Adhesion Enhancement of a Biomimetic Dry Adhesive by means of an increase to the Hamaker constant via nanocomposite formation

by

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B.A.Sc., Simon Fraser University, 2009

Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Applied Science

in the

School of Engineering Science
Faculty of Applied Sciences

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SIMON FRASER UNIVERSITY
Spring 2013

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Abstract

A novel method to increase the van der Waals adhesion of a gecko-inspired polymeric fibrillar dry adhesive through an increase of the polymer’s Hamaker constant is presented. Different metal nanoparticles (NPs) were embedded in the polydimethyl siloxane (PDMS) dry adhesive to create a nanocomposite.

The successful process involved the in-situ synthesis of Au nanoparticles within the mushroom caps of the PDMS microfibrils to enhance adhesion. Successful synthesis of the Au NPs was analyzed using Ultraviolet-Visible Spectrophotometry. To quantify the adhesion enhancement, a pull-off force test was employed to compare the adhesive samples before and after the Au nanoparticles were synthesized. The experiments performed indicate an adhesion improvement of up to 2.2x as a result of the increase in the Hamaker constant of the dry adhesive mushroom caps. A model based on the Hamaker approximation to van der Waals forces is evaluated which is in good agreement with the experimental measurements.

Keywords: biomimetics; dry adhesive; nanoparticles; gecko; van der Waals
With utmost love I dedicate this thesis to my Mom and Dad, Marody, Juan Manuel and last but not least Sharika. Without them I wouldn’t be where I am or who I am.
Acknowledgements

I would like to thank my senior supervisor, Dr. Carlo Menon for his support, counselling and encouragement throughout these last few years. His feedback and guidance helped me with the start and completion of these projects. I would also like to thank Dr. Ash M. Parameswaran, supervisor and great influence through my undergraduate and graduate degree. I am equally grateful to Dr. Woo Soo Kim and Michael Sjoerdsma for agreeing to be the examiner and chair of my committee.

Special thanks to Dr. Dan Sameoto for the initial guidance and inspiration, Dr. Saman Harirchian-Saei whose help was significant for the completion of this study. Furthermore, thanks to Jeff Krahn, Mike Henry, Yasong Li, Helia Sharif, Ausama Ahmed and everybody in the MENRVA group for their help and friendship.

To finish and most importantly, thanks to my parents and siblings for all their support, to Sharika for patiently being with me every step of the way and to all my family and friends whose constant reassurance meaningfully helped to realize this accomplishment.
# Table of Contents

Approval .............................................................................................................................ii
Partial Copyright Licence .................................................................................................. iii
Abstract ........................................................................................................................... iv
Dedication .......................................................................................................................... v
Acknowledgements .......................................................................................................... vi
Table of Contents ............................................................................................................. vii
List of Tables ..................................................................................................................... ix
List of Figures ................................................................................................................... x
List of Acronyms .............................................................................................................. xiii

1. **Introduction** ............................................................................................................ 1
    1.1. Motivation ............................................................................................................. 1
        1.1.1. Dry Adhesion for Climbing Robots ............................................................... 1
        1.1.2. Micromanipulators ........................................................................................ 3
    1.2. Objectives ............................................................................................................ 3
    1.3. Thesis Layout ....................................................................................................... 3

2. **Literature Review** ................................................................................................... 5
    2.1. Biomimetic Dry Adhesives ................................................................................... 5
    2.2. PDMS Nanocomposites ...................................................................................... 9

3. **Biomimetic Adhesives Rationalization** .............................................................. 12
    3.1. Adhesion Forces of a Gecko-like Tape ............................................................... 12
    3.2. Van der Waals Forces ......................................................................................... 12
    3.3. Singly Layered Planar Bodies ............................................................................. 14
    3.4. Hamaker Constant Calculations ......................................................................... 15

4. **Fabrication of a Nanocomposite PDMS Dry Adhesive with Metallic Nanoparticles** ..................................................................................................................... 20
    4.1. Biomimetic Dry Adhesive Fabrication ................................................................. 20
    4.2. Formation of PDMS Dry Adhesive Nanocomposite ............................................ 23
        4.2.1. Embedding of preformed NPs in PDMS ....................................................... 23
        4.2.2. In-situ Silver Nanoparticles Synthesis in PDMS ......................................... 23
        4.2.3. In-situ Gold NPs Synthesis in PDMS Dry Adhesive ....................................... 25

5. **Dry Adhesive Characterization** ........................................................................... 28
    5.1. Nanoparticles Analysis ....................................................................................... 28
        5.1.1. Preformed Nanoparticles embedded in PDMS ............................................ 28
        5.1.2. In-situ synthesized Silver Nanoparticles .................................................... 29
        5.1.3. In-situ synthesized Gold Nanoparticles ....................................................... 31
    5.2. Dry Adhesive Testing ......................................................................................... 33
        5.2.1. PDMS “mushroom” cap micro-fibrils ............................................................ 35
        5.2.2. Embedded metal NPs in dry adhesives by soft moulding ............................ 36
        5.2.3. Au NPs embedded in PDMS fibrils ............................................................. 38
6. Hamaker Approximation model corroboration with Experimental Results .................................................................................................................. 42
   6.1. Hamaker Approximation Model............................................................................................................. 42
   6.2. Validation with Experimental Results ............................................................................................... 43

7. Further Improvements to Biomimetic Dry Adhesives ................................................................. 46
   7.1. Self-Cleaning Biomimetic Dry Adhesives ............................................................................................. 46
   7.2. Electro-Adhesion and Dry Adhesives .................................................................................................. 48
   7.3. Antimicrobial dry adhesive patches for medical applications ......................................................... 50

8. Conclusions ........................................................................................................................................... 51

References............................................................................................................................................... 54

Appendices............................................................................................................................................. 63
   Appendix A. Cleaning Properties of Dry Adhesives .................................................................................. 64
   Appendix B. Characterization of Electroadhesives for Robotic Applications .............................................. 69
List of Tables

Table 3-1: Typical estimates, from literature, for the nonretarded Hamaker constants of two identical materials ($A_{131}$) interacting in vacuum at room temperature relevant to this study ........................................................ 18

Table 6-1: Hamaker constant comparison for the different interfaces studied ............... 42

Table 6-2: Predicted adhesion values using Lifshitz approximation to van der Waals forces (Hamaker Model) for a dry adhesive with Au NPs ..................... 43

Table 7-1: Approximate sizes for the particles used as contaminants to prompt a decrease in adhesion for the biomimetic dry adhesive. ......................... 47
List of Figures

Figure 1-1: Images of various climbing robots that utilize dry adhesion.  
  a) Abigaille II; b) Mini-Whegs™; c) Stickybot .................................................. 2

Figure 2-1: Samples of biomimetic mushroom-cap dry adhesives. ............................. 7

Figure 2-2: Hierarchical biomimetic dry adhesive structures for (a) micro-scale and (b) macro-scale (mm-sized posts and micro-posts on tips) ......................... 8

Figure 3-1: Singly layered planar surface as modeled with Eq. (2), for a PDMS fibrillar structure with a layer of embedded Au NPs (dark layer, b) interacting with a sapphire probe. ................................................................. 15

Figure 4-1: Dry adhesive mould fabrication steps, (a) structural Layers are spun on PMMA substrate, (b) wafer is exposed to i-line UV light in a mask aligner, (c) photoresist is developed/PMGI overdeveloped, (d) PDMS is cast on mould, (e) PDMS dry adhesive is demoulded ........................................ 21

Figure 4-2: SEM image of resulting PDMS dry adhesive, fabricated through soft-moulding as described in Figure 4-1. ............................................................... 22

Figure 4-3: Fabrication process for in-situ Ag NPs in PDMS dry adhesive caps, (a) a PDMS post array and PDMS with synthesized Ag NPs are prepared, (b) the posts are brought in contact with the PDMS nanocomposite, (c) the posts are retracted and stamped on a glass slide ............................................................... 24

Figure 4-4: Microfabricated post array with no overhanging caps initially. Used for dipping on an uncured polymer and stamping on a flat substrate to form overhanging caps ................................................................. 25

Figure 4-5: In-situ gold NPs synthesis.  (a) PDMS with mushroom-like caps dipped into a thin layer of HAuCl₄ solution (b) Au NPs embedded within caps after incubation at 37 °C ............................................................... 27

Figure 5-1: PDMS mixed with preformed metal NPs and casted on a dry adhesive mould, (a) Ag NPs, (b) Cu NPs. Posts and caps successfully formed with a large aggregation of metal NPs in the dry adhesive’s backing layer. ........................................................................................................ 29

Figure 5-2: Ag NPs in-situ synthesized in PDMS, (a) PDMS with Ag NPs, (b) PDMS dry adhesive with Ag NPs. Ag NPs aggregated into rod shaped particles, no particles were visible in the post or cap structure of the dry adhesive .......................................................................................... 30
Figure 5-3: PDMS dry adhesive, without NPs, fabricated using a pre-fabricated array of posts followed by dipping them in uncured polymer. Individual caps were not successfully formed; several posts became a conjoined array.

Figure 5-4: Colour change as a qualitative confirmation of the Au NPs synthesis in the PDMS matrix. (a) Gold solution was initially light yellow, (b) PDMS dry adhesive as initially transparent, (c) PDMS became a red ruby colour where the Au solution was in contact after incubation. Each tick mark represents 1 mm for the 3 independent images.

Figure 5-5: Ultraviolet-Visible (UV-Vis) absorption spectra of the samples with synthesized Au NPs. Colors indicate incubation time and line types refer to Au solution concentrations. Spectrum of PDMS is also shown for completeness. Vertical line indicates the peak absorption mean for the Au NPs.

Figure 5-6: UV-Vis Spectrum of a dry adhesive with in-situ synthesized Au NPs in its mushroom caps. Absorption peak is not clearly discernible due to the topology of the fibrillar dry adhesive.

Figure 5-7: Adhesion (pull-off force) test setup. A sapphire hemisphere tip is attached to a load cell using a metal screw. The load cell is secured to a linear stage mounted on an inverted microscope.

Figure 5-8: Adhesion force curve for the PDMS dry adhesive control sample. The results from this test were used as a reference to compare the adhesion change of the nanocomposite samples.

Figure 5-9: Adhesion testing for preformed Ag NPs mixed with PDMS and soft-moulded to fabricate a dry adhesive. An optical microscope image for the aggregated NPs in the dry adhesive backing is shown in Figure 5-1 (a).

Figure 5-10: Adhesive pressure comparison for the different dry adhesive gold nanocomposites. The adhesive pressure value for the control sample is shown using a solid horizontal line; measurement error for this sample is indicated with the dotted line. Values are grouped by gold solution concentration and incubation time is differentiated with the darkness of the bars.

Figure 5-11: SEM image of dry adhesive with embedded Au NPs where roughness is visibly increased. Corresponds to 5 g/L for 24 hrs.

Figure 5-12: Adhesion curve observed for a fibrillar dry adhesive with Au NPs embedded in its mushroom caps.
Figure 6-1: Pull-off force comparison between the Hamaker model and the experimental results for a contact area of $1.04 \times 10^{-6}$ m$^2$. Other constants for the Hamaker approximation model used are $D = 4.5$ nm and $b_1 = 1$ nm. ........................................................................................................ 45

Figure 7-1: Percentage adhesion recovery, after cleaning with different materials, for particles of different sizes. Materials used for cleaning were CrystalBond$^{\text{TM}}$ (wax) and Scotch tape®. .................................................................................................................................. 47

Figure 7-2: Shear electro-adhesive force comparison for different dielectric materials (polymers) on a melamine substrate. A rectangular electrode configuration, with the long side common between electrodes, was utilized. ................................................................................................................ 49
### List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
<td>Analog to Digital Converter</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
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<tr>
<td>DI</td>
<td>Deionized</td>
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<tr>
<td>ESD</td>
<td>Electrostatic Discharge</td>
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<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
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<tr>
<td>MEMS</td>
<td>Micro-Electro Mechanical Systems</td>
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<td>NP</td>
<td>Nanoparticle</td>
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<td>PDMS</td>
<td>Polydimethyl siloxane</td>
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<td>Polymethyl methacrylate</td>
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<td>PVS</td>
<td>Polyvinyl siloxane</td>
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<td>SEM</td>
<td>Scanning Electron Microscope</td>
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1. Introduction

1.1. Motivation

Many of the temporary adhesion systems in nature utilize fluids to stick to surfaces whereas dry adhesion systems use hooks, suction cups or molecular forces among other forces to adhere to surfaces [1]. Dry adhesion, and specifically adhesion that relies on van der Waals forces, is of great interest because of its reusability and broad range of application. Some of these applications are outlined in this section which summarizes the motivations that stimulated the completion of this study.

1.1.1. Dry Adhesion for Climbing Robots

Ever since the discovery that the interactions responsible for the remarkable adhesion ability found in geckos were van der Waals forces, plenty of research time has been devoted into replicating this dry adhesion mechanism. The successful manufacturing of synthetic gecko-like dry adhesives has opened the door to the development of novel kinds of climbing robots. Among some of the applications where climbing robots can excel using the capabilities achieved with dry adhesion are the cleaning and upkeep of high-rises, satellites and nuclear reactors; essentially, any place where it is or can be dangerous for a person to execute a task. Other applications have included private and military surveillance. Previously, magnets were used for climbing robots to ascend ferromagnetic walls; for non-ferromagnetic surfaces, claws have been used for scaling walls with soft and rough surfaces whereas suction cups were used to climb smooth vertical surfaces. With the successful fabrication of synthetic gecko-like adhesives, robots have been designed with capabilities to climb a wider variety of surfaces by taking advantage of this gecko-like dry adhesion mechanism. Primary benefits of dry adhesives for robotic applications include the ability to traverse multiple surfaces, passive adhesion (no power is needed to sustain attachment) and no marks or
residues remaining on the contacting surface. A few of the robots that have been
designed to use this attachment mechanism are shown in Figure 1-1.

![Figure 1-1: Images of various climbing robots that utilize dry adhesion. a) Abigaille II; b) Mini-Whegs™; c) Stickybot](image)

Note: Image taken with permission for (a) from [2]. Image (b) taken from [3], © 2005 IEEE. Image (c) obtained from [4], © 2008 IEEE.

There is still plenty of room for improvement in the development of dry adhesives for climbing robots as the dry adhesives do not behave ideally in real-life conditions. Even though a dry adhesive can carry a large load in a laboratory setting under ideal circumstances, when it’s in use as attachment for a climbing robot its performance can be severely reduced. This behaviour can be counteracted by modifying the dry adhesives to be more compliant when utilized on non-ideal conditions; modifying the material properties as explained in this study could be a viable solution for these shortcomings.
1.1.2. Micromanipulators

Another flourishing application field where dry adhesives have the potential to perform extremely well is that of micromanipulators. Pick and place operations in microfabrication are extremely important for a production line. Dry adhesives with a strong adhesive side but with a weaker or detachable side can be manufactured; a place and release movement could then be implemented into an industrial production line. However, several drawbacks exist such as Electrostatic Discharges (ESD) and small organic transfers from adhesive polymers to the part being placed, which in the macro-scale are negligible but when dealing with devices in the micro-scale becomes significant. This ESD shortcoming has the potential to be addressed with the use of nanocomposite dry adhesives, the main topic of this study, which will be discussed later.

1.2. Objectives

With the purpose of improving the performance of a fibrillar dry adhesive with mushroom caps, the subsequent objectives were recognized as an approach to enhance the performance of said dry adhesive:

1. Propose a novel strategy to enhance the performance of a biomimetic dry adhesive.
2. Propose a method to implement the novel strategy.
3. Assess if the proposed strategy is a viable solution to improve adhesion.

1.3. Thesis Layout

This study begins in Chapter 2 with an outline of the current state of biomimicking dry adhesives and their applications. It continues in the same chapter to introduce and discuss how nanoparticles (NPs) have the potential to enhance properties of the structural material for these dry adhesives. Chapter 3 discusses the forces that attach dry adhesives to other surfaces; a literature model to describe the forces interacting during dry adhesion is presented. This chapter also provides the analytical reasoning behind the strategy that was chosen to enhance the performance of the dry
adhesives. Approximations used in calculations are described in conjunction with assumptions made in modeling the proposed strategy.

Chapter 4 follows with a detailed description of the fabrication of the dry adhesives as well as the methodology to implement the selected strategy to enhance performance of the dry adhesives. Various methods to implement the chosen strategy are discussed and the selected process is outlined in detail. In Chapter 5 the analysis and results of the dry adhesive fabrication and the different implemented methodologies are described. The testing methodology and equipment utilized are also described together with a breakdown of the performance currently achieved by the dry adhesive. The improvements achieved by the proposed strategy are then tested against the currently achieved performance of the dry adhesive in Chapter 6. Likewise in Chapter 6 the experimental results are contrasted against the proposed adhesion model as described in Chapter 3.

To finish the study, further enhancements to be achieved by biomimetic dry adhesives are presented in Chapter 7. These enhancements include some preliminary work realized on dry adhesives with mushroom caps as well as with active controllable adhesion with high-voltage. Preliminary research to allow these dry adhesives to widen their usage to medical environments is also included in this chapter. Conclusions are drawn in Chapter 8 effectively wrapping up the study.

Appendices A and B present some preliminary work to further improve the biomimetic dry adhesives, as mentioned in Chapter 7. These works have been published and relate to dry adhesion as well as micro-particles and NPs as this study also does.
2. Literature Review

The main avenues of research in this study include the use of NPs as a way to increase adhesiveness of a dry adhesive. A novel dry adhesive manufacturing process that makes use of NPs to create a polymer nanocomposite, as a way to change the polymeric material’s properties is proposed. This fabrication method is postured as a means of fulfilling the objectives of this study.

2.1. Biomimetic Dry Adhesives

The term biomimetic refers to the biologically inspired design of materials and objects; the adaptation of certain processes from nature is also encompassed in its meaning, mimicking nature [5], [6]. Nature has developed some highly desired qualities worthy of studying and imitation, for example in recent years the self-cleaning capabilities of the lotus leaf and the pond skater’s ability to hover over water have been studied [5–7]. Likewise, over the past decade the reversible adhesion that some animals use to stick to a variety of surfaces under diverse conditions has been the subject of study for several research groups [1], [8], [9]. Particularly, the Tokay gecko’s (gekko gekko) notable talent to rapidly attach and detach from virtually any surface has been the main focus of investigation [10]. To achieve this remarkable climbing ability, the gecko makes use of a hierarchical array of β-keratin fibrils with millimeter to nanometer lengths [11–13] that employ van der Waals forces to stick to the surfaces it climbs [14–16]. The stiff fibrils on the gecko’s toes are built-up in a hierarchical manner which allows for the reduction of its effective modulus. This stiffness reduction facilitates the fibrils’ ability to conform to rough surfaces by means of fiber bending and buckling which in turn helps the gecko toes achieve a large contact area [17], [18]; conforming and achieving a large area in contact being the basis of strong van der Waals interactions.
The reversible adhesion attained by geckos has inspired the fabrication of numerous biomimetic dry adhesives in an attempt to replicate the gecko’s fibrillar adhesive structures [19], [20]. Several different manufacturing techniques have been developed, with newer methodologies continuously searching to improve on the dry adhesive strengths [21], [22]. Initially, fabrication methods focused on achieving the fibrillar structures and large Young’s modulus found in gecko setae by wax indenting with micro and nano-tips. These wax indents create a negative of the synthetic hairs to be moulded with stiff polymers [23], [24]. Researchers then concentrated on increasing fibrillar density using carbon nanotubes (CNTs) [25], [26] as well as casting with different polymers on moulds made by embossing [27], reactive ion etching [28] as well as using photolithography to produce negative moulds [29], [30]. Polymer soft moulding from micro-fabricated patterns has been used frequently throughout the literature because of its fairly consistent results and the fact that virtually any dimensions can be achieved. In actuality, the fibrils’ aspect ratio is limited by the structural material’s properties. Several different polymers have been used as the structural material for the dry adhesives such as polyvinyl siloxane (PVS) [31], [32], polyimide [24], [28] and the two most commonly used ST-1060 Polyurethane (BJB Enterprises) [33–35] and polydimethyl siloxane (PDMS) [36–38] among others. Research has shown that the shape of the fibrils’ tips has a strong influence on the dry adhesive’s performance [38], [39] with aspect ratio also having an important role in performance [40], [41]. The fibrillar aspect needs to be carefully controlled in order to optimize the reversible adhesion behaviour; too high of an aspect ratio leads to fiber clumping and collapse whereas a low aspect ratio may have a similar adhesive performance to that of an unstructured sample. Mushroom shaped fibrillar tips, illustrated in Figure 2-1, have been found to possess greater adhesion capabilities [19], [38], [42] when compared against flat fibrils with no overhanging caps or fibrils with spherical shaped tips. This study is centred on a mushroom-cap fibrillar dry adhesive with a manufacturing process based on [36] utilizing PDMS as the structural material; more details on the material choice will be given further in this section. The dry adhesive’s manufacturing method was studied because of its high reusability and possibility of batch fabrication making it more commercially viable.
Recently however, the research focus has shifted towards getting more consistent results, better adaptation to rough surfaces, increasing durability without sacrificing the overall adhesion. Active and passive controllable adhesion are also highly desirable adhesive qualities. Mimicking the directionality or anisotropic properties of the gecko setae is a way to achieve passively controlled adhesion; with a directional adhesive, the force required to detach the adhesive is a function of the angle the detaching force is applied. Anisotropic dry adhesives have been successfully manufactured [34], [46] and used as the attachment mechanism of legged robots [47]. Additionally, increasing the ability of a dry adhesive to conform to different substrates has been addressed by further mimicking the gecko setae by creating a hierarchical
structure, a picture of these synthetic dry adhesives shown in Figure 2-2. Arrays of nano-fibrils reside on the tips of micro-fibrillar structures allowing for adaptation and good adhesion to surface of micro and nano roughness [48], [49] (Figure 2-2 a). A third hierarchical level, on the macro-scale, could have the potential of further enhancing the dry adhesive’s performance; this has already been shown for the dual level hierarchical macro-structures without the integration of nano-fibrils [21] (Figure 2-2 b). In order to attain longer lasting adhesion and increased durability, the gecko setae besides having high adhesion is ironically also anti-adhesive [9], [14]. This “anti-adhesive” property refers to the fact that small particles, such as dust or sand which would effectively reduce adhesion, do not easily stick to the setae; if small particles do stick, the setae will self-clean as the gecko continues its stride. Mimicking this self-cleaning ability has been highly sought after with some success achieved for CNT based adhesives [50], [51] because of their intrinsic hydrophobic properties; this success however, has only achieved a partial recovery from the dry adhesive’s original adhesion. Other attempts follow more active cleaning systems but suffer from substantial fibril collapse [52], poor adhesion recovery through contact [53] or only work for adhesives with initial adhesive levels that are lower than those of an unstructured sample [54]. Other work has focused on using an oil layer to enhance the adhesion of an array of micro fibrils [55] effectively stirring away from a dry adhesion system which for this study is undesirable.

**Figure 2-2:** Hierarchical biomimetic dry adhesive structures for (a) micro-scale and (b) macro-scale (mm-sized posts and micro-posts on tips)

Note: (a): Reprinted with permission from [48]. Copyright 2009, American Chemical Society. (b) Reprinted from [21]. Copyright 2010, with permission from Elsevier.
Modifying the dry adhesive’s structural material properties in an attempt to achieve higher adhesive forces has, to the best of our knowledge, not been as widely investigated. The adhesion enhancement of a fibrillar biomimetic dry adhesive, through the modification of the adhesive’s structural material, is the main subject of study in this work.

### 2.2. PDMS Nanocomposites

PDMS is the structural material of the biomimetic dry adhesive under study. This polymer is a highly sought-after material in microfabrication, especially in microfluidics and as previously discussed, numerous dry adhesives are fabricated using this material. The abundant interest in PDMS originates from its various useful properties of which transparency, high flexibility, stability, chemical inertness and ease of molding are some of the most noteworthy [56], [57]. Most importantly, the ability of PDMS to conform to submicron features [57] because of its high flexibility and ease of moulding and demoulding together with its lower cost compared to CNTs or silicon make it a very useful polymer for many applications. Recently however, in an attempt to expand the applications of PDMS in microfluidics predominantly, metal nanocomposites which are formed by a polymer mixed with metal NPs have been extensively studied [58–61]. The main challenge with the manufacturing of these nanocomposites is the aggregation or bunching of the NPs. To avoid this undesired effect, the NPs are chemically passivated or isolated in a material’s structural matrix as a way to prevent them from joining, polymers being the most common materials of choice [58]. These polymer-metal nanoparticle composites are the gateway to many interesting and useful materials because of the many benefits attained from their coexistence.

PDMS and other polymer nanocomposites have potential applications in micro-electro mechanical systems (MEMS) where they can be used as rewritable displays [62], or in optical devices as filters [63]. Other important applications include the use of PDMS nanocomposites in biosensors [64] mainly because of the non-toxic and chemically inert properties of PDMS [58]. In order to manufacture these nanocomposites, numerous methods have been developed such as mixing NPs with PDMS precursors only to then remove the solvents and cure the mixture [65]. The
drawbacks to this manufacturing process are primarily its complexity and also that some of the solvents used are not compatible with the photoresists used in photolithography. Because photolithography is the most common and least expensive way to microfabricate dry adhesive moulds, chemical compatibility with photoresist is useful. Another commonly used method is to immobilize the NPs on a pre-treated PDMS surface [66]; this is a good method to synthesize NPs however the nanocomposite needs to be formed after the NPs have been synthesized. The simplest method to embed preformed NPs is by mixing these already synthesized NPs with the uncured polymer mixture; these NPs can be commercially purchased or synthesized before embedding them. The latter fabrication method involves NPs that have been already synthesized which in most cases leads to the NPs aggregating in the polymer matrix upon mixing; the aggregation of NPs as previously stated being very undesirable. To avoid aggregation, other methodologies such as sputtering, as well as the co-deposition of NPs and polymer have been studied [67]. The co-deposition by the use of co-evaporation gives rise to poor mechanical properties and analogous to sputtering is costly and not easily scalable. Several in-situ methods, in which the polymer and NPs are synthesized simultaneously yielding a nanocomposite, have become widely utilized. The in-situ synthesis of NPs has the advantage that the NPs are uniformly synthesized among the polymer matrix [59], [61], [63], because of the isolation of the individual particles in the host matrix, which helps in preventing aggregation. These in-situ methods for synthesizing NPs consist, as presented later in the study, of a cured PDMS sample placed in contact with a metal salt solution which reacts with the PDMS catalyst forming the NPs within the polymer structure.

In this study, different PDMS- metal NPs nanocomposites were investigated to increase the Hamaker constant of the structural material of a dry adhesive sheet. This Hamaker constant is directly related to the van der Waals attractive force responsible for the dry adhesion observed in the fibrillar structures. Different nanocomposite fabrication techniques were utilized and a novel method to integrate them to the soft-moulding dry adhesive fabrication process was developed. Ultraviolet-Visible (UV-Vis) Spectrophotometry was used to confirm the presence of metal NPs by detecting their peak surface plasmon absorption band. An indentation tester was employed to measure the adhesion force between surfaces. The resulting measurements were compared
against a control sample as well as existing models based on the Hamaker approximation showing a significant enhancement of adhesion.
3. Biomimetic Adhesives Rationalization: theoretical background

3.1. Adhesion Forces of a Gecko-like Tape

The adhesion of two surfaces in contact can be studied using contact mechanics. Johnson, Kendall and Roberts [68] as well as Derjaguin, Müller and Toporov [69] assessed the adhesion between surfaces in contact by means of surface energy approximations. The adhesion force between contacting surfaces using Hamaker’s approximation has also been described [70], which assumes that this adhesion force is only because of van der Waals forces between the interacting surfaces.

The discovery that gecko foot hair adheres to other surfaces using these van der Waals forces [11], [16] triggered a vast amount of research in this area. Many research groups have fabricated synthetic dry adhesives in an attempt to replicate this remarkable feat [30], [36], [71], [72]. Since then, some have attributed the adhesive forces in synthetic adhesives to be caused by van der Waals forces but also in part by capillary forces [19], [29], [73]. Numerous models have been proposed to explain synthetic gecko-like adhesion based on van der Waals forces [74–76] and sometimes in conjunction with capillary forces [77]. This study is centred in van der Waals forces and their effect on adhesion without considering capillary forces as has been successfully done in previous studies [15], [38], [78], [79]. The effect that van der Waals interactions in conjunction with capillary forces have on synthetic dry adhesives can be the subject of future studies.

3.2. Van der Waals Forces

Van der Waals forces are weak but ubiquitous body forces; they can be either attractive or repulsive but for like particles they will always be attractive. These forces
are mainly composed of three different dipole-dipole interactions, the orientation or Keesom interactions, the induction or Debye interactions and the dispersion or London interactions [70], [80], [81]. The Keesom interactions are between permanent dipoles whose mutual angles are, on average, favorably oriented with their opposite charges facing each other hence attracting one another. The Debye interactions exist when one permanent dipole induces a dipole in another non-polar molecule, this induction effectively creates an attractive force. London interactions are concerned with two nonpolar molecules and as such are always present. The London interactions occur between transient dipoles of nonpolar but polarizable bodies and they possibly make the most important contribution to van der Waals forces. Each of these pairs of interactions varies with the inverse sixth power of the distance between bodies. The combination of the Keesom, Debye and London interactions make up the van der Waals forces.

In this study, Hamaker’s approximation to calculating van der Waals forces will be utilized as the model to interpret the pull-off force encountered between media. The adhesion force due to van der Waals forces between two planes using Hamaker’s approximation, as shown by [70], [80], [81], can be expressed as

\[ F_{vdw} = -\frac{A_{ham}}{6\pi D^3} \]  

where \( A_{ham} \) is the Hamaker constant of the interacting materials and \( D \) is the distance between these surfaces; the negative sign indicates an attractive force (adhesive). Equation (1) is then an expression for the van der Waals force per unit area between two planes, in order to obtain the force of interaction it should be multiplied by the area in contact. In this study, the adhesion between a (macroscopic) sapphire hemisphere and the (microscopic) flat surface of the dry adhesive fibrils is investigated. More details about these surfaces can be found in section 5.2.1. The initial assumption made for this approximation is the fact that the surfaces are in such close contact that retardation is ignored. Retardation accounts for the finite amount of time it takes for the electromagnetic field from one charge to reach to the other for the interactions to occur. These surfaces are assumed to have a flat-flat contact, for an infinitely large hemisphere
radius as seen by any individual fibril, which can then be analyzed using Eq. (1) for a known surface area in contact.

3.3. Singly Layered Planar Bodies

In the same way the sapphire hemisphere interaction with the dry adhesive fibrils was treated previously, this model will treat both surfaces as planes to calculate the van der Waals force \( F_{vdw} \) between them. The difference being that one of the planes is modified to be composed of two layers of different materials. The caps of the fibrils caps will be considered as this layered surface as observed in Figure 3-1. Following this approach, a composite material can then be fabricated such that this layered material is formed. Because of the dimensions of the fibrils, this layer within the caps could be obtained by embedding NPs in the structural material (PDMS). This embedded layer can then increase the performance of the dry adhesive by the addition of its van der Waals interactions to the overall system.

From Parsegian's analysis of free energy for this system [70], we can express the van der Waals' adhesion force per unit area for a single-layer planar surface as

\[
F_{vdw} = -\frac{A_{Am/B1m}}{6\pi D^3} - \frac{A_{Am/BB1}}{6\pi (b_1 + D)^3}
\]

where \( b_1 \) is the thickness of the outermost layer. The subscripts of the Hamaker constants designate the materials interacting at the different interfaces, \( A \) corresponds to sapphire, \( m \) is the medium (air, vacuum) and \( b,b_1 \) correspond to PDMS and a material embedded within it. In order to analyze this single layered surface, two different pairs of interactions are present with their own Hamaker coefficient and separation distance. This analysis considers the Hamaker constant for the first term to be within the initial interface as Eq. (1) demonstrates but also includes the interactions caused by the layered material \( (B) \) in the second term. Each term in Eq. (2) has a different Hamaker constant calculated based on the interacting materials with the interactions existing at different fixed distances \( D \) and \( D+b_1 \) from the surface for the first and second terms respectively.
This layered approach model to the van der Waals adhesion for the dry adhesive assumes that the NPs form a uniform layer inside the PDMS mushroom caps. Following this method, in order for the NPs to be embedded within the PDMS, a layer $b_1$ exists to separate them from the surface of the fibrils' caps. The assumption of no retardation is also made, as in Eq. (1), and is valid because the separation distance ($D$) is very small even for rough surfaces; this intimate contact being characteristic of the fibrillar dry adhesives. Furthermore, because the weak van der Waals forces are short-ranged, the effect other materials, existing past $B$ and $B_1$, may have on adhesion will be almost negligible since retardation will effectively suppress further interactions because of the finite velocity of light.

### 3.4 Hamaker Constant Calculations

The Hamaker constant, more appropriately called the Hamaker coefficient because it changes with separation. This constant is directly related to the forces of interaction, so an increase in the materials constant will ideally lead to an increase in the overall attractive forces. The Hamaker constant can be calculated through a sum over all frequencies where fluctuations can occur. Each term in the summation depends on...
the frequency-dependent responses of the interacting materials to electromagnetic fields. The differences in these responses, expressed as dielectric functions and obtained from their absorption spectra, are what creates interactions. The Hamaker constant of materials 1 and 2 interacting across a medium 3, as shown by [70], [80], [81], can then be expressed as

\[
A_{132} = \frac{3}{2} kT \sum_{n=0,1,2,...}^{\infty} \left[ \frac{\varepsilon_1(iv_n) - \varepsilon_3(iv_n)}{\varepsilon_1(iv_n) + \varepsilon_3(iv_n)} \right] \left[ \frac{\varepsilon_2(iv_n) - \varepsilon_3(iv_n)}{\varepsilon_2(iv_n) + \varepsilon_3(iv_n)} \right] \text{Rel}(D)
\]  

(3)

where \(k\) is Boltzmann’s constant and \(T\) is the temperature. \(\text{Rel}(D)\) is the relativistic retardation term which for the nonretarded regions is equal to 1, as is used in this study, otherwise if retardation is considered then \(\text{Rel}(D) < 1\). The terms in the sum are the frequency dependent “dielectric functions” of the materials. This sum of discrete frequencies can then be replaced by an integration over \(n\), where

\[
dn = \frac{h}{2\pi kT}
\]  

(4)

so that

\[
kT \sum_{n=1,2,...}^{\infty} \rightarrow \frac{h}{2\pi} \int_{v=v_1}^{\infty} dv
\]  

(5)

as described in [81]; where \(h\) is Planck’s constant and \(v\) represents the frequencies of interaction. This in turn gives an expression for the nonretarded Hamaker with the basis of Lifshitz theory

\[
A_{132} \approx \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h}{4\pi} \int_{v_1}^{\infty} \frac{\varepsilon_1(iv) - \varepsilon_3(iv)}{\varepsilon_1(iv) + \varepsilon_3(iv)} \left( \frac{\varepsilon_2(iv) - \varepsilon_3(iv)}{\varepsilon_2(iv) + \varepsilon_3(iv)} \right) dv
\]  

(6)
as expressed by [80], [81], where \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) are the static dielectric constants of the three media and \( \nu_n=(2\pi kT/h)n \). The first term in Eq. (6) gives the zero frequency energy of the van der Waals interaction and includes the Keesom and Debye dipolar contributions [80], [81]. The second term in Eq. (6) gives the dispersion energy and includes the London energy contribution expressed as dielectric functions \( (\varepsilon_j(iv)) \). These are only the first terms in an infinite series for the calculation of the nonretarded Hamaker constant. Other terms seldom contribute more than 5% and are not taken into consideration for this approximation [81].

From [81], the dielectric functions that make up the London interactions are expressed as

\[
\varepsilon(iv) = 1 + \frac{n^2 - 1}{1 + \nu^2 / \nu_e^2}
\]  

(7)

where \( n \) is the refractive index of the medium in the visible range, \( \nu \) is the frequency and \( \nu_e \) is the main electronic absorption frequency in the UV region. By means of an approximation, as given by [80], [81], and also calculated based on Lifshitz theory [82] that includes the zero frequency term and making use of Eq. (7) the Hamaker constant can be calculated. The value of the nonretarded Hamaker constant of two macroscopic phases, 1 and 2, interacting across a medium, namely 3, can then be found, with available spectroscopic parameters. The expression for this Hamaker constant, as given by [80], [81], then becomes

\[
A_{132} \approx \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) \\
+ \frac{3\hbar \nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_2^2)(n_1^2 - n_3^2)}{\sqrt{(n_1^2 + n_2^2)}\sqrt{(n_1^2 + n_3^2)} \left[ \sqrt{(n_2^2 + n_3^2)} + \sqrt{(n_2^2 + n_3^2)} \right]} 
\]  

(8)

where \( \varepsilon_i \) is the static dielectric constant, as previously noted, and \( n_i \) is the refractive index in the visible range for material \( i \). The main UV absorption frequency \( (\nu_e) \) is the same for
all three materials in this approximation which is true for most materials. The downside of Eq. (8) being that it only holds for dielectric materials, such as PDMS and sapphire for this study. Because of the nature of conductive media, the Hamaker constant would be very high when $\varepsilon$ and $n$ approach infinity and this approximation would not be valid. Due to the large Hamaker constant of conductive materials resulting from these properties, conductors are an ideal candidate for increasing adhesion in the system by enlarging the Hamaker constant of the system. The Hamaker constants for some conductive materials (gold, silver and copper) as well as other materials (PDMS and sapphire), obtained from literature, used in this study are shown in Table 3-1 for reference.

**Table 3-1:** Typical estimates, from literature, for the nonretarded Hamaker constants of two identical materials ($A_{131}$) interacting in vacuum at room temperature relevant to this study

<table>
<thead>
<tr>
<th>Material</th>
<th>$A_{131}$ in $\text{zJ} \ (10^{-21} \text{ J})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>45$^a$</td>
</tr>
<tr>
<td>Sapphire</td>
<td>145-150$^{b,c,d}$</td>
</tr>
<tr>
<td>Gold</td>
<td>332$^e$, 200-400$^f$</td>
</tr>
<tr>
<td>Silver</td>
<td>488$^c$, 200-500$^b$</td>
</tr>
<tr>
<td>Copper</td>
<td>400$^b$</td>
</tr>
</tbody>
</table>

Note: Data as reported by $^a$[83], $^b$[70], $^c$[80], $^d$[81], [84], $^e$[85].

As it is observed in Table 3-1, dielectrics possess a much lower Hamaker constant when compared to conductive media. Because these conductive materials will be of interest in this study and Eq. (8) is not a valid approximation for interactions with conductors, a different approximation was used. For the purpose of calculating the Hamaker constant of a dielectric material interacting with a conductive material (metal NPs), an expression for an approximation to the dielectric constant of the conducting media is used. This dielectric constant approximation, as obtained from [81], is expressed as

$$\varepsilon(v) = 1 - \frac{v^2}{v^2}$$  \hspace{1cm} (9)
where ν_e is the plasma frequency of the free electron gas and ν is the frequency as previously defined. Equation (8) in conjunction with (9) yield the following approximate equation

\[ A_{12} = \frac{3}{8\sqrt{2}} \left( \frac{n_1^2 - 1}{n_1^2 + 1} \right) \frac{h v_1 v_2}{v_1 + v_2/\sqrt{n_1^2 - 1}} \] (10)

for a conductor (v_2) and a dielectric (v_1, n_1) interacting in vacuum (air) [81]. This approximation can then be used in conjunction with Eq. (8) to model the layered dry adhesive.

The Hamaker constant for the metal NPs layer in the PDMS structure interacting with the sapphire probe can then be expressed, from [80], as

\[ A_{132} = A_{12} - A_{32} - A_{13} + A_{33} \] (11)

where A_{ij} represents the Hamaker constant for materials i and j interacting across vacuum. A_{ij} can be found using Eq. (6) and (10), depending on the materials of interaction. Equation (11) then allows for the calculation of the Hamaker constant of material 1 and material 2 interacting across medium 3 provided the interactions across these materials have been independently calculated. Once the Hamaker constants of the interacting materials have been calculated, Eq. (2) is utilized to obtain the van der Waals forces of the overall system; the expected adhesion given some area in contact can then be found.
4. Fabrication of a Nanocomposite PDMS Dry Adhesive with Metallic Nanoparticles

With the intent to optimize the performance of a PDMS biomimetic dry adhesive through the increase of the Hamaker constant of the system, NPs were embedded in the polymeric dry adhesive. Various methods to embed the NPs were implemented, each of which overcame a different constraint as discussed later in this study. Metal NPs were chosen because of their higher Hamaker constants in comparison with their dielectric equivalents.

4.1. Biomimetic Dry Adhesive Fabrication

The dry adhesives that were utilized in this report were fabricated by casting the polymeric structural material unto a mould fabricated using a modified version of the procedure mentioned in [36]. The overall fabrication process was performed in a Class 100 cleanroom environment in order to maximize the fibrils’ yield. A base layer made of polydimethylglutarimide (PMGI, MicroChem) SF 10, made by mixing PMGI SF 19 1:1 by volume with T Thinner, was spun on a polymethyl methacrylate (PMMA, OPTIX®) 4” wafer to achieve a thickness of 1.7 µm. A laser-cut PMMA wafer was preferred over a silicon wafer because of a lower cost and increased durability (the silicon wafer was found to be more prone to break when demoulding). While the use of a PMMA wafer yields more defects on the fibrils, no significant change in performance was observed because of the redundancy inherent in the fibrillar structure; an almost negligible adhesion reduction and its much lower price point in addition to the better durability over the silicon justifies the selection. This substrate choice leads to some processing modifications, from the original recipe [36], such as avoiding temperatures above 80 °C for long periods of time to avoid deforming of the wafer. Once the PMGI was spun onto the PMMA wafer, the wafers were soft baked at 100 °C for 2 minutes and left to cool to room temperature. AZ-9260 photoresist (AZ Electronic Materials,
MicroChem) was then spun on the PMGI layer for a layer thickness of 10 µm. The wafer was then baked at 80 °C for 1 hour followed by a 100 °C hard bake for 90 seconds. After the wafer had cooled to room temperature, it was rehydrated in a DI (deionized) water bath for at least 30 minutes; this step was necessary because of the long bake time to ensure a high contrast and development rate in the resist. The wafer was then dried with N₂ before it was transferred to the ultraviolet (UV) aligner for exposure to 365 nm light. Development was carried out in a 4:1 dilution (by volume) with DI water of AZ 400K developer until the features were developed and a desired undercut in the PMGI layer was attained. The lower baking temperatures, required because of the PMMA substrate, allow for a fast undercut in the PMGI base layer with the AZ 400K hence eliminating the final processing step in [36]. A final DI water rinse and N₂ dry were completed and the wafer was left overnight before casting polymer on it. An illustration of this process can be seen in Figure 4-1.

![Figure 4-1: Dry adhesive mould fabrication steps](image)

(a) structural Layers are spun on PMMA substrate, (b) wafer is exposed to i-line UV light in a mask aligner, (c) photoresist is developed/PMGI overdeveloped, (d) PDMS is cast on mould, (e) PDMS dry adhesive is demoulded.
A 4” dry adhesive sheet can then be fabricated using this mould. PDMS (Sylgard-184®, Dow Corning) was mixed in a 10:1 ratio (by weight) of pre-polymer to catalyst and degassed for 30 minutes under vacuum to remove all air bubbles from the mixture. Air bubbles trapped within the PDMS fibrils can cause a lower yield of fibrils which in turn reduces adhesion. The PDMS mixture was then poured and spun on the mould such that a level backing layer is achieved on the dry adhesive sheet. The moulded PDMS was then baked in an isothermal oven at 80°C for 3 hours to cure the sample. After the polymer was cured, the sample was left to cool to room temperature before demoulding in order to prevent tearing of the polymer when peeling from the mould. The resulting adhesive sheet is composed of an array of fibrils with mushroom shaped caps. The diameter and height of the fabricated post structures was 10 μm with a center to center post spacing of 20 μm as measured in the mould’s AZ-9260 layer. Similarly, the PMGI layer had a thickness of 1.7 μm and an undercut of 4 μm.

Figure 4-2: SEM image of resulting PDMS dry adhesive, fabricated through soft-moulding as described in Figure 4-1.
4.2. Formation of PDMS Dry Adhesive Nanocomposite

4.2.1. **Embedding of preformed NPs in PDMS**

The simplest method to embed the metallic NPs into the PDMS was to purchase preformed NPs and mix them with the uncured polymer. This polymer-nanoparticle mixture was then casted in a previously fabricated dry adhesive mould to obtain the nanocomposite dry adhesive. The different metal NPs utilized in this processing were Ag (0.4-1 μm, Inframat), Cu (60-80 nm, SkySpring), Ag (20-40 nm, Alfa Aesar) and TiO₂ Rutile (10-30 nm, SkySpring). PDMS was mixed in a 10:1 ratio by weight of pre-polymer to catalyst and degassed before the addition of the metallic NPs. A 100:1 concentration (by weight) was utilized when mixing the PDMS and metal NPs to avoid a large increase in viscosity of the polymer. Once the mixture was casted in the mould, it was baked for 3 hours at 80 °C which fully cured the polymeric nanocomposite.

4.2.2. **In-situ Silver Nanoparticles Synthesis in PDMS**

In order to synthesize silver NPs in PDMS a recipe from [59] was followed. To begin, a 2x10⁻² M silver benzoate solution was prepared by dissolving the salt in hexanes and mixing thoroughly. A PDMS 10:1 pre-polymer to catalyst mixture was then formed and degassed under vacuum. The silver benzoate solution was then added to the polymer mixture, 3 ml of silver solution to 8 g of PDMS, and sonicated for 15 minutes. Once a homogeneous mixture was obtained and a colour change was observed, the mixture was casted in a mould to fabricate the dry adhesive. The sample was then placed on a level surface under vacuum for 48 hours followed by a 3 hour bake at 80 °C.

As a different dry adhesive fabrication method, used to embed NPs directly onto the caps, a thin layer of PDMS was spun on a glass slide and a stamping method was attempted similar to the fabrication method in [34]. A photoresist mold was fabricated following the fabrication procedure in section 4.1 with the exclusion of the first step where the PMGI layer is spun. The omission of this layer results in an array of micro-posts with no caps as shown in Figure 4-4. This mould was used to fabricate a PDMS post array with no caps of 10 μm in height. The post array was placed on a flat substrate and dipped into the uncured nanocomposite layer. After dipping the posts,
they were stamped on a glass slide to form the overhanging caps. An illustration of the processing steps followed in this fabrication method is shown in Figure 4-3. This manufacturing procedure was utilized so that the nanocomposite was only formed in the caps; the caps being the only surface of the dry adhesive that gets in contact with an external surface.

**Figure 4-3:** Fabrication process for in-situ Ag NPs in PDMS dry adhesive caps, (a) a PDMS post array and PDMS with synthesized Ag NPs are prepared, (b) the posts are brought in contact with the PDMS nanocomposite, (c) the posts are retracted and stamped on a glass slide.
4.2.3. In-situ Gold NPs Synthesis in PDMS Dry Adhesive

Another in-situ method to synthesize NPs on a cured PDMS was used for embedding gold NPs. The processing steps necessary to embed the Au NPs into the PDMS structures were obtained following a recipe from [61]. First a gold (III) chloride trihydrate (HAuCl$_4$•3H$_2$O) aqueous solution was prepared to be used for dipping the PDMS sample followed by incubation for a predetermined amount of time. Two different gold aqueous solutions were prepared by dissolving HAuCl$_4$•3H$_2$O (namely gold salt, 99.9 % purity, Sigma Aldrich) in DI water at different concentrations. Initially, the higher concentration solution (5 g/L) was prepared and then this solution was diluted further in DI water to reduce the solution concentration (2.5 g/L). The initial solution was mixed at 400 rpm for 30 minutes on a stirring hot plate set at room temperature. Some of this prepared solution was then diluted and stirred until a consistent color was seen throughout obtaining the solution with lower concentration.

Once the solutions were prepared, in order to synthesize the NPs, the fully cured PDMS dry adhesive was wetted with the gold solution and incubated for the reduction of the gold salt into Au NPs to occur [61]. The NP synthesis was achieved by dipping a
10 mm square PDMS sheet into the HAuCl₄ solution followed by incubation of the sample at 37 °C for a series of controlled times. In this process, the PDMS cross linker acts as the reducing agent and reduces the penetrating HAuCl₄ solution to Au NPs. The pore size of the PDMS matrix provides a spatial confinement on the formed NPs and therefore, it controls their size. The polymer matrix also prevents the aggregation of the Au NPs which is highly advantageous for this type of nanocomposites.

A challenge to overcome was to synthesize the NPs only in the mushroom-like caps of the dry adhesive fibrils to avoid modifying the dry adhesive’s structure not in contact with a surface. Modifying the material not in contact with a surface may lead to a decrease in adhesion, as will be explained later in the study. Therefore, a very thin and uniform layer of HAuCl₄ solution was prepared and used such that only the mushroom caps were dipped in the HAuCl₄ solution. To achieve this, a hydrophilic glass surface was prepared by immersing a micro cover glass (VWR) in Piranha solution (3:1 mixture, H₂SO₄:H₂O₂) for 30 minutes. The glass cover was then rinsed thoroughly in DI water and then dried in N₂. Once the hydrophilic surface was created, a small amount of the solution was spread on the surface yielding a thin and uniform HAuCl₄ layer. The overall process and expected fabrication outcome is shown in Figure 4-5. Once the PDMS micro-posts were brought in contact with the gold salt, the sample was placed in a temperature controlled chamber set at 37 °C. Samples were incubated using the two different solution concentrations, 2.5 g/L and 5 g/L, for 6, 14 and 24 hours. After incubation, the samples were rinsed with DI water and dried with N₂ before placing in a Petri dish to air dry overnight.
Figure 4-5: In-situ gold NPs synthesis. (a) PDMS with mushroom-like caps dipped into a thin layer of HAuCl₄ solution (b) Au NPs embedded within caps after incubation at 37 °C.
5. Dry Adhesive Characterization

Arrays of circular posts with a mushroom-like cap were successfully fabricated by soft moulding from the successfully fabricated photoresist moulds. The post structures were 10 µm in diameter, 10 µm tall and arranged in a square array with a center to center spacing of 20 µm. The overhanging caps had 18 µm diameters and were 1.7 µm thick as previously mentioned in this study. Qualitative confirmation of the synthesis of metal NPs in PDMS is first presented followed by the results from adhesion testing of dry adhesive with and without embedded metal NPs.

5.1. Nanoparticles Analysis

5.1.1. Preformed Nanoparticles embedded in PDMS

Following the procedure outlined in section 4.2.1, different metal NPs were embedded in the PDMS structure. Because of the nature of this method, where the NPs were already synthesized before embedding in the PDMS, no analysis or qualitative confirmation of the existence of NPs was performed on these samples. Images, acquired with an optical microscope, from the resulting dry adhesive sheets obtained with this manufacturing process are shown in Figure 5-1. The size range of the NPs mixed with the polymer was between 20-40 nm.

It was observed that the preformed NPs tended to aggregate, as shown in Figure 5-1. The NPs appear to be very large, and hence were not able to penetrate inside the posts or the caps of the fibrillar structure. The effect aggregation has on adhesion will be discussed in section 5.2.2. The adhesive sheet had an increase in stiffness when the PDMS nanocomposite was fully cured (qualitatively observed) in comparison with dry adhesive samples composed of only PDMS.
5.1.2. **In-situ synthesized Silver Nanoparticles**

A colour change in the mixture of PDMS and silver solution from white to yellowish brown was observed after sonication. This colour change gives a qualitative indication of the formation of Ag NPs as reported by [59]. Aggregation was not completely avoided using this method, since the silver benzoate did not completely dissolve in the hexanes, which allowed the visual inspection of the particles under an optical microscope. An image of the PDMS with the synthesized Ag NPs is shown in Figure 5-2 for the unstructured sample as well as for the backside of the moulded nanocomposite dry adhesive.

From Figure 5-2, it can be observed that the NPs were larger than 20 µm and had an appearance resembling micro-rods. The large size of the rods impeded their integration with the dry adhesive microstructure which indicated that a more creative way to embed these micro-rods into the fibrils was needed. Using the second method explained in section 4.2.2, an array of micro-pillars, imaged in Figure 4-4 was dipped in an uncured mixture of PDMS containing synthesized Ag NPs. Figure 5-3 shows the results for one of the fabrication attempts using this dipping method to produce a PDMS dry adhesive.
Figure 5-2: Ag NPs in-situ synthesized in PDMS, (a) PDMS with Ag NPs, (b) PDMS dry adhesive with Ag NPs. Ag NPs aggregated into rod shaped particles, no particles were visible in the post or cap structure of the dry adhesive.

Figure 5-3: PDMS dry adhesive, without NPs, fabricated using a pre-fabricated array of posts followed by dipping them in uncured polymer. Individual caps were not successfully formed; several posts became a conjoined array.

As it is readily observed in Figure 5-3, tilting of the sample with respect to the substrate and pressure control when indenting the posts in the uncured polymer were
issues that needed to be addressed. The use of a linear stage to control the speed and position of the post array in Figure 5-3 when lowering it to contact the uncured polymer was performed with no success. A setup similar to the one used in [86], [87] was utilized to align the samples perpendicularly to the uncured polymer. However, this did not work as expected because this did not allow for the pressure to be controlled as precision of available equipment was not adequate. This fabrication method was also a significant diversion from the original soft moulding process so a different alternative to embed the NPs in the dry adhesive was pursued.

5.1.3. In-situ synthesized Gold Nanoparticles

Visual observation of the sample’s colour change was utilized as a qualitative indication confirming the formation of Au NPs [61]. The reduction of HAuCl₄ into Au NPs results in a colour change from an initial light yellow colour of the gold salt solution to the ruby red colour within the PDMS as observed in Figure 5-4. A Cary 5 UV spectrophotometer was also used to characterize the synthesized NPs from the absorption spectra of the samples. The position of the peaks in the absorption spectra confirms the presence of Au NPs and provides information on the relative size, and concentration of Au NPs within PDMS matrix.

![Image](file.png)

**Figure 5-4:** Colour change as a qualitative confirmation of the Au NPs synthesis in the PDMS matrix. (a) Gold solution was initially light yellow, (b) PDMS dry adhesive as initially transparent, (c) PDMS became a red ruby colour where the Au solution was in contact after incubation. Each tick mark represents 1 mm for the 3 independent images.

Six different sample sets were fabricated using the two above mentioned Au salt solution concentrations (5 and 2.5 g/L) and three different incubation times of 6, 14 and
24 hours. For all samples, a red ruby colour change for the PDMS was observed which, as previously stated, suggests the formation of Au NPs in all cases. This was further confirmed by collecting the UV-Vis spectra of the samples which revealed the surface plasmon absorption bands of Au NPs, centered at a mean of $540 \pm 5$ nm as illustrated in Figure 5-5 and specified by the vertical line. This peak intensity increases by increasing the Au salt solution concentration as well as for longer incubation times. The peak intensity increase is an indication of the formation of a larger number of Au NPs.

![Figure 5-5: Ultraviolet-Visible (UV-Vis) absorption spectra of the samples with synthesized Au NPs. Colors indicate incubation time and line types refer to Au solution concentrations. Spectrum of PDMS is also shown for completeness. Vertical line indicates the peak absorption mean for the Au NPs.](image)

From Figure 5-5 it can be observed that the peak centre varies in the range of 525 nm to 545 nm for the samples prepared at different incubation times and with different gold salt solution concentrations. From the position of the peak centre we can approximate the size of the synthesized NPs to be within 5 nm to 13 nm by comparing them with the results obtained by [61]. Given that the synthesis was performed at a 10:1 concentration pre-polymer to catalyst ($\eta=0.1$) of PDMS, a nanoparticle size of 13 nm is
expected for the highest concentration of the metal salt (5 g/L). This gives an upper bound for the particle size which is of use to approximate the parameters to compare with the adhesion model. It is worthy to note that the UV-Vis spectra shown in Figure 5-5 were obtained from an unstructured PDMS sample with synthesized NPs following the same recipe as with the structured dry adhesive samples. The use of the flat PDMS samples was needed to obtain a single peak for each spectrum which yields a better understanding of the NPs formed. When the tests were performed on the structured samples, each absorption spectrum showed multiple peaks due to the topological pattern of the PDMS structure (fibrillar). The spectrum of one of the structured PDMS with Au NPs samples is shown in Figure 5-6 from which it can be seen that the centre peak is not discernible.

Figure 5-6: UV-Vis Spectrum of a dry adhesive with in-situ synthesized Au NPs in its mushroom caps. Absorption peak is not clearly discernible due to the topology of the fibrillar dry adhesive.

5.2. Dry Adhesive Testing

With the intention of characterizing the detachment (adhesion) force of the samples, a custom test setup was used to measure the pull-off force of the dry adhesive similar to the one utilized in other works [36], [88]. A 6 mm diameter sapphire
hemispherical tip (Edmund Optics, NT49-556) was used as the indenter because of its insensitivity to misalignment [86], [89]. The sapphire hemisphere was attached to a tension and compression load cell (FUTEK LRF400, 2.2 lb) using a steel rod. To digitize the reading, the load sensor was connected to a 24-bit ADC (Analog to Digital Converter) and amplifier (FUTEK USB210). The positioning of the entire setup was done with a linear stage (Zaber Technologies T-LS28-SMV) to which the load cell was fixed. In order to record the measurements performed as well as for the overall control of the test setup LabVIEW (National Instruments) was utilized with a custom script. The entire setup was mounted on an Inverted Microscope (Olympus GX-41) so that the contact area, sapphire hemisphere with the dry adhesive, could be recorded and measured. A picture of the test setup as described is pictured in Figure 5-7.

![Image of test setup](image)

**Figure 5-7:** Adhesion (pull-off force) test setup. A sapphire hemisphere tip is attached to a load cell using a metal screw. The load cell is secured to a linear stage mounted on an inverted microscope.

Each test consisted of a minimum of 300 preload-detachment cycles in an attempt to minimize measurement errors. Also, to avoid adhesion discrepancies because of fabrication differences, all samples were taken from the same adhesive
sheet. The samples were visually inspected and discarded if any major defects were encountered. The PDMS control samples were tested alongside the samples where Au NPs were synthesized for consistency of results. The probe was initially cleaned with Isopropyl Alcohol (IPA) and left to dry for at least 10 minutes before testing. The first few tests were discarded as it has been shown that adhesion decreases from what is initially recorded but reaches a steady state after a number of testing cycles [90].

5.2.1. PDMS “mushroom” cap micro-fibrils

To quantify the adhesion change due to the addition of the metallic NPs, a control sample, made of PDMS only, was characterized. The adhesion-preload curve is shown in Figure 5-8 where a 10 % variation in adhesion force is observed over a 10 % change in preload. The preload force is directly related to the area in contact, the range for which the sample was characterized was controlled using preload measurements in the LabVIEW script; contact area was also recorded during adhesion testing for comparison with the Hamaker model. A preload range is used instead of a single value because of equipment variations as a test progresses; the linear stage’s positioning varies as equipment heats up with usage.

From the values obtained in Figure 5-8, an average adhesion force of 48.36 ±2.2 mN was obtained for a 414.49 ±11.28 mN preload average value. This value was used to quantify the adhesion change caused by the embedding of metallic NPs. One thing to note from the plot in Figure 5-8 is that values that were recorded to be outside of the 400 mN-442 mN preload range were discarded so that the preload range was decreased and kept consistent with other tests.
5.2.2. Embedded metal NPs in dry adhesives by soft moulding

For the purpose of characterizing the adhesion changes of the nanocomposite dry adhesives as fabricated in sections 5.1.1 and 5.1.2, adhesion testing was carried out at different preloads for a minimum number of preload-detachment cycles. The procedure for testing of these samples was different than the one outlined in section 5.2 because the decrease in adhesion was readily observable. The adhesion curve for the preformed Ag NPs mixed with PDMS, as imaged in Figure 5-1 (a), is plotted on Figure 5-9.
Figure 5-9: Adhesion testing for preformed Ag NPs mixed with PDMS and soft-moulded to fabricate a dry adhesive. An optical microscope image for the aggregated NPs in the dry adhesive backing is shown in Figure 5-1 (a).

From the adhesion curve plotted in Figure 5-10, an adhesion decrease of approximately 80% can be perceived for the samples with Ag NPs. This decrease in adhesion performance can be explained with a decrease of area in contact between the probe and the dry adhesive. The area in contact is decreased because of a reduction in conformance between the fibrils and the sapphire hemisphere caused by the aggregation of the Ag NPs. Adhesion behaviour like the one shown in Figure 5-9 was observed for all the nanocomposites formed as explained in section 4.2.1 for preformed NPs. The Ag micro-rods (Figure 5-2) that were synthesized in the dry adhesive and soft moulded to fabricate the nanocomposite dry adhesive also had a similar performance.

However, the adhesion reduction observed for the synthesized Ag was closer to 50% when compared to the reference sample composed of only PDMS. The lesser reduction in adhesion caused by the micro-rods is theorized to be caused by the micro-rods aggregating to a lesser extent than the preformed NPs because of the in-situ synthesis. Pull-off force values for the posts that were dipped in uncured PDMS with and without synthesized NPs were much like a flat PDMS sample. Adhesion curves for other
nanocomposites made using the methods in section 4.2.1 and 4.2.2 are omitted as there was no increase in adhesion performance for the dry adhesive.

5.2.3. **Au NPs embedded in PDMS fibrils**

Adhesion (pull-off) force measurements were performed at a preload of 420 mN ± 5%, as explained in Section 5.2, for the control sample as well as the dry adhesive samples embedded with NPs; this preload corresponds to a measured contact area of 1.04 x 10^-6 m². An average of the multiple tests taken was found and the deviation from the mean was not large for all samples. The results obtained from these tests are presented in Figure 5-10 where an adhesion improvement can be observed for the majority of the samples tested. However, there is a reduction in adhesion observed for the longest incubation time (24 h) and higher gold solution concentration (5 g/L) which, as expected, is the sample with the highest concentration of gold NPs. This concentration can be correlated in the samples’ absorption spectra (Figure 5-5); a percentage concentration of Au NPs is also shown within Figure 5-10 where this was calculated taking the sample with the highest concentration of NPs as the reference.

The positive effect the synthesis of the NPs has on the performance of the dry adhesive is apparent when comparing Figure 5-5 and Figure 5-10 as the concentration of NPs relates to the adhesion measured; the exceptions observed for the highest and lowest concentrations of NPs as previously stated. In order to explain these discrepancies from the expected results, stiffness and roughness of the dry adhesive material have to be taken into account. These material properties can negatively affect the performance of the dry adhesive because of a loss of conformance of the mushroom caps with the substrate. The significant increase in adhesion observed for the lowest concentration of NPs can then be explained because in this case the addition of the NPs does not disturb other material properties such as the post stiffness. A greater conformance when compared with other nanocomposite dry adhesive samples is hypothesized to be the cause of this large increase of adhesion. Conversely, for the highest concentration of Au NPs, the adhesion significantly decreased as observed in Figure 5-10. This adhesion decrease is thought to occur because of a decrease in the adhesive’s conformance to the surface of the probe partly because of stiffness but also because of an increase in roughness on the surface of the caps. The increase in
roughness is seen because of the saturation of the mushroom caps with large and irregularly shaped Au NPs. This decrease in adhesion is shown in Figure 5-11 for the sample with highest concentration of Au NPs where the otherwise smooth caps attain an increase in roughness and consequently a reduction in conformance. It is hypothesized that the roughness of the caps increases with an increase in size of the Au NPs as well as with the amount of NPs synthesized.

Figure 5-10: Adhesive pressure comparison for the different dry adhesive gold nanocomposites. The adhesive pressure value for the control sample is shown using a solid horizontal line; measurement error for this sample is indicated with the dotted line. Values are grouped by gold solution concentration and incubation time is differentiated with a gray gradient. The NP concentration for each sample is indicated with a star and based upon the maximum NP concentration as measured in Figure 5-5.

The adhesion performance for the other adhesive samples maintains a uniform increase as the Au NP concentration also increases. This consistent increase seems to indicate that as the concentration of Au NPs increases, an increase in adhesion performance similarly occurs. As stated earlier in the study this concentration increase was measured using spectrophotometry and a ratio of the NP concentration is obtained.
using the highest absorption peak as reference. The Au NP concentration is then plotted as a percentage in Figure 5-10 for ease of comparison with adhesive performance.

![Figure 5-11: SEM image of dry adhesive with embedded Au NPs where roughness is visibly increased. Corresponds to a gold solution concentration of 5.0 g/L and an incubation of 24 hours.](image)

As can be seen in Figure 5-12 for dry adhesives with embedded Au NPs, adhesion increases with an increase of the area in contact until a plateau point is reached; once the sapphire probe is further indented and contact area increases the adhesion force is reduced from that point on. This effect is in contrast with what is observed for the PDMS dry adhesives without NPs where it reaches a plateau, or saturation level, without an increase or decrease in adhesion forces as shown in [40]. The adhesion reduction can be explained, for the nanocomposite dry adhesive, by the caps detaching from the sapphire probe after the adhesion force plateau is reached due to the probe further indenting the sample. This effect is hypothesized to be a consequence of different post and cap elasticises unlike what is found in homogenous PDMS dry adhesives. An important thing to note is that the area in contact at which the
pull-off force testing was performed, for Figure 5-12, falls within the average measured contact area for the force "plateau" value of the NP samples.

Figure 5-12: Adhesion curve observed for a fibrillar dry adhesive with Au NPs embedded in its mushroom caps.
6. Hamaker Approximation model corroboration with Experimental Results

6.1. Hamaker Approximation Model

With the intention of characterizing the force improvement to be achieved with the synthesis of the Au NPs in the PDMS fibril caps, the Hamaker constants for the different material interactions were calculated. The values are tabulated for assessment in Table 6-1 and were obtained by using Eqs. (6) and (8) to approximate the Hamaker constant of the interacting materials. The optical constants for the materials examined were obtained from several different sources [70], [80], [81].

Table 6-1: Hamaker constant comparison for the different interfaces studied

<table>
<thead>
<tr>
<th>Interacting Materials</th>
<th>Hamaker Constant A in zJ (10^{-21} J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ Air PDMS</td>
<td>87</td>
</tr>
<tr>
<td>Al₂O₃ Air Au</td>
<td>213.6</td>
</tr>
<tr>
<td>PDMS Air Au</td>
<td>109.8</td>
</tr>
<tr>
<td>Al₂O₃ PDMS Au</td>
<td>205.9</td>
</tr>
</tbody>
</table>

From Table 6-1, it can be observed that the Hamaker constant between the sapphire test probe (Al₂O₃) and the PDMS dry adhesive significantly increases if the fibril tips are nanocomposites, formed by the polymer and the Au NPs. Using Eqs. (1) and (2) in conjunction with the previously found values for the Hamaker constants (Table 6-1), the adhesion forces of the interacting media were calculated to be compared and validated with the experimental data in the next subsection. These predicted adhesion values are tabulated for easier visualization in Table 6-2.
Table 6-2: Predicted adhesion values using Lifshitz approximation to van der Waals forces (Hamaker Model) for a dry adhesive with Au NPs

<table>
<thead>
<tr>
<th>Dry Adhesive Material</th>
<th>Predicted Adhesion (mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>53.91</td>
</tr>
<tr>
<td>PDMS + Au NPs</td>
<td>121.1</td>
</tr>
</tbody>
</table>

The calculated adhesion values found in Table 6-2 were used to predict the increase in adhesion expected with the embedding of the Au NPs, a 2.25x increase was calculated for an area in contact of 1.042x10^{-6} m^2. The separation distance \( D \) used for finding these values was 4.5 nm which corresponds to the maximum \( R_a \) (average roughness) of the sapphire probe as measured with a Tencor® surface profilometer. Similarly, the thickness of the \( b_1 \) layer, as presented in Figure 3-1, is assumed for the calculation of the PDMS and Au NPs to be 1 nm which is ca. twice the packing length of PDMS as described by [91] and calculated by [92]. Disturbances in the mechanical properties of the PDMS dry adhesive can occur with the embedding of the NPs into the PDMS structures. It is important to note that the calculations obtained using this adhesion model do not account for roughness or stiffness changes in the nanocomposite material. These parameters can also have an effect on the van der Waals’ adhesion forces due to the loss of conformance of the mushroom caps with the substrate. The adhesion model that was considered however, does take into account the roughness of the sapphire probe in the separation distance. This decision was made to simplify the modeling and experimental procedure which would have required, for instance, the use of an atomic force microscope (AFM) for topographical measurements.

6.2. Validation with Experimental Results

The predicted van der Waals adhesion force for the PDMS control sample was found to be within error of the experimental results for a separation distance of 4.5 nm. This distance corresponds to \( D \) in Figure 3-1 and relates to the maximum \( R_a \) of the sapphire probe as measured with a Tencor® surface profilometer. These results are shown in Table 6-2 for the predicted adhesion and Figure 5-10 for the experimental test results. The results obtained in this study seem to indicate that the expected adhesion improvement is not strictly a direct correlation to the increase in the Hamaker constant of
the system as Eq. (1) may suggest. It can also be hypothesized from Table 6-1 that the
direct contact between the sapphire probe and the gold particles would have a stronger
effect in adhesion, which is not the case as the Au NPs behave like asperities impeding
the direct contact of the probe with the conforming surface. When the Au NPs were
located on the surface of the caps, the NPs attach to the sapphire probe because of the
higher attractive force between Au and Al₂O₃ than with the PDMS and no significant
adhesion force is measured. This unwanted outcome is the main reason why the NPs
were embedded within the adhesive’s structural material instead of simply being
attached on the surface of the fibrils. The adhesion model as previously mentioned,
does not take into account other factors that can influence adhesion such as the surface
roughness [79] or the increase in the Young’s Modulus that can occur because of the
addition of the NPs [59]. This simplification made for the adhesion model will inevitably
yield values larger than if roughness was accounted for. This is particularly important for
the sample where the largest concentration of nanoparticles exist. The roughness of the
mushroom caps increases to the point where the Au NPs are visible outside of the
PDMS structure, as shown in Figure 5-11. Due to this observation it is theorized that a
great loss of conformance of the mushroom caps to the sapphire probe exist. The loss
of conformance in turn yields a reduction in the measured adhesion forces when
compared against the adhesion model (Chapter 3).

The Hamaker model of adhesion closely agrees with the experimental results
obtained (Figure 5-10), as calculated using approximations based on Lifshitz theory.
The adhesion model yields a 125 % adhesion improvement, as described in Table 6-2,
which compares with a 119 % adhesion improvement, average measured experimental
pull-off force, obtained for the nanocomposite dry adhesive. The average experimental
adhesion improvement disregards the sample with the highest concentration of NPs as
the model doesn’t account for the parameters hypothesized to cause a reduction in
adhesion of the sample; these parameters are believed to also account for the
discrepancy ratio observed between the model and the experimental results. The
comparison of the adhesion model against the experimental results is presented in
Figure 6-1.

It should also be noted that, as previously stated, Eq. (1) corresponds to the van
der Waals forces for a plane-plane interaction and was used as an approximation to the
sapphire hemisphere probe of much larger radius than the individual caps radii in contact with the flat tips of the biomimetic dry adhesive. This approximation will inevitably lead to discrepancies between the experimental results and the model since the radius of the sapphire hemisphere is not infinite. Furthermore, retardation has to be accounted for when $D > 10 \text{ nm}$, since $D > c/v$, where $v$ is typically $3 \times 10^{15} \text{ Hz}$ for the ionization of a molecule [80], which limits the thickness of the $b_1$ layer for the analysis in the non-retarded single layer model if the Au NPs are to contribute to adhesion significantly.

**Figure 6-1:** Pull-off force comparison between the Hamaker model and the experimental results for a contact area of $1.04 \times 10^{-6} \text{ m}^2$. Other constants for the Hamaker approximation model used are $D = 4.5 \text{ nm}$ and $b_1 = 1 \text{ nm}$.  

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45
7. Further Improvements to Biomimetic Dry Adhesives

7.1. Self-Cleaning Biomimetic Dry Adhesives

Much effort has been placed in replicating the adhesion structure and strength of the geckos. However one of the most significant capabilities of the gecko’s adhesive setae is that they are self-cleaning. Synthetic dry adhesives lose adhesion when in contact with unclean surfaces. This reduction in adhesion performance can be substantial and lead to failure or it can be minor and only stop working after long usage times. This is why mimicking this self-cleaning feat has drawn considerable interest in recent years. However, nothing that has been achieved so far can rival the anti-fouling behaviour of the gecko pads. Because a self-cleaning material is yet to be found, an active self-clean mechanism to keep adhesion consistent or to recover adhesion in a practical manner can instead be implemented.

Preliminary steps towards a dry adhesive active-cleaning cycle were evaluated and a detailed description can be found in Appendix A [88]. An application of cleaning dry adhesives would be for robots that use dry adhesives as a method of attachment to surfaces. The principle behind the cleaning of the dry adhesives is that even if the adhesives are not self-cleaning, stations where robots can clean their pads without exerting energy, simply by walking over, is a step in the right direction. Several dry adhesive samples were intentionally soiled with particles in the range from a few hundreds of nanometers to almost a millimeter as presented in Table 7-1. The use of vibrations, Scotch tape ® and a wax were explored as viable solutions for the removal of these particles from the dry adhesive tips in order to recover adhesion. The results from the test carried out are plotted in Figure 7-1 where the vibration cleaning is omitted because adhesion recovery of those samples was less than 3 %. Adhesion recovery was found to be dependent on the method used and the size of the particles. Figure 7-1 suggests that larger particles have generally a better recovery with the tape cleaning
method than the smaller particles which recovered better using the CrystalBond™ wax cleaning process. This suggests that in order to achieve the best recovery a two-step cleaning process should be involved.

Table 7-1: Approximate sizes for the particles used as contaminants to prompt a decrease in adhesion for the biomimetic dry adhesive.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size (µm)</th>
<th>Material</th>
<th>Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black (C)</td>
<td>&lt; 0.5</td>
<td>Alumina (Al₂O₃)</td>
<td>45 - 250</td>
</tr>
<tr>
<td>MnO₂ powder</td>
<td>&lt; 10</td>
<td>Tin (Sn)</td>
<td>420 – 600</td>
</tr>
<tr>
<td>Nickel Powder (Ni)</td>
<td>5 – 37</td>
<td>Sand</td>
<td>590 – 840</td>
</tr>
</tbody>
</table>

Note: Table adapted from [88].

Figure 7-1: Percentage adhesion recovery, after cleaning with different materials, for particles of different sizes. Materials used for cleaning were CrystalBond™ (wax) and Scotch tape®.

Note: Figure adapted from the results in [88]. Plot layout was revised, data used remained as previously published.
From what was studied in this section, it can be seen that NPs not only can be useful for dry adhesion but if the dry adhesive comes in contact with them, they can also be detrimental to adhesion. This is why a dry adhesive with self-cleaning abilities would be very advantageous to dry adhesive and its applications. A cleaning method that can be used without the need to substantially redesign what has been already developed is then exceptionally advantageous. Cleaning robotic tracks or feet is feasible by simply having patches of tape at key areas along a nuclear reactor or inside the robot’s storage area in a satellite. For manipulators a simple lowering the end effector onto melted wax or tape and subsequent detachment could cause cleaning.

7.2. Electro-Adhesion and Dry Adhesives

After analysis of the negative effects that NPs can generate, other conceivably positive uses for dry adhesive nanocomposites are explored. Conducting composites are of great interest in MEMS and microfluidics. PDMS, as previously detailed, is widely utilized in these fields but because of its low surface energy, metals don’t adhere very well to it. The difficulty in patterning metals on polymers has led to the investigation of the embedding of NPs in its structure in order to create a conductive nanocomposite [93], [94]. These conductive nanocomposites can be suitable for use in a combination of dry adhesion and electro-adhesion as will be outlined in this section.

Electro-adhesion takes advantage of the electrostatic forces that exist between a substrate and the electrodes of an electro-adhesive sample. A high-voltage is applied on the conductive electrodes, embedded within a thin dielectric layer, producing a positively and a negatively charged electrode. The dielectric layer, which exists between the electrodes and the substrate, acts as a buffer that impedes the induced charges on the substrate to neutralize themselves with the electrodes. The charged electrodes generate an electric field which induces the electrostatic attractive forces amongst the substrate and the sample. The use of electro-adhesives for climbing robots was characterized with the published report presented in Appendix B [95]. The shear force measured for different polymers acting as the dielectrics is shown in Figure 7-2 for the attachment to a melamine surface.
With the results obtained in [96] and in part presented in Figure 7-2, the concept of using electro-adhesion to preload a PDMS dry adhesive is promising. A conductive nanocomposite layer could be created on the back of a dry adhesive sheet to function as the electrodes. An interdigitated electrode configuration showed the highest adhesion in [96] and would be the design of choice. Application of high voltage as previously explained can then apply a preload to the dry adhesive which upon removal of the applied voltage would stay attached to the substrate because of stronger dry adhesion forces. The application of an additional preload on the feet of a climbing robot (which for NP embedded PDMS dry adhesives lowers the adhesion force, Figure 5-12) can lead to energy efficient detachment from the wall. A more in-depth look into the applications of conductive nanocomposites and dry adhesives is needed nevertheless, to achieve and
better these interactions. This can be the subject of future work in dry adhesives with embedded NPs in an attempt to achieve actively controlled dry adhesion.

7.3. Antimicrobial dry adhesive patches for medical applications

By means of one of the methods outlined in Chapter 4, Ag NPs can be embedded into the PDMS dry adhesives. If the NP synthesis is successful and dry adhesion is enhanced or remains constant, very interesting applications could be realized from their mutualistic properties. Silver has intrinsic anti-microbial properties which are passed on to the nanocomposites when these Ag NPs are embedded in the polymer [59], [67]. Many commercial bandages make use of silver as a means to avoid further problems in an open wound. However, these commercial bandages utilize sticky fluids that leave residues and make it difficult with a more often than not painful detachment. These inconveniences could be eliminated with the use of dry adhesion; no residue would be deposited and ideally it would not be able to stick to body hair, hence having a painless removal.

The concept of utilizing dry adhesives as medical patches is something that has been investigated in recent years [73], [97], [98]; nonetheless, using a nanocomposite in conjunction with the dry adhesive is yet to be explored and can potentially provide a solution to skin adhesion. Its inherent properties could solve infections by stopping the spread of microbes in open wounds and is worthy of further investigation. Biodegradable properties of polymers could further increase its applications and a design framework has been established in that regard [73]. Moreover, some promising results have been found with regards to adhesion to skin [98]. Exploring this however was not the focus of this study but is important as future work for nanocomposite dry adhesives.
8. Conclusions

A novel strategy to enhance the adhesion performance of a biomimetic fibrillar dry adhesive was developed. Van der Waals attractive forces were modeled using the Hamaker approximation model which assumes all adhesion is caused by van der Waals interactions. This model indicated that an adhesion enhancement could be achieved by increasing the Hamaker constant of the interfacing materials. Conductive materials have a Hamaker constant up to 10x larger than that of the structural material of the dry adhesives. As a consequence of the sizes of the dry adhesive features, embedding metal NPs into the polymer dry adhesive became the strategy to fulfill Objective 1.

A layered approach for the Hamaker approximation to van der Waals interactions was utilized to model the NPs embedded in the PDMS fibrils. Following this model, the adhesion force of the system for a surface contact area of $1.042 \times 10^{-6} \, \text{m}^2$, corresponding to a preload of 420 mN, was calculated to be 121 mN. A distance of 4.5 nm was used as the separation between the sapphire hemisphere probe and the dry adhesive; this distance corresponds to the measured maximum $R_s$ of the sapphire probe. This estimates an adhesion improvement of roughly a 126 % when compared against the similarly calculated adhesion of a PDMS dry adhesive.

Once the strategy to enhance the performance of the dry adhesive was stipulated, different methods to embed metal NPs into the PDMS dry adhesive were pursued. The dry adhesives are manufactured by soft moulding of PDMS on a PMMA mould fabricated using photolithography in a cleanroom environment. Mixing commercially available NPs with the PDMS and casting on the mould showed a large aggregation of the NPs. This aggregation in turn generated a considerable decrease in adhesion which fails Objective 3. To solve the aggregation problem, methods to synthesize metal NPs \textit{in-situ} were proposed to implement the strategy and fulfill the second objective of the study.
The *in-situ* synthesis of silver NPs in uncured PDMS followed by casting on the PMMA dry adhesive mould led to aggregation in a lesser extent than observed for the preformed NPs. However, there was no indication the NPs were being introduced in the dry adhesive’s fibrillar structure since particles were only visible in the adhesive’s backing layer. Assessment of this method showed an adhesion decline when compared to the original dry adhesive of almost 50%. The drop in adhesion was attributed to the stiffening of the backing layer and to some extent, that of the fibrils where some Ag NPs may have been introduced; no NPs were observed in the mushroom caps. An increase in the stiffness of the material is hypothesized to show a reduction in conformation to a surface which effectively reduces its contact area. The lesser area in contact in turn sees, as expected, a decrease in adhesion.

A second *in-situ* synthesis method, for gold NPs, was also proposed where a gold solution was deposited on cured PDMS and incubated. Results for the synthesis of gold NPs showed no indication that Au NPs were aggregating, synthesis was confirmed using spectrophotometry. This method of embedding NPs into the PDMS followed the single-layer model the closest since it allowed for the NPs to be embedded only in the mushroom caps. This was important since conforming to a substrate depends on fibril stiffness, which is then not affected, and the material in closest contact dictates the van der Waals interactions; in this case the mushroom caps are what make contact with the substrate.

The adhesion performance of the samples was enhanced by modifying (increasing) the Hamaker constant of the PDMS mushroom caps by embedding NPs through the Au NPs *in-situ* synthesis. Interestingly, our results show that this improvement is not solely related to the concentration of NPs. Other factors may have predominant effects on adhesion strength, including depth at which the NPs were synthesized, and variation of both roughness and stiffness of the material due to the presence of NPs. Nanoparticles that were synthesized on top of the mushroom caps led to an almost negligible adhesion because of increased roughness. The measured adhesion for a contact area of $1.042 \times 10^{-6}$ mN was found to be $106.27 \pm 10.34$ mN. The assumed distance at which the Au NPs were synthesized within the mushroom caps was 1 nm which corresponds to ca. twice the packing length of PDMS; this provides an upper bound for the adhesion of the nanocomposite dry adhesive. The measured adhesion
value shows a 2.2x improvement over a PDMS dry adhesive which measured 48.36±4.71 mN for the same area in contact hence fulfilling Objective 3 of this study. Experimental results are in agreement with the Hamaker approximation model proposed given some justifiable assumptions. These assumptions did not violate the initial assumption made of no retardation since no retardation occurs for separation distances of less than 10 nm approximately.

Nanoparticles and larger sized particles that stick to the dry adhesive’s fibrils have a detrimental effect on its performance. An active cleaning process for biomimetic dry adhesives was presented as preliminary work towards a self-cleaning dry adhesive. Utilizing an active cleaning method serves for a more durable dry adhesive when used in robotic applications. Additional enhancements that can be achieved with NPs and dry adhesives include the embedding of NPs for antimicrobial bandages (Ag NPs) and electroadhesives for actively controlled adhesion through self-preloading. Initial groundwork was done on electroadhesion and some preliminary research was carried out for medical applications. Passive control of adhesion can also be achieved by making use of a different choice of NPs, changing the Hamaker constant, or modifying the concentration of NPs which affects stiffness of the fibrils.

Further work also includes the experimental corroboration of the hypothesis that a reduction in adhesion exists because of an increase in roughness of the fibrils. These tests can be done with an Atomic Force Microscope (AFM) taking an initial measurement of the roughness of the caps, before embedding NPs. Additionally, the roughness of the caps after embedding Au NPs can be measured and these measurements compared against the control sample. Likewise, a characterization of the stiffness changes that the polymer endures with the addition of the NPs can be subject of further study. Stiffness variations can help prove the hypothesis of the dry adhesive having better conformance with a lower amount of NPs. Capillary forces can also be of consideration in further studies which can also be affected by the changes in material properties observed in the nanocomposite biomimetic dry adhesive.
References


Appendices
Appendix A.

Cleaning Properties of Dry Adhesives

Cleaning properties of dry adhesives

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Received May 28, 2010; accepted August 25, 2010

In this paper we present a study into the cleaning properties of synthetic dry adhesives. We have manufactured the adhesive micro-fibres through a low-cost, high yield fabrication method using Sylgard 184 Polydimethylsiloxane (PDMS) as the structural material. We deliberately contaminated the adhesive samples with different sized particles in the micro and macro scales and tested different cleaning methods for their efficacy with respect to each particle size. We investigated different cleaning methods, which included the use of wax moulding, vibration and pressure sensitive adhesives. For adhesion testing we used a custom system with a linear stage and a force sensor indenting a hemispherical probe into the adhesive surface and measuring the pull-off force. To characterize the cleaning efficacy we visually inspected each sample in a microscope and weighed the samples with a microgram-accuracy analytical balance. Results showed that the moulding method induced adhesion recovery in a greater percentage than the other cleaning methods and even helped with the recovery of collapsed posts in some cases. On the other hand pressure sensitive adhesives seem to have the upper hand with regards to certain particle sizes that can potentially pose problems with the moulding method.

biomimetic, dry adhesive, PDMS, self-cleaning, gecko, climbing


1 Introduction

Gecko inspired adhesives have become the subject of much research over the past decade [1, 2]. Using Micro Electro-Mechanical Systems (MEMS) as well as micro and nano fabrication techniques, synthetic fibrillar biomimetic dry adhesives have been developed and successfully tested by many different groups [2–5]. Among these research groups, there has been a loss in performance of the adhesive sheets as the sample is tested [5]. This loss of adhesion has also been a subject of study and has been attributed to the collapse of the fibrils as well as the contamination of the fibre tips [6–9]; in some cases it has also been attributed to the testing and fabrication of the adhesive [5].

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with an optical analysis of the degree of contamination. Likewise, the force required to detach a hemispherical glass probe from interacting with the dry adhesive before contamination and after cleaning was recorded. A ratio of the average force required for pull-off was then plotted, taking into consideration the average of their standard deviations. From these values, the efficacy of the adhesion cleaning was quantified.

2 Materials and methods

2.1 Dry adhesive fabrication

In this research paper we used Sylgard® 184 from Dow Chemical as the structural material for the dry adhesives; this material has a very low surface energy that makes it easier to clean in comparison with its silicone and polyurethane counterparts that have also been studied. To fabricate the dry adhesive moulds, we altered a previously reported method [3]. In ref. [3], gold-coated silicon wafers were used as the substrate for the moulds while we used 4” PMMA (OPTIX) discs with a 2 mm thickness as substrates for this application. This was done in order to reduce costs and manufacturing time as well as increasing the mould’s lifetime; silicon wafers are prone to cracking easily during demoulding. Nonetheless the moulds fabricated using this substrate create good dry adhesive sheets although the features have lower quality. The PMMA discs are rinsed and cleaned thoroughly prior to the start of the fabrication process and are never baked above 80°C for more than 2 min because they tend to warp at higher temperatures for the increased periods of time. The rest of the fabrication process is followed as explained in [3]. Once the mould is successfully completed, the structural material (Sylgard® 184) is mixed at a ratio of 10:1 prepolymer to catalyst, degassed for 30 min under vacuum then poured onto the mould and spun at 800 r/min to cover the whole wafer. Once it is spun, it is baked at 80°C for 3 h, removed from the oven, demoulded and placed in a petri dish for two days at room temperature to ensure that curing is fully completed. This yields an adhesive sheet with a thickness of no more than 1.2 mm throughout. The resulting dry adhesive has posts with a 10 μm height including the mushroom caps, a cap diameter of 17 μm, cap thickness of 1.8 μm and an overhang of 3 μm. An SEM image of the fabricated posts is shown in Figure 1.

2.2 Dry adhesive contamination

In order to contaminate the dry adhesive sample we used a variety of particles with different sizes ranging from less than a micron (carbon black) to almost 1 mm in size. As mentioned before, there has been evidence for the self-cleaning capabilities of gecko feet by contaminating their toes with silica-alumina particles and then walking on a clean surface [11]. This is why alumina (Fisher 4991-500) has been chosen for this study in addition to carbon black, manganese dioxide (MnO2) (Aldrich No. 31-0777-0), and nickel powder (Ni) (Allied Chemical No. 58.69) for the smaller sized particles; tin particles (Sn) and sand (Ottawa Sand Std.) were used for the larger sized particles. In Table 1 we can see the different sizes for the particles and in Figure 2 we can witness the contaminated samples.

2.3 Dry adhesive cleaning

Three different cleaning methods were explored in this study in order to evaluate the efficacy of each of them with respect to the different particles; the specifics of each

![Figure 1](image1.jpg)

**Figure 1** SEM image of the dry adhesive used in the analysis.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Smaller particles size (μm)</th>
<th>Larger particles size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>45-250</td>
<td>Sn</td>
</tr>
<tr>
<td>Carbon black</td>
<td>&lt;0.5</td>
<td>sand</td>
</tr>
<tr>
<td>MnO2 powder</td>
<td>&lt;10</td>
<td></td>
</tr>
<tr>
<td>Ni powder</td>
<td>5-37</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 2](image2.jpg)

**Figure 2** Adhesive samples after contamination. (a) Sand; (b) Sn; (c) alumina; (d) MnO2; (e) Ni; (f) carbon black.
method will be explained in detail over the next few sections. The samples were contaminated by placing the particles onto a glass petri dish and then simulating a step with the adhesive in the contaminated dish. A pressure of 23 kPa was applied on the back of the adhesive to ensure particle adherence to it and then lifted and placed on a microscope slide until the cleaning was performed on it.

2.3.1 CrystalBond™ Wax cleaning method

For the first cleaning method, we explored a way of re-casting the adhesive sheet in order to help with the recovery of collapsed posts that can potentially occur and at the same time trap the contaminants that stick to the caps of the adhesives. This is where our structural material properties (Sylgard 184) are the most useful to us, because of its very low surface energy, PDMS can be demoulded with ease from other materials. We placed a previously cleaned microscope slide on a hot plate at 107°C, which is the melting temperature of the wax [13], and “painted” some CrystalBond™ onto it. The contaminated dry adhesive was then placed onto it and gently pressed (25 kPa) to ensure that the posts were fully enclosed by the wax. It was then removed from the hot plate and let to cool at room temperature. Once the sample reached room temperature it was carefully peeled from the wax and adhesion measurements were performed on it to characterize this cleaning method.

2.3.2 Scotch® Tape cleaning method

Another method used in this study to clean the adhesive was the use of Scotch® Tape. The adhesive sample was contaminated with the particles and then placed onto a piece of tape applying a pressure of 23 kPa on its backside. It was then peeled from the tape and checked for particles leftover on it. This was repeated until visually clean but no more than three times for any given sample. Adhesion force measurements were taken on the sample afterwards.

2.3.3 Shaker Table Vibration cleaning method

The last method attempted involved a shaker table. The samples were fixed onto the table using double sided tape and then a sinusoidal wave was applied to the vibration table and a frequency sweep was performed from 10 Hz to 240 Hz with the amplitude of the vibration changing according to:

\[ x(t) = a \cos \theta(t), \]

where \( x \) is the displacement amplitude, \( a \) is a constant and \( \cos \theta(t) \) the signal being input to the vibration table. The main reason for our upper frequency limit is the fact that the amplitude becomes negligible when the frequency increases, as shown in the following equation:

\[ x = \frac{\ddot{x}}{(2\pi f)^2}. \]

Once the frequency sweep was completed, the sample was removed and prepared for adhesion testing once again.

3 Results

To quantify the cleaning abilities of each different method utilized, we used a custom test setup with an electronic linear stage (Zaber Technologies T-LS28-SMV) attached to a force sensor (Transducer Techniques, TRT-100) with a hemispherical glass probe of 1.8 cm in diameter making contact with the adhesive. The setup was controlled using the LabView suite (National Instruments) and this software was used in conjunction with a National Instruments DAQ card (NI USB-6259) to monitor the output from the force sensor for preload and adhesion measurements. In addition, the samples were weighed before contamination, during contamination and after being cleaned in order to qualitatively evaluate the cleaning methods using a precision scale (Acculab L-series). Each sample tested was 1.5 cm×1.5 cm in size and was placed on 75 mm×25 mm pre-cleaned microscope slides (Premiere 9101 Plain). With the use of this test setup, each sample was measured a minimum of 5 times on all different locations cleaning the tip in between samples with Isopropyl Alcohol (IPA) letting it dry before continuing the testing.

Figure 3 shows the results of the adhesion tests carried out in this study. The results for the vibration cleaning method are not shown in this graph due to the fact that the recovery was less than optimal; only a 0 to 3% recovery was observed in the samples tested for all contaminant particles. The preload for these adhesion testing was kept constant at 550 mN ±50 mN to prevent possible post collapses and stiction in between fibres. The error bars in Figure 3 show the average of the standard deviations of the samples measured. All the samples used in this analysis were fabricated identically coming from the same adhesive sheet.

In addition to the adhesion force measurements, we

![Figure 3](image-url)
weighed and optically analyzed the samples in order to qualitatively characterize the cleaning of the samples and see if more cleaning needed to be done. The particle weight varies according to their size and density so it was very complicated to keep a constant weight of contaminants among different particles, but it was kept constant among different cleaning methods for each different contaminant. All the samples were optically inspected after each cleaning step and in the case of the tape cleaning, the cleaning was repeated for three times or until it was visually clean as mentioned earlier. The weight analysis for the cleaning methods is shown in Figure 4 where the vertical axis is the percentage of particles removed from the adhesive sample. In some cases it can be seen in Figure 4 that this percentage is very close to 100% or greater but still the samples were visually very much contaminated, as it can be observed in Figure 5 for the wax cleaning and Figure 6 for the tape cleaning, which goes to show why adhesion did not recover as expected and presented in Figure 3. One thing to note about Figure 5 and Figure 6(d), (e) and (f) is the fact that the adhesion testing was performed in the areas that were with some leftover particles as well as where the adhesive was clean. In some cases the leftover particles were on the backside of the adhesive sample such as in Figure 5(d). It is also worth mentioning that the absence of pictures for the vibration cleaning method is mainly due to the fact that the pre-contamination and post-contamination look exactly the same, only a few particles lost contact with the adhesive. Also, by visually inspecting the samples under a microscope, we found that some posts that were initially collapsed were able to recover after the wax moulding cleaning step. This is why the qualitative as well as the quantitative visual and weight measurements were important for this study.

![Figure 4](image)

**Figure 4** Percentage of cleaning done for each method. 3 different values for tape clean when more than one tape application occurred.

![Figure 5](image)

**Figure 5** Adhesive samples after Crystalbond® Wax cleaning. (a) Sand; (b) Sn; (c) alumina; (d) MnO₂; (e) Ni; (f) carbon black.

![Figure 6](image)

**Figure 6** Adhesive samples after Scotch™ tape cleaning. (a) Sand; (b) Sn; (c) alumina; (d) MnO₂; (e) Ni; (f) carbon black.

4 Discussion

Several experiments were performed in this study to evaluate the efficacy of certain cleaning methods for the dry adhesives. Many parameters can come into play with regards to adhesion such as the number of cycles loaded as well as the curing conditions and patterning of the polymer as explained in ref. [5]. Also considered in [5] is the fact that the tip of the probe can become contaminated with uncross-linked material in the PDMS causing reduced adhesion. This is why we were very careful in cleaning the tip after every sample and used the same adhesive sheet with the same curing conditions for all the samples examined.

From the results above we can see that depending on the particle size and properties different methods work better than others. We can also see that in ref. [6] the larger particles used in that study could not be easily self-cleaned due to the contact with many fibres, but looking at the methods we have presented here this may be resolved by making use of the wax or tape cleaning method while simulating the gecko steps. Similarly, as mentioned in ref. [2] the gecko self-cleaning concepts have started to be taken into consideration in recent years with the synthetic adhesives but
mainly dealing with wet-cleaning processes such as the ones outlined in [7] for mushroom microfibrils and ref. [14] for carbon nanotubes. Some of the methods we present here are not so much as the lotus leaf effect but more like the gecko self-cleaning.

Looking at the results in Figure 3, we observe that wax does not seem to work as well on larger particles. This can be explained visually with the fact that wax can get trapped behind these larger particles at the moment of casting the adhesive on the wax. This leads to wax being trapped behind the particle and detaching from the bulk of the wax leaving remnants on the adhesive which then causes a reduction in the adhesion force as can be observed in Figure 5(a). We can also observe that for certain samples the adhesion recovery is greater than 100% which can be explained as we mentioned before with the recovery of some posts that could have initially collapsed while demoulding the adhesive sheet. On the other hand we also see that the tape cleaning method tends to work very well with the larger particles because they tend to stick to it with more ease resulting in their removal with minimum pressure thus helping with the adhesion recovery. With regards to the vibration cleaning, it is possible that repeating a frequency sweep for prolonged period of times may induce a cleaning of the sample in a higher percentage than observed and it could be a subject of further study. It is also possible that with higher amplitude of vibration, the particles may fall from the adhesive at the frequencies attempted in this study but we were working at the limits of the equipment available. One important thing to notice from Figure 4 is the fact that for the carbon black recovery with the tape method we obtained a 200% recovery. This can be explained with the accuracy and repeatability of the balance used in the measurements which is ±100 μg and the amount of C black that attached to the adhesive sample was of 200 μg and hence being within the equipment error. But by looking into Figure 6(f) we can see that the sample was not as clean as the data suggested.

As we can see from our work here and others [6, 7] there is some progress being made towards making a self-cleaning adhesive and hence being able to integrate it with climbing robots [10, 12], possibly even enhancing the robot’s climbing efficacy by using anisotropic adhesives [15–17]. Some future work could include testing some of these cleaning methods while in use by one of these climbing robots or perhaps with other materials to verify the adhesive’s performance in more hazardous conditions.

5 Conclusion

Three different active-cleaning cycles for the gecko-inspired adhesives have been investigated. These methods were analyzed and experimentally tested to characterize their efficacy with different contaminants of various particle sizes. It has been shown that no one method works perfectly for every condition or contaminant. Perhaps combining them as a two-step process could lead to even better results. The experimental results suggest that the CrystalBond™ Wax cleaning (moulding) method works best but it can fail in conditions where particles are larger and the moulding could potentially decrease the adhesion because of wax trapped behind these particles. An upside of the wax is that the particles get entrapped in it and it can be reused over and over whereas using the tape cleaning method the tape will lose adhesion and get contaminated leading to a reduction in its cleaning capabilities. A good approach would be to first clean off large particles using a piece of tape and then further improve the cleanliness with the wax as a final step. Other methods could also be examined such as mechanical agitation or high pressure gases preceding the wax cleaning method to remove the larger and looser particles.

We would like to thank Jeff Krahm, Yasong Li and Helia Sharif for their assistance in the setup and logistics for the experiments as well as for their valuable insight and suggestions. We would also like to thank Dr. Byron Gates from 3D Labs for his help and provision of the particles used in testing. This work was supported by Natural Sciences and Engineering Research Council of Canada (NSERC) and the European Space Agency (ESA).

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Characterization of Electro-adhesives for Robotic Applications

Juan P. Diaz Téllez, Jeff Krahn, and Carlo Menon, Members, IEEE

Abstract—Recent research in the field of climbing robots indicates that electro-adhesion may provide an attachment method for robots to adhere to a wide range of materials. This study compares the use of several different styles and shapes of electrodes while maintaining a similar electrode area. Electro-adhesion shear force testing was performed on electro-adhesive samples made with four different insulating polymers. These results are compared in order to indicate the best type of insulating material for electro-adhesives. Shear force adhesion tests are carried out on and compared for a wide range of common building materials.

I. INTRODUCTION

The cleaning and inspection of airplanes [1], [2], nuclear power plants [3] ducting or pipes,[4] buildings[5], [6] as well as security and surveillance [7] are applications which climbing robots may excel at. Indeed, climbing robots could be utilized in numerous environments where it is either too dangerous or difficult for humans to perform inspection or cleaning operations. Several approaches to attachment include suction cups [8], magnets [4], [9] spines or claws [5], [10], biomimetic adhesives [11], [12], chemical adhesives [13] or more recently, electro-adhesives [14], [15].

The design of climbing robots has generally fallen into one of two types, both of which may prove successful utilizing electro-adhesives. Multi-legged designs [16-18], often based on the locomotion of spiders or cockroaches, may prove to be the most challenging climbing robot design to achieve. This is due to the relatively small area of the feet in contact and the control strategy required in order to achieve fluid motion. This is offset by the increased mobility of multi-legged designs over tank-like designs. Tank-like robots [19-22] are generally simpler to achieve due to the much simpler control structure and the ability to have a large area of adhesive material in contact during climbing operations.

While electro-adhesion has been in industry for several years in such applications as grippers [23], [24], clothing manufacturing robotics [25] and electrostatic chuckers [26-28], it is only in the last several years that electro-adhesion has been used as an attachment method for climbing robots [14], [15].

Electro-adhesion makes use of electrostatic forces between a wall or attachment substrate and an electro-adhesive sample. The electrostatic force is generated by applying a high voltage and inducing a negative or positive charge on conductive electrodes embedded within a thin, insulating, polymer pad. The electric field generated from the charged electrodes generates an opposing charge on the attachment substrate inducing an electrostatic adhesion between the attachment substrate and the electro-adhesive as observed in Figure 1. The insulating polymer material in which the electrodes are embedded acts as a dielectric buffer and does not allow the induced charges on the attachment substrate to neutralize themselves with the electrodes.

The surface effects contributing to the electrostatic forces created between the electro-adhesion sample and the attachment substrate when a voltage is applied to the electrodes of an electro-adhesion sample are the result of different processes for conducting materials and insulating materials. Conducting materials, such as copper, steel or aluminum, have a large number of surface electrons that are able to rearrange themselves quickly and easily on the surface of the attachment substrate. When a voltage is applied across the electrodes of an electro-adhesion sample, an equal and opposite charge is created on the surface of the conducting material and the electric field between the two creates an attracting force between the two surfaces. For insulating attachment substrates, two separate effects factor into the electrostatic attraction force. These are a result of the electrical polarization that is always present in the material and, to a much greater extent, the electrical polarization that can be induced in a material by the electrodes of the electro-adhesive sample [26]. A larger induced molecular polarization results in a greater electrostatic attractive force between the attachment substrate and the electro-adhesive sample. While [14], [15] have shown electro-adhesion in action as an attachment method, very little information was provided on the manufacturing method and materials used. This study shows

Manuscript received August 9th, 2011. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the European Space Agency (ESA).

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a simple method for manufacturing electro-adhesive samples and compares the use of several different polymer materials in manufacturing. Namely, Polyethylene terephthalate (PET), Poly(dimethylsiloxane) (PDMS), polypropylene (PP) and ST-3050 polyurethane were used in this study as polymer substrates in which thin aluminum electrodes were embedded. As well, several different electrode styles are compared for the adhesion level each electrode type is able to provide under similar test conditions. Likewise the effect that the dielectric thickness has on adhesion was investigated in this study.

The shear force provided by adhesion of a single electro-adhesive sample to a wide variety of materials including concrete, Poly-methyl methacrylate (PMMA), glass, painted steel, and both painted and bare drywall (gypsum board) was measured and a comparison is then made for adhesion to a variety of common construction materials.

II. MATERIALS AND METHODS

The samples tested in this experiment are comprised of an insulating material, which varies between samples, and two electrodes which are fabricated using aluminum foil. An extensive amount of materials can be used for both the insulating and conductive materials but it was decided to keep the electrodes (conductive) material constant throughout the experiment and instead experiment with different electrode configurations. On the other hand, as mentioned previously, the insulating material is varied to show the differences amongst an array of materials that easily conform to a surface (silicones or urethanes) and others that are stiffer (plastics). The reason to test different conforming materials is due to the fact that electrostatic chucking, on which the electro-adhesive theory is based, are very sensitive to surface roughness and it was our intention to investigate how much this would affect the electro-adhesives.

A. Sample Fabrication

1) Electrodes fabrication: The electrode for each sample consists of a pair of electrodes made with the same area to account for the positive and negative-high voltage sweep. The electrodes for all the samples were prepared using aluminum foil (Alcan®). They were cut to shape using a knife and plastic stencil to keep the measurements as precise and even as possible, the target area for each electrode was 56cm² regardless of its shape. Figure 2 shows an image of the different electrode configurations used in this study. Hereafter the electrode configurations will be referred to as types a through e as shown in Figure 2.

2) Non-Conforming Sample Fabrication: As mentioned earlier, two different materials were used to fabricate the “stiffer” samples tested. These were PET and Polypropylene (PP) sheets obtained from 3M® (PP2950) for the former and Gemex® report covers for the latter.

The fabrication involved simply gluing the desired electrodes directly to a sheet of the desired material using Locite 495® Instant Adhesive, which was found to be the least conductive bonder available. Care was taken to ensure the electrodes were spaced a minimum of 7 mm apart from each other. Finally, a second sheet is carefully placed on top of both the original sheet and electrode and then glued together. This resulted in an electro-adhesive sample with two electrodes embedded within a polymer. Curing time for the glue is minimal but samples were left for 5-10 minutes before testing was performed on them. A diagram of the fabrication process is shown in Figure 3.

3) Conforming sample fabrication: For the more conforming materials, a silicone (Sylgard 184® PDMS, Dow Corning) and a urethane (ST-3050, BJB Enterprises) were selected because of their elasticity and ease of handling. First a 1mm thick sheet of the polymer material was cured on a flat surface. Electrodes were then placed on top of the cured material and covered with a second, thicker, polymer sheet initially used to create a seal around the sample. A minimum degassing period of 1hr. was carried out for each polymer sheet to remove any entrapped air.

Fig. 2: Electrode configurations used are type: a.) Jagged b.) Rectangular in a square configuration c.) Semi-circular d.) Interdigitated e.) Rectangular in an oblong configuration. The black tape shown was used to increase the strength of the polymer materials while testing and scale bars are 5cm long for all samples.
pockets resulting from the mixing of the polymer. Curing times varied depending on the material being cured. The minimum curing schedule for the PDMS was 3 hrs at 80°C after degassing and for the ST-3050 is 8 hrs at room temperature although 5-7 days are recommended and was followed for this sample.

B. Testing Methodology

In order to test the adhesion strength in shear, the lateral force required for the sample to begin sliding was measured using a spring scale after the application of high voltage. To achieve both positive and negative high voltages, a DC-DC high voltage amplifier (E101CT, EMCO High Voltage) with output voltage maximums at ±500V was used. Each lead was connected to a separate electrode with the ground connected directly to the surrounding polymer insulator. The experiments were performed on a wide variety of different attachment substrates such as polished concrete, steel, glass, PMMA (OPTIX®), drywall and melamine (finished wood). A large piece of each of these substrate materials was attached to a horizontal surface; the different samples were then placed on the substrate and several measurements were performed including an initial calibration test with no applied voltage. The calibration measurement was performed in order to measure the shear friction force provided between the electro-adhesive sample and the attachment substrate without an applied voltage.

Shear force adhesion testing of each sample on each of the different attachment substrates consisted of incrementally increasing the DC-DC amplifier input voltage in steps of 2V. An incremental increase of input voltage by 2V corresponds to a ~667V increase in voltage across the two electrodes. After each incremental increase in applied voltage, a measurement of the ability to sustain a lateral force before slippage was performed. To measure the applied lateral force, a spring balance (Globe*) was directly attached to the sample. With the spring balance placed in line with the sample, the spring balance was pulled at a constant rate until slippage was detected. The measured applied lateral force was then recorded and the input voltage disconnected from the electrodes. After the input voltage had been disconnected from the electrodes, each electrode was connected to ground in order to eliminate any residual charge from the electrodes. Before the voltage was increased in preparation for the next test, an aluminum foil sheet was placed between the attachment substrate and the sample under test to eliminate any remaining static charge left on the attachment substrate or sample. This procedure was repeated for each test sequence.

The average surface roughness (Ra) of each attachment substrate, except for concrete, was measured using a surface profiler or profilometer (Tencor, Alpha Step 500) in a clean room environment. A small sample of each attachment substrate was placed under the diamond stylus and the average surface roughness of 5 consecutive surface profiling measurements was obtained by dragging the stylus along the surface at a rate of 50μm/s over a length of 500μm. The surface roughness of concrete was not measured as the samples were too large for the profilometer. However, the surface of the concrete was visually examined and determined to be rougher than any of the other attachment substrates.

III. RESULTS AND DISCUSSION

Several parameters were analyzed in this experiment in order to characterize how modifications to electrode type, attachment substrate and insulating polymers affect adhesion strength and performance. The tests were limited to a maximum applied voltage of 4kV due to the fact that some materials, namely PET, were unable to handle higher applied voltages without the electric field between the electrodes breaking down the dielectric material and causing a short circuit. A short circuit between the two electrodes resulted in a breakdown in electrostatic interactions and resulted in a no load condition. This is in accordance with testing performed by [14].

Figure 4 shows the measured shear force from samples made with the type b electrode configuration, as previously indicated in Figure 2. While the same electrode configuration was maintained throughout these tests, four different insulating polymer materials were used for sample fabrication. Also, all tests were performed on the same flat, clean, horizontal, melamine surface for both the intermediate and maximum applied voltages. The type b electrode pair

![Image]

Fig. 4: Comparison of shear force for different polymer materials on a melamine surface. The embedded electrode configuration used in all cases was type b.
chosen for this analysis was composed of two simple rectangular shaped aluminum electrodes separated by 0.7 mm along the longer side of each piece as can be seen previously in Figure 2. This particular configuration was chosen for these tests because of the ease of integration with the polymers used. While tests were performed on a variety of surfaces, melamine was chosen for these tests because it shows mid-range shear adhesion strength in comparison with the other surfaces.

As previously observed in Figure 4, ST-3050 polyurethane is the material that appeared to have the best overall adhesion for melamine, a condition that was also constant amongst the other materials tested upon. This seems to confirm initial observations that conformance to a surface is an important parameter to consider for designing the electro-adhesives.

Due to the lengthy fabrication time for electro-adhesive samples made with ST-3050 polyurethane, polypropylene (PP) was used as the insulating polymer material in which several different electrodes configurations were embedded. A full range of shear force adhesion measurements were performed on electro-adhesion samples with different electrode configurations embedded in PP. All testing was performed on a clean, dust-free, glass surface. Glass was chosen in this case because of the excellent adhesion that the electro-adhesion samples had to it; this made glass an ideal material upon which to obtain defining results as to which electrode configuration performed best. As can be seen in Figure 5, shear adhesion force measurements indicate adhesion force is very dependent on electrode configuration. It is important to note that even though the figures have been normalized for shear pressure, the electrode area on all of the test samples was kept constant to ensure only a single parameter changed amongst the samples being tested.

By varying the electrode configuration used for each sample amongst the electrode types shown in Figure 2, it is shown in Figure 5 that electrode configuration makes a significant difference in shear adhesion force. Of the electrode configurations tested, the type d interdigitated “comb” configuration provides superior results. Due to the significant increase in adhesion from the type d interdigitated “comb” electrode amongst the tested electrodes, the type d interdigitated “comb” electrode configuration was selected for further testing.

Another parameter to characterize is the different dielectric thicknesses. Tests were performed using the same Polypropylene sample, with type d electrodes, but altering the dielectric thicknesses from 110μm to 550μm. To correlate these tests with literature we know from [29] that

\[ F = \frac{Ae^2V^2}{2(l + 2d/\epsilon_0)} \]  

(1)

where \( A \) is the surface area of the electrodes, \( V \) is the applied voltage, \( d \) is the thickness of the dielectric, \( l \) is the separation between electrodes, \( \epsilon_0 \) is the dielectric permittivity of vacuum and \( \epsilon_ \) is the relative permittivity of the dielectric coating. From Equation 1 we can obtain

\[ P_N = \frac{e_{r}e_{0}V^2}{8d^2} \]  

(2)

where \( P_N \) is the normal pressure and \( P_L \) is the lateral pressure exerted by the electro-adhesive sheet. The measured values for the lateral pressure were plotted against the predicted values from the model and this can be observed in Figure 6 where it can be observed that as the dielectric thickness increases, the adhesive pressure decreases as expected from the model (Equation 2).

Type d electrodes were also used to test amongst a wide variety of common attachment substrates and provided consistently enhanced performance as is characterized in Figure 7, where a comparison is made for multiple substrates. As can be seen, steel achieves the best adhesion amongst the various attachment substrates tested. This can be explained using Coulomb’s law, from which Eq. 1 is derived, indicating that two oppositely charged plates in a capacitor will attract each other; this will in turn generate a much larger force than the insulators. For insulating materials, other interactions come into play such as the

![Figure 5: Measured shear force for different electrode types. All samples were made using polypropylene as the insulating polymer material and measurements were performed on a glass attachment substrate. Measurement error is less than ±0.01 kPa.](image)

![Figure 6: Shear force measurements performed on glass using a type d, interdigitated, electrode configuration embedded in Polypropylene](image)
gradient force when resistivity is high or Johnsen-Rahbeck force when resistivity is lower [22]. Another important factor to consider is the fact that it is nearly impossible to achieve perfect contact over the full interface area [28], which could explain some discrepancies.

While all of the material surfaces tested are commonly used in building construction we can see that sufficient adhesion is measured on both drywall and concrete, which showed the lowest adhesion levels, for attachment of a small climbing robot which could be used for inspection, cleaning, surveillance or security purposes. As previously mentioned, the surface roughness of all of the attachment substrates was measured except for concrete due to the size limitations imposed by our profilometer. However, under close visual examination the polished concrete appeared to have a significant amount of pitting and was considered to be the roughest of the attachment substrates. The measured average surface roughness (Ra) is shown in Figure 8 below.

As can be seen by comparing Figures 7 and 8, the average surface roughness of the attachment substrate plays a role in the conformation of our electro-adhesive sample for most attachment substrates. Steel was by far the attachment substrate that provided the greatest level of adhesion during testing. This was likely due to both the lower surface roughness and the fact that steel, a conductor, has the largest number of electrons that were free to rearrange themselves on the surface near the electrodes.

Adhesion measurements on painted steel differ greatly from those measured on steel. This could likely be explained by the fact that the paint layer was acting as an insulating layer atop the steel surface. In effect, this increases the separation distance between the steel and the electrodes of the electro-adhesive sample which in turn reduces the electrostatic force between the steel and the electrodes. Other contributing or detracting effects from the paint layer are unknown but may include molecular polarization and other surface effects. Similarly the difference in measured adhesion between painted and unpainted drywall are likely due mostly to the wide variation in surface roughness between the two surfaces but the paint itself may provide some influence on the adhesion results. For the other, non-conducting, adhesion substrates, a combination of induced electrical polarization and surface roughness seem to be the factors that have the greatest influence on lateral adhesion force. Concrete, PMMA and drywall provide similar attachment forces but vary greatly in surface roughness with concrete being the roughest surface, under visual comparison. This would indicate that the concrete surface is able to electrically polarize itself to a greater amount than either drywall or PMMA. PMMA on the other hand was one of the smoothest surfaces upon which we were able to measure the average surface roughness but adhesion results indicate that it is also the least polarizable of the attachment substrates. For all materials, the overall concentration of electrons or holes on a surface differs from one to another and effects the material’s polarization and, as a consequence, the measured electro-adhesive forces.

IV. CONCLUSIONS

The goal of this study was to characterize and determine the most useful fabrication materials for the use of electro-adhesion wall attachment in climbing robots. To achieve the best performance, several factors were considered such as attachment surface and polymer insulating materials to
achieve enhanced electro-adhesion. As well, adhesion shear force testing was performed on samples made with several different electrode configurations embedded within a single insulating polymer in order to find the most suitable electrode configuration. Our results indicate that an interdigitated “comb” electrode provides the highest adhesion force in shear over the other electrode styles tested, also as expected the dielectric thickness should be kept to a minimum. Our results also indicate that a softer material such as ST-3050 enables a higher level of conformation to rough surfaces and enhances the measured shear adhesion force. The wide range of common building materials chosen as attachment substrates indicates that shear adhesion levels even on the worst performers are large enough to accommodate a small climbing robot.

Future work includes further experimenting with the softer polymers, especially with ST-3050 polyurethane, as well as investigating other, less stiff, electrode materials. In addition, further experimentation can be done on the interdigitated electrodes regarding the optimization of different spacing and “finger” widths. It is likely that a greater electrostatic adhesion force could be achieved by reducing the spacing between the digits. However, the reduction of the spacing between oppositely charged electrodes may cause the insulating material to breakdown, causing a short circuit between the electrodes, at lower voltages, depending on the insulating material.

REFERENCES


