

ENABLING CUT-RESISTANT SUPERHYDROPHOBIC SURFACES USING A HIGHLY ENTANGLED SOFT POLYMERIC SUBSTRATE

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ABSTRACT

This paper presents a novel idea to enable superhydrophobic (SHPo) surfaces with exceptional resistance to cutting while remaining soft and stretchable. For the first time, we achieve these unprecedented mechanical properties through strategic heterogeneous integration of a highly entangled polymeric substrate with a top layer of SU-8 micro-pillars. To realize resistance to cutting in soft materials, our innovation utilizes a polymer within which the entanglement outnumbered the crosslinks so that the cutting stress can be redistributed along the long polymer chains and to many other chains. We demonstrate the unique cut-resistant property of the highly entangled hydrogel, the integration of the hydrogel to fabricate SHPo surfaces, and water-repellency tests against cutting.

KEYWORDS

Cut-resistant, soft material, PDMS, highly entangled hydrogel, superhydrophobic.

INTRODUCTION

Flexible superhydrophobic surfaces have gained significant attention due to their ability to be easily laminated to diverse materials and enable them to have strong water repellency. Inspired by the natural structure of the lotus leaf, a common approach to the design of flexible superhydrophobic surfaces is to incorporate microstructures on elastic polymer substrates so that the surface structures provide water repellency [1] while the base material sustains mechanical stress like bending or compressing. However, these surfaces are prone to damage when facing sharp and rigid objects, such as a blade, and will, in turn, lose the SHPo properties. The loss of SHPo properties may originate from various causes:

(1) The microscale features providing water repellency may get destroyed by the sharp blade, leading to a transition from the Cassie-Baxter (suspended) state to the Wenzel (flooded) state [2];

(2) The polymer substrate is broken irreversibly and cannot maintain the orientation of the hydrophobic surface structures. This is common to many polymers, such as silicone which is stretchable yet has low toughness especially when amply crosslinked short chains are broken upon cutting.

Hence, the pursuit of superhydrophobic surfaces that are physically robust and mechanically durable, especially cut resistant is an attractive area of research.

As the design of SHPo surfaces with mechanical durability that resists cutting, several groups have developed superhydrophobic coatings that can either be repaired easily (by re-depositing low-energy coating) [3] or that are ‘self-healing/repairing’ that surfaces can restore repellency with little or no outside intervention, for example, allowed the migration of colloidal particles to repair damaged areas [4] or induced to release low surface energy agents and restore superhydrophobicity upon application of heat [5], or exposure to humid environments [6], or synthetic liquid-repellent surfaces that each consist of a film of lubricating liquid locked in place by a micro/nanoporous substrate [7], bearing the cutting force by randomly introducing discrete microstructures [8] or allowing cutting by sacrificing the upper layers of a self-similar structure [9] or fabricating nanostructures to impart water repellency and a microstructure to act as ‘armor’ to resist cutting [2].

DESIGN

Our approach to addressing the challenge of cut resistance of SHPo surfaces involves a fundamental shift in the substrate material, transitioning from silicone, with its densely crosslinked short chains that are prone to irreversible fracture and thus show low toughness, to polymers predominantly composed of highly entangled long chains [10]. We assume that the presence of a large number of entanglements would facilitate tension transmission between polymer chains [11], [12] and thus minimizing the cutting force applied on each polymer chain and enabling reversible, elastic deformation.

To apply this concept to SHPo surfaces, we integrate SU-8 microstructures on a highly entangled hydrogel substrate to render the surface superhydrophobic while providing cut resistance. Note that we use highly entangled polyacrylamide (PAAm) hydrogel as the model material for the substrate due to its proven attractive mechanical properties, including high toughness and strength [10]. The cut resistance property of a highly entangled hydrogel will first be verified so that we can use it as a substrate capable of withstanding cutting forces while maintaining its integrity to support SHPo surface structures.

A robust adhesion between SU-8 and PAAm hydrogel is critical in our design, but these two materials cannot form a covalent bond. Therefore, we will have to introduce an adhesive layer that can form a covalent bond with both SU-8 and PAAm. Here we use a modified PDMS as the adhesive layer. On one side, PDMS can achieve covalent bonding to SU-8 by chemical reactions. [13] Since SU-8 is an epoxy-based negative photoresist, the epoxy groups that remain on the SU-8 surface could be sufficient to react with the aminosilane molecules. Therefore, PDMS and SU-8 bonding can be realized by grafting (3-Aminopropyl) triethoxysilane (APTES) molecules on the PDMS surface and then brought in contact with SU-8 [13]. On the other side, PDMS can covalently crosslink with hydrogel polymers by introducing benzophenone [14] to overcome elastomers’ oxygen inhibition effect [15], [16]. The benzophenone also acts as an ultraviolet-assisted grafting agent for covalently crosslinking hydrogel polymers on elastomer surfaces. In summary, if we blend benzophenone in the PDMS pre-polymer solution, then the cured benzophenone-blended PDMS (*b*-PDMS) would be able to form covalent bond to both SU-8 and PAAm hydrogel.

EXPERIMENTS

To verify our assumption, we first investigated the cut resistance of different soft polymers by comparing their response to cutting. As shown in Figure 1, a highly entangled polyacrylamide (PAAm) hydrogel and a PDMS were placed under a sharp blade, and a cutting force of ~30 kg force was added vertically downward. After confirming the cut-resistant property of a highly entangled PAAm hydrogel, we started to fabricate the SHPo surface with an enhanced cut-resistance property by introducing a highly entangled hydrogel underneath the SU-8 microstructures.

A schematic of the process flow is presented in Figure 2. We selected SU-8 to form the hydrophobic surface structures because its microstructures can be easily obtained by photolithography. To enable SU-8 pillars to be released from a silicon wafer, we first did oxygen plasma to activate the surface and then spun coated 2.5 wt% Dextran (Sigma Aldrich 31387) aqueous solution at 1500 RPM for

30 seconds on the silicon wafer. The Dextran coated wafer was baked at 110 °C on a hot plate for 1 hour. After preparing the Dextran sacrificial layer, we patterned SU-8 (Kayaku, SU-8 2050) on it using photolithography to create SU-8 pillars with a diameter of 60 µm, height of 50 µm, and pitch of 100 µm.

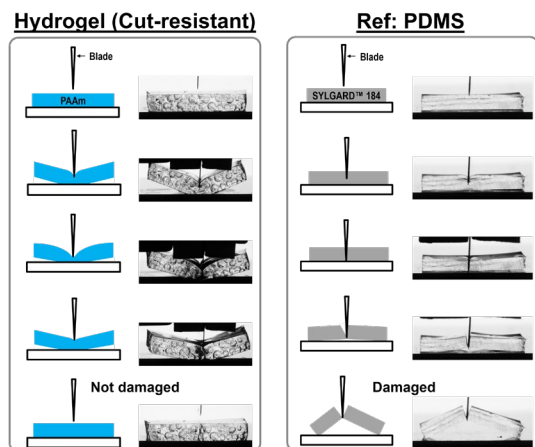


Figure 1: Comparison of the responses to cutting between a highly entangled hydrogel and a PDMS. A load of ~30 kg force was applied to the blade for both cases. (Left) The highly entangled hydrogel remained as one whole piece after cutting, showing resistance to cutting. (Right) PDMS was cut into two pieces.

To enable a robust integration of SU-8 microstructures on PAAm hydrogel, we coated a thin benzophenone-blended polydimethylsiloxane (PDMS) layer as the adhesive layer [17]. We mixed 10 wt.% benzophenone (Sigma Aldrich 427551) in ethanol solution with Part A of Sylgard™ 184 (Dow) thoroughly by the weight ratio of 1:10 and put it in an oven for 30 minutes to make sure the benzophenone was blended completely. After cooling down at room temperature, Part B of Sylgard™ 184 was added by the weight ratio of 1:10 to Part A. Because thin PDMS film was difficult to handle for transfer directly, we also needed a PDMS backing with little adhesion to facilitate thin PDMS film transfer. A 1-mm-thickness PDMS backing was synthesized by Sylgard™ 184 with a weight ratio of 10 to 1 of the base polymer solution (Part A) and curing agent (Part B). After mixing parts thoroughly and degassing under vacuum, PDMS was cured in an oven at 60°C for 2 hours. To allow thin PDMS film to be released from the PDMS backing, we vapor coated the PDMS backing with Trichloro(1H,1H,2H,2H-perfluorooctyl) silane (FOTS, Sigma Aldrich 448931) as the anti-adhesive coating. Once the backing was ready, we prepared the pre-polymer solution of *b*-PDMS as mentioned above and spun-coated it on the PDMS backing at 3000 RPM for 30 seconds, followed by curing it in an oven at 60 °C for 2 hours.

After fabricating the *b*-PDMS thin film with a backing, we needed to achieve permanent bonding between thin film and SU-8 microstructures. We did oxygen plasma treatment to the *b*-PDMS thin film, followed by dip coating in APTES solution (1 wt.% in water) for 20 minutes. Subsequently, we rinsed the surface with water several times and dried it using nitrogen gas. Finally, we brought the *b*-PDMS into contact with SU-8 pillars and baked the assembly at 110°C for 1 hour.

Separately, we need to prepare a PAAm pre-gel solution to form the highly entangled PAAm hydrogel. Acrylamide (AAM, Sigma Aldrich A8887), N,N'-methylenebisacrylamide (MBAA, Sigma Aldrich M7279), and 2-Hydroxy-4'-(2-hydroxyethoxy)-2-

methylpropiophenone (Irgacure 2959, Sigma Aldrich 410896) were used as the monomer, the crosslinker, and the photo-initiator. The deionized water was obtained from Milli-Q® IQ 7000. The monomer ratio of water to monomer, crosslinker to monomer, initiator to monomer was set to be 2, 8.0×10^{-5} , and 3.2×10^{-5} . Monomer and 0.1 M of crosslinker solution and 0.1 M of initiator solution in ethanol and water were mixed and sealed in a conical tube, vortexed for 5 seconds, and then stayed in an oven overnight to be dissolved completely without any bubbles.

To create a highly entangled PAAm substrate under the *b*-PDMS adhesive layer, the precursor was poured into a PDMS frame and covered with a glass slide. 365 nm UV light was irradiated for 6 minutes with an intensity of 45 mW/cm² to initiate the polymerization of the PAAm and hydrogel with high entanglement. Finally, the cut-resistant SHPo surface device was released by dissolving the Dextran sacrificial layer.

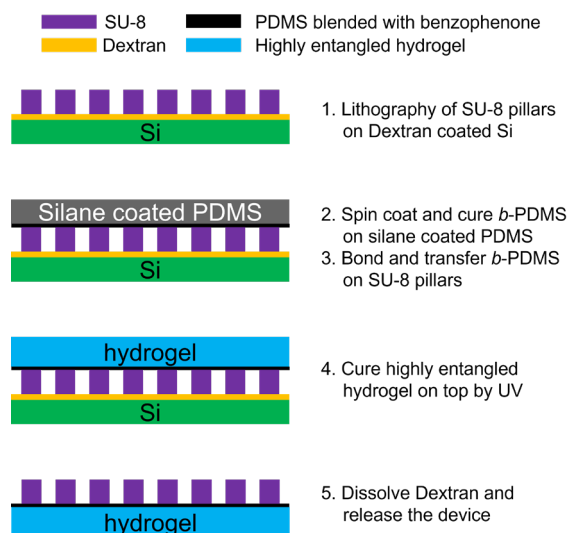


Figure 2: Process flow to fabricate a cut-resistant SHPo surface. SU-8 pillars were fabricated through traditional photolithography on a water-soluble Dextran layer coated on silicon. Then, these SU-8 pillars were covalently bonded to a PDMS thin film blended with benzophenone (*b*-PDMS). Next, a hydrogel pre-gel solution was poured on the *b*-PDMS film and crosslinked under UV. Last, the cut-resistant SHPo surface was released by dissolving the Dextran layer using water.

For a comparative study, we also constructed a SHPo surface with SU-8 pillars on a polydimethylsiloxane (PDMS) base. The SU-8 pillars were fabricated using the same method described above. The comparison/reference device was created by direct bonding of SU-8 pillars to a PDMS substrate grafted with APTES and then released by dissolving Dextran.

To evaluate the damage to the fabricated surfaces from cutting, we used the same setup for Figure 1 to apply cutting through a blade. The cutting blade was mounted to the stage, allowing vertical movement for cutting and releasing. Devices were inspected in a desktop SEM (Phenom XL G2) to visualize the damage from cutting. This will provide direct evidence on the cut resistance of different SHPo surfaces. To reveal the impact of the damage on the water repellency of the fabricated surfaces, we inspected the wetting state of water droplets on them before and after cutting. Particular focus was put on the interface where a Cassie state drop will allow lights to pass through the SU-8 microstructures.

RESULTS AND DISCUSSION

Figure 1 shows the comparison of the cut-resistant properties of smooth samples of highly entangled hydrogel and PDMS (Figure 1). Our results showed that the highly entangled hydrogel could not be cut under ~ 30 kg force while PDMS was cut into two pieces. The sharp blade could not cut into the highly entangled hydrogel but only squeezed and deformed it, indicating the high toughness of the PAAm hydrogel prepared. The presence of a thicker curled-up edge shown in Figure 1 (left) indicated that PAAm material was pushed from the cutting center to the edge. Additionally, compared to the PDMS sample, the cutting blade applied on the PAAm sample displayed a shorter displacement after contacting the material, demonstrating the integrity of the PAAm sample. Upon releasing the cutting stress, we could hardly find a cut trail left on the top PAAm surface, highlighting the high toughness and elasticity of the highly entangled hydrogel.

We believe that the reason for high-toughness performance was as follows. First, despite the sparse cross-links, the dense entanglements supplied the configuration of the polymer when the polymer was stretched or compressed, consistent with the prediction of the Lake-Thomas model [18]. Second, polymer chains were long enough due to the extremely low content of crosslinkers during fabrication and the strength of the molecular covalent bonds within polymer chains was significantly higher than that of hydrogen bonds and van der Waals forces, making them less prone to easy rupture. Third, water works as a low-viscosity lubricant between long polymer chains and provides hydrogen bonds to enhance the strength of the polymer. Consequently, the highly entangled PAAm hydrogel exhibited a high degree of elasticity and negligible hysteresis which could be easily recovered after rapid cutting. After the blade contacted the surface of the highly entangled hydrogel, the stress dissipated through the long polymer chains and entanglements rather than concentrating on defects caused by porosity.

In contrast, PDMS had much lower toughness compared to highly entangled hydrogels. Without additives and entanglements, the flexible chain structures made by silicone only provided van der Waals forces between the chains which were much smaller than hydrogen bonds in the hydrogel and could not avoid generating defects during curing. The cracks in PDMS induced by cutting easily propagate, resulting in the fracture of the entire PDMS surface. In the reference PDMS sample shown in Figure 1, the sharp blade could easily pierce (i.e., cut into) the bulk PDMS without causing significant deformation in the center or at the edge. The displacement of the blade was the same as the thickness of the PDMS pad, indicating that PDMS was cut through completely. Furthermore, upon releasing the blade, the PDMS pad broke into two pieces and moved upward with the trail of the blade due to the friction between the PDMS and the blade.

The top row of images in Figure 3 shows the as-fabricated cut-resistant SHPo surface with highly entangled PAAm hydrogel as the substrate and the reference SHPo surface with a PDMS substrate. After cutting, damaged trails were found on both surfaces. However, there is a stark difference between the two surfaces. On the hydrogel-based device, cuts were formed on the PDMS adhesion layer while both the SU-8 pillars, and the highly entangled PAAm substrate layer were kept mostly intact. Even though the adhesive layer of thin PDMS got broken, the SHPo topping maintained nearly the same morphology prior to cutting because of the high elasticity and cut resistance of the highly entangled hydrogel underneath.

In contrast, cuts on the reference PDMS-based device caused some of the SU-8 pillars to be removed from the surface where the craters of the missing SU-8 pillars indicated a cohesive failure of PDMS from cutting.

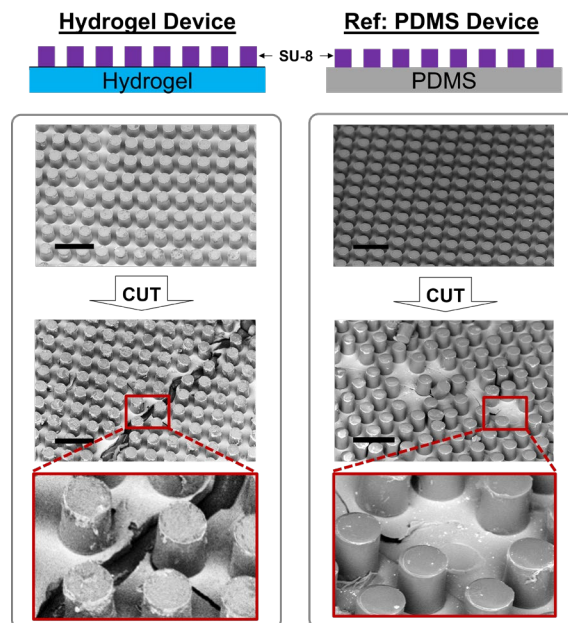


Figure 3: SEM micrographs of the cut-resistant SHPo surface made of a hydrogel substrate and the reference SHPo surface made of a PDMS substrate. Compared to the reference device where SHPo microstructures were damaged from cutting, microstructures on the hydrogel-based SHPo surface remained intact after cutting. The scale bar is 200 μm .

Figure 4 shows the water droplets deposited on the fabricated SHPo surfaces before and after cutting. For the SHPo surface with a hydrogel substrate, light could pass through the SU-8 pillars, indicating that the water droplet maintains the Cassie state. In contrast, the reference SHPo surface with a PDMS substrate showed a change of wetting state before and after cutting (Figure 4 right). Before cutting, the reference SHPo surface presented the same Cassie state as the other surface with light passing through. However, after cutting, light could no longer pass through the SU-8 pillars, indicating that it has transitioned to a Wenzel state. We also noticed the decrease in contact angles, which supports the fact of the transition from the Cassie state to the Wenzel state.

Damages from cutting on the SHPo surface with a PDMS substrate can be understood as follows: PDMS has much lower toughness compared to the highly entangled hydrogel. The huge difference between Young's Modulus of PDMS (~ 1.0 MPa) and SU-8 (~ 4.2 GPa) will lead to deformation mostly in the PDMS. Furthermore, since the covalent bond between SU-8 and PDMS was much stronger than bulk PDMS to itself [13], PDMS would not only fracture along with the cut direction but also experienced a shear fracture right beneath the SU-8 pillars when experiencing a rapid cut, forming circular concave features on the surface. This was evident by the corresponding SEM images shown in Figure 3.

CONCLUSIONS

We have presented a novel idea to enable superhydrophobic (SHPo) surfaces with exceptional resistance to cutting while remaining soft and stretchable. These unprecedented mechanical properties have been achieved by strategic heterogeneous integration of a highly entangled polymeric substrate with a top layer of SU-8 micro-pillars. We have demonstrated the unique cut-resistant property of the highly entangled hydrogel, the integration of the hydrogel to fabricate SHPo surfaces, and water-repellency

tests against cutting. We anticipate that this innovative approach will create new possibilities for the practical utilization of superhydrophobic (SHPo) surfaces.

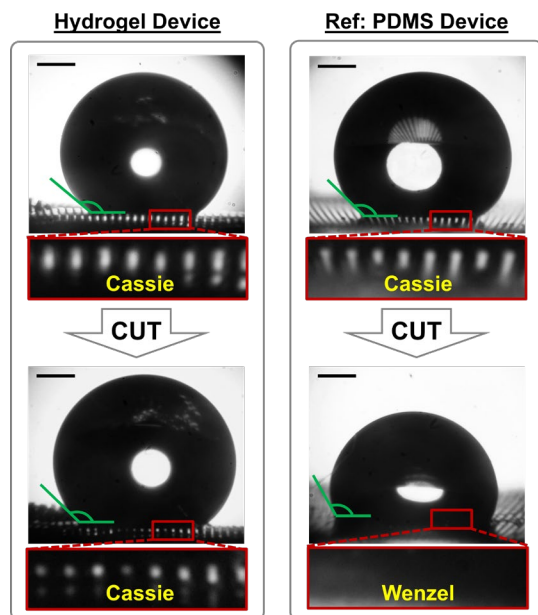


Figure 4: Comparison of water contact angle on cut-resistant SHPo surface and the reference SHPo surface. Water drops on the reference device were found to transition to a Wenzel state while our cut-resistant surface maintained a Cassie state. The scale bar is 500 μm .

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