspired chemical adhesives

Water resistant adhesives: The marine adhesives are of interest because their natural use occurs in water where most man-made adhesives are negatively impacted. Mefp-1 has been marketed (Cell-Tak™) as an adhesive to immobilize cells and tissues to inert substrates for further manipulation.[1]

Antifouling strategies: By understanding the mechanisms of bio-adhesion, it may be possible to limit biofouling. Many invertebrate species rely on a swimming larval stage to start colonization of a surface. The larval stage may then metamorphose and grow in size or reproduce to increase the colony size. For the larvae it is important to locate appropriate surfaces and to attach to these. Biofilms, such as those formed by bacterial colonies provide biochemical signals and modified surface properties (texture, chemical functionality and wettability) that larvae can exploit for site selection an attachment. This information may increase surface exploration or attachment tenacity by larvae which have been noted in some cases to settle on sites pre-colonized by specific bacterial species.[27]

Examples of antifouling coatings include enzyme releasing paint can act to hydrolyze bioadhesives. Foul release coatings act to minimise the adhesion strength through low surface energy materials. Bio-inspired antifouling coatings have been designed using the concept of Mefp-1 peptides, or DOPA units, grafted onto polyethylene glycol chains, PEG. The Mefp-1 inspired portion bonds to the surface while the PEG portion prevents cell attachement.[1,2,18,28]

Surgical adhesives: A surgical adhesive may alleviate the necessity for sutures or staples, an anestetic. It may be biodegradable as well. Surgical adhesives to date have been based on fibrin and cyanoacrylates, however these do not work in all parts of the body, for example those areas where there is high fluid concentration. Initial immunological studies of marine adhesives indicate that they may be suitable candidates for in vivo application and preliminary experiments have indicated good bond formation to animal tissue and low immunogenicity.[1,23]

2.2 Capillarity or wet adhesion

Arboreal frogs[29-31] and some river frogs, salamanders, arthropods (insects)[32] and some mammals exhibit smooth adhesive pads. A liquid film secreted onto the adhesive pad provides adhesion when the pad's surface is applied to another, by the attraction of the surfaces from the liquid surface tension (capillarity), and viscosity. It is also though that wet adhesion may play a role in hairy insect species.[29,31-33]

2.2.1 Tree Frogs

The epithelium of the tree frog's toe pad consists of a hexagonal array of flat-topped cells about 10 μm in diameter, separated from each other at their apices. A finer sub-micron peg-like structure exists on these cells. Channels that separate the cells are about 1 μm wide and the fluid film comes from pores of mucous glands that end there.[31] Toe pad detachment from a surface occurs by peeling. Frogs tend to maintain a head's up orientation on vertical surfaces to reduce peel adhesion. Resistance to shear forces may also offer peeling prevention and may be as simple as keeping the toe pads flat on the substrate.

A simple model of wet adhesion is a flat disc in contact with a fluid supported on the substrate, Figure 4. Of course this model does not take into account that toe pads present a curved surface and are soft and deformable rather than rigid. Two forces are thought to contribute to wet adhesion: Stefan adhesion, F_{SA}, and capillarity, F_C.

$$F = F_C + F_{SA} = \frac{2\pi r^2 \gamma}{h} + \frac{3\pi r^4 \eta v}{2h^2} \quad (1)$$

Where r is the pad radius, γ the surface tension, η the fluid viscosity, h the surface separation and v the speed of surface separation. From Equation 1 it is seen that capillarity forces dominate when the fluid has low viscosity or high surface tension and Stefan forces dominate when the fluid has high viscosity and low surface tension. For a constant fluid layer thickness the adhesion force should increase with the disc area if capillarity forces are involved. Stefan forces are transient, such that a small but continuous applied force will cause the disks to separate. This force may therefore be important for temporary adhesion required for walking, or if the mucous has a viscosity greater than water.[31]

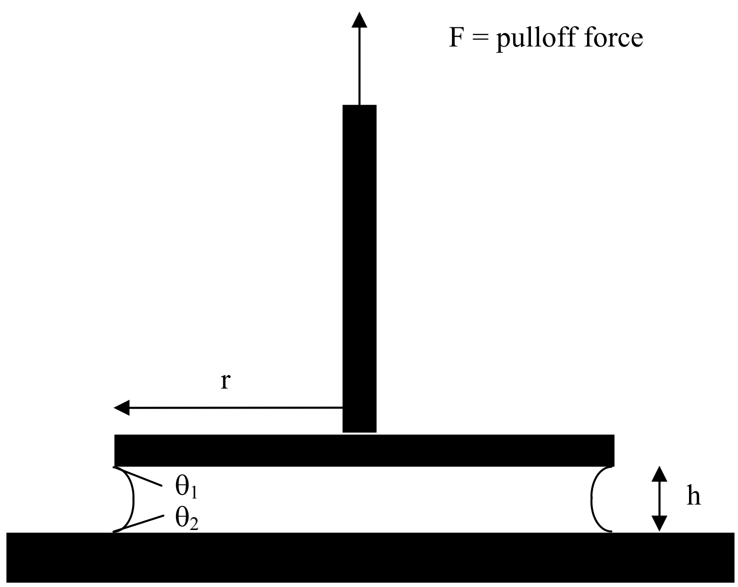


Figure 4: Simple model of wet adhesion acting between a disc and substrate.

Microscopy of toe adhesion indicates that cells away from the point of contact have a convex shape while those near the point of contact are flattened. The mucus layer thickness was measured to be between 0 and 35 nm with most thicknesses being in the 0-5 nm range. The refractive index of toe pad mucus has been measured to be only slightly higher than water and its viscosity about 1.65 times greater than water.[33] Tree frog adhesion forces have been shown to increase linearly with the area of the toe pad, indicating that capillarity is the predominant adhesion mechanism.[29,31]

With adhesion forces scaling with the toe pad area, r^2, it was surmised that larger tree frogs would not be able to adhere to surfaces as well as smaller frogs due to mass usually scaling as r^3. This is indeed the case found, however the larger frogs were not as heavy as expected and their toe pad area were proportionally larger.[29,34] Forces predicted by Equation 1 greatly overestimate the measured adhesion forces, probably due to the toe pad model not being very representative. Other models of adhesive forces including peel models come closer to the measured values but are still too great.[31]

Shear forces measured for tree frogs are larger than adhesion forces, and sliding measurements indicating that friction is involved.[33,34] The coefficient of friction measured (Shear Force/ Adhesion Force) is quite large.[31,33]

The microstructure of frog's feet (channels around the hexagonal cells) provides a mechanism to remove water or mucus from the toe pads and increase the development of surface contacts and frictional forces. The structure may also aid toe pads to conform to surface irregularities. The sub micron peg like structure on the toe pad cells may provide the first substrate-substrate contact, resulting in adhesion.[33] So although capillarity and Stefan adhesion play a part in wet adhesion of tree frogs, frictional forces are also involved, aiding in the adhesive nature in a wet environment.

2.2.2 Insects

A number of insects also have adhesive pads (ants, bees, cockroaches and grasshoppers) or they have hairy flexible setae (flies, bees and earwigs). Both groups secrete a fluid into the contact zone. The fluid has been shown to consist of a biphasic, hydrophilic-hydrophobic, emulsion. Pad friction and adhesion forces are greater when less fluid is present. The fluid may play a roll in providing adhesion to very rough surfaces by filling in the non contacting areas. Surface compliance may also be aided by the soft deformable nature of the adhesion pad cells. In a similar manner insects that are hairy, have a high probability of having the hairs conform to a rough surface and the contact area will be increased by adhesive fluid.[32]

2.2.3 Synthetic adhesives based on wet adhesion

The mechanism for tree frog adhesion has not been readily exploited, probably due to low adhesive forces generated. It is noted in several papers, however, that the channels found around the hexagonal epithelial cells are reminiscent of some car tire tread designs.[29,31,33,34]

2.3 Dry (van der Waals) Adhesion

Geckos, skinks, and anoline lizards[35] and some insect species (beetles, flies, spiders[36]) exhibit a form of adhesion which is termed dry adhesion. The adhesion is dynamic (reversible) so that the animals can climb vertical surfaces and even walk upside down. These species have evolved hair-like structures on their legs or toes that are involved in the adhesion mechanism. The setae as they are known have a branching fibrillar structure, ranging from mm to nm dimensions. A setae may be 5-15 μm in diameter and 30-130 μm long. Each seta may split into 100-1000 spatulae with diameters between 0.1 and 0.2 μm and lengths of 2 to 5 μm. The spatulae are terminated with a flat structure called the spatula, which make contact with the surface and are oriented with respect to the setal shaft.[5,37-39] Spatula are approximately 0.2-0.3 µm wide, 0.5 µm long and 0.01 µm thick.[37,40] Setae are composed of beta-keratin.[41]

Attachment occurs when the animal applies a slight loading of the setae (normal to the surface) and then a small drag back towards the body and parallel to the surface. Detachment occurs by increasing the setal shaft angle (rolling the toes) with the surface to above 30 degrees.[38]

Investigation of other lizard species, insects and beetles show that setae have finer structure as the animal mass increases. For small insects these are of µm dimensions but for geckos they are of sub-µm.[37] The increase in setae density increases adhesion. The adhesion force has been described by two models which consider a) self similar scaling where setae with terminal end radius of curvature for contact is of the dimension of the setae, and b) where the end radius curvature for contact is invariant. In both cases the number of contacts can be increased (higher setae areal density) through smaller diameter seatae. For biological species from fruit flies to lizards the number density of setae and animal mass scale linearly (log-log) with slope 2/3. This is modelled well by the self-similar scaling. However within a species the slope is closer to 1/3 which is modelled as curvature invariance.[37] Consequences of having higher setae density include damage tolerance to individual setae and poor contact due to dust.

There are many advantages to the features observed in natural dry adhesive systems. The hierarchical structure of the fibre arrays, their specific dimensions, aspect ratios and slope between the fibre and substrate, the size and shapes of the contact regions and the material properties all play a roll in the promotion of adhesion and release.

2.3.1 Measured Gecko Adhesion and Frictional Forces

Dry adhesion acts via intermolecular van der Waals forces which are largely independent of surface chemistry and highly dependent on the distance between the surfaces. The Tokay gecko has been shown to have some 200,000 setae per toe with each seta terminating in hundreds to 1,000 spatulae.[42] Measurements have been made on the shear and adhesion forces of gecko feet, setae and spatula. Adhesion forces of a single spatula have been measured to be about 10 nN. This is compared to the adhesion force of spatula on hydrophobic surfaces of 2-7 nN and 6-16 nN on hydrophilic surfaces. For single seta with 100-1000 spatulae, frictional forces were measured at about 200 µN and adhesion forces at about 40 µN. Finally the frictional forces of the two front feet were measured to be about 20 N[42] and may be as high as 10 N/cm^2.[40] The adhesion forces for a single spatula are similar to those calculated for the van der Waals force, using

$$F_{vdw} = \frac{A}{6\pi d^3} \tag{2}$$

Where A is the Hamaker constant and d is the separation of two parallel surfaces.[37,38,43]

When setae are pushed across a surface in the non-adhesion direction, normal friction behaviour is observed with the shear force (parallel to the surface) $F_{\parallel}$, is proportional to the force applied normal to the surface, $F_{\perp}$. The proportionality constant (μ = the coefficient of friction), is about 0.3 which is typical for normal adhesion.

$$F_{\parallel} = \mu F_{\perp} \tag{3}$$

However, when setae are dragged in the adhesion direction the normal friction relation of the shear and perpendicular forces no longer holds. A shear force must be maintained in order to keep the shaft angle below 30 degrees. Detachment of the setae occurs when the setae stalk is at an angle greater than 30 degrees. This means that a shear force must be applied in order to keep the shaft angle below 30 degrees.[38]

$$F_{\parallel} \geq -\frac{F_{\perp}}{\tan 30^{\circ}} \text{ or } F_{\parallel} \geq -2F_{\perp} \tag{4}$$

2.3.2 Young's Modulus

The setae structure of geckos is made of beta-keratin which can be considered as a hard polymer, with a bulk Young's modulus of ~1GPa. This value is much higher than the modulus found for materials used as pressure sensitive adhesives, PSA's, which are typically lower than 100 kPa. PSA's are tacky so that they flow and conform to the surface roughness, increasing contact and friction as well as being capable of deformation during debonding. An effective Young's modulus due to the microstructure of the setae has been measured and is on the order of 100 kPa. Thus setae possess both the characteristics of high and low modulus materials which have been surmised to allow the fibers to conform to the surface for adhesive-frictional properties and to provide hard wearing durability.[38,44]

2.3.3 Advantages of the Gecko Design

Geckos' ability to walk up smooth vertical surfaces, employing dynamic adhesion, stems from the structure of the toe pads and the mechanism used for adhesion. Fibre contact and the van der Waals forces developed by a single contact are very small. The advantages gained by having arrays of fibres include multi-point contact with rough surfaces, thus increasing the adhesive forces, the ability to limit crack propagation and spreads the load. The directional structure of the fibres and spatula are adapted so that the animal can apply the contact and shear forces required to develop the adhesive bonds, and then release the bonding through a peel mechanism.[38,45] Smaller fibre diameter and higher fibre density results in an increased ability to adhere to the surface, through increased number of contact points.[37]

Adhesive failure usually initiates near a defect that causes stress concentration and propagates by a crack that concentrates the stress and damages material ahead of the crack. Cracks in a fibrillar array extend over one fibre at a time, blunting crack propagation due to the need to initiate another crack in the next fibre. This causes the load to be spread out over the array of fibre attachments.[5,46-49] When fibres debond from surface the energy is not transferred into the surface, but is lost in the elastic relaxation of the fiber.[50] Another feature of Gecko feet and dry adhesives is their hydrophobic nature due to the underlying structure and its self-cleaning properties.[38,51]

2.3.4 Synthetic adhesives based on dry adhesion

Bio-mimetic systems to emulate natural dry adhesion have been developed based on soft (polyurethane,[47,52-59] polyurethane acrylate,[60] polydimethylsiloxane PDMS,[61-71] and polyvinyl siloxane PVS) and hard (polyimide,[61,71] and polypropylene,[72-74]) polymers and carbon nanotubes.[75-93]

Several methods have been used to produce the fibre structure including nano-imprinting, templating and growth of fibre structure. For nano-imprinting, a mechanical indenter is used, such as an AFM tip, to imprint indented structure into wax. Silicone rubber is poured over the surface and allowed to polymerize. Removal of the wax template leaves an array of silicone rubber pillars. Si rubber has a Young's modulus that is 0.57 MPa which is low compared to beta-keratin (1 to 57 GPa). Polyester is suggested as being more suitable having a higher modulus of about 0.85 GPa.[66,71,94,95]

Initial template materials included polycarbonate filters[73,96] and alumina membranes.[94,97] These materials have random and regular arrays of pores through the membrane, respectively, and fibre arrays have been fabricated using polypropylene and polyurethane. These materials are assisted into the pores be using reduced pressure.[94] Better control of fibre thickness and distribution has been achieved through the use of lithography and nano-fabrication methods, including: making moulds using lithography of silicon,[98,99] poly methylmethacrylate,[17] polyimide films with Aluminum disk masks,[100] and of the epoxy SU-8.[47] These latter techniques provide the capability to produce fibres oriented at an angle to the interface and control of the fibre shape. Ends of polymeric fibre arrays have been also been modified by dipping the fibre ends into polyurethane. The polyurethane can then be formed into different structures by placing the array in contact with a surface and permitting the polymer to dry.

Dry adhesives have been created using carbon nanotube forests.[75-93] Patterned arrays of nanotubes have been created using photolithography of catalyst on silicon wafer. The array of square blocks of nanotubes mimics the setal arrays, while the individual nanotubes mimic spatual. Nanotube forests were then transferred to flexible adhesive tape backing and could be repeatedly adhered to surfaces. In shear mode failure is cohesive leaving parts of nanotubes on the surface, but in peel mode, mimicking gecko movement, no nanotube residue is observed on the surface. Adhesion to Teflon, plastic, mica and glass has been demonstrated. Shear forces depend on height of nanotubes and size of setal array pattern and have been measured to support up to 36 N/cm^2.[77,86] Nanotube forests with a top layer that is entangled and randomly oriented have been shown to support up to 90 N/cm^2 in shear and require a normal load of 10 N/cm^2 for detachment. Shear force increased with the length of the nanotubes while total adhesive force decreases with increasing peel angle.[85]

Dry adhesive fibres have also been formed from a resist exposed to an oxygen plasma. The high electric field gradient at a surface induces a force on the polymeric resist that is large enough to overcome the surface tension and permit the growth of polymeric fibres. The resultant surface is hydrophilic, however, exposure to CF_4 plasma produces a hydrophobic coating.[102,103]

2.3.5 Potential uses of dry adhesives

Gecko inspired dry adhesives are attractive for applications where reversible or dynamic adhesion is required. These include repositionable tapes, robotic climbing devices and bandages.

Bandages with high shear strength could be quickly applied to wounds without the added damage caused by staples of sutures. The ability of gecko-inspired adhesives to bond wet surfaces has been demonstrated.[17] Steps have also been taken towards the development of materials that have biocompatibility, biodegradation, and tissue bonding properties. These materials have been shown to be effective adhesives *in vitro* and *in vivo*.[104,105] In both of these examples, the dry adhesion is facilitated by the presence of chemical adhesion.

There are numerous examples of polymer[52,55,60,66,74,106-110] and nanotube[75,77-79,81,82,84-86,88,90-93] based materials that could be, and have been demonstrated to provide adhesion in a tape like format.

With the properties of dynamic adhesion, multi-surface adhesion and self cleaning and the fact that geckos can climb vertical walls, a large effort has gone into the development of robotic systems capable of scaling vertical surfaces. This work has jointly inspired the development of novel fibre array materials as well.[42,44,58,64,66,69-71,75-77,95,105,107,111-137]

3 Research in TTCP Countries

Marine based adhesion research on bacterial, echinoderm, mussel has been extensively funded by ONR due to the continuing problem of biofouling. As indicated above this research has explored biological life cycles, attachment mechanisms, chemistry, physics and mechanics of adhesion. Some of the work investigates development of new adhesives, or adhesives that mimic naturally occurring systems, however a major focus has been the development of an understanding of biofouling mechanisms so as to develop antifouling technology. NSWC, NRL and ONR have and are sponsoring ongoing research into biofouling, and foul release coatings. Among this research are population genetic studies of adhesive characteristics,[138] adhesion strength for barnacles attached to silicone fouling-release materials,[139]; studies of the wetting characteristics of raw barnacle cement, (Eric Holmes NSWC-Caderock and Dr. Daniel Rittschof at Duke University Marine Laboratory); curing properties of barnacle (Dr. Daniel Rittschof at Duke University Marine Laboratory) and mussel cement (Dr. Jonathan Wilker, Purdue, ONR); effect of environmental variables (Dr. Dean Wendt at CalPoly San Luis Obispo); mechanical properties of curing and cured cement (Dr. Kathryn Wahl NRL and Dr. Gilbert Walker at the University of Toronto).[138-140] Research in the UK investigates the effect of surface energy and mussel inspired antifouling and foul-release polymer coatings to reduce agal attachement.[21,141] DSTO is involved with research on biofilm adhesion on various coating s and substrates including foul release coatings (Dr Wetherbee, University of Melbourne).[142] DSTO's interest also runs to bio-inspired textured materials with antifouling properties (James Cook University); Antifouling properties of superhydrophobic material (Melbourne University); and marine animal coatings/bacterial colonies that repel further bioadhesion (Dr Andrew Scardino DSTO).

Bio-inspired dry adhesion research has been sponsored by AFRL, ARL, and DARPA with most of the research being carried out in academic laboratories. An Air Force sponsored SBIR has been running to develop micro platforms capable of climbing walls and walking across ceilings. In Canada Dr Menon, Simon Fraser University, has been involved in the development of robotic systems using bio-inspired dry adhesives.

4 Conclusions

There is considerable research effort in the field of bio-inspired adhesion especially in marine based systems employing chemical adhesion and their application to antifouling coatings. Biological adhesion and fouling is an on going problem with naval platforms and presents a research environment rich with opportunities for collaborative projects especially in the testing and performance evaluation of new antifouling and foul release coatings.

Bio-inspired dry adhesives represent a new class of adhesive technology that is benefitting from nanotechnology fields including methods for nano-scale fabrication: imprinting, templating and lithography, to measurement of forces at the nN level, and imaging. Most of the research in TTCP nations is limited to the US. It is suggested that a technology watch be kept on developments in this field.

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List of symbols/abbreviations/acronyms/initialisms

AFRL	Air Force Research Laboratory
ARL	Army Research Laboratory
DARPA	Defense Advanced Research Projects Agency
DOPA	3,4-dihydroxy-L-phenylalanine
DSTO	Defence Science and Technology Organization
NRL	Naval Research Laboratory
NSWC	Naval Surface Warfare Center
ONR	Office of Naval Research
SBIR	Small Business Innovation Research
TTCP	The Technical Cooperation Panel

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Examples of adhesive systems are found in the animal kingdom that have properties which man has been challenged to achieve. One of these properties is dynamic or reversible adhesion which is necessary for animals that move and inhabit environments where gravity or fluid flow (wind or water: oceans, rivers) is present. Another property is the ability of various species to achieve adhesion to surfaces in the presence of water. Three classes of adhesion are identified among biological systems: chemical, wet and dry adhesion. Chemical systems are found in marine species that use proteins, polysaccharides and carbohydrates to achieve a variety of chemical bonding. Tree frogs and some insects take advantage of wet adhesion which takes advantage of capillarity and Stefan forces as well as structural toe pad designs that increases liquid drainage and hence frictional contact. Species that employ dry adhesion such as insect and geckos have fibrous arrays which adhere to the surface through van der Waals forces, enabling these species to climb up vertical surfaces. This paper reviews recent research in these three areas of bio-inspired adhesion.

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Bio-inspired; Adhesion; Barnacles; Mussels; Echinoderms; Tree Frogs; Geckos; Insects

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