

SHRINK-INDUCED SUPERHYDROPHOBIC SURFACES

L.R. Freschauf, J. McLane, H. Sharma, and M. Khine

University of California, Irvine, Department of Biomedical Engineering

ABSTRACT

Control of wetting properties has been investigated for applications in diverse fields, from microfluidics to contamination prevention. We present a robust, rapid, and reproducible superhydrophobic surface with hierarchical nano- and microscale structures molded into polydimethylsiloxane (PDMS). This method involves a purely structural modification free of chemical additives leading to its inherent consistency over time, thermal stress, and successive remolding from the same master mold. Because the mold is made from shrink-wrap film, it is compatible with large plastic roll to roll manufacturing and scale-up. Finally, selectively hydrophilic regions can be easily integrated into the superhydrophobic PDMS for novel microfluidics.

KEYWORDS: Superhydrophobic, Polydimethylsiloxane, Contact Angle, Sliding Angle

INTRODUCTION

Motivated by the properties of Nature's lotus leaf, superhydrophobic surfaces have become desirable because of their self-cleaning and water resistant properties. Normally achieved through structural [1,2] or chemical [3,4] alterations, superhydrophobicity allows for free movement of water across a surface due to its high contact angle and low sliding angle. Many fabrication techniques employ complex production methods such as photolithography [5,6], chemical vapor deposition [7], and self assembled monolayers [8] posing a time consuming and costly barrier. With a less intricate design, areas of study such as microfluidics and biomaterials could readily benefit from the properties of superhydrophobic surfaces. PDMS, a widely used polymer for sealing, coating, and microfluidics, has several valuable properties for our proposed application including thermal and chemical stability.

In this study, we present a rapid cast and mold method for creating superhydrophobic surfaces on PDMS. The superhydrophobicity is free of chemical alterations and achieves these properties through only structural modification. The molds are capable of recasting multiple superhydrophobic casts which are shown to retain their superhydrophobic properties for an extended period of time and range of temperatures. With this surface we further demonstrate the ability to induce temporary hydrophilic patterning on the surface, important for microfluidic applications.

THEORY

The surface tension created between water and a surface can be calculated with the use of Young's equation [9] where the three interfaces, solid-liquid, solid-vapor, and liquid-vapor, describe the resulting water contact angle (CA). In particular, as the liquid-solid surface tension increases, the CA increases due to less physical contact. According to Wenzel's theory [10], the so called roughness factor, determined by a ratio of the actual surface to the geometric surface, would cause a strong interaction between the liquid and solid phases. Thus water would fill the minute gaps created on roughened surfaces resulting in stronger interactions. However, another model was developed by Cassie and Baxter [11], where a heterogeneous surface is better described to create air pockets between the water and surface. This increase in liquid-solid surface tension is the primary key to the superhydrophobic phenomenon or lotus effect.

Superhydrophobicity is achieved when the CA exceeds 150° and the sliding angle (SA) is reduced to less than 10° . The minimal surface contact and ease of movement exhibited by water on superhydrophobic surfaces can be attributed to the creation of a heterogeneous surface containing nano- and microscale structures.

EXPERIMENTAL

By utilizing a novel shrink method, PDMS molds were made from shrink film, polyolefin (PO). A pretreatment with oxygen plasma was performed to temporarily increase the surface energy of the PO for better adhesion of metal, followed by a sputter coating of silver and gold. After the bimetallic coating, the film was heated to complete the shrinking process. This causes the stiffer metal to shrink and subsequently buckle, creating extremely rough, high aspect and multi-scale structures. Figure 1 depicts a brief process flow of this fabrication method paired with CA shots for each step.

The heterogeneous nano- and microstructures of the PDMS cast were analyzed using a scanning electron microscope (SEM) (Hitachi S-4700-2 FESEM) and a Keyence Digital Microscope (KDM) (Keyence VHX-100) shown in figure 2. These SEM images of the PDMS casts depict the roughness translated directly from the shrunk, bimetallic PO mold into the PDMS. Nanostructures can be seen on the surface of the microstructures of the PDMS leading to the enhanced hydrophobicity. Further visualization of morphology and height was achieved using the KDM displaying roughly a $70\mu\text{m}$ height range.

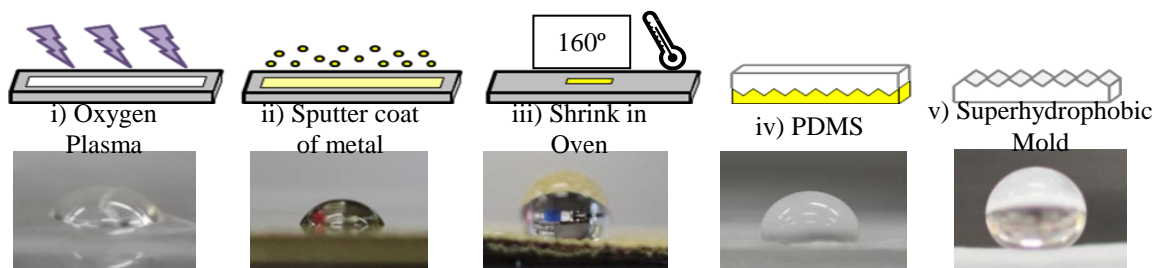


Figure 1: The process flow of the superhydrophobic PDMS casts formed from shrink film paired with their respective CA. i) PO film is plasma treated with oxygen for 30 seconds ii) Treated PO film is sputter coated with 60nm of silver and 60nm of gold iii) PO film is shrunk at 160°C iv) PDMS is poured over shrunken PO film for casting (paired photo features flat PDMS) v) Superhydrophobic PDMS cast is removed from shrunken PO.

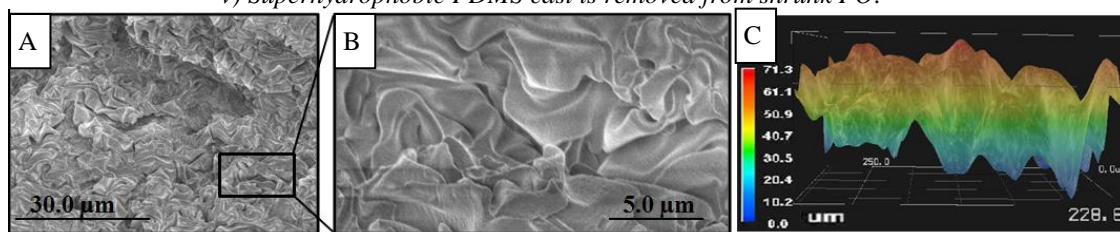


Figure 2: A) SEM image of the superhydrophobic nano- and micro- features in PDMS from a top down view, B) A magnified top down SEM view, C) A height profile taken with a KDM.

The superhydrophobic properties of the PDMS cast and flat PDMS were performed with CA and SA measurements. CA measurements were taken with a drop analysis program [12] within 1 day of separation of PDMS cast from the shrunken PO mold. A contact angle meter (Drop Shape Analysis System DSA100, KRUSS) was used to measure the CA again 4 weeks post fabrication. The SA measurements were performed using a tool clamp with a 90° rotational arm.

RESULTS AND DISCUSSION

With this method we were able to induce superhydrophobic properties on PDMS through a cast and molding method. The bimetallic layer deposited on the preshrunk PO mold provided the initial necessary mismatch in stiffness during the shrinking process to create highly structured features after shrinking is complete. When casted with PDMS, the bimetallic, shrunken PO mold transfers its physical shape. This produced heterogeneous roughening on the PDMS surface enhancing its natural hydrophobic properties. The resulting CA averaged above 150° with a maximum of 167° measured with the KRUSS system and the average SA was below 5° with a minimum of less than 2°. Figure 3 summarizes these findings compared to flat PDMS and figure 4 shows the low sliding angle. These CA measurements were taken 4 weeks post-fabrication and when compared to initial measurements taken within 24 hours we found a negligible difference (data not shown).

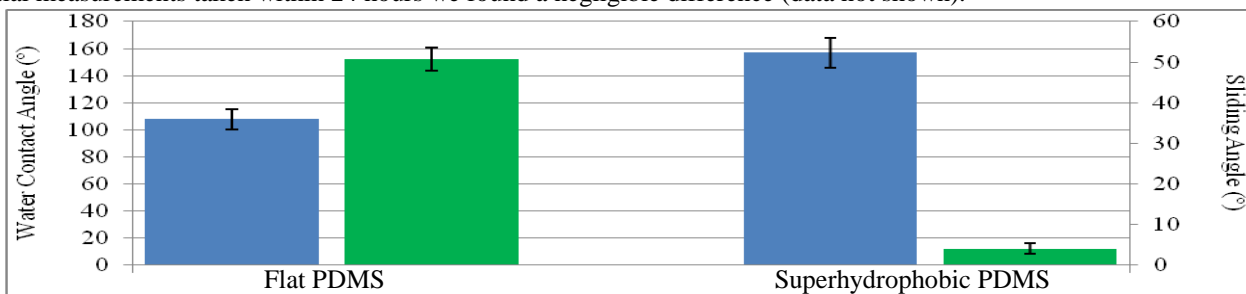


Figure 3: A graph depicting CA(blue) and SA(green) of flat PDMS(left) and our fabricated superhydrophobic PDMS(right).

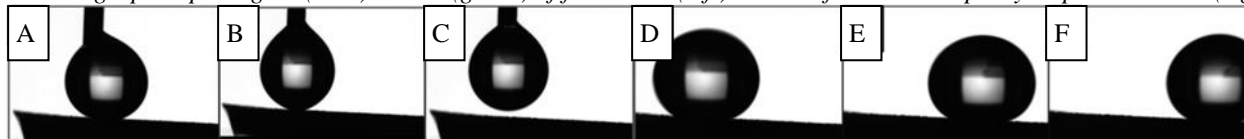


Figure 4: A-C) A droplet being placed on the surface retracts onto the dropper, D-F) A droplet rolling off the same surface immediately after placement at a 5° angle. This video can be viewed at <http://shrink.eng.uci.edu/index.html>.

The consistency of this method is due in part to the natural properties of PDMS and the method of our design. With our cast and mold method, the surface of the PDMS becomes superhydrophobic due to the highly intercut structures passed on from mold to cast. We found that over the course of three molds the CA remained consistently above 150° though the fourth mold dipped to about $148 \pm 7^\circ$ (data not shown). It should be noted, however, that the structures produced are heterogeneous

in design leading to some unavoidable variability in values. The thermal stability of these casts were also investigated and remained stable across a range of heat exposure from 25-100 °C. Samples were placed on a hotplate at 10°C intervals and allowed to acclimate to the indicated temperature over the course of 5 minutes with a 5 µL water droplet (data not shown).

In addition to superhydrophobicity, we were able to create temporary chemically induced hydrophilic patterning on the surface. This was performed using a post fabrication oxygen plasma treatment for 30 seconds through a negative mask made in house. The resulting section of PDMS is exposed to oxygen plasma which charges the surface of the PDMS and allows water to enter the rough structures on the surface. Figure 5 demonstrates this effect while exhibiting the retention of superhydrophobic regions protected by the mask against the oxygen plasma treatment.

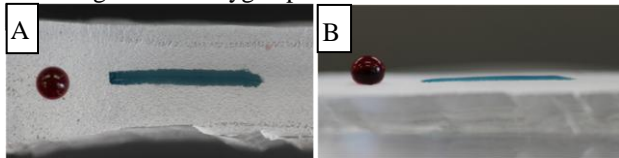


Figure 5: Selective oxygen plasma treatment results in temporary, patterned hydrophilic regions (shown with blue dye) while retaining superhydrophobicity (shown with red dye). A) A top down view, B) A profile view.

The ability to induce temporary hydrophilic channels presents the opportunity for these superhydrophobic PDMS platforms to be utilized in such methods as open channel microfluidics. The temporary nature of this hydrophilic channel also allows for the superhydrophobic PDMS platform to be used multiple times with different masking patterns.

CONCLUSION

Here we have presented a novel method of producing a superhydrophobic surface from PDMS with the use of a simple cast and mold method. This process is rapid, reproducible and yields tunable devices for creating hydrophilic regions on demand. By eliminating the need for chemical alterations to the surface, these superhydrophobic surfaces become much more robust due to the reliance solely on physical geometry at the surface. In addition, the inherent properties of PDMS as the casting material is practical because of its thermal stability, wide usage, and chemical inertness.

ACKNOWLEDGEMENTS

Special thanks to Anna Hoang of the Complex Fluids and Interfacial Physics laboratory at the University of California, Los Angeles for her aid in obtaining CA measurements. This work was supported in part by the Defense Advanced Research Projects Agency (DARPA) N/MEMS S&T Fundamentals Program under grant no. N66001-1-4003 issued by the Space and Naval Warfare Systems Center Pacific (SPAWAR) to the Micro/nano Fluidics Fundamentals Focus (MF3) Center.

REFERENCES

- [1] Q.F. Xu, J.N. Wang, K.D. Sanderson, "Organic-Inorganic Composite Nanocoatings with Superhydrophobicity, Good Transparency, and Thermal Stability," *ACS Nano*, vol. 4, pp.2201-2209, 2010.
- [2] H.Y. Erbil, A.L. Demirel, Y. Avci, O. Mert, "Transformation of a Simple Plastic into a Superhydrophobic Surface," *Science*, vol. 299, pp.1377-1380, Feb. 2003.
- [3] G.B. Gomez, L.M. Flendrig, J.M. Cooper, "Hysteresis and Reversibility of a Superhydrophobic Photopatternable Silicon Elastomer" *Langmuir*, vol. 26, pp.7248-7253, Feb. 2010.
- [4] D. Öner, T.J. McCarthy, "Ultrasuperhydrophobic Surfaces. Effects of Topography Length Scales on Wettability," *Langmuir*, vol. 16, pp.3453-3456, Jun. 2000.
- [6] S.S. Guo, M.H. Sun, J. Shi, Y.J. Liu, W.H. Huang, C. Combellas, Y. Chen, "Patterning of Hydrophilic Micro Arrays with Superhydrophobic Surrounding Zones," *Elsevier*, vol. 84, pp.1673-1676, Feb. 2007.
- [7] B. Cortese, S. D'Amone, M. Manca, I. Viola, R. Cingolani, G. Gigli, "Superhydrophobicity Due to the Hierarchical Scale Roughness of PDMS Surface," *Langmuir*, vol. 24, pp.2712-2718, Nov. 2007.
- [8] J. Genzer, K. Efimenko, "Creating Long-Lived Superhydrophobic Polymer Surfaces Through Mechanically Assembled Monolayers," *Science*, vol. 290, pp. 2130-2132, Dec. 2000.
- [9] J.S. Temenoff, A.G. Mikos, "Biomaterials: The Intersection of Biology and Materials Science," pp. 249-251, 2008.
- [10] R.N. Wenzel, "Resistance of Solid Surfaces to Wetting by Water," *Ind. Eng. Chem.*, vol. 28, pp. 988-994, Aug. 1936.
- [11] A.B.D. Cassie, S. Baxter, "Wettability of Porous Surfaces," *Faraday Soc.*, vol. 40, pp.546-551, Jun. 1944.
- [12] A.F. Stalder, T. Melchior, M. Müller, D. Sage, T. Blu, M. Unser, "Low-Bond Axisymmetric Drop Shape Analysis for Surface Tension and Contact Angle Measurements of Sessile Drops," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 364, no. 1-3, pp. 72-81, July 20, 2010.

CONTACT

L.R. Freschauf email:lfrescha@uci.edu