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Microstructured Shape Memory Polymer Surfaces with Reversible Dry Adhesion

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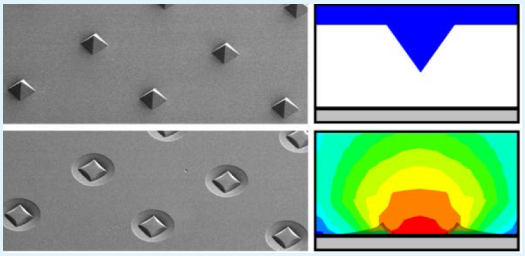
Supporting Information

ABSTRACT: We present a shape memory polymer (SMP) surface with repeatable, very strong (>18 atm), and extremely reversible (strong to weak adhesion ratio of >1 × 10^4) dry adhesion to a glass substrate. This was achieved by exploiting bulk material properties of SMP and surface microstructuring. Its exceptional dry adhesive performance is attributed to the SMP's rigidity change in response to temperature and its capabilities of temporary shape locking and permanent shape recovery, which when combined with a microtip surface design enables time-independent control of contact area.



KEYWORDS: *dry adhesives, shape memory polymer, reversible adhesion*

INTRODUCTION

Reusable dry adhesives with strong adhesion and a high degree of adhesion reversibility are attractive for a wide range of applications including temporary bonding in domestic and industrial settings, the "feet" of climbing robots, and automated assembly at both macro- and microscale. Both adhesive strength and reversibility come from a combination of bulk and surface material properties, often aided by carefully designed surface micro/nanofeatures.[1−4] Because a dry adhesive relies primarily on noncovalent molecular interactions to create its adhesion force, it is important to maximize contact area at the molecular scale. To accomplish this, the adhesive material must be compliant enough to conform closely to the surface of the substrate. However, as the adhesive material becomes more compliant it also becomes more susceptible to failure from crack formation and propagation, leading to lower adhesion. A common strategy to overcome this contradiction is to create arrays of microscopic fibrillar structures on a relatively rigid backing layer;[5] the microscopic fibrils are compliant enough to conform to the substrate, whereas the rigidity of the macroscopic structure helps to evenly distribute the load among the contact points, thereby delaying the onset of peeling. Although significant efforts have been made to study and manufacture compliant, hierarchical fibrils for dry adhesives,[6] relatively few authors have demonstrated the importance of controlling backing layer rigidity.[2,7] One such demonstration was performed using phase changing material as a backing layer, where the effective adhesive strength of the overlying elastomer was shown to increase substantially when rigidly supported.[7]

A change in elastic modulus can be effected in most polymeric materials by shifting the temperature across the polymer's glass transition (T_g). A class of thermosensitive smart materials referred to as shape memory polymers (SMPs) are specifically designed to drastically change their mechanical compliance in this way at a convenient T_g.[8] The change in an SMP's elastic modulus is accompanied by another very important property from which its name is derived: it is ability to lock itself into an arbitrary "temporary" shape and to then recover its original, "permanent" shape. This ability can be utilized to reversibly change the surface morphology of SMP, leading to switchable surface properties such as dry adhesion.[9,10] During an SMP's transformation from a temporary shape to its permanent shape, the stresses generated during attachment are released, which can serve as a unique built-in adhesion detachment mechanism. Despite these attractive features offered by SMP, strong adhesion has only been previously demonstrated when SMP is combined with an intrinsically adhesive (or sticky) rubber layer or when the surface is treated with adhesion molecules.[3,4,11,12] We hereby explore SMP as a single component to construct a strong dry adhesive, with no additional "adhesive" layer added.

RESULTS AND DISCUSSION

The SMP described above forms the basis for a not only strong but also highly reversible dry adhesive when its shape fixing and recovery capabilities are combined with a micropatterned surface design.[13] Evenly spaced microscale pyramids − termed microtips − are patterned onto an SMP surface using a reusable silicon mold (see the Supporting Information). In the

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fabrication of our SMP surface, we chose a particular thermoset epoxy-based SMP that experiences a change in elastic modulus from approximately 2.5 GPa (below 35 °C) to 10 MPa (above 65 °C) corresponding to the SMP's T_g.[14] As with most polymers, curing it in a mold captures surface details down to the nm (see the Supporting Information, Figure 3). A small section of this SMP in its rigid permanent shape is represented in Figure 1a. When heated above its T_g, it will become

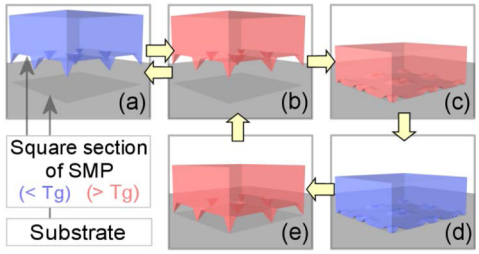

Figure 1. (a–e) Schematic illustration of the bonding/debonding between SMP surface and a substrate. (a) Section of SMP with microtips in their permanent shape at room temperature ($<T_g$). (b) To begin the bonding process, the SMP is heated above its T_g to become compliant ($>T_g$). (c) Preload is applied to cause the SMP to collapse into contact with the substrate ($>T_g$). (d) SMP is cooled to become rigid and bonded to the substrate in this temporary shape ($<T_g$). (e) To reverse the adhesion, the SMP is heated above its T_g and shape recovery causes debonding ($>T_g$).

compliant (Figure 1b) and can be easily deformed to a temporary shape. This is depicted in Figure 1c, where the SMP is pressed against a mating substrate, thereby compressing the microtips and causing the flat region between them to collapse into contact with the substrate. Note that an essential step toward forming a strong adhesive bond has been accomplished by this collapse; namely, the generation of large contact area between SMP and substrate. However, the bond is not yet very strong or stable. If pressure is released, the heated SMP, like any other elastically deformed compliant material, is susceptible to peeling failure and will try to spring back to its original shape. It is at this stage that the SMP sets itself apart from other common materials by locking in its temporary shape through cooling below its T_g (Figure 1d). The SMP will stay in this shape until it is again heated to resume its original shape, as shown in Figure 1e where the contact area, and therefore the adhesion, is nearly completely eliminated. Scanning electron micrographs of the fabricated microtipped SMP in both its permanent and temporary shapes are shown in images a and b in Figure 2, showing the microtips partially flattened and level with the collapsed intermicrotip region, all of which now make intimate contact with the substrate. The collapsed, temporary shape is reproduced using finite element software (see the Supporting Information) and is shown in Figure 2c, d along with the stress profile showing stresses concentrated near the microtips where deformation is greatest.

There is a minimum microtip height that is required to reliably cause the intermicrotip region to fully delaminate when the SMP is reheated. This height is a function of the SMP storage modulus, work of adhesion to the substrate material, detachment temperature and microtip spacing.[13] In our case, the substrate material is glass and a target detachment temperature of 90 °C is selected for consistency with previous work.[4,11] The stresses and strains generated during bonding near the microtips increase with microtip size, shown in Figure

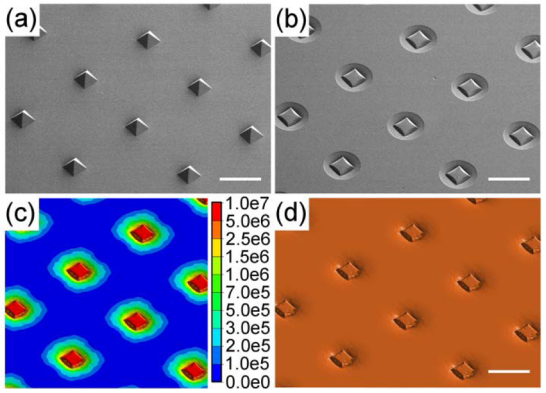

Figure 2. (a) SEM image of SMP surface in the permanent and nonbonded state, (b) SEM image of SMP surface in the temporary and bonded state, (c) Von Mises stresses generated under 30 N cm^{-2} preload in FEM, and (d) corresponding FEM image showing the same temporary shape. (scale bars: 50 μm).

3 with 100 μm spacing. Cooling below T_g traps these stresses internally within the polymer's molecular structure, eliminating the restoring force between SMP and substrate. When reheated, the stresses will be relieved and the restoring force reestablished. For delamination between SMP and substrate to occur, the released strain energy must exceed the work of adhesion of the contacting area. Experimentally, the size, measured by base-width, required for reliable delamination from glass was determined to be between 18 and 21 μm. FEM analysis was performed with the storage modulus of 10 MPa[14] and the work of adhesion of 46 mJ m^{-2} measured using atomic force microscopy (see the Supporting Information). FEM results shown in Figure 3 indicate the critical size to be between 15 and 18 μm; a consistent result given the idealizations inherent in computational analysis (see the Supporting Information).

The adhesive strength and reversibility of the resulting microtip SMP surface to a glass substrate is demonstrated in Figure 4. First, the unpatterned face (back side) of a 6.35 mm diameter section of SMP is glued to an aluminum cylinder to provide a means of loading and unloading the SMP surface (see the Supporting Information, Figure 1). The microtip SMP surface is then bonded to a glass-topped 5 kg mass using the process described in Figure 1a–d. The SMP-to-glass interface can support the full weight of the 5 kg mass as it is lifted and held, representing an adhesive strength of more than 156 N cm^{-2}. To reverse the adhesion, the load is removed and the SMP heated to 90 °C to initiate shape recovery. The adhesion is now essentially zero, as in Figure 1e, and the SMP is easily lifted away from the glass surface.

To quantify the adhesion, we performed tests using similarly constructed SMP samples with an aluminum holder. The bonding of the rigid aluminum to the side opposite to the adhesive interface of the SMP was found to have unintended consequences for the observed collapse behavior. Heating and applying pressure to the SMP during bonding causes radial expansion in our cylindrical SMP adhesive; however, this expansion cannot occur where bonded to the aluminum, and so a slight convex curvature develops on the adhesive and the contact pressure for adhesion cannot be perfectly even from center to edge (see the Supporting Information, Figure 2). This fact contributes to the observed relationship between the preload applied during bonding and the strength of the

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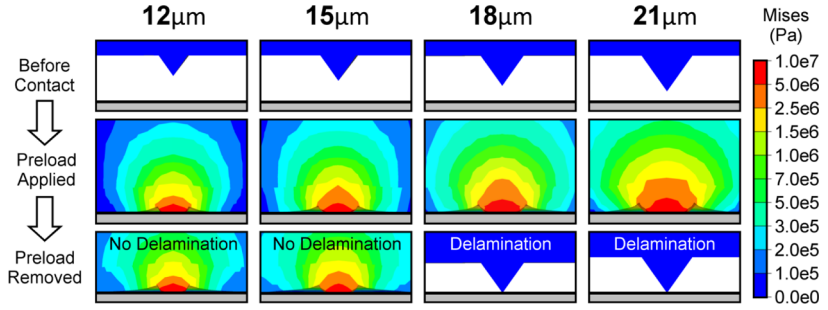

Figure 3. Von Mises stress near four sizes of microtip calculated using FEM before, during, and after an equal preload is applied to each. The larger microtips store more strain energy when compressed, allowing easier delamination when the load is removed. Perfectly elastic behavior is assumed with a modulus of 10 MPa, corresponding to 90 °C.

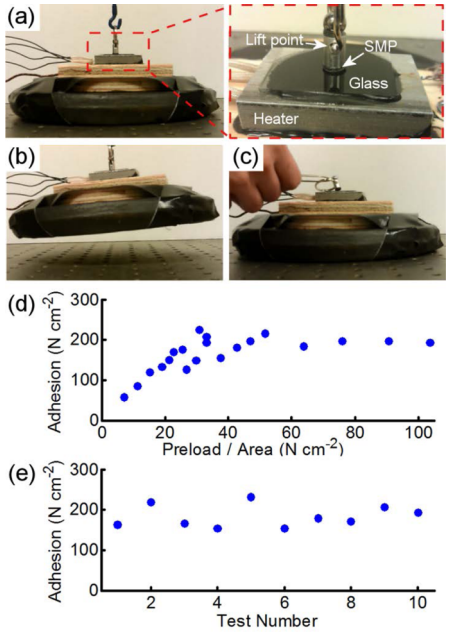

Figure 4. Demonstration of adhesive performance of an SMP microtip surface (diameter: 6.35 mm). (a) SMP is bonded to a glass surface applying preload initially at 90 °C, (b) 5 kg of mass is lifted by SMP bonded to a glass surface with the contact area of $\sim 3 \times 10^{-5}$ m^2. (c) Heating to 90 °C causes detachment with negligible residual adhesion. (d) Effect of preload on adhesion. (e) 10 consecutive cycling tests of a single SMP microtip surface.

resulting bond in Figure 4d. Adhesive strength increases steadily with increasing bonding preload because of the progressive radially outward collapse of the intermicrotip regions of the SMP to the substrate. As preload approaches approximately 30 N cm^{-2}, all intermicrotip regions are in contact with the substrate and further increases in bonding pressure yield no measurable increase in adhesion because gains in contact area become minimal. The magnitude of the preload required to reach this plateau in adhesive strength is expected to depend on the aspect ratio, i.e., the ratio of width to thickness, of the SMP adhesive layer. This point is elaborated on in the Supporting Information.

The SMP's ability to undergo solid state deformation and recover its original shape repeatedly and without deterioration has been demonstrated previously.[14] To ensure that its adhesive qualities are similarly robust, a single SMP adhesive was put through 20 bond/debond cycles and then tested to failure 10 consecutive times with results in Figure 4e. The tests indicate an average adhesive strength of 184 N cm^{-2}, an exceptionally high adhesive force compared with other macroscale dry adhesives which range from 0.1 to 100 N cm^{-2}, where the upper portion of this range has only been achieved using carbon nanotubes and polymer-based adhesives are generally below 10 N cm^{-2}.[15] Additionally, the sample does not show signs of degradation with repeated uses. In contrast to the high "temporary" shape adhesion strength (Figure 1d), the "permanent" shape adhesion strength (Figure 1e) was below the resolution of our equipment (1 mN). This corresponds to a residual adhesion less than $\sim 3 \times 10^{-3}$ N cm^{-2}, demonstrating more than 4 orders of magnitude difference between the adhesion of the temporary and permanent shape states. Shear data has not been explicitly included, but is expected to be of similar magnitude as the provided normal-direction adhesion data.

Substantial opportunities exist to expand beyond the work presented in this paper, including the characterization of the adhesive bond between the SMP material and other materials with varying chemical composition and surface roughness. It is important to keep in mind that the SMP formulation used here is but one of many formulations which have already been developed and are available in literature.[9,14] Other formulations may exhibit superior adhesion by virtue of surface chemistry or bulk material properties. Likewise, the glass transition temperature, which dictates the detachment temperature, can be tailored for specific applications.[14] The design of the adhesion interface geometry may be similarly be subject to improvement. For example, a more refined analytical/computational model may be developed to guide the optimization of the microtip size and pattern, and differently shaped microstructures may provide enhancements in adhesion through crack-trapping[16] or other mechanisms while preserving reversibility.

CONCLUSION

In conclusion, shape memory polymers can offer excellent dry adhesive performance by virtue of their shape-fixing-recovery properties and dramatic shift in elastic modulus in response to temperature change. The magnitude of the reversibility can be enhanced with simple, robust, and easily molded microstructures. Our particular SMP adhesive demonstrates tensile adhesive strength to glass twenty times greater than the typically cited shear adhesion of gecko foot pads ($\approx$ 10 N cm^{-2}),[17,18] and far exceeding most other reusable macroscale dry adhesives, while the application of heat reduces adhesion to negligible levels when detachment is desired. There is no particular upper limit to the manufacturable size of our SMP adhesive, except that issues related to thermal expansion and

Poisson's effect may necessitate mitigating design features at large scale.

■ ASSOCIATED CONTENT

Supporting Information

Details of material property tests, finite element modeling, and the SMP adhesive preparation, geometry, and testing procedures are provided. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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