Time-Dependent Wetting Behavior of PDMS Surfaces with Bio-Inspired, Hierarchical Structures

Himanshu Mishra, Alex M. Schrader, Dong Woog Lee, Adair Gallo, Szu-Ying Chen, Yair Kaufman, Saurabh Das, and Jacob N. Israelachvili

ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.5b10721 • Publication Date (Web): 28 Dec 2015

Downloaded from <http://pubs.acs.org> on January 3, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

Time-Dependent Wetting Behavior of PDMS Surfaces with Bio-Inspired, Hierarchical Structures

Himanshu Mishra^{1,††}, Alex M. Schrader^{2,‡}, Dong Woog Lee², Adair Gallo Jr.³, Szu-Ying Chen², Yair Kaufman², Saurabh Das², Jacob N. Israelachvili^{2,4*}*

¹California NanoSystems Institute, University of California, Santa Barbara, Santa Barbara, CA 93106, USA

²Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, USA

³CAPES Foundation, Ministry of Education of Brazil, Brasilia – DF, 70.040-020, Brazil

⁴Materials Department, University of California Santa Barbara, Santa Barbara, CA 93106, USA

KEYWORDS

Biomimicry; Wettability; Superhydrophobic; Cassie-Baxter; Wenzel; Cassie-impregnated; Sand dollar

ABSTRACT

Wetting of rough surfaces involves time-dependent effects, such as surface deformations, non-uniform filling of surface pores within or outside the contact area, and surface chemistries, but the detailed impact of these phenomena on wetting is not entirely clear. Understanding these effects is crucial for designing coatings for a wide range of applications, such as membrane-based oil-water separation and desalination, waterproof linings/windows for automobiles, aircrafts, and naval vessels, and antibiofouling. Herein, we report on time-dependent contact angles of water droplets on a rough polydimethylsiloxane (PDMS) surface that cannot be completely described by the conventional Cassie-Baxter or Wenzel models or the recently proposed Cassie-impregnated model. Shells of sand dollars (*Dendraster excentricus*) were used as lithography-free, robust templates to produce rough PDMS surfaces with hierarchical, periodic features ranging from 10^{-7} - 10^{-4} m. Under saturated vapor conditions, we found that in the short-term (<1 min), the contact angle of a sessile water droplet on the templated PDMS, $\theta_{\text{SDT}} = 140^\circ \pm 3^\circ$, was accurately described by the Cassie-Baxter model (predicted $\theta_{\text{SDT}} = 137^\circ$); however, after 90 min, θ_{SDT} fell to 110° . Fluorescent confocal microscopy confirmed that the initial reduction in θ_{SDT} to 110° (the Wenzel limit) was primarily a Cassie-Baxter to Wenzel transition during which pores within the contact area filled gradually, and more rapidly for ethanol-water mixtures. After 90 min, the contact line of the water droplet became pinned, perhaps caused by viscoelastic deformation of the PDMS around the contact line, and a significant volume of water began to flow from the droplet to pores outside the contact region, causing θ_{SDT} to decrease to 65° over 48 h on the rough surface. The system we present here to explore the concept of contact angle time dependence (dynamics) and modeling of natural surfaces provides insights into the design and development of long- and short-lived coatings.

1. Introduction

Biomimicry translates design principles in nature to address technological and scientific challenges. For instance, a variety of textured coatings across the animal and plant kingdoms have evolved to prevent wetting, especially from water. Commonly observed examples in nature, including leaves of lotus, rose petals, and duck feathers, motivate the engineering of inexpensive non-wetting surfaces/coatings via biomimicry. While the simplest way to mimic the texture of a surface is to use it as a template for other materials, the structural and/or chemical fragility of naturally non-wetting surfaces prevents them from direct applications. As a result, micro-/nano-fabrication techniques have been employed to develop bio-inspired topographical features.¹⁻⁵

Here, we employed sand dollars (*Dendraster excentricus*) as robust templates for creating superhydrophobic polydimethylsiloxane (PDMS). Sand dollars are sea urchins (echinoderms) from the order *Clypeasteroidea*.⁶ As marine calcifiers, they crystallize striking endoskeletons (called ‘tests’) with interconnected porosity by precipitating aqueous Ca^{2+} , Mg^{2+} , and CO_3^{2-} species into magnesium-calcite (exact ionic concentrations vary with geographies and genomes).⁶ When the organism is living, tests are covered with fuzzy bristles that have finer cilia, which participate in locomotion, prevent biofouling, and help catch and ferry food to the centrally located mouth.⁶ In addition to the unique appearance of their flattened tests, some sand dollar larvae are known to asexually clone themselves under predatory threat.⁷ The sand dollar tests used in this study were nonliving and had no bristles. Electron microscopy of sand dollar tests revealed hierarchical features in the range of 0.1-100 μm , which is typical for topography-enabled hydrophobicity (**Figure 1**).^{8,9} The features appeared to be somewhat ordered, and thus potentially amenable to mathematical modeling. In addition to the hierarchical surface features,

the mechanical robustness of sand dollars inspired us to employ them as templates for PDMS; it would be quite difficult to fabricate such textures via microfabrication techniques.

Figure 1. Scanning electron micrographs of a typical sand dollar: (a) top view shows the repetitive, ordered topography, and (b) cross section of a sand dollar show the porosity of the test's center.

Indeed, various researchers have harnessed biomimicry to develop specific surface properties. For example, wings of beetles have inspired the darkest material in the visible and infra-red regime,¹⁰ butterfly wings (*Morpho aega*)¹¹ and the compound eyes of house flies¹² were used to create antireflection coatings via atomic layer deposition of alumina; biofouling-resistant

PDMS films were inspired by the *Nepenthes* pitcher plant,¹³ shark skins,¹⁴ and bristles of echinoderms;¹⁵ cell-infused sand dollars (*Clypeaster subdepressus*) were used as scaffolds for bone regeneration,^{16,17} and sea urchin bioskeletons have been exploited to create macroporous gold.¹⁸ Techniques of microfabrication have also been employed to create bio-inspired surfaces, however, non-orthogonal hierarchical features in three dimensions are very difficult to achieve and scale up.

2. Stability of Contact Angles on Rough Surfaces

When a liquid droplet is placed on a rough surface, a layer of air could be trapped between the liquid and the solid depending on the intrinsic contact angle, θ_o , and the surface texture. The resulting apparent contact angle, θ_r , or θ_{SDT} in the present work, depends on the real contact areas between the solid and the liquid, A_{LS} , and between the liquid and the vapor, A_{LV} . In these scenarios, theoretical models proposed by Cassie and Baxter¹⁹ (with trapped air) and Wenzel²⁰ (without trapped air) are often employed to described wetting behaviors. Further, for surfaces where the intrinsic contact angle of liquids, $\theta_o < 90^\circ$, pores *outside* the contact area can be partially filled at thermodynamic equilibrium – a state described by the Cassie-impregnated, or “hemi-wicking”,²¹ model.²²⁻²⁴ Using the sand-dollar-templated PDMS (henceforth referred to as SDT-PDMS), we present a time-dependent wetting behavior that at short times (~ 1 min) is accurately described by the Cassie-Baxter model, at intermediate times (~ 90 min) by the Wenzel model, and at long times (~ 48 h) qualitatively resembles the Cassie-impregnated state. Additional scenarios not accounted for in the Cassie-Baxter, Wenzel, and Cassie-impregnated models, such as cavity sizes that are non-negligible compared to the size of the drop, a non-constant droplet volume, surface deformations, and capillary condensation are addressed as well.

Figure 2 shows schematically the time-dependent wetting behavior of water on SDT-PDMS

(documented in detail in the Results and Discussion section), but the behavior is likely general to many natural, biomimetic, and engineered surfaces. If the initial Cassie-Baxter state is metastable, meaning that pores fill over time (from panel (a) to (b) and eventually to (c), see below), a single “static,” but metastable, contact angle can no longer accurately describe the equilibrium (thermodynamic) state or the dynamics of the system. For example, natural surfaces (such as rose petals²⁵ and sand dollars) contain micro- and nano-channels which serve as conduits for the flow of liquid, either into cavities beneath the droplet or outside the contact region (panel (c)). Furthermore, when a droplet rests on a surface, the unresolved normal component of the liquid surface tension might deform the surface viscoelastically, potentially causing pinning or drastic changes in the apparent (macroscopic) contact angle over time.²⁶ We found that when water droplets are applied to SDT-PDMS, these effects have substantial short-term and long-term effects on the contact angle.

Figure 2. Schematics illustrating the decrease in the contact angle of water on SDT-PDMS. (a) After 1 min on the surface, the drop has a contact angle of $\sim 140^\circ$. (b) After ~ 90 min, pores beneath the droplet have filled, producing a smaller contact angle and a larger contact diameter. (c) After 48 h, the contact line becomes pinned, and water flows from the droplet into the pores outside of the contact region, forming a Cassie-impregnated-like state and resulting in an even smaller contact angle.

3. Experimental Section

Formulation of sand-dollar-templated PDMS. The Dow Corning's Sylgard®184 silicone polymer and cross-linker were mixed for 10 min in a 10:1 ratio by mass and poured over

1
2
3 a water-rinsed and dried sand dollar test. After degassing the PDMS with a mechanical pump for
4
5 10 min, the sample was cured in a convection oven at 80 °C and ambient pressure for 1 h. After,
6
7 the SDT-PDMS chips were peeled off of the sand dollar template, rinsed with water, and used
8
9 for measurement.
10
11

12
13 **Contact angle studies.** With the exception of the advancing and receding studies, all
14
15 contact angle measurements were conducted in a hermetically sealed glass chamber saturated
16
17 with water vapor. Liquid droplets of 1 μL were gently placed on the surface and the needle
18
19 withdrawn prior to image capture. The advancing and receding measurements at a rate of 0.1-0.5
20
21 $\mu\text{L}/\text{min}$ were taken on a DataPhysics OCA 15Pro system using an automatic elliptical fitting
22
23 program.
24
25
26

27
28 **Water-immersion fluorescent confocal microscopy.** The SDT-PDMS was placed
29
30 underneath the objective lens of an Olympus FluoView 1000MPE confocal microscope and
31
32 roughly 1 mL of water was added in the gap. For observation purposes, the water was saturated
33
34 with fluorescein isothiocyanate (FITC - green), and the SDT-PDMS was doped with Rhodamine
35
36 B by soaking it in a saturated dye solution for 2 days. A number of images were taken at ~20
37
38 different focal planes from the bottom to the top of the features to confirm full pore filling.
39
40
41
42
43
44

45 46 **4. Results and Discussion**

47 48 **4.1 The topography of sand-dollar-templated PDMS**

49
50 PDMS (Dow Corning's Sylgard®184) was chosen as a model polymer because of its
51
52 extensive applications across natural and applied sciences. After peeling the SDT-PDMS chips
53
54 from sand dollar surfaces, analysis showed regular ring-like microscopic (10-100 μm) features
55
56
57
58
59
60

with convex edges decorated with smaller (0.1-10 μm) spherical hierarchical features (**Figure 3a, 3b**). The ring-shaped structures were separated from each other and organized in a somewhat hexagonal lattice. We considered that such a surface may give rise to high contact angles of water due to its texture and the intrinsic hydrophobicity of PDMS.

Figure 3. The sand-dollar-templated PDMS (SDT-PDMS) surface was approximated to be composed of circular rings arranged in a hexagonal lattice: (a) a zoomed-in scanning electron

micrograph of a carbon-coated SDT-PDMS surface at a 15° angle and its simplistic representation as a cylinder, (b) top view of SDT-PDMS illustrating the hexagonal arrangement of surface features, and (c) a schematic of our simplified SDT-PDMS model illustrating the regularity of the patterned surface.

4.2 Advancing and receding contact angle measurements

Indeed, SDT-PDMS surfaces exhibited superhydrophobicity. Droplets of water had an advancing contact angle of $\theta_{A,SDT} = 140^\circ \pm 5^\circ$ with a hysteresis of $\Delta\theta_{SDT} (= \theta_{A,SDT} - \theta_{R,SDT}) < 20^\circ$, where $\theta_{R,SDT}$ denotes the receding contact angle. Meanwhile, on a planar PDMS surface, water droplets had an advancing contact angle of $\theta_{A,o} = 113^\circ \pm 5^\circ$ with a hysteresis of $< 10^\circ$ (**Figure 4**). Arguably, advancing and receding liquid fronts on planar PDMS surfaces pass through contiguous low-energy barriers (i.e., the advancing contact angle remains close to the equilibrium contact angle) because the low roughness of the surface can be considered to be negligible, whereas on the surface of SDT-PDMS, the liquid front is pinned discontinuously (and asymmetrically sometimes) in response to both microscale and nanoscale features (**Movie S1**). To clarify the effect of topography on the wetting behavior, we studied evaporation of water on both planar PDMS and SDT-PDMS surfaces. We found that as water evaporated, the contact line of water on planar PDMS receded while the contact angle stayed constant, whereas on SDT-PDMS, the contact angle decreased while the contact line was pinned (**Figure S1**).

Figure 4. Advancing and receding contact angles for deionized, pH 6 water on SDT-PDMS and on planar PDMS using a constant volumetric flow rate of 0.5 $\mu\text{L}/\text{min}$ and a stainless steel needle with an outer diameter of 0.55 mm. Solid circles represent advancing measurements, and unfilled circles represent receding measurements. Advancing measurements began within 1 s of the water touching the surface, and receding measurements began immediately after advancing began and ended when the fitted contact angle began dropping sharply due to syringe needle effects (typically around droplet volumes $\sim 0.05\ \mu\text{L}$). Measurements at 0.1 and 0.3 $\mu\text{L}/\text{min}$ (not shown) gave very similar contact angles.

To measure the extent to which the surface texture of SDT-PDMS would prevent wetting, 1 min after the deposition of mixed water-ethanol droplets (0-100% by volume), contact angles, θ_{SDT} , were measured (**Figure 5**). We found that $\theta_{\text{SDT}} \geq 90^\circ$ for ethanol volume fractions up to $C_v = 60\%$ (surface tension $\geq 33\ \text{mN}/\text{m}$) (**Figure S2**), in comparison to a contact angle of $< 90^\circ$ on planar PDMS for $C_v > 10\%$.

Figure 5. Short-term contact angles of water-ethanol mixtures on (a) SDT-PDMS and (b) planar PDMS, and (c) the fraction of pores, p , on the SDT-PDMS which were fully filled, as calculated from our analytical model. Contact angles were measured 1 min after depositing a 1 μ L droplet and have characteristic error of $\pm 4^\circ$. At ethanol concentrations > 50 vol%, a significant fraction of the pores are filled within 1 min. The solid blue lines show predictions of the Cassie-Baxter ($p=0$) and Wenzel ($p=1$) models.

4.3 Model predictions

The apparent contact angle, θ_{SDT} , is determined by the ratios of the real liquid-vapor and liquid-solid areas (A_{LV} , A_{LS}) to the projected area (A_{P}) such that φ_{LV} ($=A_{\text{LV}}/A_{\text{P}}$), φ_{LS} ($=A_{\text{LS}}/A_{\text{P}}$), and θ_o (intrinsic contact angle, as conventionally defined by the Young equation) via the equation¹⁹

$$\cos(\theta_{\text{SDT}}) = \varphi_{\text{LS}}\cos(\theta_o) - \varphi_{\text{LV}}, \quad (1)$$

which can predict both metastable and stable contact angles; where $\varphi_{\text{LV}} + \varphi_{\text{LS}} \geq 1$, $\varphi_{\text{LV}} \geq 0$, and $A_{\text{LS,max}}/A_{\text{P}} \geq \varphi_{\text{LS}} \geq 0$. When all pores are fully filled with liquid, $\varphi_{\text{LV}} = 0$ and **Equation 1** reduces to the Wenzel equation, where φ_{LS} is typically denoted as r .

To understand how the texturing of SDT-PDMS affects its wettability, we used scanning electron microscopy (SEM) (**Figure 3 and S3**) to measure the key dimensions and distributions of features on the SDT-PDMS surfaces. We found the average inner and outer radii of the rings and the height to be 50, 70, and 20 μm , respectively. We ignored the surface areas of slopes and smaller hierarchical features in this model. Next, we assumed a hexagonal lattice of rings separated by a distance, $l = 20 \mu\text{m}$, as representative of the surface of SDT-PDMS. Some ring-shaped features can either be in a partially wetting state (Cassie), wherein the liquid remains at the top of the features, or in a fully wetting state (Wenzel). We approximated the fraction of pores fully filled with liquid, p , using a simple analytical model (detailed calculations and diagrams are presented in **Section S1** and **Figure S4**). Using the model SDT-PDMS surface, as shown in **Figure 3c**, the values for the partially filled state ($p = 0$) were calculated as $\varphi_{\text{LV}} = 0.66$ and $\varphi_{\text{LS}} = 0.34$, and the corresponding values for the fully filled state ($p = 1$) (**Figure S4**) were calculated as $\varphi_{\text{LV}} = 0$ and $\varphi_{\text{LS}} = 1.68$. Thus, to determine the fraction of fully filled unit cells,

1
2
3 p , we set $\varphi_{LV} = (1 - p) \times 0.66$ and $\varphi_{LS} = (1 - p) \times 0.34 + p \times 1.68$. When θ_o is known, p
4
5
6 can be determined as a function of θ_{SDT} .
7

8
9 The short-term (1 min) contact angle of water-ethanol mixtures is shown in **Figure 5**
10 along with fitted p values and predicted contact angles for $p=0$ (fully non-wetting) and for $p=1$
11 (fully wetting). As the surface tension of water-ethanol mixtures decreased with the increasing
12 ethanol content (**Table S1**), we intuitively expected for the fraction of filled pores to increase.
13
14 We found p to be zero for ethanol volume fractions $< 60\%$, but p increased at higher ethanol
15 volume fractions. Given the knowledge of the time dependence of θ_{SDT} (described below), we
16 infer that ethanol-water mixtures simply fill the pores *faster* than does pure water. It is worth
17 noting that the viscosity of ethanol-water mixtures increases up to $C_v \sim 60\%$ and decreases when
18 C_v exceeds 60% ,²⁷ which indicates that interfacial energies, rather than viscosity, dominate pore
19 filling kinetics in our ethanol-water studies. The short-term wetting scenario for low ethanol
20 concentrations would be represented schematically by **Figure 2a**, whereas higher ethanol
21 concentrations correspond to **Figure 2b**.
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

4.4 Effects of waiting time on the stability of contact angles

42
43
44 While investigating the time-dependence of contact angles, we noted that the apparent
45 contact angle of water on SDT-PDMS reduced from $\theta_{SDT} \sim 140^\circ$ to $\theta_{SDT} \sim 65^\circ$ after 2 days,
46 while no change was observed on planar PDMS (both were maintained under a saturated vapor
47 environment) (**Figure 6**); a similar decrease was observed with canola oil droplets (**Figure S5**
48 and **S6**). Such a dramatic reduction in the apparent contact angle could be a practical limitation
49 for textured surfaces that rely on metastable Cassie-states. We considered several possible
50
51
52
53
54
55
56
57
58
59
60

explanations, including (1) pore filling due to inertia/weight of the liquid or capillary condensation, (2) change in surface chemistries over time, (3) mechanical deformation of the triple-phase contact line due to an unresolved normal component of the surface tension of water, and (4) contact line pinning and subsequent reduction in droplet volume through flow of liquid into pores outside the triple-phase contact line.

Figure 6. Time-dependent changes in contact angles and droplet volumes of sessile water droplets on SDT-PDMS and planar PDMS over 3000 min (50 h). The contact angle on the surface of SDT-PDMS decreased from $\sim 140^\circ$ to $\sim 65^\circ$ while on the surface of planar PDMS it remained at $\theta_o = 102^\circ \pm 2^\circ$. Both surfaces were kept in the same chamber during the measurements.

Using fluorescently labeled water and PDMS, pore filling over 70 min was directly observed with fluorescent confocal microscopy (**Figure 7**). Within 4 min of droplet deposition, ~10% of the pore volume was filled with water, and after 70 min, ~60% was filled, essentially a transition from the wetting state in **Figure 2a** to that in **Figure 2b**. Note that the unit cell volume includes both the volume within the ring structures (the pores) and that within the connected valleys between pores. First, we consider the weight of the liquid drop as a potential cause for the filling. This invokes the concept of capillary length, which is the characteristic length scale where surface tension dominates over weight, given by $\lambda = \sqrt{\gamma/\rho g}$, where γ is the surface tension (72 mN·m⁻¹), ρ is the density of water (1000 kg·m⁻³), and g is the acceleration due to gravity (9.8 ms⁻²). For water, the capillary length is approximately 2.7 mm. Since the diameters of sessile droplets employed in these experiments were ≤ 2 mm, the prospect of a water drop filling air pockets due to its own weight is ruled out. However, capillary condensation, or vapor penetration, is a possibility, given the high degree of roughness of the SDT-PDMS surface; however, due to the intrinsic hydrophobicity of the PDMS, it is unlikely that pores would fill up primarily with condensate. The alternative mechanism to capillary condensation is liquid penetration, or flow of bulk liquid from the droplet into the pore. Confocal microscopy showed that once penetration of a given cavity was initiated, full filling was attained in <1 min, releasing large air bubbles, indicative of rapid filling from the liquid above (though not due to gravity), rather than condensation slowly filling the cavity below the droplet. Moreover, when the SDT-PDMS was allowed to sit in saturated vapor for 48 hr prior to droplet deposition, no difference was observed in the wetting behavior. From pore filling observations and from our model (**Section S1**), we can deduce that the fully filled wetting state is energetically favorable.

However, mechanisms in addition to the liquid penetration of pores beneath the droplet must be involved because this could only explain a decrease in θ_{SDT} down to 110° , the Wenzel limit (Section S1).

Figure 7. Images captured using fluorescent confocal microscopy at a representative focal plane, where pore filling is displayed over time. Green regions correspond to water, red to PDMS, and black to vapor. Pores and regions between pores which become filled are labeled with white arrows. Pores are indicated with dashed circles on the image taken 4 min after adding the water. For observation purposes, the water was saturated with fluorescein isothiocyanate (FITC - green), and the SDT-PDMS was doped with Rhodamine B by soaking in a saturated dye solution for 2 days. A number of images were taken at ~20 different focal planes from the bottom to the top of the features to confirm full pore filling, but are not shown here.

Although changes in the surface chemistry of PDMS²⁸ in contact with water could lead to a reduction in the contact angle, this seems unlikely because there is no change in the contact

angle of water on the planar PDMS (**Figure 6**). Moreover, the contact angle of sessile water droplets on perfluorotridecyltrichlorosilane (FDTS)-coated SDT-PDMS surfaces decreased in a similar fashion to the uncoated SDT-PDMS (**Figure S6 and S7, and SI Experimental Section**). We also consider that the unresolved vertical component of the surface tension of water at the triple-phase contact line might bend/flex topographical features on the SDT-PDMS, which could appear as a smaller apparent contact angle. In fact, researchers have recently observed mechanical deformations of the contact line formed between a silicone gel (CY52-276A/B, Dow Corning Toray) and glycerol that could explain our observations.²⁹ We observed this event on planar PDMS using optical profilometry (**Figure S8**), but on SDT-PDMS, this was difficult due to the roughness of the surface. It is likely that when a droplet is placed on the planar PDMS, which is elastic, the deformation forms within a fraction of a second and remain constant as long as the droplet is on the surface. In the case of the SDT-PDMS, the gradual pore penetration and spreading (see below) that occur may give rise to deformations which change over time. Lastly, fluorescent confocal microscopy and contact angle studies (**Figure S9**) showed that the contact line advanced during the first hour that the droplet was on the surface, and was pinned thereafter, perhaps caused by a deformation of the surface. Subsequently, water flowed from the droplet to areas *outside* of the contact region (**Figure 2c and S10**), resulting in a lower θ_{SDT} by a combination of pinning and a substantial loss of droplet volume. In the final state, when some surface cavities outside the droplet were filled with the liquid (i.e., the Cassie-impregnated-like state), the total volume of the liquid inside the cavities is not negligible compared to the droplet volume (Figure 6 shows a 80% decrease in droplet volume over 50 h). In fact, this violates the fundamental assumption of conservation of volume of the liquid drop (and negligible volume of cavities in comparison) on which all the aforementioned theoretical models are based.³⁰ Thus,

the apparent angle in the long-time regime might fall out of scope of any of the theoretical models. Bormashenko and co-workers recently investigated transitions from the Cassie to Wenzel and then to Cassie-impregnated state by vertically oscillating liquid drops on textured PDMS, polystyrene, polyethylene, and polyetherimide at frequency, $f = 36$ Hz and amplitude, $A = 1.1$ mm, and further claimed the Cassie-impregnated state to be the thermodynamic minimum.^{22,23} They proposed that the transition to the Cassie-impregnated state is only possible when the “local” angle²² (intrinsic angle, θ_0 , in the present work) is less than 90° ; however, external vibrations can transiently reduce the local angle. Because no such energy input was applied in our studies and θ_0 was larger than 90° , we concluded that θ_{SDT} at $t > 90$ min cannot be explained by the Cassie-impregnated model. We posit that the liquid drainage outside the droplet takes place via flow through the connected valleys between the pores, where microscale channels may act as conduits for the liquid. Flows in comparably sized channels have been directly observed and studied in detail for textured hydrophobic polymer surfaces,^{31,32} and including PDMS, but further discussion of the fluid dynamics is beyond the scope of this work. In summary, it appears that the primary mechanism by which the contact angle decreases occurs on two time scales (**Figure 2**): pore filling, which happens within ~ 90 min of droplet deposition, and pinning and volume drainage, which begins to occur thereafter and can presumably progress indefinitely.

5. Conclusions

We found that tests of sand dollars, which are hydrophilic by nature, could act as physically and chemically robust templates for imparting non-wetting topographical features to many thermally- or photo-setting polymer surfaces. This biomimicking approach is simple, quick, and inexpensive and elucidates how both topographical and chemical modifications can

be combined to engineer non-wetting materials; for example, SDT-PDMS exhibited contact angles $\geq 90^\circ$ for liquids with surface tensions ≥ 33 mN/m. Scanning electron microscopy of SDT-PDMS allowed us to develop a simple model, which agreed well between measured short-term contact angles and the predictions of the Cassie-Baxter and Wenzel equations. Next, we investigated the time-dependence of contact angles on soft polymeric surfaces. The apparent contact angle of water on SDT-PDMS decreased from $\sim 140^\circ$ to $\sim 65^\circ$ over the course of 2 days, while on planar PDMS no change in contact angle with time was observed. Our contact angle and confocal microscopy experiments indicated that a combination of pore filling beneath the droplet (**Figure 2b**) and contact line pinning followed by flow of liquid outside of the contact region (**Figure 2c**) are responsible for the decrease in the contact angle. The dramatic time-dependence is particularly surprising given that the intrinsic contact angle, θ_o , was larger than 90° . For rough surfaces where θ_o is less than 90° , one would expect qualitative and quantitative differences from the time-dependent behavior shown here, in particular that Equation 1 may no longer apply, as pores outside the contact region eventually become filled with condensate at thermodynamic equilibrium.³³ Lastly, if the volume of liquid within the pores is non-negligible compared to the droplet volume, none of the aforementioned models can be applied to fully describe the wetting behavior. The concepts of contact angle stability applied to this simple bio-inspired model system should provide insight for the design and development of durable omniphobic coatings.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information contains 10 additional figures, 2 tables, 1 movie, and derivations which elaborate upon arguments made succinctly in the manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*To whom correspondence should be addressed:

Dr. Himanshu Mishra: himanshu.mishra@kaust.edu.sa; Ph. 966-54-808-2110

Dr. Jacob N. Israelachvili: Jacob@engineering@ucsb.edu; Ph. 805-893-8407

Present Addresses

† Water Desalination and Reuse Center, Biological and Environmental Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

Author Contributions

‡These authors contributed equally.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by a grant from the Procter & Gamble Company. H. M. was funded by the Elings Prize Fellowship in Experimental Science of the California NanoSystems Institute at the University of California, Santa Barbara.

ACKNOWLEDGMENT

This work was supported by a grant from the Procter & Gamble Company. H. M. was funded by the Elings Prize Fellowship in Experimental Science of the California NanoSystems Institute at the University of California, Santa Barbara. We acknowledge the use of the NRI-MCDB Microscopy Facility at UC Santa Barbara, and we thank Dr. Mary Raven for assistance with confocal microscopy. The MRL Shared Experimental Facilities (used for SEM imaging) are supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network.

REFERENCES

- (1) Wen, L. P.; Tian, Y.; Jiang, L. Bioinspired Super-Wettability from Fundamental Research to Practical Applications *Angew. Chem., Int. Ed.* 2015, 54, 3387–3399.
- (2) Leslie, D. C.; Waterhouse, A.; Berthet, J. B.; Valentin, T. M.; Watters, A. L.; Jain, A.; Kim, P.; Hatton, B D.; Nedder, A.; Donovan, K.; Super, E. H.; Howell, C.; Johnson, C. P.; Vu, T. L.; Bolgen, D. E.; Rifai, A.; Hansen, A. R.; Aizenberg, M.; Super, M.; Aizenberg, J.; Ingber, D. E.. A Bioinspired Omniphobic Surface Coating on Medical Devices Prevents Thrombosis and Biofouling *Nat. Biotechnol.* 2014, 32, 1134–1140.
- (3) Grinthal, A.; Aizenberg, J. Mobile Interfaces: Liquids as a Perfect Structural Material for Multifunctional Antifouling Surfaces *Chem. Mater.* 2014, 26, 698–708.

- (4) Ebert, D.; Bhushan, B. Wear-Resistant Rose Petal-Effect Surfaces with Superhydrophobicity and High Droplet Adhesion using Hydrophobic and Hydrophilic Nanoparticles *J. Colloid Interface Sci.* 2012, 384, 182–188.
- (5) Ralston, E.; Swain, G. Bioinspiration-the Solution for Biofouling Control? *Bioinspiration Biomimetics* 2009, 4, 1–9.
- (6) Campbell, D. D. F. (2015) "Dendroaster excentricus" *Encyclopedia of Life*, available from <http://eol.org/pages/460427>. Accessed 15 Jan 2014.
- (7) Vaughn, D.; Strathmann, R. R. Predators Induce Cloning in Echinoderm Larvae *Science* 2008, 319, 1503.
- (8) Nosonovsky, M.; Bhushan, B. Biomimetic Superhydrophobic Surfaces: Multiscale Approach *Nano Lett.* 2007, 7, 2633–2637.
- (9) Chhatre, S. S.; Choi, W.; Tuteja, A.; Park, K. C.; Mabry, J. M.; McKinley, G. H.; Cohen, R.E. Scale Dependence of Omniphobic Mesh Surfaces *Langmuir* 2010, 26, 4027–2035.
- (10) Huang, J. Y.; Liu, C.; Zhu, Y.; Masala, S.; Alarousu, E.; Han, Y.; Fratalocchi, A. Harnessing Structural Darkness in the Visible and Infrared Wavelengths for a New Source of Light *Nat. Nanotechnol.* 2015, DOI: 10.1038/nnano.2015.228.
- (11) Huang, J. Y.; Wang, X. D.; Wang, Z. L. Controlled Replication of Butterfly Wings for Achieving Tunable Photonic Properties *Nano Lett.* 2006, 6, 2325–2331.
- (12) Huang, J. Y.; Wang, X. D.; Wang, Z. L. Bio-Inspired Fabrication of Antireflection Nanostructures by Replicating Fly Eyes *Nanotechnology* 2008, 19, 1–6.

- (13) Epstein, A. K.; Wong, T.-S.; Belisle, R. A.; Boggs, E. M.; Aizenberg, J. Liquid-Infused Structured Surfaces with Exceptional Anti-Biofouling Performance *Proc. Nat. Acad. Sci. U. S. A.* 2012, 109, 13182–13187.
- (14) Schumacher, J. F.; Carman, M. L.; Estes, T. G.; Feinberg, A. W.; Wilson, L. H.; Callow, M. E.; Callow, J. A.; Finlay, J. A.; Brennan, A. B. Engineered Antifouling Microtopographies - Effect of Feature Size, Geometry, and Roughness on Settlement of Zoospores of the Green Alga *Ulva Biofouling* 2007, 23, 55–62.
- (15) Epstein, A. K.; Hong, D.; Kim, P.; Aizenberg, J. Biofilm Attachment Reduction on Bioinspired, Dynamic, Micro-Wrinkling Surfaces *New J. Phys.* 2013, 15, 1–13.
- (16) Barreiro, A. M.; Recouvreux, D. O. S.; Hotza, D.; Porto, L. M.; Rambo, C. R. Sand Dollar Skeleton as Templates for Bacterial Cellulose Coating and Apatite Precipitation *J. Mater. Sci.* 2010, 45, 5252–5256.
- (17) Petite, H.; Viateau, V.; Bensaid, W.; Meunier, A.; de Pollack, C.; Bourguignon, M.; Ouidina, K.; Sedel, L.; Guillemain, G. Tissue-Engineered Bone Regeneration *Nat. Biotechnol.* 2000, 18, 959–963.
- (18) Seshadri, R.; Meldrum, F. C. Bioskeletons as Templates for Ordered, Macroporous Structures *Adv. Mater.* 2000, 12, 1149–1151.
- (19) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces *Trans. Faraday Soc.* 1944, 40, 546–551.
- (20) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water *Ind. Eng. Chem.* 1936, 28, 988–994.

- (21) Bico, J.; Thiele, U.; Quere, D. Wetting of Textured Surfaces *Colloids Surf., A* 2002, 206, 41–46.
- (22) Bormashenko, E.; Pogreb, R.; Stein, T.; Whyman, G.; Erlich, M.; Musin, A.; Machavariani, V.; Aurbach, D. Characterization of Rough Surfaces with Vibrated Drops *Phys. Chem. Chem. Phys.* 2008, 10, 4056–4061.
- (23) Bormashenko, E. Progress in Understanding Wetting Transitions on Rough Surfaces *Adv. Colloid Interface Sci.* 2015, 222, 92–103.
- (24) Boreyko, J. B.; Baker, C. H.; Poley, C. R.; Chen, C.-H. Wetting and Dewetting Transitions on Hierarchical Superhydrophobic Surfaces *Langmuir* 2011, 27, 7502–7509.
- (25) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal Effect: A Superhydrophobic State with High Adhesive Force *Langmuir* 2008, 24, 4114–4119.
- (26) Style, R. W.; Hyland, C.; Boltyanskiy, R.; Wettlaufer, J. S.; Dufresne, E. R. Surface Tension and Contact with Soft Elastic Solids *Nat. Commun.* 2013, 4, 1–6.
- (27) Khattab, I. S.; Bandarkar, F.; Fakhree, M. A. A.; Jouyban, A. Density, Viscosity, and Surface Tension of Water+Ethanol Mixtures from 293 to 323 K *Korean J. Chem. Eng.* 2012, 29, 812–817.
- (28) Delamarche, E.; Schmid, H.; Michel, B.; Biebuyck, H. Stability of Molded Polydimethylsiloxane Microstructures *Adv. Mater.* 1997, 9, 741–746 .
- (29) Style, R. W.; Boltyanskiy, R.; Che, Y.; Wettlaufer, J.S.; Wilen, L. A.; Dufresne, E. R. Universal Deformation of Soft Substrates Near a Contact Line and the Direct Measurement of Solid Surface Stresses *Phys. Rev. Lett.* 2013, 110, 066103-1–066103-5.

(30) Whyman, G.; Bormashenko, E.; Stein, T. The Rigorous Derivation of Young, Cassie-Baxter and Wenzel Equations and the Analysis of the Contact Angle Hysteresis Phenomenon Chem. Phys. Lett. 2008, 450, 355–359.

(31) Sbragaglia, M.; Peters, A. M.; Pirat, C.; Borkent, B. M.; Lammertink, R. G. H.; Wessling, M.; Lohse, D. Spontaneous Breakdown of Superhydrophobicity Phys. Rev. Lett. 2007, 99, 156001-1–156001-4.

(32) Peters, A. M.; Pirat, C.; Sbragaglia, M.; Borkent, B. M.; Wessling, M.; Lohse, D.; Lammertink, R. G. Cassie-Baxter to Wenzel State Wetting Transition: Scaling of the Front Velocity Eur. Phys. J. E: Soft Matter 2009, 29, 391–397.

(33) This assumes a supersaturated vapor environment, which is necessary to prevent evaporation of the droplet.

Table of Contents Entry

Sand-dollar-templated (SDT) PDMS is a simple, lithography-free surface. Shown is a droplet of water on the SDT-PDMS with an advancing contact angle, $\theta_{A,SDT} = 140^\circ$, and a scanning electron micrograph of a characteristic feature on the SDT-PDMS surface.