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A STUDY OF SHAPE MEMORY POLYMERS AND THEIR USAGE IN THE DEVELOPMENT OF DIRECTIONAL
DRY ADHESIVES

BY

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Mechanical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2016

Urbana, Illinois

Adviser:

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ABSTRACT

This thesis first introduces shape memory polymers and their unique phase-changing and recoverability properties. The underlying thermodynamic explanations along with their fundamental governing equations are presented. A few possible potential areas of interest for applications of this unique polymer are also shown, but the one of particular interest is biomimetic dry adhesives. For the experimental section, a shape memory polymer (SMP) surface with geometrically asymmetric micro-wedge array is fabricated as a reversible directional dry adhesive through a double exposure angled lithography technique. The unique shape fixing and recovery properties of SMPs and surface microstructuring enable highly reversible adhesion strength upon thermo-mechanical loading, and the tilted wedge geometry gives rise not only to its capability for varying adhesion strength based on loading direction, but also the reduction of strain energy input necessary to achieve contact area saturation with the opposing surface. To characterize the directional adhesion strength of the fabricated micro-wedge surface, adhesion tests are performed in the forward shear, backward shear, and normal directions based on the tilting direction of the micro-wedges. The adhesion strength is measured as a function of the applied preload for the three directions investigated, and is compared to a computational analysis by modeling the adhesive failure as the initiation of crack growth in linear elastic fracture mechanics. Additionally, reversibility is demonstrated by heating the micro-wedge surface above its T_g , allowing the structure to recover its original shape after being deformed, resulting in almost zero adhesion strength. The adhesion tests demonstrate that the forward shear direction is capable of adhesion strengths that are greater than that of the backward shear direction by a factor of over 3, confirming its capability for directional adhesion. Finally, additional novel shapes are introduced, taking advantage of the angled exposure technique and properties of negative photoresist to “cleave” a unique wedge pattern based on the shape of the patterns on the photomask used in fabrication.

ACKNOWLEDGEMENTS

I would first like to thank my advisor, Seok Kim, who has been exceptionally supportive throughout the entire project. No matter the circumstances or hardships encountered throughout my academic journey, he has always been kind and understanding. This thesis surely could not have been finished without his assistance. Likewise, I would like to thank my laboratory group mates, Zining Yang, Jun Kyu Park, Anthony Keum, Alex Kahn, and Jeff Eisenhaure, for their contributions as well. Jeff in particular was of tremendous help, as his past work and experience in shape memory polymers laid the foundation of the experimental section of this thesis. I would also like to thank the entire MechSE department for their unending support all the way from the moment I first arrived on campus as an undergraduate in 2013. I would also like to thank the MechSE department for awarding me with the MechSE Outstanding and Excellence Fellowship, which was of great help throughout my graduate-level academics and research. Finally, I need to thank my friends and family for their outpour of love and support, and reminding me every step of my academic journey why I am here. Thank you all so much.

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1. INTRODUCTION

1.1 SHAPE MEMORY POLYMERS

Shape memory polymers refer to a broad range of polymers that, as their name implies, exhibit a behavior that allows for the storing of a configurational memory of a certain “permanent shape” that is recovered post-deformation through external stimuli. An analogy of this mechanism can be understood through how an empty disposable plastic water bottle may be deformed by external forces that squeeze it into certain temporary shapes, but the “external stimulus” of blowing air into the water bottle would provide sufficient internal pressure to revert it to its original shape.

The recovery of the shape memory polymer structure’s original shape can be induced by a significant number of stimuli; the shape memory polymers that are currently well-characterized can be stimulated by optics, electromagnetic fields, chemical means, or temperature [1]. These stimuli act as the “trigger” mechanism, which allows for access to its lowest energy configuration through its effects on the polymer network once the stimuli are introduced to the structure. This is due to the introduction of the stimulus that alters the fundamental structure of the polymer structure which allows a means for the structure to minimize the mechanical strain that was stored in its temporary shape [2].

It is important to note that the stimulus is unique to the specific material in question. In other words, “shape memory polymers” encompass a wide range of materials that, due to some mechanism, is allowed to recover a certain shape despite any potential deformation. Furthermore, a stimulus that corresponds to one type of shape memory polymer may not necessarily have an effect on another. Therefore, a model that is valid in the simulative characterization of a certain class of shape memory polymers may be an incorrect model to use for another type.

The effects of shape memory behavior were first characterized by Vernon et al. through a 1941 patent of an organic acid called methacrylic acid resin, best known as the precursor to the commonly

used material poly(methyl methacrylate) (PMMA, or commonly referred to as “Plexiglas”) [3,4]. The material was first discovered to exhibit the curious property of “shape recovery”, which allowed the familiar ability to recover its initial shape through a sufficient thermal stimulus. However, despite the advent of such a peculiar phenomenon that was possible in polymers, most of the applications of its effects were limited to a few number of industrial uses [5]. It was not until recently that the behavior of shape memory polymers and their potential applications began to spark curiosity in the field of academia. Today, a growing number of papers can be found dealing with specialized applications of shape memory polymers in the fields of biological applications, hydrogels, composites, and biomimicry.

There is another class of materials that exhibit similar behaviors, called “shape memory alloys”, which refer to metals as opposed to polymers. These materials are best known by their current industrial uses in automobiles, aerospace, biomedical, and robotic applications [6]. In comparison, however, shape memory polymers as a material are advantageous in that they allow for a significant amount of strain before recovery; most shape memory polymers allow for strains of above 200%. Furthermore, shape memory polymers are relatively cheap, lightweight, biocompatible, and biodegradable, which allows for a significantly broader spectrum of potential applications of these polymers in the future, particularly in the fields of biomedicine and microfabrication [5].

1.2 POTENTIAL APPLICATIONS OF SHAPE MEMORY POLYMERS

Treatment of Intracranial Aneurysms

Intracranial aneurysms (colloquially referred to as simply “brain aneurysms”) describe a life-threatening cerebrovascular occurrence in which a weak region in a vein or artery causes a localized ballooning of the wall where blood collects until it eventually ruptures. Currently, the two medical treatment options for aneurysms currently available are a surgical clipping of the affected region, or

endovascular embolization. The latter refers to introducing a coiled material to the site of a propagating aneurysm, by promoting proper clotting and sealing the affected region to stabilize the pressure between the inner and outer artery wall. However, the issue with current treatment options is that the currently available biocompatible materials used in this procedure do not properly adhere to the biological substrate around it.

The introduction of shape memory polymers would significantly improve the reliability of the endovascular embolization procedure; this is entirely due to the unique shape recovery effect of shape memory polymers. The polymer would be inserted into the ballooning region by being deformed into a geometry that allows for the insertion of the polymer in its temporary shape. With the introduction of the appropriate stimulus, the recovery effect is triggered, whereby the shape memory polymer begins to undeform into its permanent shape. However, if the inserted polymer is larger than the aneurysm site, the polymer will simply deform in a way to match the contours of the diseased region, acting to prevent a possible rupture in the future by providing a tight seal.

Self-tightening surgical suturing

The current methods of applying sutures to a deep wound is akin to tightening shoelaces, where a single string is woven around the wound in an appropriate pattern, and then tension is manually applied by the medical treatment specialist to close the wound to promote proper healing. Because the tightening is done by hand, it is virtually impossible to maintain an acceptable level of precision in the quality of the sutures, solely based on it being a function of the medical specialist's finesse and skill. Should the sutures be applied too tightly, there may be scarring or localized tissue damage in the patient. On the other hand, if the sutures were to be applied too loosely, the wound would not be properly sealed, which can delay healing or even introduce infections. However, should the sutures be

made of a shape memory polymer, the wound can be closed and tightened at a relatively well-quantified fashion, depending on how well the shape memory polymer being applied is characterized.

Biomimetic Dry Adhesive Surfaces

Dry adhesive surfaces refer to surfaces that can provide an adhesive behavior that originates not from chemical means, but from microscopic non-covalent van der Waals molecular interactions. The inspiration for this originates from the structure of gecko toes, shown by Figure 1 [7]. In the microscopic scale, it is apparent that the gecko toe is not a single structure, but is rather a hierarchical array of slender hair-like setae. This gives rise to the gecko toe's remarkable adhesive abilities evident in its ability to adhere to both smooth and rough surfaces alike, making it favorable to traditional adhesives that are chemical-based. Thus, the successful fabrication of a surface with design principles that parallel the surfaces seen in the animal kingdom would serve as a significant breakthrough in the field of adhesives.

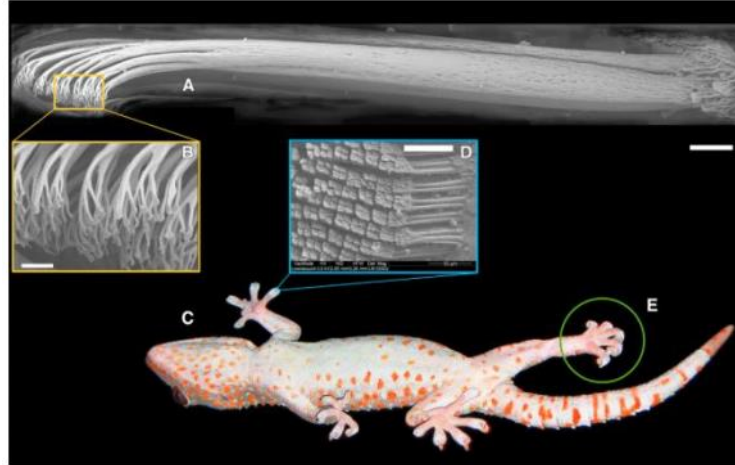


Figure 1. Gecko adhesive system. (A) Micrograph of a single gecko seta. (B) Nanoscale array of hundreds of spatular tips of a single gecko seta. (C) Ventral view of a tokay gecko (*Gekko gekko*) climbing a glass surface. (D) Array of setae are arranged in a nearly grid-like pattern. (E) Toe peeling during detachment. Scale bars: 50 μm (D), 5 μm (A), 1 μm (B) [11].

In the case of dry adhesives, it is important that, because the van der Waals interactions are significantly weaker than that of other bonding mechanisms, a maximization of the contact area in the microscopic scale becomes critical. Thus, the array of fibrils must be compliant enough to be able to conform to the contours of the target substrate. The more compliant a material is, however, the more susceptible it becomes to forming cracks, which consequently damages the adhesive surface the more it is used. If one decides to alter the aspect ratio of the fibrils rather than the material properties, the fibrils may begin to stick to each other, and it also becomes more susceptible to being contaminated by ambient debris. It is evident that in all current fabricated dry adhesives, there is an inherent trade-off between the strength of adhesion and the durability of the adhesive surface.

In the case of shape memory polymers, however, due to their unique stimulus-induced changes that are possible in its mechanical properties, as well as its shape recoverability, a dry adhesive surface fabricated with shape memory polymers would not have to sacrifice either the conformity for durability,

or vice versa. Furthermore, the adhesive surface would be a reversible one, meaning it can be cyclically detached and reattached without loss of performance.

If the dry adhesive surface is fabricated with shape memory polymers, the necessary compliance to successfully conform to the target surface shape can be accomplished by simply heating the surface to the critical temperature, independent of geometry or scale. Once the adhesive surface has conformed to its substrate to a desired degree, the structure can be cooled down below the critical temperature, increasing its stiffness and strengthening its bond with the target surface. When detachment is desired, the surface can be reheated to the critical temperature, softening the surface to ease separation, as well as allowing the structure to regain its original shape.

An extensive study of a fabricated microstructured dry adhesive surface was conducted, and the details are outlined in the upcoming sections. This surface is capable of reversibility, directionality, and high adhesive strengths.

1.3 LIMITATIONS OF SHAPE MEMORY POLYMERS

Although shape memory polymers are evidently diverse in its potential applications, there are certain limitations common in all of these polymers. The most significant limitation for these polymers is in its ability to regain its permanent shape. It has been shown experimentally that the recovery ability of shape memory polymers is not perfect, and the recovered shape is increasingly distorted with each deformation-recovery cycle [8]. Another limitation that shape memory polymers face is the permanent shape recovery time, which is partially due to their recovery ability being entropically-based. When the soft segments of the polymer are activated by a stimulus, the macroscopic recovery of the structure to its permanent shape is the collective conformational changes of the individual polymer chains reaching its lowest energy state, which would affect its recovery time. Furthermore, for thermally-actuated shape

memory polymers, the limiting factor in shape recovery is most likely the thermal conductivity of the collective polymer. In other words, the recovery rate is limited by how effectively the heat can conduct through the solid polymer. Figure 2 shows the recovery process for a typical shape memory polymer material that is thermally activated, showing the recovery time is typically on the order of tens of seconds [9].

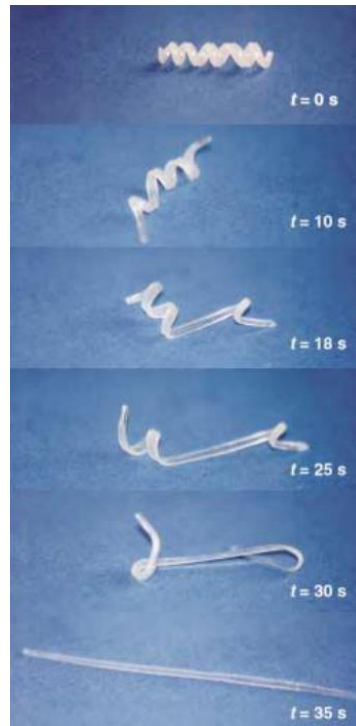


Figure 2. Time dependence of shape recovery behavior in shape memory polymers [10].

2. THEORETICAL ANALYSIS OF SHAPE MEMORY POLYMERS

2.1 PHYSICAL CHARACTERIZATION

Shape memory polymers in general are best characterized in currently available literature by those that are thermally-stimulated. The basic structure of the polymer network is outlined in Figure 3. As can be seen from the figure, the polymer network is composed of two main components: a hard “cross-linked” component and a soft “switching” component [1]. The hard component is mainly composed of the cross-linked chain network that mainly determines the permanent recoverable shape of the polymer. The soft component, on the other hand, is the part of the polymer that is responsible for the “shape memory” effect, due to its molecular properties being extremely sensitive to the applied stimuli: in this case, the temperature of the polymer.

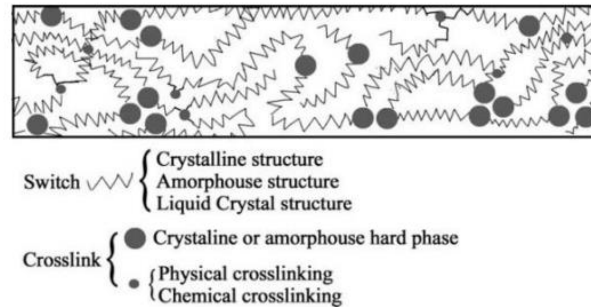


Figure 3. The two main components of the shape memory polymer structure: the hard “cross-linked” component and the soft “switching” component [1].

The sequence for the shape recovery behavior begins with the deformation of the structure, by applying the sufficient thermal conditions for activating the soft components of the polymer, given by T_g , the glass transition temperature. In this “rubbery” state, the overall entropy increases, lowering the overall elastic modulus, and allowing the chain to be deformed while in this “softer” state. The thermodynamic effects will be further outlined in the next section. When the polymer is cooled in this new temporary shape, however, it takes its current configuration as its overall local minimum energy

state for the system and remains in a deformed, temporary state. Once the polymer is heated once again to above T_g , the most favorable overall configuration, the permanent shape, becomes available, due to the stimuli's effect on the soft "switching" component of the polymer.

A 3-D plot of this process is shown in Figure 4 for convenience of understanding this process [11]. This plot uses data obtained during a mechanical load test to observe the deformation behavior (shown by the strain %) throughout the recovery process. The plot shows data for both shape memory polymers and rubber under similar loading conditions, in order to compare the shape memory polymer behavior to that of rubber, whose recovery behavior is commonly understood. As can be seen in the plot, the most significant difference between the shape memory polymer and the rubber is in the unloading behavior, in which for a constant temperature below T_g , the strain does not change. However, the recovery phase of the shape memory polymer is initiated with the increase of temperature, specifically at one that is above T_g . In the case of rubber, however, there is virtually no effect of temperature on the strain, and is entirely dependent upon the applied force. This comparative plot outlines the unique thermal properties that are present in shape memory polymers that are not found in other materials that may exhibit similar recovery behavior.

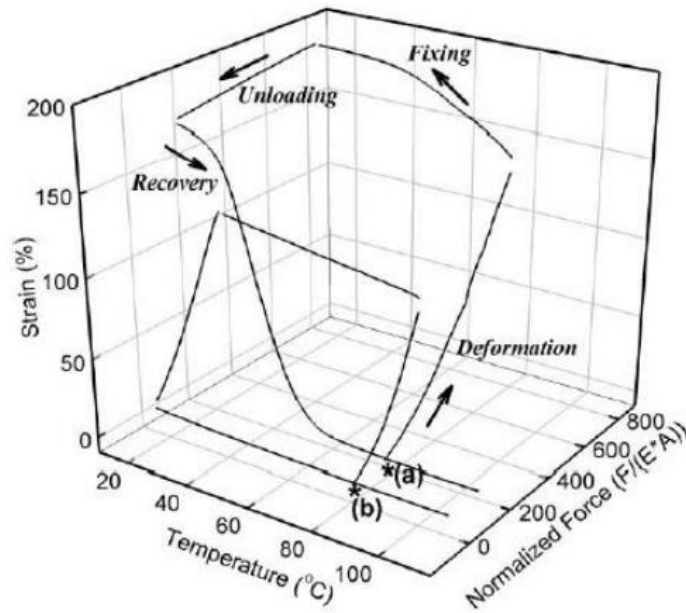


Figure 4. 3-D plot of deformation and shape recovery cycle behavior for (a) shape memory polymers and (b) rubbers [11].

In general, the entirety of all shape memory polymer materials can be reduced down to three main categories in the basic mechanism that allows for shape recovery behavior [12]. Figure 5 illustrates these three models of the effects of the stimulus on the polymer. The first of these is the simple model in which there are linear chains of the shape memory polymer in a solution, where the structure is able to recover from a reversible collapse through the introduction of its corresponding stimulus (i). The second is like a network of covalently crosslinked gels that undergo either reversibly expand or contract depending on the stimulus (ii). 3 Finally, the third characterization is that of an adsorbed chain on a surface in which either swelling or collapse of the chains are observed through the introduction of the stimulus, which alters the hydrophobicity of the chain-surface interface (iii). Though the characterization and feasibility of each model was presented by Kumar et al., the focus of our characterization—as well as those of most literatures—will focus on the model of individual chains that are crosslinked into a gel,

as shown in (ii) of Figure 5, as it most closely corresponds to the actual physical nature of a thermally-induced shape memory polymer.

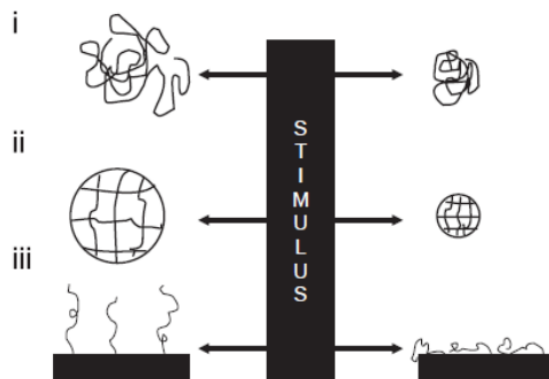


Figure 5. Three classifications of common shape memory polymers: (i) simple model in which there are linear chains of the shape memory polymer in a solution, (ii) network of covalently cross-linked gels, (iii) adsorbed chain on a surface in which either swelling or collapse of the chains are observed through the introduction of the stimulus [12].

2.2 THERMODYNAMIC CHARACTERIZATION

As stated beforehand, T_g , also known as the glass transition temperature, is the determining factor for the shape memory behavior in common shape memory polymers. Temperatures below T_g exhibit rigid behavior. This is due to the inactivation of the soft “switching” components, as stated in the previous section, which does not allow for much macroscopic conformational changes. In terms of entropy, below this critical temperature, it will tend to remain in its current macroscopic shape due to a decrease in entropy. This is because the soft “switching” component of the shape memory polymer network are inactive, which tends to make the chains more ordered. This in turn decreases the entropy, which therefore removes a significant amount of conformations that the chains can undergo. Thus, any change in the strain at this state will be entirely energetic, as it will be due to an increase in internal

energy due to the stretching of bonds, rather than the alteration of chain configuration [9]. For temperatures above T_g , however, a “rubbery” state is achieved in the polymer, which effectively means the elastic modulus will be decreased. In a thermodynamic perspective, this becomes the state in which the behavior of the shape memory polymer becomes entropically dominant. When the polymer is increased past this threshold temperature, the behavior of the polymer chains can then be characterized as entropic springs. In other words, the overall conformational states due to the rotation about the chain covalent bonds that were previously unavailable become valid states due to the thermal activation of the soft “switching” component. Thus, the most favorable shape, which happens to be the permanent shape, is recovered. In the macroscopic structure of a shape memory polymer sample that is heated past the critical temperature T_g , there will naturally be regions which are both activated and inactivated, as shown in Figure 6.

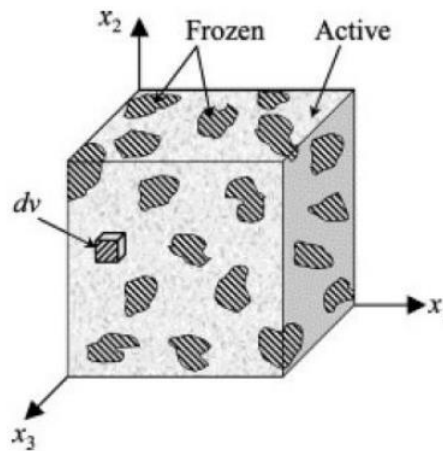


Figure 6. 3-D simplified representation of the shape memory polymer structure, contrasting active and frozen regions within the structure [13].

The active regions refer to the areas in which the soft components are activated and act as entropic springs, while the frozen regions refer to the areas in which the polymer has not yet been “switched”

and is locked into its configuration. Quantifying the volumes for both regions, we have the following expressions:

$$\Phi_{frozen} = \frac{V_{frozen}}{V_{total}} \quad (1)$$

$$\Phi_{active} = \frac{V_{active}}{V_{total}} \quad (2)$$

$$\Phi_{frozen} + \Phi_{active} = 1 \quad (3)$$

From these volume fractions, which are functions of temperature due to the nature of shape memory polymers being thermally activated, we can find the expression for the elastic modulus of the polymer, as well as the intrinsic stress in the polymer based on the deformation. The respective expressions are shown below, in equations 4 and 5. The extensive calculations are done by Gopi et al. [13].

$$E = \frac{1}{\frac{\Phi_{frozen}}{E_e} + \frac{\Phi_{active}}{E_s}} \quad (4)$$

$$\sigma = E(\epsilon - \epsilon_s - \epsilon_T) \quad (5)$$

Where equation 4 shows the overall elastic modulus of the shape memory polymer, and equation 5 describes the internal stress. In equation 4, the E_e and E_s terms refer to the elastic modulus of the frozen regions and the active regions respectively. The elastic modulus for the frozen region is energetically driven based on our thermodynamic assessment above, and should be a constant value. However, the elastic modulus for the active regions is entropically determined, meaning that it should be given by the following expression:

$$E_s = 3NkT \quad (6)$$

where this expression is derived from the engineering stress for elastic materials by taking the slope of the curve at the origin of the stress-strain relationship expression to obtain the initial elastic modulus [14]. N refers to the number of chains in a given volume (not to be confused with the degree of polymerization), k is the Boltzmann constant, and T is the temperature of the shape memory polymer. The simplified stress term due to a one-dimensional deformation, given by equation 5, is a characterization to model the intrinsic stress that is stored within the shape memory polymer, based on the various strain parameters and its elastic modulus that is shown by equation 4. The first strain term ϵ represents the total strain of the polymer, and is defined as the sum of the stored, thermal, and mechanical strains. The stored strain term, shown by ϵ_s , is a temperature-dependent component of the strain that represents the history of the polymer conformation. The thermal strain term, ϵ_T , is a familiar strain term that represents the collective strain due to the thermal expansions of both the frozen and active regions of the shape memory polymer. It is evident that a thermodynamic modeling of shape memory polymers proves a useful tool in both the explanation of the thermally-driven mechanisms which give rise to its recovery behavior, as well as the quantification of its mechanical properties as a function of temperature.

The following section outlines a process for the fabrication and experimental testing of a directional dry adhesive making use of these shape recovery properties of shape memory polymers, as outlined in the relevant paper that I also authored [33]. The following section primarily summarizes the work done for this self-publication, and it should be noted that Chapters 3 and 4 reference the figures and text.

3. FABRICATION AND TESTING OF A DIRECTIONAL REVERSIBLE DRY ADHESIVE SURFACE

3.1 Overview of Device

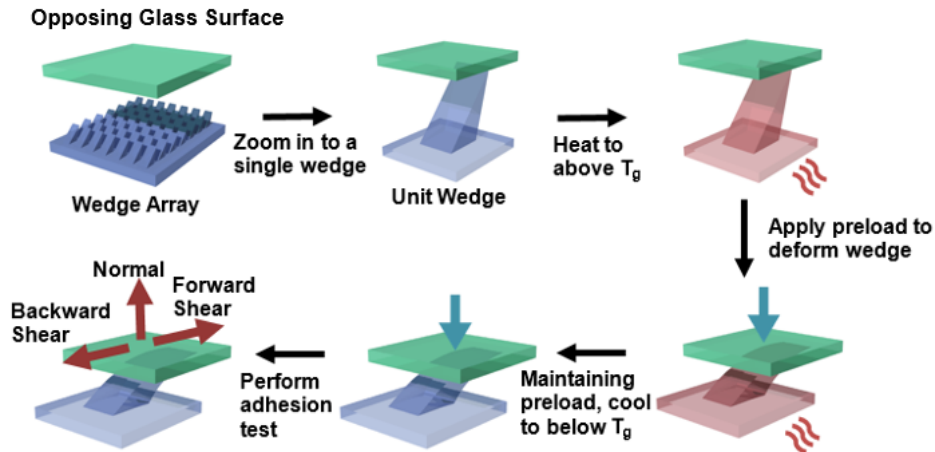


Figure 7. Overview of the process of wedge preload deformation and adhesion testing. The first step indicates the final fabricated wedge array of shape memory polymer (SMP), and the final step indicates the testing done to quantitatively characterize the adhesive strength per area of surface.

Dry adhesives offer various advantages over wet adhesives including reusability, longevity, greater adhesion, robustness, and potential for reversibility [15]. A reversible dry adhesive design that has shown great success in past studies is a biomimetic array of micro- or submicro-scale fibrillar structures, inspired by nature's gecko foot hairs [7, 16-23]. These designs make use of individual fibers to enhance the robustness of the adhesive interface, particularly when mated to microscopically rough or uneven surfaces, compared with chemically similar flat-surfaced adhesives. The bulk surface adhesion strength is then primarily dependent upon the collective contact area of the individual deforming fibers.

In past studies on fibrillar-structured dry adhesives, the most favorable results were found through the fabrication of a compliant microfiber array on a relatively rigid backing layer, whereby the former structure contributes to its conformity to the opposing surface, while the latter structure inhibits peeling by providing more uniform load distribution, thus increasing its overall adhesive strength [24]. However,

as evidenced in published past experiments, applications of such designs still typically yielded relatively low adhesion, within the range of sub 1 atm adhesive strengths. Although some studies demonstrating higher maximum adhesive stresses exist [25-27], there remains substantial room for improvement, as past studies have yet to develop versatile systems suitable for general use; strength is but one aspect of an adhesive, among other qualities such as directionality, reusability, and reversibility.

Advancements to dry adhesives can be found through the implementation of responsive materials, which enables material property “switchability” of the structure [28]. One such investigation was done, utilizing a shape memory polymer (SMP) as the primary adhesive material [29]. SMPs refer to a broad range of such responsive materials that, as their name implies, exhibit a behavior that allows for the storing of a configurational memory of a certain “permanent shape” that is recovered from a deformed shape, i.e. “temporary shape,” through an external stimulus that is specific to the material. One common stimulus to activate the shape memory behavior is temperature: heating the polymer beyond a certain glass transition temperature (T_g) initiates its material compliance transition from “rigid”, on the order of 1 GPa, to “compliant”, on the order of 10 MPa. These unique properties have been utilized in combination with surface microstructuring, e.g. microtip patterning, to produce an SMP-based dry adhesive with both high normal adhesive strength and reversibility [29].

Dry adhesives generally rely on van der Waals forces, rather than chemical means to generate adhesive forces. It follows that a superior adhesive surface design is achieved by maximizing the area of contact between the adhesive surface and the opposing surface with as little input energy as possible. As seen in the results of past studies, the utilization of SMP as the primary adhesive material combined with surface microtip patterning allows for direct manipulation of the material compliance and the contact area, which contributed to their impressive results in adhesive strength and reversibility [29].

This chapter strives to propose a method to expand upon that past investigation by introducing an asymmetrically tilted wedge-shape structure, in order to exhibit directional shear adhesion capabilities. The structures fabricated in the past demonstrated high normal adhesion strength and reversibility. However, because of the symmetric shape design of the microtip, the surface not only requires high preload to achieve contact area saturation but also is intrinsically incapable of directional shear adhesion, which would otherwise enable multiple adhesion strength states as a function of loading conditions [29]. Here, we present a micro-wedged SMP surface capable of high reversible adhesion based on the shape memory effect, and directional shear adhesion upon loading conditions based on asymmetric shape design in the micro-wedge. Such a surface allows not only multiple high shear adhesion states upon loading conditions, but also zero-adhesion states via thermo-mechanical loading. Furthermore, the tilted wedge geometry gives rise to the reduction of strain energy input necessary to achieve contact area saturation with the opposing surface. In other words, by using deflection of thin wedges, rather than bulk compression, as the primary mode of deformation, a large contact area can be obtained with a relatively small preload applied.

A two-step angled exposure technique is utilized to fabricate a mold comprised of an array of tilted asymmetric wedge structures. Further steps produce a positive SMP replica, the surface of which is tested for its forward shear, backward shear, and normal adhesion capabilities as a function of the preload, as indicated in Figure 7. The introduction of asymmetric wedge structures implies that there will be inherent directionality of the adhesive, i.e., the shear adhesive strength should be higher for the forward shear direction than the backwards direction. This behavior is verified through both experiment and computational analyses and will be presented in the upcoming sections.

3.2 Fabrication of the Adhesive Surface

The micro-wedge structure is shown in Figure 8. It consists of a periodic array of SMP wedges fabricated as part of a continuous thin layer of SMP on a glass backing layer. The fabrication of the master mold relies on a multi-step angled exposure technique through the use of SU-8 50 negative tone photoresist (MicroChem). The SU-8 mold then undergoes a double-molding process to obtain a flexible polydimethylsiloxane (PDMS) negative mold structure that would facilitate the peeling of the negative mold from the more rigid final SMP structure.

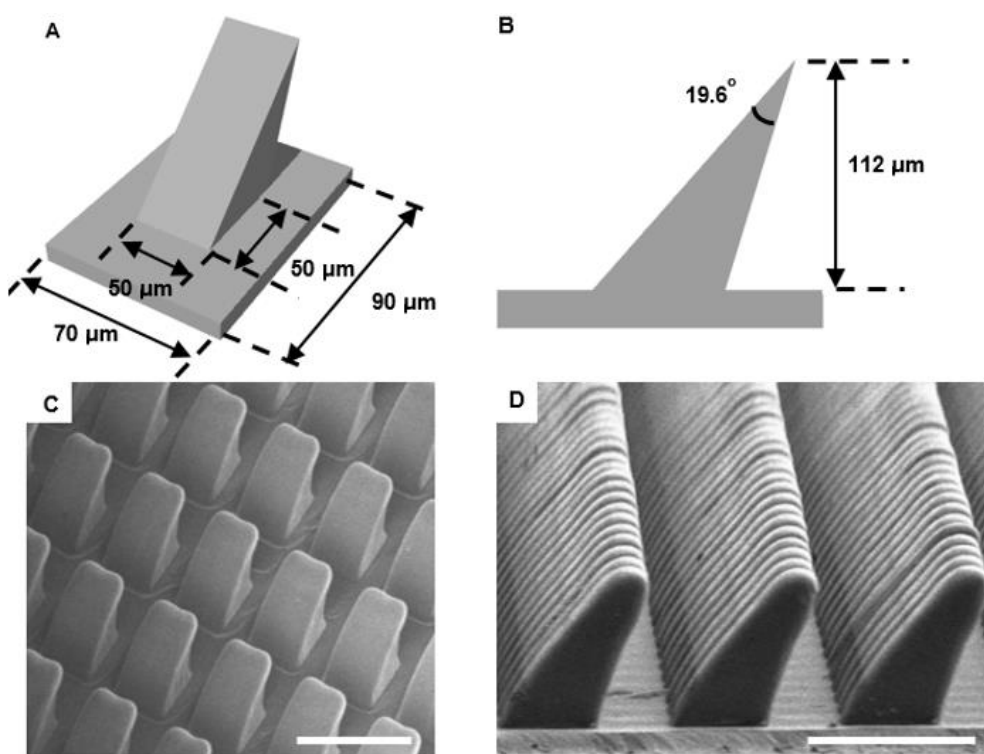


Figure 8. (A) Dimensions of a single SMP wedge in isometric view, (B) Dimensions of a single SMP wedge in side view, (C) Isometric SEM image of SMP wedge array, and (D) Tilted side view SEM image of SMP wedge array. Scale bars for SEM images are represented in white, with lengths corresponding to 100 μm.

The SU-8 negative mold was first fabricated by spincoating a negative photoresist, i.e., SU-8 at a spin speed of 1000 rpm for 30 seconds. After softbaking at 65°C for three hours, the SU-8 was then left to rest for five minutes before undergoing a two-step angled exposure as shown in Figure 9 through the

use of a custom fabricated stage, with the UV illumination source being provided by a Model 60 Flood Exposure (ABM). The iron-oxide photomask used was of a periodic array of opaque squares with side and spacing dimensions respectively corresponding to the base and lateral pitch lengths of the wedge in Figure 8A. Following the exposure, the mold underwent a post-exposure baking step of three minutes at 65oC and 10 minutes at 95oC. After allowing the mold to rest at room temperature for five minutes, it was then developed in a SU-8 developer, and gently rinsed with isopropanol, obtaining the final negative mold structure.

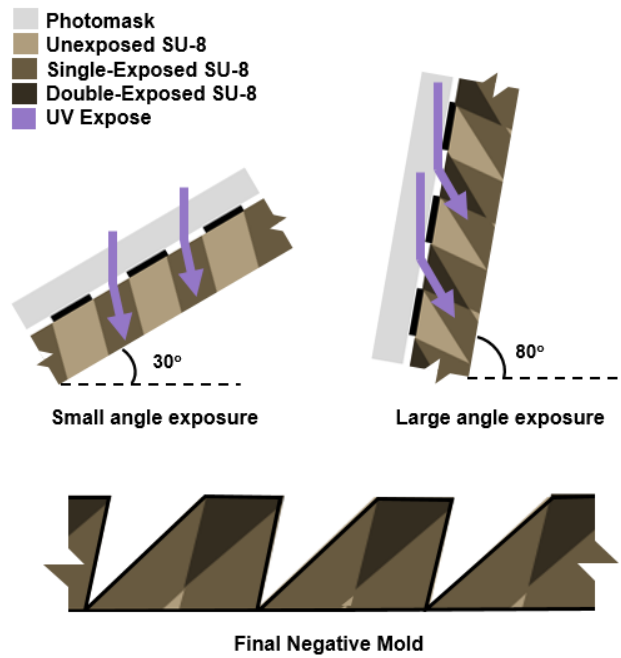


Figure 9. Two-step UV exposure technique utilized in creation of the SU-8 mold. Note the angle of exposure within the SU-8 differs from the angle to which the substrate is tilted by due to optical refraction. SU-8 50 has a refractive index of 1.61[30], yielding a maximum theoretical exposure angle of 38.4° when the substrate is tilted by 90°.

The SU-8 mold was used to produce a positive PDMS wedge array that corresponds to the shape of the desired final structure. A double molding procedure then follows in order to cast the SMP into the desired shape, with a visual representation of the process shown in Figure 10. The positive PDMS mold was cured with an 8:1 base prepolymer to curing agent mixing ratio in order to obtain a more rigid

polymer compared to the standard 10:1 ratio, as to prevent the protruding PDMS wedges from sticking to adjacent wedges. Similarly, the negative PDMS mold was cured with a 13:1 mixing ratio to facilitate the peeling process by allowing the mold a higher strain before tearing occurs. The final SMP structure is cured on a glass backing layer in order to ensure the adhesive surface is level and parallel to the surface of the surrounding testing setup.

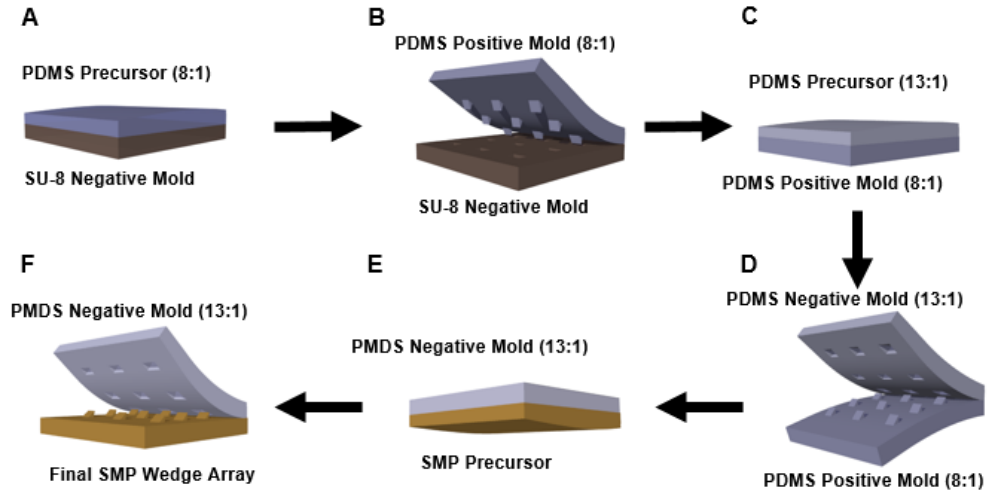


Figure 10. Double molding procedure utilized to obtain final SMP structure. (A) An 8:1 mixing ratio of base to curing agent of PDMS precursor is poured onto the SU-8 negative mold, following the steps shown in Figure 9, and is cured. (B) The resulting PDMS positive mold is then peeled from the SU-8 negative mold. (C) A 13:1 mixing ratio of PDMS precursor is poured onto the positive PDMS mold after applying a nonstick coating onto the positive mold to prevent sticking, and is cured. (D) The resulting PDMS negative mold, with the same pattern as the SU-8 negative mold, is then peeled from the PDMS positive mold. (E) SMP precursor is sandwiched between the substrate and the PDMS negative mold and is cured. (F) The PDMS negative mold is peeled from the substrate, revealing the final wedge array.

The particular formulation of thermosensitive SMP utilized in the fabrication procedure is a thermally-activated type whose precursor is created by mixing a 1:1:1 ratio by molar mass of EPON 826, Jeffamine D230, and neopentyl glycol diglycidyl ether (NGDE), respectively [31]. This particular mixing ratio, referred to as “NGDE2,” is one among several mixing recipes, chosen for its relatively convenient glass transition temperature (T_g) of about 40°C, which is low enough to enable rapid heating and easy

handling but high enough to prevent undesired reconstitution at room temperature, at which the adhesion tests are performed [31].

3.3 Experimental Adhesion Test

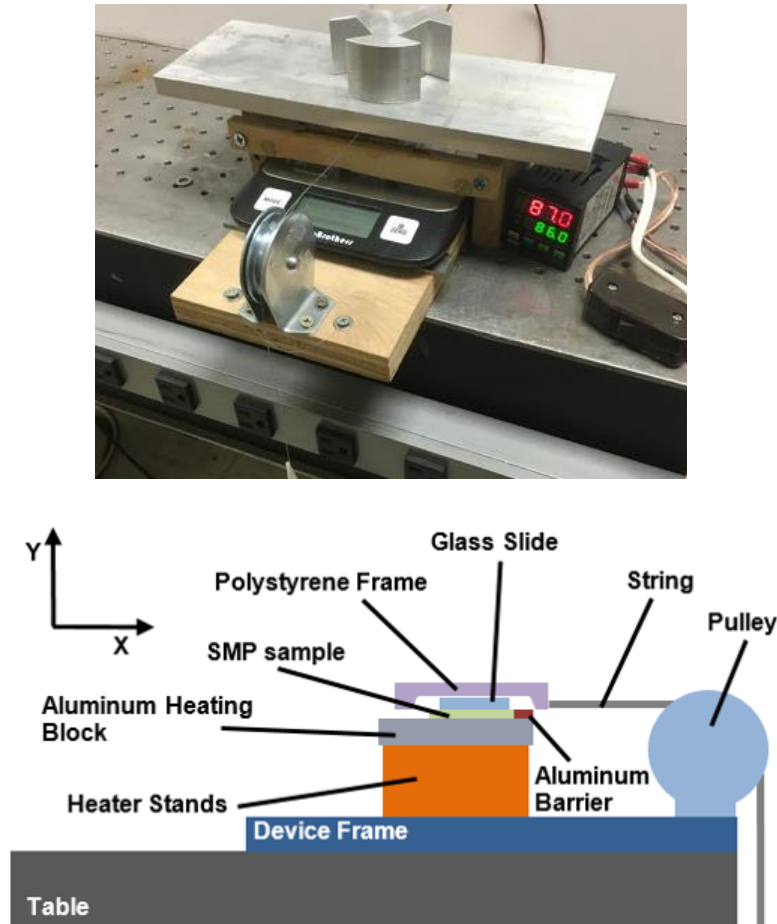


Figure 11. Testing setup used to obtain experimental data. Top image shows testing setup with preload applied (represented by the weight resting on the aluminium slab), taken with a digital camera. The temperature controller shown regulates heat input into the heating block based on instantaneous temperature measurements using a thermocouple.

The normal and shear adhesion strengths of the SMP sample with micro-wedge array were found experimentally through the use of the custom built testing setup presented in Figure 11. The tests

specifically investigated the results of the following: forward shear adhesion, where the force is applied parallel to the contact interface in the same direction as the wedges point towards, backward shear adhesion, where the force is applied in the opposite direction of the wedges, and normal adhesion, where the force is applied perpendicularly to the contact interface. For each test, the effective area of the entire micro-wedge sample against an opposing glass surface is 8.9 mm^2 and the force at the time of adhesive failure was obtained for bonds formed at preloads of 0.0625, 0.125, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 atm.

For both the shear adhesion tests, the data were obtained through a testing setup with an integrated heater and scale, to provide a constant heat source and accurate preload measurements, respectively. The opposing glass surface is secured onto a polystyrene frame as shown in Figure 11, allowing a shear load to be applied through the connected string in tension. The sample to be tested was first placed and secured on the heater, and the opposing glass surface is placed on the SMP array. The sample is then brought up to a temperature of 85°C , well above the SMP glass transition temperature, and the appropriate preload is applied onto the glass and polystyrene frame component. The sample is then brought to room temperature with the preload continuously applied while the sample is cooled. When the desired temperature is confirmed by inspecting the thermocouple probing the heater, the adhesion test is conducted by steadily increasing the load in the desired direction and recording the load value at the moment of failure between the sample and the glass surface. The tests are repeated three times for each of the preloads investigated, with the results of the experimental tests presented in Chapter 3.4.

The adhesive reversibility of the micro-wedge system was also tested to ensure it can easily release from a surface upon re-heating. The micro-wedge sample is first fully bonded to a substrate using the previously described procedure for several levels of preload up to 2 atm, then with the preload removed it is re-heated to above the SMP T_g . From this procedure it was confirmed that the adhesion strength of

the micro-wedge array after its shape recovery was too small to be properly quantified using the testing setup, of which the measurable adhesive strength is 0.02 lb (about 0.1 atm), based on the resolution of the device which measures the final load. This effectively demonstrates that the surface is capable of tuning its adhesion between high- and almost zero-adhesion states based on thermo-mechanical loading conditions.

Finally, in order to verify the shape fixing capabilities of the shape memory polymer material for the purposes of the adhesion test, the fabricated adhesive surface was first deformed, and was imaged using scanning electron microscopy (SEM). The procedure for preparing the sample for imaging was identical to that of the adhesion testing, as shown in Figure 7. However, once the sample is cooled, the opposing glass surface is separated from the SMP surface. The adhesive surface is then imaged with SEM. The collapsed state of the wedges is shown in Figure 12 below.

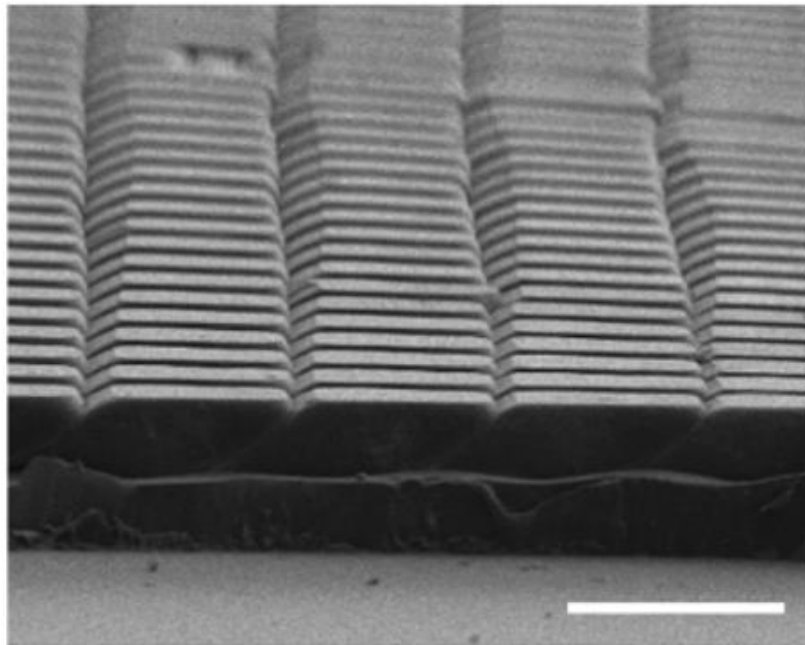


Figure 12. Fully collapsed wedge array in SEM, with given scale bar representing 100 μm . This collapsed state of the adhesive surface shows the theoretical maximum possible contact area the surface is capable of obtaining during the preloading step.

3.4 Experimental Testing Results and Discussion

Figure 7 shows the experimental adhesion strength data for the three loading conditions, provided at each value of preload used. The adhesion strength was measured three times for each preload and appropriate error bars are included.

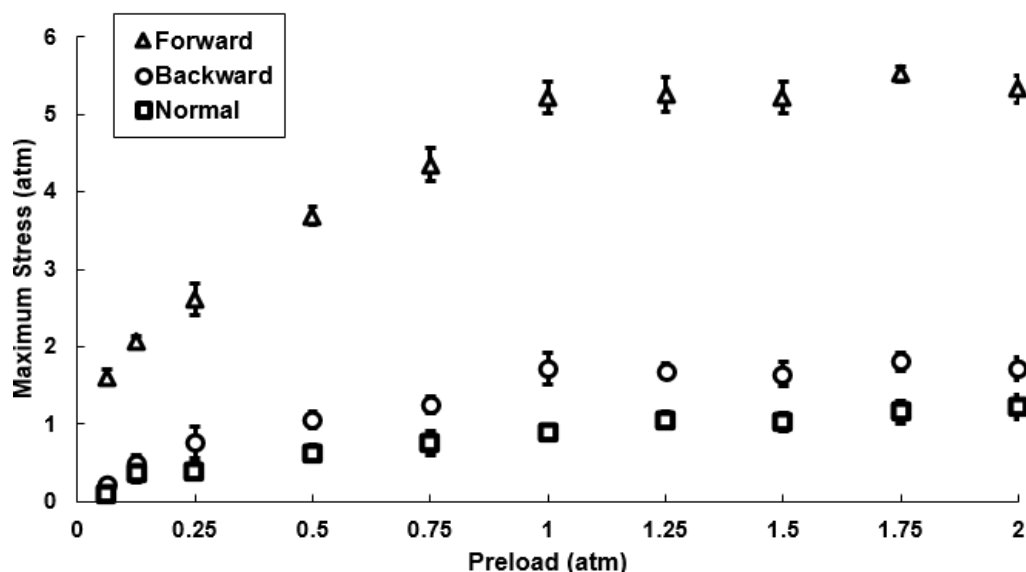


Figure 13. Experimental data plot for forward shear, backward shear, and normal adhesion tests, with error bars for repeated trials included. The tests were performed with the setup shown in Figure 5, using the same sample for all adhesion tests.

The experimental data all show a point of saturation for the maximum adhesive loads the SMP sample was capable of achieving, occurring approximately 1 atm preload stress regardless of loading condition. The obtained results thus confirm that the angled geometry of the wedge structures yield significantly enhanced compliance compared to past work utilizing microtip SMP surfaces [29]. This enhancement allows the structures to maximize their adhesive contact area with relatively low preload values, while still maintaining a respectable shear adhesive strength, peaking at around 5 atm for the forward loading direction. Furthermore, directionality of the fabricated micro-wedge array is clearly evident by inspection of Figure 7.

The transition from backward to forward loading demonstrates an adhesion strength increase exceeding a factor of three. The experimental tests also included a normal adhesion test as a reference while the purpose of micro-wedge arrays is to create directional shear adhesion. The results in Figure 7 indicate a significantly higher adhesion in forward loading compared to both backward shear and normal loading.

4. COMPUTATIONAL ANALYSIS OF FABRICATED ADHESIVE

4.1 Preliminary Theoretical Analysis

The adhesion strength of the wedges was computationally modeled through the use of the finite element analysis (FEA) software (Abaqus, Dassault Systèmes). The ideal wedge structure was modeled in the software, which was then followed by applying the appropriate preloads to obtain the theoretically deformed shape at each preload value. Preloads beyond 1 atm were not investigated, since the wedge structure is predicted to fully collapse at this preload, and any additional compressive stresses are assumed to have negligible impact on the final adhesive contact area.

The adhesion failure mode is modeled as a propagating crack by the relationship below in Equation 7:

$$\gamma_o = G = \frac{K_I^2 + K_{II}^2}{E} \quad (7)$$

where γ_o is the work of adhesion between the glass and SMP, while G is the strain energy release rate.

K_I and K_{II} are the stress intensity factors in mode 1 and mode 2 loading respectively. The E term in the denominator is the modulus of elasticity of the bulk material.

The significance of the first two terms in the above equation is that the maximum adhesive stress the wedge structure can tolerate is assumed to be at the instance when the strain energy release rate (G) is exactly equal to the work of adhesion between the glass and SMP surfaces (γ_o), which is taken to be 46 mJ/m² based on prior experimental data [29]. Since the adhesion failure is modeled as a crack propagation phenomenon, with the assumption of plane stress, the second and third terms of the above equation are equated.

The stress intensity factor in linear elastic fracture mechanics is known to be a product of the stress applied on the structure and a coefficient that is dependent upon the geometry and loading conditions of the structure. Therefore, for a structure with its geometric and material parameters held

constant, the stress intensity factor scales linearly with the applied stress. This geometric scaling factor is obtained through Abaqus by dividing the calculated stress intensity factor value by the applied input stress, and has units of MPa $\sqrt{\text{mm}}$. Rearranging Equation 7 and substituting for the geometric factor, we obtain:

$$2 E_{SMP} \gamma_o = K_{IC}^2 + K_{IIC}^2 = \left[\left(\frac{K_I}{\sigma} \right) \frac{F_{fail}}{A_{contact}} \right]^2 + \left[\left(\frac{K_{II}}{\sigma} \right) \frac{F_{fail}}{A_{contact}} \right]^2 \quad (8)$$

where F_{fail} is the load at which the adhesion fails, and $A_{contact}$ is the total contact area that the wedge makes in contact with the opposing glass surface. This method is originally based on a crack forming within a homogeneous material. To adapt these equations to the present study of a crack between dissimilar materials (SMP and glass), the value of the elastic modulus may be adjusted to account for the effect the dissimilarity [32].

In this case, it is recognized that the elastic modulus of the glass is much greater than that of the SMP, and so to a close approximation we model the system as a homogenous material with an elastic modulus equal to twice that of the SMP. Thus, in Equation 8 above, the E term from Equation 7 is substituted by $2E_{SMP}$. The FEA model likewise includes this substitution. Additionally, in Equation 8 are: equivalent fracture toughness terms (K_{IC} and K_{IIC}) for mode 1 and mode 2 loading directions respectively, the stress intensity terms (K_I and K_{II}) for mode 1 and mode 2 directions, a stress term σ which refers to arbitrary applied stress values during FEA, and an area term $A_{contact}$ which corresponds to the total contact area between a single wedge and the corresponding opposing glass surface.

From Equation 8, we can rearrange the terms to solve for the load at failure, F_{fail} . In order to obtain the maximum adhesive stress, we simply divide F_{fail} by the unit area of the wedge and backing layer. This final result is shown in Equation 9.

$$\sigma_{failure} = \frac{F_{fail}}{A_{unit}} = \frac{A_{contact}}{A_{unit}} \sqrt{2 E_{SMP} \gamma_o} \left[\frac{\sigma}{K_I^2 + K_{II}^2} \right] \quad (9)$$

A_{unit} is the $70\ \mu\text{m}$ by $90\ \mu\text{m}$ area that represents the entire area encompassed by a single repeating unit wedge, as represented in Figure 8A.

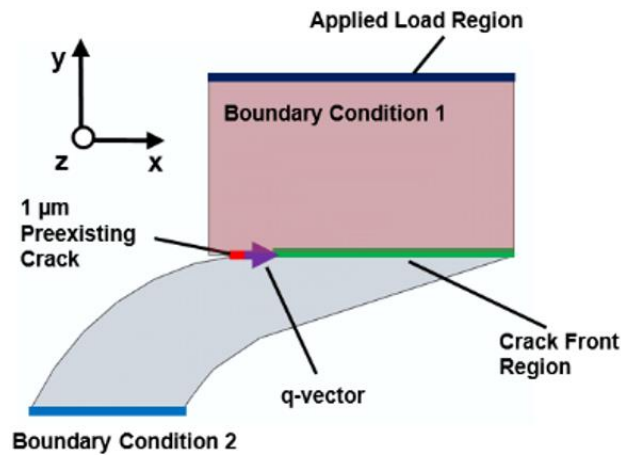


Figure 14. FEA input conditions for the corresponding fully collapsed structure corresponding to Figure 12. The rectangular partition above the crack front region refers to the partition to which boundary condition 1 applies to, whereas the line encompassing the base of the wedge partition indicates the region to which boundary condition 2 applies to. The q-vector outlines the direction to which the crack initially propagates, from the $1\ \mu\text{m}$ preexisting crack.

This equation indicates the stress at failure in terms of the input stress, material properties of the SMP, and the geometrically-determined stress intensity factor for the applied input stress. While the parameters for the areas, modulus of elasticity, and work of adhesion are already known, the input stress value (σ) and the corresponding stress intensity factors (K_I and K_{II}) were calculated via the FEA software as shown in Equation 9. The basic overview of the parameters utilized in the FEA software are indicated in Figure 14, as well as Table 1.

Table 1 – Description of FEA (Abaqus, Dassault Systèmes) parameters used in analysis, corresponding to Figure 14.

	Initial Collapse	Forward Shear	Backward Shear	Normal
FEA Model Element Type	3D Solid	2D Shell	2D Shell	2D Shell
Applied Load Region Direction	-y	+x	-x	+y
Boundary Condition 1 (Constrained Parameters)	z-rotation	z-rotation, y-displacement	z-rotation	z-rotation, x-displacement
Boundary Condition 2	Pinned/Fixed	Pinned/Fixed	Pinned/Fixed	Pinned/Fixed

An uncollapsed wedge was first modeled and then deformed in compression to simulate preloading the wedge array to achieve adhesive contact, for each preload value corresponding to an experimentally tested stress. In the FEA analysis, the wedges were found to be fully collapsed with a preload of 1 atm, determined as the point at which the adhesive contact area was found to be larger than the wedge pitch; thus, preloads from 1 to 2 atm are expected to have similar adhesive strength values. Furthermore, for the backward shear analysis, y-displacement was neglected in boundary condition 1 constraints to avoid self-compression between the wedge surface and the glass, since the crack cannot propagate under compression.

Following the preload simulation, an FEA fracture mechanics analysis was performed to simulate the adhesive delamination as a crack growth phenomenon. An initial crack of 1 μm was assumed to exist, as indicated in Figure 14. The calculated stress intensity factor has a magnitude linearly proportional to the applied stress, and the values found through the analysis are used in Equation 9 to calculate the maximum theoretical adhesive strength for each preload configuration.

4.2 Results of FEA Modeling of Adhesion Strength

Because there are 10 total cold-state configurations, corresponding to the 10 different applied preloads tested from 0.0625 atm to 2 atm, six total models (instead of 10 because preloads beyond 1 atm were assumed to be identical, and thus redundant) corresponding to the deformed shape and dimensions of a single wedge at the prescribed preload, are modeled in the software's computer-aided design (CAD) feature. The final deformed shapes of the wedge for each of the first six preload values are shown in Figure 15 below.

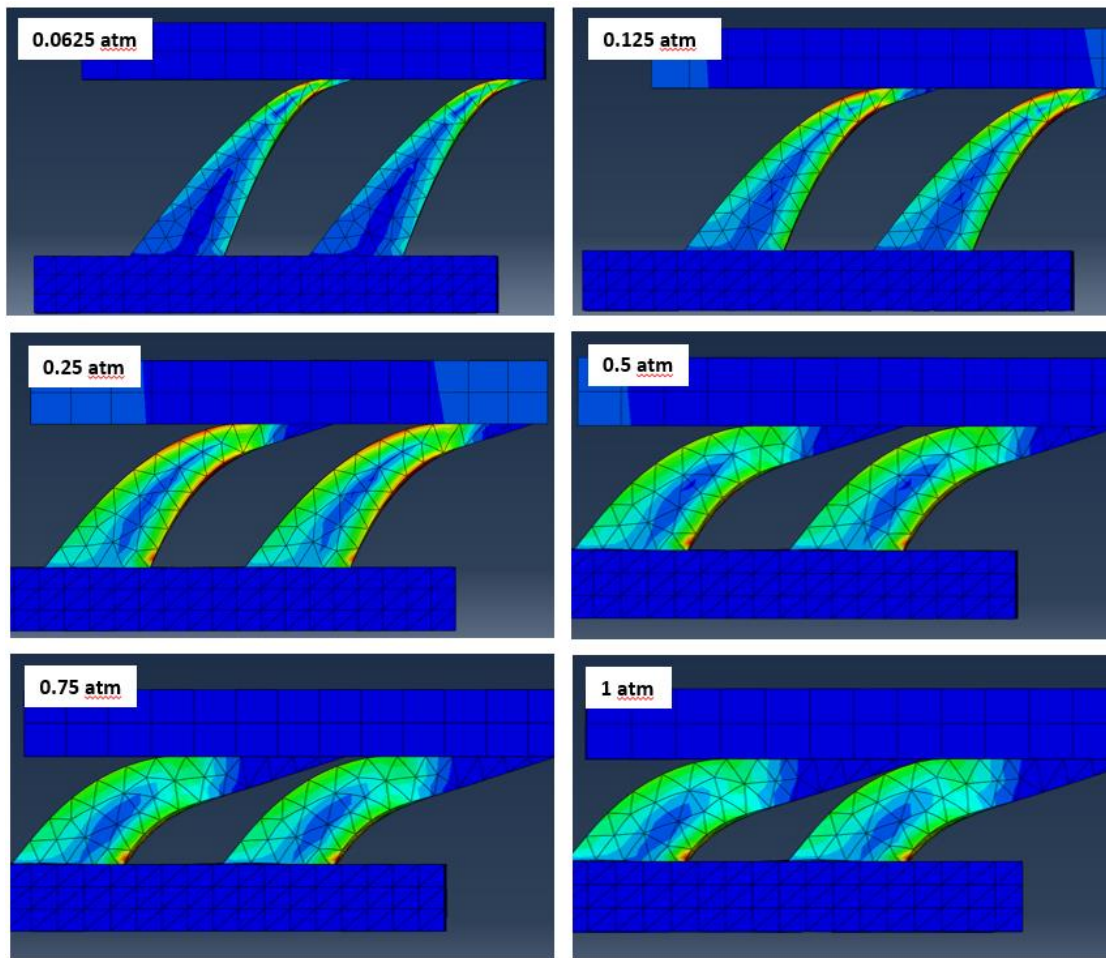


Figure 15. The final deformed shape of the wedge for the respective applied preload. Each of the six final deformed states shown share the same initial state, and the final shape is only a factor of preload. Two consecutive wedges are modeled as opposed to just one in order to obtain the point at which the two wedges make contact. This point is at 1 atm, evident by inspection of the figure, and it signifies the fully collapsed state. Von Mises stress is shown in color with absence of scale bars, showing the relative internal stresses at various points on each wedge.

The results for applying the stress intensity factors attained from the FEA software (Abaqus, Dassault Systèmes) into Equation 9 for each of the preload values are plotted in Figure 16, for all three testing configurations. There is a clear confirmation of the directionality behavior of the adhesive, by comparing the relative magnitudes of adhesive strengths for the forward and backward directions. As expected, the forward adhesion shows the largest peeling resistance and is the most favorable loading direction.

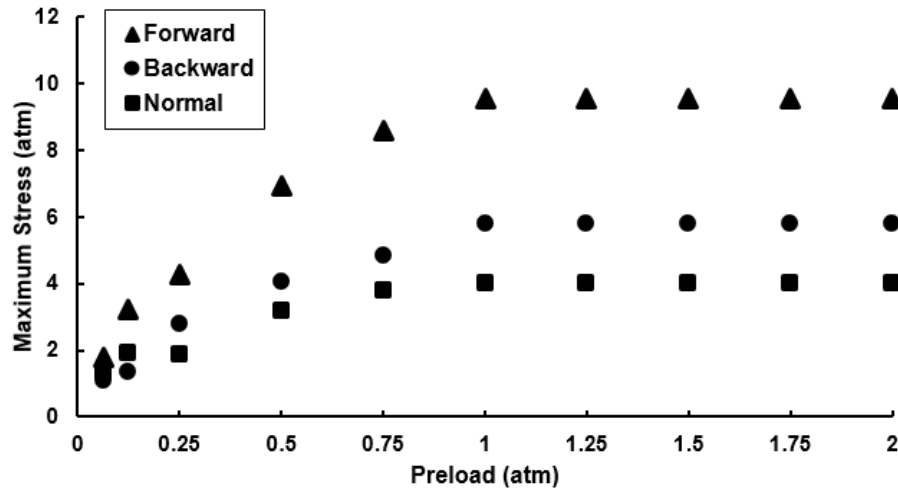


Figure 16. FEA Results for theoretical Forward Shear, Backward Shear, and Normal adhesion. The analysis was done with the general parameters outlined in Table 1, with the main difference between the three tests being the direction of the load represented by the dark blue line in Figure 6. The stress intensity factor per applied load, in conjunction with Equation 3 yields the theoretical maximum adhesive stress at each configuration.

4.3 Comparison of Experimental and Computational Results

The results in Figure 16 are nearly double that of the adhesive strengths found experimentally, which is generally to be expected. One source of this disparity could be from setting the bonded glass-wedge structure as a single, homogeneous and continuous solid, so that the fracture mechanics analysis for Equations 7, 8, and 9 becomes valid. This simplification in modeling does not take the microscopic roughness and defects of the SMP wedge surface into account, which would ignore any voids along the

contact area that would facilitate peeling and reduce the adhesive strength obtained. The round tip shape of fabricated micro-wedges is not accounted for in the FEA model and likely contributes to lower experimental adhesive strength. Further, the FEA model did not consider the effects of tilting surface misalignment or any slight differences between wedges along the entire array as would be expected in the experimental test. As such, the discrepancy between the results in Figure 13 and Figure 16 can be attributed to the ideality of the modeling techniques utilized.

4.4 Fabrication of Novel Shapes in Wedges

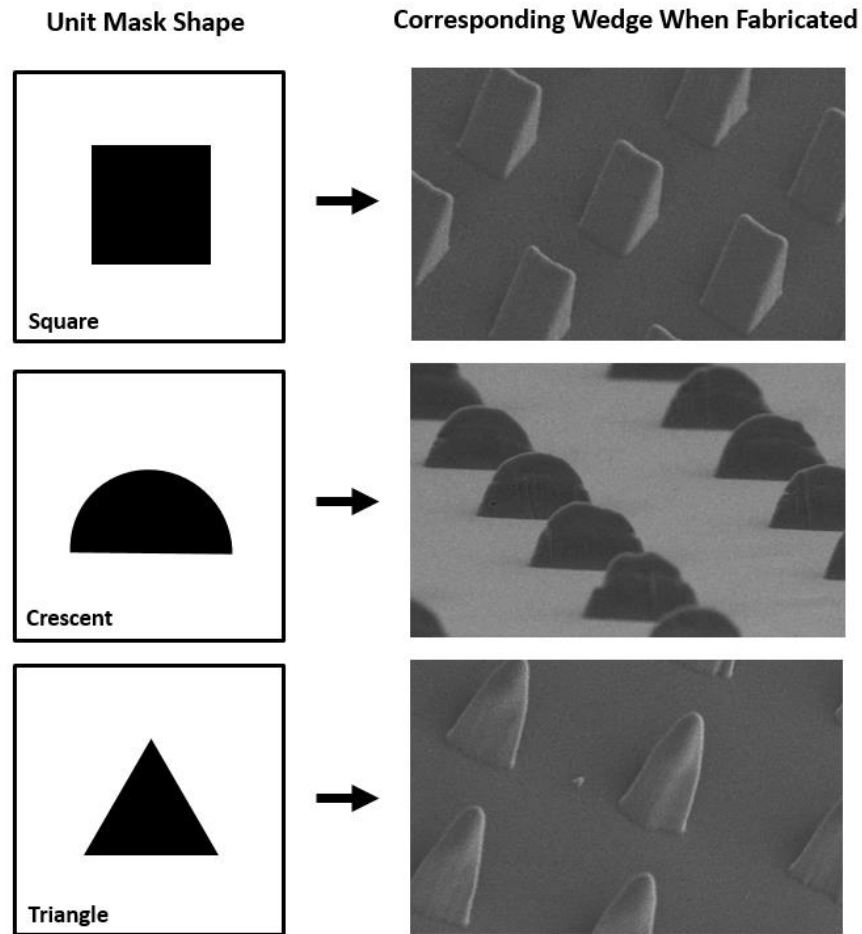


Figure 17. Possible unit mask shapes (left) and the corresponding SEM image of the wedge structure when each pattern is used in fabrication (right), showing the shape of the wedge faces. In this particular arrangement, the “small angle exposure” angle in Figure 9 is 0° , as opposed to the 30° used in the experimental fabrication previously, so the fabricated wedges are not tilted.

By altering the shape of the individual patterns in the photomask during the fabrication steps, various novel shapes become possible, two new shapes of which are shown in Figure 17. The process shown in Figure 9 remains consistent in that the fabrication method is still the same angled exposure technique. However, by changing the shape and dimensions of the photomask patterns, novel shapes can be attained, each of which has its own unique features. Figure 17 presents the unit pattern shape of

the photomask array, and the corresponding shape that is attained when used to fabricate the wedge patterns.

This investigation into different possible shapes is possible entirely due to the unique properties of SU-8 being a negative photoresist in the fabrication of the negative mold. Thus, the obtained structure is the negative “pit” that takes on the shape of the unexposed regions of the SU-8, that get completely removed after the development step of fabrication. The angled exposure procedure can be thought of as “cleaving” or “chiseling” the SU-8 structure at different angles.

The implications of this process’ subsequent “cleaving” steps is that multiple geometries can be obtained using the same pattern, but orienting the photomask differently. For example, the triangular pattern can be flipped upside-down in order to create a wedge that has the edge now where the face would have been. This concept is illustrated below in Figure 18 using a triangular photomask pattern as an example:

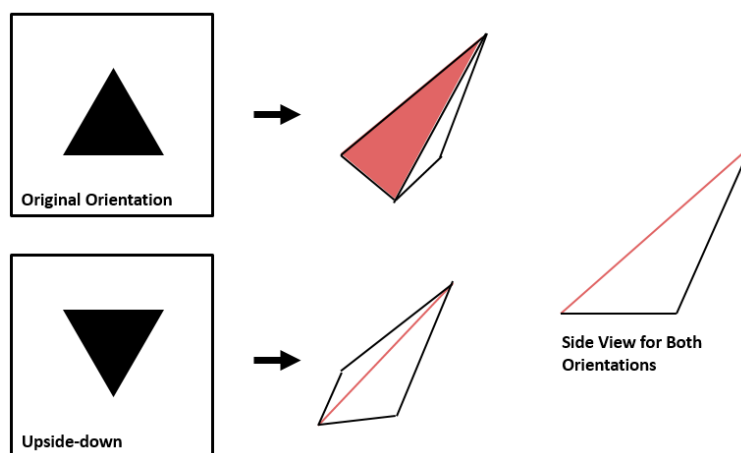


Figure 18. Example image of alternate shape wedge that can be obtained from orienting the photomask in a different manner. Shown is a triangular pattern and the two possible outcomes in an isometric top-down view. The shaded regions (in red) indicate the “face,” indicated by the feature with the longest projected length as viewed from the side.

Although there are virtually an infinite number of possible geometries for the wedge shapes, it is evident that the square pattern was the most optimal pattern to fabricate an adhesive, as the shape geometrically maximizes the contact area for the same contact length that makes contact with the opposing surface, along the direction in which the wedges point. However, different shapes are able to make use of additional unique features dependent upon its geometry. In addition to the contact area, some wedge shapes, the triangle in particular, is easier to deform, as there is less mass concentrated towards the back face of the wedge. Thus, less material is needed to be compressed, and therefore, less input energy is needed to deform the same amount vertically.

Using the same FEM software (Abaqus, Dassault Systèmes) as for the previous computational analysis, the different possible shape geometries are investigated in terms of its ability to be deformed in the direction perpendicular to the opposing surface. In order to emphasize its respective capabilities in deformation, the “small exposure angle” was again set at 30° in order to achieve a tilted wedge geometry, identical to the technique used in the experimental steps. The corresponding CAD models are shown in Figure 19, along with the resulting deformation of each geometry after a 0.6 atm preload. For the sake of expanding the analysis, an additional geometry not fabricated and shown in Figure 17 is shown: the structure obtained by using a circular pattern, revealing a cylindrical-shape wedge.

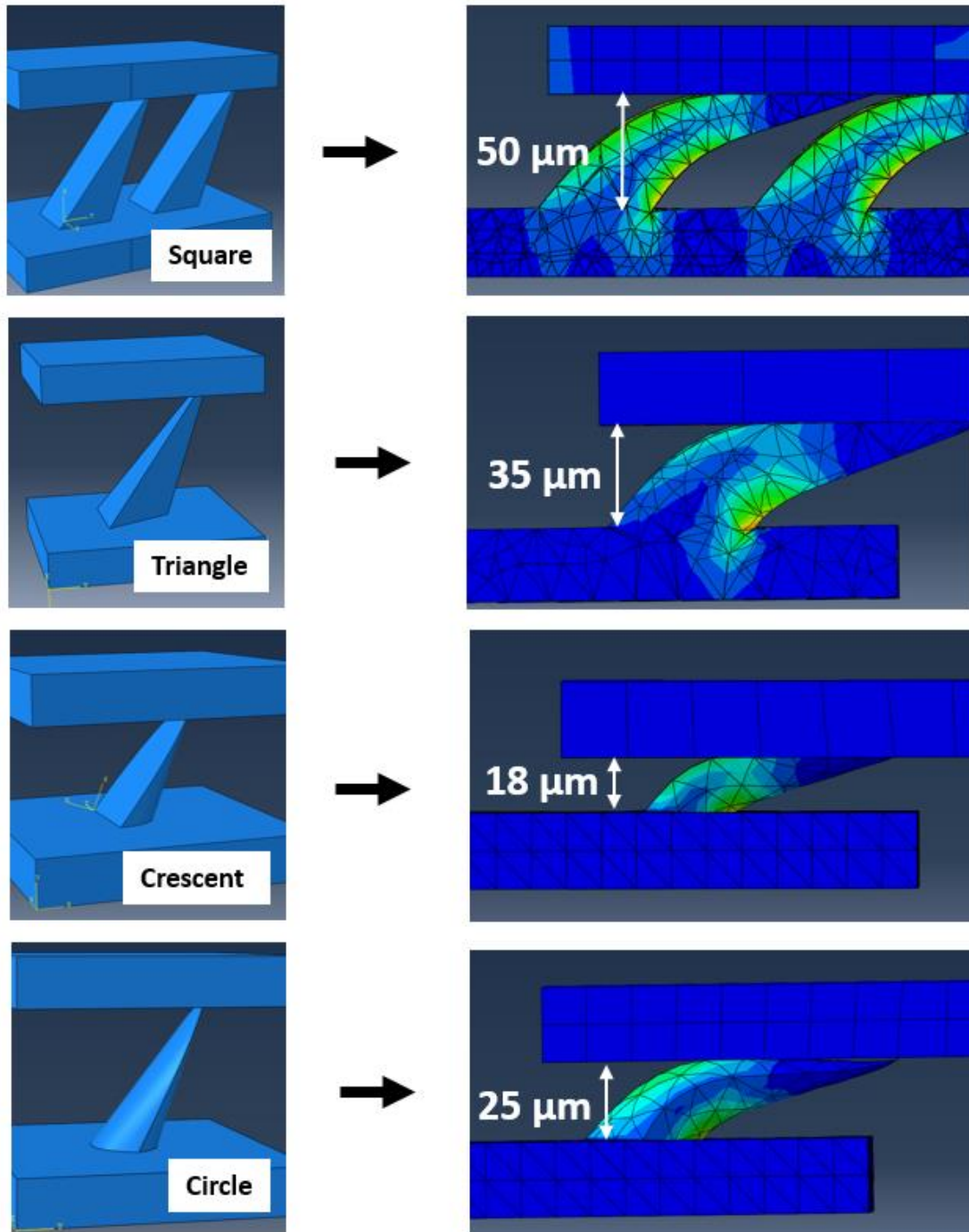


Figure 19. CAD models of each of the four shapes is first created (left column) and then assigned appropriate properties and deformed at a preload of 0.6 atm. The vertical distance between the opposing surface and the base surface is measured for each shape in order to determine ease of deformation for each shape.

From these results, it is evident that, as predicted, the wedge from the square pattern has the highest bulk stiffness in the vertical preload direction, as it had the smallest vertical deflection (shown by the highest gap measured in Figure 19) at 50 microns. It should be noted that for the crescent shape, the gap distance should be doubled for a proper quantitative comparison, as the projected aspect ratio of the semi-circular shape is half of the other three patterns, because it is quite literally half of the circle pattern. Therefore, the bulk vertical stiffness values in descending order are: square, with 50 μm ; crescent, with 36 μm (18 μm raw data multiplied by 2, as due to its aspect ratio); triangular, with 35 μm ; and circle, with 25 μm . However, one should note that the circular pattern's wedge, although the easiest to deform, would yield the smallest contact area, as the face that makes contact with the opposing surface is a line, traced by the midpoint of the arc along the wedge, as opposed to a surface as shown in the other three patterns.

The analysis of these novel shapes shows that there is significant potential in terms of modifying the properties of an adhesive surface, simply by changing the geometry of the patterns in the photomask. By only altering the photomask and its orientation during exposure, one is able to tune parameters such as contact area maximization or preload minimization to his or her liking.

5. QUALITATIVE DEMONSTRATION PROGRESS

5.1 BRIEF OVERVIEW OF THE PROPOSED DEVICE

Following the experimental work on the adhesive behavior of the microsurface, as well as the FEA results, much work has been done in order to create a versatile adhesive device. The proposed device consists of an array of micro-wedged array where its net adhesive area is significantly larger than that of the sample adhesive shown in Chapter 3, in order to hold a practical amount of weight that demonstrates its ability to be used commercially, for example. Thus, it is essentially a “scaled up” version of the sample adhesive used for testing. Furthermore, the device proposed is heated internally through Joule heating as a current is passed through the bulk adhesive material. A single unit of the adhesive can be shown below in Figure 20.

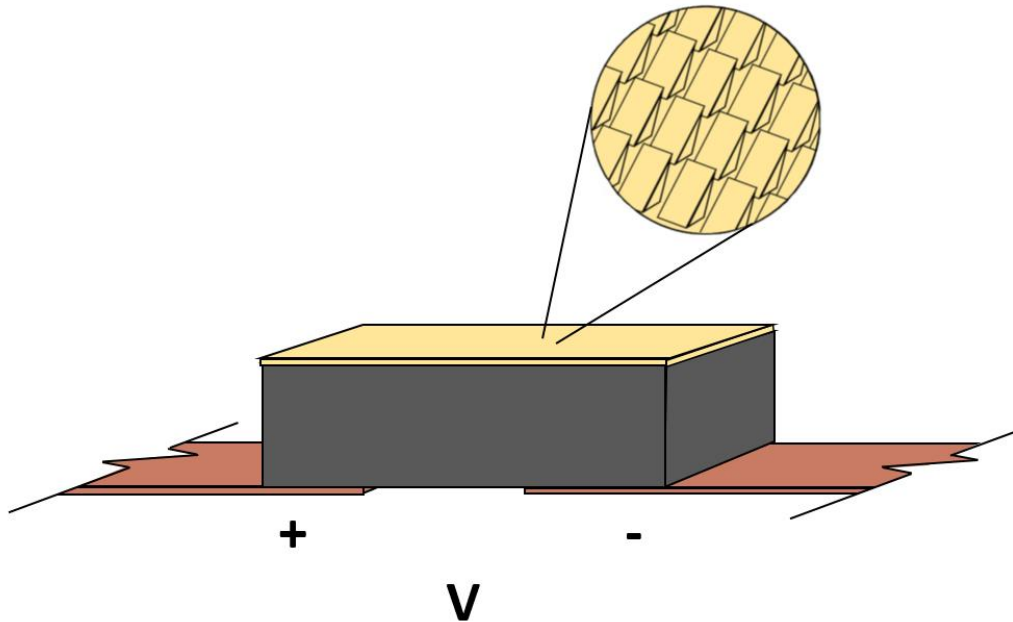


Figure 20. The basic overview of the final device. This figure shows a unit adhesive island, arranged in an array of series and parallel based on the power source capabilities. When the ends of the islands are subjected to a voltage drop, current passes through the bulk carbon black embedded SMP (shown in gray), which heats the thin layer of a microstructured surface of SMP (shown in yellow) above the polymer's T_g , thereby inducing the SMP's compliant state, making the individual microwedges able to deform easily when pressed against the opposing surface.

5.2 BASIC FABRICATION STEPS

In Figure 20 on the previous section, we can see that, based on the colors presented in the figure, there are three distinct regions in the device. The fabrication for the middle region, where the bulk of the heat generation takes place as the current is run through the island, is made of a material whose precursor recipe is essentially the same as the basic NGDE2 shape memory polymer recipe as used in Chapter 3, except the polymer precursor is mixed with a certain amount of carbon black powder and mixed thoroughly. The exact amount of this carbon black by weight was investigated based on its effects on the Joule heating performance of the final device, which will be presented in the following section. The optimal percentage of carbon black by weight was also investigated by Eisenhaure et al. and the basic premise is that there is a critical threshold of the amount of carbon black for optimal electrical conductivity, which can be seen as a percolation problem [34].

Once the desired amount of carbon black is added and mixed with the SMP precursor, it is flattened out between two flat surfaces in order to create a thin wafer of this carbon black-embedded SMP. Once it is cured with the same curing conditions as the plain SMP, it is peeled away and cut into desired shapes, as necessary for the device. In Figure 20, the red region represents the copper tape (or any other conductive material with negligible resistance), and the cut islands of SMP are secured onto the copper tape by using the same carbon black-embedded SMP precursor and using this paste material as a “glue” layer. This is then set in the oven to cure once more, and then each island is molded with a PDMS negative mold using plain SMP without any carbon black in order to obtain the final structure shown in Figure 20.

5.3 FABRICATING THE DEVICE

The preliminary work for the device was planned by first testing the heating capabilities of the carbon black-embedded SMP structure, as a function of the mixing ratio by comparing the weight of the carbon black to that of the overall structure. Various percentages were tested, and the heating performance was based on both the resistance as well as the raw temperature measurements using a thermocouple with an applied voltage difference. The data is presented below.

Table 2 – Overall testing data on the effect of carbon black on the resistance and peak temperatures. The “composite islands” refer to a mixture of an array of 30% composite squares surrounded by a 15% bulk material, based on the optimal setup from Eisenhaure et al. [34].

Composite Islands, 15% Adhesive			
	Resistance (ohms)	Power (W)	Peak T (at 5 min, saturation)
Trial 1	768	0.29	39
Trial 2	167	1.35	59
Trial 3	105	2.14	74
Trial 4	113	1.99	67
15% Islands, 15% Adhesive			
	Resistance (ohms)	Power (W)	Peak T (at 5 min, saturation)
Trial 1	274	0.82	43
Trial 2	198	1.14	47
Trial 3	206	1.09	61
Trial 4	224	1.00	62
Composite Islands, 30% Adhesive			
	Resistance (ohms)	Power (W)	Peak T (at 5 min, saturation)
Trial 1	67	3.36	87
Trial 2	35	6.43	135
Trial 3	34	6.62	142
Trial 4	79	2.85	94
Composite Islands, 30% Adhesive, Separated			
	Resistance (ohms)	Power (W)	Peak T (at 5 min, saturation)
Trial 1	695	0.32	58
Trial 2	465	0.48	61
Trial 3	460	0.49	62
Trial 4	2390	0.09	37
Composite Islands, 30% Adhesive, Separated			
	Resistance (ohms)	Power (W)	Peak T (at 5 min, saturation)
Trial 1	19.3	11.66	178
Trial 2	52.7	4.27	181
Trial 3	47.8	4.71	180
Trial 4	50.5	4.46	162

From the data shown, it is clear that generally, a higher percentage of carbon black by weight in the overall structure yields a much better thermal performance. However, for the purposes of the device,

the composite structure was concluded to be the best carbon black mixture to use in the overall structure for the bulk adhesive islands, because the 30% islands tended to be “chalky” when describing its brittleness.

The fabrication steps in the previous section were utilized in order to fabricate the final device, as shown below.

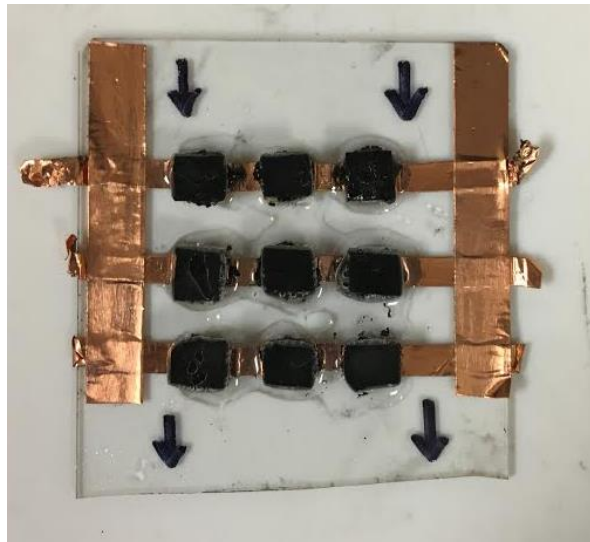


Figure 21. One of the final devices fabricated: a 3x3 fabricated device, based on the proposed design in Figure 20. The arrows indicate the direction the microstructural wedges are oriented.

Unfortunately, a proper qualitative demonstration for the adhesive capabilities has not yet been done yet, and is the logical next step of the work completed up until this moment. The device shown above, however, has been tested to confirm its electrically conductive capabilities, and has been successfully heated up using a power source, as shown in the next page in Figure 22. The final device displays a relatively small resistance, which is convenient in that there can be a lesser amount of voltage difference in order to obtain a necessary amount of power for proper Joule heating.



Figure 22. A second final device fabricated, with the resistance of the entire device shown using a multimeter. The final device has a resistance of 81 Ω.

An issue that was encountered during the attempted adhesion testing of the device was that the adhesive displayed poor normal adhesion, which became a challenge when attempting to load the device after being adhered to a target surface using the same phase changing steps for the microstructure, as shown in Figure 7. Although the normal adhesion shown in the testing portion based on the data from Figure 13 shows a normal adhesion that is within the same order of magnitude of the forward shear adhesion, it seems that when fabricating the adhesives using surface areas of an amount needed for a proper qualitative demonstration, the normal adhesion scales poorly, and this is a challenge that needs to be addressed in order to create a properly functioning adhesive device capable of handling higher loads.

Should such a device be able to be fabricated, further improvements can be added to embellish the device's impressive adhesive versatility. For example, the device shown in Figure 21 has a backing layer

of glass, making the bulk device rigid. This is a limitation on the possible surfaces the adhesive can mate to, as target surfaces which have a countour with features that exceed the length scales of the microstructure cannot be efficiently adhered to. A flexible backing can instead be used in order to add further versatility to the device. Furthermore, the device can be scaled virtually indefinitely, as it is simply an array of simple resistors. The device can be supported with the only limitation being the power source's capabilities. These proposed features are shown below in Figure 23.

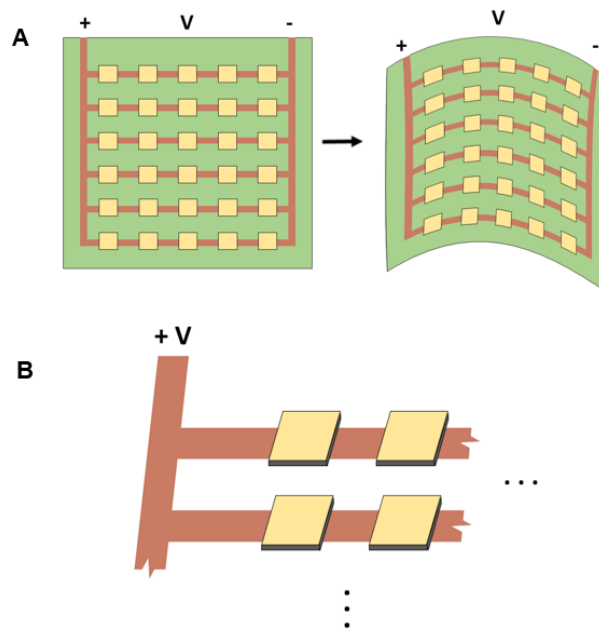


Figure 23. (A) Flexibility, which allows adhesion of the islands (shown in yellow) to a curved surface, due to the flexible backing (shown in green), and (B) scalability, which allows for direct manipulation of the effective adhesion force and dimensions of the device (bottom).

6. CONCLUSION AND FUTURE WORK

The study presented in this thesis involves an extensive research on the characteristics of shape memory polymers (SMPs) and their unique phase-changing properties. Several potential applications were discussed utilizing this material, but the one that was the focus of this thesis was that of the directional dry adhesives. The SMP material allows for both shape recoverability, as their name implies, which gives rise to reversibility. Furthermore, the adhesive surface fabricated holds directionality because of the double-angle exposure technique utilized in fabrication, as well as switchability in adhesion, meaning it is capable of switching between states of high adhesion and near-zero adhesion. Such a surface has potential in uses of medical adhesives, or biomimetic robotic applications.

The experimental data was compared with FEA modeling data, confirming the adhesive saturation behavior shown in the experimental tests. Furthermore, there is potential for additional wedge shapes to be fabricated, as seen in Chapter 4.4, with SEM images of three total shapes already fabricated. This shows that one can also tune the shape of the adhesive microstructure, and the shapes depend on both the shape of the patterns on the photomask, as well as exposure orientation.

There is much room for study beyond the work done in this thesis. For example, the experimental section, in future works, can include the tests comparing across the novel shapes proposed in Chapter 4.4, testing and comparing between samples for parameters such as adhesive strength, saturation preload, and directionality capabilities. Furthermore, only three shapes (square, crescent, and triangle) were presented in its fully fabricated form, but because of its flexibility, a wide variety of shapes, including the effect of exposure orientation, can be studied in the future. Finally, as proposed in Chapter 5, the qualitative testing can be demonstrated by loading the fabricated device with weights in order to present the full practical capabilities of the adhesive.

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