Enhanced Shear Adhesion by Mechanical Interlocking of Dual-Scaled Elastomeric Micropillars With Embedded Silica Particles

This paper is dedicated to the memory of Professor Kahp-Yang Suh (1972–2013), an extremely innovative and dedicated researcher in the field of surface/interface science. His generosity to share his knowledge and inspirations in fabrication and adhesion research has made this work possible.

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Enhanced shear adhesion of mechanically interlocked dual-scaled micropillars embedded with silica particles is demonstrated. Arrays of elastomeric polyurethane acrylate micropillars with variable pillar diameter, height, aspect ratio (AR = diameter/height), and spacing ratio (SR = pillar-to-pillar distance/diameter) are decorated with silica particles of 100 nm to 1 μm on the pillar heads. The high-density protrusions provided by a silica particle assembly (1 μm diameter) on the micropillar heads (5 μm diameter, AR = 8, SR = 2) increase the shear adhesion strength by an order of magnitude from 4.1 (between pristine micropillars) to 48.5 N cm⁻². The adhesion strength is proportional to the particle size and the AR of micropillars, and inversely proportional to the SR. A simple mathematical model is derived by incorporating the interdigitation state of interlocking adhesion forces generated by the contacts between pillars and particle protrusions. Our model and SEM images also suggest that only ≈20% of micropillars participate in the actual contact.

1. Introduction

Adhesion plays an important role in many bioorganisms. For example, gecko clings on almost all kind of surfaces using van der Waals force via hierarchical fibers on its toes.¹⁻² Mussels and barnacles use special proteins for wet adhesions based on chemical bonding.³⁻⁴ Fruit burrs, dragonfly’s head arrester and microtrichia on beetle’s inner wings exploit mechanical interlocking of structural features (e.g., hook and loop) to lock or adhere to external surfaces.⁵⁻⁶ Another intriguing example is our
fingerprint. Although it is still under debate, the small ridges on the surface of fingerprints have been suggested to provide a nonlinear modulation of frictional force, which in turn increases the gripping capability of fingers besides of its fundamental function as biometrics and sensing enhancement capability.[9,10] This intuition has been adapted to many useful technologies, including patterned rubber gloves, separable fastening devices, and packaging.[11–13]

In natural adhesion systems, the adhesion strength is generally governed by the materials characteristics, such as elastic modulus, surface energy, surface charges, as well as the surface geometry (e.g., size, shape). Specifically, in mechanically interlocked fibers, the total adhesion strength is determined by the competition of van der Waals force and deflection force of the interlocked fibers.[8,14] Van der Waals force, $F_{\text{vdw}}$, is characterized by material intrinsic properties, $F_{\text{vdw}} = A\sqrt{R/D_0}$. Here, $A$ is the Hamaker constant, $R$ is the radius of fiber, and $D_0$ is the cut-off distance between the neighboring fibers, typically 2 nm. On the other hand, the disjoining force from the deflection of fibers, $F_{\text{def}}$, is measured as $F_{\text{def}} = 2EI\Delta\phi/(l_0 - l/2)^3$. Here, $E$ is the elastic modulus, $I = \pi R^4/4$ is the moment inertia, $\Delta\phi$ is the deflection angle, $l_0$ is the fiber length, and $l$ is the overlapping length of fibers. In general, the separation takes place when the deflection force overwhelms the van der Waals force.[15]

Compared to gecko-like adhesion, the interlocking system has provided rather large and robust adhesion where the governing force of interlocking adhesion is approximately linear to the yield point of the interweaving fibers.[16,17]

Previously, we have demonstrated enhanced shear adhesion ($\approx 10$ N cm$^{-2}$) when interdigitating high AR nanohair arrays made from elastomeric PUA (elastic modulus $E = 19.8$ MPa, diameter 100 nm, AR = 10). It has produced a van der Waals force interaction by 2–3 orders of magnitude higher than deflection force[15] from the nanohair array with a relatively large SR of 3. We have also explored the adhesion behavior on buckled micropillars made of shape memory polymers (SMPs; $E = 2.5$ GPa at 22 °C and 3.6 MPa at 80 °C, diameter 1 μm, AR = 4).[18] We found that dry adhesion can exist from with three possible interlocking adhesion states: interdigitation, indentation, and interweaving depending on pillar spacing and symmetry, pillar–pillar alignment, external load, bending of the lever arm of the pillars. When the preload is small, the pillars remain straight and can interdigitate with pillars from the other set of pillars when the SR is large, and the adhesion could be amplified by increasing the effective contact area.[15] In the indentation state, pillars are buckled and indented face-to-face with counter pillars after preloading. In the interweaving state, the buckled pillars are entangled with and sliding against the counter buckled pillars. The interlocking adhesion was dominated by interweaving pillar–pillar contact at a small SR (1 or 2).

Shear adhesion strength up to $\approx 70$ N cm$^{-2}$ was achieved when interlocking 1 μm diameter SMP pillars with AR = 4 and SR = 1. In this paper, we exploit the combination of the two systems using soft and high AR micropillars with SR varied from low to high, and introduced particles on the heads of the pillars to create interweaving interlocking behaviors for enhanced shear adhesion.

We prepared dual-scale micropillars (5 μm diameter) of different ARs (up to 8) and SRs (2–4) from elastomeric PUA by embedding silica nanoparticles on the heads of the pillars. The nanoparticle suspension was first drop cast onto polydimethylsiloxane (PDMS) mold with a micropore array, followed by solvent evaporation. Then, an ultraviolet (UV)-curable urethane acrylate was dropped into the mold to fill the rest of the channel, producing PUA micropillars with nanoscale protrusions on the top part of the pillars. The presence of such undulations allows for additional, sequential locking in the shear direction when a perpendicular force (i.e., preload) is applied to the micropillars. The protrusions can be precisely controlled using different sized particles with high durability. The shear adhesion strength was increased by an order of magnitude from 4.1 to 48.5 N cm$^{-2}$ when silica particle (1 μm in diameter) was assembled on the heads of the pillars (5 μm diameter, AR = 8, SR = 2). We further showed that the adhesion strength could be tuned by varying the particle size, AR, and SR of the pillars.

2. Materials and Method

2.1. Preparation of Nanoparticle Suspensions

Silica nanoparticles with diameter of 100 nm were provided by Nissan chemicals, Ltd. (Japan). Nanoparticles were harvested from isopropanol solution by centrifugation at 6 000 rpm for 30 min using Eppendorf Centrifuge 5804R. Pelletized silica particles were separated from the solvent by overnight evaporation in an oven at 65 °C. Silica particles with 500 nm and 1 μm particles were purchased from Alfa Aesar as powders. Silica particle suspensions were prepared by dissolving the particles in 1 wt% in ethyl alcohol (200 Proof, Decon Laboratories, Inc., USA). Suspensions were shaken in M16700 Barnstead Thermolyne (ThermoScientific, USA) for 15 min followed by mixing in ultrasonic mixer, Branson 2210 (Emerson Industrial Automation, USA) for 60 min at room temperature.

2.2. Fabrication of Nanoparticles-Embedded Micropillars

PUA micropillar arrays (5 μm diameter) of different ARs and SRs were fabricated by replica molding from the PDMS mold, prepared by mixing Sylgard 184 (Dow Corning)
prepolymer and crosslinker (10:1 wt/wt), followed by degassing in vacuo for 1 h, and baking in an oven at 65 °C for 1 h. Silica particle suspension was drop-cast over the PDMS mold, followed by blading using a glass slide in one direction (see Figure 1). The speed of manual blading was controlled such that the evaporation of the solvent was not too fast over the sample area (≈10 s cm⁻²). Typically, a blading speed of about 1 mm s⁻¹ was proper for 1 wt% silica particle suspensions. After the solvent was completely evaporated, the overflown silica particles on the mold surface were removed by 3M Scotch tape. Then, a UV-curable PUA prepolymer (Minuta Tech, Korea) was back-filled into the mold with a polyethylene terephthalate (PET) film (250 μm thick, McMaster & Carr, USA) as a supporting backplane. The PUA prepolymer with silica particles was photopolymerized in the mold by exposure to UV light (97436 Oriel Flood Exposure Source, Newport Corp., USA) at an intensity of 2 000 J cm⁻², followed by peel off the PDMS mold to obtain the nanoparticles-embedded dual-scale micropillars.

2.3. Preparation of FITC-Dyed Particles

Fluorescein isothiocyanate (FITC)-dyed particles were prepared as described in literature. Brieﬂy, an aminofunctionalized (FITC-APS) dye was prepared by mixing 2 mL ethanol and 1.5 mg FITC (Sigma–Aldrich) and 0.24 mL 3-(aminopropyl) triethoxysilane (APS, Sigma–Aldrich) and stirred for 12 h at room temperature. FITC-functionalized particles were prepared by mixing 1 wt% silica particle suspension in ethanol (6.5 mL) with 551 μL H₂O, 48.15 μL tetraethyl orthosilicate (TEOS), and 20.8 μL FITC-APS for 48 h at room temperature.

2.4. Shear Adhesion Tests

The macroscopic shear adhesion force was measured by pulling interlocked pillars using a custom-built device. The shear adhesion force was translated into shear adhesion strength by taking the maximum/pull-off force per unit area after a preload (≈300 g) was applied by gently finger rubbing. A hanging scale with precision of ± 5 g (American Weigh Scales, USA) was used to pull in parallel direction of the substrate with interlocked micropillars.

2.5. Characterization

The surface morphology was characterized by scanning electron microscope (SEM) using FEI 600 Quanta FEG environmental SEM. The samples were coated with 9 nm Au/Pd prior to observation. The ﬂuorescent images of FITC-functionalized particles was observed using Olympus BX61 Motorized Microscope. First, the particles-embedded micropillars were inscribed using a razor blade, followed by dispersion in water and drop cast on a glass slide. After evaporation of water, the clusters of micropillars were imaged under the ﬂuorescent mode.

3. Results and Discussion

3.1. Embedding Particles in Polymer Micropillars

The particle-embedded dual-scale micropillar arrays were fabricated according to the procedure shown in Figure 1. First, 1 wt% silica particle suspension in ethanol was drop-cast on the PDMS mold, followed by infiltration of PUA prepolymer and UV curing. To make a uniform distribution of particles in the tips of micropillars, the suspension drops were spread by a glass slide and bladed in one direction. Compared to the pristine micropillars with smooth surface (see Figure 2a), it was clear that the silica particles were uniformly assembled on the top part of the pillars, creating protrusions for later study of the interlocking adhesion (see Figure 2b–d).

First, we investigated the distribution of particles on pillar heads as a function of particle size. As seen in Figure 2, when the nanoparticle size was small (100 nm), a relatively random distribution of the nanoparticles was observed on the surface of micropillars. When the particle size was

![Figure 1. Schematic illustration of the fabrication procedure to create dual-scale micropillars embedded with silica particles on the heads.](www.mre-journal.de)
increased to 500 nm and 1 μm, the particles were nearly close-packed. To further examine the distribution of particles within the whole micropillars, we labeled the particles using FITC dye. Fluorescent images in Figure 3 showed that the distribution of particles was highly dependent on particle sizes. Consistent with the SEM images, pristine PUA micropillars showed smooth pillars surface with little fluorescence (Figure 3a). The pillars embedded with 100 nm FITC-silica particles were found with particles randomly assembled over the entire surface of the micropillars with slightly high concentration near the heads (Figure 3b). Five hundred nanometer silica particles were found mostly assembled on the top of the micropillars, but some of them also spread over the sidewall.

**Figure 2.** SEM images of micropillars (5 μm diameter) embedded with silica particles of different diameters. (a) Pristine micropillars. (b–d) Particle diameter of 100 nm (b), 500 nm (c), and 1 μm (d).

**Figure 3.** Fluorescence images showing the distribution of silica particles of variable sizes in PUA micropillars (5 μm diameter and aspect ratio 8). For visualization purpose, micropillars were broken from the substrate, and the silica particles were dyed with FITC. (a) Pristine micropillars. (b–c) Particle diameter of 100 nm (b), 500 nm (c), and 1 μm (d).
When the silica particle size was increased to 1 μm, non-close packed silica particles were localized only on the top part of the micropillars (see Figure 3d).

This phenomenon can be understood by the competition between capillary force and gravitational force when embedding particles inside the mold during solvent evaporation. When the particles are small, capillary force is significantly high to pull the particles up following the meniscus of the solvent. Since the solvent used in this experiment is ethanol, which can wet the PDMS mold, the 100 and 500 nm particles appeared not only on the top of the pillars but also throughout the side walls, even though the concentration of 500 nm particles was much lower than that of 100 nm as evident from the fluorescent intensity. When the particles are sufficiently large, the gravitational force becomes dominant, thus drawing the particles in the suspension down to the bottom of the mold. As the result, the 1 μm particles sit only on the top of the pillars.

To quantify the role of particles size, we calculated the particle settlement rate according to literature. The settling of unimodal suspension under normal gravity is given by:

\[ v = \frac{2}{9} \frac{\alpha^2 (\rho_p - \rho) g}{\eta} \left( \frac{r_p}{\rho} \right)^2 \]  

(1)

where \( \alpha \) is the radius of particles, \( \rho_p \) is the density of particles, \( \rho \) is the density of fluid, \( g \) is the gravity acceleration, and \( \eta \) is the viscosity of the fluid. From Equation (1), it is clear that the velocity of particle settlement, \( v \), increases in a parabolic manner with the radius of particles. The velocity ratio of 100 nm, 500 nm, and 1 μm silica particles is 1:25:100. Therefore, given the same evaporation time, the larger particles will settle quicker to the bottom of the mold in comparison to smaller ones.

### 3.2. Shear Adhesion Strength of the Mechanically Interlocked Dual-Scale Micropillar Arrays

The adhesion strength between mechanically interlocked dual-scale micropillars was measured using a hanging scale (see setup in Figure 4a). Two identical micropillar arrays were put together against each other under a load (≈300 g). A shear force parallel to substrates was applied while the scale was attached to one end of the substrate to measure the maximum force (see the schematic of interlocking micropillars and shear force application in Figure 4b). The mechanical interlocking-based adhesion is highly dependent on the geometry of micropillars, including size, AR, SR, and surface roughness (i.e., the number and size of particles protrusion). A typical interlocked micropillar arrays is shown in Figure 4c. It is apparent that many micropillars were interdigitated with each other, while some were buckled. This may be due to the misalignment of the micropillars and low elastic modulus of PUA, causing the pillars to collapse during engagement. Previously, we have shown that there are three modes of interlocking behaviors, including interdigitation, interweaving and indentation, of two complimentary pillars are dependent on the preload, spacing of the pillars, and buckling during engagement. Interdigitation instead of indentation is likely to happen when \( \alpha = 1 + SR > \sqrt{3} \). Therefore, we expect that all samples tested here would have interdigitation state of mechanical interlocking. We will show later that after successful interdigitation, interweaving type of interlocking was introduced when the heads of the micropillars was covered with particles protrusions. Our calculation with geometrical simplification is shown in Figure 4d.

As shown in Figure 5, the adhesion strength increased with increase particle size regardless of the AR of micropillars. In Figure 5a, the adhesion strength of micropillar array (diameter 5 μm, SR = 2, and AR = 8) was tripled, from...
2.9 (pristine pillars) to 8.82 N cm$^{-2}$ (pillars embedded with 100 nm particles), and could be further increased to 25.5 N cm$^{-2}$ from pillars embedded with 500 nm particles. Pillars embedded with 1 μm particles had the highest adhesion strength, 48.5 N cm$^{-2}$. This may be attributed to the fact that larger protrusions on the heads of the micropillars were formed using larger particles, thus increasing the chance for interlocking. Figure 5a also showed a nonlinear decay of adhesion strength with increasing the SR of the micropillar arrays, which could be explained by the reduced density of interlocked micropillars. The same trend was observed in micropillars with lower ARs, 6 and 4, as shown in Figure 5b and c, respectively. Again, particle-embedding contributed to significant increase of adhesion strength up to one order magnitude as compared to the pristine micropillars array. However, the slope of increasing adhesion strength decreased as the AR increased. It can be understood from the fact that the force to separate two interweaving pillars is smaller when the base length ($L_1$ in Figure 4d) is shorter. When $L_1$ is long, the deflection of the pillar becomes large with pulling, which, in turn, may increase the required force to separate two interlocked pillars.

### 3.3. Comparison With the Theoretical Models

To better understand the dry adhesion mechanism of particle-embedded dual-scale micropillars, the theoretical adhesion strength is calculated based on Johnson–Kendall–Roberts (JKR) theory. Here, an equilibrium contact area is considered to be formed when the shear force is applied to the samples. In the JKR model, the adhesion force, $F_{JKR}$, is given by

$$F_{JKR} = \frac{3}{4} \pi Wd$$

Here, $W$ is the work of adhesion, $d$ is the effective diameter of contact. Giving the measured $W$ of PUA ≈ 143.8 mN m$^{-1}$ from our previous work, and the estimated $d$ is 500 nm, the adhesion strengths of 2.34 × 10$^{-2}$, 1.32 × 10$^{-2}$, and 8.46 × 10$^{-2}$ N cm$^{-2}$ for micropillars with SRs of 2–4, respectively. These values are about 1–2 orders of magnitude lower than the measured adhesion strength. Moreover, the model could not explain the increasing adhesion strength with the embedding of particles since the JKR model is mainly based on single contact point for each micropillar, regardless of the AR and...
particles embedding. Therefore, the roughness of the pillars could not be accommodated in the current system.

Alternatively, we employed a mathematical model incorporating the side contact of cylindrical micropillars when they were brought in contact against counter micropillars. The adhesion force based on side contact of micropillars, $F_{sc}$, is given by\textsuperscript{18,23,24}:

$$F_{sc} = \left(\frac{\pi E_y W^2 d^2}{8(1 - \nu^2)}\right)^{1/4} \left(\frac{L_c}{2}\right)^{3/4}$$

(3)

Here, $E_y = E_m \phi + E_p(1 - \phi)$ is the effective elastic modulus,\textsuperscript{25} where $E_m$ and $E_p$ are the elastic modulus of polymer matrix and particles, respectively, $\phi$ is the fraction of particles in the pillar, $\nu$ is the Poisson’s ratio, and $L_c$ is the side contact length of micropillars. In our system, some of these values are given as follows: $E_m = 19.8$ MPa, $E_p = 69$ GPa (silica particles), and $\phi \cong 0.1$. For 5 $\mu$m diameter PUA micropillars with $\nu = 0.4$, $L_c = 40$ $\mu$m (AR = 8, by assuming the maximum contact length), Equation (3) yields the adhesion strength of $F_{sc} = 1.71$, 0.96, and 0.62 N cm$^{-2}$, respectively, for the corresponding micropillars with SR = 2–4. These values were comparable to experimental measurements of pristine micropillars, 1.78, 0.74, and 0.6 N cm$^{-2}$, respectively. However, this model failed to explain the increased adhesion with enlarged heads of the micropillars from particles embedding. The logical components for increasing $F_{sc}$ according to Equation (3) are the changes of work of adhesion and/or increasing contact length. However, since we use the same PUA materials and it is impossible to have contact length larger than the actual length of micropillar itself, then there is no way to increase the adhesion, theoretically. Therefore, this model is also invalid for our current system.

We then introduced a simple mathematical model based on interlocking adhesion of solid cylinders in the interweaving state. In this model, the adhesion force is purely generated from mechanical bending force required to separate interweaving solid cylinders. There are several assumptions made in this model to simplify the calculation. First, the particles embedded on the heads of micropillars are considered to be a repetitive arm to lock the micropillars during shear force application (see definition in Figure 4d). In this case, the arm length corresponds to the density and sizes of particles on the head of micropillars. Second, the particles embedded in polymeric micropillars are assumed to behave as a composite, where the elastic modulus is derived from the uniform distribution of particles filler in polymer matrix. From the Castiglano’s first theorem, the force to separate two interweaving solid cylinders is\textsuperscript{17,18}:

$$P = \frac{\pi^2 E_y I}{3} \left(\frac{L_2^2 R}{2} + L_2 L_1 + 2L_2 R^2 + R^2 L_1 + \frac{4\pi R^5}{4}\right)$$

(4)

Here, $P$ is the force required to separate interlocking cylinders, $\delta P$ is the deflection of micropillar during force application, $E_y$ is the effective elastic modulus, $I$ is the moment of inertia, $L_i$ is the micropillar height, $L_2$ is the arm length, and $R$ is the bent radius. Using this model, we are able to estimate the maximum adhesion strength in the current system with variation of embedded-particles sizes.

We hypothesize that $n$-layer of protrusions as large as the particle radius, $r$, in micropillar heads act as sequential interweaving states of interlocking adhesion with the total arm length, $L_2 = nr$. Although the apparent interlocking micropillars were shown in the interdigitated state (Figure 4c), the actual contact produced an interweaving state from particle protrusions. Our calculation showed that this model matched well with the adhesion behavior in our current system with 20% possible interdigitation of the total micropillars population. For example, in micropillars with AR = 6 and SR = 3, with the arrangement of particles shown in Figure 2, the number of particle layer is approximately 10, 5, and 3 $\mu$m from the tips for 100 nm, 500 nm, and 1 $\mu$m particles, respectively, giving the respective number of particle layer $n$ as 100, 20, and 6. Taking the 20% of theoretical values calculated in Equation (4), we obtained adhesion strength of 4.76, 18.1, and 41.4 N cm$^{-2}$ for micropillars embedded with particles of 100 nm, 500 nm, and 1 $\mu$m, respectively. These values were close to experimental ones, that is 6.1, 16.4, and 27.3 N cm$^{-2}$, respectively. The difference between experiments and theoretical values could be attributed to the presence of defects in micropillar arrays and non-uniform pre-loading during contact process, thus, substantially lowered the percentage of the interlocked pillars.

In addition, we investigated the shear adhesion strength with different AR and SR as a function of particle size. As seen from Figure 5, in most cases of variable particle sizes and SRs, the model matched well with the experimental measurements. We note that the theoretical values shown in Figure 5 were 20% of the values calculated from Equation (4). It should be noted that for all pillars with variable ARs and small SR of 2, the model over-estimated the adhesion strength. The observation agreed well with our previous estimation that the probability of interdigitation between two pillars of SR = 2 is very low.\textsuperscript{18} Nevertheless, even at low SR, the adhesion was enhanced by embedding particles in the micropillars.

4. Conclusion

Enhanced shear adhesion strength has been demonstrated between mechanically interlocked elastomeric micropillar arrays with embedded silica particle on the heads of the micropillars by more than an order of magnitude as compared to those without particles (e.g., 48.5 N cm$^{-2}$ vs.
The experimental data with several adhesion models have been compared in order to understand the adhesion mechanism. The calculation suggests that the interlocking adhesion model of solid cylinders with interweaving state matches well with the experimental results. The calculation and SEM images further show that approximately 20% of micropillars are engaged with each other in the interweaving state of the interlocking adhesion. This approach offers a new concept to design dry adhesives with strong adhesion for potential technological applications, including replaceable fastener and smart packaging.

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