



Boiling Heat Transfer on Surfaces with Extreme Wettabilities

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REGENTS OF THE UNIVERSITY OF MICHIGAN

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Final Report

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Final Project Report: Boiling and Condensation on Surfaces with Extreme Wettabilities

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Summary of Achievements: This project has so far lead to 14 publications in high impact journals, as well as, widespread domestic and international popular press coverage. Many of these publications involved multiple collaborators from AFRL. One patent disclosure, that included collaborators from AFRL, was also filed. This patent has already been licensed out from the University of Michigan and is being commercialized. Results from this work have also been presented over 25 different invited talks. The project involved five undergraduate students, two graduate students and a postdoctoral research associate. Two of the major achievements from this project, development of some of the first ever self-healing durable superhydrophobic surfaces, and some of the first ever durable omniphobic surfaces, are discussed in detail below. A list of all 14 manuscripts published based on this work is provided in the end. 5 more publications based on this work are either submitted or in preparation.

Achievement 1: Development of Self-Healing Superhydrophobic Surfaces with Exceptional Mechanical Durability

One of the first requirements for developing surfaces that enhance boiling and condensation heat transport is the development of mechanically durable non-wetting surfaces. The last decade saw a drastic increase in the understanding and applications of superhydrophobic surfaces (SHSs). Water beads up and effortlessly rolls off a SHS due to its combination of low surface energy and texture. Whether being used for drag reduction, stain repellency, self-cleaning, fog harvesting or heat transfer applications (to name a few), the durability of a SHS is critically important. Although a handful of purportedly durable SHSs have been reported, there are still no criteria available for systematically designing a durable SHS. In the first part of this work, we discuss two new design parameters that can be used to develop mechanically durable SHSs via the spray

coating of different binders and fillers. These parameters aid in the rational selection of material components, and allow one to predict the capillary resistance to wetting of any SHS from a simple topographical analysis. We show that not all combinations of sprayable components generate SHSs, and mechanically durable components do not necessarily generate mechanically durable SHSs. Moreover, even the most durable SHSs can eventually become damaged. In the second part, utilizing our new parameters, we design and fabricate physically and chemically self-healing SHSs. The most promising surface is fabricated from a fluorinated polyurethane elastomer (FPU) and the extremely hydrophobic small molecule 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (F-POSS). A sprayed FPU/ F-POSS surface can recover its superhydrophobicity even after being abraded, scratched, burned, plasma-cleaned, flattened, sonicated, and chemically attacked.

Introduction

Superhydrophobic surfaces (SHSs) have garnered much attention over the last few decades for their ability to be self-cleaning,¹ drag-reducing,² stain-resisting³ and anti-fouling.⁴ By trapping pockets of air in their porous texture, SHSs display water contact angles $> 150^\circ$ and low roll-off angles.⁵ The design and optimization of such surfaces have been well studied.¹⁻¹⁷ However, most natural and artificial SHSs suffer from poor mechanical durability, as their fragile and porous surface texture can be easily removed even by the swipe of a finger.¹² Only a few SHSs have been reported to exhibit mechanical durability, as characterized by sand impact,¹⁸⁻²² rubbing with a soft cloth,^{3,23-25} tape peel tests^{7,19,26-28} or sandpaper abrasion.^{9,12,14-16,19,24,29-40} However, all such reports present single material systems. The development of design criteria to aid in the systematic fabrication of durable SHSs, generalizable to multiple chemistries or fillers, is

expected to be extremely useful to the field. In the first part of this work, we aim to develop such criteria.

Even the most durable SHSs will eventually become damaged by extreme or repeated mechanical abrasion, which damages their low surface energy and/or texture. SHSs that can regenerate their surface texture and chemistry,⁴¹⁻⁴³ akin to the lotus leaf's ability to regenerate its nano-structured wax,¹ would be highly desirable. Herein we also report mechanically durable SHSs that exhibit physical and chemical self-healing. The developed surfaces can fully recover their water-repellency even after being abraded, scratched, burned, plasma cleaned, flattened, sonicated and chemically attacked. These surfaces, and the design parameters used to develop them, may find immediate usage in a wide range of academic and industrial sectors across the globe.

Designing a Durable SHS: Chemistry and Miscibility

The lowest possible surface energy, γ_{SV} , is achieved with a monolayer of $-\text{CF}_3$ groups ($\gamma_{SV} \approx 6 \text{ mN/m}$).⁴⁴ Chemically grafting such monolayers requires specific substrate chemistry. Moreover, the thin monolayer only renders the uppermost surface hydrophobic, and any surface degradation will expose the higher surface energy material underneath. In contrast, the incorporation of highly perfluorinated compounds within a coating allows one to achieve equally low surface energies without the need for chemical grafting^{45,46}. Moreover, these unbound species can diffuse to the surface, restoring the low surface energy after mechanical or chemical attack (discussed later), and reducing the formation of hydrophilic defects upon damage.¹² Such coatings can be universally applied to any substrate, and impart low surface energy throughout the entire thickness of the coating. In this work, we fabricated a library of SHSs using sprayed

blends of polymeric binders and hydrophobic fillers. Due to its low surface energy, ($\gamma_{SV} \approx 10 \text{ mN/m}$), we primarily focus on systems incorporating 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (F-POSS),⁴⁵ although the developed design parameters are generalizable to other material systems, as shown here. Spray coating was chosen as the primary methodology for the application of the superhydrophobic coatings. Spray coating is inexpensive, scalable, and allows control over the surface energy and texture of our coatings via simple changes in experimental parameters.

As the fillers used in this work are soluble small molecules rather than non-deformable particles, they cannot induce texture directly. We observed the microscale texture formation during spray coating to be strongly dependent on the miscibility between the binder and filler components. Chemically similar blends yielded smooth, non-superhydrophobic coatings, but very chemically dissimilar blends yielded highly superhydrophobic, but mechanically fragile coatings (discussed below). This motivated the quantitative study of the miscibility, and its relation to durable superhydrophobicity.

The cohesive energy of any material species can be broken into its dispersive, polar, and hydrogen bonding Hansen solubility parameters, ($\delta_D, \delta_P, \delta_H$).⁴⁷ A miscibility sphere can be experimentally constructed for any compound, with its center at some point in a 3D space defined by these three solubility parameters, and its volume encompassing all good solvents and excluding all non-solvents. We determined the miscibility spheres for several hydrophobic fillers and a wide variety of binders (Figure 1a), by screening their solubility in a large number of solvents. The overlap between the Hansen spheres of the binder and filler is indicative of their chemical similarity, and the extent to which they phase separate and form texture during the

spray-coating process. In order to quantify a polymer's miscibility with the filler, we developed the miscibility parameter S^* , which is given as,

$$S^* = \frac{\Delta R - R_{binder} + R_{filler}}{2R_{filler}} \quad (1)$$

Here ΔR is the distance in 3D solubility space between the centers of the filler's sphere and the binder's sphere, with their radii denoted by R_{filler} and R_{binder} , respectively.

Similar to Hansen's Relative Energy Difference⁴⁷ value, S^* is defined such that the filler is completely immiscible with a binder when the two spheres do not overlap ($S^* > 1.0$, also see schematic in Figure 1a). Alternately, binders with $S^* < 0$ have solubility spheres that completely encompass the filler's sphere, and are hence fully miscible (at a given concentration, see Figure S5). In between these two extremes is the regime of partial miscibility, which turns out to have far-reaching consequences for the sprayed superhydrophobic surface's durability.

The S^* parameter allows one to predict if the filler will phase separate from the binder during spray coating. This phase separation manifests in the sprayed surface's root-mean-squared roughness, S_q . For example, we determined the solubility spheres for a polyurethane and an epoxy, which are both commonly used hydrophilic adhesives. For the epoxy, $S^* \approx 0.2$ with F-POSS, and an epoxy+5wt% F-POSS blend, when sprayed, resulted in a smooth surface with $S_q = 0.8\mu\text{m}$. Conversely, for the polyurethane, $S^* \approx 1.6$, and a polyurethane+5wt% F-POSS blend, when sprayed in the exact same manner, resulted in a very rough surface ($S_q = 41\mu\text{m}$). Thus, immiscibility alone can induce roughness during the spray coating process. However, a large S_q does not guarantee superhydrophobicity.⁴⁸

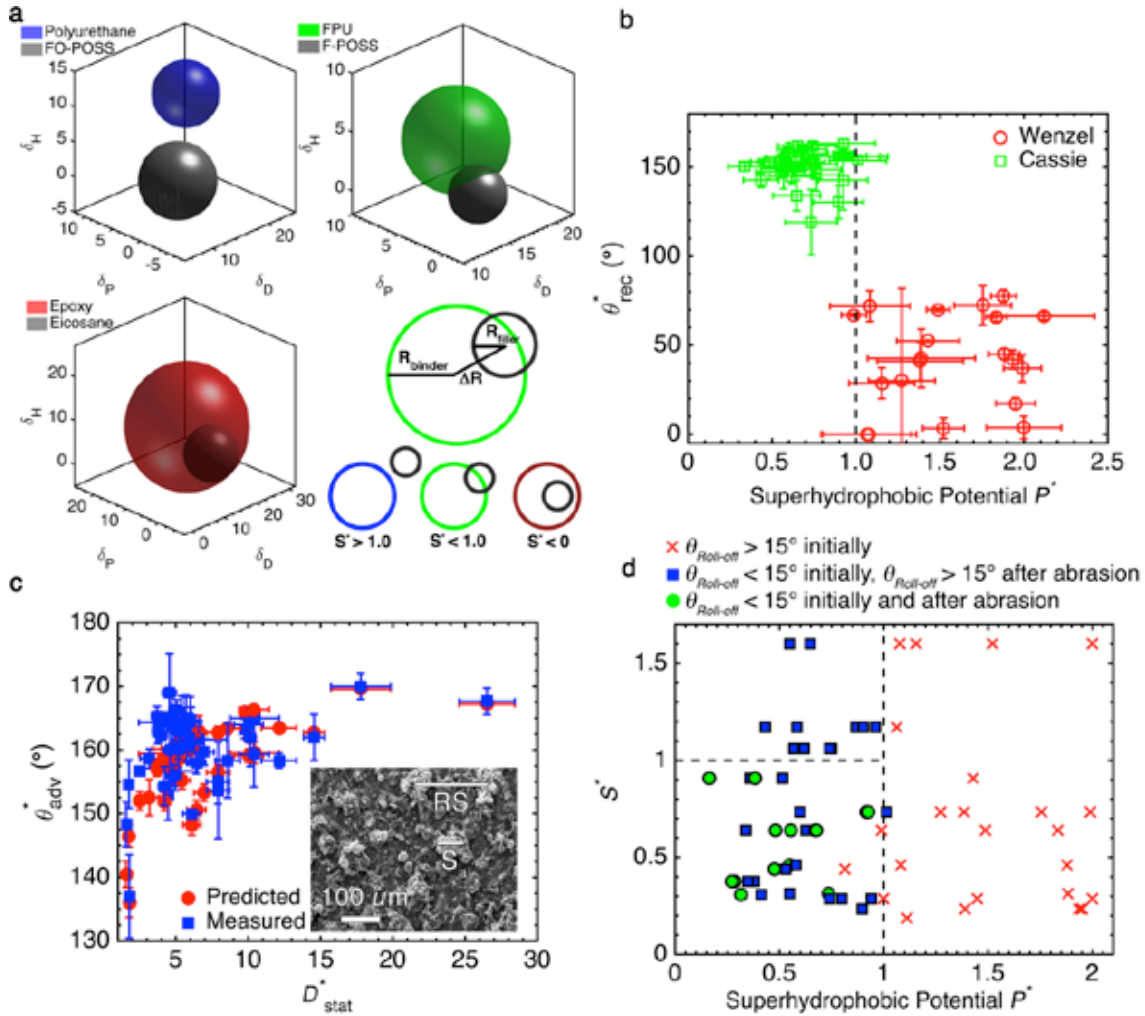


Figure 1: Designing SHSs. **a**, Visualization of the S^* parameter for three binders in 3D Hansen space. FO-POSS: fluorooctyl polyhedral oligomeric silsesquioxane. FPU: fluorinated polyurethane. F-POSS: fluorodecyl polyhedral oligomeric silsesquioxane. **b**, The apparent receding contact angle *versus* the P^* parameter. The sharp transition at $P^* = 1.0$ denoted an Young's contact angle of 120° . **c**, Measured and predicted apparent advancing contact angles *versus* the developed statistical porosity parameter. This plot includes all the different systems from Table 1. The inset shows an SEM micrograph of the FPU/F-POSS sprayed surface, with representative RS_m and S_{al} values indicated. **d**, A Phase diagram for all the surfaces sprayed developed in this work (see Table 1). Only surfaces with $P^* < 1.0$ can be superhydrophobic ($\theta_{Roll-off} < 15^\circ$, $25 \mu\text{L}$), and additionally only surfaces with $0 < S^* < 1.0$ can be mechanically durable ($\theta_{Roll-off} < 15^\circ$ after 100 abrasion cycles). The non-SHS that exhibited $P^* < 1.0$ was a blend of FPU/FO-POSS. For this blend, $\theta = 91^\circ$, although the sprayed texture required $\theta_c = 114^\circ$. This is an example where the texture is sufficient to produce a SHS, but the chemistry does not exhibit low enough surface energy.

Designing a SHS: Surface Texture

Water on SHSs can exist in the Cassie-Baxter state, in which air pockets are trapped in the surface's porous texture.⁴⁹ However, water can displace these air pockets, leaving the surface in a wetted, Wenzel state.⁵⁰ SHSs should ideally be designed such that the Cassie-Baxter state is energetically preferred.¹ We developed a method to predict when the Cassie-Baxter state would be energetically favorable over the Wenzel state using only the topographical statistics of a given surface. Because each binder/filler combination exhibited a distinct, characteristic surface morphology, we wished to develop universal metrics that characterize surfaces with widely varying topographies. To do so, we measured three statistical surface properties (methods): peak periodicity, RS_m , auto-correlation length, S_{al} , and Wenzel roughness, r (the ratio of the actual surface area to its projected area).⁵⁰ RS_m represents the length along the surface between large surface features, and can be thought of as the center-to-center distance between texture elements.⁵¹ S_{al} denotes the length at which a surface no longer exhibits self-similarity, and can be thought of as the average size of the largest texture features. We, therefore, can define the statistical porosity D_{stat}^* of the surface as (inset, Figure 1c),

$$D_{stat}^* = (RS_m / S_{al})^2 \quad (2)$$

where the second power is added to convert from properties measured along one-dimensional height profiles to the porosity of a two-dimensional surface.¹¹ Larger values of D_{stat}^* indicate surfaces with higher porosity.

For the Cassie-Baxter state to be favored over the wetted, Wenzel state, it must be the global energy minimum.⁵² For a given surface topography, the free energies of the two states can be balanced. The non-wetted state is energetically preferred only if the Young's contact angle of the material, θ , exceeds a critical value, θ_c . This critical Young's contact angle is given by

$\cos \theta_c = (\phi_s - 1) / (r - \phi_s)$,⁵² where ϕ_s is the fraction of solid in contact with water (note $D_{stat}^* \approx \phi_s^{-1}$). Stated differently, recalling that Young's water contact angles cannot exceed 120° even on a fully perfluorinated monolayer,¹⁰ there exists some minimal texture that any surface, regardless of surface chemistry, must exhibit in order to achieve an energetically favorable Cassie-Baxter state. Substituting this maximum contact angle as θ_c yields,

$$\cos \theta_c = \cos 120^\circ = (1 / D_{stat}^* - 1) / (r - 1 / D_{stat}^*)$$

or

$$-0.5 = (1 - D_{stat}^*) / (r D_{stat}^* - 1)$$

We can then define a surface's superhydrophobic potential, P^* , such that only for values of $P^* < 1.0$ is the Cassie-Baxter state the global energy minimum. Doing so yields

$$P^* = 2(D_{stat}^* - 1) / (r D_{stat}^* - 1). \quad (3)$$

For any surface that exhibits $P^* > 1.0$, the wetted state is energetically preferred, regardless of surface chemistry. Note that water can exist in a metastable Cassie-Baxter state through the addition of re-entrant texture,¹⁰ and hence a value of $P^* > 1.0$ does not necessarily indicate wetting. P^* is useful because surfaces are often created with a given topography, and then subsequently rendered superhydrophobic by applying a low surface energy layer on top.¹ As such, measuring P^* allows one to determine *a priori* if such a surface will become superhydrophobic before applying such a (often expensive) low surface energy monolayer. Moreover, if a surface is superhydrophobic in spite of a $P^* > 1.0$ value, one can say with certainty that water will exist in a metastable state, and such a surface should be used with caution. By measuring the dynamic contact angles on many surfaces, both wetted and non-wetted, we probed the effectiveness of P^* .

When water initially advances on a SHS, it displays a maximum apparent contact angle, θ_{adv}^* .⁵³ If any texture elements become wetted, the apparent angle at which water recedes, θ_{rec}^* , will decrease. Thus, θ_{adv}^* is a measure of the SHS's inherent porosity (*i.e.* fraction of air pockets), ignoring how stable the air pockets may be, and θ_{rec}^* gives an indication of their stability.⁵⁴ We measured θ_{rec}^* for more than fifty combinations of F-POSS and various polymeric binders, as a function of P^* (Figure 1b). These binders included both crosslinked networks, such as different urethanes, acrylates, epoxies, and cyanoacrylates, as well as linear polymers such as polystyrene, polymethylmethacrylate and polyisobutylene (methods, Table 1). We observed a high θ_{rec}^* only for systems with a stable Cassie-Baxter state, *i.e.* $P^* < 1.0$. This was confirmed by the sharp jump in θ_{rec}^* at a value of $P^* = 1.0$. The specific value of $P^* = 1.0$, corresponding to an Young's contact angle $\theta \approx 120^\circ$, indicated that all the surfaces had a high percentage of F-POSS at the solid-liquid interface, although there were vast differences in topography. Thus, we were able to predict if an F-POSS-containing surface could be superhydrophobic solely by measuring P^* . Without measuring P^* , there is no easy way to determine if a randomly textured surface has the potential to become superhydrophobic, *a priori*. Moreover, for surfaces with $P^* < 1.0$, recasting the Cassie-Baxter relation⁴⁹ in terms of D_{stat}^* effectively predicted θ_{adv}^* (Figure 1c). We observed that the predictive power of D_{stat}^* and P^* extended to other SHSs not containing F-POSS. These SHSs included polymer blends with other hydrophobic fillers like eicosane, octa-isobutyl POSS (IB-POSS) and fluoro-octyl POSS (FO-POSS), as well as other SHSs such as three commercially available superhydrophobic formulations, lithographically fabricated microstructures,⁵⁵ textured metals treated with self-assembled monolayers^{56,57} and binders filled with hydrophobic

particles.⁵⁸ As such, the design parameters developed in this work are applicable to SHSs produced using a wide range of binders, fillers, and fabrication techniques.

For each binder (fixed S^*), we varied P^* by adjusting the amount of hydrophobic filler in the blend. Combining the S^* and P^* parameters allowed us to construct a phase diagram for the different possible surfaces created when spraying the binder/filler blends (Figure 1d). Here we denote surfaces with a red $\times$ when the water roll-off angle was $\theta_{\text{Roll-off}} > 15^\circ$ (not superhydrophobic), and surfaces that exhibited $\theta_{\text{Roll-off}} < 15^\circ$ (superhydrophobic) as blue squares. These two regions were demarcated by a line at $P^* = 1.0$, *i.e.* we never observed a SHS for which $P^* > 1.0$.

Low surface energy species are known to preferentially migrate to the solid-air interface.⁵⁹ For binders with $S^* > 1.0$, the final surface was always very mechanically weak, with a powdery consistency, because the filler was completely immiscible with such binders. Green circles in Figure 1d denote surfaces that remained superhydrophobic after mechanical abrasion (discussed below). These mechanically durable SHSs were only observed when a binder exhibited partial miscibility with the filler ($S^* < 1.0$), *i.e.* we never observed a durable SHS with $S^* > 1.0$. Finally, we note that increasing the amount of filler within a sprayed blend was not always efficacious. As the binder can be much more mechanically resilient than the filler molecules, any excess filler within the blend, beyond what is required to achieve superhydrophobicity ($P^* < 1.0$), can lower the overall durability. For example, a perfluorinated polyether, PFPE, with 25wt% F-POSS remained superhydrophobic after abrasion, but PFPE with 35wt% F-POSS did not, although the S^* and P^* values were equivalent. Overall, choosing

components that satisfy $S^* < 1.0$ helps ensure that the final surface will be durable, and choosing a sufficient filler content such that $P^* < 1.0$ assures that the surface will be highly water repellent.

Durability of SHSs: Mechanical Abrasion

We utilized the industry standard of rotary Taber abrasion to evaluate the mechanical durability of our sprayed binder/filler blends. The stresses generated by Taber abrasion can be found using a cylinder-cylinder Hertzian contact mechanics analysis.⁶⁰ Depending on the elastic modulus of the coating, the exerted shear stress ranges from tens to hundreds of kPa (Figure 2a). Considering the porosity of the surface, the texture elements experienced shear stresses on the order of a few MPa. This is similar or greater than the less systematic durability characterization techniques employed in the literature.^{9,12,14-16,19,24,29-40} For example, in a recent report,¹⁶ the authors' durable SHS was abraded with sandpaper along a total length of 800 cm, without degradation of high contact angle. We reproduced such an evaluation for our FPU/F-POSS blend, which maintained high contact angles, as well as low roll-off angles, even after 1 kilometer (100,000 cm) of abrasion using the same sandpaper and applied load (Figure 2b). Thus, we have good confidence in claiming that the surfaces created in this work can also withstand the other metrics of mechanical durability reported elsewhere.

One hundred Taber abrasion cycles sufficiently differentiated durable and non-durable SHSs, *i.e.* non-durable surfaces were either completely removed, or water wet the remaining coating, after 100 abrasion cycles. Only surfaces that exhibited $\theta_{\text{Roll-off}} < 15^\circ$ after 100 abrasion cycles are shown as green circles in Figure 1d. All such surfaces exhibited partial miscibility with the hydrophobic fillers ($0 < S^* < 1.0$). We then continued Taber abrasion of our partially

miscible blends (Table 1). We compared the durability of these systems to three commercially available, and purportedly durable, SHSs (Figure 2c). None of the commercial coatings maintained a low $\theta_{\text{Roll-off}}$ after 100 abrasion cycles. We extended the abrasion testing of our binder/filler blends exhibiting $S^* < 1.0$ and found them to be quite resilient to mechanical wear (Figure 2d). Whereas all other evaluated SHSs became wettable within 100 abrasion cycles, the non-wetting properties of our surfaces endured significantly longer. When blended with F-POSS, coatings incorporating the PFPE, SF-100 and FPU binders remained superhydrophobic for up to about 400, 500, and 800 Taber abrasion cycles, respectively. Combinations of the polyurethane Desmophen 670BA and IB-POSS, or the FPU and FO-POSS, both exhibited $\theta_{\text{Roll-off}} < 15^\circ$ for ~800 cycles. In fact, all such systems only became wettable once almost the entire coating was abraded away. For example, a 100 μm -thick FPU/F-POSS coating maintained $\theta_{\text{Roll-off}} < 15^\circ$ even when $> 90 \mu\text{m}$ of its thickness was removed. Note that the coating mass loss was not linear with the number of abrasion cycles – large aggregates were removed first. Abrasion of smooth FPU/F-POSS blends and other partially miscible systems ($S^* \approx 0.4 - 0.9$), deposited by alternate means (methods), confirmed that the abrasion process did not induce superhydrophobicity ($P^* \approx 1.3 - 1.9$ after abrasion, see Figure S3). Rather, only the SHSs fabricated from partially miscible components maintained $P^* < 1.0$ (Figure 2d) during abrasion, whereas fully miscible ($S^* < 0$) and fully immiscible ($S^* > 1.0$) systems did not.

As further proof that partial miscibility is required for mechanically durable SHSs, we chain extended the FPU by incorporating propylene glycol into the crosslinked network (methods). The chain-extended FPU exhibited a three-fold increase in elastic modulus, and a 12% reduction in mass loss during abrasion of the smooth binder (no F-POSS), as compared to

unmodified FPU. However, the increased number of urethane linkages altered the Hansen sphere for the crosslinked network, changing the miscibility with F-POSS from $S^* \approx 0.6$ to $S^* \approx 1.1$. As such, whereas a sprayed blend of FPU+15wt% F-POSS ($P^* = 0.48$) remained superhydrophobic after 800 abrasion cycles, a sprayed blend of the chain extended FPU+15wt% F-POSS ($P^* = 0.56$) was no longer superhydrophobic after only 100 abrasion cycles (Figure 2d). This counterintuitive result emphasizes the fact that the binder with the correct miscibility ($0 < S^* < 1.0$), not the most mechanically durable binder, can yield the most mechanically durable SHSs. Moreover, the blend of FPU/F-POSS also withstood a host of other potentially damaging exposures (methods). After ultrasonication, a fluoro-solvent rinse, acid and base submersion, knife scratching (Movie 3), accelerated weathering, ultraviolet exposure and being held at 350 °C for 3 days, the coating always maintained $\theta_{\text{Roll-off}} < 10^\circ$ (methods, Figure 2b).

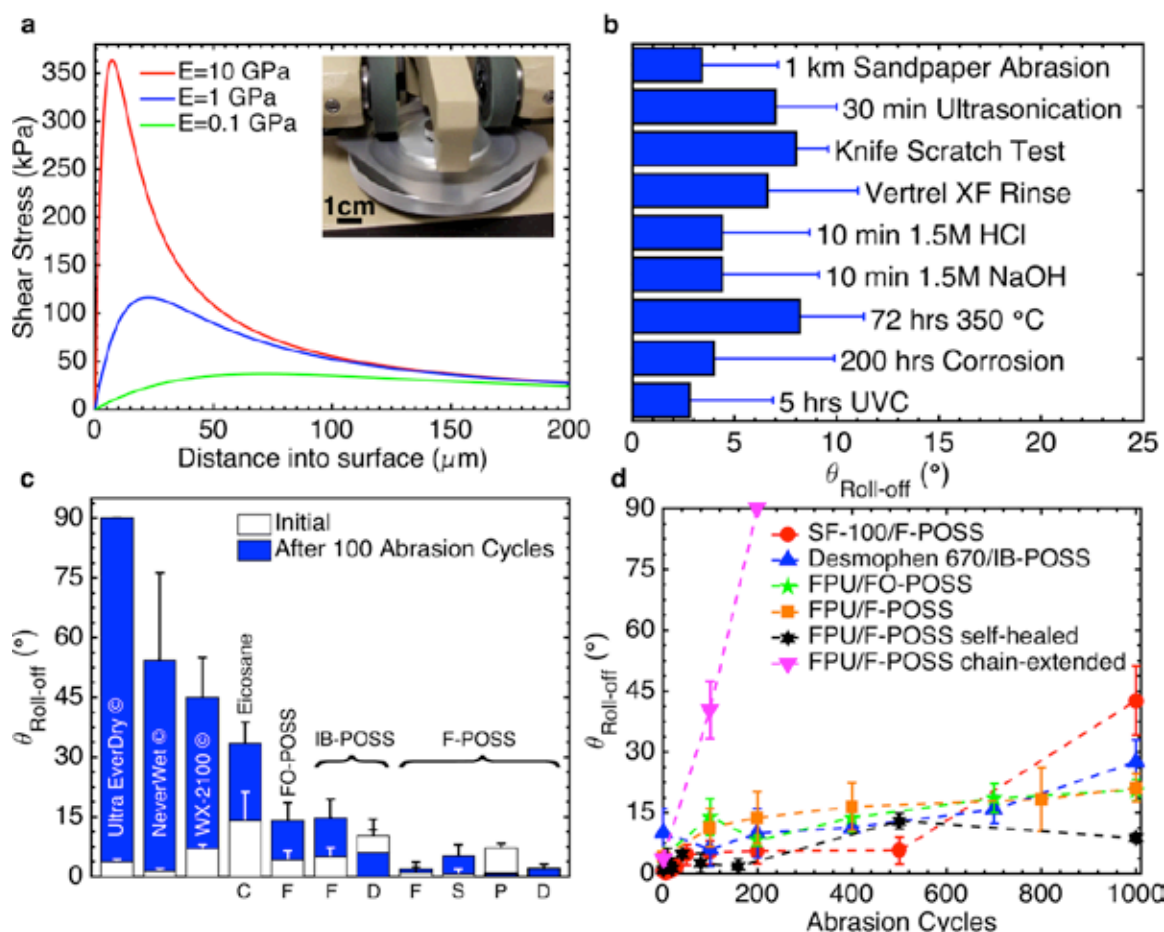


Figure 2. Mechanical durability. a, The shear stress experience during Taber abrasion as a function of depth into the coating. The values are found using Hertzian contact mechanics (see SI). The inset shows the Taber abrasion machine. b, Additional durability characterizations that the FPU/F-POSS coating could withstand without self-healing. c, The roll-off angles for three commercially available SHSs and eight of the SHSs fabricated in this work (with $S^* < 1.0$), initially and after 100 abrasion cycles. C: chlorinated rubber, F: FPU, D: Desmophen 670BA, S: SF-100, P: PFPE. d, The droplet roll-off angles for four representative durable SHSs fabricated in this work. The data for the propylene glycol chain extended FPU/F-POSS, and the self-healed FPU/F-POSS are also shown. All roll-off experiments used 25 μL droplets.

Physical and Chemical Self-Healing SHSs

In the remainder of this work we focus on our most durable coating, the FPU binder blended with 15wt% F-POSS. Due to the surface migration of F-POSS upon heating and the elastomeric ($T_g \ll \text{room temperature}$) nature of the FPU, the fabricated coating can both chemically and

physically self-heal. For example, the as-abraded coating maintained $\theta_{\text{Roll-off}} < 15^\circ$ up to about 800 abrasion cycles. Beyond this, $\theta_{\text{Roll-off}}$ increased with the number of abrasion cycles. But if the coating was placed on a hotplate for a few minutes, the water repellency was easily restored ($\theta_{\text{Roll-off}} < 5^\circ$, Figure 3a). With self-healing, the FPU/F-POSS coating maintained $\theta_{\text{Roll-off}} < 15^\circ$ even after 4,000 abrasion cycles. Other blends created using different elastomers, such as SF-100/F-POSS, FPU/FO-POSS, or Desmophen 670BA/IB-POSS, also exhibited a self-healing nature. The self-healing and superhydrophobic nature of Desmophen 670BA/IB-POSS system is notable because neither of the components contains any fluorinated species.

The low surface energy of F-POSS causes it to migrate to the solid/air interface,⁵⁹ imparting different binder/F-POSS blends with a robust, self-healing nature. For example, oxygen plasma, which has the capability of hydrolyzing F-POSS,⁶¹ rendered the FPU/F-POSS coating hydrophilic within minutes ($\theta^* = 0^\circ$, although P^* remained unchanged). However, upon heating, the low surface energy was fully restored (Figure 3b). We found that the time required for full superhydrophobic recovery decreased with increasing temperature, consistent with a diffusion-controlled process. The coating maintained low $\theta_{\text{Roll-off}}$ when held at temperatures up to about 400 °C, the point at which F-POSS begins to degrade (Figure 3c). However, even when > 75% of the mass had degraded, the coating maintained $\theta_{\text{Roll-off}} < 15^\circ$. We also repeatedly treated the coating with O₂ plasma and found that the water repellency was fully recovered by heating even after 10 successive treatments (Figure 3d).

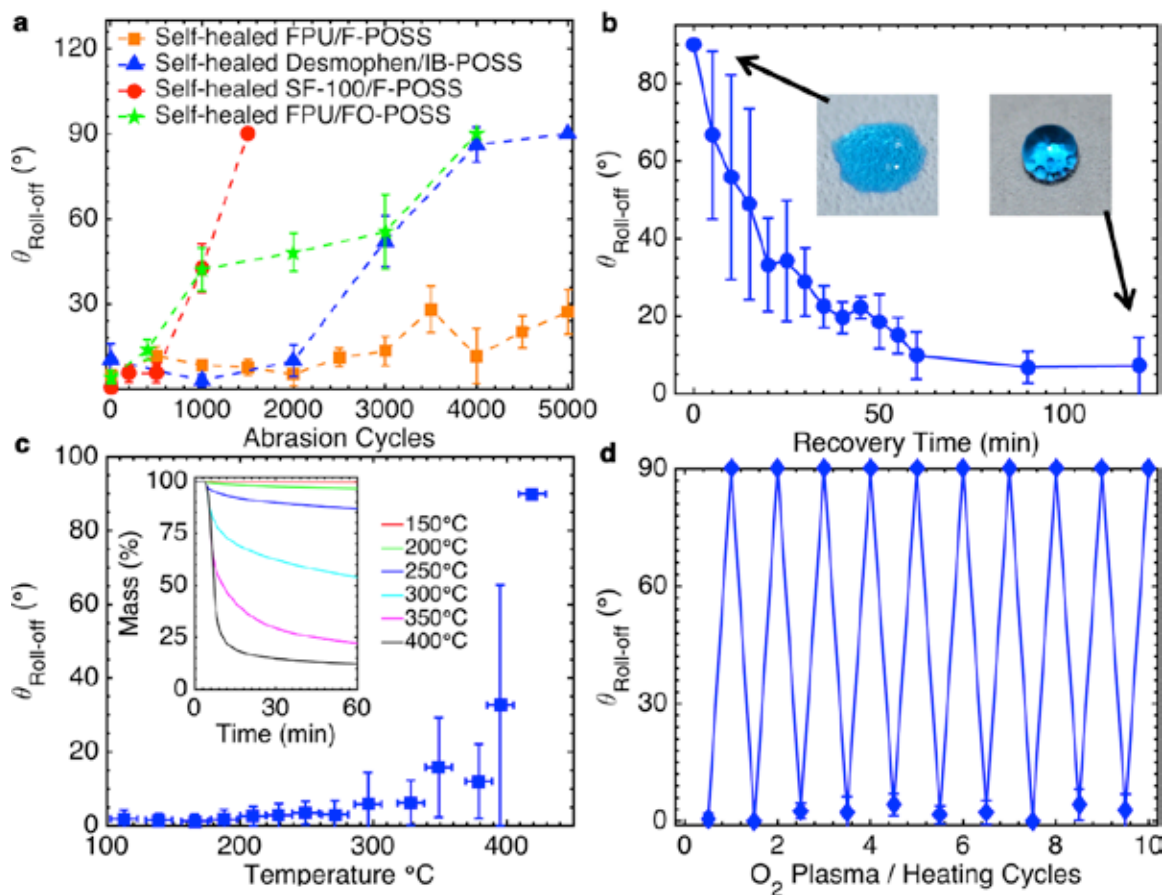


Figure 3. Self-Healing SHSs. a, The roll-off angle for four binder/filler blends after self-healing, as a function of the number of abrasion cycles. b, The roll-off angle of the FPU+15wt% F-POSS coating after O₂ plasma treatment, as a function of recovery time at 80 °C. As the fully fluorinated chains bloomed to the surface, the surface energy decreased, and water was more easily repelled. The insets show water droplets (dyed blue) after O₂ plasma treatment, and after thermal recovery. c, The roll-off angle of the FPU/F-POSS coating versus temperature held for 1 hour. The inset shows TGA of the same coating, at different temperature points. d, Ten successive O₂ plasma/recovery cycles, highlighting that the self-healing nature of the FPU/F-POSS coating was quite robust.

Even after mechanical wear, a robust SHS should also exhibit a large capillary resistance or breakthrough pressure, P_b , defined as the pressure required to force a transition from the Cassie-Baxter to the Wenzel state.^{10,11,52,62-64} Although the FPU/F-POSS coating maintained $P^* < 1.0$ over 5,000 abrasion cycles (Figure 4a), indicating an energetically favorable Cassie-Baxter state, a pressure-induced wetting transition is usually irreversible without some form of energy input.¹⁰

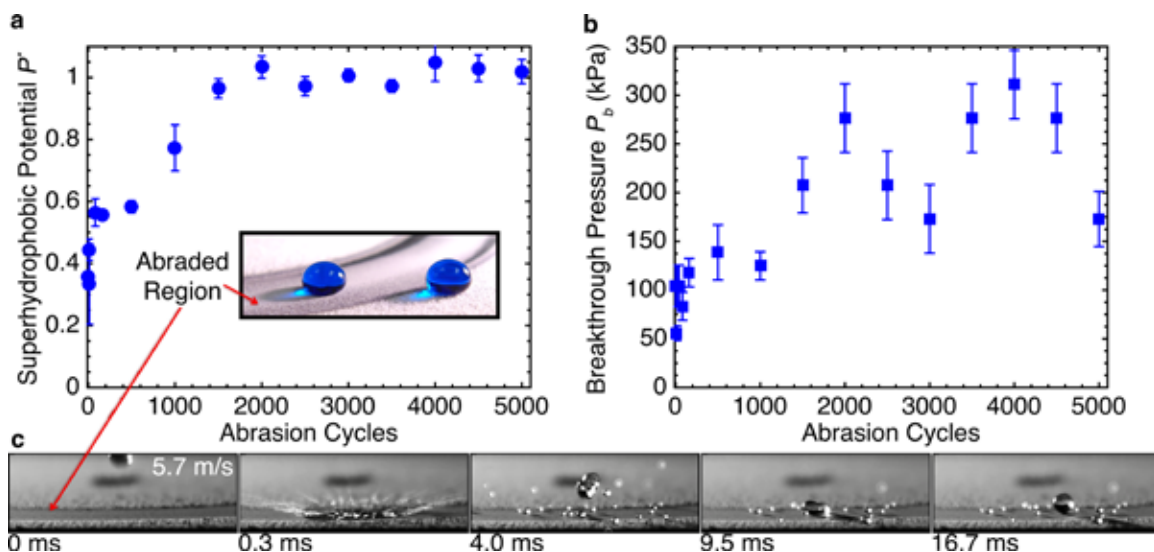


Figure 4. Capillary resistance. a, The P^* parameter as a function of the number of abrasion cycles for the FPU/F-POSS coating after self-healing. The inset shows water droplets (dyed blue) displaying high contact angle even after 5,000 abrasion cycles. b, The breakthrough pressure of the FPU/F-POSS coating as a function of abrasion, after self-healing. c, A water droplet, dropped from a height of ~ 1.7 m, impacts the abraded region (4,000 abrasion cycles) of the FPU/F-POSS coating at a velocity of 5.7 m/s (see Movie 1). After breaking up, the satellite droplet bounces at least four times after impacting the surface. The surface is tilted at 1.5° .

To evaluate the breakthrough pressure, we completely submerged our self-healed FPU/F-POSS coating in a pressurized water tank and observed when wetting occurred (methods). The breakthrough pressure of this coating was initially $P_b = 100 \pm 20$ kPa and never decreased below $P_b = 50$ kPa, even after 5,000 abrasion cycles (Figure 4b). Remarkably, the pressure resistance increased to a maximum of $P_b = 310$ kPa after 4,000 abrasion cycles, due to the decrease in S_q with increasing abrasion. As such, even water droplets impinging the abraded surface at an impact velocity of ~ 6 m/s completely rebounded, leaving the surface dry (Figure 4c and Movie 1). The maximum measured breakthrough pressure of 310 kPa corresponds to a droplet impact velocity of ~ 25 m/s ($P_{\text{impact}} = \rho V^2/2$), and a static water height of 31 m. Whereas often SHSs only maintain high contact angle after mechanical damage, the surfaces reported here preserve

all their advantageous, water-repellant properties (high θ^* , $\theta_{\text{Roll-off}} < 15^\circ$, high P_b), even after harsh mechanical abrasion.

The thermal recovery of low surface energy due to F-POSS migration will only result in a SHS if the texture is also maintained. Although abrasion damages the texture of the FPU/F-POSS coating, we found that the abraded texture was still sufficient for superhydrophobicity (Figure 4a). Further, we also observed that the texture could be partially restored during the thermal treatment. For example, after 1,000 abrasion cycles, the FPU/F-POSS coating exhibited $S_q = 2.6 \mu\text{m}$. Thermal recovery at 100 °C for 120 seconds increased this value to $S_q = 3.3 \mu\text{m}$ (measured at identical locations) (Figure 5a). Thus, abrasion also slightly compressed the coating. To further explore this, we subjected the coating to compressive stresses up to 350 MPa. Although flattening the texture elements significantly reduced the coating's porosity ($P^* \approx 2.0$, Figure 5b), such damage was reversible, and upon heating, the coating quickly recovered its original porous state ($P^* \approx 0.6$) (Figure 5b,c). Environmental scanning electron microscopy (ESEM) allowed us to observe this self-healing *in situ* (Figure 5d, Movie 2). As the compression set of elastomers is typically non-zero,^{65,66} the use of elastomeric materials in the fabrication of SHSs may be advantageous in terms of their ability to recover from compressive stresses that flatten their porous texture, as shown here.

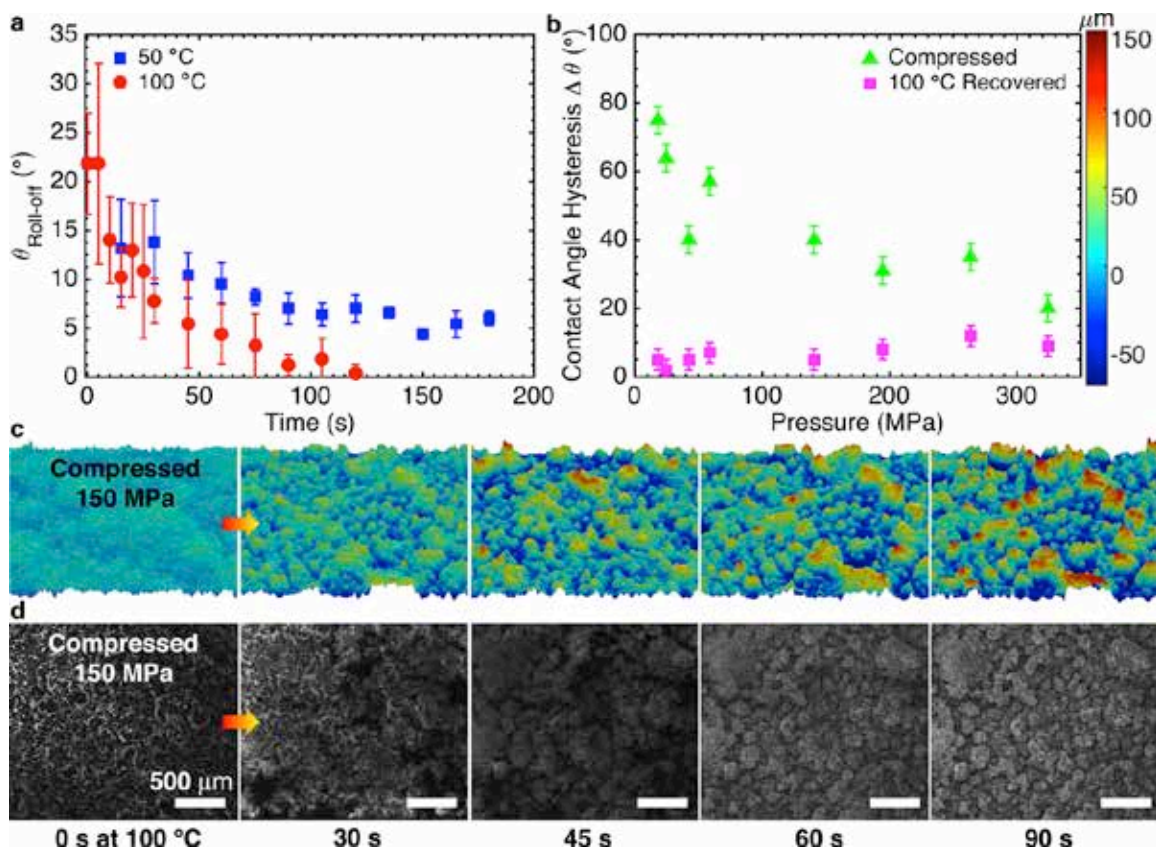


Figure 5. Texture recovery. a, The self-healing properties of the FPU/F-POSS coating as a function of time and temperature, after 1,000 Taber abrasion cycles. S_q increased from 2.6 μm to 3.3 μm during self-healing. b, The contact angle hysteresis for the FPU/F-POSS coating before and after thermal recovery from compression, as a function of the compressive load. Note that the compressed coating's hysteresis decreased with an increase in applied load because the surface became smoother after compression. All compressed surfaces were fully wetted. c, Height maps of the FPU/F-POSS coating after 150 MPa compression, as a function of recovery time at 100 °C. d, The recovery of the texture was also imaged *in situ* using environmental scanning electron microscopy (Movie 2).

Conclusion

In summary, we have explored how miscibility between hydrophobic fillers and polymeric binders allows one to control the formation of surface texture during spray coating in order to fabricate superhydrophobic surfaces. The S^* parameter quantifies the miscibility between the two sprayable components, and the P^* parameter characterizes the stability of the

non-wetted state. Superhydrophobic surfaces should be designed such that $S^* < 1.0$, to afford mechanical durability, and $P^* < 1.0$, to provide a robust non-wetting state. Utilizing these two design criteria, we have fabricated superhydrophobic surfaces with unprecedented mechanical durability. Some of these surfaces also exhibited a self-healing nature, both chemically and physically, and were able to fully recover their superhydrophobicity after a wide variety of extreme chemical and physical exposures. These surfaces, and the design parameters used to develop them, may find immediate usage in a wide range of academic and industrial sectors across the globe.

Table 1. Surface properties of coatings in this work before and after 100 rotary Taber abrasion cycles

Base	% F-POSS	P^*	D^*_{stat}	Initial θ_{adv} [°]	Initial θ_{rec} [°]	Initial $\theta_{Roll-Off}$ [°]	100 cycle θ_{adv} [°]	100 cycle θ_{rec} [°]	100 cycle $\theta_{Roll-Off}$ [°]	100 cycle mass loss [%]
Neverwet	-	1.79	7.4	165	162	1	132	37	54	17
Ultra Ever Dry	-	1.36	4.0	161	152	1	155	0	90	14
Cytonix WX 2100	-	1.04	1.4	164	156	18	122	77	90	6
FPU ($S^* = 0.64$)	0	1.84	7.2	115	66	55	-	-	-	-
FPU	1	0.99	14.3	106	67	90	106	63	90	1
FPU	3	1.49	25.5	121	66	90	122	78	76	3
FPU	5	0.31	1.5	148	112	62	151	102	75	8
FPU	10	0.34	2.5	162	150	10	159	124	22	20
FPU	15	0.48	3.9	165	159	2	161	154	2	32
FPU	20	0.56	3.5	163	153	5	161	144	10	40
FPU	25	0.67	6.4	166	153	2	164	152	2	86
FPU	30	0.68	4.8	165	160	2	163	144	3	81
FPU	35	0.63	4.4	160	151	1	146	113	24	56
FPU-PG ($S^* = 1.06$)	5	0.62	5.3	163	145	8	153	98	81	44
FPU-PG	10	0.57	8.2	161	152	7	158	116	57	40
FPU-PG	15	0.75	4.7	162	148	7	161	113	90	27
FPU-PG	20	0.74	5.6	164	151	3	159	123	40	26
PMMA ($S^* = 1.17$)	0	1.06	5.1	155	0	90	-	-	-	-
PMMA	2	0.76	5.5	160	83	14	135	0	90	109
PMMA	5	0.43	4	160	143	11	159	123	35	99
PMMA	10	0.58	3.4	163	153	7	159	128	24	104
PMMA	35	0.90	5.9	166	156	2	162	127	26	129
PMMA	50	0.86	4.2	164	156	0	127	84	63	100
SF-100 ($S^* = 0.74$)	0	1.99	2.9	93	37	64	-	-	-	-
SF-100	5	1.38	3	129	41	90	-	-	-	-
SF-100	10	1.75	2.9	140	72	83	-	-	-	-
SF-100	15	1.27	4.5	158	123	13	167	113	37	22
SF-100	20	1.01	3.8	163	157	1	165	133	21	30
SF-100	25	0.92	3.5	169	163	0	166	164	1	55
SF-100	35	0.60	7	167	159	2	145	107	34	38
PDMS ($S^* = 0.32$)	0	1.88	3.8	123	45	90	-	-	-	-
PDMS	15	0.73	5.4	154	119	47	158	137	10	20
PDMS	30	0.55	5.4	160	153	4	157	0	66	46
PFPE ($S^* = 0.46$)	0	1.88	18.6	113	78	53	-	-	-	-
PFPE	5	2.12	0.5	127	66	66	-	-	-	-
PFPE	15	1.08	7	155	72	47	163	20	90	45
PFPE	25	0.55	3.7	156	147	7	163	142	8	33
PFPE	35	0.58	4.1	165	153	2	164	0	90	100
Vytaflex ($S^* = 1.60$)	0	2.00	1	73	4	90	-	-	-	-
Vytaflex	1	1.52	9.6	149	0	90	-	-	-	-
Vytaflex	5	1.08	4.5	150	0	90	-	-	-	-
Vytaflex	10	1.15	3.1	135	29	90	-	-	-	-
Vytaflex	15	0.65	4.5	158	134	11	159	55	39	28
Vytaflex	35	0.55	5.2	160	150	2	161	130	17	-
PS 45 ($S^* = 0.48$)	0	1.15	26.6	157	123	14	-	-	-	-
PS 45	15	0.60	1.9	157	131	14	156	114	37	26
PS 45	25	0.58	1.4	155	142	15	152	111	38	14
PS 1.2 ($S^* = 0.48$)	15	0.94	8.5	159	153	0	-	-	-	100
PIB ($S^* = 0.19$)	0	1.27	19.3	118	61	90	-	-	-	-
PIB	15	1.18	10.4	164	143	14	161	118	90	48
Araldite ($S^* = 0.23$)	0	1.95	2.9	101	17	90	-	-	-	-
Araldite	5	1.94	12.5	128	43	90	127	62	87	-
Araldite	15	1.39	1	137	43	90	132	69	90	3
Araldite	25	0.89	9	158	130	14	158	16	90	25
Desmophen 670BA ($S^* = 0.91$)	0	1.43	41.9	85	49	90	-	-	-	0
Desmophen 670BA	2.5	0.52	8.9	161	141	8	148	94	74	17
Desmophen 670BA	5	0.36	7.8	166	157	5	159	125	23	20
Desmophen 670BA	10	0.38	8.4	166	160	4	162	129	16	24
Desmophen 670BA	15	0.17	2.3	165	156	9	164	162	2	27

Methods

Materials:

All solvents, pre-polymers, and crosslinking agents were used as-received. Fluorinated solvents HCFC-225ca/cb (Asahiklin-225, Asahi Glass Co.) and HFC-43-10mee (Vertrel XF, DuPont) were purchased from Techspray and TMC Industries, Inc. respectively. Poly(methyl methacrylate) (PMMA), polystyrene (PS, 45 kDa or 1.2 kDa) and polyisobutylene (PIB) were purchased from Scientific Polymer. Luxecolor 4FVBA fluorinated polyol resin (55% solids in n-butyl acetate) was purchased from Helicity Technologies, Inc. Desmophen 670BA polyol was provided by Bayer MaterialScience, A.G. Isocyanate crosslinkers Desmodur N3200 and Wannate HMDI (4,4'-Diisocyanato-methylenedicyclohexane) were provided by Bayer MaterialScience, A.G. and Wanhua Chemical Group Co., Ltd. respectively. Crosslinker ratios were 9.7 and 3.4 wt. % respectively with FPU, and 28.5 wt. % N3200 with 670BA. Propylene glycol, a chain-extending agent that increases the modulus of the final cross-linked polyurethane network, was obtained from MP Biomedicals, LLC. A polyurethane elastomer (Vytaflex 40) was purchased from Smooth-On, Inc., and was prepared according to manufacturer directions. CNR (chlorinated polyisoprene) was provided by Covestro. Polydimethylsiloxane elastomer (Dow Corning Sylgard 184) was obtained from Krayden, Inc. and a 10:1 base:crosslinker ratio was used according to manufacturer directions. Acrylate-terminated perfluoropolyether resin (CN4001, purchased from Sartomer USA, LLC) was mixed with 5 wt. % radical photoinitiator (Irgacure 2022, provided by BASF Corporation) to yield a UV-curable fluorinated polymer matrix. Cyanoacrylate adhesive (3M Scotch-Weld SF100) was purchased from Pack-n-Tape, Inc. Two-part epoxy adhesive (Selleys Araldite 90 seconds) was used in an approximate 1:1 volume ratio of the components, per manufacturer instructions.

Fluorodecyl and fluoro-octyl polyhedral oligomeric silsesquioxanes (F-POSS, FO-POSS) were prepared by condensing perfluorinated triethoxysilanes as previously reported⁴⁵. Octaisobutyl polyhedral oligomeric silsesquioxane (IB-POSS) was purchased from Hybrid Plastics, Inc. Eicosane was purchased from Acros Organics.

Coating sample fabrication:

Spray coating solutions were prepared by solubilizing the filler, polymer or pre-polymer, and cross-linker or photoinitiator (if applicable) at an overall solution concentration of 100 mg/mL. The weight fraction of filler in the total solution was varied from 0 to 50%. The solvents used for F-POSS and FO-POSS blends were: pure Vertrel XF (for FPU and PFPE), pure AK-225 (for SF100, 670BA, PMMA, chain extended FPU and PDMS), 50:50 Chloroform:Vertrel XF (for Vytaflex 40, PS and Araldite epoxy) and 50:50 AK-225:Hexane for PIB. Pure chloroform was used for IB-POSS blends with 670BA and FPU. Pure toluene was used for blends of eicosane and CNR.

No significant effect on spray coating morphology was observed between these solvents, as they have similar volatility and surface tension. The solutions were applied to 10 cm × 10 cm 6061 aluminum sheets with an ATD Tools 6903 high-volume-low-pressure spray gun. 20 mL of coating solution was applied to each plate, which resulted in coatings that were approximately 100 μm thick. However, because the surfaces are both porous and extremely rough, the thickness cannot be well-defined, and during abrasion tests the mass % lost was tracked instead. Spray coated samples were held at room temperature for at least one day and then cured as necessary prior to further testing (polyurethanes: 80 °C two days; PDMS: 150 °C 1 h; epoxy and cyanoacrylate: room temperature at least 2 h; PFPE acrylate resin: 15 min simultaneous exposure to 254 and 365 nm UV mercury lamp irradiation under N₂ atmosphere).

Hansen Solubility Parameter Studies:

Hydrophobic filler miscibility in the polymer binders was analyzed with the aid of the HSPiP software package and associated database of Hansen solubility parameters. All solvents were used without further purification, including acetone, THF, chloroform, ethylene glycol, toluene, cyclohexane, hexane, dodecane, DMSO, ethanol, n-butyl acetate, MEK and o-fluorotoluene (Fisher), as well as 1-hexanol, chlorobenzene, perfluorodecalin, hexafluorobenzene, p-chlorobenzotrifluoride, diisopropylamine and pentafluorobutane (Sigma-Aldrich). Additionally, DI water, AK-225, and Vertrel XF were used.

Crosslinked polymers and elastomers were swollen in a selected number of solvents until a consistent mass was achieved. Samples were weighed and then the solvent was extracted using a vacuum oven at 100 °C. The goodness of a solvent was determined by ranking the swelling ratio (divided by the mass of the solvent) from 1 to 6, with 1 being solvents that swell the polymer the most. These were then input into the HSPiP software in order to determine the center and radius of the given system, or to determine other solvents necessary to better define the radius of the Hansen sphere.

The Hansen sphere for F-POSS was determined only using fluorinated solvents, as the fluorine-fluorine interaction is crucial in solubilizing the highly fluorinated compound⁴⁵. As an example, hexafluorobenzene and dodecane have the exact same Hansen parameters and similar molecular volumes. However, F-POSS is completely insoluble in dodecane even at 1 mg/ml, whereas F-POSS is soluble up to 800 mg/ml in hexafluorobenzene. Thus, rather than confounding the results by including alkanes and other proximal molecules, only fluorinated solvents were used.

Along similar lines, the Hansen sphere for F-POSS was found for various solution concentrations. Although the Hansen radius is known to be weakly dependent on concentration⁽⁴³⁾, we found a strong dependence when evaluating fluorinated systems such as F-POSS (Figure S5b,c).

Wettability Measurements:

Advancing and receding contact angle measurements were obtained via the sessile drop method using a Ramé-Hart 200 F1 contact angle goniometer. A water droplet suspended from a vertical dispensing needle was brought into contact with the substrate, and its volume increased and decreased to obtain the advancing and receding contact angles. A circular drop profile on the live video feed in the DROImage Advanced software was used to obtain contact angle data. At least three points were measured for each surface at each abrasion condition. Droplet roll-off angles were obtained by placing at least five 25 μL water droplets distributed across the surface with a micropipette, and using the manual tilting stage of the goniometer to gradually increase the angle. The tilt angle was recorded when each droplet rolled off, and the average across the droplets was calculated. Droplets that did not roll off were recorded as $\theta_{\text{Roll-off}} = 90^\circ$ for averaging purposes. The large error bars in some of the abraded samples in Figure 2 arose from averaging areas that wet with areas that remained superhydrophobic.

Abrasion Testing:

Abrasion testing based on ASTM standard D4060 was performed with a Taber Model 5135 Rotary Abraser with CS-10 resilient abrasive wheels. 250 g weights were placed on the rear of the wheel arms such that the applied normal load was ~ 60 g, and the sample was then rotated relative to the freely spinning abrasion wheels such that a shearing abrasion action occurred.

Excess debris was removed continuously with a vacuum nozzle. The result was a circular region on the sample that was consistently mechanically damaged.

The manual sandpaper abrasion test performed previously¹⁶ was automated using a Taber Model 5750 Linear Abraser. A 2.5×2.5 cm spray coated sample was mounted facing downwards on the reciprocating head, and brought in contact with 240 grit sandpaper, with an applied load of ~ 250 g. The sample was then moved under load on the static sandpaper, and the test was continued until water droplets were pinned. Water roll-off angles were measured periodically to confirm the retention of superhydrophobicity (Figure S2b).

Imaging and Metrology:

Scanning electron micrographs were obtained with a Philips XL30 SEM after sputter coating the samples with gold to reduce charging effects. Two-dimensional height-maps ($2.4 \text{ mm} \times 2.4 \text{ mm}$) of the surfaces were obtained with an Olympus LEXT OLS4000 3D Laser Measuring Microscope with the 10X objective, and at least five were collected for each sample at each abrasion condition. This data was subsequently analyzed to yield statistical topographical parameters using MATLAB (see Supporting Information: Justification of Statistical Parameters).

Thermal Degradation Analysis:

A sample of FPU+15 wt% F-POSS was placed on a hot plate at temperatures from 150 – 425 °C in increments of 25 °C, 1 hour per temperature point. After each baking step, the advancing, receding and roll-off angles were measured (Figure 3c). To correlate the onset of degradation of the Cassie-Baxter state with chemical degradation of the sample, thermogravimetric analysis was performed with a TA Instruments Discovery Series TGA using a 6 mg sample scraped from the same spray-coated surface. This sample was heated from 25 –

600 °C at 10 °C/min in a 10 mL/min N₂ gas purge flow while continually monitoring its mass (inset, Figure 3c).

UV Exposure:

A sample of FPU+15 wt% F-POSS was placed under 254 nm UVC mercury lamp (UVP, LLC) at a distance of 5 cm. The contact angles were measured after five hours of continuous exposure.

O₂ Plasma Exposure:

A sample of FPU+15 wt% F-POSS was exposed to O₂ plasma (Harrick Plasma PDC-001) using RF source power of 30 Watts and a pressure of ~200 mTorr for 20 min. Contact angles were measured to verify the complete wetting of the surface. To recover the water repellency, the coated surface was placed on a hotplate at a certain temperature (80 °C or 150 °C). For the time-dependent recovery, the substrate was removed from the hotplate after temporal increments and the contact angles were measured. For the O₂ plasma cycling, the substrate was placed on a 150 °C hotplate for 20 min before measuring contact angles. The O₂ plasma exposure followed by the 150 °C recovery is denoted as one cycle in the inset of Figure 3d.

Corrosion Testing:

Corrosion testing was done in accordance to ASTM B117. Briefly, steel tabs measuring 25 mm × 75 mm were spray-coated with the FPU+15 wt% F-POSS coating. The coated pieces were hung in a salt-spray fog chamber (Bemco Inc.) kept at 35 °C for 200 hours. A 25 mm scratch was made along the length of the coating so that the steel underneath was exposed. After the accelerated corrosion, the contact angles were measured.

Compression Testing:

Compression testing was done using a Carver 4350 compression molder with a 30 ton capacity. Samples of known dimensions were placed between aluminum plates and a certain force was applied and held for 60 seconds. The contact angles were then measured immediately following compression. The coating was then self-healed on a 100 °C hotplate for 5 minutes, and contact angles were recorded again.

Breakthrough Pressure Testing / Droplet Impact:

Pressure stability was measured both statically and dynamically. Static pressure testing was done using a pressure tank (TCP Global) with a 7 cm head of DI water. The pressure was regulated using compressed air. Samples were submerged and the pressure was raised to the set level for 60 seconds at a ramp rate of no more than 5 psi per second. After the pressure was released, samples were removed to determine if they remained dry. Due to the inhomogeneity of the surfaces, breakthrough was considered to have occurred when the sample was fully wetted upon removal from the water tank.

Dynamic pressure testing was done using impacting water droplets and a high-speed camera (Fastec Imaging HiSpec 1) at 2000 fps. The breakthrough pressure was considered when the droplet became pinned on the surface upon impact. As the maximum droplet height for our experimental setup was 1.7 m, corresponding to an impact velocity of 5.7 m/s, many surfaces exhibited breakthrough pressures too high to measure using droplet impact.

**Achievement 2: Development of Smooth, All-Solid, Low-Hysteresis, Omniphobic Surfaces
with Enhanced Mechanical Durability**

To develop surfaces that enhance heat transport with liquids besides water, such as jet fuel, oils, alcohols and refrigerants, it is imperative to develop durable omniphobic surfaces. The utility of omniphobic surfaces stems from their ability to repel a multitude of liquids, possessing a broad range of surface tensions and polarities, by causing them to bead up and either roll or slide off. These surfaces may be self-cleaning, corrosion-resistant, heat-transfer enhancing, stain-resistant or resistant to mineral- or bio-fouling. The majority of reported omniphobic surfaces use texture, lubricants, and/or grafted monolayers to engender these repellent properties. Unfortunately, these approaches often produce surfaces with deficiencies in long-term stability, durability, scalability, or applicability to a wide range of substrates. To overcome these limitations, we fabricated an all-solid, substrate-independent, smooth, omniphobic coating composed of a fluorinated polyurethane and fluorodecyl polyhedral oligomeric silsesquioxane. Liquids of varying surface tension, including water, hexadecane, ethanol, and silicone oil, exhibit low contact angle hysteresis ($< 15^\circ$) on these surfaces, allowing liquid droplets to slide off, leaving no residue. Moreover, we demonstrate that these robust surfaces retained their repellent properties more effectively than textured or lubricated omniphobic surfaces after being subjected to mechanical abrasion.

Introduction:

Hydrophobic or oleophobic surfaces prevent droplets of a desired liquid from spreading across the surface, causing them to bead-up and, under certain conditions, roll or slide off. Omniphobic surfaces, on the other hand, possess the ability to repel most liquids, regardless of

their polarity or surface tension. Applications of omniphobic surfaces include ‘non-stick’ coatings, bio- and mineral-fouling resistance, corrosion-prevention, chemical- and stain-resistance, and prevention of protein and cell adhesion.⁶⁷⁻⁶⁹ These surfaces may also be useful in applications where liquid mobility is required, such as in digital microfluidic devices.⁷⁰ Patterning of omniphobic coatings enables the manufacture of non-wetting surfaces with wettable open channels for microfluidic devices,⁷¹ as well as surfaces that improve efficiency in phase-change heat transfer and fog-harvesting applications.⁷² In the majority of these applications, the key requirement is that all liquids form mobile droplets on the surface that readily dewet without leaving any residue. The disparate strategies to achieve such repellent surfaces have yielded numerous surfaces with widely varying mechanical durability and effectiveness.⁶⁷

A liquid droplet placed on a smooth and chemically homogenous surface exhibits a characteristic equilibrium contact angle within the drop. This contact angle is determined by the balance between the liquid surface tension (γ_{LV}), the solid-liquid interfacial tension (γ_{SL}), and the solid surface energy (γ_{SV}). As the surface becomes more resistant to wetting by a given liquid, its contact angle increases.⁷³ Contact angles deviating from this equilibrium value are often observed on surfaces possessing roughness and/or chemical heterogeneity, thereby causing local variation in liquid-solid interactions. A range of contact angles may be measured, from the minimum value when a liquid recedes from the surface (θ_{rec}), to the maximum value when a liquid advances over the surface (θ_{adv}).⁷⁴ The difference between θ_{adv} and θ_{rec} is known as contact angle hysteresis ($\Delta\theta$). Ideally, an omniphobic surface should exhibit a low $\Delta\theta$ for essentially all contacting liquids, because minimizing $\Delta\theta$ reduces the tilting angle required to allow a droplet to slide on the surface, according to the Furmidge relation as:

$$(mg \sin \alpha) / w = \gamma_{LV} (\cos \theta_{rec} - \cos \theta_{adv}) \quad (1)$$

where α is the tilting angle, w is the width of the droplet, mg is the force due to gravity, and γ_{LV} is the liquid surface tension.⁷⁵ Minimizing the contact angle hysteresis with all liquids thereby enhances the liquid-repellency of an omniphobic surface.

Approaches to producing liquid-repellent surfaces include fabricating rough surface textures that entrap air pockets beneath the liquid, infusing porous surfaces with immiscible liquid lubricants, and modifying smooth surfaces with reactive low-surface-energy molecules.⁶⁷ These methods each have potential drawbacks, which limit their long-term stability, durability, and scalability for industrial applications, in addition to reducing applicable substrate materials, as discussed below.

Textured surfaces with overhanging or “re-entrant” microscale features are capable of maintaining a composite solid-air interface beneath liquids with a broad range of surface tensions.^{10,76} Droplets on these so-called superomniphobic surfaces exhibit extremely high contact angles (approaching 180°) and minimal $\Delta\theta$, and therefore easily roll or even bounce off.⁷⁷ However, reliance on entrapped air to maintain the non-wetted Cassie-Baxter state makes such surfaces vulnerable to transitioning to a wetted Wenzel state under elevated pressure across the liquid-air interface (*e.g.* due to droplet impact or immersion). This transition is more prone to occur with lower surface tension liquids, which exhibit lower contact angles.⁷⁸ The micro- and nano-scale features on these surfaces are also vulnerable to mechanical damage, which introduces defects that may cause irreversible wetting. It is especially challenging to maintain the necessary re-entrant geometry for superomniphobicity after abrasion.^{67,79} Past efforts to produce durable superomniphobic surfaces with low hysteresis have included monolithic fluorinated aerogels,⁸⁰ or polymer – nanoparticle coatings fabricated using a layer-by-layer methodology.⁸¹

The pressure stability of textured superomniphobic surfaces may be increased by replacing the entrapped air with a relatively non-volatile, inert liquid lubricant, such as a perfluoropolyether.⁶⁸ The surface chemistry of the porous material may be modified to enhance lubricant wetting, thereby enabling a broad range of immiscible liquids to essentially float on top of the surface. Liquid droplets exhibit significantly lower contact angles on these lubricated surfaces than on textured superomniphobic surfaces, but with comparably low hysteresis and improved pressure stability. The liquid lubricant also imparts limited self-healing capabilities, as it can flow into damaged regions on the surface.⁶⁸ However, the lubricant may be depleted over time due to evaporation or displacement by other liquids, especially under high shear flows.⁸² In certain cases, interaction between the lubricating liquid and floating liquid droplets may accelerate lubricant depletion by allowing a small amount of lubricant to be removed with each liquid droplet that slides from the surface.^{83,84} The porous substrate also remains vulnerable to mechanical damage, which reduces the stability of the lubricant film.

Alternatively, a smooth homogenous surface with low surface energy may be produced by covalently grafting small molecules to smooth substrates. For example, a densely-packed liquid repellent monolayer of trifluoromethyl (CF_3) groups may be produced by the self-assembly of perfluoroalkyl compounds with a reactive terminal functional group, such as a thiol or alkoxysilane.^{85,86} Low hysteresis can also be achieved with flexible grafted poly(dimethyl siloxane) chains, which yields a mobile liquid-like surface, but with much lower contact angles.⁸⁷ Near-perfect monolayers of these molecules may yield negligible hysteresis and essentially zero sliding angles with a broad range of liquids. However, achieving complete surface coverage with these molecules is challenging, and highly dependent on reaction conditions and substrate surface chemistry. For example, silanes only react well with hydroxyl-rich oxide surfaces such as

silica, alumina, and titania.⁸⁸ Surface cleanliness and activation is critical to minimizing hysteresis, both of which can also be dependent on the substrate roughness.

To address the aforementioned drawbacks of textured superomniphobic surfaces, lubricated surfaces, and self-assembled monolayers, we have developed an all-solid, omniphobic coating that can be applied to a broad range of substrates via spin or dip coating. The produced omniphobic coatings are suitable for applications when liquid dewetting is desirable but high contact angles are not strictly required. These applications include self-cleaning surfaces, immersion photolithography, droplet microfluidics, non-stick coatings, stain-resistance, and enhancing heat transport during condensation. Previous approaches to fabricate smooth, all-solid low-hysteresis coatings have been somewhat involved, and include layer-by-layer deposition, polymer matrices containing lubricant domains, and sol-gel deposition of mixed silanes.⁸⁹⁻⁹¹ The coating in this work relies on the partial phase separation of a highly fluorinated molecule from a polymeric matrix to produce surfaces with low contact angle hysteresis ($< 15^\circ$) for most liquids, including water, hexadecane, toluene, ethanol, and silicone oil, regardless of their polarity or surface tension. These liquids slide easily from coated surfaces without leaving any residue. The all-solid nature of the coating addresses the pressure stability and long-term performance concerns with textured and liquid-infused surfaces. Furthermore, the coatings are mechanically durable and can be applied to a broad range of underlying substrates.

Results and discussion:

Fluorodecyl polyhedral oligomeric silsesquioxane (F-POSS) was selected as the fluorinated additive in this work because of the high density of perfluorinated groups it possesses, in addition to its extremely low surface energy. F-POSS was produced using previously reported synthetic methods.⁴⁵ Unfortunately, F-POSS molecules typically form large

crystals (tens of micrometers across) when deposited from solution, resulting in rough films with high contact angle hysteresis. For example, a solution of F-POSS was drop-cast onto Si wafers from a solution of dihydrodecafluoropentane (HFC 43-10) and allowed to dry. The resulting surface showed high contact angle hysteresis with both water ($\theta_{adv}/\theta_{rec}=149^\circ/110^\circ$), and hexadecane ($\theta_{adv}/\theta_{rec}=94^\circ/49^\circ$). The production of smooth F-POSS films requires a volatile solvent with a high F-POSS solubility in order to delay precipitation and minimize crystallization. Deposition was performed using a spin coating methodology (methods) to minimize the time available for F-POSS crystallization. The optimal solvent was determined to be an equal volume ratio mixture of HFC-43-10 and hexafluorobenzene (HFB). The former is a highly volatile fluorinated solvent (boiling point 55°C) with limited solubility for F-POSS (~ 25 mg/mL), while the latter is less volatile (boiling point 80°C), but is an excellent solvent for F-POSS (~ 750 mg/mL). This 1:1 (v:v) solvent blend yielded films that were smoother and exhibited lower contact angle hysteresis than those spin cast from pure solutions of either solvent or alternative solvent mixtures.

Films of pure F-POSS spin cast at 5000 rpm from 1:1 HFC-43-10:HFB exhibited very low contact angle hysteresis with liquids possessing a broad range of surface tensions and polarities, including water ($\theta_{adv}/\theta_{rec}=124^\circ/120^\circ$), hexadecane ($80^\circ/77^\circ$), ethanol ($75^\circ/70^\circ$), and 5 cSt silicone oil ($64^\circ/59^\circ$) (Table S1). For all non-solvents of F-POSS, $\Delta\theta$ was $\leq 5^\circ$, significantly lower than previously reported for pure F-POSS films, especially with low surface tension liquids.^{45,92,93} The solid surface energy (calculated to be 10.1 ± 0.7 mJ/cm² using the Fowke's method) approached that of an atomically ordered trifluoromethyl monolayer (~ 9 mJ/cm²), despite the evident nanoscale roughness of the film.⁹⁴

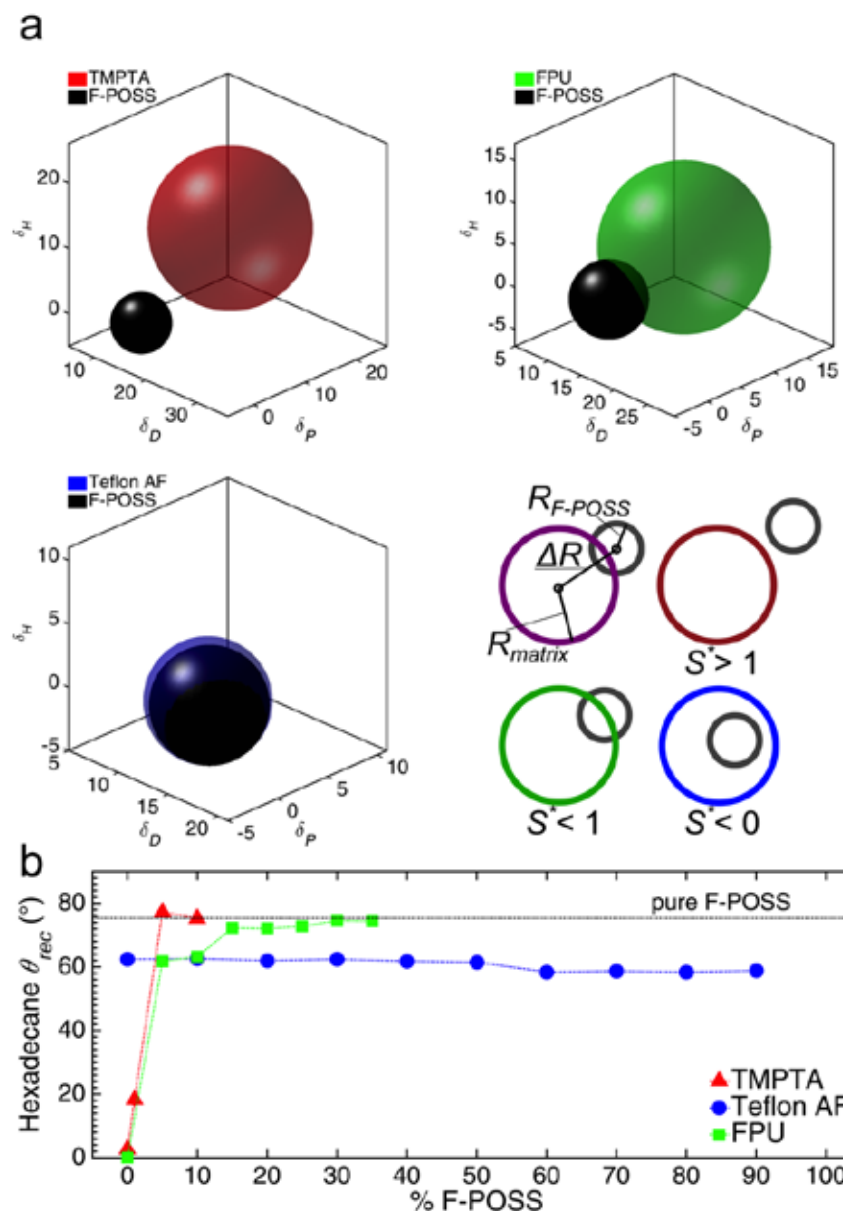


Figure 6. (a) Hansen solubility spheres illustrating the miscibility between the F-POSS and TMPTA (immiscible, $S^* \approx 1.3$), FPU (partially miscible, $S^* \approx 0.6$), and Teflon AF (miscible, $S^* \approx 0.0$), polymer matrices. (b) Receding contact angles with hexadecane for varying fractions of F-POSS in TMPTA, Teflon AF, and FPU. Error is $\pm 2^\circ$. Note that the immiscible TMPTA based coatings reach the receding contact angle values for a pure F-POSS film at ~ 5 wt.% F-POSS, the partially miscible FPU based coatings reach those values at ~ 30 wt.% F-POSS, while the miscible Teflon AF based coatings never yields receding contact angle values obtained for F-POSS films.

The low surface energy of F-POSS results in poor adhesion to substrates and limits its utility as a coating. Therefore, it is necessary to blend F-POSS with an inherently durable matrix.

Selecting a suitable matrix polymer requires consideration of its miscibility with F-POSS and its solvents, as these factors determine the stability, durability, and liquid repellency of the resulting coatings. We previously reported a miscibility parameter, based on Hansen solubility theory, which quantifies the extent to which a molecular filler, such as F-POSS, phase separates from a polymer matrix.⁹⁵ For any compound, a sphere may be constructed in Hansen solubility space that is centered on the dispersive, polar, and hydrogen bonding parameters of the compound. The sphere will possess a radius in which, ideally, all its good solvents are encompassed. The Hansen solubility spheres for F-POSS and a fluorinated polyurethane (FPU) reported in our previous work,⁹⁵ as well as those of additional polymer matrices evaluated in this work were determined experimentally by screening their solubility in solvents with known Hansen solubility parameters (Fig. 6a). The geometric overlap between the spheres allows for quantification of the miscibility between two species. The miscibility parameter, S^* ,⁹⁵ was calculated for each matrix as follows:

$$S^* = \frac{\Delta R - R_{matrix} + R_{F-POSS}}{2R_{F-POSS}} \quad (2)$$

where ΔR is the distance between the centers of the F-POSS and matrix spheres, and their radii are R_{F-POSS} and R_{matrix} , respectively. For matrices which are completely immiscible with F-POSS (no sphere overlap), $S^* > 1$, and for matrices which are fully miscible with F-POSS and whose spheres completely overlap, $S^* \leq 0$ (see schematic in Fig. 6a). Between these two extremes is a regime of partial miscibility. As F-POSS is an extremely low surface energy material, any immiscibility with the matrix polymer will drive it to the surface of a blended film during deposition.

Three polymer matrices were selected with varying Hansen parameters, and therefore varying miscibility with F-POSS. All matrix materials were fully soluble in the HFC-43-10:HFB solvent blend at the concentrations tested. Films of each polymer with varying fractions of F-

POSS were spin coated and their liquid repellency and durability evaluated. As there is no broad consensus in the literature on a method for testing the durability of liquid-repellent surfaces,⁹⁵ we selected a commonly used industrial methodology for evaluating the durability of coatings. This automated test, using a consistent abradant and applied pressure, was performed using a Taber Linear abraser with a CS-5 felt insert and an applied pressure of ~20 kPa. The contact angles of water and hexadecane were periodically measured on the abraded surfaces. A receding contact angle approaching zero corresponded to the point at which a liquid did not slide from the surface without leaving residue, regardless of tilting angle. The receding contact angle with hexadecane is representative of the capability of the surface to repel low surface tension liquids, and was used to compare films. A significant reduction in the receding contact angle during abrasion indicated either the F-POSS molecules on the surface or the entire coating had been removed from the substrate. Abrasion was halted when a significant portion of the underlying substrate was exposed or when hexadecane no longer receded from the surface, or both.

The first matrix evaluated was trimethylolpropane triacrylate (TMPTA), a nonfluorinated UV-curable network polymer, which has negligible miscibility with F-POSS ($S^* \approx 1.3$) (Fig. 6a). Spin coating a blend of TMPTA with just 5 wt.% F-POSS yielded a film with contact angles approaching that of the pure F-POSS film discussed above (water $\theta_{adv}/\theta_{rec} = 124^\circ/115^\circ$, hexadecane $81^\circ/78^\circ$), (Fig. 6b). This suggested that the F-POSS molecules completely migrated to the upper surface of the polymer film (the polymer-air interface), which was undesirable, as a loosely adhered thin film of F-POSS on a surface could easily be abraded away or delaminated with solvents. This blended film lost liquid repellency after only 50 abrasion cycles (water $\theta_{adv}/\theta_{rec} = 105^\circ/47^\circ$, hexadecane $61^\circ/7^\circ$), although the TMPTA matrix appeared undamaged.

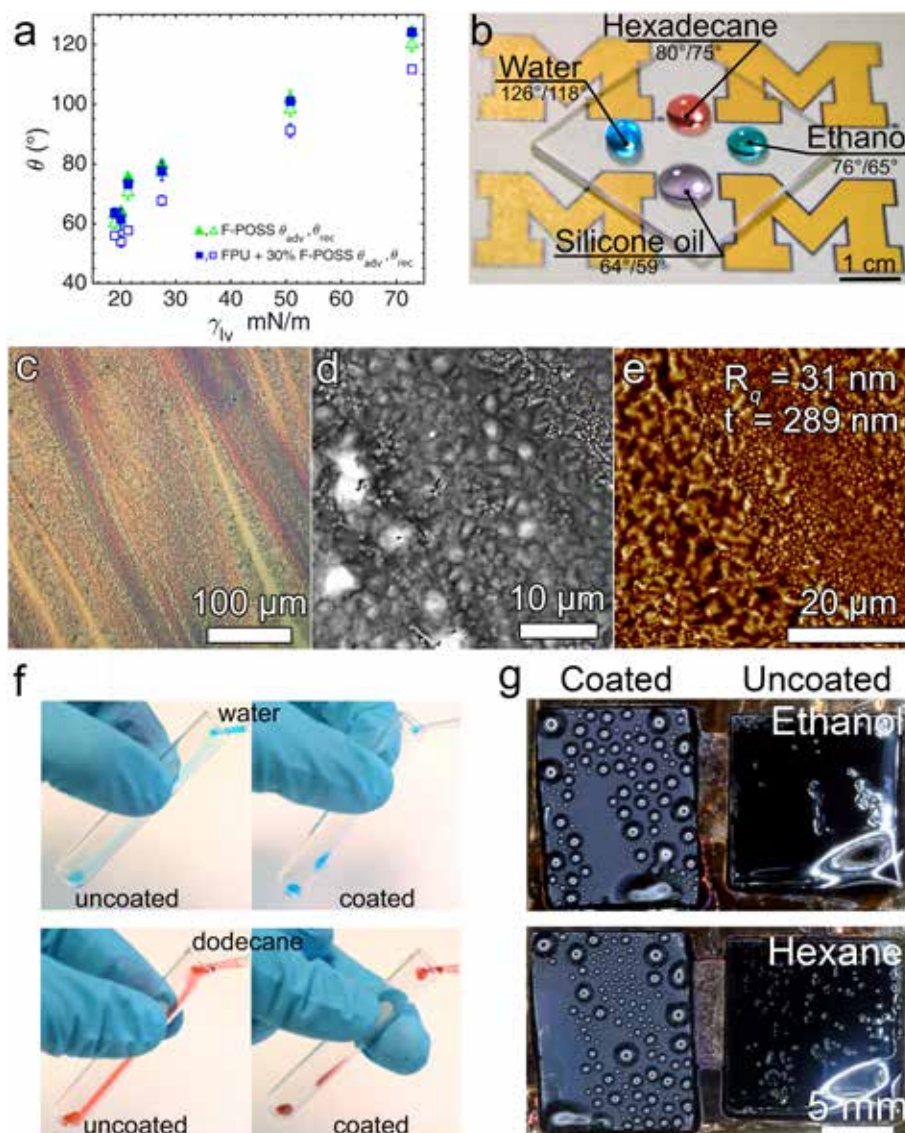


Figure 7. (a) Advancing and receding contact angles for liquids of varying surface tensions and polarities on spin coated F-POSS and FPU + 30% F-POSS films. Standard error is $\pm 2^\circ$ (b) An image of various liquid droplets on a spin-cast film of FPU + 30% F-POSS film on top of a glass slide. The image highlights the transparency and non-wettability of the fabricated surfaces. All of these liquids will readily slide off the surface if it is tilted (Movie S1). (c) Optical micrograph, (d) SEM, and (e) AFM for a FPU + 30% F-POSS film. (f) Images of water and dodecane being added to 5 mL glass test tubes which are uncoated or coated with FPU + 30% F-POSS. Note that the droplets do not wet the inner surface of the coated tubes (Movie S2). (g) Condensation of ethanol and hexane on cooled, coated and uncoated silicon substrates. Dropwise condensation was observed on the substrates coated with a FPU + 30% F-POSS film. The blurred droplets are in the process of dewetting the surfaces; exposing dry areas and facilitating continued condensation. The uncoated substrates exhibited filmwise condensation.

By contrast, adding even up to 90 wt.% F-POSS in a highly fluorinated polymer which was completely miscible with F-POSS (Teflon AF, $S^* \approx 0$) did not yield contact angles equal to

pure F-POSS. The maximum contact angles with hexadecane remained significantly lower than that of the fully fluorinated F-POSS monolayer ($\theta_{adv}/\theta_{rec} = 70^\circ/62^\circ$ versus $80^\circ/77^\circ$). This suggests that the F-POSS remained within the polymer matrix and did not completely cover the solid-air interface. Therefore, the CF_2 groups present in Teflon AF raised the overall surface energy of the film (approaching 19 mJ/cm^2) versus a dense CF_3 monolayer ($< 10 \text{ mJ/cm}^2$).⁹⁶ Although pure Teflon AF still exhibited reasonably low contact angle hysteresis and high contact angles (water $\theta_{adv}/\theta_{rec} = 125^\circ/113^\circ$, hexadecane $69^\circ/62^\circ$), it is not inherently durable, and films of this material and its F-POSS blends were completely destroyed after mild mechanical abrasion (< 50 Taber abrasion cycles).

A partially fluorinated polyurethane (FPU; methods) yielded partial miscibility ($S^* \approx 0.6$). While phase separation did occur, receding contact angles approaching those of pure F-POSS films were not observed until $> 15 \text{ wt.}\%$ F-POSS, which indicated that a significant portion of the F-POSS molecules could be dispersed within the bulk of the film, reducing the surface energy throughout the composite film. A blend of FPU and $30 \text{ wt.}\%$ F-POSS exhibited contact angle values approaching that of pure F-POSS (water $\theta_{adv}/\theta_{rec} = 127^\circ/118^\circ$, hexadecane $82^\circ/74^\circ$) (Fig. 7a,b). This composite was also much more durable and better adhered to the underlying substrate, as demonstrated by the mechanical durability testing described below. As the surface possessed only nanoscale roughness and did not cause significant light scattering (Figs. 7c-e), the FPU + F-POSS films were optically transparent (Fig. 8a). Virtually all high and low surface tension liquids slid readily on the surface, except for certain strong FPU solvents with low surface tension and high polarity (*e.g.* tetrahydrofuran and acetone) as well as the most highly fluorinated solvents, which dissolve F-POSS. The coating was applied to a variety of smooth substrates: steel, aluminum, glass, polystyrene, poly(methyl methacrylate), in addition to silicon,

and the contact angle hysteresis was consistently $< 11^\circ$ for water and $< 9^\circ$ for hexadecane. High-speed spin coating was not critical for achieving low contact angle hysteresis, as dip coated films on silicon exhibited low contact angle hysteresis with both water ($\theta_{adv}/\theta_{rec} = 129^\circ/116^\circ$) and hexadecane ($\theta_{adv}/\theta_{rec} = 81^\circ/72^\circ$). This signifies that samples unsuitable for spin coating due to curvature or size could also be successfully coated. For example, the coating was applied to the interior of small test tubes by simply filling them with the coating solution, then pouring it out. This treatment dramatically lowered the retention of dyed water and dodecane, as compared to the uncoated tubes (Fig. 7f).

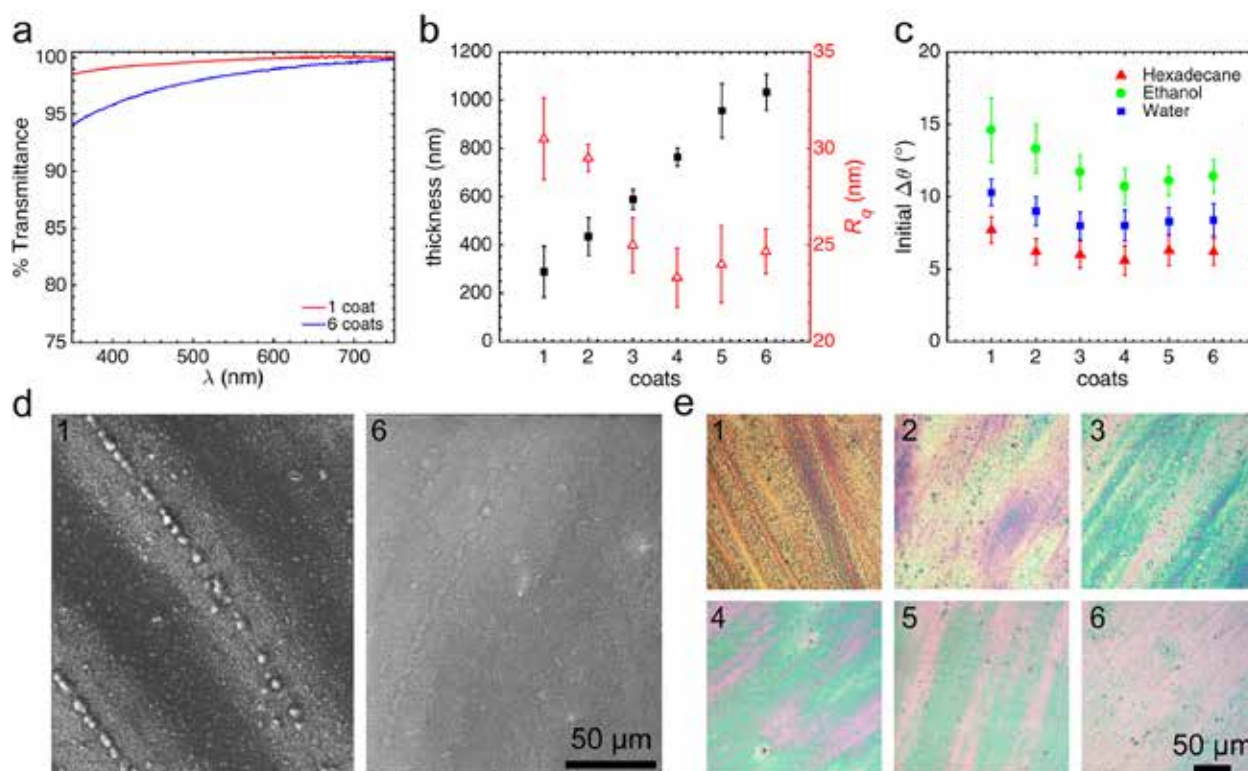


Figure 8. (a) High optical transparency is maintained even after multiple coats of FPU+30% F-POSS. (b) Multiple coats increase the film thickness, and increase the coatings mechanical robustness. A concurrent decrease in root-mean-squared roughness (R_q) was also observed using AFM measurements. (c) Reduced roughness yielded a decrease in the contact angle hysteresis with water, hexadecane, and ethanol (Table S5). (d,e) The reduced roughness and increased uniformity with multiple coats was also visible in SEMs and optical micrographs.

Microscale droplets condensing from a vapor, particularly for low surface tension liquids, may become immobile on both textured superomniphobic and lubricated surfaces.^{83,97} This is problematic for applications such as fog harvesting and condensation heat transfer.^{83,97} In our testing, a silicon wafer coated with FPU + 30% F-POSS, maintained at -10 °C, within a vacuum chamber saturated with vapors of ethanol or hexane, enabled the stable dropwise condensation and continual removal of both these low surface tension liquids (Fig. 7g). These results highlight the suitability of the developed omniphobic coatings for improving condensation heat transfer.^{83,97}

The thickness, t , of the spin-coated FPU + 30% F-POSS could be increased by spin coating the solution multiple times on the same substrate (Fig. 8b). Thicker samples should survive an increased number of abrasion cycles before failure. This strategy of increasing coating thickness to improve abrasion resistance is not possible with lubricated surfaces or self-assembled monolayers. For textured superomniphobic surfaces, increasing the thickness to improve durability would only be effective if the initial re-entrant geometry could be preserved during abrasion, which is usually unlikely. Spin coating multiple times also yielded more uniform surfaces, leading to decreased contact angle hysteresis with water, hexadecane, and ethanol ($\Delta\theta$ decreases from 10° to 8°, from 8° to 6°, and from 15° to 11°, respectively), concurrent with a decrease in the overall roughness of the coating (Fig. 8b-e). This effect was more pronounced on substrates that were significantly rougher than silicon wafers, such as mill-finished steel and aluminum, as the coating material could fill in surface scratches. For example, coating rough steel substrates ($R_q = 1440 \pm 80$ nm) five times significantly decreased contact angle hysteresis of water, hexadecane, and ethanol when compared versus a single coat ($\Delta\theta$ decreases from 26° to 11°, from 21° to 7°, and from 47° to 21° respectively).

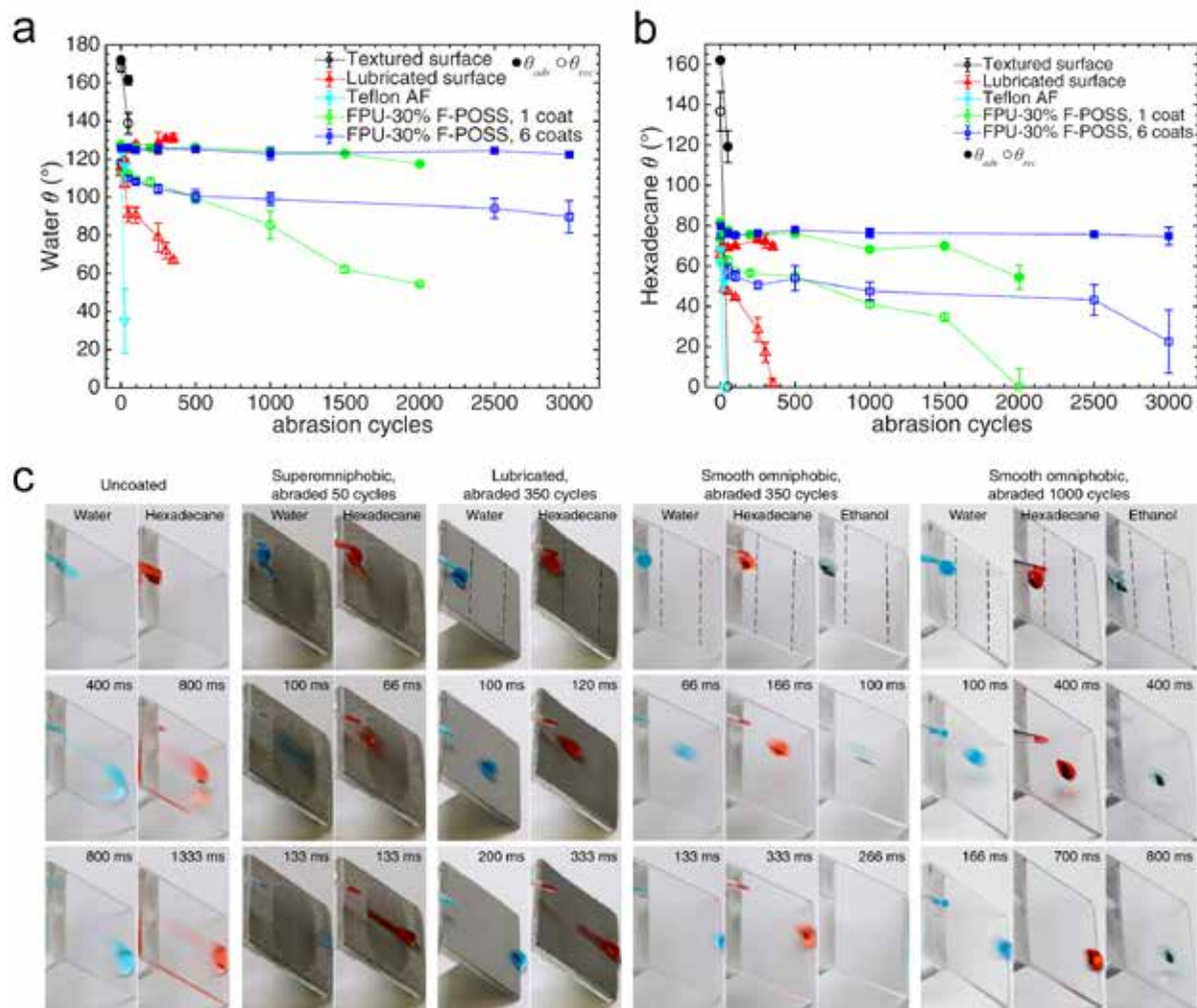


Figure 9. Advancing/receding contact angles with (a) water and (b) hexadecane with increasing linear abrasion cycles for a textured superomniphobic surface, a lubricated omniphobic surface, a spin-coated film of Teflon AF ($t \approx 200 \pm 50$ nm), and one coat ($t \approx 290 \pm 50$ nm) or six coats ($t \approx 1030 \pm 40$ nm) of the smooth omniphobic FPU+30% F-POSS coating (Fig. 3b). (c) ~ 20 μ L liquid droplets sliding on the abraded samples inclined at 45° in video frames compiled from Movie S4. The ~ 12.5 mm wide abraded track is located in the center of the 25×25 mm samples, perpendicular to the droplet sliding direction. Hexadecane readily wetted the superomniphobic and lubricated samples after 50 and 350 abrasion cycles, respectively, but slid readily on the smooth omniphobic coating even after 1000 cycles. However, ethanol, a polar low-surface-tension solvent, pinned irreversibly on the 1000 cycle abraded sample.

The abrasion resistance of our thickest FPU + 30 wt% F-POSS film (6 coats, $t = 1030 \pm 40$ nm) was compared to the resistance for a thinner ($t = 290 \pm 50$ nm), single coat FPU + 30 wt% F-POSS film, a superomniphobic surface (FPU + 50 wt% F-POSS spray-coated with an airbrush), a lubricant-infused textured surface (perfluoropolyether drop-cast on an

etched, fluorosilanized aluminum surface fabricated based on methods reported in literature⁹⁸), and a spin coated Teflon AF film (Fig. 9). The Teflon AF, spray-coated, and lubricant-infused surfaces reached a zero receding contact angle with hexadecane relatively quickly during the abrasion testing (Fig. 9b), at 25, 50, and 350 cycles, respectively. However, the FPU + 30 wt% F-POSS spin coated films maintained high contact angles significantly longer (after 2500 cycles on the sample with 6 coats, water $\theta_{adv}/\theta_{rec} = 123^\circ/99^\circ$, hexadecane $77^\circ/50^\circ$). While low surface tension liquids completely adhered to the abraded textured and lubricated surfaces, they still slid from the FPU + 30 wt% F-POSS 6 coats sample when tilted after 350 abrasion cycles (Fig. 9c). Hexadecane remained mobile on the coating even after 1000 abrasion cycles. As long as the coating remained free from macroscopic scratches, the contact angles with water and hexadecane remained relatively constant after an initial decrease. Coating failure due to scratching through to the substrate began to occur beyond 3000 cycles in certain samples, but not until 8000 cycles in others. A standard tape peel test was performed on the same sample to evaluate its adhesion to the underlying silicon substrate. No delamination was observed after peeling the tape from a scratched surface. The coating remained liquid repellent despite the apparent removal of some surface F-POSS molecules (initial: water $\theta_{adv}/\theta_{rec} = 126^\circ/118^\circ$, hexadecane $80^\circ/75^\circ$, final: water $124^\circ/107^\circ$, hexadecane $79^\circ/59^\circ$). A cyclic bending test was also performed, with the linear abraser, on a flexible polyester substrate coated with six layers of FPU + 30 wt% F-POSS. Each forward stroke flexed the sample to a minimum bend radius of ~ 2.3 mm. After 1000 bending cycles, there was no visible delamination or cracking of the coating, and the contact angles in the bent area were virtually unchanged (initial: water $\theta_{adv}/\theta_{rec} = 124^\circ/113^\circ$, hexadecane $80^\circ/73^\circ$, final: water $123^\circ/111^\circ$, hexadecane $79^\circ/71^\circ$).

Conclusion

We have demonstrated a facile, spin-coating methodology to produce highly liquid-repellent surfaces that allow liquids with a broad range of surface tensions and polarities to slide off without residue. We optimized the deposition of smooth coatings containing a highly fluorinated small molecule (F-POSS), utilizing a blended fluorinated solvent to minimize crystallization, yielding surfaces with very low contact angle hysteresis with a broad range of liquids. An inherently durable fluorinated polyurethane in which the F-POSS is partially miscible was added as a matrix polymer in order to produce a mechanically durable omniphobic coating that adheres to a variety of substrates. The coating may also be applied to non-planar substrates via dip coating. The smooth, all-solid nature of the coating allows it to be inherently pressure stable, as well as more abrasion resistant than textured and lubricated omniphobic surfaces. This approach may facilitate novel applications where repelling all types of liquids from a transparent substrate is critical. These surfaces may be especially useful for developing surfaces that enhance heat transport during both boiling and condensation.

A list of manuscripts supported by this grant:

1. “Low Interfacial Toughness Materials for Effective Large-Scale De-Icing”, Kevin Golovin, Abhishek Dhyani, M. D. Thouless[#], and **Anish Tuteja[#]**, *Science, in revision* (*Science* is interested in publishing the manuscript as a report after revision).
2. “Design of surfaces for controlling hard and soft fouling”, Alex Kate Halvey, Brian Macdonald, Abhishek Dhyani, and **Anish Tuteja[#]**, *Philosophical Transactions of the Royal Society – A*, 2018, 20180266, <http://dx.doi.org/10.1098/rsta.2018.0266>.
3. “Characterization of superhydrophobic surfaces for drag reduction in turbulent flow”, James W. Gose, Kevin Golovin, Mathew Boban, Joseph M. Mabry, **Anish Tuteja**, Marc Perlin and Steven L. Ceccio, *Journal of Fluid Mechanics*, Volume 845, 25 June 2018, pp560-580.
4. “Smooth, All-Solid, Low-Hysteresis, Omniphobic Surfaces with Enhanced Mechanical Durability”, Mathew Boban, Kevin Golovin, Brian Tobelmann, Omkar Gupte, Joseph M. Mabry, and **Anish Tuteja[#]**, *ACS Applied Materials & Interfaces*, 2018, 10 (14), pp 11406–11413.
This work was highlighted through press releases from Michigan Engineering and University of Michigan News. Also highlighted by the National Science Foundation, National Academy of Engineering, The Verge, LiveScience, AZO Materials, Business Standard, NetNewsledger.com, Financial Express, Futurity, Brinkwire, Eureka!, Indian Express, Science Alert and hundreds of other national and international news outlets.
5. “A predictive framework for the design and fabrication of icephobic polymers”, Kevin Golovin and **Anish Tuteja[#]**, *Science Advances*, 22 Sept 2017, Vol. 3, no. 39, e1701617.
6. “Designing Self-Healing Superhydrophobic Surfaces with Exceptional Mechanical Durability”, K Golovin, M Boban, JM Mabry, and **Anish Tuteja[#]**, *ACS Applied Materials & Interfaces*, 2017, 9 (12), pp 11212–11223.
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7. “Open-channel, water-in-oil emulsification in paper-based microfluidic devices, C Li, M Boban, and **Anish Tuteja[#]**, *Lab on a Chip*, 2017, 17, 1436-1441
8. “Rational Design of Hyperbranched Nanowire Systems for Tunable Superomniphobic Surfaces Enabled by Atomic Layer Deposition”, Ashley R Bielinski, Mathew Boban, Yang He, Eric Kazyak, Duck Hyun Lee, Chongmin Wang, **Anish Tuteja[#]**, Neil P Dasgupta[#], *ACS Nano*, 2017, 11 (1), pp 478–489.
9. “High-resolution velocity measurement in the inner part of turbulent boundary layers over super-hydrophobic surfaces”, H Ling, S Srinivasan, K Golovin, GH McKinley, **A Tuteja**, J Katz, *Journal of Fluid Mechanics*, 2016, 801, 670-703

10. “Bioinspired surfaces for turbulent drag reduction”, Kevin B. Golovin, James W. Gose, Marc Perlman, Steven L. Ceccio and **Anish Tuteja**[#], *Philosophical Transactions of the Royal Society A*, **374**: 2016, 0189.

11. “Paper-Based Surfaces with Extreme Wettabilities for Novel, Open-Channel Microfluidic Devices”, C Li, M Boban, SA Snyder, SPR Kobaku, G Kwon, G Mehta, and **Anish Tuteja**[#], *Advanced Functional Materials*, 2016, 26 (33), 6121-6131

12. “Designing Durable Icephobic Surfaces”, Kevin Golovin, Sai P. R. Kobaku, Duck Hyun Lee, Edward T. DiLoreto, Joseph M. Mabry, and **Anish Tuteja**[#], *Science Advances*, 11 Mar 2016, Vol. 2, no. 3, e1501496.

This work was highlighted through press releases from Michigan Engineering and University of Michigan News. Also highlighted by Science, The Wall Street Journal, NPR, German Public Radio, Channel 4 News, Phys.org, Chemistry World, ScienceNews.org, AAAS EurekAlert, The Telegraph, engadget, nanowerk, TechTimes, Daijiworld, ZeeNews, Chennai Online, Big News Network, New Kerala, Yahoo!, e! Science News, UPI, HNGN, Western Daily, Press, MSN, ScienceDaily, redOrbit, MaterialsGate, Christian Science Monitor, and hundreds of other national and international news outlets.

13. “Membranes with selective wettability for the separation of oil–water mixtures”, *MRS Communications*, Gibum Kwon, Ethan Post, and **Anish Tuteja**[#], Volume 5, Issue 3, September 2015, pp. 475-494

14. “Wettability Engendered Templated Self-assembly (WETS) for Fabricating Multi-phasic Particles”, *ACS Appl. Mater. Interfaces*, Sai P.R. Kobaku, Gibum Kwon, Arun K. Kota, Raghuraman G. Karunakaran, Philip Wong, Duck Hyun Lee, and **Anish Tuteja**[#], 2015, 7 (7), pp 4075–4080.

This work was highlighted in hundreds of media outlets (TV, Radio, Newspapers and Websites) including: Michigan Engineering, University of Michigan News, M Record, Detroit News, Greenfield Daily Reporter, Michigan Radio, Washington Times, Sun Herald, Olympian Online, KSL-TV, Daily Press, World News, Miami Herald, WOHL-TV, Oklahoma News, WBNS-TV, Monroe News, India West News, Yahoo India News, Middle East Molecular Biology Society- ENews, Gazette Online, and Technology.org

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