

Design and Application of Surfaces that Control Liquid and Solid Fouling

by

Brian C. Macdonald

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Materials Science and Engineering)
in the University of Michigan
2022

Doctoral Committee:

Professor Anish Tuteja, Chair
Professor Zhan Chen
Professor Jinsang Kim
Professor Geeta Mehta

Brian C. Macdonald

macdobri@umich.edu

ORCID iD: 0000-0002-5337-903X

© Brian C. Macdonald 2022

Dedication

To my wife

Because we are just kids with cars and money

Acknowledgements

Having gone through the experience of this PhD, one thing has rung true to me: So much randomness and serendipity plays into the successes in life. With this in mind, it would be impossible (and crazy) not to recognize all of those who have helped me get to this point. First and foremost, I would like to thank my research advisor Prof. Anish Tuteja. He has given me a unique and gratifying opportunity to contribute to the lab and gave me the freedom to explore my creativity in solving complex, open-ended problems. Thank you Prof Jinsang Kim for both your feedback and allowing me to audit your excellent classes. Thank you Prof. Zhan Chen also for your feedback, as well as our fruitful collaboration on multiple works. Thank you Prof. Geeta Mehta for also providing very helpful feedback.

I also owe noteworthy gratitude to all of my peers both inside and out of the Polymers, Surfaces, and Interfaces research group. To my group members, it has been nothing short of a pleasure working with, and learning from you. Thank you to my first group research mentor Catherine Snyder, Sarah Snyder for the fun conversations in the office, Alex for the shenanigans within the lab, Brian T for confusing us all by having my name (and for the work we did together), Dhyani for the great work we did and great discussions, Matt Boban for the early mentorship, Jiayue for the brief work we did together, Jun for suffering through and overcoming a very difficult project with me, Jing for the great and exciting work we did together, Jiaqi for carrying on my work and becoming the ‘ice-cream manager’, and Fan-Wei for the reminder that “I don’t

know”. Outside of those mentioned in the lab I would also like to thank all of the friends I have made here at U of M. Those include Jonathan, Patrick, Nate, Randy, Sarah, Brian I, Izzy, Laura, Max, Paul, Joey, Duncan, Reggie (I knew you from undergrad), Avi, Mike, and Aaron. These have beyond a doubt been the best years of my life and it was made possible by spending so much quality time with you.

I would also like to thank some key mentors I have had during my academic journey that have played a vital part in my success to this point. From my time at community college, I would like to thank Prof Mamta Agarwal for mentoring me, believing in me when I hardly believed in myself, and seeing my potential as a future scientist. Thank you to Prof Mo Tavakoli for seeing in me what I could not; the ability to become an engineer. Thank you also for constantly taking care to mentor me, and exposing me every opportunity you could. I would like to thank Prof. David Kisailus for giving me my first research opportunity, and helping me cement my decision to get a PhD. I would lastly like to thank both Dr. Sourangsu Sarkar and Dr. Richard Novak for your patience and mentorship.

I would like to thank those in my family who made this possible. I particularly want to thank my grandfather and grandmother. Without your help, none of this would have been remotely possible.

Lastly I would like to thank my wife Kathy, whom moved here with me from California to support me through this PhD journey.

Table of Contents

Dedication	ii
Acknowledgements.....	iii
List of Figures	xii
List of Tables	xviii
Abstract	xix
Chapter 1 – Introduction	1
1.1 Introduction to Surface Fouling.....	1
1.2 Controlling Liquid Fouling.....	3
1.2.1 Wettability Theory	4
1.2.2 Design Strategies for Liquid Control.....	8
1.3 Controlling Solid Fouling	13
1.3.1 Notable Examples of Solid Fouling.....	14
1.3.2 Solid Fouling Surface Design Strategies	20
1.3.3 Design Challenges of Fouling Complexity.....	26
1.4 Research Overview	29
Chapter 2 - Rapid and Robust Surface Treatment for Simultaneous Solid and Liquid Repellency	32
2.1 Introduction.....	32

2.2 Results and Discussion	34
2.2.1 Liquid Repellency	38
2.2.2 Solid Repellency	42
2.2.3 Liquid-like Surface Characterization	45
2.2.4 Durability	51
2.3 Conclusion	56
2.4 Materials & Methods	57
2.4.1 b-PDMS and cb-PDMS Synthesis	57
2.4.2 Glass Silanization.....	57
2.4.3 Control Surfaces.....	59
2.4.4 Surface Characterization	60
2.4.5 Surface Energy.....	61
2.4.6 AFM.....	61
2.4.7 Ellipsometry	61
2.4.8 Solid Adhesion Tests	62
2.4.9 Scaling Tests	63
2.4.10 Durability Tests.....	64
Chapter 3 - Polysiloxane-based Liquid-Like Layers for Resistance of Polymer and Wax Deposition	65
3.1 Introduction.....	65

3.2 Results and Discussion	69
3.2.1 Surface Characterization	69
.....	71
3.2.2 Fouling Quantification via AFM and Contact Angle	72
3.2.3 Sum Frequency Generation Analysis of Highly Mobile Tethered PDMS	79
3.3 Antifouling Mechanism	83
3.4 Conclusion	84
3.5 Materials and Methods.....	86
3.5.1 Materials	86
3.5.2 Surface Silanization	86
3.5.3 Polymer Fouling Procedure	87
3.5.4 Characterization	88
Chapter 4 - Bioinspired Superoleophobic Zwitterionic Nanowires for Enhanced Marine Fouling Prevention	90
4.1 Introduction.....	90
4.2 Results and Discussion	93
4.2.1 Fabrication of the Zwitterionic Nanowires	93
4.2.2 Chemical Characterization of the Zwitterionic Nanowires	94
4.2.3 Wetting Characterization of the Zwitterionic Nanowires	96
4.2.4 Marine Algal Fouling Test on the Zwitterionic Nanowires and Other Surfaces	97

4.2.5 Marine Algal Fouling Release on the Zwitterionic Nanowires and Other Surfaces....	98
4.3 Conclusion	101
4.4 Materials and Methods.....	101
4.4.1 Materials and Fabrication.	101
4.4.2 Contact angle measurements.....	102
4.4.3 Algae fouling experiments	103
4.4.4 Open channel shear flow.....	103
4.4.5 Optical density measurements.	104
4.4.6 XPS	105
4.4.7 TEM	105
Chapter 5 - Design of Abrasion Resistant Polymeric Coatings with Durable Anti-Fog Performance	106
5.1 Introduction.....	106
5.2 Results and Discussion	110
5.2.1 Optimization of Coating Toughness	110
5.2.2 Reducing Coating Friction Coefficient.....	113
5.2.3 Abrasive Wear Resistance	117
5.2.4 Antifog Performance.....	119
5.2.5 Comparison to Commercial Anti-fogging Coatings	124
5.3 Conclusion	130

5.4 Materials and Methods.....	130
5.4.1 Antifog Coating Fabrication	130
5.4.2 Dynamic Mechanical Analysis (DMA)	132
5.4.3 Tabor Abrasion	132
5.4.4 Scanning Electron Microscopy	135
5.4.5 Dynamic Friction Coefficient	135
5.4.6 Linear Stylus Profilometry.....	136
5.4.7 FTIR.....	136
5.4.8 Dynamic Mechanical Analysis (DMA)	137
5.4.9 Hansen Solubility Parameters:.....	138
5.4.10 Friction Coefficient.....	140
5.4.11 Experimental structure for fogging test	142
5.4.12 Comparison to Commercial Antifog Solutions.....	146
5.4.13 UV-Vis Optical Properties.....	149
Chapter 6 - Durable Water-Resistant Composite Antifog Coatings	150
6.1 Introduction.....	150
6.2 Results and Discussion	152
6.2.1 Evaluation of Wear Resistance	152
6.2.2 Antifog Performance.....	157
6.3 Conclusion & Ongoing Work	163

6.4 Materials and Methods.....	164
6.4.1 Antifog Coating Fabrication	164
6.4.2 Graphene Oxide Synthesis.....	165
6.4.3 Tabor Abrasion	166
6.4.4 FTIR.....	167
6.4.5 Fog Testing	167
6.4.6 Optical Microscopy.....	169
6.4.7 Linear Stylus Profilometry.....	169
Chapter 7 - Facile anti-frosting/anti-icing coating with enhanced longevity	170
7.1 Introduction.....	170
7.2 Results and Discussion	174
7.2.1 Chiller Apparatus	174
7.2.2 Peltier Apparatus.....	177
7.3 Conclusion and Future Directions	181
7.4 Materials and Methods.....	182
7.4.1 Testing Apparatus and Conditions.....	182
7.4.2 Coating Fabrication (redo).....	184
7.4.3 Anti-Ice SBMA Network Coated Aluminum	185
7.4.4 PEG-Polyurethane Coating Fabrication.....	185
Chapter 8 – Summery and Future Outlooks	186

8.1 Future Directions	189
8.1.1 Solid and Liquid repellent Liquid-Like Layers	189
8.1.2 Multifunctional Marine Antifouling Surfaces	191
8.1.3 Durable Polymeric Antifog Coatings.....	192
8.1.4 Polymer Antifrost Coatings	193
Bibliography	195

List of Figures

Figure 1: Summery of the applications which require the control of hard and soft fouling.....	3
Figure 2: Depiction of Youngs contact angle on a smooth surface and the potential wetting behavior.....	4
Figure 3: Contact angle hysteresis conducted via Sessile drop and sliding drop methods.....	5
Figure 4: The relation between the cosine of the equilibrium contact angle and the cosine of the apparent contact angle.....	7
Figure 5: (Above) Demonstration of the minimum texture angle and (Below) dependence of robustness factor (A^*) on surface energy and spacing ratio (D^*) (Top) various surface geometires and their corresponding ψ_{min}	10
Figure 6: The contact angle hysteresis vs the apparent contact angle for three different state-of-the-art liquid repellent surfaces.....	12
Figure 7: Ice accretion at varying length scales.....	15
Figure 8: Protein repellency mechanism for a hydrophilic, brush-like grafted polymer.....	17
Figure 9: Varying examples of marine fouling species and the fouling of ship hulls.	19
Figure 10: (A) Illustration of varying size and modulus of fouling species as well as (B) corresponding antifouling surface design strategies. Adapted from ¹⁸	21
Figure 11: Antifouling performance of various surface design strategies and select foulants.	26
Figure 12: Graphical depiction of the natural marine fouling process.	28
Figure 13: Precursor molecular wieght and hysteresis	35

Figure 14: Effect of reaction time and thickness on hysteresis	37
Figure 15: The proposed mechanism for the bidentate attachment of 1,3-dichlorotetramethyldisiloxane.....	38
Figure 16: CB-PDMS liquid like layer shedding fluorinated krytox lubricant	42
Figure 17: Solid Antifouling Properties of Liquid-Like Layers	44
Figure 18: Liquid-Like layer property characterization.....	47
Figure 19: AFM micrographs of cb-PDMS and surfaces of comparison	48
Figure 20: AFM micrograph of bare silicon	48
Figure 21: Logarithmic plot displayinh the measured ice adhesion shear strength as a function of shear rate	50
Figure 22: Durability of b-PDMS and cb-PDMS	52
Figure 23: AFM Micrographs of abraded cb-PDMS	53
Figure 24: Durability of cb-PDMS to icing/deicng cycles	53
Figure 25: Abrasion and wetting properties of abraded textured omniphobic coatings	54
Figure 26: Confocal micrographs of damaged textured surfaces	55
Figure 27: Confocal micrographs of damaged lubricant infused surfaces	56
Figure 28: PDMS Silanized Glass	58
Figure 29: Ice & solid fouling testing apparatus.....	63
Figure 30: Resultant surface chemistries after silane exposure and their structure.	68
Figure 31: AFM micrographs of bare silicon and functionalized silicon.	71
Figure 32. Roughness and thickness of silanized samples.	71
Figure 33. A) Change in root mean square (RMS) surface roughness after polymer fouling.	73
Figure 34. AFM micrograph array of fouled silicon and functionalized silicon samples	73

Figure 35. Change in dynamic receding water contact angle after polymer fouling.	75
Figure 36: Comparison of fouling from Polystyrene/Toluene and Polystyrene/DMF solutions..	77
Figure 37. RMS roughness, change in receding contact angle and AFM micrographs of wax fouled surfaces	78
Figure 38. SFG spectra collected from: (A & B) coating/toluene interfaces and (C & D) the coating/water interfaces.	81
Figure 39: Bioinspired zwitterionic nanowire coating for simultaneous fouling reduction and fouling release.	93
Figure 40: Fabrication and chemical characterization of the zwitterionic nanowires.	95
Figure 41: Contact angle measurement on zwitterionic NWs and uncoated NWs under different conditions.	97
Figure 42: Algae fouling test on ZNWs and other coatings.	100
Figure 43. Design of durable antifog coatings.	109
Figure 44: Mechanical enhancement of the PVP-PETRA antifog coating.	111
Figure 45: Raw stress-strain data of PVP and PVP-PETRA films.	112
Figure 46. Miscibility parameter (S^*) of PVP and surfactants	113
Figure 47: Miscibility and coefficient of friction for PVP-surfactant coatings.	116
Figure 48: Linear Tabor abrasion setup for antifog coated polycarbonate and the microstructure of the CS-5 felt tip abrasion tip.	117
Figure 49: Polycarbonate and coated polycarbonate substrates after sequential abrasion.	119
Figure 50: Water contact angle of selected coatings.	120

Figure 51: A) Polycarbonate and antifog coated polycarbonate within controlled environmental chamber (Rel Humidity = ~65% and substrate temperature of ~14 °C). The coatings containing surfactant also contain 20% PETRA.....	123
Figure 52. Image correlation factor (ICF) of surfaces.	124
Figure 53: Abrasion resistance and contact angle data for commercial antifog coatings.....	126
Figure 54: Comparative fogging trends between PS20 and commercial antifog coatings.	127
Figure 55: Transparency properties of coated samples.....	129
Figure 56: Post abrasion substrates after all abrasion cycles outlined in Table 8. 20% PETRA and 15% surfactant was added to the coatings indicated.....	133
Figure 57: FTIR spectra for PETRA with UV exposure	137
Figure 58: Relative dynamic interfacial friction coefficients	141
Figure 59: Schematic diagram of the test chamber.....	143
Figure 60: The humidity and temperature evolution during the experiments.	145
Figure 61: Image correlation factor plots for successive, cyclical (15) fogging tests.	146
Figure 62: Longevity of static water contact angle performance with extended exposure time to normal environmental conditions.	148
Figure 63: Design schema of durable water resistant antifog coatings.	151
Figure 64: Coated polycarbonate after 1000 CS-7 abrasion cycles.....	153
Figure 65: Optical micrograph array of PVP and PVP composite coatings and sequential abrasion, water swelling, and further abrasion.	155
Figure 66: Thin coatings (600nm) subjected to abrasion, water submersion/swelling, followed by drying, and 1000 additional abrasion cycles.....	156

Figure 67: Root-mean-square roughness measurements (R_q) of coated samples after 1000 abrasion cycles before and after water swelling. A) Thick 700nm and B) thin 600 nm coatings.....	157
Figure 68: Contact angle properties of each PVP-based coating.....	158
Figure 69: Optical images of PVP/1%Graphite composite coating before and after water submersion/swelling and drying. Potential mechanism of particle surface migration.	160
Figure 70: Fogging performance of PC, PVP, and PVP/1% Graphite. A) Comparison between polycarbonate (PC) and PVP B) comparison between PC, PVP, and PVP after submersion in water for 2 hours followed by drying C) PVP and PVP/1%Graphite D) PVP/1% graphite fogging for a fresh sample and a sample submerged into water for 2 hours followed by drying.	161
Figure 71: Small local contact angle of water condensates between solid lubricating particles and large contact angle of large sessile drop.	162
Figure 72: Schematic of modified Hummers method and FTIR spectra graphite and graphene oxide.....	166
Figure 73: Experimental schematic of fogging apparatus	168
Figure 74: Temperature profile for the sample surface and the PID controlled base temperature.	169
Figure 75: Formulation and fabrication process of SBMA anti-freezing coatings.....	173
Figure 76: Chiller thermal profile for a given coolant temperature. A) Thermal profile for surface temperature (T_s) for -10 °C coolant and B) -20 °C coolant.....	175
Figure 77: Frost delay testing of bare aluminum substrates and SBMA coated aluminum.	176
Figure 78: Ice initiation time for coating thickness of 150 μ m, 100 μ m, and 50 μ m.....	177
Figure 79: Temperature profile comparison between Chiller and Peltier apparatus.	178
Figure 80: Frost formation time of bare aluminum utilizing different freezing apparatuses.....	179

Figure 81: Ice initiation time of pure polySBMA (0%) and crosslinked 0.25% PEGDA/SBMA	180
Figure 82: Ice initiation time for 100µm thick PEG-Polyurethane (1:1 mass ratio) coatings.	181
Figure 83: Schematic of chiller test section and image of secured sample for testing.	182
Figure 84: Peltier freezing test section.....	183
Figure 85: Photographs of Peltier plate test section. A) Aluminum est section with insulation and B) Fully constructed and insulated sample on the test section.	184

List of Tables

Table 1: Liquid contact angles on b-PDMS, cb-PDMS, and F-17 functionalized surfaces	40
Table 2. Surface energy, water contact angle and DMF contact angle of silicon, and silicon grafted with C12, F17, t-BCSE, and t-PDMS	69
Table 3. Static water, DMF, and Toluene contact angle of a 2.5 μ L droplet selected surfaces. ...	76
Table 4: Example of flow parameters in highest flow rate (2 gpm).	104
Table 5: List of experiments demonstrating material and additive effects on sequential abrasion resistance	134
Table 6: Experimental Hansen Solubility Parameter data for surfactants.	139
Table 7: Hansen solubility parameters calculated by HSPiP software from date of Table S1. *PVP parameters were taken from the HSPiP database.	140
Table 8: Select Surfactants and corresponding HLB values and S^*	140
Table 9: Average steady-state friction coefficients of polycarbonate and antifog coated	142
Table 10: % increase in average contact angle for t=1min the PVP-based coatings. Thick (700nm) and thin (600nm) coating sets were evaluated.	159

Abstract

Surfaces which maintain the ability to control liquid and solid accretion are of significant industrial and everyday value. The applications for such materials may include antifogging glasses, self-cleaning surfaces, frost and fouling resistant heat exchangers, ice-phobic airplane wings, antibacterial surfaces, and marine antifouling ship hulls. Over the past few decades, researchers have attempted a host of design strategies that effectively control surface fouling. Some surface design strategies include lubricant infused surfaces able to repel many liquids and solids, liquid omniphobic textured surfaces, hydration-layer forming covalently attached superhydrophilic brushes, and ice-phobic elastomers. However, the inability of these innovations to limit fouling of varying size, Young's Modulus, and complexity, as well as withstand the harsh conditions of natural and/or industrial environments, has limited their broad implementation. This thesis presents multiple advancements in the design of surfaces able to rationally control the accretion of multiple forms of matter, and in some cases yield exceptional durability.

The first two chapters involve a novel surface reaction technique able to easily render a chemically bound polysiloxane liquid-like lubricating layer onto various surfaces. These grafted chains can readily shed a wide range of liquids with broad ranging surface tension, and solids of various size and Young's Moduli. In a second work, we demonstrated the ability of these liquid-like layers to significantly limit the adsorption of small-scale polymer and wax deposits. They also demonstrated significant durability to abrasion, UV exposure, heat, and chemical damage. Such a

surface design, with exceptional durability and broad antifouling properties, has rarely been demonstrated.

The design of surfaces able to broadly control material accretion was also further investigated within the realm of marine environments. Chapter 4 demonstrates the design of a unique surface able to combat complex algae accretion. A combinatorial approach was envisaged where biocidal nanowires were coated with hydration layer-forming zwitterionic polymer brushes. The hydration layered nanowires demonstrated the ability to both limit the settlement and kill algal, and bacterial species. This surface which combined two widely studied and distinct surface designs, outperformed a host of different state-of-the-art surfaces in their ability to broadly control marine fouling.

In the last three chapters, surfaces were designed to control phase changing water accretion. Chapter 6 & 7 detail the engineering of antifog polymers. Most antifog polymers contain an inherent limitation dilemma between performance and abrasion resistance. To overcome this dilemma, a hydrophilic polymer antifog coating was developed which simultaneously enhanced the durability and the fogging performance through the addition of miscible hydrophilic slip additives. Depending on the additive, we can achieve high performance, wear resistance, and/or water resistance. Lastly, an innovative zwitterionic anti-freezing polymer coating was developed with the ability to absorb water and facilitate a non-freezing water state within the bulk matrix. This coating yielded freezing delay times of almost 13X that of bare aluminum.

The culmination of this work adds value to the field of surface engineering by demonstrating multiple surface design strategies able to control the accretion of several states of matter with varying complexity. In addition, these works push the boundary of applicability with regard to not only performance, but also durability. With the techniques and knowledge gained

from this thesis, surfaces and coatings can be designed, operate within complex fouling processes, demonstrate robustness within harsh environments, and above all, achieve high levels of performance.

Chapter 1 – Introduction

1.1 Introduction to Surface Fouling

Surfaces that impart control over liquid, solid, or vapor accretion provide an evolutionary advantage to numerous plants, insects, and animals. Examples include superhydrophobic feathers, furs, and leaves that enable the rapid shedding of accreted water; anti-freeze proteins that prevent the freezing of arctic fish, animals, and plants; patterned surfaces that can provide insects a drink of water in the middle of the desert; and superhydrophobic hairs that enable insects to walk on or breathe under water. Over the last few decades, synthetic analogs of these natural surfaces have been fabricated to support a broad spectrum of commercial and residential applications. Applications that emerge from liquid repellency include stain resistant garments ¹, drag reducing coatings ², self-cleaning surfaces ³, anti-corrosion surfaces ⁴, and membranes for enhanced liquid-liquid separation ⁵. Surfaces able to resist or shed solids can find applications in the de-icing of airplane wings, preventing marine fouling of ship hulls and infrastructure, averting pathogenic contamination within hospitals, proteins on medical equipment, counteracting wax and asphaltene accumulation within crude oil pipelines, and inhibiting scale formation on heat exchanger surfaces ⁶. Finally, surfaces that control vapor condensation and evaporation can enable energy efficient condensation ⁷, boiling ⁸, avert frost formation ⁹, and deter fogging ¹⁰.

The design of surfaces becomes more complex when matter accretion control is required across multiple phases and length scales or requiring a degree of durability. In most prior work,

surfaces have been engineered to control the adherence of a single state of matter. However, in many real-world situations, two, and sometimes even three states of matter work in concert, or in series towards forming the final bulk accumulating species. This causes many strategies focused on shedding or controlling one state of matter, to be ineffective. One relevant example is that of frost and ice formation. Frost forms as water vapor from a humid atmosphere condenses on a cold surface. The small droplets formed via condensation, can then act as nucleation sites for larger ice crystals to grow ^{11, 12}. Design strategies aimed at delaying frost formation, such as the use of hydrophilic surfaces, generally lead to stronger adhesion of larger-scale ice ¹³. Similarly, superhydrophobic surfaces that can repel and prevent freezing of supercooled water droplets ^{14, 15}, are readily filled with condensate at cold temperatures, leading to dramatically higher adhesion to ice once the condensed water eventually freezes ^{12, 16}. Often these finely designed surfaces are not capable of enduring harsh, real-world conditions. Surfaces able to control the accretion of liquids, ice, marine life, and condensation are rarely evaluated in terms of their wear, thermal, and ultraviolet (UV) resistance, despite the obvious necessity.

Engineering of surfaces aimed at mitigating or controlling matter accretion is also differentiated in terms of the fouling species length-scale. For example, marine biofouling is associated with the accumulation of foulants over multiple length scales, ranging from $\sim 100\text{nm}$ to $\sim 1\text{m}$. Most anti-fouling surfaces developed in the literature focus on resisting the attachment of only a single fouling species and / or foulants within a small size range, and thus have limited success in passively deterring the attachment of the different marine foulants present in real-world conditions. Figure 1 depicts the design of surfaces to control specific forms of matter, their phase, composition, and various associated applications. This chapter includes sections of text taken from

review articles previously published in Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences¹⁷ and Science.¹⁸

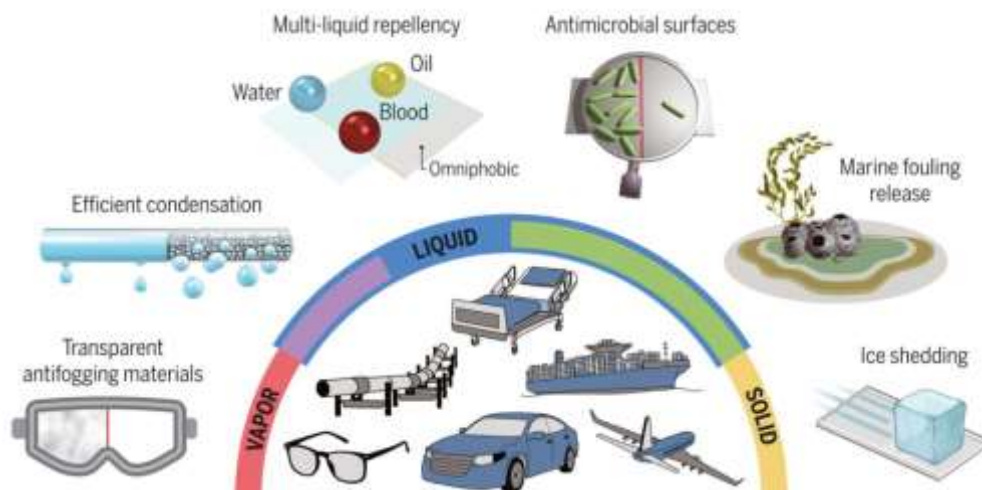


Figure 1: Summary of the applications which require the control of hard and soft fouling.

1.2 Controlling Liquid Fouling

The control of undesired liquid accretion of surfaces is important for a wide variety of applications which include stain resistant garments¹⁹, surface fogging²⁰, drag reduction²¹, self-cleaning paints²², and water harvesting²³. Multiple surface designs have been successful in controlling these liquids, but the problem becomes increasingly complex depending on the user requirements and environmental conditions. For example, surfaces that are able to repel water (hydrophobic) can still remain philic to low surface tension liquids (oleophilic). Therefore surfaces must be designed that can dewet liquids with broad surface tension, requiring complex surface structures. Surfaces must also be engineered to control condensing water for harvesting, or into a specific shape for fogging applications. By engineering surfaces in terms of their surface energy and structure, and composition, a substrate may be able to dewet a broad range of liquids, cause significant attraction/wetting, or force a liquid into a specific shape.

1.2.1 Wettability Theory

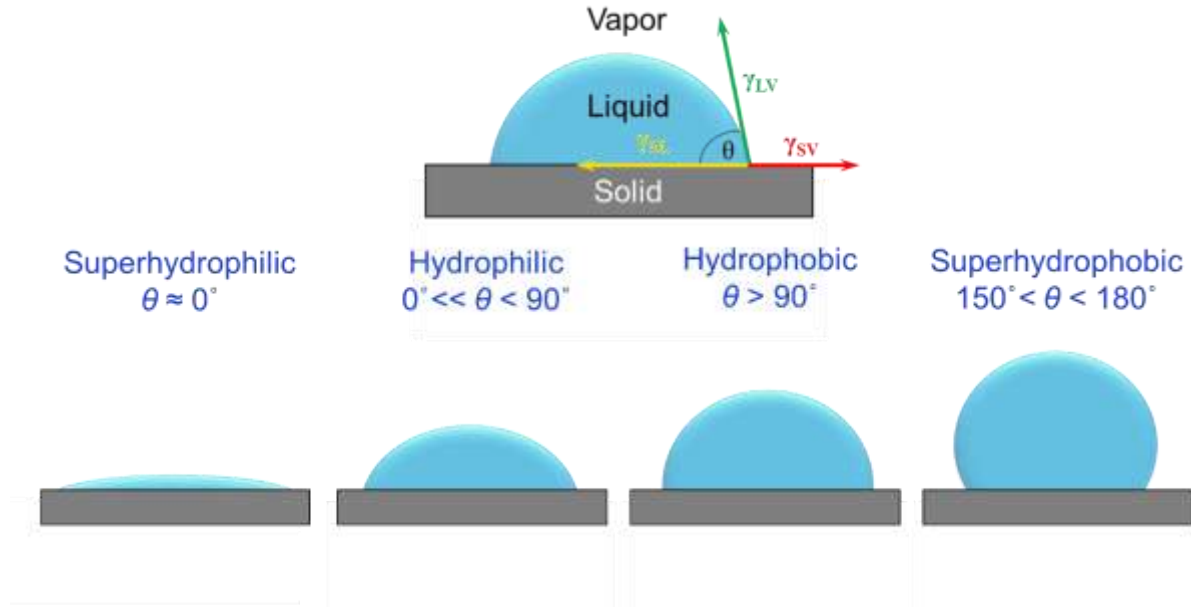


Figure 2: Depiction of Young's contact angle on a smooth surface and the potential wetting behavior.

(Above) A liquid droplet on a smooth homogeneous surface and the equilibrium contact angle caused by the balance of surface tensions within the system. (Below) Possible wetting behavior and associated conventional ranges of contact angle.

The shape a droplet takes when in contact with a particular surface can be described by its Young's contact angle. On smooth, chemically homogeneous, nonreactive, and nondeformable surfaces, the equilibrium contact angle (θ_E) for any contacting liquid is given by the Young's relation²⁴ as:

$$\cos\theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

Here γ_{SV} , γ_{SL} , and γ_{LV} are the interfacial surface tensions for the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively. Figure 2 demonstrates this force balance. Surfaces can be readily classified based on their contact angles with various contacting liquids. For example, based on water contact angles, surfaces are classified as superhydrophilic (contact angle $\sim 0^\circ$),

hydrophilic (contact angle $< 90^\circ$), hydrophobic (contact angle $> 90^\circ$) and superhydrophobic (contact angle $> 150^\circ$) (Figure 2). Similarly, based on oil contact angles, surfaces can be classified as being superoleophilic, oleophilic, oleophobic, and superoleophobic. Oils typically possess much lower surface tension values than water. Thus, most oleophobic surfaces are also hydrophobic. However, a few counter-intuitive surfaces that are hydrophilic and oleophobic have been reported in the literature ^{5, 25}. Therefore, surfaces that display contact angles $> 90^\circ$ or $> 150^\circ$ with all contacting liquids, including different oils, alcohols, solvents, acids, and bases are classified as omniphobic or superomniphobic, respectively.

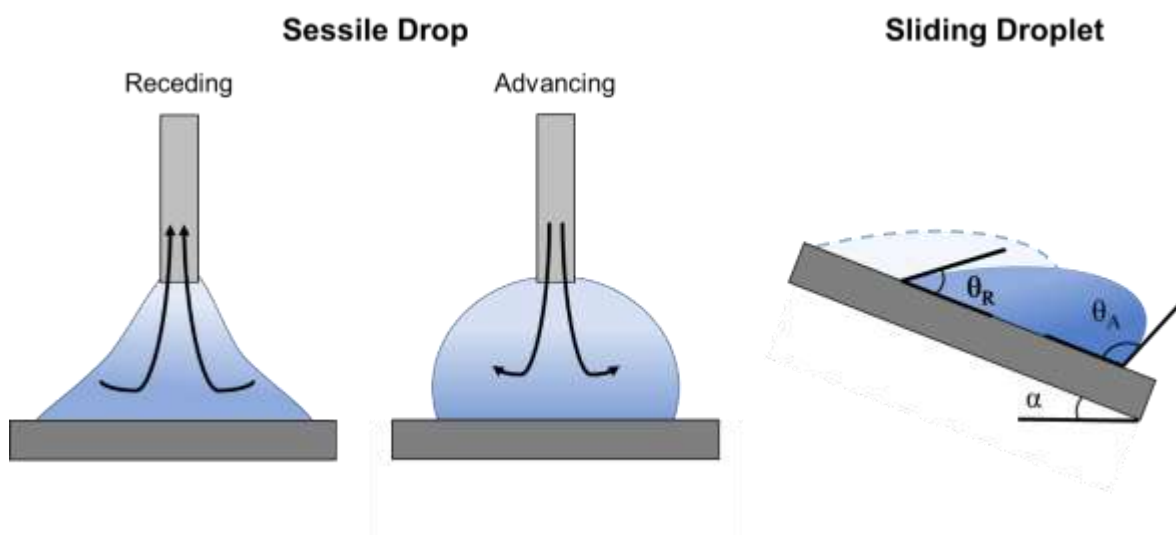


Figure 3: Contact angle hysteresis conducted via Sessile drop and sliding drop methods.

The contact angle for a droplet provided by the Young's relation is based on an ideal, smooth surface. However, on real surfaces, multiple contact angles can be measured and correspond to the numerous metastable states (local energy minima) ²⁶. The maximum and minimum observable contact angles for a given system, particularly for a mobile droplet, are called the advancing and receding contact angles respectively. The difference between these two contact angles is termed the contact angle hysteresis ($\Delta\theta$). Physically, contact angle hysteresis is a measure

of the energy dissipated during the motion of the three-phase contact line for a liquid droplet on a solid surface ²⁶. The contact angle hysteresis can be measured utilizing two common methods: the Sessile drop, and the sliding drop methods (Figure 3). The Sessile drop method is conducted by extruding a liquid that is in contact with a surface from a syringe orifice and recording the angles during extrusion and aspiration (Figure 3). The other more straightforward sliding drop method, involves recording the advancing and receding contact angles while a droplet moves down a tilted surface with an angle α (Figure 3).

For a smooth surface, the highest water contact angle reported in the literature is $\sim 130^\circ$ ²⁷. However, contact angles with water as high as $\sim 180^\circ$ can be obtained when resting on textured surfaces ²⁸. A droplet in contact with a rough surface may take one of two states to minimize its Gibbs free energy: the Wenzel state or the Cassie-Baxter state (Figure 4). In the Wenzel state, the droplet makes contact with the full surface area of the surface to generate a fully wetted interface. In the Wenzel state, the apparent contact angle θ^* (the contact angle on a textured surface) can be determined by the Wenzel relation below:

$$\cos\theta^* = r\cos\theta_E \quad (2)$$

Here r is the surface roughness, or the ratio between the actual and the projected surface area ($r \geq 1$). Thus, roughness always enhances the inherent wetting ($\theta^* < 90^\circ$, if $\theta < 90^\circ$) or non-wetting ($\theta^* > 90^\circ$, if $\theta > 90^\circ$) characteristics of droplets in the Wenzel state. It is important to note that due to the enhanced interfacial area while in the Wenzel state, textured surfaces display high contact angle hysteresis ²⁹. One unique state of Wenzel wetting is hemiwicking/superwetting

(Figure 4), which occurs when an intrinsically hydrophilic surface is coupled with texture to cause complete wetting of the droplet ($\theta^* \sim 0^\circ$).

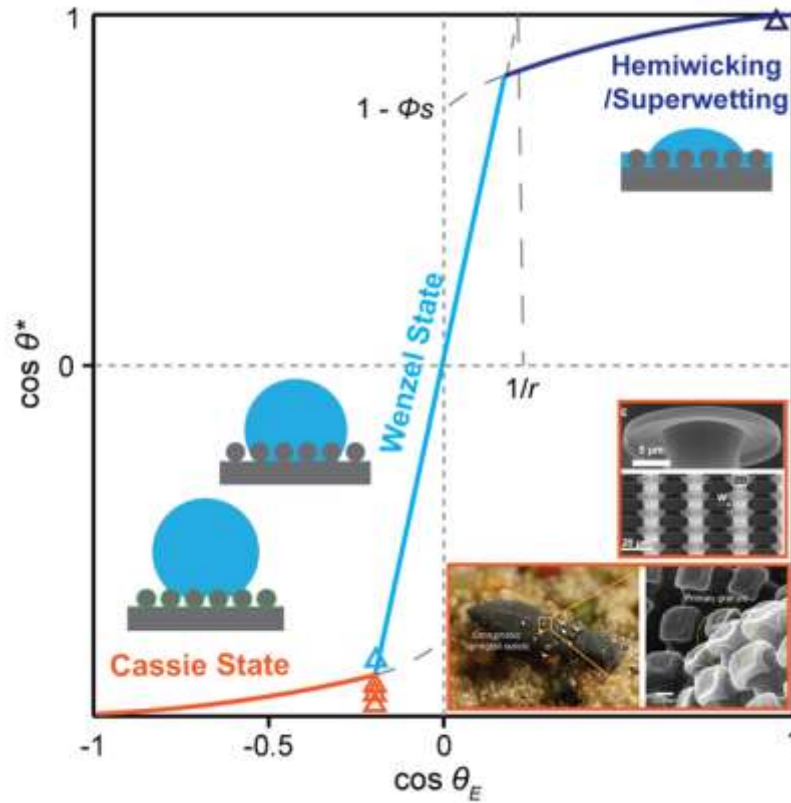


Figure 4: The relation between the cosine of the equilibrium contact angle and the cosine of the apparent contact angle.

Wettability domains on rough surfaces for including Cassie-Baxter State³⁰, Wenzel state³¹, Hemi-wicking state³². Right inset: oleophobic springtail with re-entrant features³³, and synthetic doubly re-entrant surface textures³⁴. Adapted from¹⁸.

When a liquid does not fully penetrate into a surface structure, this situation is known as the Cassie-Baxter state. Here, the contacting liquid droplet rests partially on the surface structure and pockets of entrapped air. The contacting liquid penetrates into the surface texture until the local texture angle (ψ) for the solid-liquid-vapor three phase contact line becomes equal to the equilibrium contact angle (θ_E)^{35, 36}. For the Cassie-Baxter state apparent contact angle (θ^*) is given as:

$$\cos\theta^* = r_\phi \phi_s \cos\theta_E + \phi_s - 1 \quad (3)$$

Where r_ϕ is the roughness of the wetted area and ϕ_s is the areal fraction of the liquid-air interface occluded by the surface texture (Figure 4). Here, the Cassie-Baxter state is distinguished as the air-infused composite interface, as opposed to lubricant infused surfaces discussed in the next section. Small values of ϕ_s in the Cassie-Baxter state result in higher contact angles and smaller contact angle hysteresis; this is the preferred state for the design of superhydrophobic and superoleophobic surfaces. Additionally, unlike the Wenzel state, in the Cassie-Baxter state, it is possible to obtain $\theta^* \gg 90^\circ$, even if $\theta_E < 90^\circ$ ^{35, 36}.

1.2.2 Design Strategies for Liquid Control

Engineering Surface Structure

There are numerous natural superhydrophobic surfaces including a variety of plant leaves, insect legs, and insect wings²² (Figure 4). However, only one natural oleophobic surface has been identified thus far – the skin of various springtails (see inset Figure 4). Because of the unique organic environment they inhabit, springtails must breathe through their skin, and therefore must be able to prevent a fully wetted interface of oily liquids on their bodies. This is achieved by a periodic microstructure which arc back upon itself, termed as a re-entrant structure^{37, 38} (see inset Figure 4). Re-entrant structures have a unique ability to support an air-solid-liquid composite interface for both oils and water. This structure has been proven to be necessary to support the composite interface for low surface tension liquids^{35, 38}. Surfaces with re-entrant texture possess local texture angles $\psi < 90^\circ$ (also see Figure 5), and allow for the formation of a composite

interface for low surface tension liquids, given that $\theta_E \geq \psi_{min}$ ^{38,39}. Here, ψ_{min} is the minimum local texture angle of a surface feature (see Figure 5).

The systematic design of such omniphobic and superomniphobic surfaces requires the maximization of two important parameters relating to the composite interface: the magnitude of the apparent contact angle (θ^*) and the magnitude of the breakthrough pressure (P_{br}). P_{br} is pressure required to transition the Cassie-Baxter state to the Wenzel state³⁶. Relating to the Cassie-Baxter state, θ^* values are a function of the surface porosity. This porosity can be defined in terms of the spacing ratio $D^* = (R+D)/R$ ^{35,36} in the case of cylindrical geometries. Here R is the radius of the cylinder, and $2D$ is the inter-cylinder spacing. The Cassie-Baxter relation can now be modified to:

$$\cos\theta^* = -1 + \frac{1}{D^*} [\sin\theta_E + (\pi - \theta_E) \cos\theta_E] \quad (4)$$

Increasing values of D^* correspond to higher surface porosity, leading to higher θ^* and generally lower $\Delta\theta$ values. P_{br} on the other hand can be expressed in terms of the dimensionless parameter A^* , called the robustness factor³⁸. In terms of cylindrical surface geometry, A^* can be expressed as^{36,40}:

$$A^* = \frac{P_{br}}{P_{ref}} = \frac{\ell_{cap}}{R(D^* - 1)} \frac{(1 - \cos\theta_E)}{(D^* - 1 + 2\sin\theta_E)} \quad (5)$$

Where $P_{ref} = 2\gamma_{LV}/\ell_{cap}$ is the reference pressure – conceptualized as being near the minimum possible pressure differential across the liquid-vapor interface for a millimeter-sized liquid droplet or puddle; $\ell_{cap} = \sqrt{\frac{\gamma_{LV}}{\rho g}}$ is the liquid capillary length; ρ is the liquid density and g is the acceleration

due to gravity. The robustness factor thus incorporates properties of the solid texture (R, D), the contacting liquid (ℓ_{cap}), and θ_E . Surfaces for which $A^* \leq 1$ for a given contacting liquid cannot support a composite interface and transition to the Wenzel state; this scenario is highly desirable for superwetting surfaces. Meanwhile values of $A^* \gg 1$ imply a robust composite interface^{36, 38}. Optimal nonwetting surfaces require $D^* \gg 1$ and $A^* \gg 1$ with a contacting liquid to simultaneously display both high apparent contact angles and high robustness. However, according to equation (5) increasing D^* will decrease A^* . This issue can be solved by minimizing surface energy, imparting doubly re-entrant features³⁴ ($\psi_{min} \approx -90^\circ$), and/or by the addition of hierarchical scales of texture⁴¹. Figure 5 A&B illustrate these 3 strategies.

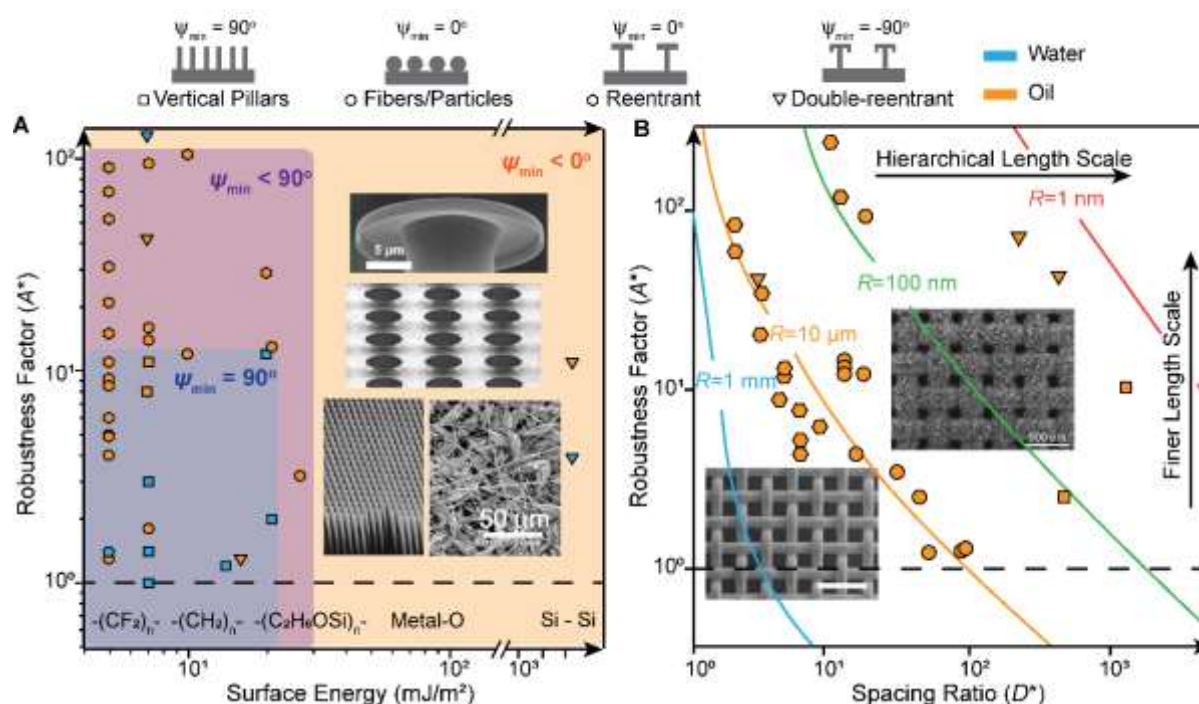


Figure 5: (Above) Demonstration of the minimum texture angle and (Below) dependence of robustness factor (A^*) on surface energy and spacing ratio (D^*) (Top) various surface geometries and their corresponding ψ_{min}

Lubricant Infused Surfaces

Another liquid repellency approach is inspired by the carnivorous *Nepenthes* pitcher plant, which generates a lubricating surface on the outer rim by locking in water within a porous structure. Any insect or small rodents that attempt to walk on the slippery rim fall into the base of the plant where they are consumed. Inspired by the natural design of such structures, many omniphobic lubricant-infused (LIS) surfaces have been developed⁴²⁻⁴⁵. These engineered surfaces usually contain a liquid silicone or fluorinated lubricant that is stabilized within a textured / porous solid through capillary forces. The stabilization of the lubricant within the further enhanced when functionalized with a low surface energy surface coating. Unlike the dry surface structures discussed earlier, LIS surfaces do not rely on high θ^* to achieve omniphobicity. Instead, these surfaces are able to readily dewet droplets as the lubricating liquid offers little resistance to mobile droplets, even despite the low θ^* values (see Figure 6).

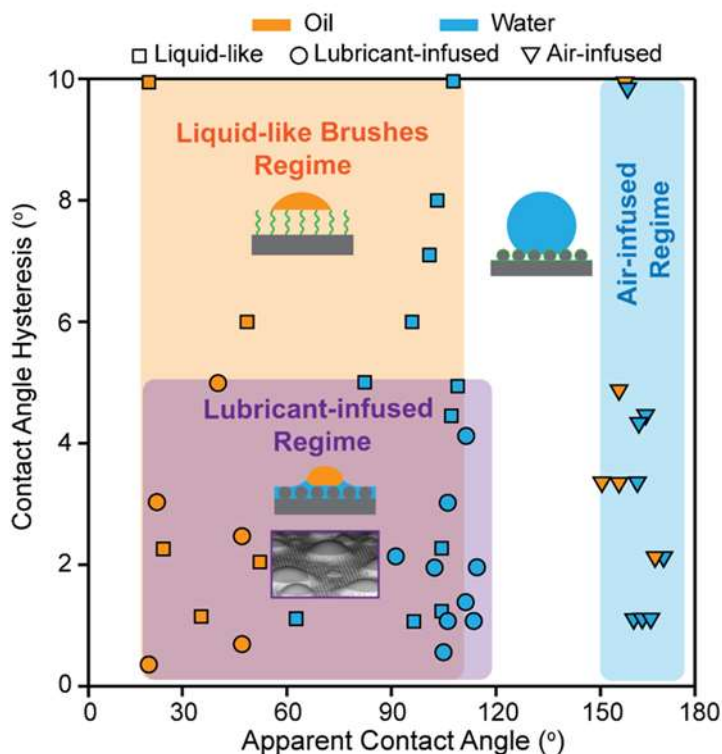


Figure 6: The contact angle hysteresis vs the apparent contact angle for three different state-of-the-art liquid repellent surfaces.

Adapted from ¹⁸

Liquid-Like Layers

A similar approach to LIS surfaces involves the bonding of highly mobile polymer chains to surfaces ^{46, 47}. This approach attempts to capture the properties of LIS surfaces by grafting polymer chains that are implemented at temperatures far above their glass transition temperature, leading to high interfacial mobility with any contacting liquid (or solid, as discussed below). These can also be conceptualized as a tethered lubricant, and have been shown to yield low $\Delta\theta$ and sliding angles with a variety of contacting liquids. The key advantage of these surfaces is that unlike LIS surfaces, despite the miscibility of the chains and the contacting fluid, there will be no removal of the grafted polymer ⁴⁸. Meanwhile LIS surfaces are compromised and depleted when the lubricant is contacted with a miscible liquid; thus diminishing the properties. However, depending on the

underlying substrate coverage, in many cases the liquid-like polymer chain coated surfaces yield slightly higher $\Delta\theta$ than lubricant-infused coatings (see Figure 6) ^{46, 47}.

1.3 Controlling Solid Fouling

The undesired adhesion of solid contaminants to a surface, particularly when the adhering material damages the desired properties of that surface, can be labelled as solid fouling. This broad category of fouling includes the surface adhesion of a diverse array of contaminants such as ice, clathrate hydrates of natural gases, wax, inorganic scale deposits, polymers in solution, proteins, as well as a wide range of biofouling materials. Some examples of industrial problems caused by these materials include the attachment of marine organisms to ship hulls ^{49, 50}, icing of power lines and airplanes ⁵¹⁻⁵³, deposition of asphaltenes and wax on systems in petroleum processing ^{54, 55} and biofilm growth on medical devices ^{56, 57}. Due to consequential issues, it is important to engineer surfaces that control their accretion.

Solid fouling materials vary widely in composition and chemical structure, as well as in their physical properties and modes of deposition. Many surfaces have been fabricated to control their adhesion, however research efforts have traditionally focused on only a single type of solid foulant when designing a surface. Moreover, they rarely have been able to address sequential fouling where one foulant templates the growth for another more complex adherent. Therefore, an effort to design a surfaces able to control the solid fouling of two, or more foulants that vary in size and chemical composition would prove widely beneficial.

1.3.1 Notable Examples of Solid Fouling

Ice

One of the most significant examples of solid fouling is that of ice accretion. Ice is able to take on length-scales on the order of nucleates of frost, to sheets of solid glaze⁵⁸, and its accretion causes significant costs in removal. Ice accretion causes issues such as airplane^{51, 52, 59} and power line de-icing^{53, 60} as well as locks and dams⁶¹ and roads. Ice fouling also impacts renewable energy technology, impeding the function of solar panels⁶² and wind turbines⁶³. Some common approach to combat ice accretion are surface heating by hot air or electrothermal pulses^{52, 63}, and mechanical shock or vibrations⁵³, but both are costly and time consuming. In the case of airplane wing icing, low-freezing temperature organic solutions are sprayed onto the wings to melt and remove the ice, but is also time consuming in the context of commercial flying⁵⁹.

Ice is considered as a hard foulant with a modulus on the order of 1 GPa^{64, 65}. However it varies greatly in length scale. For example small-scale ice nucleates are on the order nanometers⁶⁶⁻⁶⁸, while bulk ice can easily accumulate on industrial equipment in sheets which are meters long and inches thick. The varying Scale of ice is illustrated in Figure 7 below. In order to design surfaces to prevent each scale of ice, multiple design strategies are required to control their accretion.

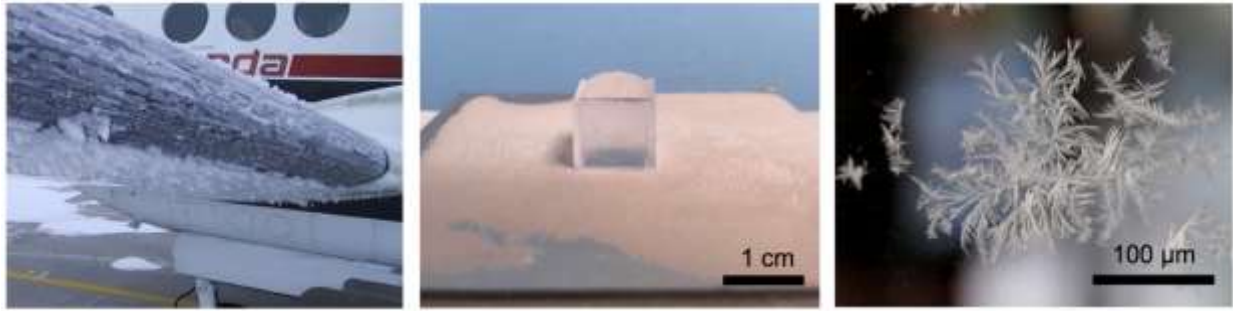


Figure 7: Ice accretion at varying length scales

(left) Large-scale glaze ice accretion on an airplane wing (center) Standard cubic ice for testing (right) Nucleating ice formation. Image adapted from ¹⁷.

Clathrates

Clathrates, or gas hydrates, are ice formations with periodic inclusions of gas molecules. This ice structure is stabilized by intermolecular forces, primarily hydrogen bonding and van der Waals interactions. Typical clathrate gasses include propane, methane, cyclopentane, ethane and carbon dioxide ^{69, 70}. One of the greatest hindrances caused by clathrates is within oil and gas pipelines, where it builds up within the interior and causes blockages, and therefore reduced production ^{69, 71}. The current industrial solutions to the clathrate blockages are additives of methanol or glycol to inhibit nucleation, or anti-agglomeration agents ⁷¹⁻⁷⁴. In 2003, the cost of remedying clathrate blockages cost up to \$220 million in 2003 ⁷⁴

Inorganic Scale

Inorganic scale is a form of mineral deposit that has proved problematic for a number of industrial processes. The unchecked deposition and growth of organic scale can cause a host of issues including increased friction in pipes, surface corrosion, and heat transfer efficiency loss (up to 40% thermal efficiency decreases) ⁷⁵⁻⁷⁸. Much like the case of clathrates, most approaches to the challenge of inorganic scale have been preventative; this has mainly been achieved via the addition

of nucleation inhibitors into the bulk working fluids ^{75-77, 79}. Despite being effective, the inhibitors can contaminate the fluids and the environment. Mechanical approaches to deposit removal have also been necessary, but are energy intensive and lead to costly operational downtimes ^{75, 79}. Passive surface design approaches are therefore critical in minimizing harm done by inorganic scale fouling.

Wax & Asphaltenes

Wax and asphaltene deposition are a problematic form of fouling that primarily effects crude oil and gas industries. Leading to production losses, and costly labor and downtime as a result of cleaning the blockage ^{80, 81}. Current strategies to mitigate this form of fouling again include preventative measures such as the addition of inhibiting polymers ⁸², n-alkanes ⁸³, wax crystal modifiers ⁸⁴, dispersants ^{85, 86}, and microbes ^{87, 88}. Unlike the previously mentioned foulants, crude oil pipe fouling is a complex process involving constituents such as resins, asphaltenes, wax, scales, and water; this makes it difficult to perform controlled laboratory tests on the phenomenon. In addition, there are also a host of physical environmental variances such as shear stresses, abrasives, and notable temperature changes ⁸⁹. There is thus both a vacancy and opportunity to develop surfaces able to better remedy this issue.

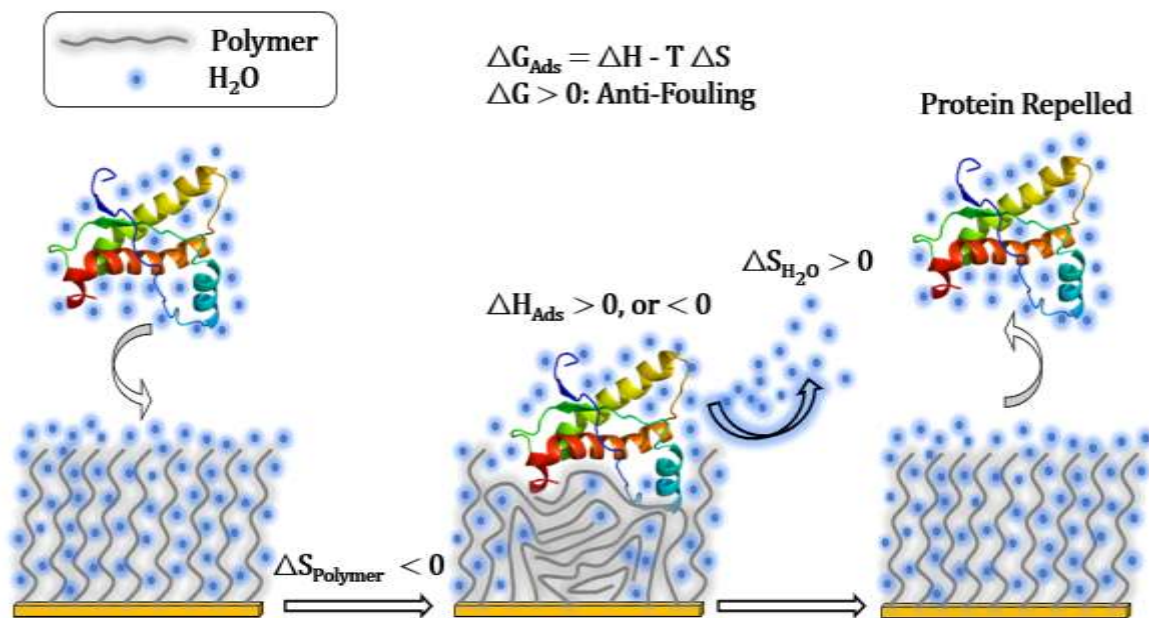


Figure 8: Protein repellency mechanism for a hydrophilic, brush-like grafted polymer.

Figure taken from ¹⁷, and adapted from ^{90,91}. Protein adsorption onto grafted PEG results in the release of the hydration barrier from both the polymer and the protein. This process increases the entropy for water but is outweighed by a decrease in conformational entropy for the polymer. The net result is entropically unfavorable for protein adsorption. (ΔH_{Ads}) for the protein-polymer interaction can either be favorable or unfavorable depending on the paired species.

Protein Fouling

Protein fouling is problematic for any situation where biological fouling occurs as it is the first step in any larger-scale biological fouling process ⁹²⁻⁹⁴. Proteins are complex biomaterials which consist of one or more ordered polypeptide chains ⁹¹. These polypeptides can have a wide array of functionalities, causing either hydrophilic or hydrophobic character. Within aqueous solutions, proteins take on a metastable globular form where the majority of the hydrophobic functionality is ordered within the interior, while the hydrophilic side-groups are oriented to the exterior ⁹¹. The metastability of proteins is a result of a decrease in conformational entropy for the ordered interior nonpolar groups which is somewhat overcome by their hydrophobic interactions, as well as by the enthalpic stabilization of the outer hydrophilic groups by surrounding water

molecules⁹¹. This makes proteins susceptible to chemical, thermal, or mechanical perturbations, which can lead to unfolding, and adsorption. Low surface energy, or “hydrophobic” surfaces, although able to repel high surface tension fluids, will cause protein adsorption by disrupting their metastable state. Additionally, even though proteins vary broadly in modulus^{95, 96}, their small length scales do not allow for the low surface modulus approaches previously discussed to be a sufficient solution to combat adhesion. Therefore, hygroscopic disordered polymer brush surfaces must be implemented to create a hydration layer which enhances the change in Gibbs free energy of adsorption⁹⁰. This strategy is illustrated in Figure 8 and discussed more in the next section.

Polymer Fouling

Unlike protein fouling, organic polymer fouling has been infrequently studied. Polymer fouling, can lead to: contamination during polymerization reaction processes⁹⁷, down time during reactor cleaning cycles⁹⁷, ineffective filtration⁹⁸, and inefficient heat exchangers⁹⁹. In biological settings, algae and diatoms secrete extracellular polymeric substance (EPS) when adhering to a given surface^{93, 100}. EPS strengthens their attachment, and can be problematic for a variety of marine applications^{93, 100}. Polymers in solution, although unlike the metastable proteins, exhibit a similar surface adsorption mechanism. Currently, there are few reports which specifically address the design of surfaces that control the adhesion of polymer deposits.

Biofouling

The contamination of surfaces by biological matter and organisms, or biofouling, is problematic for a multitude of fields and applications. Within the medical realm, biocontamination can be dangerous for implants¹⁰¹⁻¹⁰⁴, surgical equipment¹⁰⁵⁻¹⁰⁷, catheters¹⁰⁸⁻¹¹¹, and hospital beds¹¹². Biofouling is also problematic for food packaging and storage¹¹³⁻¹¹⁶, filtration¹¹⁷⁻¹²¹, as well as marine vessels^{49, 122, 123} and infrastructure^{124, 125}. Biofouling offers a unique challenge in that it

is multiphasic, multistep, and can engender biological organisms which possess the ability to divide, and to adjust based on the properties of the underlying surface⁹⁴. As stated previously, the biofouling process typically begins with protein adsorption on a surface, which serves as a conditioning layer for larger order organisms⁹²⁻⁹⁴. This process can occur within seconds, or minutes⁹⁴. The adsorbed proteins can also hamper the performance of immunological assays^{126, 127}, lead to thrombosis for medical implants^{128, 129}, and aid in the formation of platelets within certain microfluidic devices¹²⁸. It has been demonstrated that even 10ng/cm² of the protein fibrinogen adsorbed on a surface can lead to blood platelet formation¹²⁸.

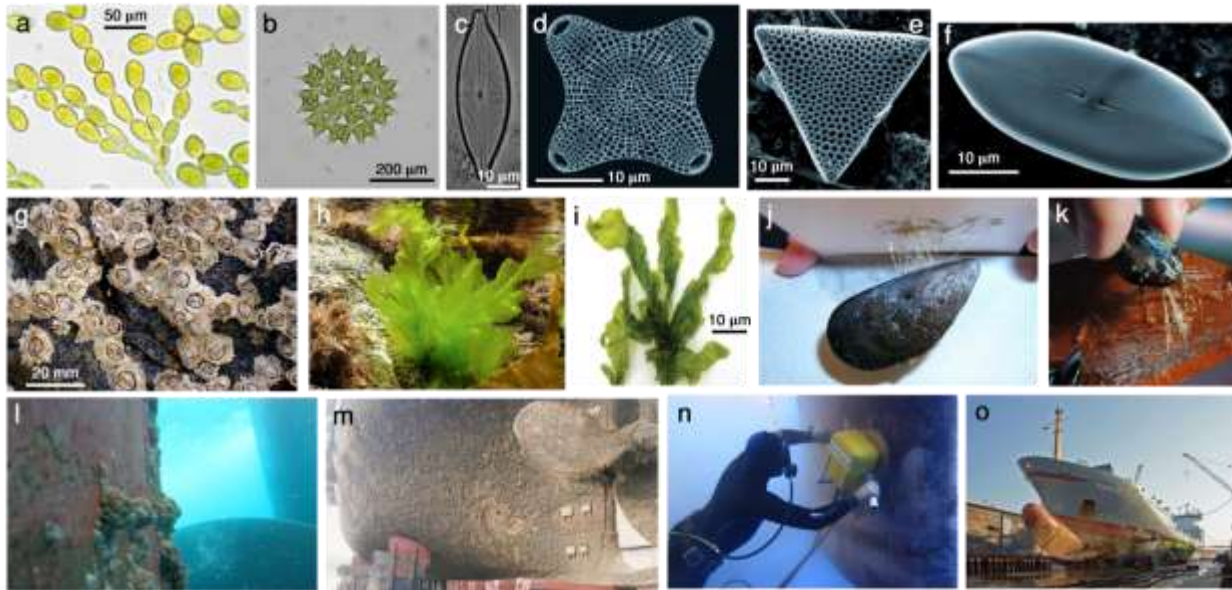


Figure 9: Varying examples of marine fouling species and the fouling of ship hulls.

Diversity of marine species including **a)** a high magnification view of spores of *Lemanea*, a genus of freshwater red algae (Photo credit: Chris Carter) **b)** nonmotile coenobium (group of cells) of *Pediatrum*, a genus of green algae **c)** Diatom frustule of *Cymbella inaequalis* **d, e, f)** SEM images of several marine diatom species **g)** *Chthamalus stellatus* barnacle photographed near the upper shoreline, Lundy Island, UK **h, i)** *Ulva lactuca* a.k.a. sea lettuce **j)** common blue mussel, *Mytilus edulis*, adhering to Teflon® (Credit: Jonathan Wilker of Purdue University, NSF) **k)** and a mussel collected in Boston Harbor clinging to a clay slab, attached by an array of thin filaments called byssus threads (Credits: Zhao Qin and MIT). Also shown is **l)** biofouling on a ship hull and **m)** hard macrofouling at the stern, consisting of mostly barnacles, **n)** underwater ship hull cleaning using Brushcart system requiring labor and expensive machinery, **o)** fouled ship docked and undergoing hull cleaning procedures extending operation down time. Image from¹⁷.

Marine Biofouling

Marine fouling adherants are a special class of foulants in that they represent a diverse community of organisms with varying sizes, preferences to surface settlement, attachment, as well as release mechanisms. The species include mussels, barnacles, algae, bacteria, and proteins. All of which work in concert to develop well-attached marine fouling layers. This causes marine fouling to be time-dependent, and possess a unique evolutionary attachment sequence. Marine organisms are an important part of the biosphere, however they can be highly damaging to underwater sensors and increase drag of marine vessels to up to several multiples^{130, 131}. This in turn raises their fuel consumption^{49, 132}, and environmental pollution. Furthermore, ship maintenance for removal of these organisms extends down time and cleaning expenditures⁴⁹. Figure 9 depicts the various species of marine foulants and the fouling of ship hulls. To prevent marine biofouling, biocidal paints were developed, but have since been largely banned due to the broader ecological damage they caused¹³³.

1.3.2 Solid Fouling Surface Design Strategies

Multiple challenges exist pertaining to the control solid fouling species, including size, modulus, chemistry, and general complexity of fouling. Many common foulants can be classified with respect to their scale and modulus as shown in Figure 10. For example: A hard foulant such as ice can exist across a broad range of length scales; each of them requiring unique surface design strategies in order to impart fouling control (Figure 10A). Meanwhile proteins (a precursor to macro-biofouling), are extremely small in scale, but maintain unique chemistries which allow them to foul most surfaces with relative ease. Fouling complexity is further worsened when two, or more foulants work in concert or in series to produce a complex layer that is much stronger, or more difficult to remove than its single constituents. This complexity of fouling has led to many unique

surface design strategies; usually for a specific foulant and length-scale. These various design strategies are illustrated in Figure 10B)

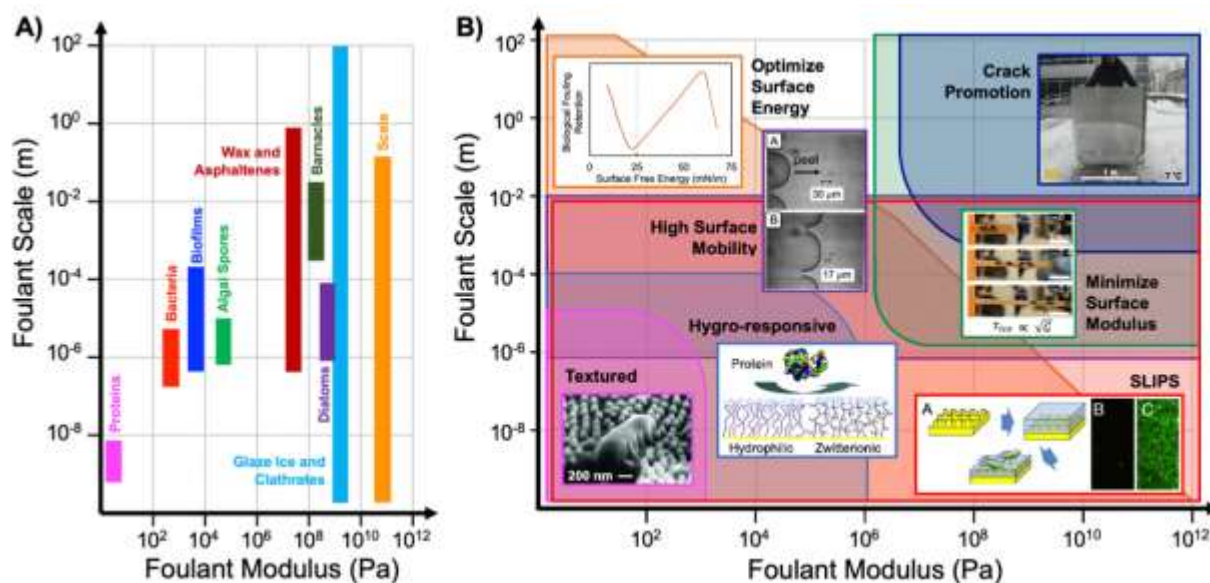


Figure 10: (A) Illustration of varying size and modulus of fouling species as well as (B) corresponding antifouling surface design strategies. Adapted from ¹⁸.

Two major modes of classification of solid foulants include scale, and modulus. In terms of Young's modulus for example, hard foulants comprise of ice, inorganic scale, waxes and asphaltenes, and natural gas hydrates, while soft foulants include bacteria, biofilms and proteins. Although the range of foulant scale is large, some notable small-scale foulants include single bacteria, algal spores, and diatoms, as well as proteins. While glaze-ice and inorganic scale sheets are relatively large in length-scale. With respect to the factors of foulant length scale and modulus, a multitude of surface design strategies have been developed to control foulant accretion; this is demonstrated in Figure 10. Notable surface design methodologies relevant to this thesis are elaborated on further below.

Surface Energy Optimization

Surface energy optimization has been investigated in order to control the accretion of a wide range of surface foulants¹⁸. One common form of surface energy optimization also utilized to minimize liquid accretion, is the minimization of surface energy. This strategy involves selecting or creating a surface chemistry which lowers the substrate surface energy. This has been achieved via silanization¹³⁴, and substrate material selection¹³⁵. By minimizing the energy of a surface, the potential adhesive interaction between the surface and a fouling material is reduced, and is known as the work of adhesion, W_a . The phenomenon is articulated by the following equation:

$$W_a = \gamma_{s_1v} + \gamma_{s_2v} - \gamma_{s_1s_2} \quad (6)$$

Where γ_{s_1v} and γ_{s_2v} are the interfacial free energy for the foulant and the foulant-substrate interface respectively^{136, 137}. This approach has proven useful for ice^{13, 138}, clathrates¹³⁴, inorganic scale⁷⁹, and wax/asphaltenes¹³⁹. Additionally, rather than exclusively minimizing the surface energy, specific substrate γ_{sv} ranges were found to be optimal in foulant accretion reduction. One such example is provided by Baier, who showed that the attachment of different biological foulants, such as bacteria, on surfaces is minimized over a narrow range of surface energies, typically between 20 – 30 mN/m^{140, 141}.

Surface Modulus Reduction

Surface modulus reduction can also be an effective strategy in minimizing fouling accretion. Unlike the modification of surface energy which may only change by a factor of 100, this approach is advantageous in that surface modulus can be tuned by nearly five orders of

magnitude ¹⁷. The stress required to remove a rigid object from a softer surface has been demonstrated to correlate to the following expression:

$$\sigma \propto \sqrt{\frac{W_a E}{t}} \quad (7)$$

Where W_a is the work of adhesion, E is the elastic modulus, and t is the thickness of the film.¹⁴²,¹⁴³. Surface Modulus reduction has proven highly effective for the removal of ice fouling resulting in ice adhesion strengths as low as 14 kPa. ¹³⁸. Various reports have also demonstrated low modulus surfaces to deter the adhesion of small, and moderately rigid foulants. For example, low-modulus coatings have been shown to significantly reduce the attachment of rigid-walled algal sporelings ¹⁴⁴ and pseudo-barnacles ¹⁴⁵. However, mechanical durability will be compromised as the surface becomes increasingly soft, making practical application challenging.

Lubricant Infused Surfaces

As discussed in section 1.2.2, lubricant infused surfaces (LIS) are porous surfaces with an entrapped, stabilized lubricant. This surface is able to repel a broad range of liquids by minimizing the contact angle hysteresis. LIS surfaces have also proven to minimize the adhesion of solid foulants. In the case of accreted ice, it does not adhere to any solid component, but instead rests on a lubricating layer ⁹, ⁴³. This same mechanism of foulant-LIS interaction has also been successful for other hard and soft foulants including bacteria ¹⁴⁶, micro- ¹⁴⁷ and macro-scale marine species ¹⁴⁸, and inorganic scale ¹⁴⁹. LIS surfaces have also demonstrated significant reduction in the accretion of ice nucleates, or frost. In one report, molecularly smooth LIS surfaces were able

to delay the freezing by nearly preventing heterogeneous ice nucleation^{9, 150}. Many different lubricants, typically hydrophobic oils or water¹⁵¹⁻¹⁵³, may be incorporated within a functionalized porous texture¹⁵³⁻¹⁵⁵, or infused within a polymeric network^{153, 155, 156}. However, $\hat{\tau}_{ice}$ values for many oil containing lubricated surfaces can increase after only a few icing-de-icing cycles due to gradual depletion of the lubricant^{138, 157-160}. The depletion of lubricant also raises the concern within harsh environments where regular abrasive wear is possible.

Textured Surfaces

Textured surfaces offer multiple foulant-dependent mechanisms for the control of various foulant accretions. Inspired by the bactericidal structure of Cicada wings, bio-inspired nanopillar surfaces were developed that were able to impale and kill bacterial cells¹⁶¹. Further bio-inspiration was derived from the skin of sharks. Sharklet patterns inspired by shark placoids have been shown to significantly prevent the settlement of different marine foulants such as the algae *Ulva*¹⁶². Unlike the nanopillars, sharklet patterns are not necessarily lethal. Textured surfaces have also proved effective for ice fouling. Atop superhydrophobic surfaces with $\theta_{rec} > 150^\circ$, ice has demonstrated significant reductions of $\hat{\tau}_{ice}$. These surfaces reduce the total contact area between the solid surface and the ice, and has lead to $\hat{\tau}_{ice}$ values as low as 40 kPa^{15, 155}. However, such low $\hat{\tau}_{ice}$ values are only obtained when water is frozen while in the Cassie-Baxter state¹². If the water freezes within the structure, such as the case during frost formation, $\hat{\tau}_{ice}$ will increase dramatically due to the increase in contact area¹². However texture can be used to inhibit frost formation when the feature size is smaller than the critical ice nucleation radius¹⁶³. Despite the benefits of textured surfaces in controlling various solid fouling, these surfaces lack in durability, and in the case of abrasive surface wear, the fouling properties will worsen.

Hygro-Responsive Surfaces

Hygro-responsive surface have proven to be highly effective in controlling the fouling of adherents such as proteins, bacteria, algae, and ice^{152, 153, 164-167}. One of the earliest and most effective discoveries in the application of hygro-responsive surfaces has been the utilization of polyethylene glycol brushes^{90, 168-175}, and later zwitterionic brushes¹⁷⁶⁻¹⁸³ for their prevention of protein adsorption. Proteins are difficult to control due to their tendency to readily adsorb onto surfaces (particularly hydrophobic surfaces). Zwitterionic polymers particularly have been useful due to their ability to generate a strong hydration layer in aqueous environments which acts as a barrier between the surface and the protein^{184 176, 177}. This strong hydration layer is a result of the strong electrostatic interactions the polymer generates with water due to the repeated positive and negative charges. As described in more detail in section 1.3.1, adsorbed proteins serve as a conditioning layer for larger, more problematic foulants such as bacteria and algae. Multiple reports have found that the inhibition of protein adhesion via zwitterionic brush coatings limits the adhesion of bacteria and algae^{164, 167, 185-187}. Hygro-responsive coatings have also proven to be useful in the control of multiple forms of ice accretion. Hydration layer generating hygro-responsive surfaces have demonstrated reduced $\hat{\tau}_{ice}$ and can withstand multiple icing-deicing cycles for bulk ice^{152, 153, 166}. In addition to the removal of ice, certain hygro-responsive surfaces polyelectrolyte brushes^{188, 189}, hydrogels¹⁶⁶, charged crystals^{190, 191}, natural anti-freeze proteins^{192, 193} have proven the ability to disrupt ice nucleation and growth.

High Surface Mobility

High mobility surfaces have been developed to overcome the shortcomings of LIS surfaces with regard to lubricant depletion. As discussed in section 1.2.2, high mobility surfaces are greatly

effective in prevention the accretion of liquid matter. These surfaces act as a tethered lubricant, allowing interfacial slip between the surface and the adhered solid matter such as bulk ice¹⁹⁴. This is due to the nature of the highly flexible surface-tethered chains which exist much below their glass transition temperatures; making them a tethered liquid layer¹⁹⁵. Due to the liquid-like nature of high-mobility surfaces, one example is demonstrated their ability to create a pristine interface, significantly reducing the nucleation of inorganic scale¹⁹⁶. These surfaces have not been widely assessed in terms of durability, but is investigated in Chapter 2.

1.3.3 Design Challenges of Fouling Complexity

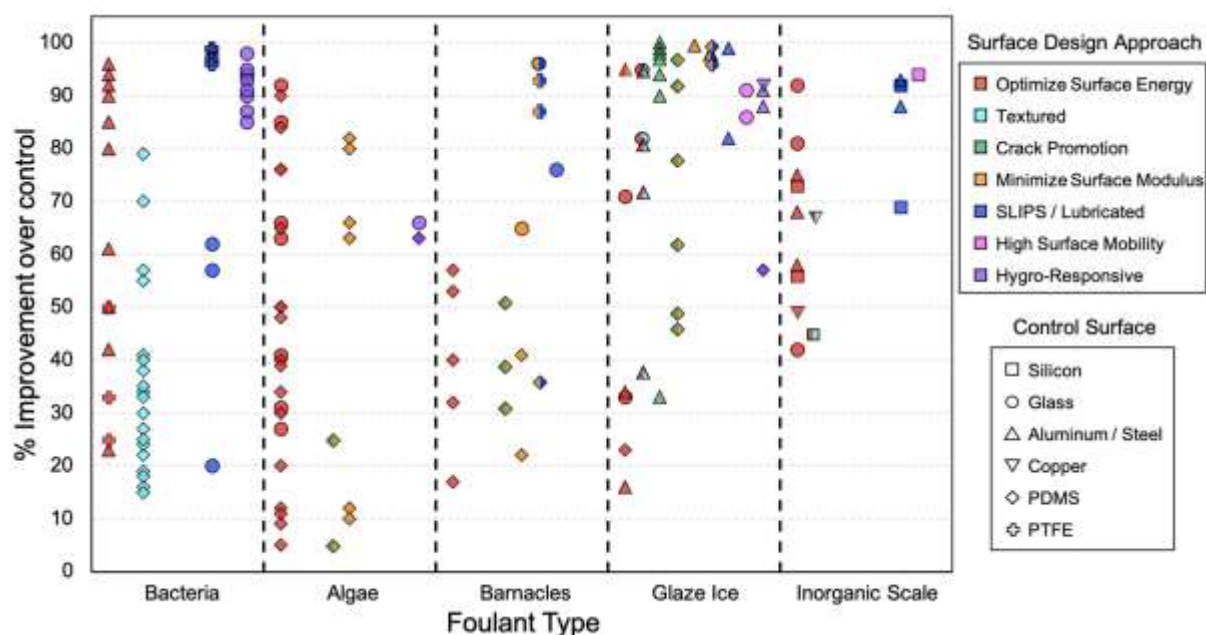


Figure 11: Antifouling performance of various surface design strategies and select foulants.

Surface performance in their ability to mitigate fouling of bacteria, algae, barnacles, glaze ice, and inorganic scale. Literature data was sorted according to the surface design aspect which dominated in contributing to the surface's performance. For surfaces where two design aspects contributed significantly to performance, split color markers are used to indicate both approaches. Literature reports were only included in this plot if performance data was reported alongside control data for one of a select number of common control surfaces (listed on plot). Surface performance is reported using a particular performance matrix for each foulant (amount of adhered bacteria, % of adhered algae remaining after shear flow, barnacle adhesion strength, ice adhesion strength or mass gain after extended exposure to a scaling solution) in order to ensure that all values are comparable. Figure Adapted from¹⁸.

Despite the effectiveness of the aforementioned solid fouling design strategies, there still remains many gaps in their ability to control fouling across multiple length scales and species. Figure 11 above illustrates this point by demonstrating the antifouling effectiveness of each surface design strategy in their ability to prevent, or remove select foulants such as: bacteria, algae, barnacles, glaze ice, and inorganic scale. Figure 11 clearly illustrates that the majority of reports thus far have only been successful in controlling the adhesion of one singular foulant. This problem is caused by the differences in fouling length-scale, and the complexity of various fouling process.

There are many examples of challenging, complex, stepwise fouling processes. One of the clearest examples of the general fouling complexity problem in nature, is marine fouling. As depicted in Figure 12, when a surface is submerged underwater in a marine environment, it provides a fresh surface on which an ecosystem can develop. First, an organic layer composed of humic acids, uronic acids, carbohydrates, amino acids and proteins is formed within the first few minutes of fouling^{100, 197, 198}. This film acts as a conditioning layer planktonic bacteria attachment on top of the film. This serves as a nutritional layer for unicellular organisms such as protozoa and diatoms which bind via mucus or extracellular polymeric substance (EPS) secretion^{93, 100}. The surface environment allows for the proliferation of species of larvae, algae and algae spores which colonize within several days, followed by increasingly complex organisms such as tunicates, mussels and barnacles over the course of several weeks^{93, 199}. Each step of the process, with the integration of a new foulant, further increases the hydrodynamic drag for a marine vessel, and therefore demands a new surface design strategy to control the fouling process. Figure 11 further illustrates the lack of broad design strategies for marine fouling, where the early, small settlement is mostly prevented by surface chemistry (hygro-responsive) approaches, while large and rigid barnacles are often removed by surface modulus design approaches. However biofouling is just

one of multiple examples of complex fouling processes; others include: wax fouling, icing accretion, and clathrate depositions, but will not be elaborated on in significant detail in this chapter.

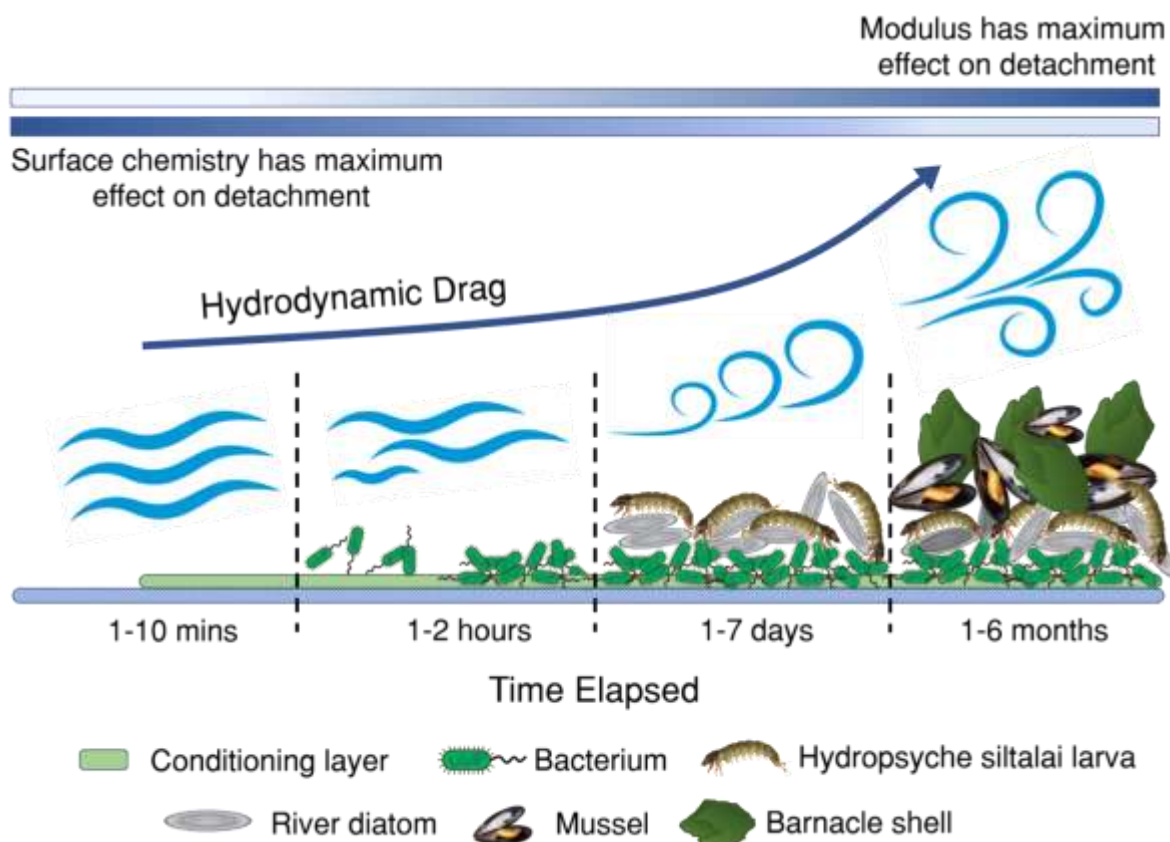


Figure 12: Graphical depiction of the natural marine fouling process.

Within the first few minutes, a layer of organic macromolecules, known as the conditioning layer, is formed and fouls the surface. After 1-2 hours of submersion, planktonic bacteria colonizes the conditioning layer. Within several days the substrata becomes a habitat for larger unicellular organisms such as diatoms, followed by multicellular species of larvae, algae and algae spores. After several weeks, the surface experiences fouling from increasingly complex organisms such as tunicates, mussels and barnacles. A consequence of fouling on a ship hull is the increased drag experienced by the vessel in motion which increases costs and extends downtime during hull maintenance. Adapted from ¹⁷.

To be commercially applicable, surfaces must be evaluated in terms of their ability to broadly control material accretion and/or deliberately designed in such a way through a combinatorial approach. Following the example of marine fouling, Figure 11 demonstrates some

overlap of effectiveness for a few surface design strategies, where surface energy and hygro-responsiveness demonstrate broad applicability for bacteria, algae, and barnacles. However these strategies, which work well for small and soft bacteria, do not fully translate to the more complex algae and barnacles accretion. In addition, texture is almost exclusively effective for bacteria; minimal successful examples exist for algae and barnacles. Figure 11 also demonstrates need for more combinatorial approaches. In terms of effectiveness, only combinatorial solutions for glaze-ice and barnacles have been utilized, but opportunities may still exist for other (1 or more) foulants. Lastly, as more innovative surface designs are developed, it will become increasingly important to consider mechanical durability for the harsh environments of nature and industrial applications.

1.4 Research Overview

As presented in this chapter, there remains a whole host of design strategies able to control the accretion of solid and liquid foulants. Unfortunately, there are large vacancies in surface designs that are able to control multiple states of matter; surface durability is also a significant concern. This work, although eclectic in nature, largely aims in bridging the gaps of the current state of the field in an attempt to more broadly control solid and liquid fouling, and in some cases enhance durability.

In the first two chapters, we investigate a relatively new class of materials called liquid-like layers. These layers, as described in section 1.2.1, are tethered lubricating layers that yield most of the properties of a lubricant infused surface, but without the problem of depletion by mechanical abrasion or miscible solvents. In chapter 1, we developed a rapid surface chemical process to render a PDMS liquid-like layer onto silicon within minutes. This PDMS liquid-like layer demonstrated omniphobicity to a broad range of liquids of high and low surface tension.

These layers also yielded very low adhesion values for a wide range of solids, including ice, even when compared to low surface energy fluorinated silane. We also uncovered and characterized the shear thinning mechanism by which this surface imparts facile release of the solid adherents. The PDMS liquid-like layers lastly proved highly durable to abrasive, thermal, UV, and chemical damage. To follow on to this work, in chapter 3 I investigated the small-scale solid fouling resistance of the PDMS liquid-like layers. Here I showed that the liquid-like layers are able to limit the adsorption of a wide range of polymers dissolved in solution; this also included the preventing wax fouling. With the collaboration of Professor Zhan Chen's group, we were able to reveal the highly disordered nature of the PDMS chains which led to a thermodynamically unfavorable adsorption process.

Chapter 4 is an attempt to bridge the gaps of marine antifouling surfaces by combining a biocidal approach and a facile release/prevention via a hydration layer. This was achieved by engineering a high aspect ratio nanowire array followed by the growth of a superhydrophilic SBMA brush onto the structures. These SBMA functionalized surfaces are able to both kill bacteria and algae by puncturing the cell walls, as well as easily remove the debris under shear stress. We confirmed the hydration layer formation by oil-within-water contact angle measurements as well as the reversed. Instead of using an oversimplified single-species algal system, we used a multi-species bacteria-algae system found in the state of Florida; more representative of a natural environment. We found that the combination of biocidal nanostructures along with a hydration layer greatly limited both the settled algae/bacteria, but even more so facilitated their facile release.

In Chapter 5 and 6 we focus on surfaces able to control fogging while enhancing their durability. Although many polymeric antifogging coatings have been developed ²⁰⁰⁻²⁰⁴, a very small minority have assessed their durability. In Chapter 5 we demonstrated a simple design

methodology to simultaneously enhance the fogging properties and the abrasive wear properties of polyvinyl pyrrolidone (PVP). This was achieved by the simple addition of miscible hydrophilic slip additives where the resulting coatings were able to outperform a few notable commercial products. Another design strategy revealed in Chapter 6 was also implemented which included the blending of solid slip additives such as graphite. This was done in order to achieve not only a durable polymer antifog coating, but also one that is water resistant. These coatings proved to be antifogging and durable after hours of being submerged into water. Thus, with these works, we were able to bridge a gap between liquid fouling control (antifogging) and real-world applicability (durability).

The final chapter deals with the control of frost phenomena. Ice and frost accretion is a serious problem affecting a wide range of industries which include, but are not limited to: aircraft, ships, refrigerators, and heat exchangers^{155, 205-207}. In this work, we developed a novel frost testing apparatus which is highly consistent and reliably yields multi-phase transition freezing events that result from the surface properties. With this apparatus we demonstrated the design of an SBMA coating that is able to absorb water vapor and facilitate a non-freezing water state within the coating at sub-freezing temperatures for long durations of time.

Chapter 2 - Rapid and Robust Surface Treatment for Simultaneous Solid and Liquid Repellency

This chapter is paraphrased from our work published in *ACS AM I* ²⁰⁸. The work was originally started by Dr. Kevin Golovin, but Dr. Mathew Boban, Dr. Alex Halvey, and I added to, and eventually finished it. This section demonstrates a surface design that is able to control the fouling of not only liquids, but also a wide range of solids, while remaining durable.

2.1 Introduction

As mentioned in the first chapter fouling, in its most general sense, involves a foreign contaminant adsorbing to an interface and compromising one or more surface properties.²² Fouling is a ubiquitous hindrance, which includes the bio-fouling of marine vessels,²⁰⁹ the accretion of ice on power lines,²¹⁰ and the adsorption of contaminants to water purification membranes.²¹¹ Fouling can be broadly subdivided into two categories: the unwanted adsorption of liquids or the unwanted adhesion of solids. Literature reports typically address these foulant categories with separate surface designs. However, practical application frequently requires a single surface which demonstrates fouling resistance across a broad range of both liquid and solid contaminants ¹⁸. For example, coatings for medical implants need to resist fouling by complex bodily fluids, proteins, and bacterial biofilms; anti-ice coatings must reduce fogging and frost nucleation as well as the adhesion of glaze ice; and anti-marine fouling coatings must limit the sequential attachment of soft

proteins, bacteria, algae, mussels, and barnacles. Additionally, in order for a surface to be commercially relevant, it must be facile to apply, and highly resistant to environmental damage.

The repellency of a surface towards a given liquid has been well studied and involves two aspects: high resistance to wetting and high droplet mobility. Wetting resistance may be characterized by high contact angles (θ), while droplet mobility is characterized by low contact angle hysteresis ($\Delta\theta$, the difference between the advancing and receding contact angles).²¹² Many liquid-repellant or superomniphobic surfaces developed in the past decade rely on low surface energy and re-entrant features to entrap air underneath a contacting liquid droplet in order to simultaneously achieve contact angles $> 150^\circ$ and low $\Delta\theta$ with a broad range of liquids.^{35, 213, 214} However, pressure perturbations,²¹⁴ droplet impact,⁴ flow,²¹⁵ evaporation,²¹⁶ and mechanical damage^{217, 218} can all allow liquids to displace this air and cause irreversible wetting. Additionally, these highly textured / porous surfaces often cannot decrease adhesion to solids and may even increase the strength of solid adhesion. This is because many solid foulants can penetrate into the porous texture, dramatically increasing the interfacial contact area and thereby the adhesion between the foulant and surface.²¹⁹⁻²²¹

Lubricated surfaces replace the entrapped air within a textured surface with a liquid, such as a perfluoropolyether, that preferentially wets the solid, textured surface and is immiscible with a broad range of contacting liquids which float on top of the lubricant, and readily slide off.²²² Lubricated surfaces can also allow the facile release of solid contaminants such as ice,²²³ and the lubricant can flow into physically damaged regions, allowing for self-repair.²²² However, such surfaces are resistant to fouling by immiscible contaminants only. Additionally, the surface texture is still susceptible to mechanical damage, and the lubricant may be readily depleted, especially by simple abrasion,²²⁴ condensation of low surface tension liquids,^{45, 225} or under high shear flows.⁴⁸

To improve upon the limitations of textured and lubricated surfaces for simultaneous solid and liquid repellency, a third approach, the covalent tethering of flexible molecular chains or brushes to a surface, has been reported.^{194, 196, 226-234} Such grafted coatings consist of materials with glass transition temperatures far below ambient conditions, generating a mobile, liquid-like interface that can drastically reduce $\Delta\theta$ with most contacting liquids.^{194, 226-228, 230, 231, 233, 234} However, previous reports of these surfaces typically require complex fabrication involving different solvents, catalysts, and surface pretreatment,^{196, 226-228, 231, 233, 235-238} and solid adhesion on liquid-like surfaces has been minimally studied.^{194, 196, 232} Here, we report an extremely rapid, solvent- and pretreatment-free method to generate an ultra-thin film of low surface energy, linear, liquid-like poly(dimethylsiloxane) on silicon wafers. We present a systematic investigation and detailed characterization of this treatment method, demonstrating that the liquid-like morphology of resultant surfaces is the key contributing factor to anti-fouling performance. This transparent surface treatment demonstrates exceptional durability, low adhesion with a broad variety of solids, and $\Delta\theta \rightarrow 0^\circ$ with an unprecedented range of liquids, including fluorinated solvents.

2.2 Results and Discussion

To fabricate our coating, denoted b-PDMS, silicon was exposed to a room-temperature vapor of volatile, bi-functional, chlorine-terminated dimethylsiloxane (1,3-dichlorotetramethyldisiloxane) for three consecutive, five-minute periods with a 2-propanol rinse between each exposure. The glass transition temperature of polydimethylsiloxane (PDMS) is -123 °C, therefore linear PDMS is a liquid at room temperature. The surface-grafted, linear PDMS chains can be similarly described as liquid-like, generating a mobile interface that effectively masks surface defects and lowers the barriers for the advancing and receding of liquids, thereby reducing $\Delta\theta$. Additionally, these liquid-like grafted layers can simultaneously induce interfacial

slippage^{138, 239, 240} (i.e. a non-zero slip velocity at the solid-solid interface) between the coating and any contacting solid, enabling their facile debonding from the surface.

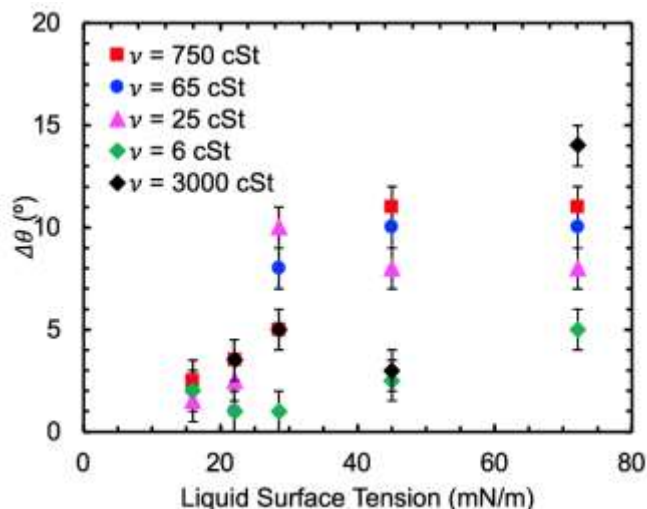


Figure 13: Precursor molecular weight and hysteresis

Contact angle hysteresis ($\Delta\theta$) of b-PDMS surfaces fabricated with bi-functional methylsiloxane precursors of varying chain lengths, as a function of liquid surface tension. All five precursors were exposed to the Si wafers for 10 minutes in the vapor phase. The vapor pressure of the shortest precursor is likely responsible for the increased reactivity and resultant omniphobic properties.

The anti-fouling performance of the b-PDMS surfaces is strongly dependent on the molecular length and reaction time. Exposure to the shortest precursor, 1,3-dichlorotetramethyldisiloxane ($n = 2$), resulted in the lowest contact angle hysteresis for the largest number of liquids (Figure 13). The chlorine terminated siloxane precursors of varying length ($n = 2, 3, 4, 6$, or 30-50) were purchased from Gelest. For a single exposure period to the precursor, a time of ten minutes optimized the surface coverage and linear grafted chain morphology, generating a b-PDMS surface with thickness ~ 4 nm (Figure 13A). The lower θ_{rec} and higher $\Delta\theta$ on samples exposed for less than 10 minutes most likely resulted from chemical inhomogeneity due to unreacted silanol groups on the silicon surface. Beyond the optimal 10-minute exposure, the θ_{rec} again decreased along with increased θ_{adv} , raising $\Delta\theta$. This increase was likely due to a

higher degree of self-polymerization of the b-PDMS, resulting in higher roughness and the development of longer molecules, which have been previously shown to impede the motion of the three-phase contact line.²³⁵ The thickness of the b-PDMS film increased from <1 nm after 30 seconds of exposure to > 6 nm after 1 hour of exposure. However, a slightly modified reaction scheme, consisting of a series of three, five-minute exposures to the precursor, minimized $\Delta\theta$ and led to the best overall performance, at a thickness of 2.5 ± 0.2 nm. This divided reaction likely minimizes uneven self-polymerization which can occur in longer exposure periods, without sacrificing surface coverage. Low relative humidity (< 25%) during silanization was also found to be necessary to minimize $\Delta\theta$. Increased $\Delta\theta$ values for longer exposure times, and at increased reaction speeds caused by higher humidity, can likely be attributed to a resultant increased degree of self-polymerization, increased heterogeneity, and higher roughness, all of which can impede the motion of the three-phase contact line.²³⁵ While longer exposure periods lead to increased $\Delta\theta$, this increase is not caused by increasing film thickness. When exposed to 10 cycles of oxygen plasma (15 minutes) and re-exposure to the precursor (10 minutes). The oxygen plasma step hydrolyzed the surface methyl groups and rendered the surface completely wettable by water.^{241, 242} The resulting silanol groups were then reacted with the precursor to yield a b-PDMS surface with increased thickness, but the same $\Delta\theta$ as the original 4 nm thick surface. Repeating this procedure ten times yielded a 15 nm thick b-PDMS film that still exhibited $\Delta\theta \approx 3$ (Figure 14 B).

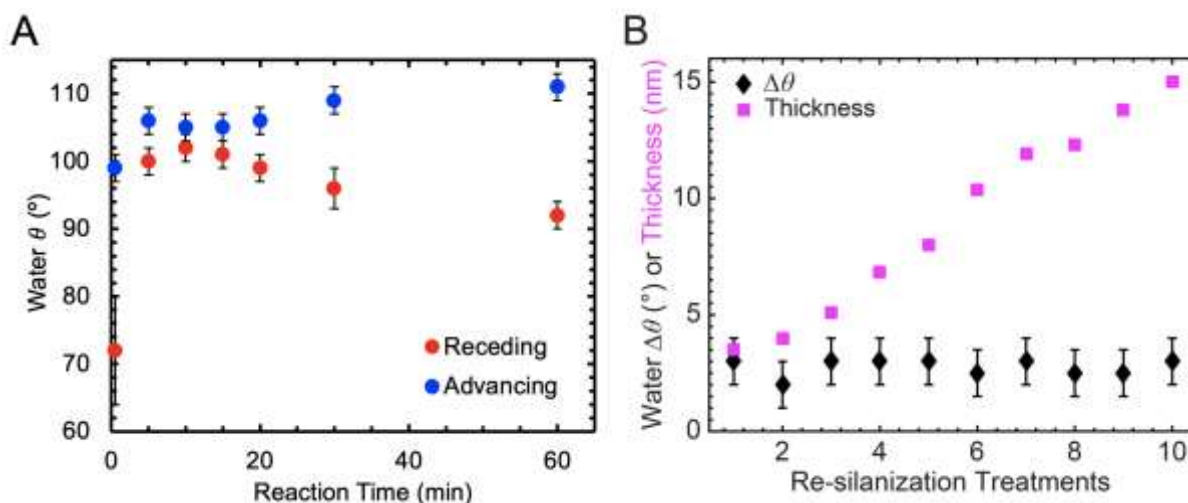


Figure 14: Effect of reaction time and thickness on hysteresis

A) The advancing and receding water contact angles on the b-PDMS film as a function of exposure time to the precursor. B) Exposing the optimal b-PDMS surface to O₂ plasma and subsequently re-silanizing the surface yielded a surface with identical $\Delta\theta$ to that prior to plasma treatment. However, the thickness was increased, and this could be repeated for at least ten subsequent exposures.

Due to steric hindrance, the bidentate 1,3-dichlorotetramethyldisiloxane can only react with a fraction of the silanol groups on a completely hydrolyzed silicon wafer. To reduce the surface energy of the fabricated surface further, we capped the residual silanol groups on the silicon surface, as well as terminal silanol groups at the end of the linear siloxane chains, with a low molecular weight, monofunctional, hydrophobic silane – trimethylchlorosilane. Whereas the b-PDMS surface exhibited $\theta \approx 104^\circ$ with water, the capped surface (cb-PDMS) exhibited $\theta \approx 106^\circ$, which approaches the intrinsic contact angle of a dense methylated surface, $\theta = 110^\circ$ (Figure 15).²⁴³ The thickness of the PDMS coating increases negligibly after capping. The cb-PDMS surface also has a surface energy of 22.9 ± 0.2 mN/m and a roughness of 2.9 ± 0.2 nm. Note that the capping procedure required ~ 1 hour of additional exposure, resulting in a more omniphobic surface but a less rapid fabrication procedure.

The homogeneity of a PDMS surface is thus controlled in multiple ways. The first is by slowing the reaction to limit disorderly polymerization of PDMS chains. This is done by working in a low humidity environment and using multiple, short reaction cycles with a rinse in between, instead of one extended exposure period. Use of the smallest molecular weight siloxane precursor also helps to avoid steric hindrance during polymerization and minimize defects. Lastly, the capping reaction to convert b-PDMS to cb-PDMS minimizes exposed hydroxyl groups and improves surface homogeneity. Maximizing homogeneity serves to minimize the contact angle hysteresis of a surface and to limit the nucleation and adhesion of solid contaminants.

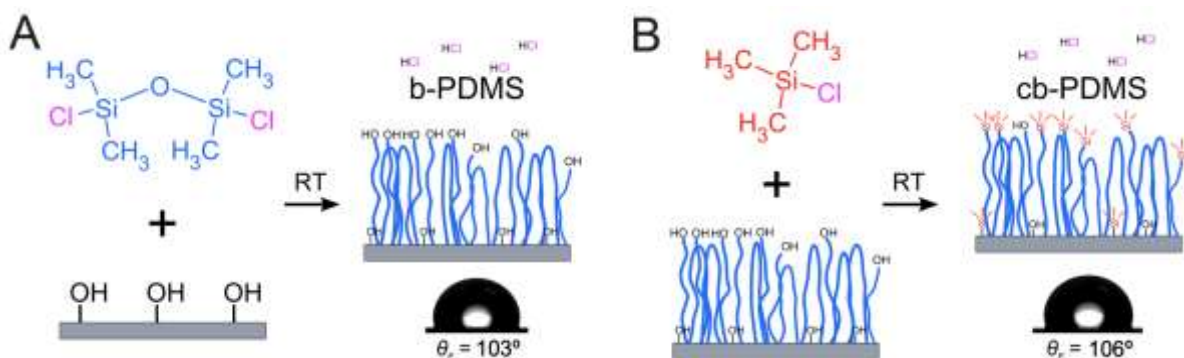


Figure 15: The proposed mechanism for the bidentate attachment of 1,3-dichlorotetramethyldisiloxane.

A) A Si wafer with surface silanol groups is exposed to the vapor of the bi-dentate siloxane at room temperature. The siloxane reacts with the silanol groups, as well as atmospheric water vapor, to yield grafted chains of poly(dimethylsiloxane) (PDMS). Hydrochloric acid is given off as a reaction product. The final surface is quite hydrophobic with the static water contact angle $\sim 103^\circ$, but polar silanol groups remain on the surface and on chain ends. B) The reacted wafer is subsequently exposed to a vapor of trimethylchlorosilane, which converts most of the remaining silanol groups to fully methylated Si atoms. Note that we show the likely case where complete reaction is not achieved, due to steric hindrance.

2.2.1 Liquid Repellency

We measured advancing and receding contact angles for different probe liquids with a wide range of surface tensions and polarities on both b-PDMS and cb-PDMS surfaces, including several liquids not previously reported in the literature (Table 1).^{226, 227} To compare the performance of

the fabricated surface with a low surface energy coating widely used in the literature, we also vapor deposited a monolayer of perfluorodecyldimethylchlorosilane on silicon (denoted F-17). The fabrication of this F-17 monolayer required a much more time- and energy-intensive process (pretreatment with oxygen plasma followed by 48 h of vapor deposition at 100 °C under vacuum) than the b-PDMS grafted surface. The surface energy of the perfluorinated monolayer ($\gamma_{SV} \sim 14$ mN/m) is significantly less than that of PDMS ($\gamma_{SV} \sim 23$ mN/m), resulting in higher contact angles with most liquids when compared to b-PDMS or cb-PDMS coated surfaces. However, as long-chain perfluoroalkyl monolayers are highly crystalline, surface defects can act as pinning points for liquid droplets.²⁴⁴ As a result, for every probe liquid evaluated, the contact angle hysteresis on the F-17 monolayer was significantly higher than on either the b-PDMS or the cb-PDMS films despite its lower surface energy.

Interestingly, some fluorinated solvents with very low surface tensions exhibited higher contact angles, in addition to lower $\Delta\theta$, on the PDMS films than on the F-17 monolayer. Fluorine-fluorine interactions are known to play a large role in the solvation of fluorinated species.^{245, 246} This is likely why several fluorinated liquids did not recede from the F-17 monolayer. Moreover, we also observed higher contact angles with the PDMS-based systems for perfluorodecalin and Krytox 100 (a short-chain perfluoropolyether²²²), indicating a high interfacial tension between the liquids and the grafted PDMS. Typically, the surface tension of the highest surface tension liquid that fully wets a surface is a reasonable estimate of the surface energy of the solid, as first proposed by Zisman.²⁴³ However, quite remarkably, we observed both non-zero receding contact angles and extremely low $\Delta\theta$ for liquids with significantly lower surface tensions than the solid surface energy of PDMS.

Table 1. $\theta_{adv}/\theta_{rec}$ for various liquids on a silicon wafer covered with a perfluorinated monolayer (F-17), bidentate PDMS film (b-PDMS), and capped bidentate PDMS film (cb-PDMS). The standard error is $\pm 2^\circ$ for all measurements.

Table 1: Liquid contact angles on b-PDMS, cb-PDMS, and F-17 functionalized surfaces

$\theta_{adv}/\theta_{rec}$ for various liquids on a silicon wafer covered with a perfluorinated monolayer (F-17), bidentate PDMS film (b-PDMS), and capped bidentate PDMS film (cb-PDMS). The standard error is $\pm 2^\circ$ for all measurements.

Liquid	$\gamma_{LV}(\text{mN/m})$	F-17	b-PDMS	cb-PDMS
Water	72.8	119°/109°	104°/102°	107°/105°
Dimethylformamide	37.1	80°/70°	65°/60°	68°/64°
Hexadecane	27.5	64°/58°	36°/34°	35°/34°
Toluene	28.4	65°/60°	26°/25°	32°/30°
Acetone	25.2	59°/53°	27°/26°	31°/30°
1-Propanol	23.7	56°/49°	24°/23°	33°/32°
Ethanol	22.1	55°/48°	26°/25°	32°/31.5°
2-Propanol	23.0	50°/44°	19°/11°	22°/19°
o-Fluorotoluene	28.0	68°/52°	28°/26.5°	27.5°/27°
p- Chlorobenzotrifluoride	24.0	61°/43°	25°/24°	25°/24°
Hexafluorobenzene	21.0	41°/35°	20°/18.5°	21°/21°
Perfluorodecalin	19.0	27°/23°	28°/27°	35°/34°
Krytox 100	16.0	23°/11°	32°/30°	32.5°/31.5°
Asahiklin 225	16.0	27°/17°	11°/10°	13°/12°
Pentafluorobutane	15.0	17°/0°	10°/10°	14.5°/14°

Vertrel XF	14.0	8°/0°	9°/9°	12°/12°
Methoxyperfluorobutane	13.0	12°/0°	10°/10°	14.5°/14°

We found only a few liquids that could completely wet the b-PDMS and cb-PDMS films, including linear liquid PDMS, linear alkanes shorter than octane, small alkyl-amines, and ultra-low molecular weight perfluoropolyethers. These liquids exhibit a combination of very strong solubility for PDMS,²⁴¹ low molecular weight, and/or very low surface tension. However, unlike lubricated systems, where the repellency is lost when the lubricant is contacted by a miscible solvent, the tethered PDMS films retained their ultra-low $\Delta\theta$ with all other liquids after the removal of the wetting liquid. This is because the PDMS chains are covalently bonded to the underlying substrate (Figure 1).

As previously mentioned, lubricated surfaces cannot repel liquids that are miscible with the lubricant. To highlight the significant advantage of the cb-PDMS surface over a lubricated system, we placed 10 μL droplets of Krytox 100 (a representative fluorinated lubricant) on a cb-PDMS surface inclined by 0.5° (Figure 13). This very low surface tension liquid ($\gamma_{LV} \sim 16 \text{ mN/m}$) easily dewetted from the cb-PDMS surface. It also slid around without leaving a residual trail, while maintaining a relatively high contact angle ($\theta \approx 32^\circ$) and low hysteresis $\Delta\theta = 1^\circ$. The surface remained undamaged after this demonstration.

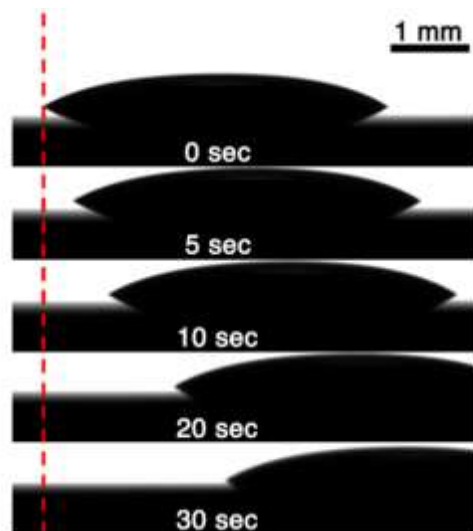


Figure 16: CB-PDMS liquid like layer shedding fluorinated krytox lubricant

A droplet of Krytox 100 (a perfluoropolyether lubricant, $\gamma_{LV} = 16$ mN/m) was placed on the cb-PDMS surface at a tilt angle of 0.5° . The droplet easily slid from the surface, displaying negligible hysteresis, and did not leave a wetted trail.

2.2.2 Solid Repellency

Next, we evaluated the adhesion of solid foulants with a wide range of surface bonding types to b-PDMS, cb-PDMS and F-17 treated surfaces. These solids include ice (hydrogen bonding), cyanoacrylate superglue (covalent bonding), calcined gypsum (polar bonding), paraffin wax (van der Waals interactions), and crosslinked PDMS elastomer (Figure 17A). In all cases, the solid adherent was deposited in a liquid state, ensuring complete solid/solid contact. We observed that the non-polar, liquid-like b-PDMS and cb-PDMS films significantly reduced adhesion for all solids, regardless of bonding type, compared to the F-17 monolayer. This was surprisingly true even for elastomeric PDMS adhesion. The same tests were also carried out on bare silicon, but multiple solid foulants failed cohesively during debonding (Figure 17A). Remarkably, the cb-PDMS surface demonstrated an ice adhesion strength of only $\tau_{ice} = 18 \pm 1$ kPa, significantly below the threshold value for an icephobic surface ($\tau_{ice} < 100$ kPa).¹³⁸ Both b-PDMS and cb-PDMS surfaces also remain icephobic, without significant increases in τ_{ice} , after 10 cyclic icing/de-icing

cycles (Figure 17A). Thus, although perfluorinated surfaces have lower surface energy, the mobile interface of the liquid-like b-PDMS and cb-PDMS surfaces more effectively facilitated the removal of a range of different solids via interfacial slippage. The phenomenon of interfacial slippage was first verified by Newby *et al.*, who demonstrated that the adhesion strength of liquid-like silane monolayers during transverse debonding does not depend on the work of adhesion between the surface and the adherent, but rather the mobility of the grafted surface chains.²⁴⁰ We similarly observed minimal dependence of adhesion on the type of hard foulant, as would be expected for a surface exhibiting interfacial slippage.^{138, 239} The higher adhesion observed between superglue and the b-PDMS surface likely resulted from the residual silanols bonding with the highly reactive cyanoacrylate groups, and this adhesion reduced significantly after capping.

Interestingly, while it has been suggested that reducing the τ_{ice} of liquid-like siloxane surface requires increasing the surface thickness,¹⁹⁴ this performance was achieved for a surface with thickness < 5 nm. As discussed previously, our data suggests that careful control over the precursor polymerization reaction is essential to achieve optimum surface performance. Full surface coverage and homogeneity are the critical properties and can be achieved independent of layer thickness (Figure 14A).

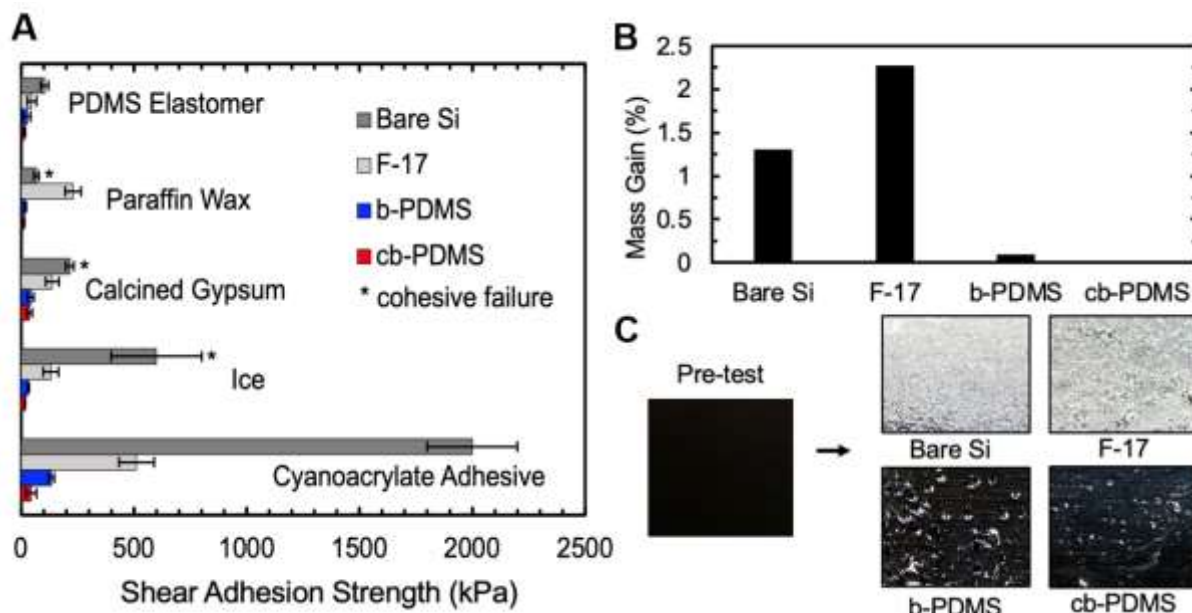


Figure 17: Solid Antifouling Properties of Liquid-Like Layers

A) The shear adhesion strength for five different solids on silicon wafers treated with b-PDMS, cb-PDMS, or F-17. B) The mass gain in % of bare silicon, F-17, b-PDMS, and cb-PDMS following the completion of the scaling test C) 1.2 x 1 cm images of a pre-test specimen (which appears identical for all tested surfaces) as well as bare silicon, F-17, b-PDMS, and cb-PDMS after all DI water has evaporated and the scaling test is complete. The images are oriented as the samples were during testing (the water level fell downward).

The b-PDMS and cb-PDMS surfaces also demonstrate anti-scaling performance, showing a near-complete reduction in inorganic scale deposition, and a significantly better performance than the lower surface energy F-17 surface (Figure 17B&C). In our testing, all samples were submerged at an angle of 70° from the horizontal in an aqueous CaSO_4 solution, which was then slowly evaporated on a hotplate until dry, allowing the salt to crash out of solution and deposit on the test surfaces.¹⁹⁶ While the F-17 surface is more hydrophobic than b-PDMS and cb-PDMS, and has a lower roughness when compared to b-PDMS, cb-PDMS, and bare silicon (Figure 18), it is unable to limit scale fouling, accumulating even more CaSO_4 per unit area than bare silicon. This is likely because the crystalline nature of long-chain perfluoroalkyl monolayers leads to surface defects that can act as non-homogenous pinning points for liquid droplets.²⁴⁴ These defects may

also provide nucleation sites for depositing scale, resulting in significant fouling. In contrast, a negligible amount of CaSO_4 deposits onto the b-PDMS and cb-PDMS surfaces during solution evaporation. The surfaces displayed in Figure 17C do not undergo any type of cleaning following the scaling test, and demonstrate the ability of linear, liquid-like PDMS to resist nucleate fouling by presenting a nearly defect-free surface, due to the mobility of the surface chains.

2.2.3 Liquid-like Surface Characterization

To illustrate the effect of a linear, liquid-like surface morphology on anti-fouling performance, we compared the properties of b-PDMS to chemically similar surfaces generated by reactions with both a mono-dentate (trimethylchlorosilane) and a tri-dentate (methyltrichlorosilane) methylated silane, as well as both methylated and fluorinated crystalline monolayers (Figure 18). Both the mono- and tri-dentate silanes resulted in surfaces with decreased water contact angles, and significantly increased $\Delta\theta$ and τ_{ice} values, as compared to b-PDMS surfaces. The inability of trimethylchlorosilane to polymerize on the surface, leads to imperfect coverage and likely unreacted silanol groups which are exposed to fouling liquids and ice. Conversely, tri-dentate methyltrichlorosilane can polymerize rapidly, forming a network with significantly uneven topography and without free chain movement to enable interfacial slippage. This surface's asperities are expected to interact with fouling liquids and ice, limiting their ability to recede and shed.

The fluorinated crystalline surface (F-17) has lower surface energy and roughness when compared to b-PDMS, yet still displays higher $\Delta\theta$ and τ_{ice} values. As previously mentioned, surface defects typically found in highly crystalline surfaces can act as pinning points for liquid droplets.²⁴⁴ The methylated crystalline silane suffers from similar surface defects at a higher surface energy, again resulting in increased $\Delta\theta$ and τ_{ice} values. The comparison of b-PDMS to the extremely similar

methyated crystalline silane demonstrates poignantly the importance of the flexible chain morphology of b-PDMS in enabling foulant release.

The n-decyl and perfluorodecyl crystalline surfaces, with surface energies of 27.3 ± 0.1 and 14.2 ± 0.4 mN/m respectively, display τ_{ice} values of 457 ± 149 and 131 ± 34 kPa respectively. The mono-dentate (trimethylchlorosilane) surface has a surface energy of 31.1 ± 0.9 mN/m and an $\tau_{ice} = 567 \pm 214$ kPa. These values all correspond well to the relationship established between water wettability and ice adhesion strength for smooth surfaces by Meuler *et al.*, $\tau \propto 1 + \cos(\theta_{rec})$.¹³ Note that τ_{ice} of the tri-dentate (methyltrichlorosilane) silane surface is significantly higher than the Meuler prediction, likely due to its high roughness and surface heterogeneity. Remarkably, despite a surface energy of 23.3 ± 0.2 mN/m, b-PDMS displays an ice adhesion strength of only 32 ± 3 kPa. This is a nearly four-fold reduction in ice adhesion strength compared to the more hydrophobic F-17 surface and a significant deviation from the Meuler relationship previously mentioned. Previous reports have shown that the Meuler relationship holds only for high modulus interfaces where slippage does not occur.^{138, 239, 240} This b-PDMS result demonstrates the critical influence of interfacial slippage in facilitating the facile release of solid foulants, even compared to coatings with lower surface energy.

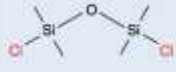
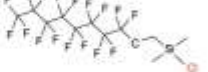
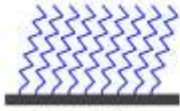
Silane Type	b-PDMS	tri-methyl	tri-chloro	n-decyl	perfluorodecyl
Chemical Precursor					
Surface Morphology	 linear, liquid-like	 monolayer	 network	 crystalline	 crystalline
water $\theta_{adv}/\theta_{rec}$	104°/102°	87°/76°	90°/62°	106°/97°	119°/109°
hexadecane $\theta_{adv}/\theta_{rec}$	36°/34°	34°/10°	33°/10°	19°/6°	64°/58°
τ_{ice} (kPa)	32 ± 3	567 ± 214	1222 ± 450	457 ± 149 kPa	131 ± 34 kPa
Surface Energy (mN/m)	23.3 ± 0.2	31.1 ± 0.9	29.1 ± 0.4	27.3 ± 0.1	14.2 ± 0.4
Roughness (nm)	1.4 ± 0.3	1.9 ± 0.1	7.4 ± 3.1	3.4 ± 0.2	0.6 ± 0.1

Figure 18: Liquid-Like layer property characterization

A comparison of b-PDMS surface properties with multiple methylated control surfaces as well as the F-17 monolayer. The linear, liquid-like morphology of the b-PDMS surface, generated by controlled polymerization of a bifunctional siloxane precursor, leads to exceptional anti-fouling performance even when compared a surface (F-17) with lower surface energy and roughness.

Atomic Force Microscopy was utilized to further characterize the morphologies of the surfaces in this test set (Figure 19). The b-PDMS and cb-PDMS surface scans, as well as both crystalline surfaces, correspond closely with the morphology of bare silicon (Figure 20), which has a roughness of 1.4 ± 0.4 nm. The scan of the surface generated by reaction with trimethylchlorosilane displays inconsistent coverage, which corresponds well with the performance reported in Figure 18. The surface generated by reaction with methyltrichlorosilane clearly displays the effects of rapid, network polymerization in the form of large material agglomerates on the surface. The roughness of this surface is over five times greater than its silicon

substrate due to this effect, which is again consistent with the poor anti-fouling performance reported in Figure 17.

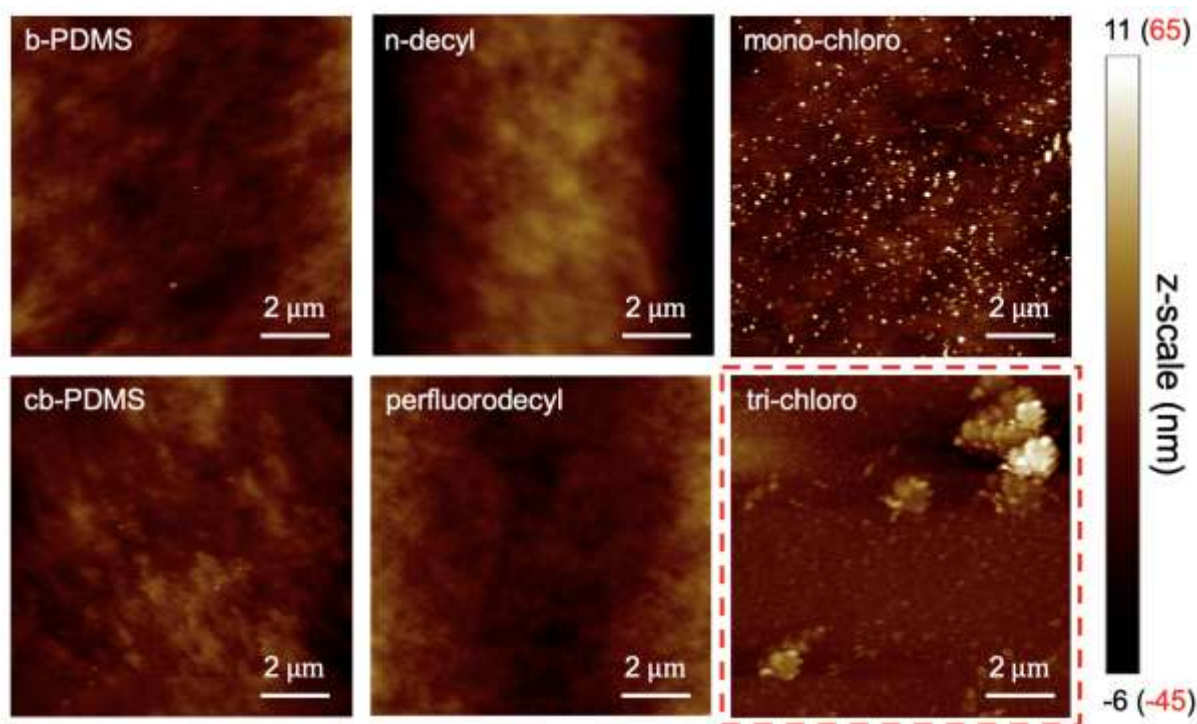


Figure 19: AFM micrographs of cb-PDMS and surfaces of comparison

AFM micrographs for the surfaces described in Figure 4, as well as cb-PDMS. The n-decyl, perfluorodecyl, b-PDMS and cb-PDMS surfaces all approach the morphology of bare silicon. Note that the z-axis range shown is the same for all surfaces except the tri-chloro surface, indicated in red, which requires a larger range in order to capture its high degree of roughness.

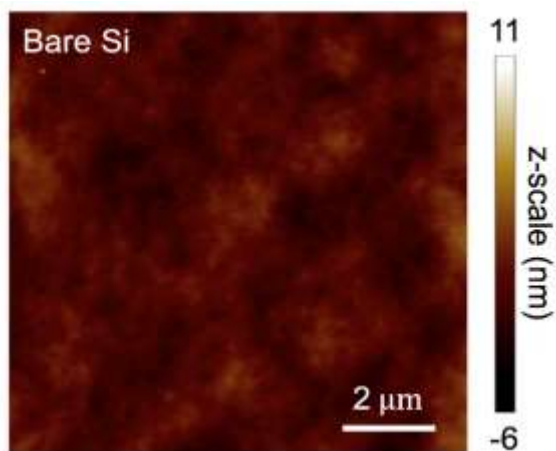


Figure 20: AFM micrograph of bare silicon

The liquid-like behavior of b-PDMS and cb-PDMS layers was confirmed at $-10\text{ }^{\circ}\text{C}$ by measuring the ice adhesion shear strength over a large range of shear velocities (from $4\text{ }\mu\text{m/s}$ to 2 mm/s). The b-PDMS and cb-PDMS surface used for this test were generated by a single, 10-min exposure to the bPDMS precursor, followed by the standard capping procedure, resulting in a layer thickness of $\sim 4\text{ nm}$. The shear stress, τ , for shear thinning liquids is known to follow a power-law dependence on shear rate over a certain range, as $\tau = K\dot{\gamma}^n$. Here K is the consistency index, and n is the power law index (Newtonian fluids exhibit $n = 1$ and shear thinning fluids exhibit $0 \leq n \leq 1$).²⁴⁷ A strong dependence of the ice adhesion strength on the shear rate ($\dot{\gamma}$) was observed for both b-PDMS and cb-PDMS, indicating a large viscous component. The shear rate was determined by $\dot{\gamma} = v/h$, where v is the linear velocity and h is the measured b-PDMS thickness of 4 nm .²⁴⁸ Plotting τ vs. $\dot{\gamma}$ in logarithmic space (Figure 21) allowed for the determination of $K = 186\text{ Pa}$ and $n = 0.58$ for b-PDMS, and $K = 187\text{ Pa}$ and $n = 0.51$ for cb-PDMS. K effectively represented the minimum possible ice adhesion strength observable on these two surfaces at infinitely low shear rates. The power law index represents the degree of shear-thinning behavior. These values indicated that the two surfaces shared similar minimum ice adhesion values, but the cb-PDMS surface was more shear thinning, resulting in the lower ice adhesion strengths observed for larger shear rates. It is recognized that there is typically an onset shear rate for the shear thinning behavior of PDMS.²⁴⁹ However, the extremely thin film (4 nm) makes all practical velocities yield shear rates well above the onset shear rate of $\sim 1\text{ s}^{-1}$. For example, even at a linear speed of 10 nm/s , $\dot{\gamma} = 2.5\text{ s}^{-1}$, therefore the onset shear rate could not be measured directly using our experimental setup. These results were consistent with the non-Newtonian, shear thinning behavior of liquid PDMS.²⁵⁰ For comparison, a methylated crystalline surface (n-decyldimethylchlorosilane functionalized)

was evaluated by the same method. No significant dependence of the ice adhesion strength on the shear rate ($\dot{\gamma}$) was observed, as expected for a non-liquid-like surface (Figure 21).

For comparison, a methylated crystalline surface (n-decyldimethylchlorosilane functionalized) was evaluated by the same method. No significant dependence of the ice adhesion strength on the shear rate ($\dot{\gamma}$) was observed, as expected for a non-liquid-like surface (Figure 5).

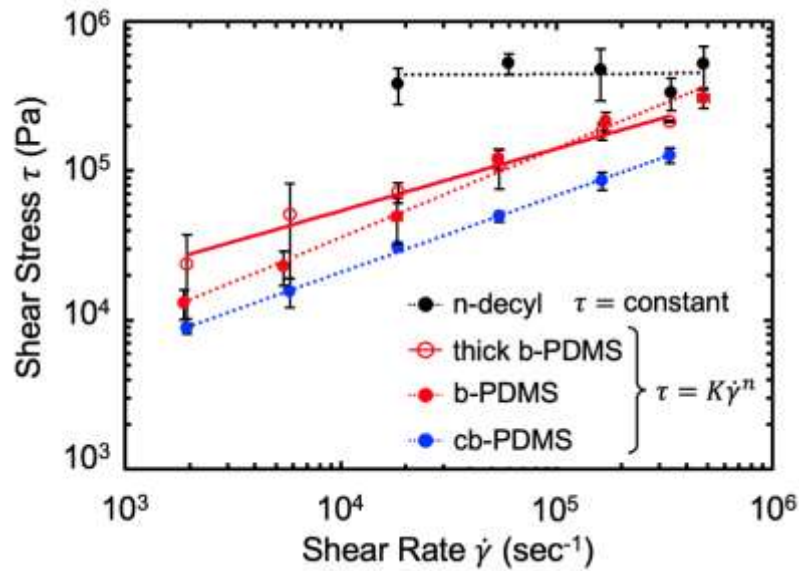


Figure 21: Logarithmic plot displaying the measured ice adhesion shear strength as a function of shear rate

Results for the b-PDMS, cb-PDMS and methylated crystalline surfaces. The b-PDMS and cb-PDMS surface show a power law dependence of τ on $\dot{\gamma}$, while for the crystalline surface, τ is independent of the shear rate.

To evaluate the relationship between shear stress and shear rate as a function of coating thickness, we fabricated a b-PDMS coating with increased thickness using the procedure depicted in Figure 14B. This coating underwent 5 re-silanization treatments and had a measured thickness of 9.2 ± 0.1 nm, a nearly 4x increase over the thickness of standard b-PDMS samples (2.5 ± 0.2 nm). The ice adhesion shear strength of this surface was measured over a large range of shear velocities (from 4 $\mu\text{m/s}$ to 2 mm/s). As was true for the standard b-PDMS and cb-PDMS samples, the shear stress, τ , vs. shear rate, $\dot{\gamma}$, data fits a power law ($\tau = K\dot{\gamma}^n$) well (Figure 21). For the thick

b-PDMS surface we observed $K = 500$ Pa and $n = 0.49$. These values indicated that the thicker b-PDMS has a larger minimum ice adhesion value than the other two PDMS surfaces, possibly due to a lack of homogeneity caused by repeated functionalization cycles, but is the most shear thinning of the three, resulting in the smaller increases in τ observed for larger shear rates.

2.2.4 Durability

To evaluate the robustness of the b-PDMS and cb-PDMS surfaces against harsh environmental conditions, we subjected them to a number of durability characterizations (Figure 22). First, the surfaces were heated in air for several hours at 250 °C (24 hours) and 350 °C (1 hour). The surfaces were also immersed in boiling water and hexane. While there was some increase in the contact angle hysteresis after these severe thermal exposures, the coating did not degrade and remained adhered to the underlying substrate. UV exposure also resulted in minimal increase in the contact angle hysteresis. Extended mechanical abrasion (5,000 cycles, Taber linear abrader, CS-5 abrasive felt, 20 kPa load) had negligible impact on both θ_{adv} , θ_{rec} and $\Delta\theta$ with water (Figure 22A) and hexadecane (Figure 22B). As the cb-PDMS thickness was only ~ 3 nm, any surface degradation would result in a catastrophic contact angle decrease, especially for the receding angle of hexadecane. This was not observed, indicating that this level of abrasion did not damage the coating. Post-abrasion AFM scans additionally confirmed that, while the surface roughness decreased after abrasion, the coating remained homogenous (Figure 23). The water contact angles on cb-PDMS after 5,000 abrasion cycles were $\theta_{adv}/\theta_{rec} = 107^\circ/105^\circ$.

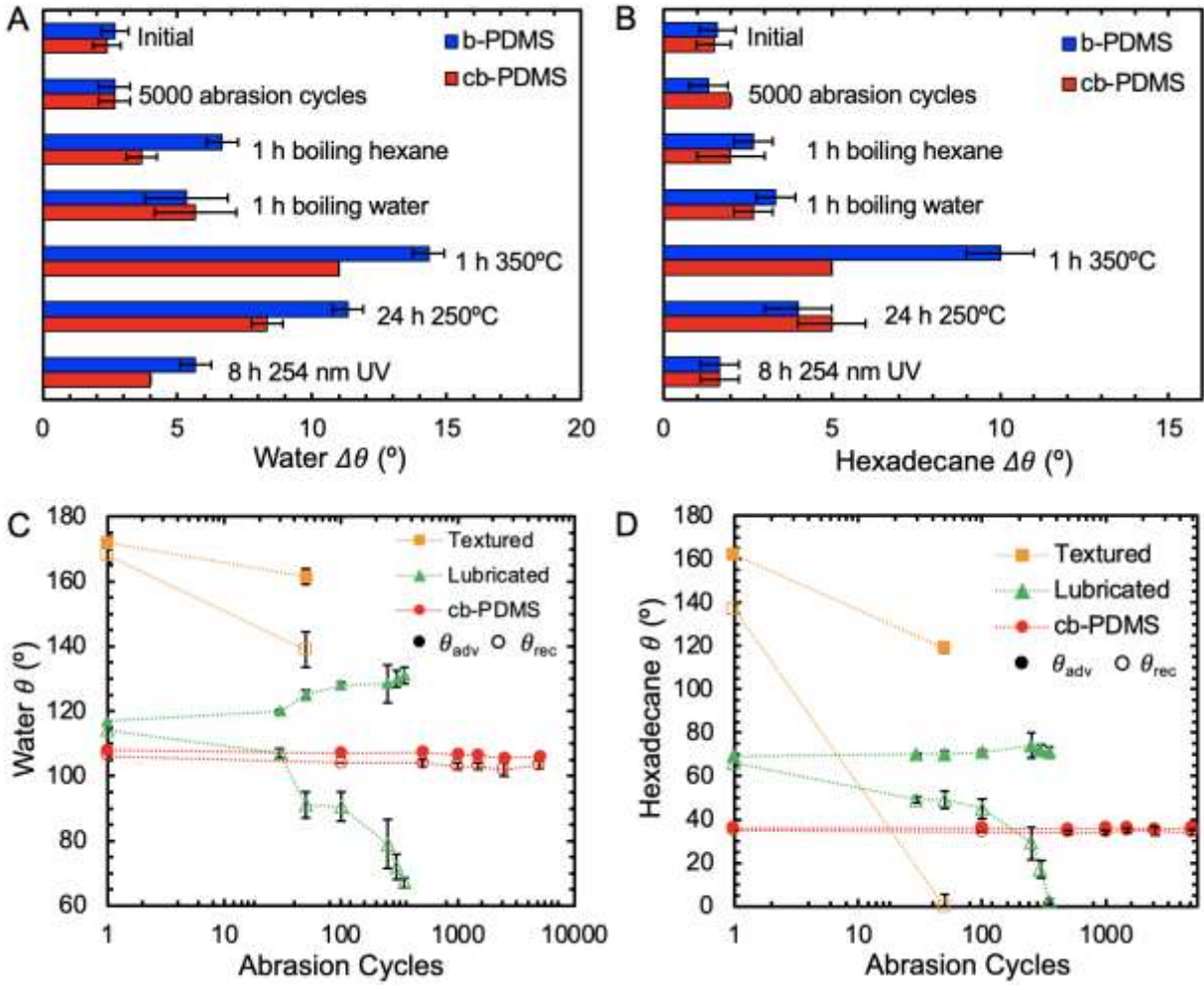


Figure 22: Durability of b-PDMS and cb-PDMS

A, B) Contact angle hysteresis for water and hexadecane on the b-PDMS and cb-PDMS surfaces after exposure to various harsh environments. C, D) θ_{adv} and θ_{rec} for water and hexadecane on the capped bidentate PDMS surface (cb-PDMS), as well as a lubricated surface, and a textured superomniphobic surface, as a function of the number of Taber linear abrasion cycles. The x-axis is a log scale with the data plotted at one abrasion cycle representing the pre-abrasion contact angles for each surface.

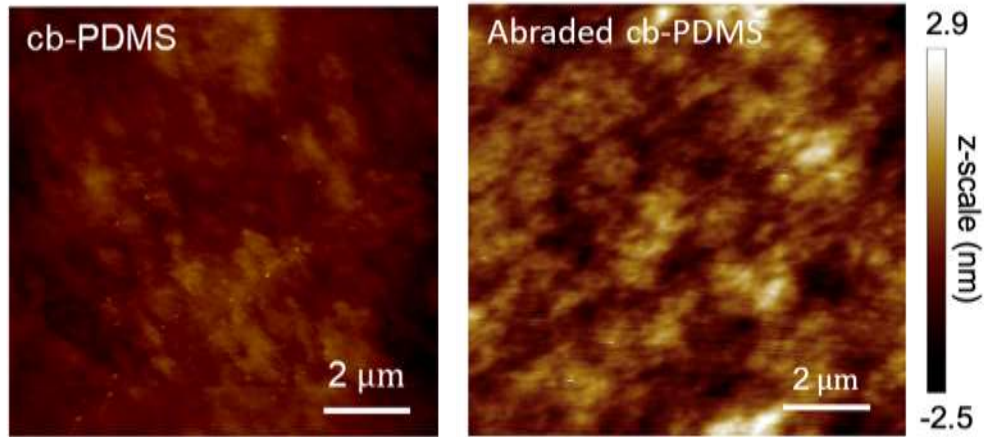


Figure 23: AFM Micrographs of abraded cb-PDMS

To further demonstrate the durability of the b-PDMS and cb-PDMS surfaces, a series of 10 cyclic icing and de-icing tests were performed. While the variation in the ice adhesion strength measurements does increase after multiple icing cycles, particularly for b-PDMS, the ice adhesion strengths of the b-PDMS and cb-PDMS surfaces remain fairly constant and both surfaces remain icephobic (Figure 24).

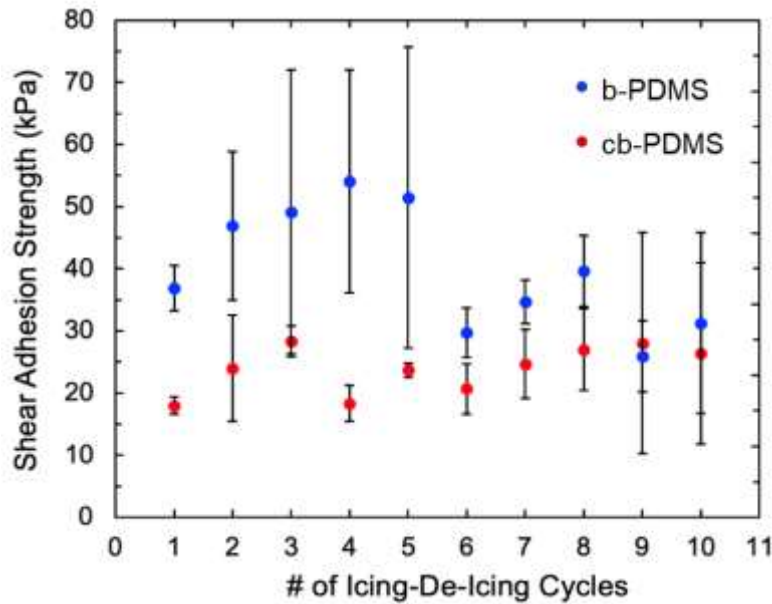


Figure 24: Durability of cb-PDMS to icing/deicing cycles

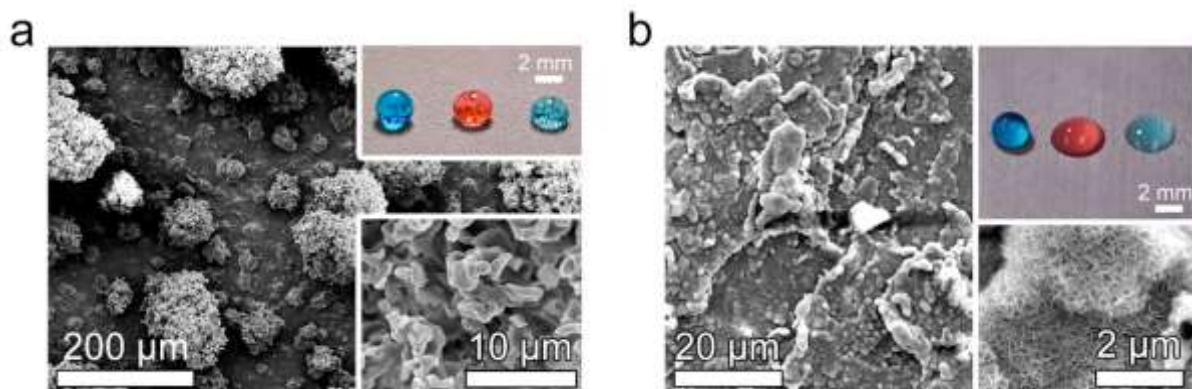


Figure 25: Abrasion and wetting properties of abraded textured omniphobic coatings

Surfaces for comparison. **A)** SEM of the spray-coated, textured superomniphobic surface, which is composed of large aggregates which are in turn composed of individual dried droplets of FPU+50% F-POSS **B)** SEM of the etched, boiled, and fluorosilanized aluminum surface prior to adding lubricant, showing large scale texture from the hydrochloric acid etch process, and nanoscale texture formed from boehmite crystals. Insets in (A) and (B) show SEMs at higher magnifications, as well as photographs of dyed $\sim 15 \mu\text{L}$ droplets of water (blue), hexadecane (red), and ethanol (green) on these surfaces. The droplets on the textured superomniphobic surface are all in the Cassie-Baxter state, with entrapped air supporting them. Reprinted with permission from previous work.²²⁴ Copyright 2018 American Chemical Society

The cb-PDMS surface, as well as the Textured and Lubricated control surfaces, were imaged in 3D before and after undergoing Taber abrasion. The Textured and Lubricated surfaces were imaged by confocal scanning laser microscope (Olympus LEXT OLS5100), while cb-PDMS was imaged by AFM. The Textured surface suffered significant mechanical damage after only 75 cycles of Taber abrasion, including the breakup of FPOSS/FPU agglomerates on the surface and scratching of the underlying substrate. The roughness of this surface decreased from $30 \mu\text{m}$ to $7 \mu\text{m}$ following 75 abrasion cycles (Figure 26). Similarly, the Lubricated surface suffered mechanical damage after 350 cycles of Taber abrasion, with the surface roughness decreasing from $4 \mu\text{m}$ to $3 \mu\text{m}$. The visible damage to the microstructure of this control surface also indicated catastrophic

damage to the more fragile, functionalized surface nanotexture, leading to lubricant instability and partial depletion (Figure 27).

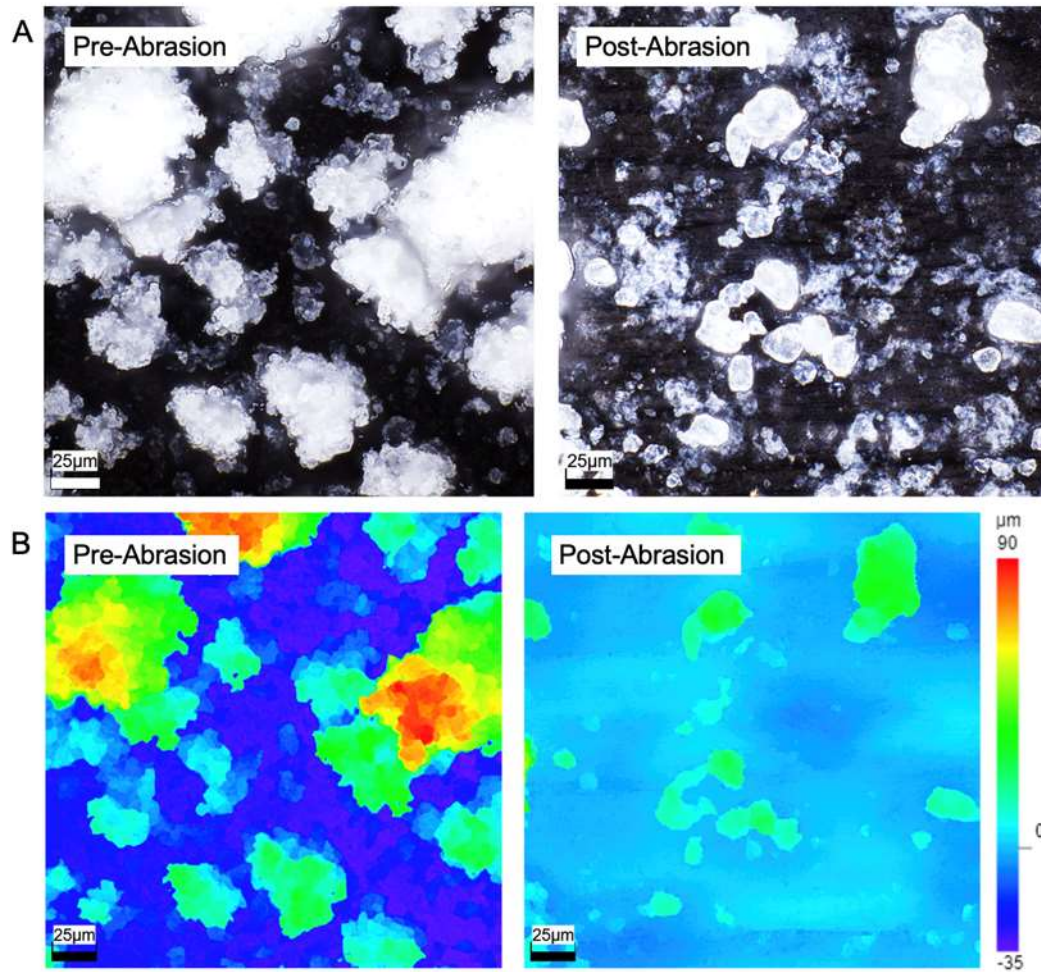


Figure 26: Confocal micrographs of damaged textured surfaces

A) Color confocal images of the Textured surface captured before and after 75 cycles of Taber abrasion. Abrasion causes significant breakup of surface agglomerates and some substrate scratching. **B)** The images from A depicted as height profiles, demonstrating the greatly reduced roughness of the Textured surface following abrasion.

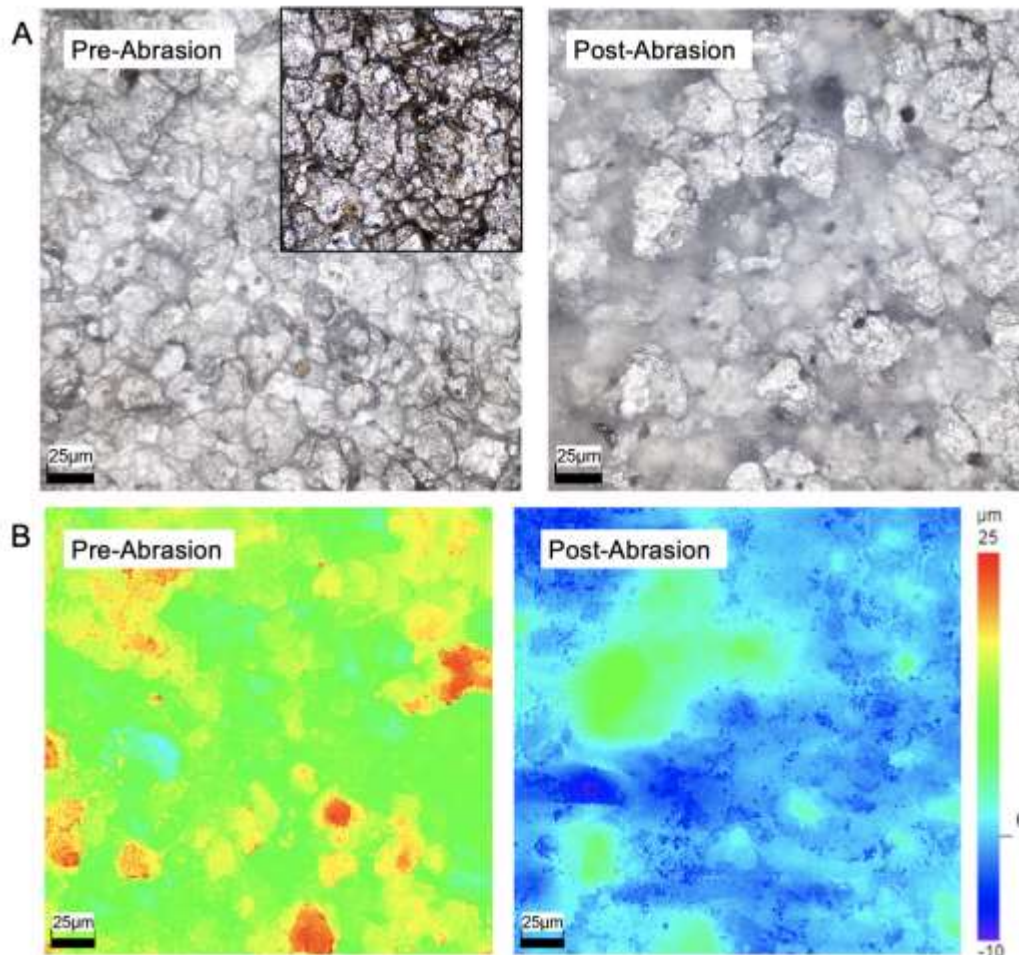


Figure 27: Confocal micrographs of damaged lubricant infused surfaces

A) Color confocal images of the Lubricated surface captured before and after 75 cycles of Taber abrasion. Abrasion causes significant damage to the surface microtexture. The inset in the Pre-Abrasion image depicts the surface prior to the addition of lubricant. **B)** The images from A depicted as height profiles, demonstrating the reduced roughness of the Lubricated surface following abrasion.

2.3 Conclusion

In summary, we have demonstrated an extremely simple and rapid approach to graft a layer of liquid-like PDMS chains to silicon and glass by exposure to a vapor of a volatile, bi-functional, chlorine-terminated siloxane precursor at room temperature. The resulting, exceptionally durable films readily repel a broad range of liquids with varying surface tension and polarity, including fluorinated solvents. The surfaces simultaneously demonstrate low adhesion to various solids, including ice, wax, plaster, and super glue, as well as exceptional anti-scaling performance. Our systematic investigation into the

properties and behaviors of these coatings establishes the utility of the highly-mobile interface enabled by a liquid-like, linear chain morphology. Such coatings, capable of resisting damage and broadly reducing both liquid and solid fouling, may find utility in protecting a wide range of surfaces found in architecture, marine, transportation, biomedical, microfluidic, and photolithography applications.

2.4 Materials & Methods

2.4.1 b-PDMS and cb-PDMS Synthesis

All reactions were performed at room temperature and pressure on silicon chips (University Wafer test grade, 500 μm thickness, 1.5 nm native oxide layer, <100> orientation) of either $\sim 1\text{ cm}^2$ or $\sim 8\text{ cm}^2$ area (larger chips were used for abrasion, scaling and solid adhesion test samples), pre-rinsed with toluene, 2-propanol, and water. All exposures to the precursor occurred in a 47 mm diameter closed polystyrene petri dish along with 50 μL of the bi-functional, chlorine-terminated PDMS (1,3-dichlorotetramethyldisiloxane, Gelest). After silanization, the pieces were rinsed with toluene, 2-propanol (Fisher Scientific), and deionized water, then dried with compressed air. Note that we found plasma cleaning did not improve b-PDMS silanization, and thus it was not done for any of the reported PDMS surfaces. Low relative humidity (< 25%) during silanization was found to be necessary to consistently produce the contact angles reported in Table 1. To fabricate capped (cb-PDMS) surfaces, b-PDMS treated wafer chips were placed in a closed container with 200 μL of trimethylchlorosilane (Gelest) for 1 hour. Each sample was then washed with toluene and 2-propanol.

2.4.2 Glass Silanization

Glass also has a silanol-rich surface which is highly reactive to the silanes used in this work. However, it was found that typical borosilicate glass required prior activation with oxygen

plasma (30W, 30 min) and extended exposure times to the 1,3- dichlorotetramethyldisiloxane and trimethylchlorosilane (1 h and 3 h, respectively) to yield low $\Delta\theta$ approaching that on silicon. This modified process yielded dynamic water contact angles on 3" x 3" borosilicate glass substrates (McMaster-Carr) of 106°/101° for b-PDMS and 108°/102° for cb-PDMS. The cb-PDMS coating is transparent on glass (Figure 28). Optical transparency was characterized using a UV-Vis Spectrophotometer (Varian Cary® 50) with a wavelength range from 200 nm to 800 nm. It is also worth noting here that while hydrochloric acid, which can cause the corrosion of common metals, is generated by the b-PDMS and cb-PDMS functionalization processes, metals such as aluminum can be functionalized with chlorosilane following the deposition of a protective silica layer ²³¹.

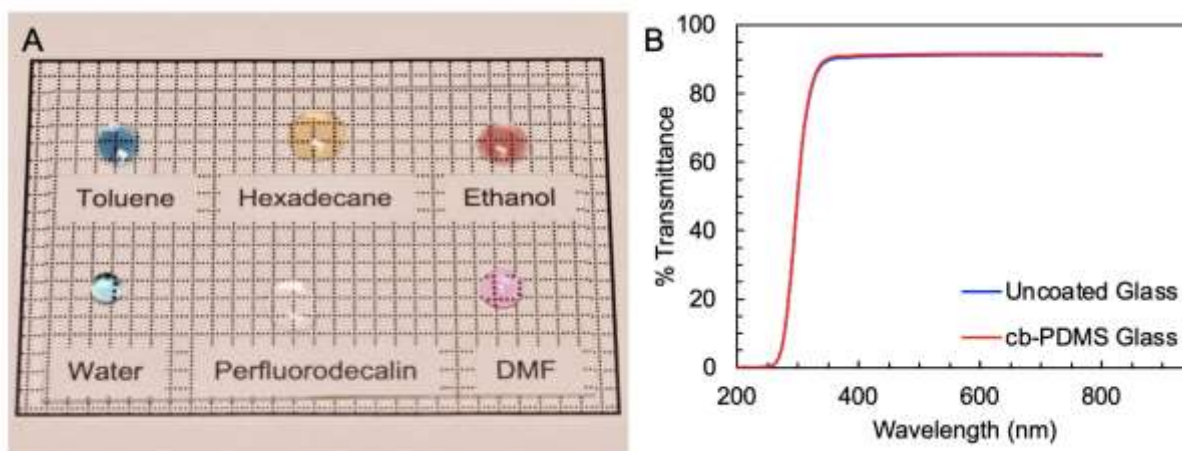


Figure 28: PDMS Silanized Glass

A) photograph of 20 μ L droplets of liquids with broadly varying surface tensions and chemistries placed on a transparent, cb-PDMS-treated glass slide. The inset shows the chemical structure of the bidentate 1,3-dichlorotetramethyldisiloxane. B) UV/Vis spectra of an untreated glass slide and a slide with the cb-PDMS coating

2.4.3 Control Surfaces

Methylated silane surfaces were prepared using precursors with mono-dentate (trimethylchlorosilane, Gelest) or tri-dentate (methylchlorosilane, Gelest) chlorine functionality on silicon chips pre-rinsed with toluene, 2-propanol, and water. Samples functionalized with the mono-dentate precursor were placed in a closed container with 200 μL of trimethylchlorosilane for 1 hour. Samples functionalized with the tri-dentate precursor were placed in a 47 mm diameter closed polystyrene petri dish along with 50 μL of methyltrichlorosilane for three consecutive, five-minute exposures, with a 2-propanol rinse between each exposure. After functionalization, all samples were rinsed in toluene, 2-propanol, and deionized water, then dried with compressed air.

To prepare methylated crystalline surfaces, whole or segmented silicon wafers were rinsed with water, ethanol, and acetone, then dried with compressed air. The silicon wafers were plasma treated within a 30 W Harrick Plasma PDC-001 chamber at a pressure of 250 mTorr, for 30 minutes. The plasma treated substrates and 150 μL of n-decyldimethylchlorosilane (Gelest) were then placed inside a Bel-Art™ Space Saver Vacuum Desiccator and cyclically pumped down and purged with nitrogen (15 times). The vacuumed desiccator and contents were then placed inside an 80 °C oven for 48 hours. The silanized silicon samples were then washed with toluene, ethanol, and acetone.

To prepare fluorinated crystalline surfaces, silicon wafers were plasma treated within a 30 W Harrick Plasma PDC-001 chamber at a pressure of 250 mTorr, for 15 minutes. The plasma-cleaned wafer was then exposed for two 24 h periods to a vapor of perfluorodecyldimethylchlorosilane (Gelest) at 100 °C at <5 mmHg in a vacuum oven. The silanized silicon samples were then washed with 2-propanol, Vertrel XF, and deionized water, then dried with compressed air. The thickness of the F-17 silane surface is 0.8 ± 0.1 nm. Note that this mono-

functional silane was selected to minimize self-polymerization and roughness, yielding films with optimal contact angles with low contact angle hysteresis approaching that of the b-PDMS. While the more commonly used perfluorodecyltrichlorosilane precursor will react faster, within a few hours, it is prone to yielding rougher films with typical water $\Delta\theta > 15^\circ$.

Superomniphobic and lubricated control surfaces were prepared abrasion testing. The textured superomniphobic surface was produced by spraying a fluorinated polyurethane (Luxecolor 4FVBA, Helicity Technologies) + 50 wt.% fluorodecyl polyhedral oligomeric silsesquioxane (F-POSS), 50 mg/mL in pure Vertrel XF with an airbrush (Paasche VLS) onto a microscope slide, similar to previously described methods.²²⁴ The coating was held at room temperature for 12 h to allow the solvent to evaporate completely, then cured for 2 days at 80 °C. The lubricated surface was produced as follows. First, an aluminum substrate (6061 T6 alloy, McMaster-Carr) was etched in 2.5 M hydrochloric acid (Fisher Scientific) for 20 min, agitated in a bath sonicator for 10 minutes to remove aluminum particles, and was then placed in boiling water for 20 min to convert the outer layer to boehmite (γ -AlO(OH)) nano-crystals. This textured substrate was then reacted with a vapor of (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxy silane (Gelest) in a vacuum oven at ~5 mTorr and 80 °C for 24 h. Krytox GPL-100 perfluoropolyether oil (acquired from Miller-Stephenson Chemical Company) was then drop cast onto these now superhydrophobic substrates to produce a lubricated surface. Excess oil was removed by holding the samples vertically overnight.

2.4.4 Surface Characterization

Advancing and receding contact angle measurements were performed with the sessile drop method using a Ramé-Hart 200 F1 contact angle goniometer. A ~10 μ L water droplet suspended from a 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 fit in the DROImage Advanced software was used to obtain contact angle data. At least three points on the substrate were measured for each reported mean value. The standard error was $\pm 2^\circ$. Probe liquids were used as received, and included: acetone, 1-propanol, 2-propanol, ethanol, toluene, hexadecane, dodecane, decane, octane, heptane, hexane, cyclohexane, and pentane (Fisher Scientific), diiodomethane, dimethylformamide, and methoxyperfluorobutane (Sigma Aldrich), hexafluorobenzene (SynQuest), Krytox GPL 100 and GPL 103 perfluoropolyethers, Vertrel XF dihydrodecafluoropentane (Chemours), pentafluorobutane (Alfa Aesar), *o*-fluorotoluene, perfluorodecalin, and 4-chlorobenzotrifluoride (Acros Organics).

2.4.5 Surface Energy

Surface energy values were calculated via the Owens-Wendt method²⁵¹ with de-ionized water and hexadecane as the probe liquids. 2.5 μ L of each liquid was dispensed onto the surface and the static contact angle was measured with a Ramé–Hart 200 F1 goniometer.

2.4.6 AFM

Tapping-mode atomic force microscopy was conducted in air with a Veeco Innova AFM. Veeco RTESP-300 tips were used for imaging and a scan rate of 0.500 Hz was set for each sample.

2.4.7 Ellipsometry

Variable-angle spectroscopic ellipsometry (J. Woollam Co. M-2000) was performed in reflection mode using incidence angles of 55° through 75° in 5° increments to measure grafted PDMS and F-17 thickness. The data was fit using the CompleteEASE software program, with the optical constants of silicon and native oxide taken from within the program, and the optical constants of the test surfaces determined using an experimental fit.

2.4.8 Solid Adhesion Tests

The adhesion of solids was determined using a lab-built shear force testing apparatus as previously described.¹³⁸ For each test, a 1 cm³ poly(methyl methacrylate) cuvette, open at the top and bottom was placed on the surface to be tested and filled with an adherent: ice, paraffin wax (PW, Sigma Aldrich), cyanoacrylate adhesive (CA, 3M SF-100), calcined gypsum (CG, Sheetrock Easy Sand 5), or polydimethylsiloxane elastomer (PDMS, Dow Corning Sylgard 184). At least four measurements were performed for each material. In the case of ice, the surface was mounted to a Peltier plate held at -10 °C and deionized water was poured into the cuvette and allowed to freeze to the surface. Our ice adhesion setup is exposed to ambient air where frost formation can occur, but the application of liquid water to the surface melts any frost within the cuvette boundary, allowing complete ice-surface contact. PW was melted at 150 °C on a hot plate, transferred to the cuvette on the substrate held at 50 °C, and then slowly cooled to room temperature. As CA only fully cures in thin layers, one face of a 1 cm³ plastic cube was coated with the adhesive and placed onto the sample surface and allowed to cure at room temperature. CG was prepared by mixing gypsum powder at 1 g/mL in deionized water for five minutes, pouring into the cuvette, and leaving overnight at room temperature, then heating at 50 °C for 3 h to fully harden. PDMS was prepared by mixing the base and crosslinker 10:1 by weight as recommended and pouring into a cuvette on the surface on a 120 °C hot plate and curing for one hour. For each cuvette filled with each of the five materials, the tip of a force gauge mounted to a linear motion stage was brought into contact with one side of the cuvette ~1 mm above the base. A controlled shear rate (74 µm/s) was applied to the cuvette until it detached from the substrate, and the peak force was recorded. The shear rate was later varied from 4 µm/s to 2 mm/s during additional ice adhesion tests evaluating the shear-

thinning behavior of b-PDMS, cb-PDMS, and a methylated crystalline surface (n-decyldimethylchlorosilane functionalized).

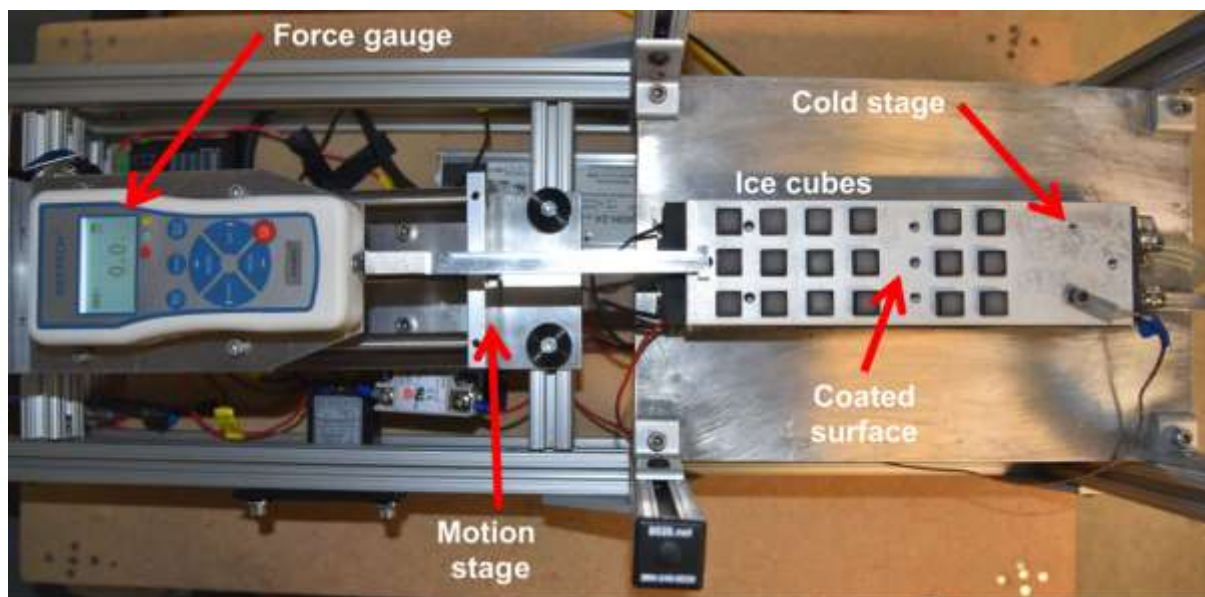


Figure 29: Ice & solid fouling testing apparatus.

A force gauge is mounted to a linear motion stage. Square molds of dimensions 1 cm x 1 cm x 0.6 cm (LxWxH) are filled with the solid adherent in liquid form, and then solidified. The force gauge then impacts the solid along the interfacial plane. Here ice on the cold stage is demonstrated, but the other solids were tested using the same apparatus only at 20 °C as opposed to -10 °C. More details can be found elsewhere [26, 36].

2.4.9 Scaling Tests

Scaling tests were carried out using a method adapted closely from Zhao *et al.*¹⁹⁶ To make the scaling solution, 1.26 g of Calcium Sulphate Dihydrate (Acros Organics) was added to 1000 mL of DI water (0.1g CaSO₄/100mL) in a wide glass beaker and mixed at room temperature with a PTFE stir bar at 400 rpm for 1 hour, until fully dissolved. Bare silicon wafer chips, as well as chips functionalized with b-PDMS, cb-PDMS, trimethylchlorosilane, and F-17 were submerged in this solution at a 70° angle from the horizontal position. The samples were ~8 cm² in size, supported by wedges of acrylic, and secured by double sided tape. The tape fully covered the back side of each sample to limit scaling only to the front. Once the samples were submerged, the beaker was placed on a hot plate held at 80°C until all the DI water evaporated. Samples were weighed before

and after testing on a balance with a resolution of .0001 g (Mettler Toledo ML-104). To account for any differences in the size of each sample, scale accumulation is represented as percentage mass gain.

2.4.10 Durability Tests

Boiling tests with both water and hexadecane were carried out by suspending samples for one hour in a beaker of the boiling liquid on a hotplate. Thermal durability in air was evaluated by placing samples directly on a clean hotplate surface held at 250°C or 350°C and covered with an overturned glass petri dish for twenty-four hours or one hour respectively. UV durability was evaluated by placing samples at a distance of 14 cm from two, 19.8W, 254 nm bulbs (Ushio G40T10) for eight hours. Mechanical abrasion was performed using a Linear Taber Abrasion machine with a CS-5 resilient felt abrader and a 250 g load (~20kPa). For abrasion, samples were clamped down and abraded for up to 5000 cycles at 60 cycles/min and a stroke length of 2". All durability tests were carried out for a minimum of three samples each.

Chapter 3 - Polysiloxane-based Liquid-Like Layers for Resistance of Polymer and Wax Deposition

This chapter details the work I carried out based off of the discoveries of the previous chapter. The work was done with the collaboration of Professor Zhan Chen's group, whom performed SFG experimentation and analysis. This work investigates the small-scale antifouling properties of the tethered liquid-like layers and is currently being submitted to *Langmuir*.

3.1 Introduction

Fouling is a process where undesired matter accumulates on a solid surface, causing a decline in performance, or even damage. Some examples include the fouling of gas-oil pipelines²⁵², medical devices and implants²⁵³, heat exchangers²⁵⁴, marine infrastructure and ship hulls⁹⁴, and ice on aircraft²⁵⁵. Fouling species can be readily segregated with respect to their length-scale, modulus, and chemical nature²⁵⁶. For example, ice, barnacles, and inorganic scale are examples of foulants that are both large, and relatively hard, while species such as bacteria and proteins are significantly smaller and softer. These differences have led to a range of diverse design strategies for fouling prevention, and/or fouling removal²⁵⁶. For large, high modulus foulants such as ice and barnacles that elastically deform surfaces when under stress, lowering the bulk elastic modulus and decreasing the surface interfacial free energy is often beneficial for facile foulant release²⁵⁷,²⁵⁸. In addition, lowering the interfacial free energy between the foulant and surface is often employed to lower the work of adhesion given as $W_a = \gamma_{s_1v} + \gamma_{s_2v} - \gamma_{s_1s_2}$ ²⁵⁹. Here γ_{s_1v} and

$\gamma_{s_1s_2}$ are the interfacial free energy of the foulant and the energy of the adhered interface respectively ²⁵⁹. Surface energy can be minimized by utilizing fluorinated materials to as low as 0.0067 J m^{-2} ²⁶⁰. However, the surface design strategies significantly differ with small-scale and/or soft organic foulants such as bacteria, algae, wax, and proteins. These fouling species delineate in their behavior when compared to larger adherents, and often require unique surface topography ²⁶¹⁻²⁶³, or high surface energy, hydration layer forming polymer brushes to prevent their accretion ^{169, 183, 264}.

Small-scale organic fouling within nonpolar solvent systems have been relatively less studied despite their economic impact. In the petrochemical industry organic wax fouling occurs within crude oil pipelines and heat exchangers, causing blockages and severe decreases in heat transfer efficiencies. Wax blockages can lead to extremely costly facility shutdowns and remediation for pipelines under 400 meters of water can reach \$1 million/mile ²⁶⁵. Even lesser studied is organic polymer fouling. Polymer fouling is problematic for a wide range of industrial application such as: reaction vessels ²⁶⁶⁻²⁶⁸, microfluidic devices ²⁶⁹, jet fuel injectors ^{270, 271}, heat exchangers ²⁷², and fuel tanks ²⁷³. To date, there are few reports focused on the design of surfaces to prevent polymer adsorption. Recently Wang *et al*, analyzed fluorine terminated (F1) monolayers for their ability to prevent polymer accretion ²⁷⁴. The F1 monolayer was compared against multiple alkyne layers containing either no fluorine, three fluorine atoms, or seventeen fluorine atoms by conducting fouling tests within solutions of polystyrene, polyvinyl acetate, poly(4-chloro styrene), Poly(N -isopropyl acrylamide), polyethylene glycol, polyacrylic acid, poly(adipic anhydride), and poly(hydroxyl propyl methacrylate) in DMF. In a later report, it was found that more hydrophobic solvents such as toluene reduced the antifouling efficacy of F1 layers, and that ATRP grown fluoropolymer brushes yielded better polymer fouling resistance. Wang and Zuilhof generated

thick (75nm) heavily fluorinated branched brush layers via ATRP in order to minimize the enthalpy of adsorption between brush and polymer, and found that the polymer glass transition temperature (T_g) played an important role in preventing adsorption²⁷⁵. They concluded that higher T_g decreased polymer adsorption, but did not study extremely low T_g brushes.

Tethered liquid-like layers have recently been investigated for their liquid and solid repellent properties^{46, 208, 226, 276-281}. Liquid-like layers are grafted, linear polymers that exist in the liquid state at temperatures far above their T_g . These surfaces have mostly been investigated as low hysteresis, omniphobic surfaces. Omniphobic surfaces possess the ability to reduce adhesion of a broad range of liquids of varying surface tension. A surface's non-wetting ability is typically manifested by its apparent contact angle (θ), and contact angle hysteresis ($\Delta\theta$) – the difference between the advancing and receding contact angle. High θ and low $\Delta\theta$ are desirable for omniphobic surfaces. Due to their low T_g of ~ -125 °C, one of the most prominent examples of omniphobic grafted liquid-like layers are those consisting of linear polydimethyl siloxane layers (PDMS)^{194, 208, 230, 231, 238, 277, 279, 282-286}. These liquid-like PDMS chains are highly mobile at room temperature and offer minimal resistance to mobile droplets. However, the solid antifouling properties of such surfaces have only minimally been studied^{194, 208, 277, 279, 282}. The study of PDMS liquid-like layers' ability to prevent small, soft polymer adsorption has yet to be investigated.

In this report we investigate the potential of tethered liquid-like layers to inhibit the adsorption of polymer and wax compounds in solution. Silicon, and silicon grafted with linear was Heptadecafluoro tetrahydrodecyl dimethyl monochlorosilane (F-17), n-decyldimethylchlorosilane (C-12), 1,3-Bis(chlorodimethylsilyl)propane (t-BCSE), and 1,3-Dichloro-1,1,3,3-tetramethyldisiloxane (t-PDMS) (see Figure 30) were chosen to compare the effects of surface energy, thickness, and silane mobility. As demonstrated previously, grafted linear PDMS chains

have significant interfacial mobility^{226, 281}. This chain mobility yields low $\Delta\theta$ ($\Delta\theta < 3$) (Table 2) for a range of high and low surface tension liquids, as well as an ease of solid fouling removal^{46, 226, 278, 281}. t-BCSE was additionally investigated as a theoretically less mobile species containing Si-O within the backbone (Figure 30). The ethylene spacer is intended to decrease the chain mobility due to the presence of ethylene groups alternated with silicon-oxide bonds along the main chain. t-BCSE has not to our knowledge been previously implemented as a linear grafted surface. Assessing the fouling properties of t-PDMS and t-BCSE will help in understanding the extent to which grafted chain mobility plays a role in the polymer fouling process. Alternatively, C-12 is investigated as a control layer with comparable surface energy (Table 2), but a more rigid chemical structure as the chains can crystalize on the surface at room temperature. To investigate the potential effects of adhesive work, a very low surface energy F-17 silane is also included in the study. In addition, unmodified bare silicon is included as a control.

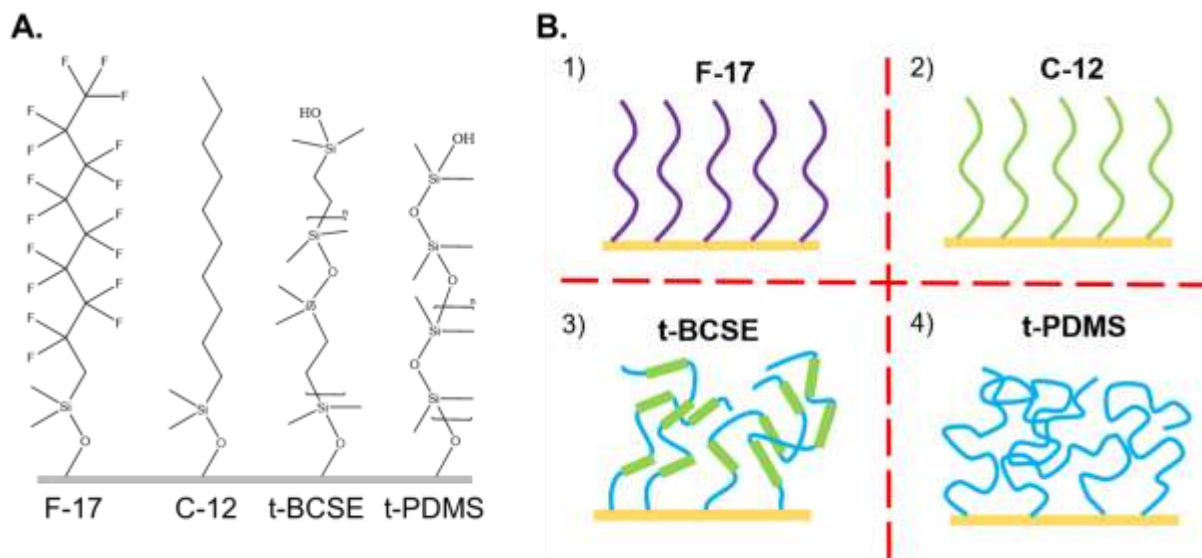


Figure 30: Resultant surface chemistries after silane exposure and their structure.

A) (Left to Right) Fluorinated silane (F-17), alkyl silane (C-12), t-BCSE, and t-PDMS. B) Structures of each modified surface. F-17 and C-12 yield more orderly, rigid structures, t-BCSE is semi liquid-like with rigid (green) segments, and t-PDMS is fully liquid-like.

Table 2. Surface energy, water contact angle and DMF contact angle of silicon, and silicon grafted with C12, F17, t-BCSE, and t-PDMS

Surface	Surface Energy (mN/m)	Water Contact angle ($\theta_{Adv}/\theta_{Rec}$)	DMF Contact angle ($\theta_{Adv}/\theta_{Rec}$)
PFPE	13.58	120°/111°	86°/75°
F-17	14.47	120°/105°	80°/70°
C-12	23.74	109°/90°	47°/35°
t-PDMS	23.31	103°/100°	65°/60°
t-BCSE	26.82	104°/97°	66°/56°
Silicon	46.43	-	-

3.2 Results and Discussion

3.2.1 Surface Characterization

Atomic force microscopy (AFM), ellipsometry, and contact angle measurements were utilized to characterize each surface. The RMS roughness was measured and averaged by obtaining three spatially distanced (at least 50 micrometers apart) AFM scans of each surface to capture inter-sample uniformity. Figure 32A yields the average roughness values for silicon, and the silanized silicon samples. Compared to bare silicon, the addition of C-12 and F-17 only marginally increased the roughness (0.051nm, 0.17nm, and 0.17nm respectively), indicating the formation of uniform monolayers. t-PDMS yielded a comparably low RMS roughness of 0.07nm. This smoothness may be a result of the highly mobile chains conforming to the probed surface. t-BCSE exhibited a slightly higher roughness of 0.29nm when compared to the other silanes. As with the

roughness measurements, Figure 32B shows similar thickness between C-12 and F-17 monolayers with values of 0.79nm and 0.78nm respectively. These values are reasonable for the silane molecular length of the monofunctional ‘grafted-to’ silanes. t-PDMS and t-BCSE are considered ‘grafted-from’ polymer layers which grow via a step-growth polycondensation reaction in the presence of water vapor, and therefore yielded comparatively thicker layers thicknesses of 2.63nm and 2.19nm respectively. Table 2 reports the surface energies for the different coatings considered in this work and the surface energies decreases in order of: t-BCSE, C-12, t-PDMS, F-17, and PFPE. The contact angle data yields high adv/rec of 120°/111° and 120°/105° for low surface energy fluorinated PFPE and F-17 layers respectively, and 109°/90° for the C-12 layers. t-PDMS and t-BCSE demonstrate contact angles of 103°/100° and 104°/97°, but with comparatively low $\Delta\theta$. t-PDMS yields low $\Delta\theta$ as a result of the dense, highly mobile silicone chains²²⁶. The slight increase of $\Delta\theta$ for t-BCSE indicates a reduced mobility of t-BCSE chains (compared to t-PDMS) as a result of the repeating ethylene – silicone bonds (reduced density of flexible Si-O-Si bonds). We see a similar reduction in $\Delta\theta$ for PFPE compared to F-17 due to the presence of flexible C-O-C bonds and a low glass transition temperature of $\sim -100^{\circ}\text{C}$ ^{287, 288}. Similar observations can be made when DMF is utilized as the contacting fluid on these surfaces. Note that the observed contact angles with DMF are typically lower than with water due to the lower surface tension of DMF ($\gamma_{lv} = 35.8 \text{ mN/m}$)²⁸⁹.

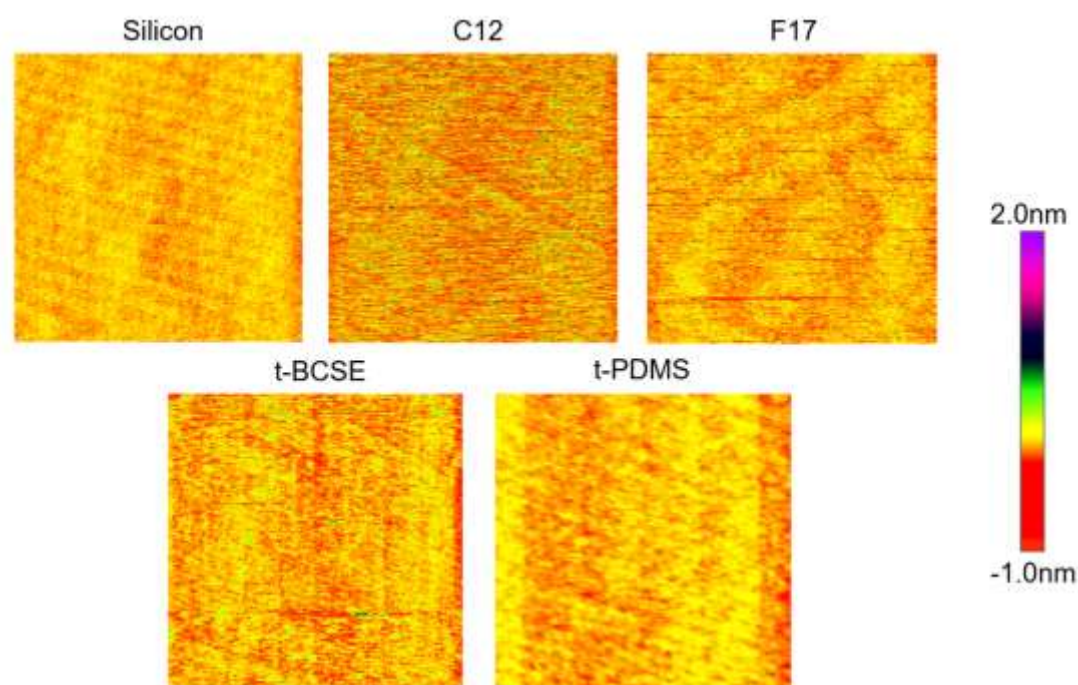


Figure 31: AFM micrographs of bare silicon and functionalized silicon.

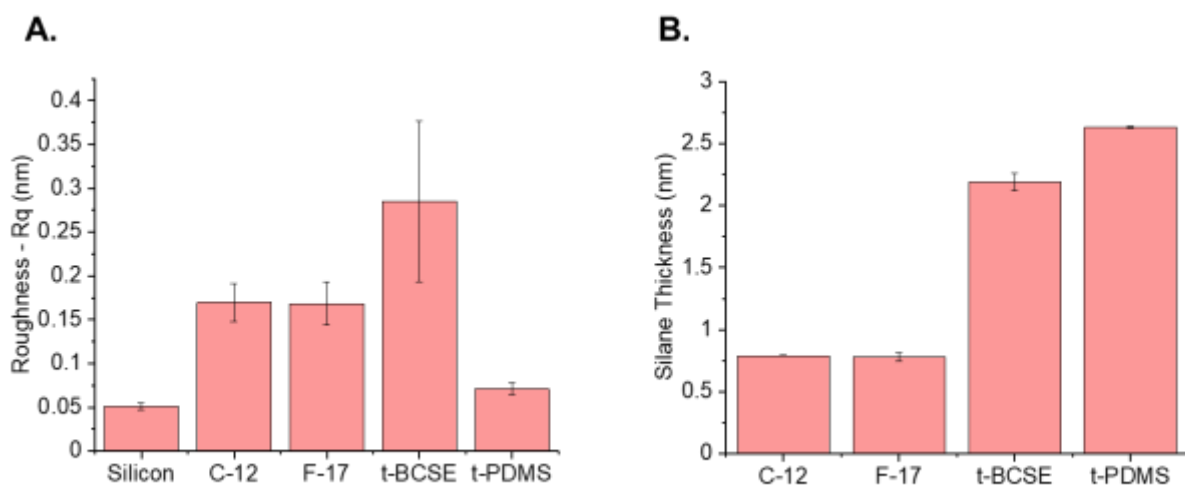


Figure 32. Roughness and thickness of silanized samples.

A) Root mean square roughness for the different surfaces in this work (measured via AFM). B) Thickness of silanized surfaces measured with ellipsometry.

3.2.2 Fouling Quantification via AFM and Contact Angle

AFM scans were collected to measure the surface roughness changes after polymer fouling in a similar fashion as Wang *et al*^{274, 275, 290}. Figure 33 shows the change in surface roughness after silicon and silanized silicon substrates were fouled by different polymer solutions in DMF and water. In our work, DMF-soluble polymers included: poly(ethylene glycol), Poly(4-vinylphenol), Poly(vinyl chloride), Polymethyl methacrylate, Polystyrene, and Polyvinylpyrrolidone. Water soluble polymers included polyethylene glycol (also used for polymer-DMF fouling). For all tested polymer solutions, t-PDMS and t-BCSE typically showed much smaller increases in roughness/fouling when compared to silicon, C-12, and F-17. Figure 34 displays the AFM micrographs for the different fouled substrates surfaces. Similar to the RMS roughness data, the micrographs qualitatively show the degree of fouling on each surface where silicon, C-12, and F-17 tend to foul to greater degrees than t-BCSE and t-PDMS, with t-PDMS yielding the least amount of visual fouling.

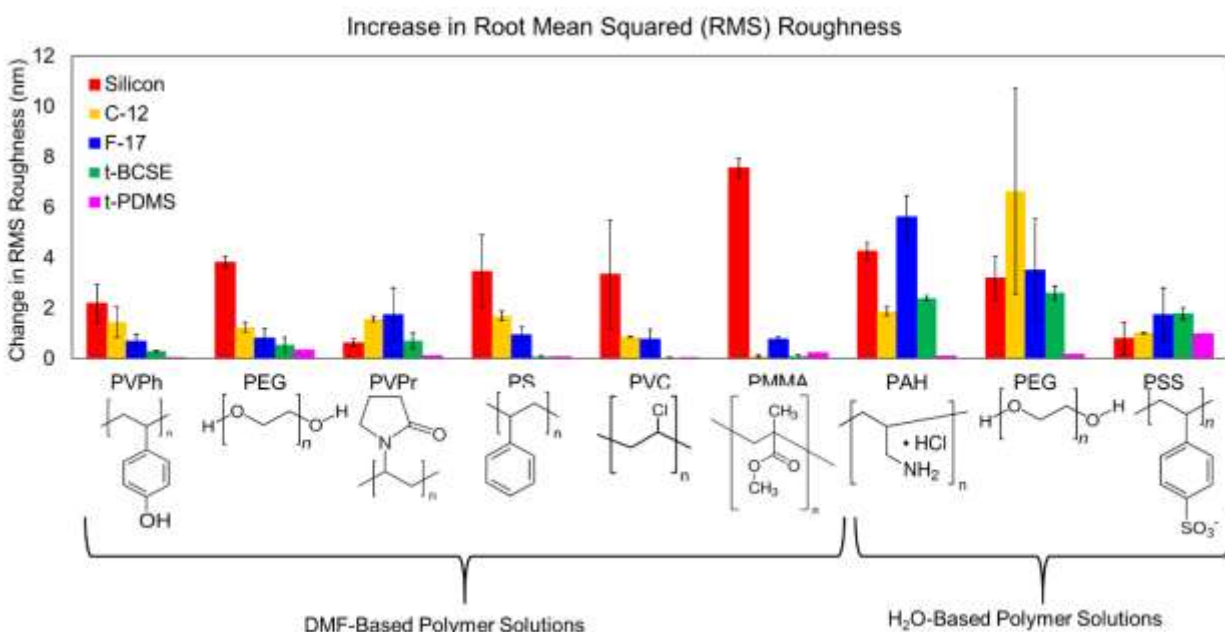


Figure 33. A) Change in root mean square (RMS) surface roughness after polymer fouling.

Surface roughness was measured via AFM.

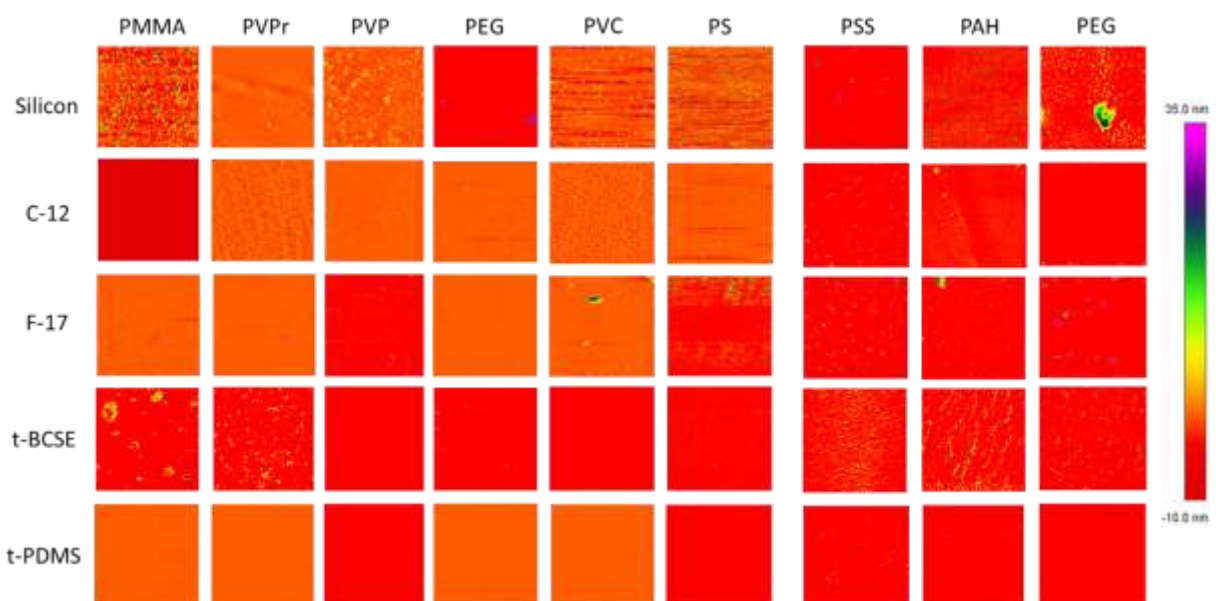


Figure 34. AFM micrograph array of fouled silicon and functionalized silicon samples

A) AFM micrograph array of DMF/polymer fouled substrates (left 6 rows) and of H₂O/polymer fouled substrates (right 3 rows). Each micrograph is a 10x10 μm box.

The change in the receding water contact angle was utilized as a secondary method to quantify the fouling behavior of various polymer solutions. The change in receding contact angle is a simple yet powerful method of analysis that captures the effects of fouling on a much larger scale than the 10 μ m x10 μ m box size of AFM. With this technique, we typically observed large changes in receding contact angle as the fouling on a given surface increased ²⁹¹. Figure 35 displays the changes in receding contact angle for the different coated surfaces post-fouling. The receding contact angle findings generally overlap with the AFM data shown in Figure 33. For the DMF/polymer solutions, the change in receding angles overlapped well with the RMS roughness data, with the t-PDMS and t-BCSE regularly outperforming, the C-12, F-17 and silicon surfaces. Similarly for the different polymer systems, the change in receding angles for silicon, C-12, F-17, and t-BCSE were relatively high, while changes in t-PDMS receding angle remained low for all different polymer-solvent combinations tested. This data again highlights the ability of linear liquid-like layers to reduce polymer fouling.

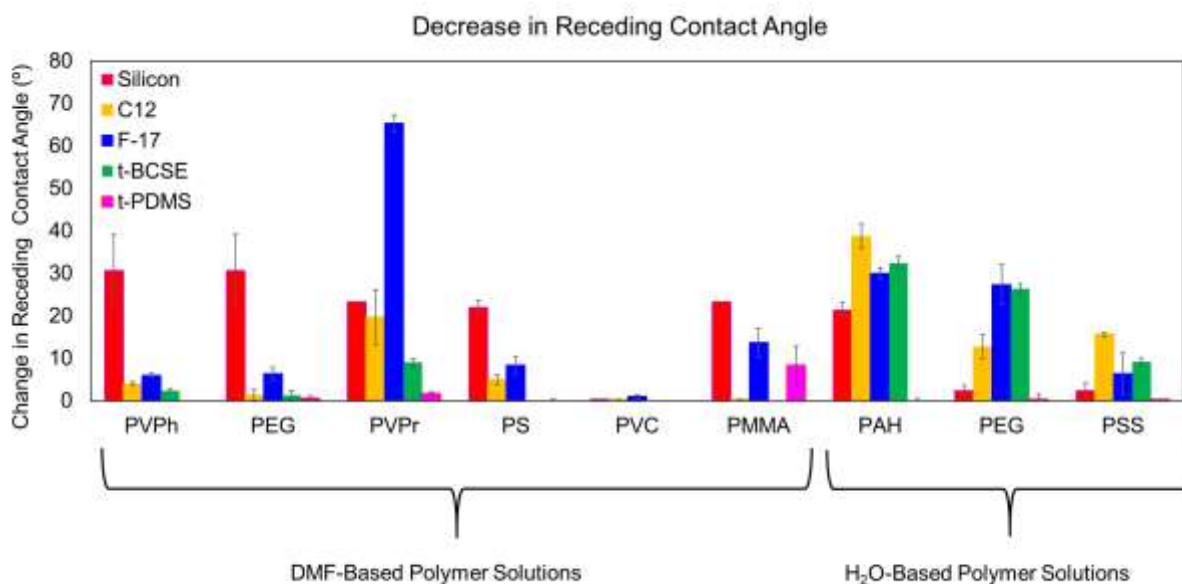


Figure 35. Change in dynamic receding water contact angle after polymer fouling.

Between water-polymer and DMF-polymer fouling data sets, it is clear that a reduction in surface energy does not directly correlate with reduced fouling. C-12, t-BCSE, and t-PDMS have relatively similar surface energies (see Table 2), and yet displayed very different fouling behavior. This disparity can be related to the molecular structure and mobility of the different grafted polymers. The chain mobility for these molecules increases in order of C-12 < t-BCSE < t-PDMS and correspondingly polymer fouling resistance also tends to increase with increasing chain mobility.

Table 3. Static water, DMF, and Toluene contact angle of a 2.5 μ L droplet selected surfaces.

Surface	Water Contact	DMF	Toluene
	Angle	Contact Angle	Contact Angle
Silicon	48.1°	<5°	<5°
C12	98.4°	53.7°	21.8°
F17	108.7°	72.9°	60.7°
PFPE	114.6 °	82.5°	67.2 °
t-BCSE	103.1°	64.6°	20.1°
t-PDMS	103.0°	61.7°	28.8°

Solvent effects on the fouling process were further investigated by conducting similar experiments in toluene. Toluene, possesses a much lower surface tension (γ_{LV} =27.8 mN/m), than both DMF (γ_{LV} =35.8 mN/m) and water (γ_{LV} =72.8 mN/m) ²⁸⁹. Depending on the solvent, polymer behavior can vary significantly both in the free and tethered state ²⁹². Polystyrene fouling in toluene (100mg/ml) was conducted on each surface and compared with the polystyrene/DMF data. Commercially available perfluoro poly ether (PFPE) silane ($T_g \sim -100^\circ\text{C}$) was also included in the sample set in an attempt to leverage the low surface energy properties of fluorine groups and the flexibility of the polyether segments. As shown in Figure 36, the toluene/polystyrene solutions fouls each surface to a greater extent than for the DMF/polystyrene solutions of the same concentration. This phenomenon was also observed by Wang *et al* ²⁷⁴. Across both solvent systems, t-PDMS reduced fouling compared to all other tested monolayers. t-BCSE also succeeded in reducing fouling, but to a lesser extent than t-PDMS. To our surprise, the PFPE silanized surface did not resist fouling comparatively well as displayed by the RMS roughness and receding contact

angle changes. Despite retaining highly flexible polyether groups and low surface energy, the ‘grafting-to’ process for PFPE may have inhibited its functionality. Unlike t-BCSE and t-PDMS, the ‘grafted-to’ process for the bulky PFPE silane may yield low surface coverage when compared to the ‘grafted from’ surfaces ²⁹³. Low surface coverage, and subsequent exposure to a greater fraction of unreacted bare silicon may lead to increased fouling.

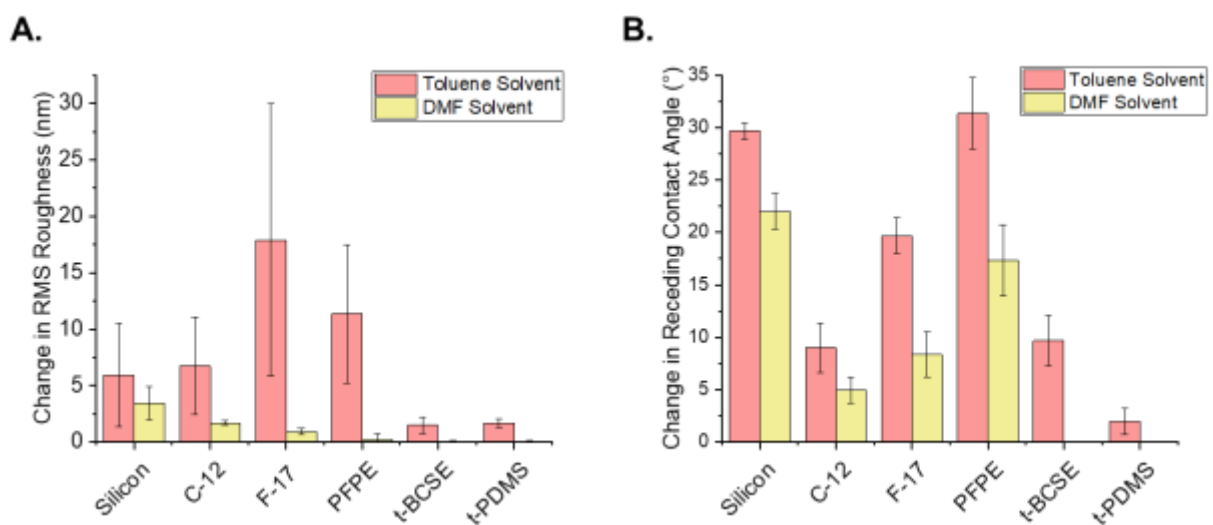


Figure 36: Comparison of fouling from Polystyrene/Toluene and Polystyrene/DMF solutions.

A) Change in RMS roughness after polystyrene fouling. B) Change in receding contact angle after polystyrene fouling. Error bars originate from post-fouled samples.

Paraffin wax fouling resistance was also investigated for the different coatings. Wax is a component of crude oil, and can adsorb to pipeline inner walls, causing costly blockages. 100mg/ml paraffin wax was dissolved in toluene and the same set of original substrates which included silicon, C-12, F-17, t-BCSE, and t-PDMS were probed for fouling resistance. Each substrate was submerged into the wax/toluene mixture for 15 hours and the fouling was evaluated

in the same manner as previously mentioned. Figure 37 yields the post wax fouling change in RMS roughness, receding contact angle, and AFM micrographs of the investigated surfaces. Much like the data previously described, there was minimal comparative relationship between the coating surface energy and fouling resistance. Fouling decreased as a function of chain flexibility with t-PDMS reducing the greatest degree of wax adsorption, followed by t-BCSE. The change in receding contact angle for the C-12 monolayer yielded somewhat inconsistent data compared to the AFM data were potentially related to the similarity between the wax and C-12 chains. Our measurements also showed a large change in receding contact angle for the surface with the lowest energy, F-17. The micrographs better illustrate the fouling of different coated of surfaces where t-PDMS is seen to be free of any notable fouling by the paraffin wax.

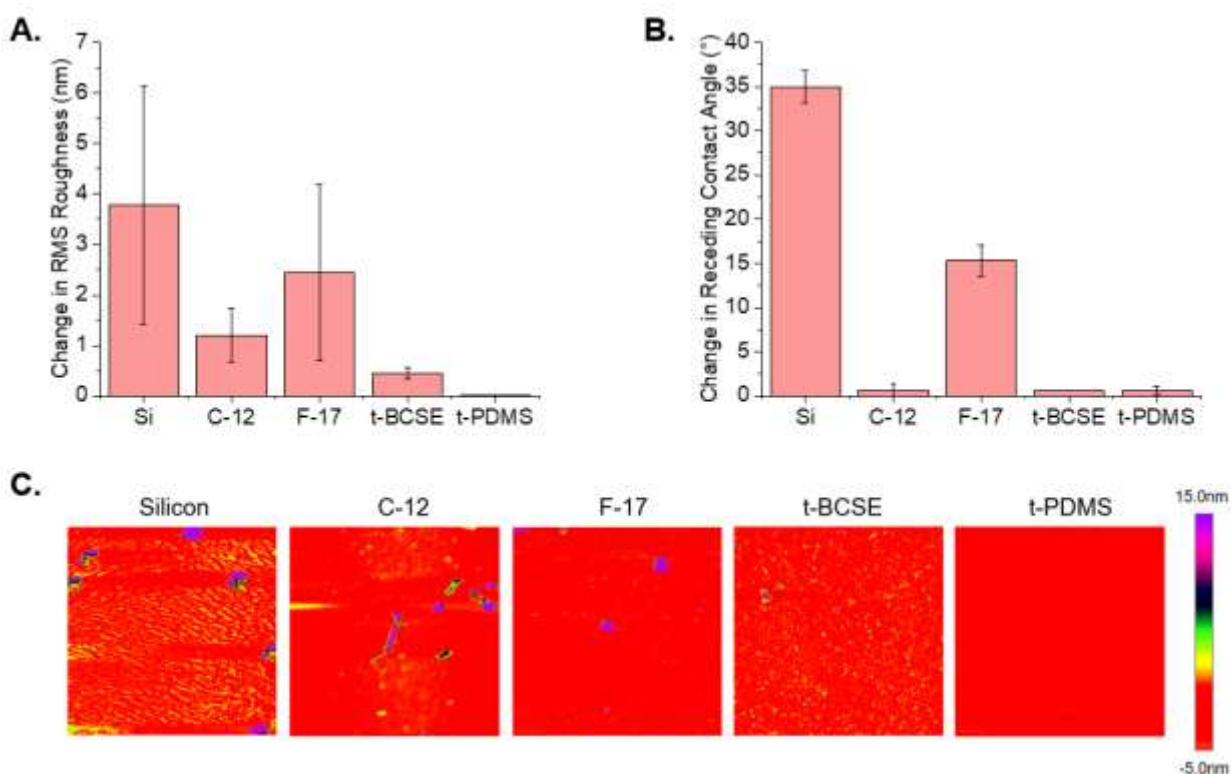


Figure 37. RMS roughness, change in receding contact angle and AFM micrographs of wax fouled surfaces

Wax fouled surfaces quantified by A) change in RMS roughness, and B) change in receding contact angle. Error bars represent standard deviation between post fouling data points C) AFM micrographs (10x10nm box size) of wax fouled surfaces.

3.2.3 Sum Frequency Generation Analysis of Highly Mobile Tethered PDMS

To gain molecular understandings of the different polymer fouling behaviors on different coatings, surface-sensitive sum frequency generation (SFG) vibrational spectroscopy was applied to investigate the interfacial structures of the coatings. SFG is a second-order nonlinear optical spectroscopy which can probe molecular structures of surfaces and interfaces with a sub-monolayer sensitivity²⁹⁴⁻³⁰⁶. SFG spectra were first collected from the interfaces between the investigated coatings and toluene (deuterated). Deuterated toluene was used here to avoid spectral confusion. All the SFG C-H stretching signals detected below were contributed from the surfaces, instead of toluene (which contains C-D bonds and does not have C-H bonds). Strong SFG signals at 2915 cm⁻¹ and 2960 cm⁻¹ were detected from t-PDMS/toluene and BCSE/toluene interfaces, corresponding to the symmetric and asymmetric stretching modes of the Si-CH₃ groups respectively (Figure 38A & B)³⁰⁷. Additionally, the symmetric C-H stretching mode of the methylene (Si-CH₂-) group (around 2870 cm⁻¹³⁰⁷) was also detected from the t-BCSE/toluene interface, indicating the presence of gauche defect in the (-Si-CH₂-CH₂-Si-) chain of t-BCSE. Interestingly, the SFG signal intensities of t-PDMS/toluene and BCSE/toluene interfaces are very similar, despite of the different structures of the two molecules. It is well known that silicone materials have very low glass transition temperatures, indicating that the silicone molecules/functional groups are very flexible. Here SFG spectra from both t-PDMS and t-BCSE in toluene are dominated by contributions from Si-CH₃ groups, showing that both surfaces are dominated by Si-CH₃ groups and thus both materials are flexible in toluene. Since both the t-PDMS and t-BCSE samples show very low water contact angle hysteresis (3° and 4° respectively), their surface coverages are believed to be very homogeneous. Therefore, the t-BCSE sample

should have lower surface Si-CH₃ group density in comparison to the t-PDMS sample since the two silicon atoms connecting the methyl groups in BCSE are farther apart compared to the ones in t-PDMS. SFG signal intensity is related to the surface functional group coverage and orientation distribution (or ordering). If the ordering is the same on t-PDMS and t-BCSE surfaces, SFG signal intensity from the t-PDMS surface should be much higher, which was not observed. This indicates that the methyl groups at the t-BCSE/toluene interface are more ordered than the ones at the t-PDMS/toluene interface. We believe that the relatively more disordered methyl groups at the t-PDMS/toluene interface are related to the stronger rotation mobility of the siloxane groups in t-PDMS or more flexible compared to that of the (Si-CH₂-) groups in t-BCSE³⁰⁸. The methyl groups at the PDMS/toluene interface therefore adopt more random orientations and are more flexible.

The SFG spectrum collected from the C-12/toluene interface contains contributions from many functional groups including the (-CH₂-) group, (Si-CH₃) group and (C-CH₃) group. The presence of the methylene group (C-CH₂-) C-H symmetrical stretching mode at 2850 cm⁻¹ demonstrates that the inversion symmetry in the (C-CH₂-) alkyl chain is broken, which is related to the gauche defects caused by the inhomogeneous coverage of the substrate³⁰⁹. This can be further corroborated by the large water contact angle hysteresis on the C-12 sample (19°). The Si-CH₃ group SFG signal collected from F-17/toluene interfaces (~2915 and 2955cm⁻¹) are much weaker compared to those collected from the other three interfaces, indicating that the Si-CH₃ groups near the substrate are either disordered or lying down at the interface.

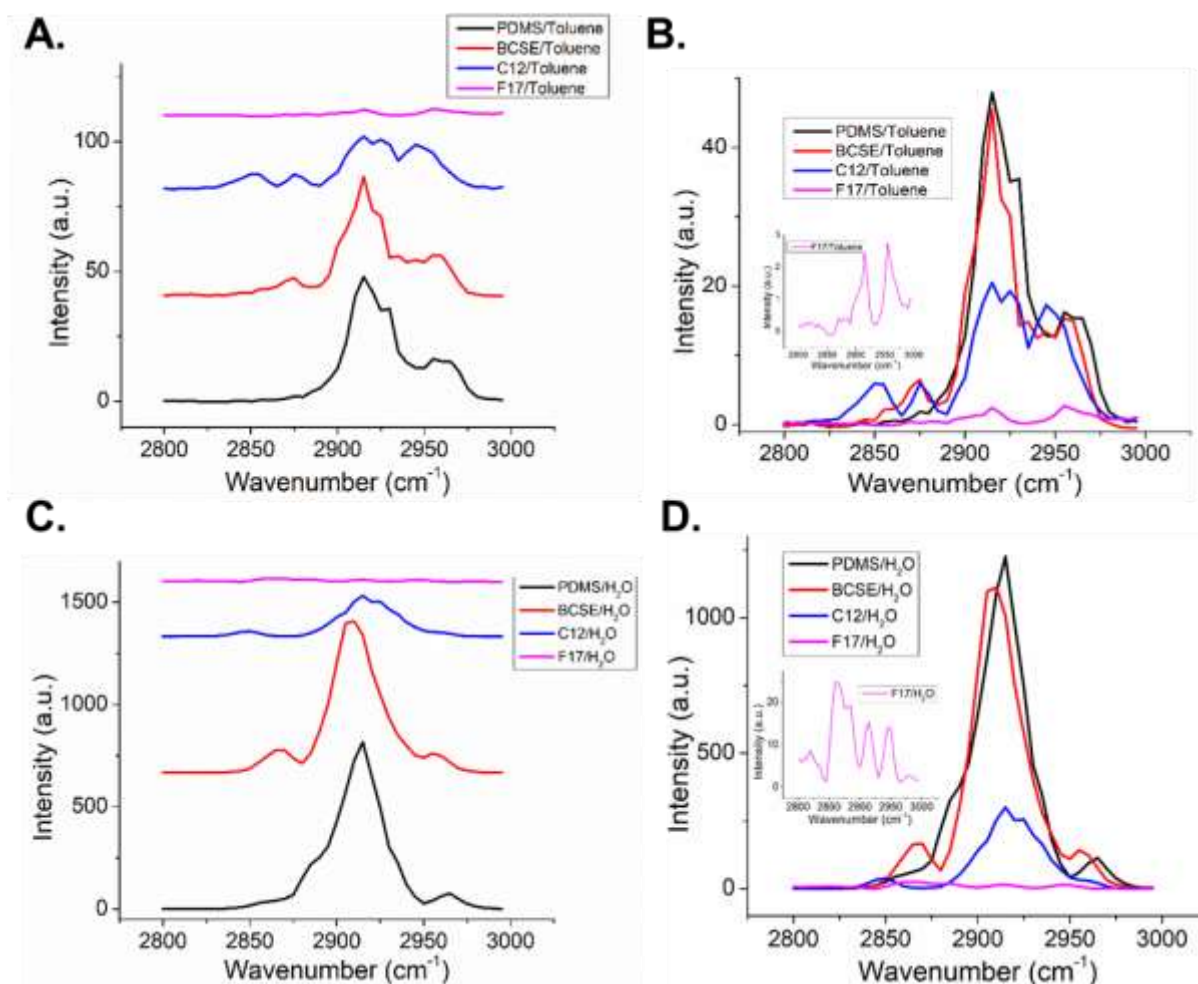


Figure 38. SFG spectra collected from: (A & B) coating/toluene interfaces and (C & D) the coating/water interfaces.

The SFG spectral features collected from t-PDMS/water and t-BCSE/water interfaces were similar to those collected from the t-PDMS/toluene and t-BCSE/toluene interfaces, respectively (Figure 38C & D), showing similar structures of these two surfaces in different chemical environments. Therefore both surfaces of t-PDMS and t-BCSE are also flexible in water. The much stronger SFG signal intensities detected from the water interfaces compared to those from toluene interfaces were caused by the much larger Fresnel coefficients of the water interfaces than the toluene interfaces. Total (or near total) reflection occurred at the water interfaces but not at the toluene interfaces because of the much smaller water refractive index. Excluding the Fresnel coefficient

difference, SFG spectra observed from the water interfaces and the toluene interfaces have similar signal strength. Figure 38 shows that the spectra collected from t-PDMS (or t-BCSE) are not identical in water and in toluene. The 2915cm^{-1} / 2960cm^{-1} peak ratio (symmetrical / asymmetrical stretching modes of Si-CH_3) from the water interface was higher than the ratio from the toluene interface, corresponding to some differences of methyl groups at PDMS/water and BCSE/water interfaces ³¹⁰. No additional structure differences were detected from the two water interfaces besides the detection of the Si-CH_2 groups from t-BCSE interface ($\sim 2870\text{ cm}^{-1}$). Therefore, the molecular structures of t-PDMS and t-BCSE are overall well maintained when the contacting medium switched from a very hydrophobic solvent (toluene) to a very hydrophilic one (water), indicating that they are stable and likely homogeneous, as well as flexible.

On the other hand, the C-12/water and F-17 water interface spectra were very different from the C-12/toluene and F-17/toluene interface spectra, respectively. For the C-12 interfaces, the C-CH_3 group signal at 2875cm^{-1} and the Si-CH_3 group signal at 2955cm^{-1} observed from the C-12/toluene interface spectrum were not present at the C-12/water interface spectrum. For the F-17/water interface, SFG signals located at 2875, 2915 and 2950cm^{-1} can be observed, which differ significantly from the signals detected from the F-17/toluene interface. These drastic signal differences between toluene and water interfaces indicate substantial structural changes of the C-12 and F-17 surfaces when the contacting medium is altered. Therefore, C-12 and F-17 surface structures are demonstrated to be relatively unstable in comparison to the t-PDMS and t-BCSE structures. Since t-PDMS and t-BCSE possess more stable surface structures, their surfaces are less likely to be disrupted, hence less fouled by various polymers. Comparing t-PDMS with t-BCSE, the t-PDMS surface with more disordered (or flexible) surface Si-CH_3 groups shows better antifouling performance than t-BCSE. Also, the presence of Si-CH_2 groups (which are less flexible

compared to the Si-CH₃ groups) at the surface of t-BCSE detected by SFG resulted in worse antifouling performance.

3.3 Antifouling Mechanism

The SFG results reveal that the ‘grafted from’ t-BCSE and t-PDMS surfaces are high in grafting density and stable, likely yielding a great degree of flexibility at the liquid-surface interface because of the dominating presence of the flexible Si-CH₃ groups at the interface. The amount of flexibility (or conformational freedom) was found to be greater in linear t-PDMS, than for linear t-BCSE due to the respective increase in concentration of siloxane bonds (See Table 2). The surface’s stable, but flexible properties enable the surface to remain relatively unchanged when modifying the contacting medium from hydrophobic toluene to polar water. In contrast, C-12 and F-17 coated surfaces yielded lower grafting density resulting from the ‘grafting to’ process, and their structures changed notably depending on the contacting medium. Contrary to expectations, reduction of surface energy alone, as in the case of F-17 or PFPE, did not lead to a notably reduced degree of polymer or wax fouling. Although greater in grafting density, we believe that the high stability and high conformational entropy led to a greater degree of polymer antifouling for t-PDMS and t-BCSE, compared to F-17 or C-12. Between ‘grafted from’ surfaces of similar surface energy, t-PDMS repeatedly outperformed t-BCSE in fouling resistance which can be related to increases in t-PDMS flexibility or mobility. The flexibility of the surface renders the liquid-like property.

Our findings prove that highly disordered, or flexible grafted chains are necessary to preventing polymer adsorption. This is similar to certain aspects of protein antifouling but new to polymer fouling. Unlike the findings of Wang *et al* ²⁷⁵, who measured a greater degree of polymer

antifouling when increasing the grafted brush T_g , we find the opposite result showing that low T_g , disordered brushes are important for polymer antifouling. The high conformational entropy of the polysiloxane brushes make it energetically unfavorable for polymer adsorption. In order for polymer to adsorb to the siloxane brushes, a drastic decrease in conformational entropy would be required. Our findings on the importance of chain mobility and flexibility in resisting polymer fouling are similar to those found in protein antifouling investigations^{127, 311, 312}. However it is well supported that for protein antifouling, a strong hydration layer is more dominant than the effects of chain flexibility^{127, 313-315}. Yet, in the case of polymer fouling, solvent barrier effects tend to play lesser role than chain mobility due to the weak van Der Waals forces between grafted polymer and solvent. Wang *et al.* found that single terminal fluorine (F1) chains did greatly reduce polymer adsorption via a solvent barrier mechanism when compared to fluorinated chains of a similar length²⁷⁴. Yet in a later investigation they found that si-ATRP grown fluoropolymer brushes performed better in more nonpolar solvents than F1 chains²⁹⁰. It is important to note that the si-ATRP grown fluoropolymers contain bulky repeating fluorinated side groups, causing more inter-chain free volume, and enhanced mobility when compared to the likely crystalized F1 chains. Our grafted linear PDMS although slightly higher in surface energy than fluoropolymers, have much greater mobility, and therefore yielded superior antifouling performance.

.

3.4 Conclusion

In this report we investigated the potential of highly mobile liquid-like layers in their ability to resist fouling of polymers and wax in solution. Linear PDMS was grafted to silicon using a simple vapor-phase polycondensation reaction, yielding ~2.5nm thick brushes. To prove their efficacy, three differently modified surfaces were also investigated. Low adhesive forces were

investigated by modifying silicon with fluorosilane (F-17), and structural differences were probed by modifying silicon with a more rigid alkyl silane (C-12). Another polysilicone t-BCSE, served as a liquid-like layer with alternating segments of stiff ethylene. The surface coatings based on C-12, t-BCSE, and t-PDMS yielded similar surface energies while maintaining differing structural properties. Silicon was used as control surface. Overall, the t-PDMS coated surfaces outperformed all other surfaces and significantly reduced the adsorption of a range of different polymers in different solvents. A similar experiment was also conducted with paraffin wax in toluene, and t-PDMS was able to significantly reduce wax adsorption when compared to silicon, F-17, C-12, and t-BCSE.

SFG was utilized to investigate the molecular level interface properties for each of the modified surfaces in order to help rationalize a mechanism. The results uncover that both t-BCSE and t-PDMS are high in grafting density and yield a great degree of random conformational freedom at the liquid-surface interface. However it was found that the degree of conformational freedom or flexibility at the liquid-surface interface was greater for t-PDMS, than for t-BCSE. t-PDMS retains a higher concentration of siloxane bonds than t-BCSE, making it more mobile or liquid like. The high mobility and more liquid like property, or conformational entropy of the grafted PDMS chains make it energetically unfavorable for polymer adsorption. Our findings run counter to the limited existing studies on polymer antifouling design, but rather is more analogous to the generally understood mechanisms for protein antifouling surfaces. Liquid-like siloxane layers have repeatedly demonstrated their potential as liquid omniphobic and facile solid shedding surfaces, and now offer promise in their ability to resist polymer and wax foulants.

3.5 Materials and Methods

3.5.1 Materials

Silicon wafers 4", Type N-1-10, 500-550 microns thick were purchased from the Lurie Nanofabrication Facility within the University of Michigan (LNF). The silanes consisted of Heptadecafluoro tetrahydrodecyl dimethyl monochlorosilane (F-17), n-decyldimethylchlorosilane (C-12), Bis(Methyldichlorosilyl)- Ethane, and 1,3-Dichloro-1,1,3,3-tetramethyldisiloxane (1-3 PDMS), and were ordered from Gelest Inc. Optool polyfluoro polyether (PFPE) was purchased from Daikin-America Inc. Polymer fouling experiments were conducted with six N,N-Dimethylformamide (DMF) soluble polymers, and three water soluble polymers. The DMF soluble polymers included poly(ethylene glycol) ($M_w \sim 20,000$, Sigma Aldrich), Poly(4-vinylphenol) ($M_w = 25,000$, Sigma Aldrich), Poly(vinyl chloride) ($M_w = 43,000$, Sigma Aldrich), Polymethyl methacrylate ($M_w = 35,000$, Scientific Polymer Products), Polystyrene ($M_w = 45,000$, Scientific Polymer Products), and Polyvinylpyrrolidone ($M_w = 40,000$, Scientific Polymer Products). 100mg/ml of polymer in DMF were prepared for each species. Hydrophilic polymers included poly(ethylene glycol) ($M_n \sim 20,000$, Sigma Aldrich), poly(allylamine hydrochloride) ($M_w \sim 45,000$, Sigma Aldrich), and Poly(sodium 4-styrenesulfonate) ($M_w \sim 70,000$ Sigma-Aldrich). 100mg/ml solutions of hydrophilic polymer in filtered deionized water were prepared for experimentation. The total volume of each solution was 10mL.

3.5.2 Surface Silanization

Before silanization of F-17 and C-12, silicon wafers were pre-treated with O_2 plasma using a Harrick Plasma PDC-001 with an RF source power of 30 watts and a pressure of ~ 200 mTorr for 30 min. Once treated, the silicon samples were loaded into 2-liter desiccators with 150 μ L of either

C-12, or F-17. Each desiccator only utilized one silane type to avoid contamination. Once loaded into a desiccator with silane, the desiccator was exposed to a vacuum of 25psi, and cyclically purged with nitrogen 10 times in order to render an inert atmosphere. The vapor phase reaction was left for 48 hours under vacuum before removing the samples. Once finished, excess silanes were removed from C-12 and F-17 modified silicon by washing with Toluene and Vertrel XF respectively. Similar to our previous report, tethered PDMS (t-PDMS) substrates were prepared by exposing 50 μ L 1-3 PDMS oligomers to 1cm² silicon substrates at room temperature²⁰⁸. Once finished, the PDMS modified substrates were washed with toluene in order to remove excess unbound silanes. Despite slight variations in humidity (45%-55%) within the lab space, this procedure yielded consistent advancing and receding contact angles, roughness, and thickness values. The reaction took place within a 47mm closed petri dish and ran for 5min. t-BCSE samples were also prepared in vapor phase by placing the silicon substrates into a 60mL glass septa-jar with 100g of the silane. The jar was closed and placed into a 120 C oven for 48 hours. The functionalized silicon samples were rinsed with toluene to remove excess unbound silanes.

3.5.3 Polymer Fouling Procedure

Unmodified silicon, C-12 modified silicon, and F-17 modified silicon substrates were cut down to 1cm² pieces for experimentation. PDMS modified silicon substrates were 1cm² to begin with. 100mg/ml polymer solutions were utilized for all experiments. Silicon control, F-17, C-12, t-BCSE, and t-PDMS coated surfaces were all placed in a vial of polymer solution for 15 hours at room temperature. Once finished, the samples were taken out of solution and rinsed within their respective solvents. Those fouled within DMF-polymer solutions were rinsed with 5ml of fresh DMF, while those within water-based polymer solutions were rinsed with 5mL of filtered

deionized water. The rinsing step included submerging the substrates taken from the polymer solution, and lightly swirling by hand for ~30 seconds. Each substrate was taken from solution one by one in order to avoid drying before the rinse step. Immediately after rinsing, the samples were dried with air, and placed onto a hotplate set to 50 °C for 10 minutes to remove solvent. When a given substrate is submerged into a polymer solution for an adequate duration, polymer deposits will adhere to the surface. This generally resulted in an increase in the RMS roughness for the fouled surfaces, and relatively little to no change for those that had not fouled.

3.5.4 Characterization

Atomic force microscopy (AFM) was utilized to view the increase in roughness as a result of polymer fouling. Root mean square (RMS) roughness was measured using a Bruker Innova AFM in tapping mode using an rTESP tip. 10µm box sizes were utilized to accurately capture the fouling of surfaces. Advancing and receding contact angles were measured using a Ramé-Hart 200 F1 contact angle goniometer using the standard sessile drop. Dynamic water contact angle measurement was used as a secondary data set by taking into consideration the change in receding contact angle. Contact angle hysteresis, which is the difference between the advancing and receding angles can be correlated with the degree of polymer fouling. However, in some cases, the advancing angle would decrease significantly as a result of the deposited polymer hydrophilicity leading to irregular contact angle hysteresis. Yet in every fouling situation, the receding contact angle would decrease, making this quantification more accurate. Deionized water, toluene, and DMF were used as probing fluids. Ellipsometry was conducted with a Woollam ellipsometer and silane layer thickness was measured using Cauchy parameters. Figure 31 demonstrates the AFM and ellipsometry surface characterization of the silane modified substrates.

SFG is a second-order nonlinear optical spectroscopic method which provides vibrational spectra of surfaces/interfaces²⁹⁴⁻³⁰⁶. Details regarding SFG theory, experiment, and data analysis have been reported extensively²⁹⁴⁻³⁰⁶ and will not be repeated. Here only a brief introduction of the SFG technique and related experiments in this study is presented. The sub-monolayer surface/interface sensitivity of SFG is due to the selection rule of a second-order nonlinear optical process. According to the selection rule, SFG signal can only be generated from a medium with no inversion symmetry under the electric dipole approximation. Most bulk materials have inversion symmetry, while surfaces/interfaces do not. SFG has been extensively applied to study surfaces and interfaces including buried solid/liquid interfaces²⁹⁴⁻³⁰⁶. In this study, for a typical SFG experiment, two input laser beams were used: a frequency-fixed 532 nm visible laser beam and a frequency-tunable infrared laser beam with wavenumber tunability from 1000 to 4300 cm⁻¹. The visible beam was generated by frequency doubling the 1064 nm (20 ps pulse width) output from an EKSPLA Nd:YAG laser. The tunable IR beam was produced using an EKSPLA optical parametric generation, optical parametric amplification and difference frequency generation system with LBO and AgGaS₂ crystals. The two input laser beams were overlapped both spatially and temporally at the interface. The beam spot sizes on the sample interface were around 500 μm in diameter. The sum frequency (SF) signal was then generated and collected using a photomultiplier tube normalized by the input visible and IR beam intensities. All SFG spectra were collected using the SSP polarization combination (s-polarized sum frequency output, s-polarized visible input, and p-polarized IR input).

Chapter 4 - Bioinspired Superoleophobic Zwitterionic Nanowires for Enhanced Marine Fouling Prevention

This work was co-authored with Dr. Jing Wang and aims to utilize a combinatorial approach to create surface which both kills algae and easily removes it. Here, I focused on the challenge of creating a hydration layer onto the biocidal nanowires and experimental design, while Dr. Wang also partook in experimental design, as well as conducted the characterization, algae tests/analysis, and theoretical adhesion analysis. The publication of this work is currently in preparation.

4.1 Introduction

Marine biofouling has remained a persistent problem throughout human history^{316, 317}. It not only inhibits maritime deep-water exploration and travel throughout the ocean and large lakes, costing billions of dollars per year³¹⁷, but also increases at least 20% in the greenhouse gas emissions from ships, which take around 80% of global trade by volume³¹⁸. Marine fouling is a complex and dynamic process, where various species accrete, compete, and cooperate in the attachment to the exposed surfaces, forming strong live developing biofilms with multiscale and multi-adhesion mechanisms^{316, 317}. Therefore it is possible to disrupt antifouling coatings by replacing their surface chemistry and burying their surface micro/nano structures^{50, 319, 320}, and further it can adhere strongly once attaches on the surface and dynamically adapt to shear flow environments^{162, 320-322}. Therefore, it is challenging to achieve both high prevention on marine fouling and easy removal of the accumulated biofilm in a single antifouling coating.

The current design strategies of marine coatings aim towards either fouling reduction or fouling release³²³. Fouling reduction aims to significantly delay the fouling growth^{324, 325}, while the fouling release works to actively remove the accumulated biofilms^{141, 323-325}. In the past century, only extremely toxic marine paints have proven to be effective in reducing and releasing marine fouling simultaneously³²⁶⁻³²⁸. After banning these paints due to their environmental issues in 2008, new non-toxic marine coatings have been developed in the past decade. These non-toxic coatings mainly used two methods to achieve antifouling: (1) creating physical barrier for attachment, for example, lubricant layer³²⁹; and (2) mildly killing marine microbials through natural biocidal chemicals^{330, 331}, or mechanical biocidal effect such as nanostructured surfaces³³². However, they have not achieved effective simultaneous fouling reduction and release compared to the previous toxic paints.

The physical barrier and biocidal coatings yield significant limitations for marine antifouling coatings. In particular, the physical blocking layer composed of air is generally known on superhydrophobic surfaces inspired by Lotus leaf, which can effectively prevent fouling for a short period of time (e.g., 1-10 days)³³³. However, once water breaks through the quasi-stable air layer, the fouling species can freely settle and strongly attach to the surface, meaning that superhydrophobic surfaces can only reduce fouling but not release fouling. Another more recently developed blocking layer is formed by liquids (oils or water)³³⁴⁻³³⁶. Inspired by the Pitcher plant rim, these lubricant-infused surfaces with an oil layer on the surface have shown significant fouling release performance because of its low adhesion strength to biofoulants^{147, 148, 334, 335}, but it cannot prevent different fouling species to settle and accumulate (Figure 39).

On the other hand, surfaces with hydrophilic polymers (e.g., zwitterionic polymers) can form a stable layer of interfacial water^{313, 337, 338}. This hydration layer has particularly been

effective in preventing protein adsorption, a problematic early fouling species^{167, 336, 339, 340}. Different from surfaces with an oil layer, these surfaces with a hydration layer have demonstrated mild effectiveness in both fouling reduction and release (Figure 39)^{167, 336, 339, 340}. Another strategy using mild mechanical biocidal effect usually prevents or reduces the fouling. In our recent work, we demonstrated the ability to limit the attachment and promote the death of complex marine fouling; however, the biocidal properties alone were not able to achieve strong fouling release performance³³².

Herein, we report a cross-species bioinspired zwitterionic nanowire (ZNW) coating (Figure 39), which employs synergetic antifouling strategies: liquid lubrication, anti-protein zwitterion, and mechanical biocidal from nanostructures. This zwitterionic nanowire (ZNW) coating forms nanostructured hydration layer, and demonstrates simultaneous fouling reduction and fouling release, outperforming the state-of-the-art non-toxic marine coatings. The zwitterionic nanowires were fabricated through atomic layer deposition (ALD) surface-directed self-assembly and surface-initiated atom transfer radical polymerization (si-ATRP), resulting in core-shell-shell nanostructures with precise thickness control in nanometer scale. The fabricated zwitterionic nanowires showed underwater superoleophobicity and underoil superhydrophilicity, indicating the formation of nanostructured hydration layer. We tested this zwitterionic nanowire coating and different control surfaces in algae fouling and low-shear stress fouling release tests. Our ZNW coating showed 70% fouling reduction in a static fouling environment compared to the uncoated planar control, which is >25% improvement compared to our previously reported mechanical biocidal coatings³³². In addition, the zwitterionic nanowires achieved 60% fouling release under low shear stress, at least 4 orders of magnitude lower than regular water jet cleaning¹⁶⁷. Further, we explored the synergetic antifouling and fouling-release mechanism of this coating by multi-

scale microscopic imaging techniques and theoretical adhesion analysis. This zwitterionic nanowire coating with nanostructured hydration demonstrates application potentials in maritime industry, deep ocean exploration, and biomedical industry, and the cross-species inspired synergetic design method provides new design frameworks for non-toxic antifouling coatings.

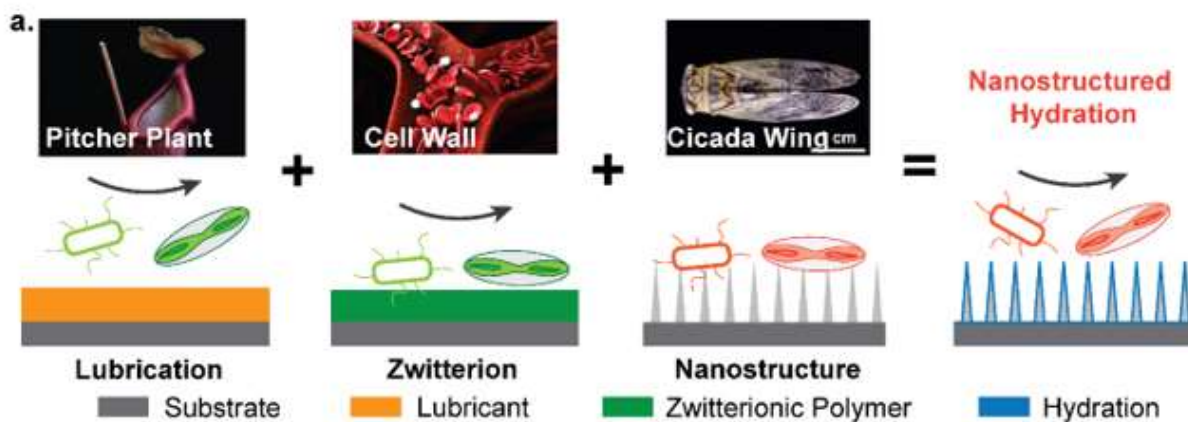


Figure 39: Bioinspired zwitterionic nanowire coating for simultaneous fouling reduction and fouling release.

Schematics of different bioinspired antifouling strategies and our cross-species inspired synergetic antifouling effects from lubricated pitcher plant rim, anti-blood clogging zwitterionic lipid membrane, and mechanical biocidal cicada wing.

4.2 Results and Discussion

4.2.1 Fabrication of the Zwitterionic Nanowires

We fabricated nanowires (NWs) through ALD-aided surface-directed self-assembly process (Figure 40A) reported in our previous works^{332, 341}. In particular, the substrate was coated with ALD ZnO seed layer followed by a hydrothermal synthesis process to grow ZnO NWs. Through this process, close-packed NWs were formed with a diameter of ~50 nm and inter-NW distance of ~40 nm³³². As ZnO nanowires were not stable in aqueous solution, we further coated a protection layer of 10-nm Al₂O₃ on the ZnO NWs by atomic layer deposition. This surface-

directed self-assembly process with ALD overcoats is highly substrate independent, and we can apply the NWs onto various shapes.

In previous reports^{167, 342}, zwitterionic polymers were successfully grafted on surfaces for different biomedical and maritime applications. These surfaces were usually inert materials (e.g., SiO₂) as the surface-initiated atom transfer radical polymerization (si-ATRP) process needs acid or base catalyst to effectively graft the initiator molecules on the nanoparticles. However, this conventional si-ATRP process cannot be used for highly unstable photo catalytic materials ZnO, because the acid or base catalyst is highly reactive with ZnO and can easily corrode ZnO nanostructures into Zn ions^{343, 344}, even with nanometer-scale Al₂O₃ protection layer. Therefore, we modified the surface initiation reaction by utilizing a small amount of water and heat as a catalyst to hydrolyze the silane prior to the subsequent SBMA-ATRP polymerization (See Materials & Methods). The zwitterionic polymerization yielded a conformal SBMA brush layer onto the ZnO/Al₂O₃ core-shell NWs (Figure 40B & C). This fabrication process of zwitterionic NWs is scalable (e.g., on 10-cm glass slide) and the fabricated zwitterionic NW coating on glass slide was highly transparent compared to uncoated glass, which can enable applications requiring high light transmittance.

4.2.2 Chemical Characterization of the Zwitterionic Nanowires

To confirm the ZnO/Al₂O₃/zwitterion core-shell-shell nanostructures, we first confirmed the nanowire structure through scanning electron microscope (SEM) analysis. From Figure 40B, the zwitterionic nanowires were closely packed with an aspect ratio of around 16, which is above the mechanical biocidal requirement for nanowire structures³⁴⁵. We further analyzed these nanowires by transmission electron microscope (TEM) with element mapping (Figure 40C). The TEM image in Figure 40C clearly shows the core-shell-shell structure of the nanowires with the

crystal structure of ZnO, the amorphous Al₂O₃, and the poly sulfobetaine methacrylate (pSBMA). In addition, the element mappings of Zn, Al, and S also confirm the observation of these three layers. Moreover, we noticed that the thickness of the Al₂O₃ layer on the zwitterionic NWs was reduced from 10 nm to 5 nm, indicating that even the mild water catalyst and heat can corrode the ceramic protecting layers. We also applied X-ray photoelectron spectroscopy (XPS) analysis on the zwitterionic NWs to further identify their chemical composition. The XPS spectrum recognized all the key elements in the zwitterionic NWs. In particular, the sulfur and nitrogen were almost in 1 to 1 ratio in CPS (See Materials & Methods), which indicates the successful grafting of pSMBA on ZnO/Al₂O₃ core-shell nanowires.

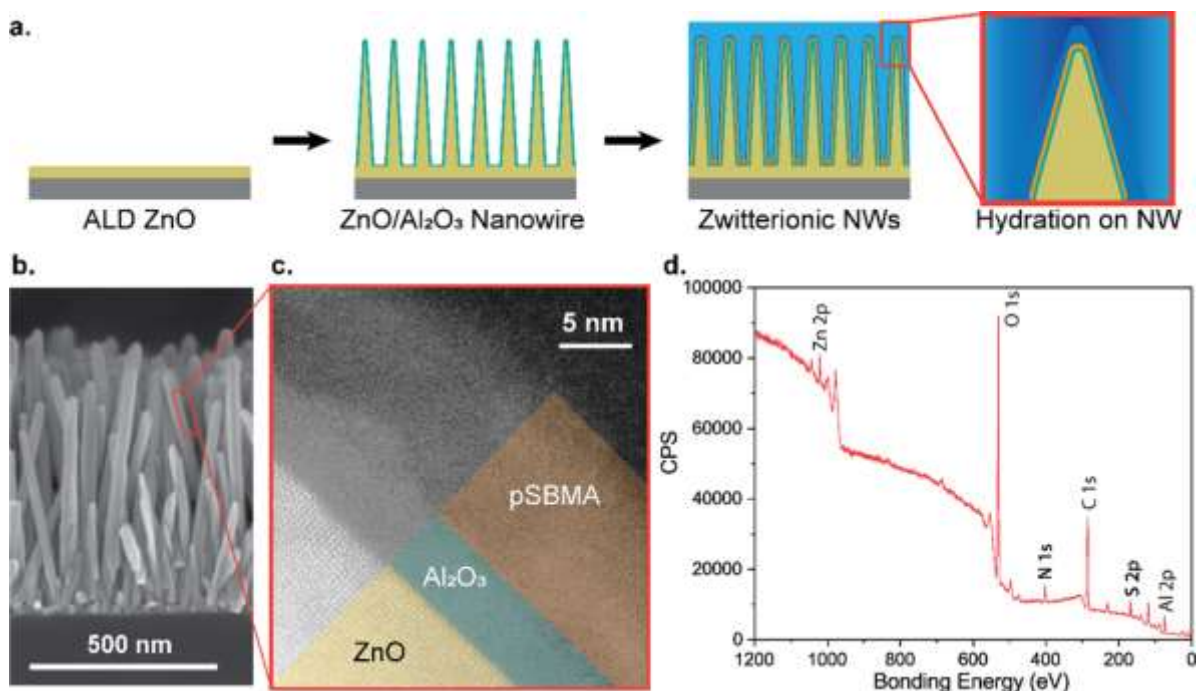


Figure 40: Fabrication and chemical characterization of the zwitterionic nanowires.

a. Schematics of the fabrication process of zwitterionic nanowires. b. SEM image of the zwitterionic nanowires. c. TEM image of the zwitterionic nanowire, demonstrating the core-shell-shell structures. d. XPS spectrum of zwitterionic nanowires.

4.2.3 Wetting Characterization of the Zwitterionic Nanowires

Zwitterionic polymers are known for their high affinity to water molecules because of their inner, spatially separated positive and negatively charged functional groups^{313, 337, 338}. The water molecules are highly attracted to the charged groups and form strong, stable water layer, resulting in the repellency of various proteins. This water layer also serves as a lubricating layer, which blocks not only other immiscible liquids such as oils, but also larger biofouling species coming into contact with the solid zwitterionic polymers^{167, 339, 346}. Therefore, before the fabricated zwitterionic NWs were tested with marine fouling species, we characterized their wetting performance under three different testing conditions. First, the zwitterionic NWs were tested for their wetting stability under contaminating environments compared to other surfaces, including zwitterionic planar surface, uncoated NWs (i.e., ZnO/Al₂O₃), and uncoated planar (i.e., Al₂O₃). We placed a pool of oil next to the testing surfaces as the contamination source. Then water contact angle measurements were performed on these surfaces after each week for 4 weeks. From Figure 41A, uncoated surfaces with and without NWs showed around 20° contact angle change after 4 weeks. In strong contrast, zwitterionic pSBMA coated surfaces with and without NWs did not show any changes in water contact angle. This owes to the strong affinity of zwitterionic polymers to water molecules, and macroscopically, water can easily displace the oil contaminant layer on zwitterionic surfaces.

Second, we measured underwater contact angles of oils with different surface tension on the zwitterionic NWs and uncoated NWs. In particular, oil drops were put on the testing surfaces within a bath of water. On zwitterionic NWs, their underwater contact angles of different oils were all above 150°, and the underwater contact angle hysteresis of different oils were all below 5° (Figure 41B). This indicates that the zwitterionic NWs are underwater superoleophobic to oils with

surface tensions ranging from 12 mN/m to 27 mN/m. In contrast, oils with different surface tension were all in the Wenzel state on the uncoated NWs with contact angle hysteresis larger than 25°.

Finally, the reverse experiment was completed by measuring water contact angles within an oil bath for the zwitterionic NWs and uncoated NWs. The probing liquid was in this case was water while the environment liquids were different oils. From Figure 41B, the zwitterionic NWs were superhydrophilic in different oils, that is, water drop spread on the surfaces in the oil bath. In comparison, the uncoated NWs were in the Wenzel state hydrophobic for most of the oils except for dodecane and silicone oil.

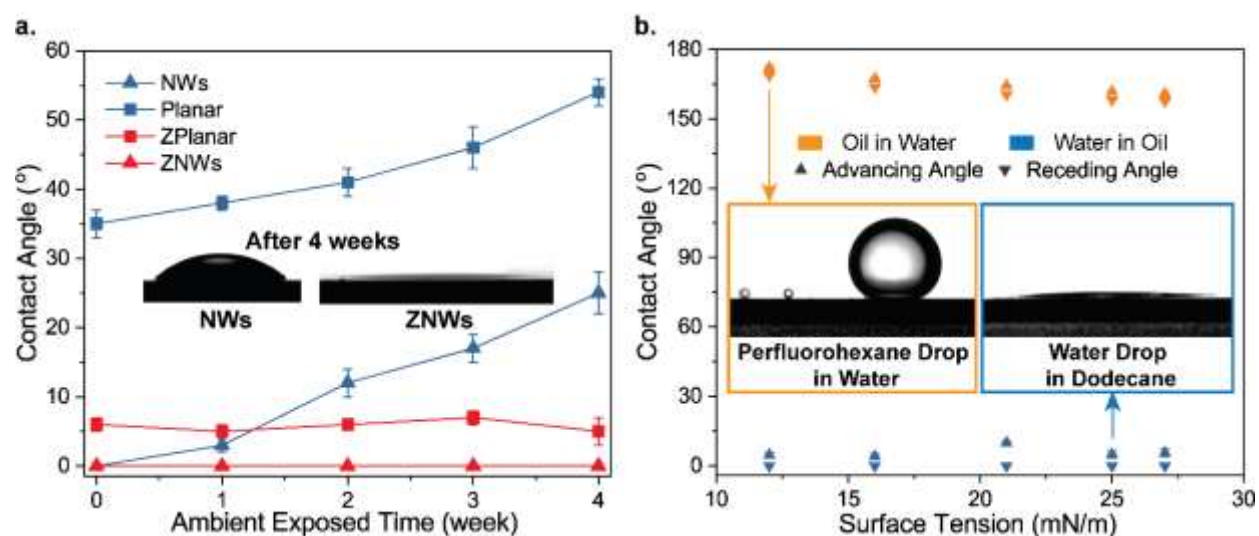


Figure 41: Contact angle measurement on zwitterionic NWs and uncoated NWs under different conditions.

a. Contact angle measurement after different contamination time. b. Advancing and receding contact angle measurement underwater for different oils and under different oil for water. The error bars were obtained from at least 3 independent measurements.

4.2.4 Marine Algal Fouling Test on the Zwitterionic Nanowires and Other Surfaces

Among marine fouling species, algae mixtures are one of the most common and widespread biofoulants in most waters. In this report and our previous works^{332, 347}, we used the algae

mixtures, containing few different diatoms and cyanobacteria, as a model marine fouling system. In particular, different surface coatings were submerged into a concentrated algae fouling solution (more than most natural environments) and remained statically in position for 14 days. These surfaces included ZNWs, uncoated NWs, zwitterionic planar surfaces, uncoated planar surfaces, zwitterionic micropillars, and uncoated micropillars (See Materials & Methods). Before we pulled the testing surfaces out of the algae solution for fouling analysis, these fouled surfaces were analyzed under an optical microscope to obtain the fouling area coverage fraction. The fouling area coverage fraction is defined as the percentage of fouled area in total measuring area. The fouling area coverage fraction for each surface was then measured after being pulled out and placed in simulated seawater. No obvious difference in fouling coverage fraction was noticed through this process, indicating that the sample transfer process from one medium to another would not remove the biofilm.

From the optical microscopic images in Figure 42A, the ZNWs were the least fouled surface among all testing surfaces, significantly less than the planar surfaces and the micropillars with and without zwitterionic polymer coating. Quantitatively, less than 30% of the surface area of the ZNWs was covered with marine algae (Figure 42B), while 100%, >75%, and 55% of the surface area was covered by algae on uncoated planar and micropillar surfaces, zwitterionic planar and micropillar surfaces, and uncoated NWs, respectively. This improvement in reducing fouling illustrated the advances of using both nanostructured hydration layer and mechanical biocidal effect.

4.2.5 Marine Algal Fouling Release on the Zwitterionic Nanowires and Other Surfaces

After 14-day algal fouling, these surfaces were cleaned by shear flow to test their fouling release performance. Different from current water jet cleaning method, we applied an open-

channel flow to generate wall shear to remove the attached biofilm. This open channel flow can generate a shear stress of 0.4 Pa (see Materials & Methods), which is at least 4 orders of magnitude lower than the shear stress generated by a high-pressure water jet for ship hull cleaning¹⁶⁷. We applied 30-min of such shear flow on the fouled surfaces, and observed that only zwitterionic polymer coated surfaces showed fouling release performance (Figure 42B&C). In particular, the fouling coverage fraction on ZNWs dropped from 28% to less than 10% (Figure 42B), which was also demonstrated by the optical microscopic images (Figure 42A). The other zwitterionic coated planar and micropillar surfaces were also less covered by algae after 30-min shear flow; however, their coverage fractions were still higher than NWs (Figure 42B).

Furthermore, we performed optical density measurements on these fouled surfaces after 30-min shear flow. The optical density measurement is a destructive method to quantitatively characterize the fouling coverage in a 3-dimensional manner. It measures the absorbance of the biological stain through a UV-Vis spectrometer, representing the total attached cells on the surface (see Materials & Methods). From the optical density measurements shown in Figure 42C, the uncoated micropillar surfaces had nearly twice of attached cells than the uncoated planar surfaces, which was not reflected by the optical microscope measurements. Interestingly, the optical density of the uncoated planar surfaces was only 4 times higher than the ZNWs after 30-min shear flow; while their area coverage fraction was more than 10 times higher than ZNWs (Figure 42B). This indicates that algae cells intend to grow in horizontal plane on favorable planar surfaces, and that ZNWs force algae cells to grow more vertically as they cannot settle and attach well on such surfaces.

We also characterized the fouling release performance with the percent removal after different time of shear flow. From Figure 42D, the percent removal increased with shear flow time

on ZNWs in the 30-min shear flow test; while the percent removal plateau after 10-min of shear flow on zwitterionic coated planar and micropillar surfaces. In addition, the percent removal reached >60% on ZNWs and tended to increase with shear flow time. In comparison, the percent removal was only less than 20% on zwitterionic coated planar and micropillar surfaces. This reveals that the mechanical biocidal effect from the NW structures also contributes to the fouling release together with the zwitterionic polymers. To note, the low shear stress applied in this study is in similar order of the shear stress from a boat in its cruise speed, indicating that the accumulated marine fouling in static condition could be removed when driving the boat off the bay.

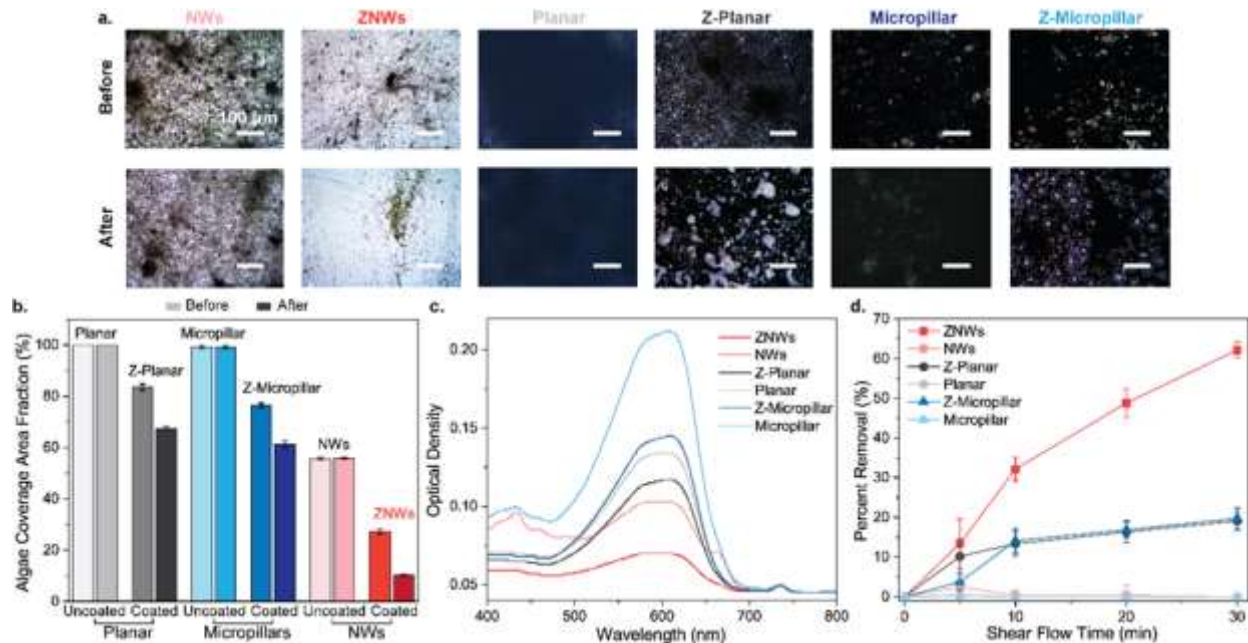


Figure 42: Algae fouling test on ZNWs and other coatings.

a. Optical microscopic images of different samples after 2 weeks of fouling and after 30-min of shear flow. b. Algae coverage area fraction on different samples before and after 30-min of shear flow. c. Optical density of different samples after 30-min shear flow. d. Percent removal on different sample after different shear flow time. The error bars were obtained from at least 3 independent measurements.

4.3 Conclusion

In this work we have developed a bioinspired superoleophobic, superhydrophilic interface capable of both the prevention and release of complex marine algae. This was achieved by a unique combinatorial approach; the joining of a mechanical biocidal nanowire array with a hydration layer formed by a polySBMA brush. The SBMA nanowires were engineered utilizing an Si-ATRP process whereby the surface initiator was anchored in a simple non-destructive process by utilizing water and heat as hydrolysis catalyst. In an underwater environment, the SBMA nanowires demonstrated substantial phobicity to oils, and while in an oil environment, significant hydrophilicity, indicating the formation of a strong hydration layer in the presence of water. The unique mechanical biocidal nanowires combined with a strong SBMA-induced hydration layer elucidated the effect of both the ability to greatly reduce algae settlement, as well as the ability to release settled foulants when compared to the planar control, planar SBMA brush, non-functionalized nanowire arrays, non-biocidal micropillars and SBMA micropillars. Lastly, this was achieved for a complex algae system representative of a natural environment. This is in opposition to the use a single species system, a widely practiced protocol in anti-algae surface investigations. This bioinspired coating offers great promise and insight into the field as we aim to design surfaces to effectively inhibit the detrimental effects of complex marine fouling on surfaces within nature.

4.4 Materials and Methods

4.4.1 Materials and Fabrication.

The Al₂O₃/ZnO NWs were fabricated using our previous method^{332, 341}. 20 nm of ZnO was coated through atomic layer deposition (ALD), followed by 60-min of hydrothermal synthesis of ZnO nanowires (i.e., nanowires with 1 μm length). Then the ZnO nanowires were coated with 10

nm of Al₂O₃ using atomic layer deposition (ALD). The substrates were first treated in 50W oxygen plasma (Plasm Etch Inc.) for 20 minutes. The plasma treated substrates were submerged into a 8mg/ml (3-TRIMETHOXYSILYL)PROPYL 2-BROMO-2-METHYLPROPIONATE (Gelest) in 1% H₂O/Ethanol (Sigma Aldrich) solution. The solution and substrate were then heated on a 85°C hotplate for 2 days, followed by 110°C for 12 hours. Once complete, the samples were rinsed with 2-propanol (Sigma Aldrich) and gently blown dry. The SBMA-ATRP solution was prepared similar to Chernyy *et al*³⁴⁸; 3.75g of [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA) purchased from Sigma Aldrich, was dissolved in a mixture of 6.35mL deionized water and 18.75mL of Methanol (Fischer). The solution was mixed in a two-neck 100mL round-bottom flask with nitrogen bubbling for 3 hours. 166.25mg of 2,2'-Bipyridyl (Sigma Aldrich) was mixed into the solution with for 30 minutes, then 76.25mg CuBr and 30mg CuBr₂ was mixed for an additional 30 minutes under constant nitrogen bubbling and stirring. The solution turned from transparent to dark red/brown after copper catalyst was added. With the surface-initiated substrates placed at the bottom of a 50mL glass septa-jar (Fischer), the ATRP solution was quickly poured into the jar and the cap closed. Nitrogen was then bubbled in for the duration of the reaction. Once the reaction was finished (1 hr), the samples were removed and rinsed with DI water, followed by sonication in DI water until all residual polymer was removed.

4.4.2 Contact angle measurements

The underwater and underoil contact angle measurements were performed with a Ramé-Hart 200-F1 contact angle goniometer using the sessile drop method. Advancing and receding contact angles were obtained by measuring the angle while the liquid was slowly added to or removed by a micro-syringe from a ~5 µL droplet in contact with the surface.

4.4.3 Algae fouling experiments

The algal fouling tests were similar to our previous works^{332, 347}. Specifically, two grams of biomass (i.e., algae biofilm) was weighted through an analytical balance with a resolution of 0.0001 g and was introduced to a petri dish (diameter: 100 mm) with 50 mL of seawater and F/2 (purchased from <https://www.amazon.com/>) mixture. Samples were submerged into the algae culture environment for 14 days. We took microscopic images on these fouled surfaces using a Nikon LV150N Optical Microscope. The algae coverage area fraction was quantified with obtained microscopic images through ImageJ analysis.

4.4.4 Open channel shear flow

We built up a shear flow setup based on open channel flow with a controlled flow rate. The water pump can provide maximum flow rate as ~15 gpm, and the flowmeter is in the range of 2 gpm. We used a valve to control the flow rate. The open channel was made of acrylic that is 1-m long (L_c) and 27-mm wide (w). At the highest flow rate, we can calculate the length that the flow needs to be fully developed by calculating the Reynolds number ($Re = 4VR/\nu$) and Froude number ($Fr = V/(gh)^{1/2}$), where R is hydraulic diameter, V is the flow velocity, ν is the kinetic viscosity, g is the gravity constant, h is the flow height. The hydraulic diameter is $R = A/P$, where A is the flow cross-sectional area, and $P = w+2h$ is the wetted perimeter. For open channel flow, the length of the flow development zone (L) can be determined using the equation of Kirkgöz and Ardiçlioğlu (1997)³⁴⁹:

$$L/h = 76 - 0.001Re/Fr \quad (8)$$

The wall shear on the bed of the channel can be described by the equation from Guo and Julien (2005)³⁵⁰:

$$\frac{\tau_b}{\rho ghS} = \frac{4}{\pi} \tan^{-1} \exp\left(-\frac{\pi h}{w}\right) + \frac{\pi}{4} \frac{h}{w} \exp\left(-\frac{h}{w}\right) \quad (9)$$

where τ_b is the wall shear in the channel bed, ρ is the density, S is the slope of the channel (1:5000). The wall shear (τ_b), the development zone (L) and all dimensionless numbers (We and Fr) are calculated shown in Table 4.

Table 4: Example of flow parameters in highest flow rate (2 gpm).

Flow rate (m³/s)	Flow height h (m)	Re	Fr	Developed zone L (m)	Wall Shear τ_b (Pa)
1.26×10 ⁻⁴	4.3×10 ⁻³	1067	4.94	0.34	0.37

The open channel flow setup we built in this quarter can be used for study fouling release property of various surfaces and fouling under flow environment instead of a steady-state environment³⁵¹. In the next quarter, we will test the fouling release behavior of the NWs and design experiment for fouling under flow conditions.

4.4.5 Optical density measurements.

The fouled surfaces were firstly rinsed by saltwater (0.8 M NaCl) to remove unattached algae, followed by soaking in DMSO (Sigma-Aldrich, Inc.) for 15 min to remove the chlorophyll in the algae. Then the samples were gently rinsed by saltwater again and stained with trypan blue (from Thermo Fisher Scientific) for 15 min. Further, we rinse off the excess dye by saltwater.

Finally, 10 mL of DMSO was used for each sample to extract the blue stain, and absorbance of the liquid was measured by UV–vis spectrometry.

4.4.6 XPS

XPS was conducted using a Kratos Axis Ultra X-ray Photoelectron Spectrometer

4.4.7 TEM

A Thermo-Fisher Talos F200 was used for imaging and element mapping. The microscopy was operated in STEM mode and a Velos software was used for collecting STEM images including HAADF, LAADF and BF images and EDS element maps. TEM was done by Dr. Kai Sun, Dr. Eric Kazyak, and Julia D. Lenef from University of Michigan.

Chapter 5 - Design of Abrasion Resistant Polymeric Coatings with Durable Anti-Fog Performance

In this chapter, I present a unique design strategy for the engineering of polymer abrasion resistant antifog coatings. The work was done in collaboration with Natick Army Research labs for their soldier defense systems. For this work, I designed the coating concept, conducted the experimental work and wrote the manuscript while Dr. Jing Wang, Dr. Brian Tobelmann, and Fan-wei Wang aided in the design and experimentation of fog testing. To our knowledge, this is the first time a systematic approach has been done for the design of abrasion resistant polymer-based antifog coatings.

5.1 Introduction

Surface fogging is caused by condensed micro-droplets on cold surfaces which scatter light, rendering normally transparent surfaces hazy ²⁰. Fogging occurs when the water contact angle on the surface is greater than 40° ²⁰. Fog adversely effects the visibility of lens applications such as prescription glasses ³⁵², safety eyewear ³⁵³, swimming goggles ³⁵⁴, camera lenses ³⁵⁵, and hazmat face-shields ³⁵⁶. Broader effects of fog include the reduction of efficient solar energy conversion ³⁵⁷, and the hygiene of medical devices ³⁵⁸. To mitigate the surface fogging, highly hydrophilic coatings (i.e., water contact angle < 40°) are preferable as they can easily maintain the optical transparency and clarity ³⁵⁹, and be dried faster by convection when compared to hydrophobic surfaces ³⁶⁰

Antifogging design strategies generally aim towards one, or both of the following avenues: manipulating the substrate surface chemistry, and/or the surface geometry modification. A simple way to increase surface energy and reduce contact angle is via plasma treatment^{361, 362}. However plasma treated materials succumb to ‘hydrophobic recovery’, where the material loses its hydrophilic properties as a result of ambient contamination and diffusion of low energy groups to the surface^{362, 363}. Microfabricated surfaces have been investigated for antifog applications through Wenzel wetting³⁶⁴ to achieve low contact angles. Notable examples include microfabricated nanocones and nanopillars, which demonstrated significant antifogging ability^{365, 366}. Microfabricated surfaces however require highly precise and expensive processing conditions, making scalability a concern. Durability is also an issue as the microstructures are highly susceptible to damage and wear, which nullifies their properties. Ceramic coatings such as Titania and Zinc Oxide have also been investigated for antifog applications since their wettability can increase upon UV exposure^{20, 367-370}. However, despite their performance and inherent durability, ceramic coatings often require high temperature calcination, eliminating the possibility of using plastic substrates such as common polycarbonate safety glasses or goggle lenses.

Hydrophilic surfaces can be achieved via high-surface-energy polymers, including polyethylene glycol³⁷¹, polyvinyl alcohol²⁰⁰, polyvinyl acetate²⁰⁰, and polyvinyl pyrrolidone²⁰¹, as well as recently developed zwitterionic and amphiphilic polymers²⁰²⁻²⁰⁴. These hydrophilic polymers have low water contact angles (e.g., $< 40^\circ$), and most are able to absorb moisture to further reduce the water contact over time^{201, 204}. However, these antifogging coatings suffer from their poor durability, particularly under mechanical abrasion or prolonged exposure to fogging conditions.

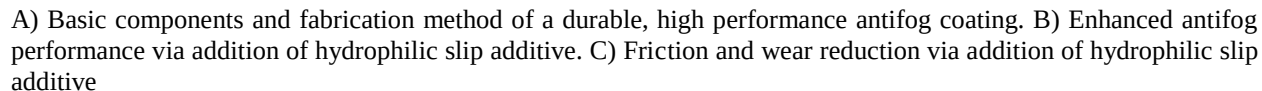
The mechanical durability of the anti-fogging polymeric coatings can be described by the Ratner-Lancaster relation:

$$W \sim k\mu \left(\frac{1}{H\varepsilon_u\sigma_u} \right) \quad (10)$$

where W is the wear rate, μ is the friction coefficient, H the hardness, and ε_u and σ_u are the strain and stress at tensile break respectively^{372, 373}. The relation illustrates that the polymer wear coefficient is proportional to the interfacial friction coefficient and inversely proportional to the film hardness and product of strain and stress at tensile break³⁷². Particularly, wear rate is defined as the volume loss of a polymeric coating per unit travel distance of mechanical abrasion. Therefore, increasing the hardness, tensile stress and strain at break, and reducing the surface frictional coefficient lead to polymer wear resistance. This design relation induces two major challenges in improving durability of the hydrophilic antifogging coatings. On one hand, hydrophilic polymers tend to have a narrow range of miscibility, limiting the number of additives which can be leveraged to enhance their hardness and tensile properties. On the other hand, the high surface energy of the hydrophilic antifogging polymer coatings inherently results in high work of adhesion, which can lead to a high friction coefficient^{374, 375}. Although several attempts have been made to engineer a wear resistant polymer antifog coating^{201, 376-378}, none have provided a relatively simple and systematic approach that results in the enhancement of both properties.

Herein, we report the systematic design and fabrication of durable polymeric antifogging coatings. These coatings are a crosslinked polyvinyl pyrrolidone (PVP) matrix with the addition of two critical chemicals for enhancement on antifogging performance as well as mechanical durability. We develop a simple two-step coating process to apply these coatings to a wide variety of plastic surfaces as shown in Figure 43A. This facile fabrication process can be readily scaled

Figure 43. Design of durable antifog coatings.



5.2 Results and Discussion

5.2.1 Optimization of Coating Toughness

Polyvinyl pyrrolidone (PVP) in the presence of hydrogen peroxide is able to self-crosslink condensation of local succinimide groups under UVC with the presence of H_2O_2 ^{201, 379}. The reaction results in a stiff polymer network (A), allowing it to be resistant to dissolution in humid or aqueous environments. Thus, it has been used as one of the antifogging coating materials that can stand cyclic fogging conditions without loss its antifogging properties. The addition of benzophenone facilitates the bonding of the bulk coating to polymeric substrates after exposure to UVA radiation²⁰¹. However, this crosslink PVP is brittle and can be easily fractured (Figure 44). To increase the toughness of the crosslinked PVP, we added a miscible tetrafunctional oligomer pentaerythritol tetraacrylate (PETRA) (Figure 44A) with different percentages in PVP and hydrogen peroxide to generate a semi interpenetrating polymer network (Si-IPN) through a self-reaction between acrylate groups. The self-reaction of PETRA was confirmed via FTIR (see section 5.4.7), which demonstrates a sufficient decrease in acrylate peak after 10 minutes of UV. Substrate UV exposure was minimized to avoid degradation of the underlying polycarbonate³⁸⁰.

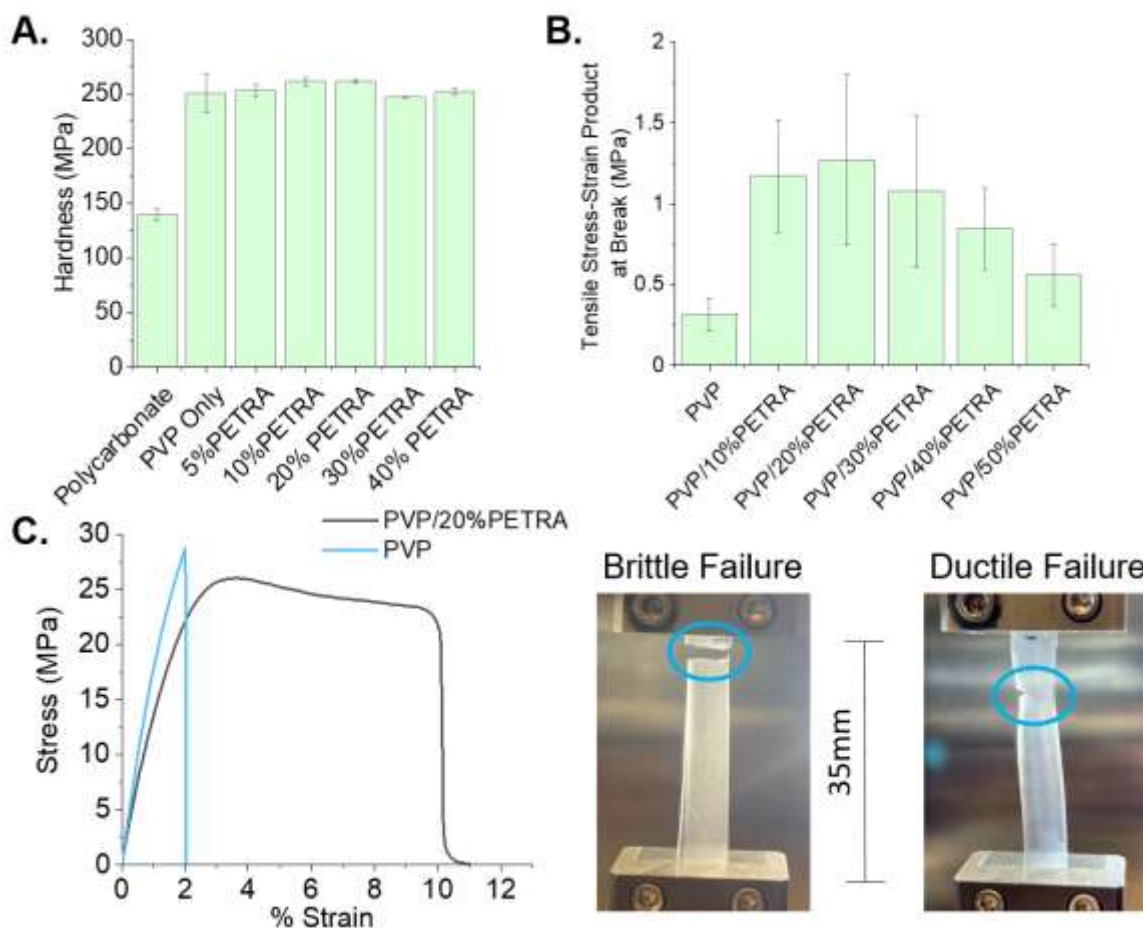


Figure 44: Mechanical enhancement of the PVP-PETRA antifog coating.

A) Indentation hardness of polycarbonate, crosslinked PVP and crosslinked PVP with increasing concentration of PETRA. B) Stress-Strain product at break/tear onset for crosslinked PVP and crosslinked PVP with increasing concentration of PETRA. C) Increase in coating toughness through addition of PETRA and transition from brittle to ductile failure.

Figure 44A exhibits the hardness of the PVP coatings as a function of PETRA mass ratio%. By addition of crosslinked PVP, the hardness is increased by over 100MPa when compared to polycarbonate. The hardness of PVP with different amounts of PETRA is effectively unchanging with the addition of PETRA up to 40%. However, the toughness of PVP was enhanced by adding PETRA. Through the tensile tests on cross-linked PVP and PVP-PETRA films (Figure 44B and C), we demonstrated that the ductility was notably increased with the addition of up to 20%

PETRA. Figure 44B also illustrates an increase of the stress-strain product at breaking point from 0.3 MPa to 1.3 MPa for crosslinked PVP and crosslinked PVP with 20% PETRA respectively. As shown in Figure 44C, the crosslinked PVP exhibited a brittle failure while PVP/20%PETRA exhibited a ductile tearing failure. Interestingly, the increase of PETRA additive after 20% resulted in a transition of the coating from ductile tearing back to brittle failure (Figure 45). Therefore, the maximum enhancement on coating toughness was achieved via a 20%PETRA/PVP film, which would also enhance the mechanical durability of the coating.

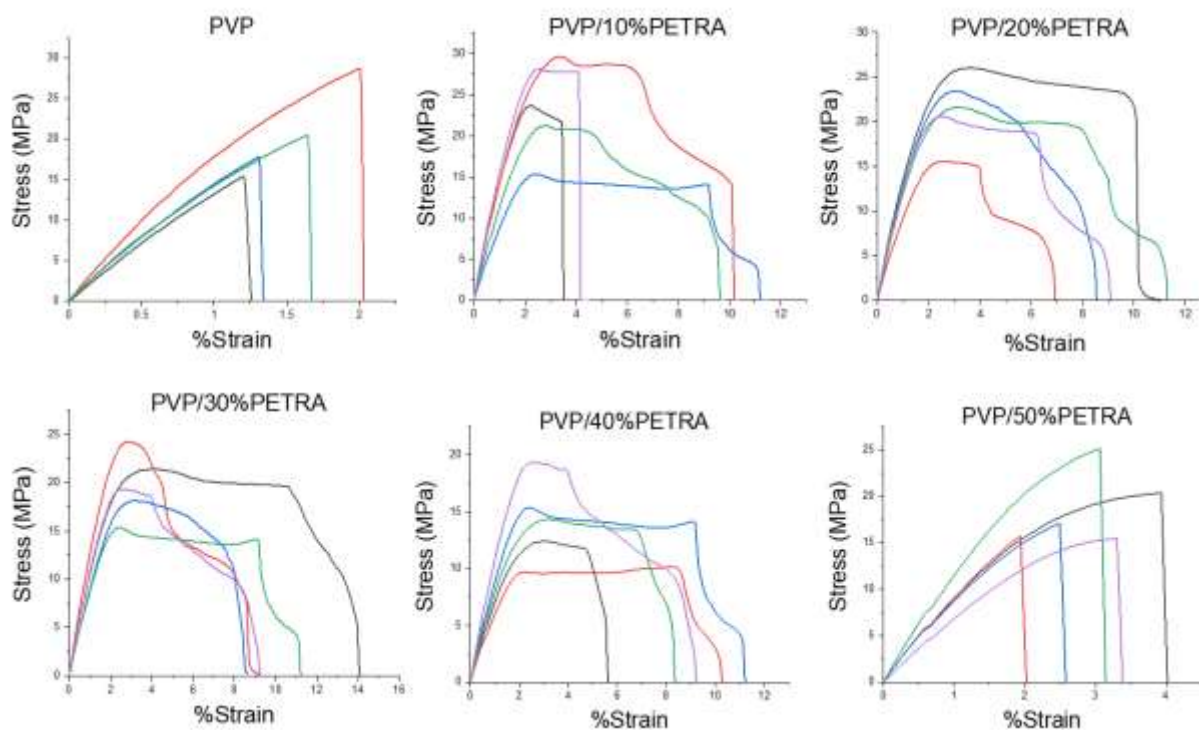


Figure 45: Raw stress-strain data of PVP and PVP-PETRA films.

5.2.2 Reducing Coating Friction Coefficient

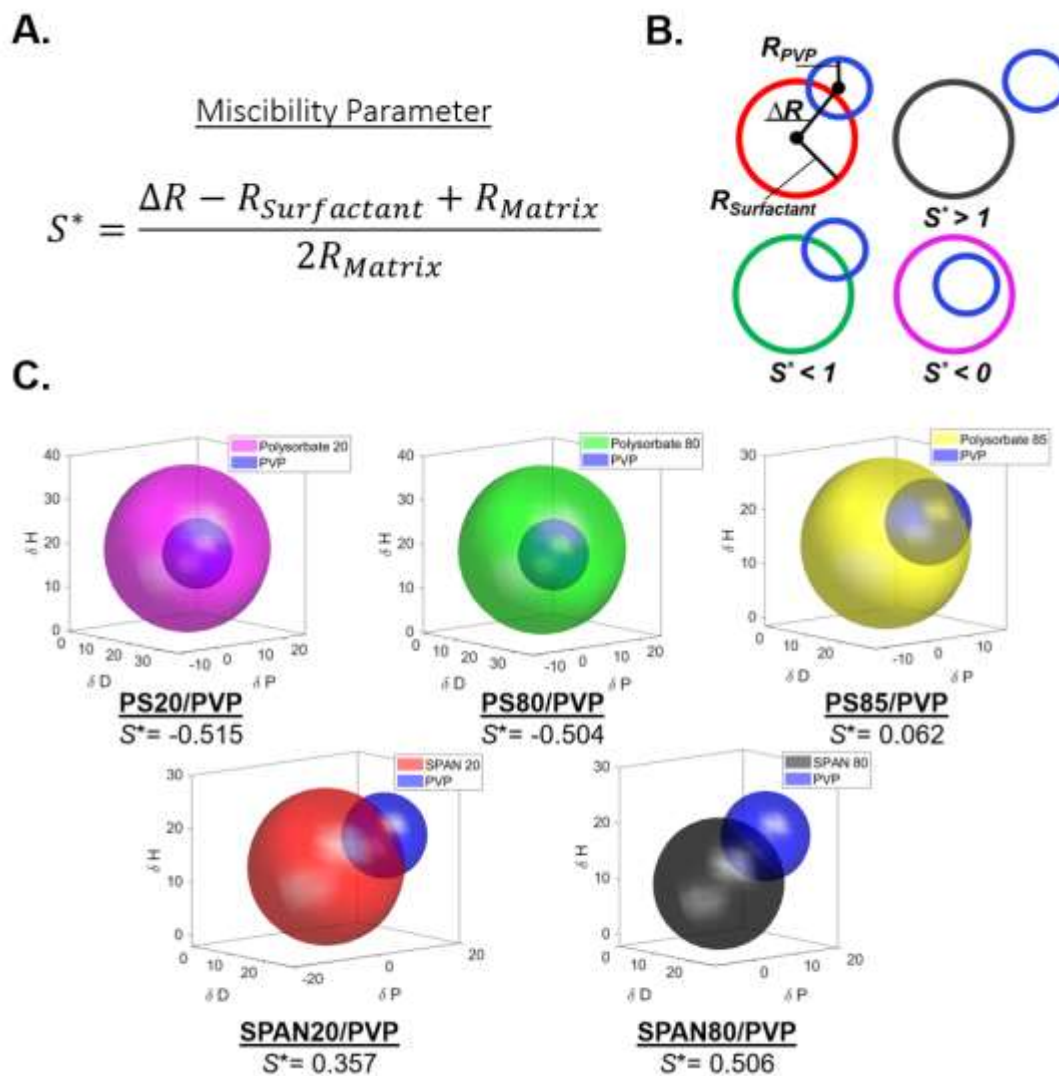


Figure 46. Miscibility parameter (S^*) of PVP and surfactants

A) Equation defining the miscibility parameter between two compounds. B) Graphical depiction of miscibility parameter in Hansen Space where $S^* > 1$ results in phase separation, $S^* < 1$ partial miscibility, and $S^* < 0$ as effectively miscible. C) The Hansen spheres of PVP and PS20, PS80, and SPAN80.

To further enhance the wear resistant properties of the coating, the frictional coefficient must be reduced. Herein, we introduced miscible slip additives into the PVP-PETRA network to form a lubricating layer. Slip additives are relatively low molecular weight macromolecules that are blended into a polymer matrix. Owing to differences in surface energies between the PVP matrix and free macromolecules, and diffusion, these slip agents partially migrate to the surface, forming an interfacial, ultra-thin lubricant layer³⁸¹. Identifying slip additives that are miscible with PVP and/or other antifog polymers while maintaining antifogging properties presents a unique challenge. The majority of slip additives, for example fatty amides³⁸², are not sufficiently hydrophilic to be miscible with antifog polymers. Therefore, we selected a class of amphiphilic macromolecular surfactants as slip additives to study their miscibility, friction, and antifog performance. Specifically, they include sorbitan monooleate (SPAN80), sorbitan monolaurate (SPAN20), polyoxyethylene sorbitan trioleate (PS85), polyoxyethylene sorbitan monooleate (PS80), and polyoxyethylene sorbitan monolaurate (PS20). These amphiphilic macromolecules were selected because of their broad solubility resulting from their asymmetric polar molecular structure.

The surfactants and their miscibility with PVP were analyzed utilizing Hansen solubility parameter. Specifically, the Hansen solubility parameters are the sum of cohesive energy densities consisting of hydrogen bonding, polar forces, and dispersive forces intrinsically exerted by a given compound³⁸³. Through solubility experimentation and the HSPiP software, the solubility parameters were estimated and a sphere in Hansen space was generated for each molecule (See materials & methods)). The Hansen solubility spheres of each component provide the calculation of relative miscibility (S^*). Depicted in Figure 46A&B, S^* can be conceptualized as the degree of spherical overlap between two Hansen spheres and indicates the level of miscibility between two

molecules^{224, 384}. For example, a negative S^* means that the two molecules are miscible, and the more negative S^* is, the more miscible of the two molecules. Figure 46C displays the Hansen solubility spheres and S^* values between the surfactants and PVP. It shows a decrease of S^* in the order of SPAN80, SPAN20, PS85, PS80, and PS20. Only PS80 and PS20 have negative S^* , illustrating that they are miscible with PVP/PETRA as shown in Figure 46A.

The surfactant hydrophilic-lipophilic balance value (HLB) is another important dimensionless parameter for this miscibility design. HLB values relate to the hydrophilic or hydrophobic degree of a nonionic surfactant³⁸⁵. In general, molecules with HLB values >10 are hydrophilic, while those with HLB values <10 are hydrophobic. For antifogging applications, hydrophilic chemistry is preferred and therefore higher HLB value of the slip additives is needed. Based this criteria, polysorbates have higher HLB values than Span surfactants, making PS20 the most hydrophilic slip additive for the requirement of optical clarity and antifogging.

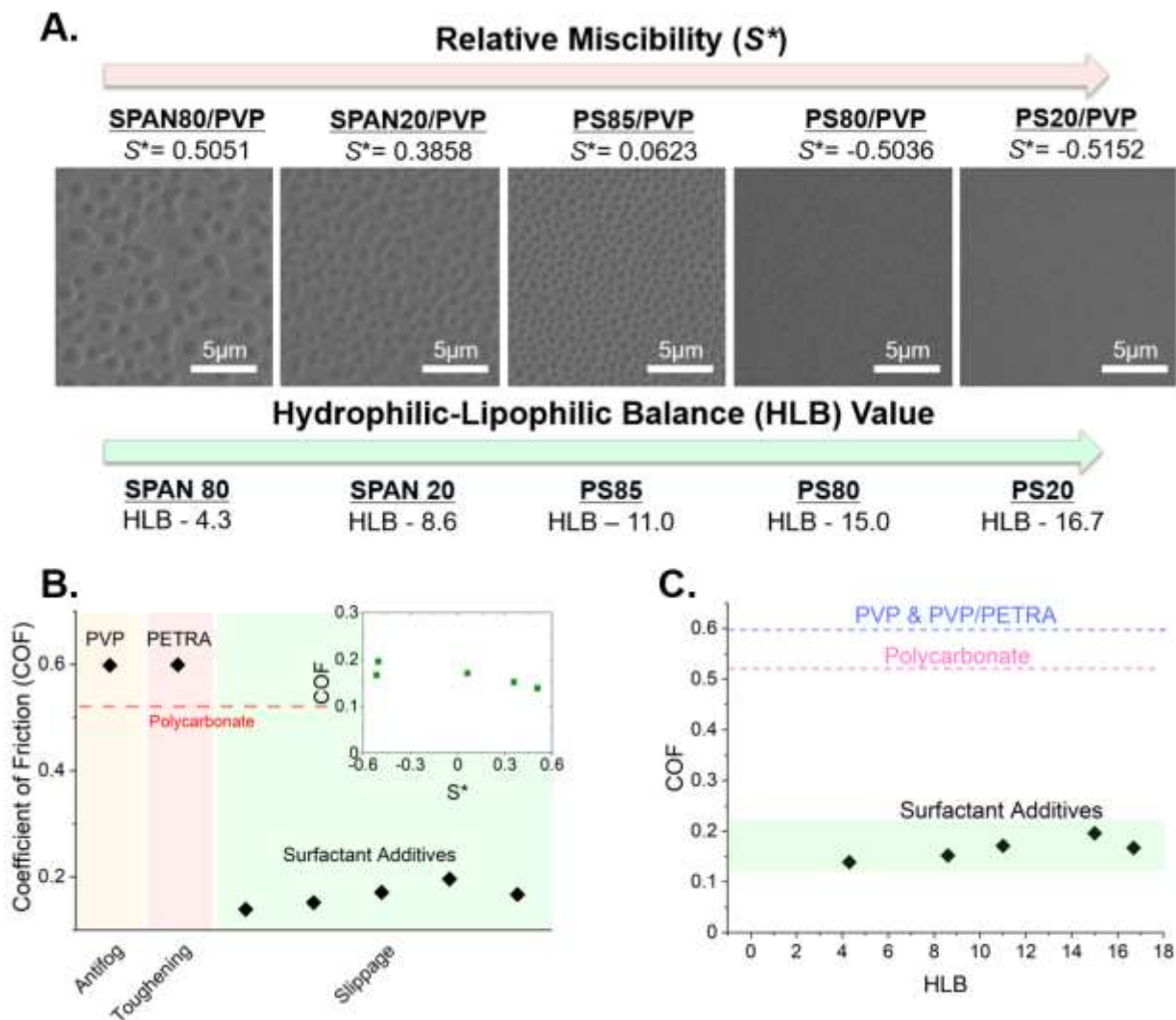


Figure 47: Miscibility and coefficient of friction for PVP-surfactant coatings.

A) Relative miscibility (S^*) of surfactant/PVP systems, and hydrophilic-lipophilic balance (HLB) value of surfactant additives. SEM micrograph insets demonstrate the surface phase separation of PVP and surfactant due to S^* . B) Effect of antifog coating toughness and slippage enhancement on the coefficient of friction (COF). Inset depicts the effect of S^* on the COF. C) The effect of HLB value on COF. Neither HLB value nor S^* have an effect on the COF.

Further, we measured the friction coefficient of PVP with different additives, demonstrating that the slip additives can significantly reduce friction. Antifogging PVP and toughened PVP/20%PETRA increase the surface friction relative to polycarbonate (red dashed line). This is consistent with the direct relationship between surface energy and friction^{374, 375}. The addition of

15% surfactant into the PVP/20%PETRA matrix induces a nearly three-fold reduction in COF. Interestingly, with regard to surfactant blended films, the COF is both independent of S^* (Figure 47B inset) and HLB value (Figure 47C). Therefore, the surfactant slip additive can be chosen on the basis of hydrophilic properties in order to maximize the antifogging properties of the coating.

5.2.3 Abrasive Wear Resistance



Figure 48: Linear Tabor abrasion setup for antifog coated polycarbonate and the microstructure of the CS-5 felt tip abrasion tip.

The abrasive wear resistance of different antifogging coatings was tested using a standard linear Tabor Abrasion apparatus with a CS-5 abrader (Figure 48). As shown in Table 5 in Materials & Methods, polycarbonate, PVP, and PVP-PETRA can be easily abraded after a few abrasion cycles with 300 grams of load. In comparison, the crosslinked PVP with 15% of PS80 was able to survive 5000 cycles of abrasion under the same condition, and even remained intact by another 1000 cycles of abrasion with a 550g load (See section 5.4.3). When including the toughening agent PETRA (e.g., 20%), the coatings can survive the same abrasion as PVP-PS80, and an additional

two sequences of 1000 abrasion cycles with increased load to 1050g. In addition, the enhanced wear resistance of PVP with 20% PETRA and 15% surfactant slip additive is independent of the choice of slip additives as shown in Table 5 in Materials & Methods. This observation agrees well with the friction coefficient of coating with different slip additives as shown in Figure 47.

Figure 49 yields the qualitative results of abraded samples which underwent sequential wear cycles of 5000 (300g), 1000 (550g), 1000 (800g), and 1000 (1050g) abrasion cycles. The visible effects of macro-abrasion can be readily seen by the eye on polycarbonate, coated polycarbonate with PVP and PVP/20% PETRA. For coatings of PVP/20%PETRA with 15% surfactant, there are no visible macroscale abrasive wear patterns. SEM micrographs in Figure 49 show samples with 2Kx and 12Kx magnification respectively and display large periodic abrasive rupture patterns. Samples containing 15% PS20 (or other surfactant) only retained minor scratching as found under both 2Kx and 12Kx SEM. This is also true for all other coatings with slip additives (see section 5.4.3). The change in surface root-mean-square (RMS) roughness after abrasion was can also be found in Figure 49. Polycarbonate, and polycarbonate coated with PVP, and PVP/PETRA yielded notably high changes in roughness after abrasion, indicating obvious abrasive wear. Meanwhile, substrates coated with PVP-PETRA with 15% surfactant yielded minimal changes in roughness after all sequentially harsh abrasion cycles.

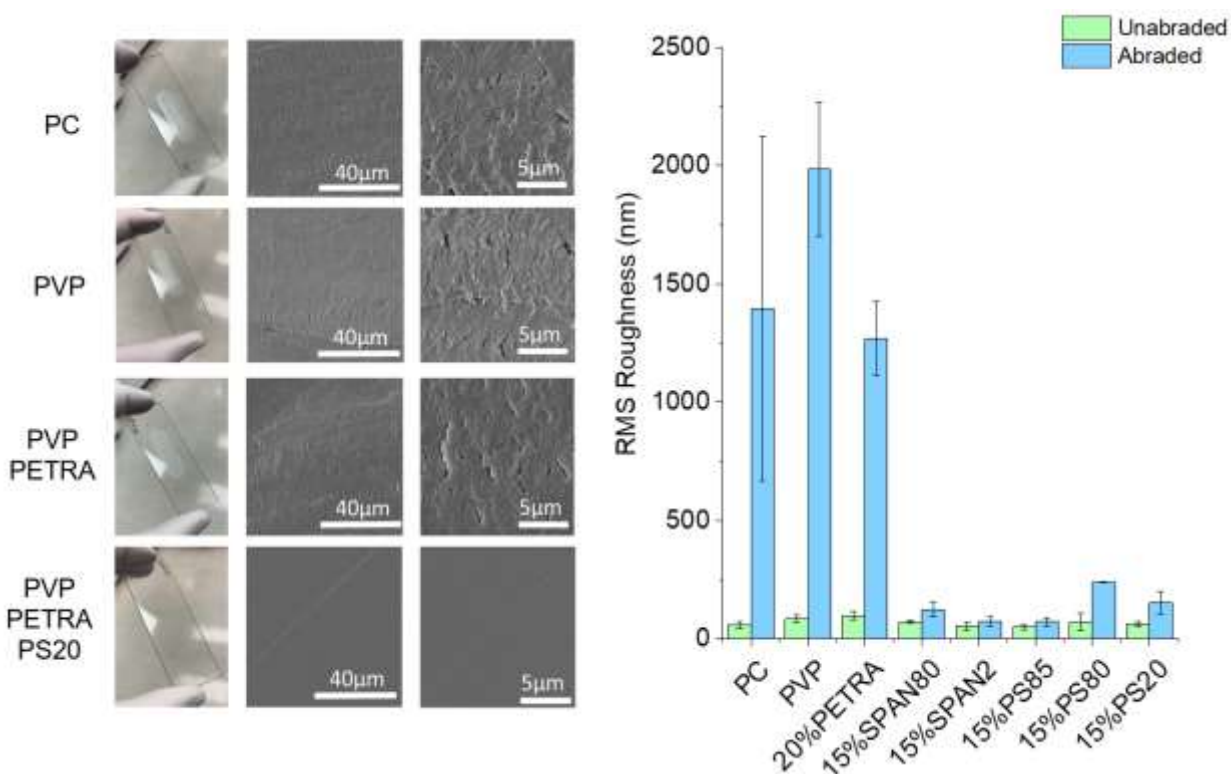


Figure 49: Polycarbonate and coated polycarbonate substrates after sequential abrasion.

CS-5 abrasion cycles (5000-300g, 1000-550g, 1000-800g, and 1000-1050g). A) Post-abrasion polycarbonate (PC), crosslinked PVP, toughened PVP-20%PETRA, and PVP-20%PETRA-15%PS20 under normal viewing, SEM at 2Kx, and 12Kx. B) Change in RMS roughness before and after abrasion.

5.2.4 Antifog Performance

For a hydrophilic antifog surface, its water contact angle must be less than 40° ²⁰. Figure 50A displays the static water contact angle of polycarbonate, PVP, and PVP with increasing concentration of PETRA. As expected, hydrophobic polycarbonate showed very minor changes in contact angle over 5min due to evaporation. PVP-based coatings are water absorbing, causing the contact angle to significantly decrease as a function of time. PVP coated polycarbonate reduces the contact angle below the 40° threshold and the addition of up to 20%PETRA did not notably change the contact angle despite its hydrophobic properties. This minimal effect on contact angle

is advantageous due to PETRA's enhancement on wear resistance. For the remainder of this text, the shorthand name for coatings containing set PVP, 20% PETRA, and 15% of variable surfactant will be labeled as PS20, PS80, PS85, SPAN20, and SPAN80. Figure 50B demonstrates the effect HLB value has on the water contact angle of the surfactant additive coatings. The addition of SPAN 80 notably increases the contact angle of the antifog coating beyond that of pure PVP. As the HLB value increases up to 16.7 for PS20, the contact angle is reduced to near that of PVP.

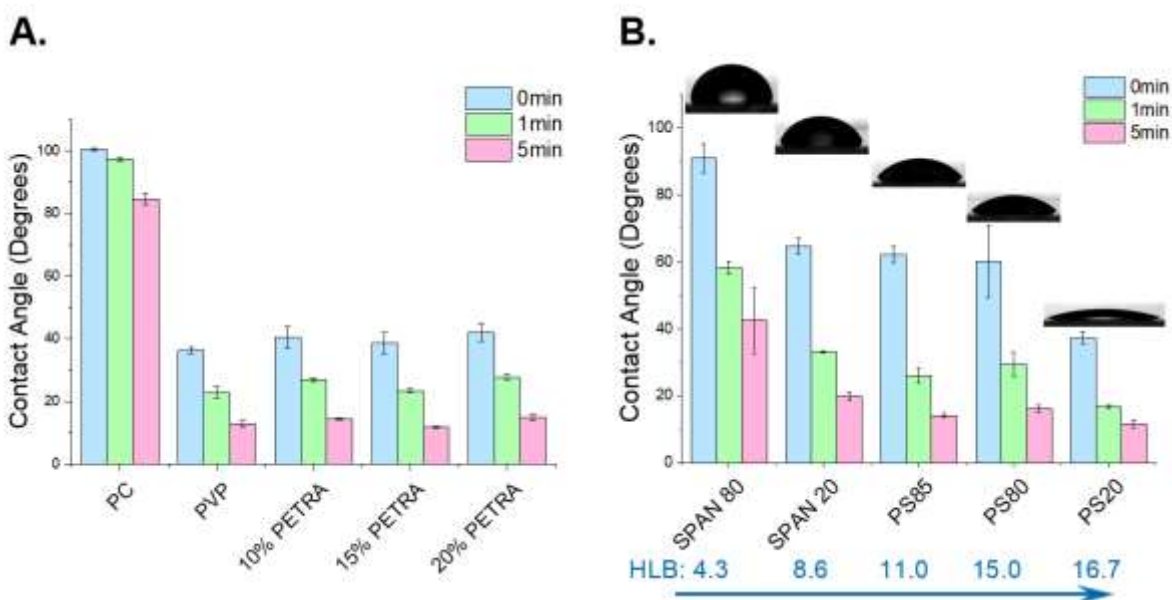


Figure 50: Water contact angle of selected coatings.

A). Water contact angle of polycarbonate (PC), PVP, and PVP with increasing mass % of PETRA. B) Contact angle of PVP/20%PETRA with 15% of varying surfactant and HLB value.

Antifog testing was conducted in a controlled humidity and surface temperature environmental chamber (see section 5.4.11). Briefly, the surface temperature of all samples were reduced to 14 ± 0.5 °C and the relative humidity maintained to $54 \pm 1\%$ (below dew point). The analysis and quantification of fogging was underwent utilizing a similar yet enhanced version of

the system created by Lee *et al.* ²⁰⁴. Our aggressive variation of their testing method for long term fogging under controlled, sustained humidity, and surface temperature has not to our knowledge been demonstrated for antifogging analysis. Unlike most other antifog testing methodologies, we demonstrate the ability to not only discriminate between antifogging and fogging, but also the ability to determine efficacy between antifogging solutions over long periods of sustained fogging conditions.

The visual results of the fogging experiment are presented in Figure 51 as an image grid containing polycarbonate, and polycarbonate with polymer films. At nearly the 8-10min point, the substrate reaches the cooling temperature and fogging begins on the polycarbonate control surface. PVP demonstrated antifogging properties up to 20 minutes, while the SPAN series having lower HLB values fogged almost immediately as a result of their high contact angles. The higher HLB value of the polysorbate slip additives all demonstrate enhanced antifogging properties. Figure 52 presents the change in image correlation function over time for each surface within the environmental chamber. Figure 52A demonstrates the performances of polycarbonate (PC), PVP, and PS20. As PC fogs after ~10min, the image distortion increases continuously for the duration of the experiment. PVP was able to prevent fogging for ~15minutes (~5minutes of antifogging) with the image correlation function factor (ICF) dropping below 0.90 until it fully fogs to ~0.50. The PS20 coating was able to fully eliminate fogging throughout the duration of the entire experiment, and without a reduction in ICF lower than 0.96. This demonstrates a significant enhancement in antifog properties when compared to crosslinked PVP alone. Figure 52B compares the performance of the PS20 coating to the more hydrophobic SPAN 80 and SPAN 20 coatings. Here it can be seen that both SPAN coatings are unable to prevent fogging, and perform worse than polycarbonate. Another differing phenomenon is the recovery of correlation factor

(transparency) for PVP, and the SPAN coatings. This can be explained as a transition from small-scale dropwise condensation to greater scale filmwise condensation, which increases transparency. Although a recovery is observed, it does not occur rapidly enough to be considered sufficiently antifogging. The polysorbate-based coatings performed exceedingly well, with some variance between as shown in Figure 52C. The differences between each polysorbate additive coating are also related to their HLB value. PS85, having the higher HLB value fogs near the 0.90 threshold, but recovers almost immediately. This rapid, but quickly dissipating fog can be visually inspected at the 10 minute panel of Figure 51. For the higher HLB value PS80 and PS20 coatings, no fogging occurred throughout the duration of the experiment, and minor differences come from image distortion from prolonged uneven water condensation. PS20 had minimal uneven condensation, no fogging, and proved to be exceedingly wear resistant.

The most optimal formulation PS20, was also examined in terms of repeated antifogging capacity. The same fogging procedure previously utilized was applied to expose the PS20 formulation for sequential fog testing. For this experiment, 20 minute fog cycles were used and an initial heating step to ensure similar levels of condensation for each cycle. Figure 52D demonstrates the ICF of the PS20 sample for the final 20th minute of each cycle. The full minute-by-minute correlation factor for each cycle can be found in Figure 61 in Materials & Methods. The dashed lines for polycarbonate and PVP indicate the correlation factors at fog onset for the 10 minute interval. These samples being monolithic in nature do not change appreciably in performance between cycles and are assumed as constants. Figure 52D shows that even after 15 cycles, the highly durable PS20 coating is able to remain antifogging with image correlation factor values above the visibility limit. It is also important to note that although this fogging procedure

is 20 minutes, it still is significantly more aggressive than human breathing cycles, and proves promising for antifogging longevity.

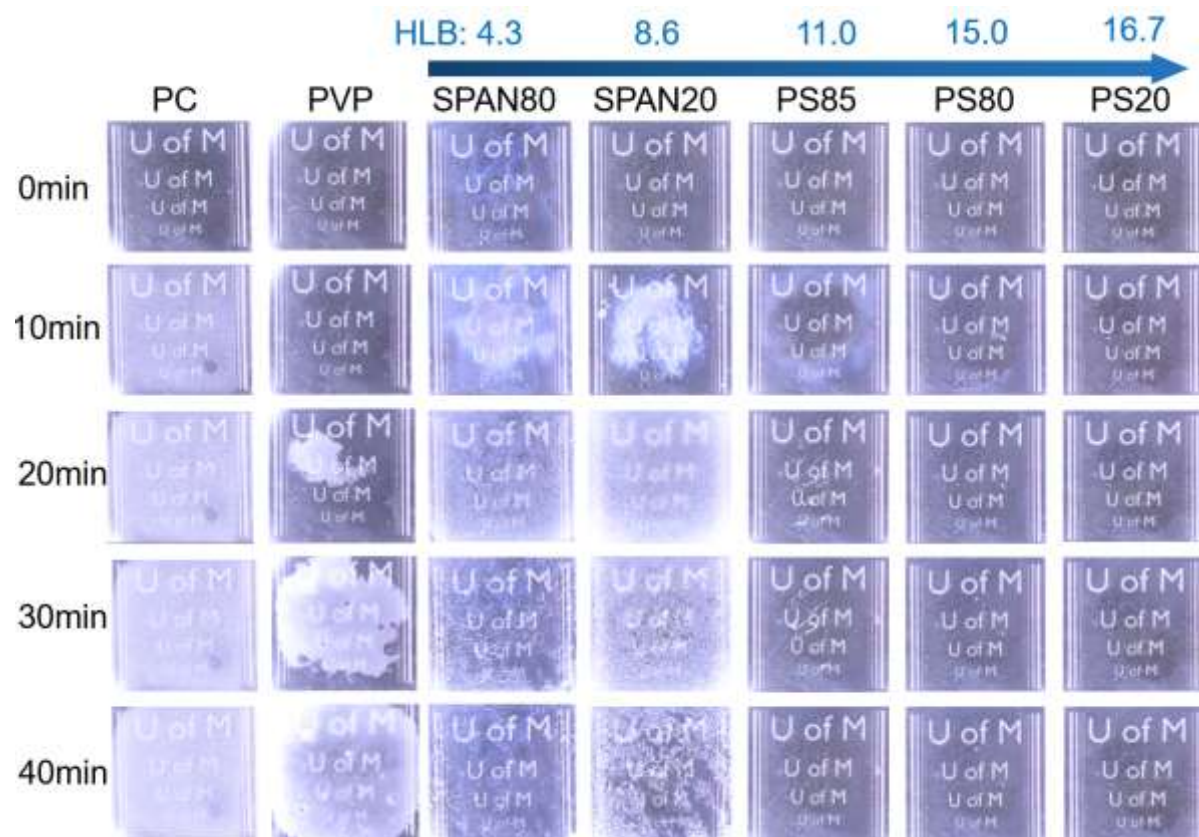


Figure 51: A) Polycarbonate and antifog coated polycarbonate within controlled environmental chamber (Rel Humidity = ~65% and substrate temperature of ~14 °C). The coatings containing surfactant also contain 20% PETRA.

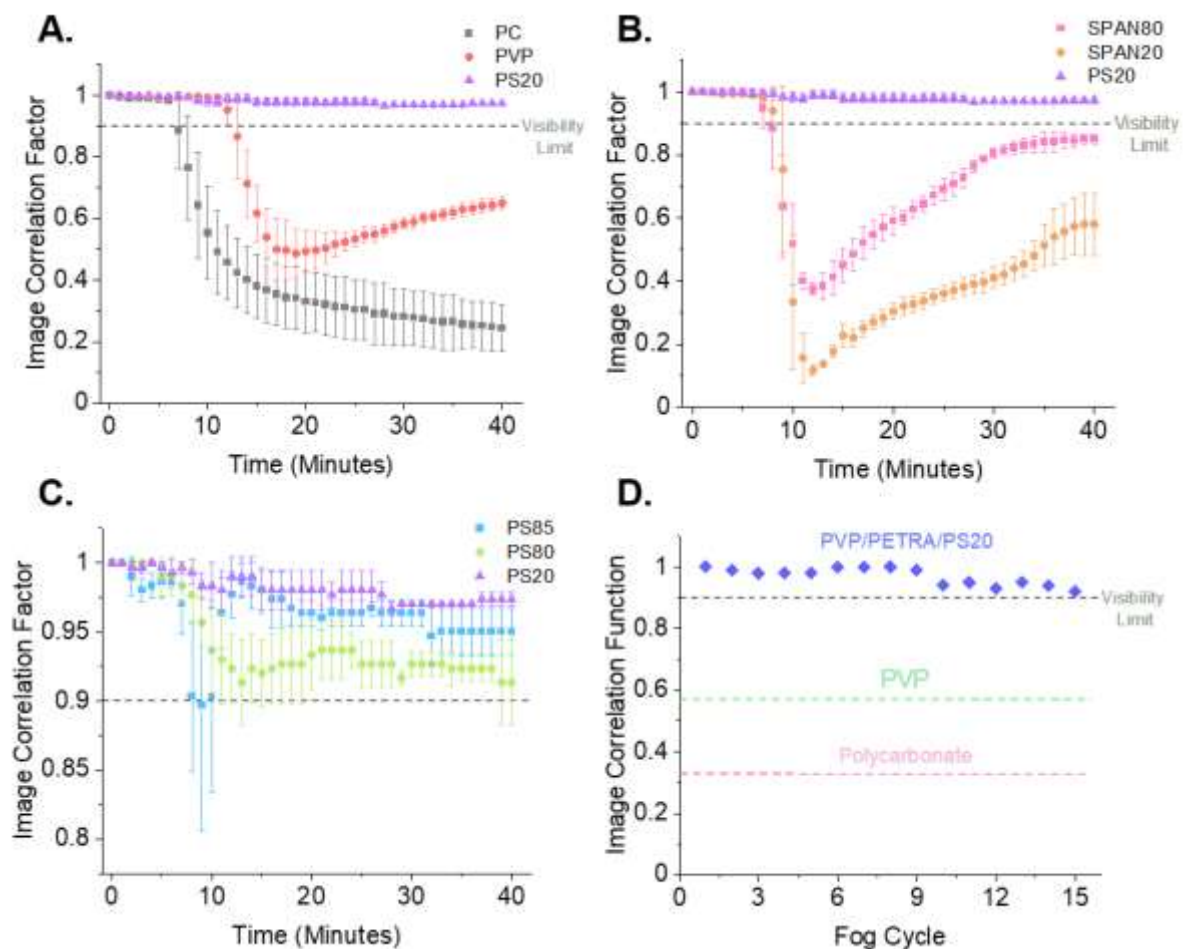


Figure 52. Image correlation factor (ICF) of surfaces.

Coatings denoted as surfactants were all in proportions of 15% and containing 20% PETRA. A) ICF of optimal PS20 compared to PVP and PC. B) ICF of optimal PS20 coating compared to PVP containing higher HLB value surfactants SPAN20 and SPAN80. C) ICF of PS20 and high HLB polysorbate additive coatings PS80 and PS85. D) ICF of PS20 for the 20th minute of 15 consecutive fogging cycles. PVP and polycarbonate reference lines indicate ICF of fogged samples for a single cycle.

5.2.5 Comparison to Commercial Anti-fogging Coatings

To validate the wear and antifog performance of the optimized PS20 antifog coating formulation, it was subjected to testing against three commonly sold temporary antifog treatments, and one commercial polyurethane-based antifog coating. Figure 54A demonstrates the antifog performance of the PS20 coating against temporary coatings such as Optix, Ops Drops, Revision

wipes, and Exxene HCF-100 commercial antifog coating. The samples were fog tested in the same manner as previously described. The tests reveal that Optix and the PS20 coatings demonstrate excellent, sustained antifogging properties despite Optix being a temporary solution. Ops Drops performed to a lesser degree while Revision appeared to yield negligible antifogging benefits. Exxene was able to delay fogging for ~20 minutes, but fogged soon after as indicated by a decline in image correlation factor. Durability analysis was also investigated in the same way as articulated in section 5.4.3. The Figure 53A finding agrees well with the durability data of surfactant additive antifog coatings. Since the temporary agents exist as free antifogging macromolecules on the surface, they impart a lubricating, or slip effect and therefore a degree of wear resistance. However unlike our coating which contains embedded slip additive within the film network, these ephemeral antifog solutions can only offer wear resistance for a short duration and can be easily removed mechanically. Exxene does not contain any additive, but is characteristically durable as a polyurethane and therefore proved to be highly wear resistant. However, the wear resistance inherently compromises the performance of antifogging. These results fall in line with our general framework of polymer antifog coatings; high surface energy coatings are generally antifogging, but are poor in abrasion resistance, while lower surface energy interfaces generally demonstrate poor antifogging, but relatively good abrasion resistance. Although Exxene is highly wear resistant, it yields comparatively high contact angles, unlike our PS20 coating. Figure 53B demonstrates the effect of water contact angle for the examined coatings and treatments. The temporary antifog solutions (Optix and Ops Drops) yielded low contact angles due to their hydrophilic properties and high degrees of freedom when compared to crosslinked coatings. Exxene yielded relatively high contact angles but offered time-dependent absorbing capabilities

over the course of 5 minutes. Unlike Exxeene, the contact angle of our PS20 durable antifog coating yielded comparatively low contact angle values.

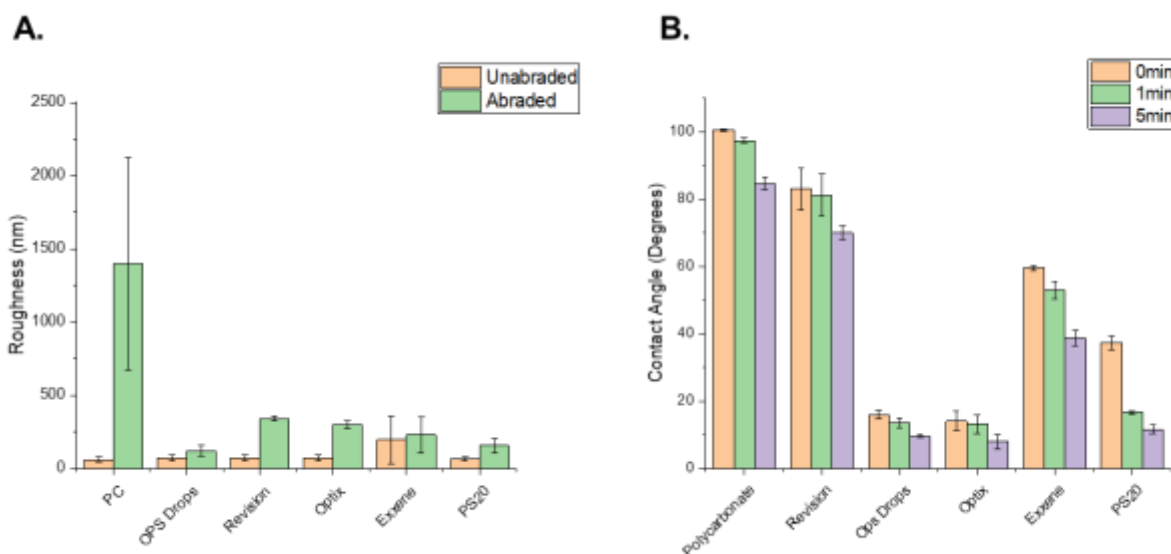


Figure 53: Abrasion resistance and contact angle data for commercial antifog coatings.

A) Roughness of antifog commercial coatings and PS20 coating after abrasion. B) Contact angle of commercial of antifog commercial coatings and PS20 coating after abrasion.

We lastly demonstrated the regenerative properties of our optimized coating to replenish the PS20 surfactant to the surface after wiping cycles. Figure 54B demonstrates the antifogging behavior of polycarbonate coated with Optix and the PS20 formulation after 500 Tabor abrasion cycles with a microfiber lens wipe. Fog testing was conducted immediately after wiping, and a day later for a separate sample. As shown in the figure, the antifog properties of PS20 slightly decline after wiping, but eventually improves as the test progresses. When fogging was conducted 1 day after the 500 microfiber wipes, the coating sustained a >90% ICF. This proved the ability of the PS20 coating to regenerate surfactant after being removed by a microfiber cloth. For comparison, we demonstrated the full depletion of antifog properties of Optix coating after 500 microfiber

wipes, which led to immediate and non-recoverable fogging. Lastly, we investigated the low contact angle longevity of our coating and plasma treated polycarbonate, Optix, Exxene, and crosslinked PVP. Over the course of 5 weeks, our coating maintained low contact angle while all other formulations experienced a gradual increase (Figure 54).

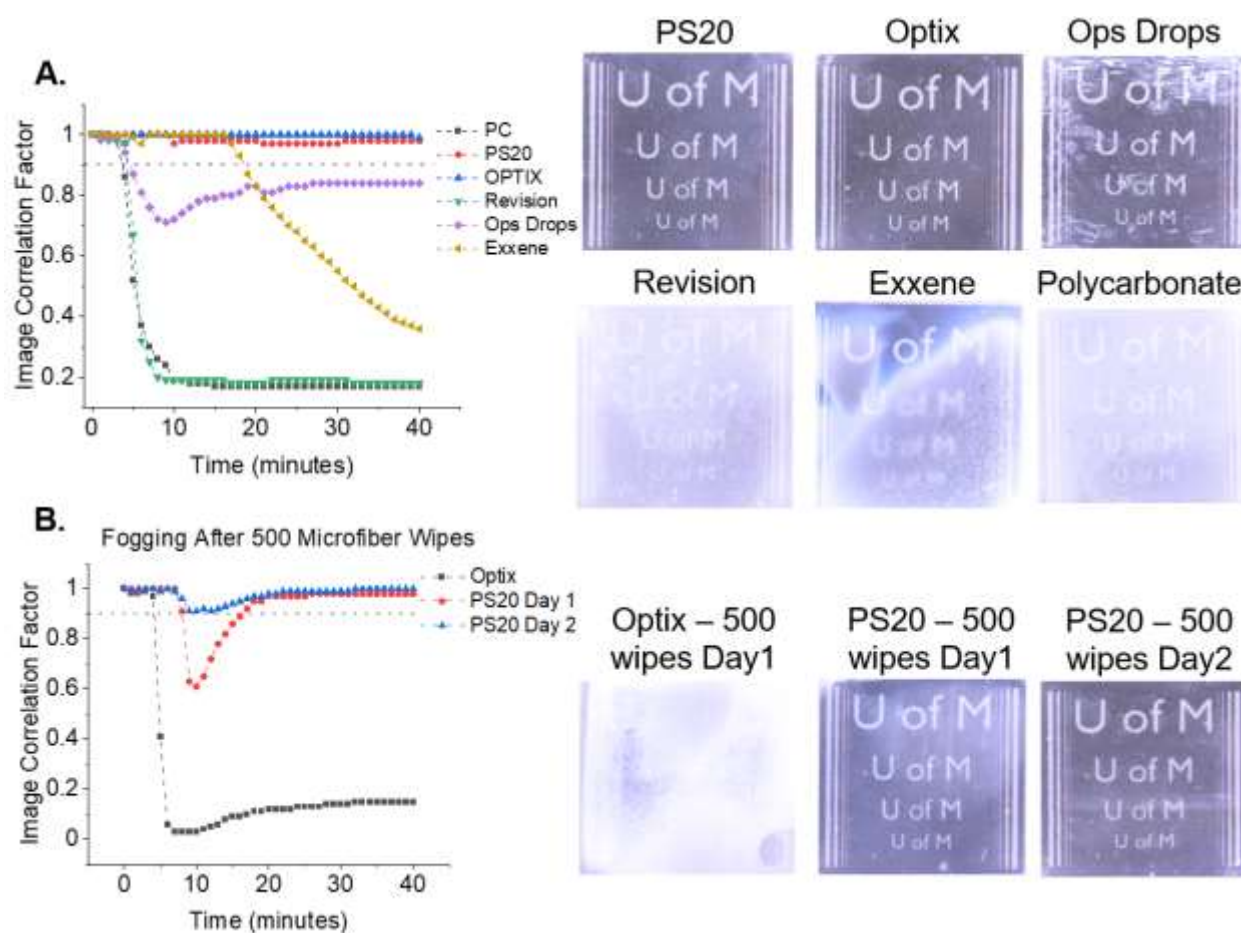


Figure 54: Comparative fogging trends between PS20 and commercial antifog coatings.

A) Comparative antifog performance of wear resistant PS20 coating, to single use Revision wipes, Optix, and Ops drops. PS20 is also compared to Exxene commercial antifog coating and polycarbonate. The upper image tile corresponds to samples exposed to fogging conditions at the 40 minute interval. B) Fog testing after Tabor Abrasion wiping each treated sample 500 times with a microfiber lens wipe. Optix was tested immediately after wiping and one PS20 coating was tested immediately after whipping while another was given 24 hrs to replenish the PS20 slip additive. The lower image tile correspond to the 10 minute interval during fogging conditions.

As we have demonstrated, the optimal slip agent must be both hydrophilic and friction reducing for durable antifog coatings. The effect of S^* was initially expected to govern the reduction of friction coefficient via phase separation to the surface³⁸⁶, but is shown to be more consequential for transparency effects (Figure 55), and relatively inconsequential to the friction coefficient. Figure 55 demonstrates the optical properties of the coated substrates. As shown, no discrimination can be made between coatings for transmittance UV-Vis alone since all curves overlap. However, UV-Vis %Haze spectra for each coating yielded notable differences and therefore these should be focused on. By simple visual inspection, differences in coating opacity could be noted. As seen in Figure 55B, S^* tends to correlate to the %Haze for each coating. Coatings containing 15% SPAN80 with an $S^* = 0.505$ (the highest S^* of our sample set) exhibited a comparatively high haze value owing to the degree of immiscibility between SPAN80 and PVP. The remaining coatings containing surfactant yielded relatively low haze values comparable to the polycarbonate base despite their differences in S^* . This was surprising for the case of SPAN 20 and PS85 where SPAN 20 had a lower %Haze than PS85. PS20 yielded the lowest haze owing to the great solubility with PVP.

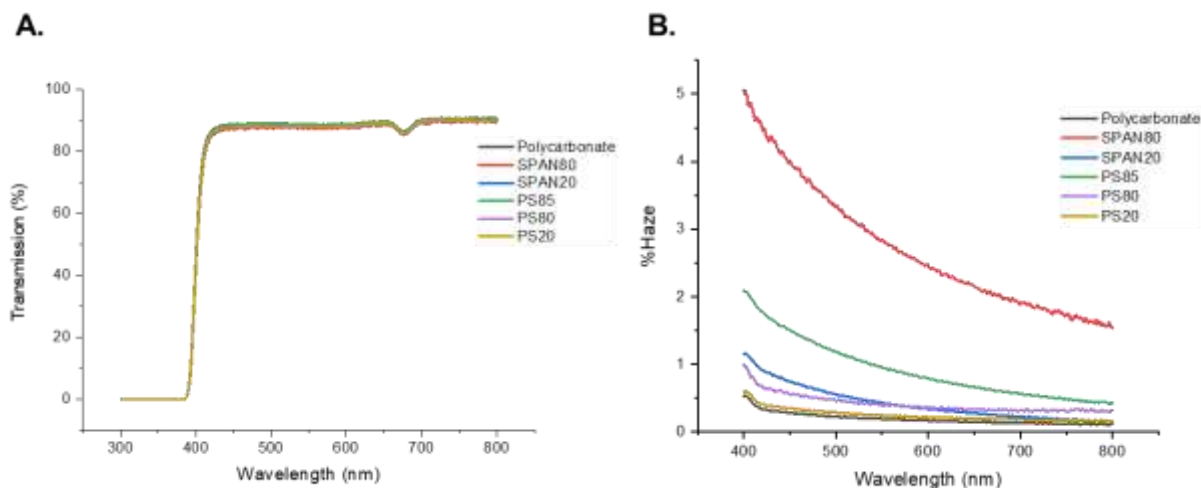


Figure 55: Transparency properties of coated samples

A) %Transmission UV-vis B) %Haze

The molecular structure of the surfactant slip additives is key for the surface migration in crosslinked PVP. The bipolar, asymmetric nature of the chosen surfactants may have facilitated surface migration despite the S^* value. This allowed for the usage of the surfactant with the greatest HLB value of 16.7 (PS20) and lowest value of S^* , for optimal surface wear properties and antifogging behavior. To test this claim, we conducted a simple test of substituting the surfactant with a more symmetric amphiphilic oligomer, polyethylene glycol 400 (PEG400). However after ~10 CS-5 cycles, the coating abraded indicating that a symmetric hydrophilic slip additive does not readily migrate to the surface, nor facilitate wear resistance. Lastly, the broad applicability of hydrophilic PS20 slip additive to crosslinked polymers was conducted by mixing it into a crosslinked PEGDA coating. Although not to the same extent as PVP, the simple addition of PS20 to the PEGDA network enhanced both the wear resistance and antifog properties.

5.3 Conclusion

In this work, we have engineered a set of abrasion resistant antifog coatings that can be easily applied onto a variety of plastic substrates with varying geometry. Based on a classic wear model of polymers, coating toughening agents and low-friction slip additives were introduced to conventional antifog polymer PVP, which enhanced the abrasion resistance of coating by approximately 13 times. Further, HLB value and Hansen solubility parameters (S^*) were investigated as criterion for optimizing antifogging abilities and friction reduction. We illustrated that friction reduction is independent with HLB and S^* , while the optical clarity and the antifog ability can be improved by lower S^* and higher HLB values, respectively. Our optimized PVP antifog coating demonstrates continuous antifogging performance, strong wear resistance, and outperformed commercially available antifog coatings in terms of antifog performance, wear resistance, and yielded good cyclical performance. This simple design and fabrication with the incorporation of a toughening agent and slip additives to existing hydrophilic antifog polymers offers a new strategy for simultaneously enhancing the antifog properties and wear resistance of the coatings.

5.4 Materials and Methods

5.4.1 Antifog Coating Fabrication

Solution Parameters

A 0.0265 g/ml solution of 1300KDa Polyvinyl Pyrrolidone (PVP) (Purchased from Sigma Aldrich) and 0.001 g/ml benzophenone (purchased from Sigma Aldrich) was made by dissolving the polymer in a solution containing 1-Propanol (Purchased from Fischer Scientific), distilled water, and 15% Hydrogen peroxide (Purchased from Fischer). The respective volume ratio of the solvents is 93.1:0.029:0.040. Surfactants and cross-linker were later dissolved in solutions of 1-propanol

in order to dilute and add to the PVP solution in constant volumes and concentrations. Polysorbate 20 (Purchased from Thermo Fisher Scientific), Polysorbate 80 (Purchased from SAFC), Polysorbate 85 (Purchased from Sigma Aldrich), Span 20 (Purchased from Sigma Aldrich), or Span 80 (Purchased from TCI) were dissolved in 1-Propanol in varying concentrations. Pentaerythritol tetraacrylate (Purchased from Sigma Aldrich) was also dissolved in 1-Propanol in varying concentrations. Constant volume of PETRA and surfactant solutions were added to the solvent mixture to achieve a volume ratio of 89.5 1-Propanol: 0.027 DI water: 0.039 15% H₂O₂: 0.019 PETRA/1-Propanol solution: 0.019 Surfactant/1-Propanol Solution (PVP now at 0.0254mg/ml). All contents were stirred in a glass septa-jar until fully dissolved (>2hrs). Concentrations of PETRA or Surfactant are with respect to the mass of PVP.

Coating Fabrication

Impact resistant polycarbonate strips (Purchased from McMaster-Carr) of 1 inch width and 1/16 inch thickness were cut to 4 inch slides for testing. Polycarbonate strips were first cleaned with isopropyl alcohol and blown dry before exposure to 30W oxygen plasma (Harrik Plasma Cleaner PDC-001) for 10 minutes. Once plasma treated, the samples were coated using a home-built automated spray coating apparatus. The plasma treated samples were placed at a distance of 20cm from the spray gun. The spray gun (HVLP mini touch up ATD-6903) parameters were set to a linear speed of ~20cm/s, 2 spray passes, and spray pressure of 20 Psi. The solutions were dispensed into the spray reservoir, and sprayed onto the plasma treated polycarbonate. This allowed for coatings of consistent thickness and roughness to be deposited. Immediately after, the coatings were subjected to UVA (UVP 100W Longwave Mercury Spot Lamp) and UVC (UVP XX-40S Bench Lamp 2.6mW/cm²) at a distance of 12cm for 10 minutes.

5.4.2 Dynamic Mechanical Analysis (DMA)

Sample Preparation

The thin polymer strips were fabricated by developing a 0.053g/ml solution of PVP in 1-propanol, water, and 30% H₂O₂ with volume ratios of 0.931:0.029:0.040 respectively. PETRA/1-Propanol solutions were also developed and added to the PVP solution with a volume of 2ml. The PETRA/1-Propanol solutions varied depending on the desired mass ratio of PETRA/PVP. 5mL of the final PVP-based solutions was dispensed into a silicone mold with dimensions of 76.2x50.8x1.2mm and allowed to dry for 2 days. The dried film and mold were then placed under UVC for 30 minutes (to ensure that the strip is cured sufficiently). Once cured, the polymer sheet was cut to ~7.5-8mm widths and lengths of ~76mm. The cut samples were immediately sandwiched between two glass plates and allowed to uniformly dry completely for >10hrs in relative humidity <20%.

DMA Testing Specifications

An RSA-G2 DMA (TA Instruments) was utilized to conduct tensile tests on PVP and PVP/PETRA thin strips. Each sample was secured with untextured flat grips, with spacing of 35mm. A strain rate of 0.035µm/s was used for each sample. The relative humidity of the testing room was maintained at 20-22%.

5.4.3 Tabor Abrasion

Abrasion Testing

All substrates were abrasion tested with a Taber Linear abrader Model 5750 with a stroke length of 1 inch and frequency of 60 cycles/minute. 32x32 mm samples were abraded with a stroke length

of 0.5 inches. A CS-5 abrasion tip was used for each test and was purchased from the Taber manufacturer. Between each test, the CS-5 was washed with IPA to remove potential debris or surfactant. The number of cycles varied between ~5 and 5000 depending on the test. The weight varied between 300g and 1050g.

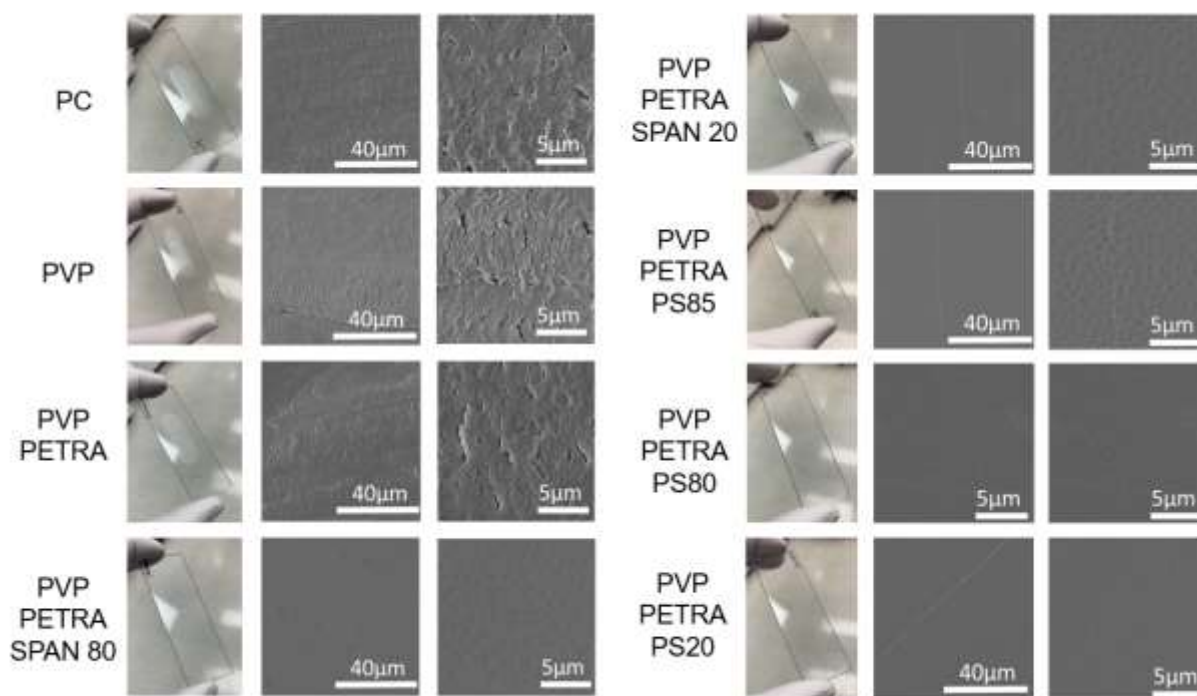


Figure 56: Post abrasion substrates after all abrasion cycles outlined in Table 9. 20% PETRA and 15% surfactant was added to the coatings indicated.

Table 5: List of experiments demonstrating material and additive effects on sequential abrasion resistance

Resistance to CS-5 Tabor Abrasion under increasing mass. A ✓ indicates the absence of visible abrasion after abrasion cycles and ✗ indicates the presence of obvious abrasion. Each cycles were done in succession per sample.

PVP Coating Composition		Abrasion Cycle and Qualitative Result			
%PETR A	Slip Additive	5000 Cycles (300g)	1000 Cycles (550g)	1000 Cycles (800g)	1000 Cycles (1050g)
0%	10% PS80	✗	✗	✗	✗
	15% PS80	✓	✓	✗	✗
	20% PS80	✓	✓	✗	✗
10%	10% PS80	✗	✗	✗	✗
	15% PS80	✓	✓	✓	✓
	20% PS80	✓	✓	✓	✓
15%	10% PS80	✓	✗	✗	✗
	15% PS80	✓	✓	✓	✓
	20% PS80	✓	✓	✓	✓
20%	10% PS80	✓	✓	✓	✓
	15% PS80	✓	✓	✓	✓
	20% PS80	✓	✓	✓	✓
20%	10% PS20	✓	✓	✓	✓
	15% PS20	✓	✓	✓	✓
	20% PS20	✓	✓	✓	✓
20%	10% SPAN80	✓	✓	✓	✓
	15% SPAN80	✓	✓	✓	✓

	20% SPAN80	✓	✓	✓	✓
20%	15% SPAN20	✓	✓	✓	✓
20%	15% PS85	✓	✓	✓	✓
	Polycarbonate	✗	✗	✗	✗
	Crosslinked PVP	✗	✗	✗	✗
	Crosslinked PVP and 20% PETRA	✗	✗	✗	✗

Controlled Wiping Simulation

To simulate the effect of normal, everyday wiping, a common microfiber lens wipe was attached to a 1x1 inch block of soft foam and mounted to the raster arm of the Taber Abrader. The samples were mounted to the apparatus in the same fashion as prior and wiped with the custom lens wipe fixture with a stroke length of 1 inch and frequency of 60 cycles/min. If 32x32 mm samples were wiped, 1 inch polycarbonate spacers were placed on either side of the sample to allow full range of motion of the raster arm.

5.4.4 Scanning Electron Microscopy

Scanning electron micrographs were obtained with a Tescan MIRA3 FEGSEM. A beam intensity of 7, accelerating voltage of 7kV, and working distance between 9-11mm was used for each micrograph.

5.4.5 Dynamic Friction Coefficient

The steady state dynamic friction coefficient was measured with a Shimpo model FG-7005 force gauge. The force gauge was attached horizontally to a motorized stage which traveled at a

controlled velocity of 74 $\mu\text{m/s}$. An aluminum block with dimensions of 44x50x24mm and with a standard nonwoven cleanroom wipe (Texwipe TX606) adhered to the 44x24mm face was pushed across each surface with the force gauge. The substrates were secured onto a level adjacent stage statically with double sided tape. Force data was taken every 0.2 seconds and was pushed for 60 seconds.

5.4.6 Linear Stylus Profilometry

Surface roughness was measured via a Dektak 6M stylus profilometer (courtesy of Lurie Nanofabrication Facility). A 5mg stylus force, a segment length of 2000 μm , and a raster time of 120 seconds was used for each measurement. At least 4 spatially separated segments were measured for each sample (abraded and unabraded).

5.4.7 FTIR

Fourier transform infrared spectroscopy (FTIR) was conducted by a Thermo Scientific Nicolet 6700 FTIR spectrometer with an ATR (diamond crystal) and a frequency range of 400-4,000 cm^{-1} . Antifog samples were coated on polycarbonate and analyzed as a function of UV time. To confirm the crosslinking of adjacent pyrrolidone groups within PVP and within the presence of H_2O_2 , the C=O group was tracked for samples with varying UV time. Figure 57A demonstrates that a 10 minute UV time – the UV time utilized for our experiments – was sufficient to produce crosslinking of adjacent PVP. To investigate the self-reacting nature of the toughening agent, pure PETRA solutions were made to analyze the curing properties. The parameters consisted 0.090g/ml in a 0.091:0.900 mixture of 30% hydrogen peroxide and 1-Propanol. The PETRA solution was sprayed onto small polycarbonate strips (1/2 x 1 inch) and cured under UV with varying time. Figure 57B displays a segment of an FTIR spectra for pure PETRA on polycarbonate. The peak at

820 cm^{-1} pertaining to acrylate functional groups shows a decrease with increasing UV time³⁸⁷. This indicates that PETRA oligomers self-crosslink in the presence of hydrogen peroxide and UV irradiation. After 10 minutes, there is a notable decrease of the acrylate peak which indicates crosslinking, and the formation of a partial Si-IPN.

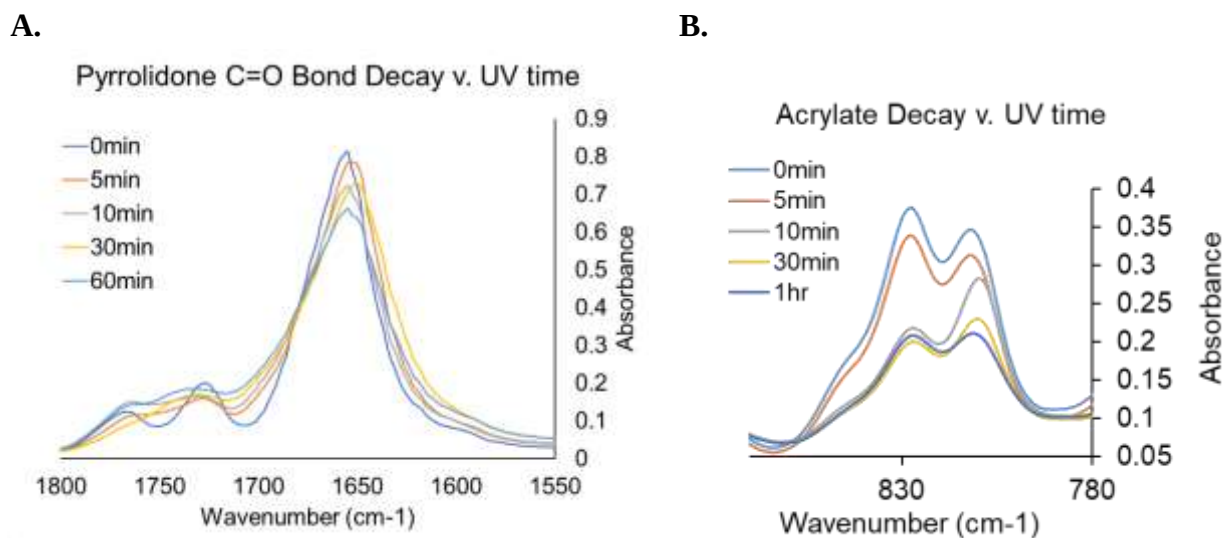


Figure 57: FTIR spectra for PETRA with UV exposure

A) Change in C=O bond for a PVP antifog coated polycarbonate as a function of UVC exposure time. B) Change in acrylate peak of pure PETRA coated polycarbonate with increasing UVC exposure.

5.4.8 Dynamic Mechanical Analysis (DMA)

The thin polymer strips were fabricated by developing a 0.053g/ml solution of PVP in 1-propanol, water, and 30% H_2O_2 with volume ratios of 0.931:0.029:0.040 respectively. PETRA/1-Propanol solutions were also developed and added to the PVP solution with a volume of 2ml. The PETRA/1-Propanol solutions varied depending on the desired mass ratio of PETRA/PVP. 5mL of the final PVP-based solutions was dispensed into a silicone mold with dimensions of 76.2x50.8x1.2mm

and allowed to dry for 2 days. The dried film and mold were then placed under UVC for 30 minutes (to ensure that the strip is cured sufficiently). Once cured, the polymer sheet was cut to ~7.5-8mm widths and lengths of ~76mm. The cut samples were immediately sandwiched between two glass plates and allowed to uniformly dry completely for >10hrs in relative humidity <20%. Figure 45 depicts the raw stress-strain data for each coating formulation. Per formulation, each curve represents a tested sample. What can be observed, is that PVP alone exhibits brittle fracture under an applied strain. However upon addition of only 10% PETRA, we see an immediate increase in ductility as demonstrated by the irregular stress-strain curves as well as visual observation of tearing rather than brittle fracture. The phenomenon continues until 50% PETRA is added where there is a transition from ductile, back to brittle fracture.

5.4.9 Hansen Solubility Parameters:

Hansen solubility parameters were measured by dissolving a small amount (3-5 drops) of surfactant into 10ml of solvent. The solvents consisted of DI water, Methanol (Fisher Scientific), Ethanol (Fisher Scientific), 1-Propanol (Fisher Scientific), 2-Propanol (Fisher Scientific), Dimethyl Formamide (Fisher Scientific), 1-Hexanol (Sigma-Aldrich), Dimethyl Sulfoxide (Fisher Scientific), Ethyl Acetate (Sigma-Aldrich), Toluene (Fisher Scientific), Benzene (Fisher Scientific), Cyclohexane (Acros Organics), Decane (Sigma-Aldrich), Pentane (Fisher Scientific), n-Heptane (Acros Organics), O-Xylene (Acros Organics), Perfluorohexane (Alfa Aesar), Formamide (Sigma-Aldrich), Acetonitrile (Fisher Scientific), Acetic Acid, (Fisher Scientific) Propylene Carbonate (Alfa Aesar), Methyl Acetate (Acros Organics), Chloroform (Fisher Scientific), and 30% Hydrogen Peroxide (Fisher Scientific). Once added to the solvent, the solutions were mixed briefly in a vortexer (Vortex-Genie 2 - Scientific Industries, Inc). The solutions were visually inspected to determine their solubility within each solvent and noted. The

data (either miscible or immiscible) was plugged into the HSPiP version 5.3.09 and Hansen solubility parameters and sphere radii were generated.

Table 6: Experimental Hansen Solubility Parameter data for surfactants.

Solvent	PS20	PS80	PS85	SPAN20	SPAN80
Water	yes	Yes	yes	no	no
Methanol	yes	yes	yes	yes	no
Ethanol	yes	yes	yes	yes	yes
1-Propanol	yes	yes	yes	yes	yes
2-Propanol	yes	yes	yes	yes	yes
DMF	yes	yes	yes	yes	yes
1-Hexanol	yes	yes	yes	yes	yes
DMSO	yes	yes	yes	yes	no
Ethyl Acetate	yes	yes	yes	no	no
Toluene	no	yes	no	yes	yes
Benzene	yes	yes	no	yes	yes
Cyclohexane	no	no	yes	yes	yes
Decane	no	no	yes	yes	yes
Pentane	no	no	yes	yes	yes
n-Heptane	no	no	yes	yes	yes
O-Xylene	no	yes	no	yes	yes
Perfluorohexane	no	no	no	no	no
Formamide	yes	yes	no	no	no
Acetonitrile	yes	yes	no	no	no
Glacial Acetic Acid	yes	yes	yes	yes	yes
Propylene Carbonate	yes	yes	no	no	no
Methyl Acetate	yes	yes	yes	no	no
Chloroform	yes	yes	yes	no	no
30% H2O2	yes	yes	no	no	no

Table 7: Hansen solubility parameters calculated by HSPiP software from data of Table S1. *PVP parameters were taken from the HSPiP database.

	δD	δP	δH	R
PS20	17.06 $\pm$ 1.4	7.93 $\pm$ 1.2	19.3 $\pm$ 0.7	18.9
PS80	16.76 $\pm$ 0.65	7.81 $\pm$ 1.25	19.22 $\pm$ 0.65	18.9
PS85	13.57 $\pm$ 0.65	3.64 $\pm$ 1.25	14.17 $\pm$ 0.95	15.7
SPAN20	13.15 $\pm$ 2.6	0.10 $\pm$ 1.35	12.6 $\pm$ 1.35	14.6
SPAN80	13.67 $\pm$ 1.8	0.09 $\pm$ 2.35	9.64 $\pm$ 1.2	11.7
PVP*	18.1	10	18	8

Table 8: Select Surfactants and corresponding HLB values and S*

Slip Additive	Hydrophilic-Lipophilic Balance (HLB)	Miscibility Parameter (S*)
PS20	16.7	-0.515
PS80	15.0	-0.504
PS85	11.0	0.062
SPAN20	8.6	0.357
SPAN80	4.3	0.506

5.4.10 Friction Coefficient

The steady state dynamic friction coefficient was measured with a Shimpo model FG-7005 force gauge. The force gauge was attached horizontally to a motorized stage which traveled at a controlled velocity of 74 μ m/s. An aluminum block with dimensions of 44x50x24mm and with a standard nonwoven cleanroom wipe (Texwipe TX606) adhered to the 44x24mm face was pushed

across each surface with the force gauge. The substrates were secured onto a level adjacent stage statically with double sided tape. Force data was taken every 0.2 seconds and was pushed for 60 seconds. Figure 58 depicts the raw data of relative friction coefficients for each substrate and Table 5 displays the average dynamic friction coefficient for the plateaued region.

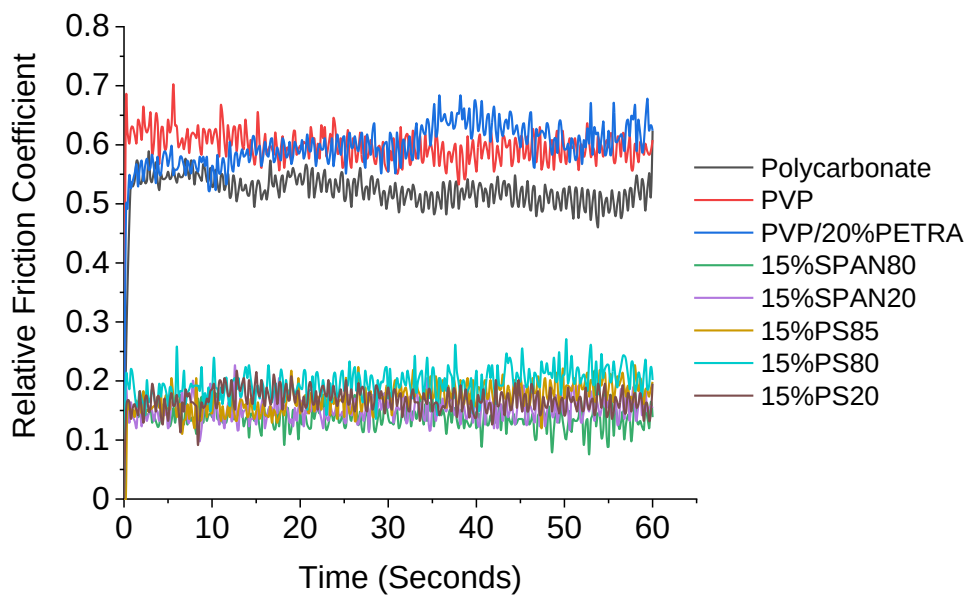


Figure 58: Relative dynamic interfacial friction coefficients

Samples include polycarbonate, PVP, PVP/20%PETRA, and PVP/20% PETRA with 15% surfactant.

Table 9: Average steady-state friction coefficients of polycarbonate and antifog coated

Surface	Average Friction Coefficient
Polycarbonate	0.522
PVP	0.598
PVP/20%PETRA	0.599
15% SPAN80	0.139
15% SPAN20	0.152
15% PS85	0.171
15% PS80	0.196
15% PS20	0.167

5.4.11 Experimental structure for fogging test

Experiments were conducted in a stainless-steel chamber (Figure 59A) with an observation window (the outer diameter of 6 inches and the inner diameter of 4 inches) (Figure 59B). The coated polycarbonate plates (35 mm x 35 mm x 1 mm) (Figure 59C) were held with a cylindrical glass (the diameter of 1.5 inches and the height of 0.5 inches) (Figure 59D) and an aluminum plate (32 mm x 32 mm, with text design) (Figure 59E) by a holder (Figure 59F) with a square Teflon window (the inner dimension of 25 mm and outer dimension of 47 mm) fixed on the cooling platform with screws. The aluminum plates were mounted onto a copper pillar (20 mm x 20 mm) (Figure 59G) using fast drying silver paint (Ted Pella, Inc., USA). Liquid cooling channels (Figure 59H) were built into the opposite end of the copper pillar with ethylene glycol (Arcos Organics, USA) pumped through by a MS immersion thermostat (Lauda, Germany) and cooled by 1/2 HP glycol chiller (Penguin Chillers, USA). The temperature is controlled by the circulator in the

precision of ± 0.1 °C. The entire portion of copper was insulated from the environment with a Teflon enclosure (the diameter of 11.5 cm) (Figure 59I) and was mounted to the test chamber. A type-T thermocouple (OMEGATM, USA) was used to measure the temperature of the sample surface. A temperature/humidity gauge iTHX-W3-2 (OMEGATM, USA) (Figure 59J) was mounted on the top of the chamber to obtain the humidity/temperature readings. A self-made humidity-controlled box (Figure 59K) was linked with the top of the chamber to blow humid air into the chamber. The other side of the box was connected to an air supply with an adjustable valve. The dry air from the air supply was blown to the box which storage water to gain humidity and then to the chamber to control the humidity. The air went out of the chamber through the air outlet (Figure 59L) at the bottom of the chamber.

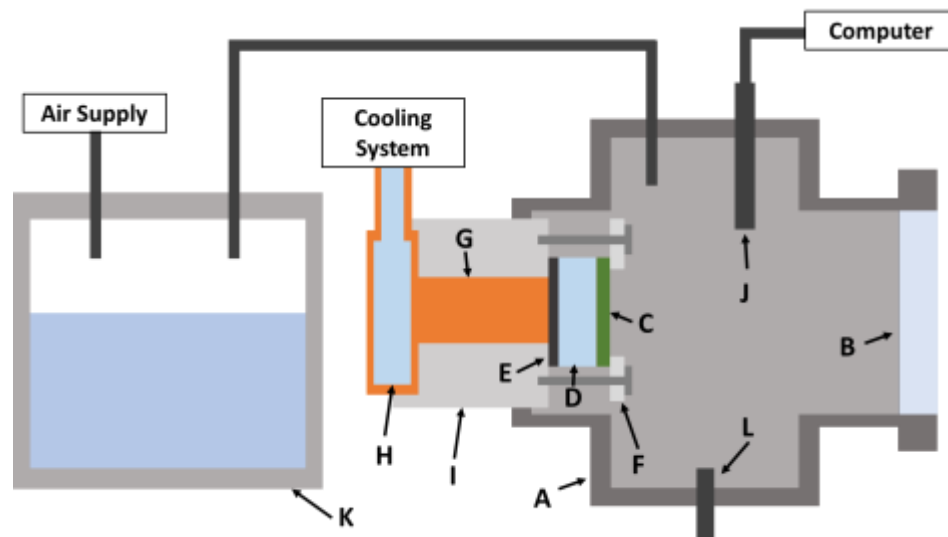


Figure 59: Schematic diagram of the test chamber.

(A) the test chamber (B) observation window (C) sample (D) cylindrical glass (E) aluminum plate with text (F) Teflon window and screws (G) copper pillar (H) cooling channel (I) Teflon enclosure (J) humidity and temperature gauge (K) humidity controlling box (L) air outlet.

Experimental setup for fogging test

The circulator was first held at the temperature of 40.0 ± 0.1 °C to control the surface temperature of the sample at 28 ± 1 °C to prevent any fogging before the test. After the humidity was controlled at 65 ± 1 % relative humidity and the temperature was 22 ± 2 °C, the target value of the circulator was changed to 5.0 ± 0.1 °C (surface temperature of the sample would be 14 ± 0.5 °C) and the experiment started. The fogging evolution on the sample was captured by a single-lens camera D3200 (Nikon, Japan) with a 150 mm f/2.8 Macro 1:1 lens (Irix, Switzerland) and a 28 mm long spacer (Photo Plus, USA) at the rate of 1 frame per minute controlled by RC-N2II ShutterBoss II timer remote switch (Vello, USA) with a light source VM-160 LED macro ring light (Bolt, USA). The experiment duration was 45 min for normal fogging tests and 20 min for the cyclic fogging test (15 cycles in total). The detailed humidity and temperature change during the experiment are listed in the supplemental materials. A reference image was placed behind the substrate, and between them, a 1 inch glass spacer to enhance the effect of image distortion from fog. Images were captured every minute, for 40 minutes. The reference image provides the ability to visually display fogging properties over time and is used to measure image distortion caused by fogging. Image distortion was analyzed with an open source ImageJ plugin utilized and developed by Lee *et al* ²⁰⁴.

Humidity and temperature change during the experiments

The humidity and temperature change are as shown in Figure 60, where the humidity changed from 65 ± 1 % to 54 ± 1 % and stayed stable from about 10 minutes after the experiments began. The sample-to-sample variation of different test samples and different coatings is within ± 1 %, showing the consistency of the experimental manipulation. On the other hand, the temperature changed from 29 °C to 14 °C and maintained stable from about 10 minutes, which is

similar to the trend of the humidity. Near 10 minutes, the temperature became lower than 15 °C which is estimated to be near the dew point of the system (estimated under the condition of 65 % relative humidity and 22 °C temperature), leading to the beginning of the fogging which can be observed from the experiments.

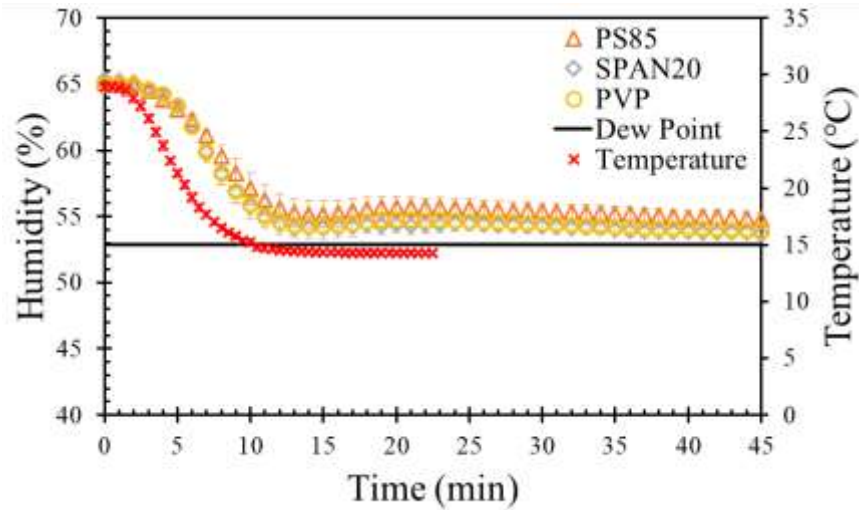


Figure 60: The humidity and temperature evolution during the experiments.

The red cross denotes the temperature corresponding to the secondary y-axis. The hollow orange triangle, the hollow grey diamond, the hollow yellow circle respectively denote the humidity records during the fogging tests of PS 85 coating, SPAN 20 coating, and PVP coating. All the error bars are obtained from the standard deviations from triplet trials.

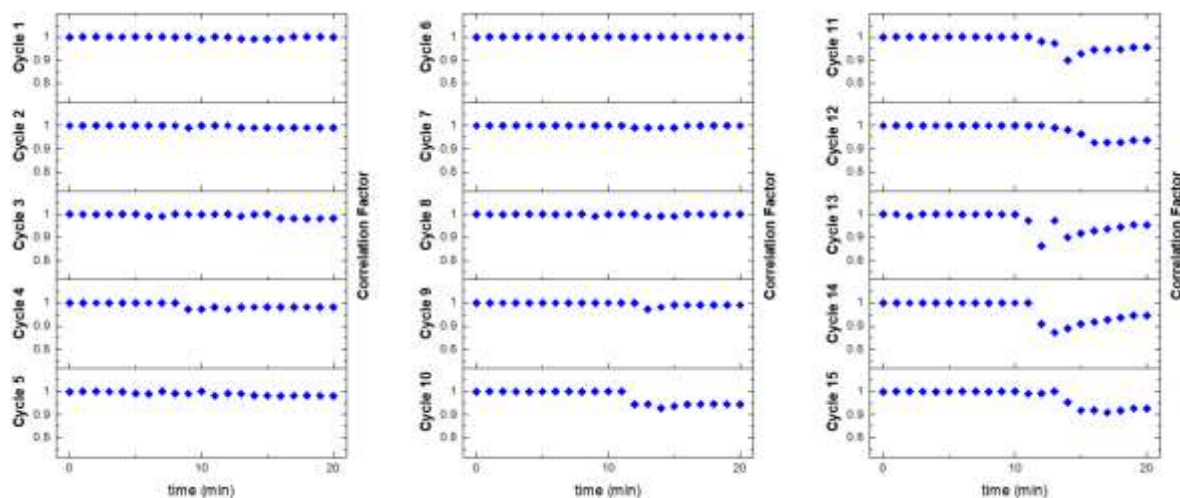
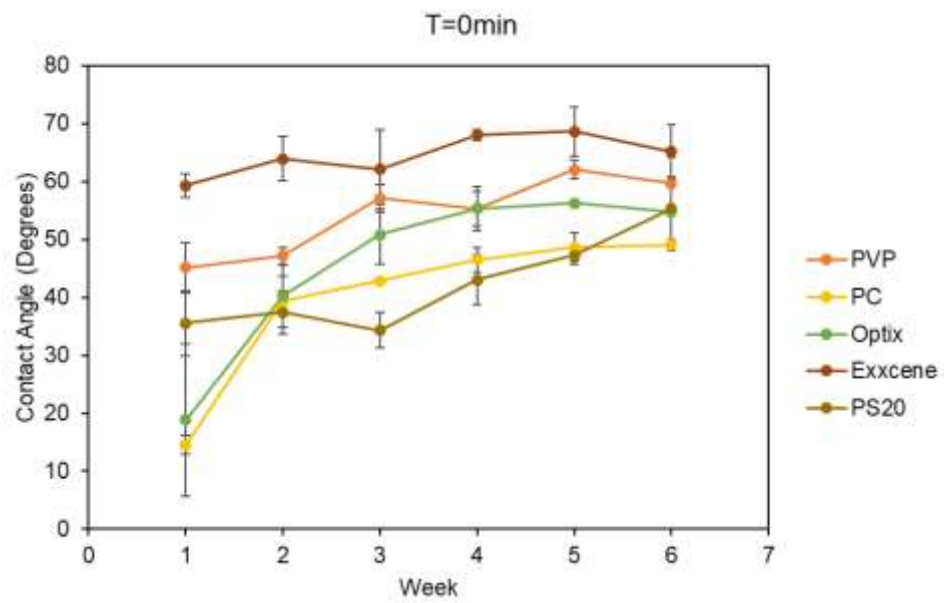


Figure 61: Image correlation factor plots for successive, cyclical (15) fogging tests.

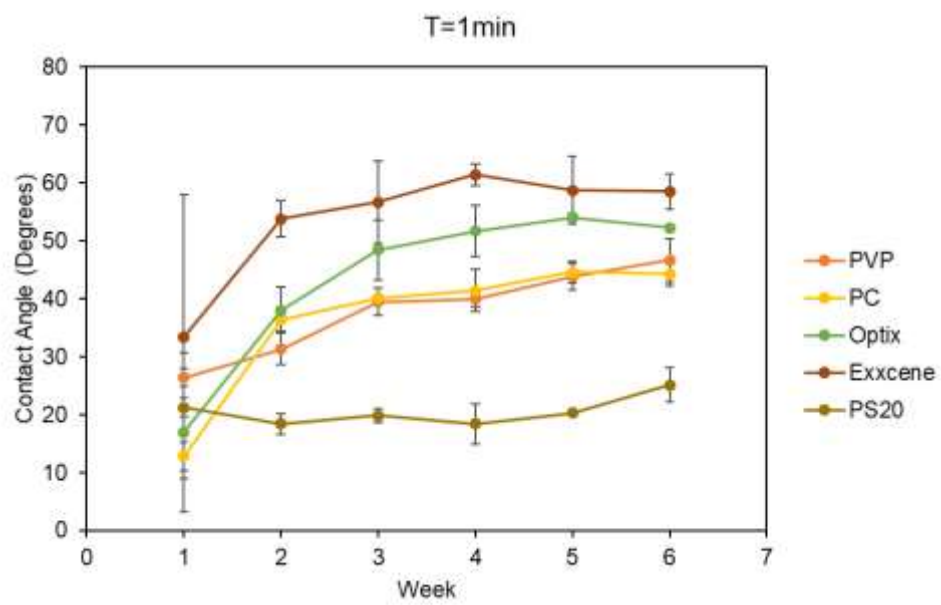
5.4.12 Comparison to Commercial Antifog Solutions

Optix 55 (Purchased from Amazon), Revision Military Anti-Fog Cloth (Purchased from Amazon), and Gear Aid McNett Tactical OP Drops (Purchased from Amazon) temporary antifog solutions were all applied to the substrates using the directions indicated by the manufacturers. The Exxene HCF-100 Anti-Fog Coating formulation (donated by Exxene Corporation) was applied to the substrates via flow coating method and cured on a 110 °C hotplate for 1 hour.

A.



B.



C.

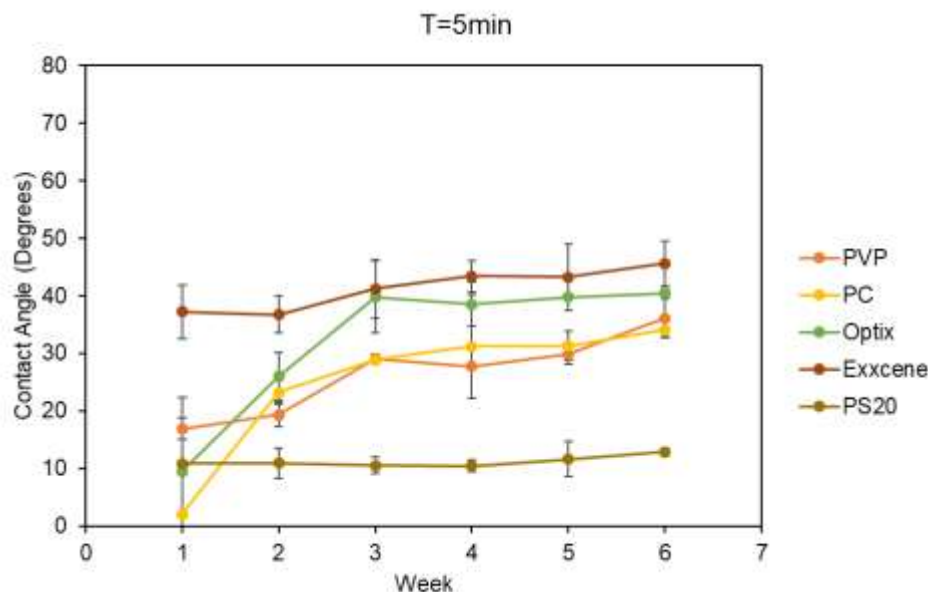


Figure 62: Longevity of static water contact angle performance with extended exposure time to normal environmental conditions.

Contact angle at A) time = 0min, time = 1min, and time = 5min.

The comparative performance longevity of each antifog formulation was assessed by coating fabricating each coating and monitoring the contact angle of each week. The samples were kept in open-air normal laboratory conditions between sampling and like previous contact angle measurements, time-series contact angle data was taken to observe the absorbency of the coatings. As shown in contact angle previously, polymer coatings (PVP, PS20, Exxcene) decreases notably with time, indicating the absorption of water. Plasma treated polycarbonate and Optix do not show considerable contact angle change over the course of 5 minutes (contact angle change here is due to evaporation and pinning of the contact line). Over the course of 5 weeks, increases in contact angle due to ambient air contamination increases the contact angle for all coating except the PS20 durable antifog coating. This is particularly true for the Optix antifog coating being that it exists

as a thin layer of hydrophilic molecules. The crosslinked PVP and Exxene coatings also yield increases in contact angle, owing to contamination. The PS20 coating being both crosslinked and imbibed with hydrophilic slip additive allows for significant enhancements in hydrophilic longevity.

5.4.13 UV-Vis Optical Properties

Transmittance and transmission haze were measured with a Shimadzu UV-2600. Transmittance haze is the fraction of light scattered when the incident light passes through a transparent material and describes the optical clarity of a material ³⁸⁸. Experimentally, haze was measured by the total transmittance of the sample (T_s) and the diffusion rate of both the sample (DT_s) as well as the instrument (DT_{ins}) using a UV-vis spectrophotometer equipped with an integrating sphere. The haze percentage was calculated by the following equation:

$$\text{Haze} = (DT_s - DT_{ins})/T_s \times 100\% \quad (2)$$

Chapter 6 - Durable Water-Resistant Composite Antifog Coatings

Despite the surprising high performance of the antifog coatings described in the last chapter, this chapter focuses on overcoming the shortcomings with regard to water resistance. The key component which enhanced the durability and antifog properties in the Chapter 5 is prone to leeching in water environments due to its water solubility. Thus, in this chapter we demonstrate the simple ability of utilizing hydrophobic solid slip-additives to incur antifogging, durability, and water resistance. This work was aided by Jiaqi Guo and Jing Wang, and is still currently in progress.

6.1 Introduction

In the previous section, a durable antifog coating was engineered which could be easily spray-coated and cured onto a variety of substrates. This coating derived great performance largely due to the addition of hydrophilic slip additives (or hydrophilic surfactants). When these slip additives were blended into the antifogging PVP network, the relative interfacial coefficient of friction was significantly reduced, thereby engendering a highly wear resistant coating. This overcame a notable design dilemma of polymer antifog coatings; as a coating's surface energy is increased to reduce the water contact angle (and minimize light distortion or fogging), the interfacial friction can also increase, leading to poor wear resistance. The hydrophilic slip additives are able to migrate to the air-solid interface and reduce the friction for an abrading counterface.

The hydrophilic slip additives also greatly increased the antifog properties of the coatings. At the solid-liquid interface, the hydrophilic slip additives retain high degrees of freedom compared to the crosslinked PVP, leading to significant wetting and superior antifogging properties.

Despite the unique antifogging capabilities of the hydrophilic slip additive infused PVP coatings, a second, more deleterious dilemma exists with respect to the longevity of the coatings. The most optimal slip additives are water soluble, or hygroscopic, which leads to the depletion of the additive when in prolonged contact with water. This will inevitably occur since fog/condensation will accumulate on the solid interface. Another potential scenario emerges for the application of swimwear, or rain which will eventually cause the coating to come into contact with water. There is therefore a need to develop a facile coating design which preserves antifogging abilities, durability, and water resistance.

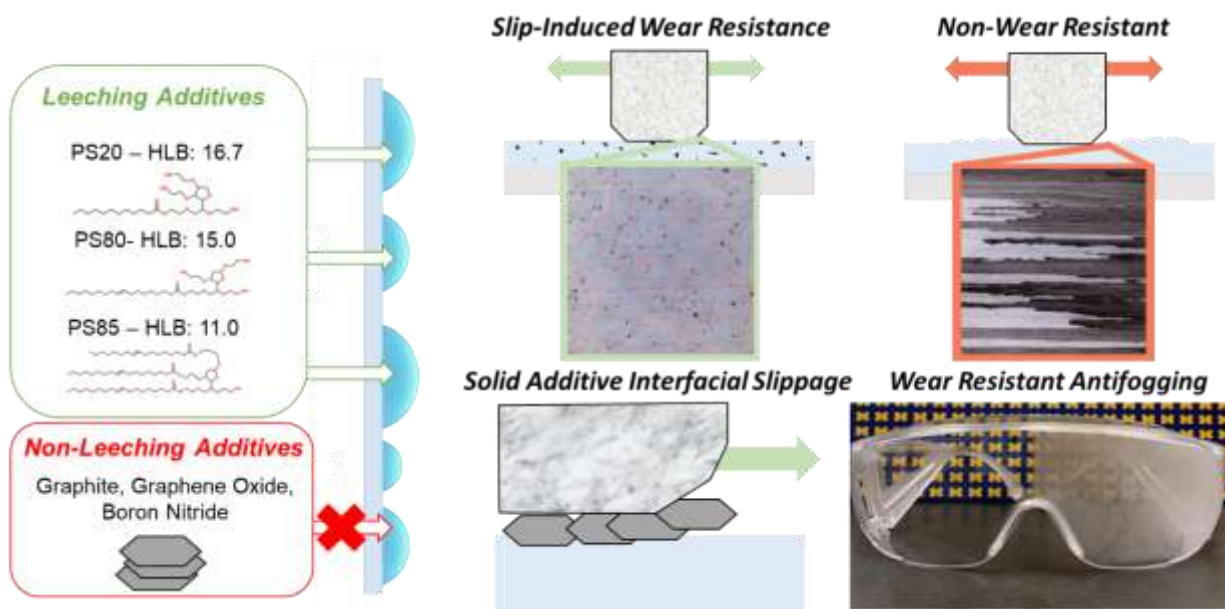


Figure 63: Design schema of durable water resistant antifog coatings.

Solid slip additives such as graphite are added in small concentrations are embedded within a PVP matrix. The solid slip additives allow for localized interfacial slippage which greatly enhances the wear resistance without diminishing antifog performance.

As described in the previous chapter, the Ratner-Lancaster relation (7) demonstrates that in order for a polymer material to be wear resistant, its friction coefficient (μ), stress (σ_b) and strain (ε_b) at break, and hardness must be optimized. We found that friction coefficient is the most tunable variable when attempting to maintain a consistent antifog polymer matrix composition. Therefore, friction coefficient must continue to be minimized. In order to generate slip during shear abrasion while maintaining water-resistant antifogging properties, solid lubricating agents were investigated (Figure 63). Solid lubricants have been widely utilized in a range of industrial applications such as antiblocking^{386, 389-391} and industrial wear reduction³⁹²⁻³⁹⁵. Herein we demonstrate the simple design of a composite antifog coating that is both wear and water resistant by blending antifog polymers such as polyvinyl pyrrolidone (PVP) with small amounts of solid slip additives which included graphite, graphene oxide, boron nitride, and nanoclay. We evaluate the coatings water-resistant properties with respect to durability and antifogging; meanwhile qualitatively optimizing for transparency. The final result is a simple polymer composite antifog coating that can be readily spray coated and UV cured onto a variety of plastic substrates.

6.2 Results and Discussion

6.2.1 Evaluation of Wear Resistance

The composite PVP-Solid slip additive coatings were prepared by mixing volumes of 50mg/ml solid slip additive/1-propanol solutions into 10ml of PVP solutions (see materials & methods), and sprayed onto (with home built automated spray coating apparatus) oxygen plasma treated polycarbonate and cured under UVA/UVC. Wear resistance was conducted with a Tabor Abraser with a coarse, felt-tip CS-7 abradant. Pure crosslinked PVP coated polycarbonate was prepared as a control to evaluate the comparative wear resistance of the composite coatings. The concentration of solid lubricant to be added to PVP was chosen as to achieve the minimum amount

required that allowed for wear resistance based on some preliminary experiments. Adding excess was avoided to promote the optical transparency of the composite films.

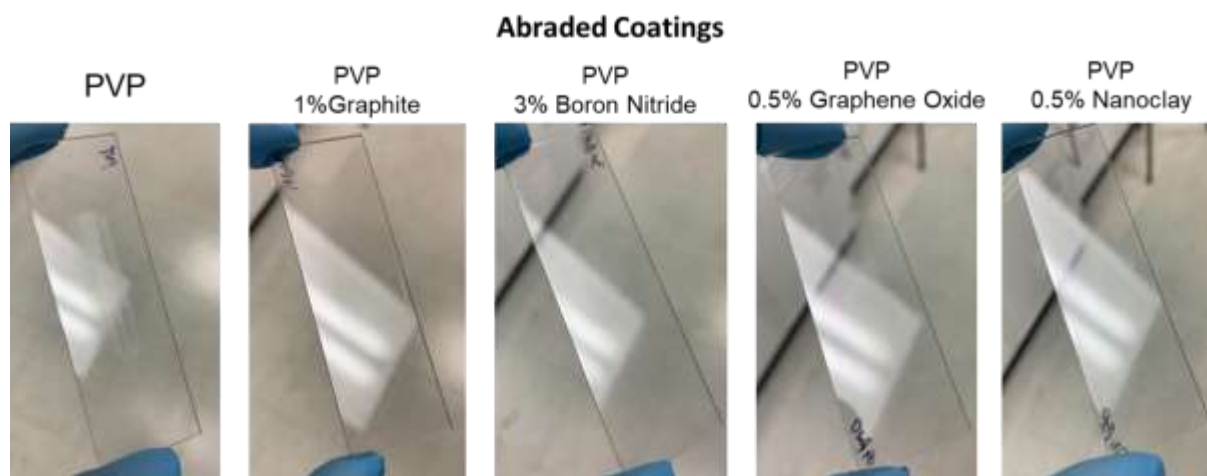


Figure 64: Coated polycarbonate after 1000 CS-7 abrasion cycles.

Figure 64 above yields the eye-view abrasion resistance of each of the coated samples. 1000 CS-7 abrasion cycles (300g of mass) were abraded across each sample. Here the significant abrasion of PVP can be seen similar to what was reported in the previous chapter. The results are in-line with the Ratner-Lancaster relation of high friction, which is related in part to the surface energy (and wettability) of the substrate ³⁷²⁻³⁷⁵. Unlike PVP, the composite PVP coatings containing, 1% graphite, 3% boron nitride, 0.5% graphene oxide, and 0.5% nanoclay all visibly resisted 1000 abrasion cycles. In addition, it is noteworthy to consider qualitatively, the degree of relative transparency of each coating. To obtain a more magnified view of each coating, optical microscopy was utilized and can be viewed in Figure 65 below. Here, the significant abrasion of PVP can be viewed much clearer. What can also be seen, are the particles within respective composite coatings and their degree of aggregation. Qualitatively, the 1% graphite, and 3% boron nitride coatings yield low levels of aggregation, compared to the 0.5% graphene oxide, and 0.5%

nanoclay samples. The aggregation of the latter two can be seen visibly by eye, which indicates poor optical properties, and may be related to the particle miscibility within the PVP matrix. The abrasion resistance between each of the composite coatings is minimal after the first 1000 cycles, however some minor wear and scratching can be seen. Between each of these, all were initially wear resistant except the 0.5% graphene oxide coating with a notable dark wear pattern. After submerging the samples into water for 24 hours and allowing them to dry, all of the samples can be observed to self-heal as a result of the swelling. PVP, due to its significant abrasion only marginally self-heals when compared to the lightly scratched composite coatings. This is most clearly observed in with the graphene oxide composite sample where the abrasion area self-heals after swelling in water, followed by drying. All composite coatings then displayed wear resistance to 1000 more abrasion cycles, indicating water resistant durability.

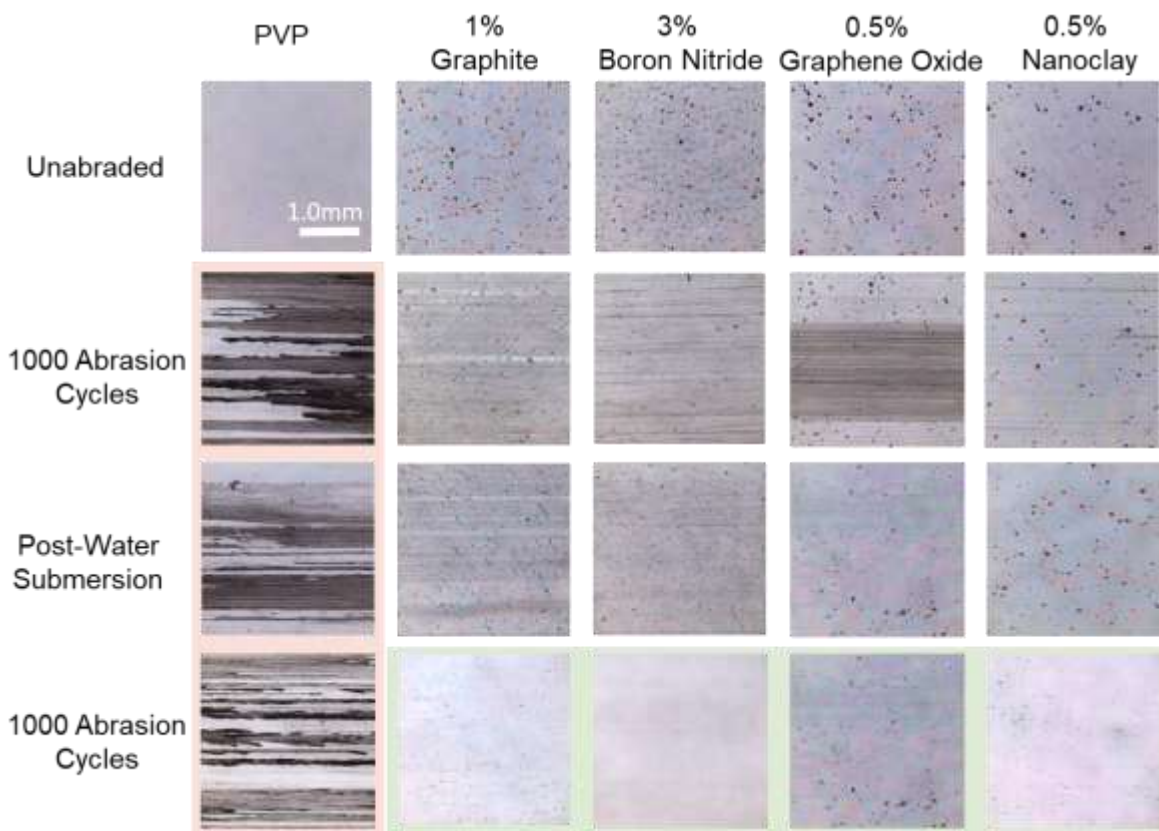


Figure 65: Optical micrograph array of PVP and PVP composite coatings and sequential abrasion, water swelling, and further abrasion.

To understand the durability and contact angle properties with respect to thickness, the PVP and PVP/additive solutions were diluted by ~15% prior to spray coating. This resulted in a thickness reduction of 700nm (thick), to 600nm (thin). The thickness and wear resistant properties were also probed and the optical micrographs can be found in Figure 66. The same trend follows here with PVP considerably abrading compared to the composite coatings with solid slip additives. Meanwhile, for the unabraded coatings (top row) reduction of thickness slightly reduces the levels of aggregation of particles. This is particularly the case for the 1%graphite coating. A thinner coating is expected to limit the effects of aggregation since the absolute number of particles is reduced within the coating, thereby reducing the opportunities of light scattering as a function of coating thickness. Once again, outside of some minor scratching and wear, all of the composite

coatings with solid slip additives demonstrated significant qualitative improvements in wear resistance.

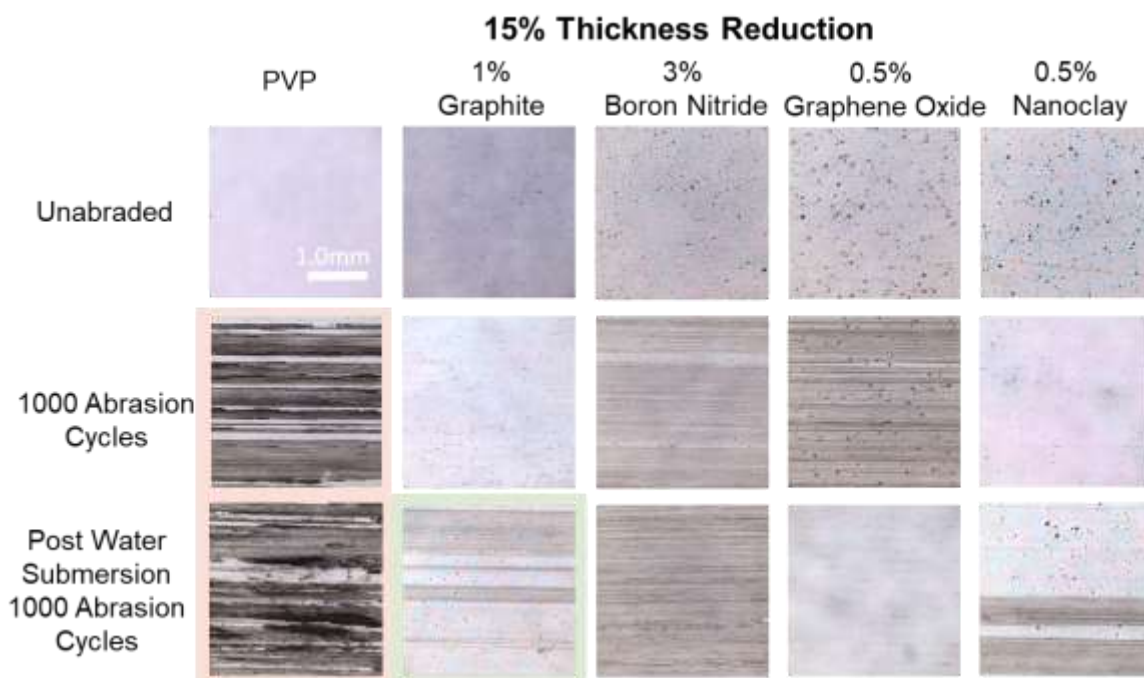


Figure 66: Thin coatings (600nm) subjected to abrasion, water submersion/swelling, followed by drying, and 1000 additional abrasion cycles.

Figure 67 yields the roughness measured via a stylus profiler. The profiles were gathered after the first 1000 CS-7 abrasion cycles, and another 1000 cycles were underwent after water submersion and drying. In accordance with the qualitative data presented in Figure 65 & Figure 66, we can see the roughness of PVP increase greatly relative to the composite coatings. The measured roughness in some cases slightly decreased after the wear cycles; some of the rough aggregates are smoothed over by the abradant in this case. This occurred in the case of the thick 3%Boron nitride and thin 0.5% nanoclay. However despite the coating thickness, the 1% graphite composite PVP coating endured minimal changes in roughness after all abrasion cycles.

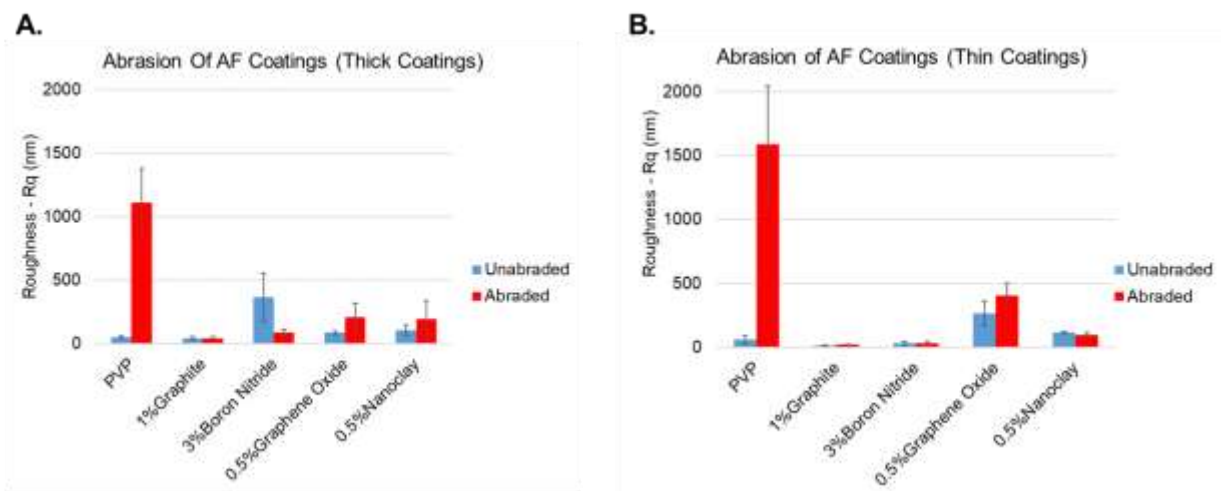


Figure 67: Root-mean-square roughness measurements (Rq) of coated samples after 1000 abrasion cycles before and after water swelling. A) Thick 700nm and B) thin 600 nm coatings.

6.2.2 Antifog Performance

To gain understanding of the wetting properties and the effects to long durations of water exposure, contact angle measurements were obtained. Since all coatings are crosslinked hydrophilic networks, water will absorb into their volume. Therefore, a static contact angle of a sessile droplet was measured for $t=0\text{min}$ (approximately), $t=1\text{min}$, and $t=5\text{min}$. Samples were measured as-cured prior to water submersion/swelling. What can be seen in Figure 68A in the case of graphite and boron nitride, is that the contact angle remains nearly constant despite the addition of hydrophobic slip additive. In the case of nanoclay and graphene oxide, the contact angle is increased. These two composites are also both the two systems that yield the most severe particle aggregation despite having the lowest concentrations. After submerging the coatings in water for 24 hours and allowing to dry, the coating contact angles were measured again (Figure 68B). Surprisingly, the pure PVP coating greatly increased in contact angle; the contact angle increased by 53.5% (Table 10). The graphite and boron nitride composite coatings also increased by a similar

magnitude, while graphene oxide and nanoclay coating contact angles only increased by 4.7% and 26.3% respectively (Table 10). The thin coatings yielded dissimilar properties, where increases in contact angle are observed. However the results vary for boron nitride and graphite additive coatings. For these, the contact angles increased to a greater extent than PVP, while the nanoclay and graphene oxide coatings increased in contact angle to the greatest extent (Table 10). These changes in contact angle do however contain some inconsistencies.

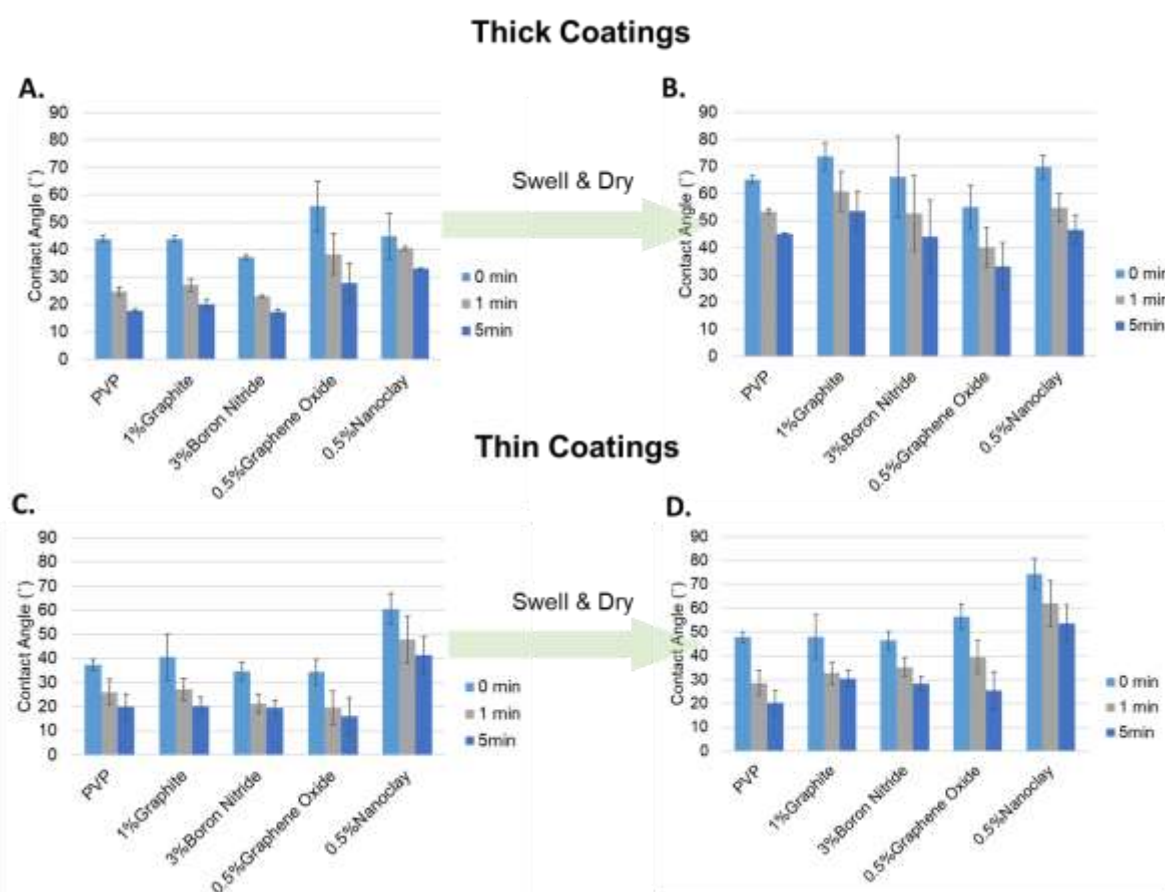


Figure 68: Contact angle properties of each PVP-based coating.

A 2.5 μ L droplet was deposited onto each surface and allowed to absorb and wick into each coating and measurements were gathered for ~0min, 1min, and 5min. Thick coatings were ~700nm and thin coatings as ~600nm

Table 10: % increase in average contact angle for t=1min the PVP-based coatings. Thick (700nm) and thin (600nm) coating sets were evaluated.

Coating Thickness	PVP	1% Graphite	3% Boron Nitride	0.5% Graphene Oxide	0.5% Nanoclay
700nm	53.5%	55.5%	56.3%	4.7%	26.3%
600nm	9%	17%	39%	50%	23%

A potential difference in the contact angle data between the thick and thin coating data sets could be the duration of water swelling between the two sets of samples; the 700nm samples underwent 24hrs of water submersion and swelling while the thin coatings underwent 2hrs, but with stirring. Variables of thickness and duration of swelling are difficult to separate, but one clear distinction is the greater increase in contact angle of the graphite and boron nitride composite coatings when comparing the thin to the thick coatings. The high degree of increase in hydrophobic properties was surprising for the thick coatings. In addition to the removal of free, uncross-linked polymer chains, one potential explanation is the migration of hydrophobic groups to the solid-air interface during the drying process^{204, 396-398}. This phenomenon was also observed by Lee *et al.* who measured high contact angles for PVA/PAA antifogging/anti-ice polymer coatings²⁰⁴. Understanding the effects of thickness and water swelling on the PVP contact angle indeed warrants further exploration. Yet one potential mechanism to understand some of the severe increases in contact angle for solid additive composite PVP coatings would be the migration of the particles to the air-solid interface (solubility driven surface blooming) during the drying step³⁹⁹. Figure 69 demonstrates the dry surface structure changes of the graphite before and after water submersion/swelling and drying. Prior to swelling, the graphite is well dispersed randomly throughout the PVP matrix. After 2 hours in water followed by drying, the particles self-assemble into a striated pattern. This indicates that some degree of surface migration/rearrangement is occurring at the interface. Migration may also impact the contact angle.

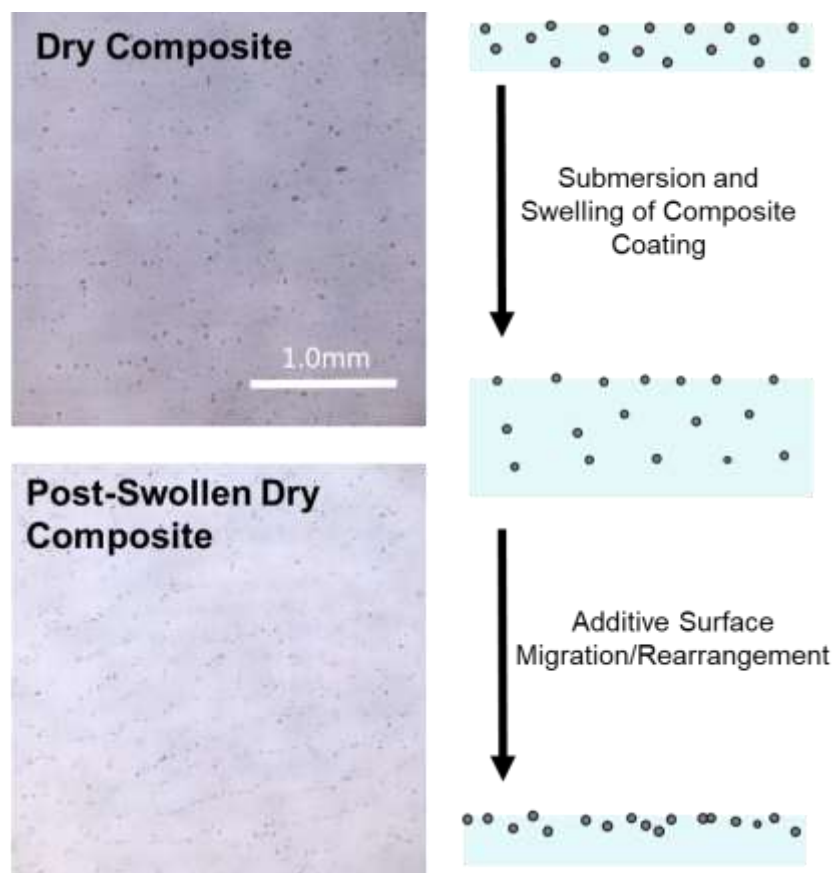


Figure 69: Optical images of PVP/1%Graphite composite coating before and after water submersion/swelling and drying. Potential mechanism of particle surface migration.

Fog testing was conducted in an apparatus similar to Chapter 5. However instead of utilizing a chiller as the cooling source, a peltier plate was utilized with a larger environmental chamber (Materials & Methods). Briefly, the coated sample was placed onto the cooling source, which included the Peltier plate with a glass spacer on top to ensure proper optical distortion from fogging. The sample surface was cooled to a temperature between 15-13°C with an air temperature of 23°C and a relative chamber humidity of ~63% (See Materials & Methods). PVP, polycarbonate and one composite coating was tested for fogging performance. Being that the 1% Graphite demonstrated the best qualitative optical properties and significant wear resistance, it was chosen to be tested compared to the controls. Fogging can be observed as a gradual or sudden reduction in the image correlation factor as fogging distorts the background image. As shown in Figure 70A,

PVP is confirmed to delay fogging onset by ~5minutes when compared to hydrophobic polycarbonate. After water submersion and drying of PVP, the fogging time is generally maintained (~1min shorter fog time) despite the subtle increase in contact angle (Figure 70B). Surprisingly, despite the addition of hydrophobic graphite within the PVP matrix, the fogging time is slightly greater than PVP by ~1min (Figure 70C). When the 1% graphite composite coating underwent the same swelling procedure as pure PVP, the fogging time was minimally altered. However, the fogging behavior did change from a rapid fogging event, to a more gradual fogging as indicated by the gradual decrease in image correlation factor displayed in Figure 70D.

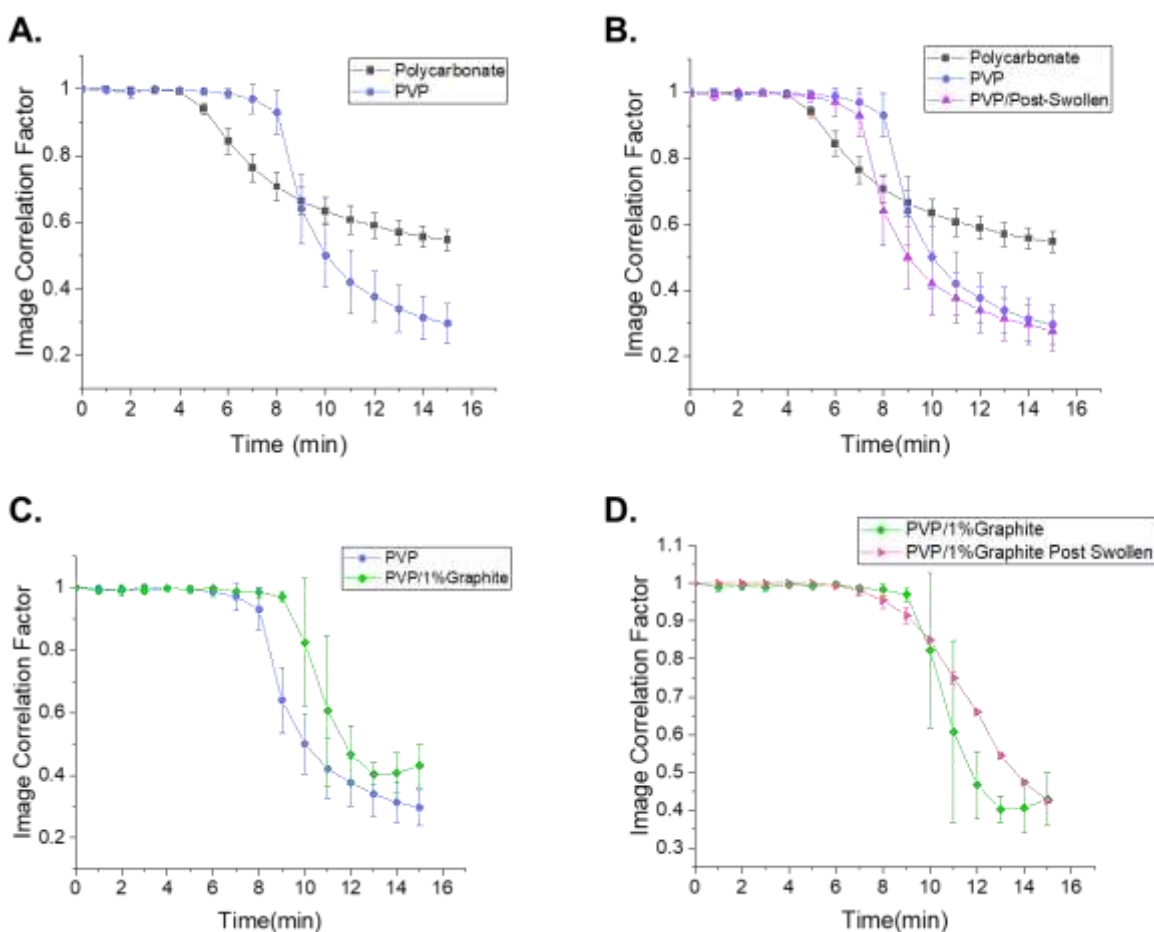


Figure 70: Fogging performance of PC, PVP, and PVP/1% Graphite. A) Comparison between polycarbonate (PC) and PVP B) comparison between PC, PVP, and PVP after submersion in water for 2 hours followed by drying C) PVP and PVP/1%Graphite D) PVP/1% graphite fogging for a fresh sample and a sample submerged into water for 2 hours followed by drying.

The behavior of fogging in Figure 70 is unexpected when considering the contact angle data found in Figure 68 and the fact that hydrophobic graphite particles are added to the PVP matrix. Contact angle is related to the surface energy or degree to which a polymer is hydrophilic in this context. Despite the increases in contact angle, the fogging properties are virtually uninhibited for the 1% Graphite/PVP coating. This goes against the simple heuristic requiring the contact angle to be below 40° in order for light to be undistorted by the hemispherical droplets²⁰. In the case of graphite where the contact angle is above 40° , the potential mechanism is two-fold: The concentration of graphite is small enough to allow PVP to dominate the fogging properties, meanwhile the small water vapor condensates will preferentially tend to condense onto PVP as opposed to embedded graphite particles at the air-solid interface⁴⁰⁰. As illustrated in Figure 71, condensing water is able to locally wet the PVP matrix and absorb into the polymer, delaying fogging. Meanwhile, the sessile droplet is wetted onto an areal fraction of both hydrophilic PVP and the hydrophobic graphite, increasing the contact angle.

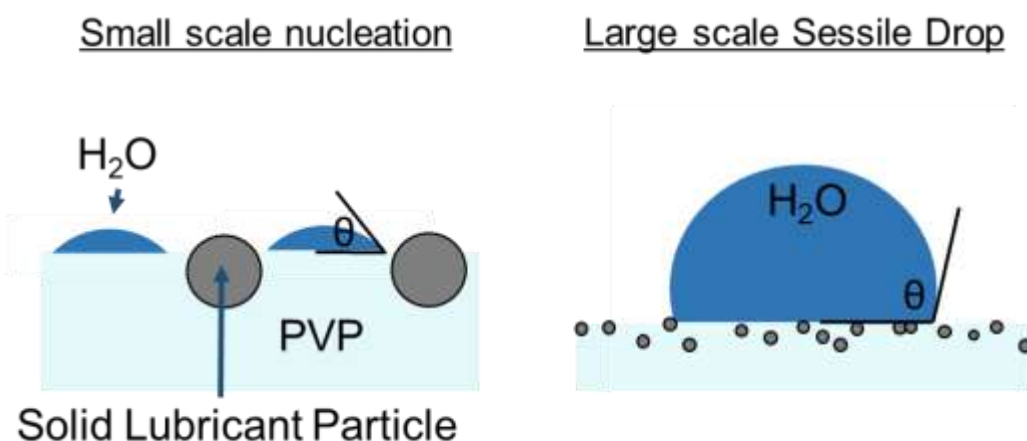


Figure 71: Small local contact angle of water condensates between solid lubricating particles and large contact angle of large sessile drop.

6.3 Conclusion & Ongoing Work

In this work, we have designed a water-resistant, wear resistant polymer antifog coating that can be spray-coated onto plastic substrates and rapidly UV-cured. By blending small fractions of solid slip-additives into the PVP crosslinked matrix, the new composite interface can yield under shear stress without notable damage as a result of the lamellar inter-slip nanostructure of the graphite, boron nitride, graphene oxide, and nanoclay. Particularly in the case of a 1% graphite/PVP composite, the wear resistance was significantly improved compared to the pure PVP. This was confirmed via optical microscopy and changes in surface roughness. The durability carried over even after severe water exposure and swelling for hours, indicating that the slip additives do not extract when exposed to water. The 1%Graphite composite demonstrated the most notable water resistant durability. The composite coating to our surprise was even able to yield a fogging delay time that was similar, and slightly longer than that of pure PVP despite retaining a fraction of hydrophobic particles. At such small particle concentrations, this phenomenon is rationalized by the local water droplets preferentially condensing and absorbing into the hydrophilic PVP matrix as opposed to the hydrophobic graphite particles. The composite coating also demonstrated water resistance in its ability to maintain fogging delay after water exposure and drying. Thus, we demonstrate the successful design of an antifog coating that yields water resistance to both durability and antifogging.

Although we have demonstrated a proof of principal design for water resistant antifog coatings, some further work is warranted. One of the most noteworthy aspects to investigate are the optical properties of the coatings as a function of solid slip-additive concentration. Being that these coatings find primary applications in eyewear, it is important to investigate the limits to which these additives can be included in terms of transparency. Similarly, the additive

composition, as well as the thickness of the coating in relation to transparency must also be investigated. Another avenue of study for this work would include quantifying the solubility of the solid additives in PVP and other polymer matrixes. As discussed earlier, a more thorough investigation of the impact of thickness and water swelling duration of the polymer films must be completed. Lastly the broad applicability of solid slip-additive design strategy with multiple polymer matrices such as PEG, PVA, PAA, and SBMA should be completed.

6.4 Materials and Methods

6.4.1 Antifog Coating Fabrication

Solution Parameters

A 0.0265 g/ml solution of 1300KDa Polyvinyl Pyrrolidone (PVP) (Purchased from Sigma Aldrich) and 0.001 g/ml benzophenone (purchased from Sigma Aldrich) was made by dissolving the polymer in a solution containing 1-Propanol (Purchased from Fischer Scientific), distilled water, and 30% Hydrogen peroxide (Purchased from Fischer). The respective volume ratio of the solvents is 93.1:0.029:0.040. All contents were stirred in a glass septa-jar until fully dissolved (>2hrs). 50 mg/ml solutions of graphite (Purchased from Sigma Aldrich), Graphene Oxide (made in house), Boron Nitride (purchased from Sigma Aldrich), and nanoclay (purchased from Sigma Aldrich) dissolved in 1-Propanol (Fisher). Due to the low volumes added, varying amounts were pipetted into the main PVP solution (10mL) and gyrated for at least 15 minutes.

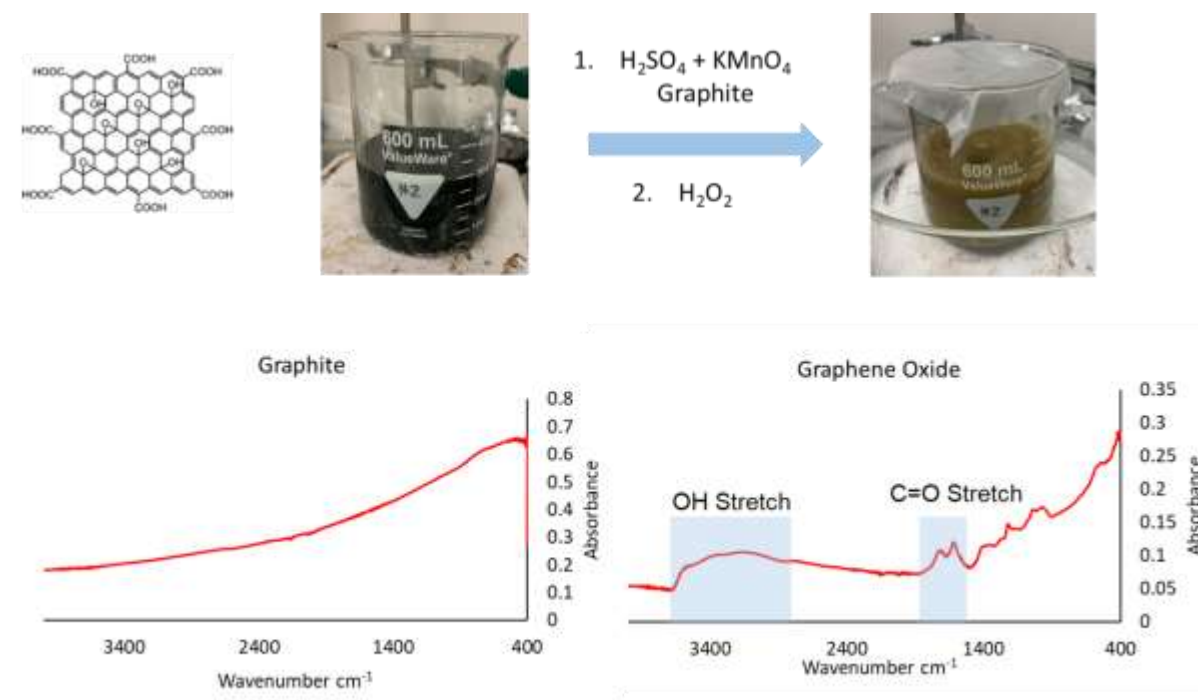
Coating Fabrication

Impact resistant polycarbonate strips (Purchased from McMaster-Carr) of 1 inch width and 1/16 inch thickness were cut to 4 inch slides for testing. Polycarbonate strips were first cleaned with isopropyl alcohol and blown dry before exposure to 30W oxygen plasma (Plasma Etch Inc.) for

10 minutes. Once plasma treated, the samples were coated using a home-built automated spray coating apparatus. The plasma treated samples were placed at a distance of 20cm from the spray gun. The spray gun (HVLP mini touch up ATD-6903) parameters were set to a linear speed of ~20cm/s, typically 1 spray pass, and spray pressure of 20 Psi. The solutions were dispensed into the spray reservoir, and sprayed onto the plasma treated polycarbonate. This allowed for coatings of consistent thickness and roughness to be deposited. Immediately after, the coatings were subjected to UVA (UVP 100W Longwave Mercury Spot Lamp) and UVC (UVP XX-40S Bench Lamp 2.6mW/cm²) at a distance of 12cm for 10 minutes.

6.4.2 Graphene Oxide Synthesis

Graphene oxide was synthesized utilizing a modified Hummers method⁴⁰¹. 1g of graphite (Sigma-Aldrich) was dissolved into 100ml of 90 wt% sulfuric acid solution and stirred within an ice bath for 1hr. 4g of potassium permanganate (Sigma-Aldrich) was stirred into the solution for 4hrs (violet color solution). 100ml of water was added with continued stirring for 1hr, followed by another 200ml and stirring for 30 minutes. 20 ml of 30% hydrogen peroxide (Fischer) was then added under stirring whereby the solution turned light brown. Excess water was added and the particles were centrifuged and washed 6 times. The figure below illustrates this process and the measured FTIR spectral differences between pure graphite and graphene oxide.



110

Figure 72: Schematic of modified Hummers method and FTIR spectra graphite and graphene oxide.

6.4.3 Tabor Abrasion

Abrasion Testing

All substrates were abrasion tested with a Taber Linear abrader Model 5750 with a stroke length of 1 inch and frequency of 60 cycles/minute. 32x32 mm samples were abraded with a stroke length of 0.5 inches. A CS-7 abrasion tip was used for each test and was purchased from the Taber manufacturer. Between each test, the CS-7 was sonicated in acetone (Fisher) to remove potential debris and solid additives. The number of cycles varied between ~5 and 5000 depending on the test.

6.4.4 FTIR

Fourier transform infrared spectroscopy (FTIR) was conducted by a Thermo Scientific Nicolet 6700 FTIR spectrometer with an ATR (diamond crystal) and a frequency range of 400-4,000 cm⁻¹.

6.4.5 Fog Testing

Fog testing was conducted using a home-built setup as described in the Figure 73. This setup is similar to that of chapter 5; the difference being the usage of a PID controlled Peltier plate and a large acrylic environmental chamber. In series, a 0.5mm square of aluminum (32x32mm) with a reference image was placed behind the substrate, and between them, a 1 inch glass spacer to enhance the effect of image distortion from fog. Images were captured every minute for 40 minutes. The reference image provides the ability to visually display fogging properties over time and is used to measure image distortion caused by fogging. Image distortion was analyzed with an open source ImageJ plugin utilized and by Lee *et al*²⁰⁴. The fogging evolution on the sample was captured by a single-lens camera D3200 (Nikon, Japan) with a 150 mm f/2.8 Macro 1:1 lens (Irix, Switzerland) and a 28 mm long spacer (Photo Plus, USA) at the rate of 1 frame per minute controlled by RC-N2II ShutterBoss II timer remote switch (Vello, USA) with a light source VM-160 LED macro ring light (Bolt, USA).

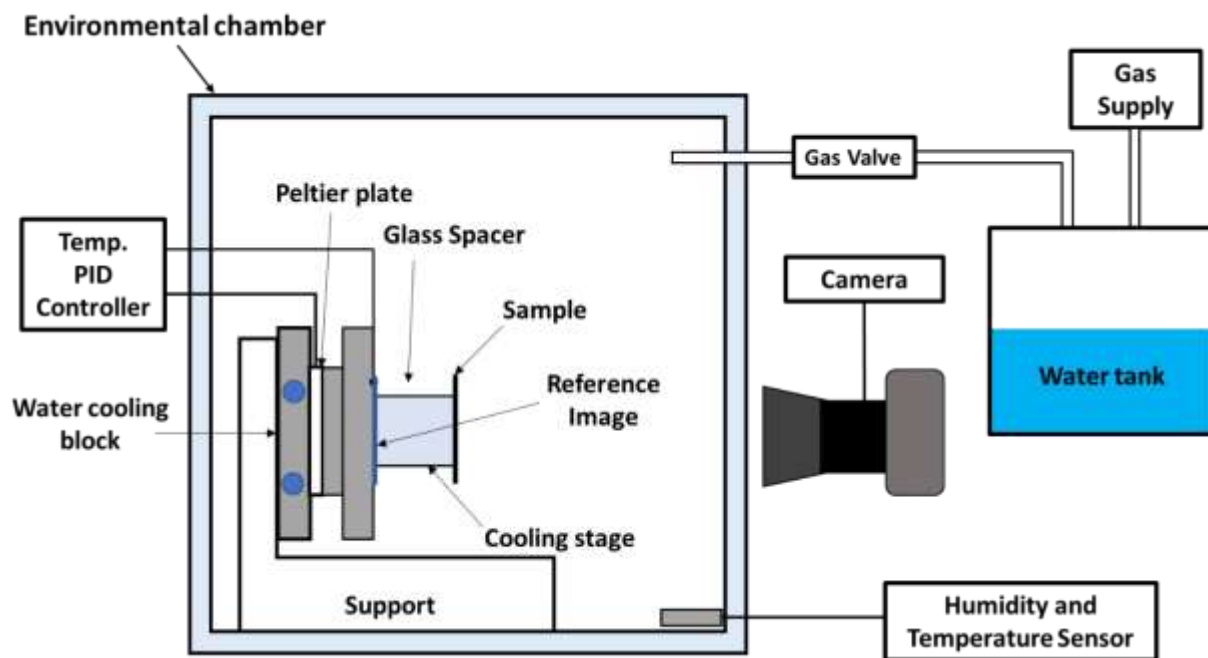


Figure 73: Experimental schematic of fogging apparatus

The humidity was maintained between 65-63% and the ambient temperature was maintained to 23°C in order to yield a consistent dew point. Below is the temperature profile for the sample surface and the base temperature setting controlled by the PID controller (Auber instruments).

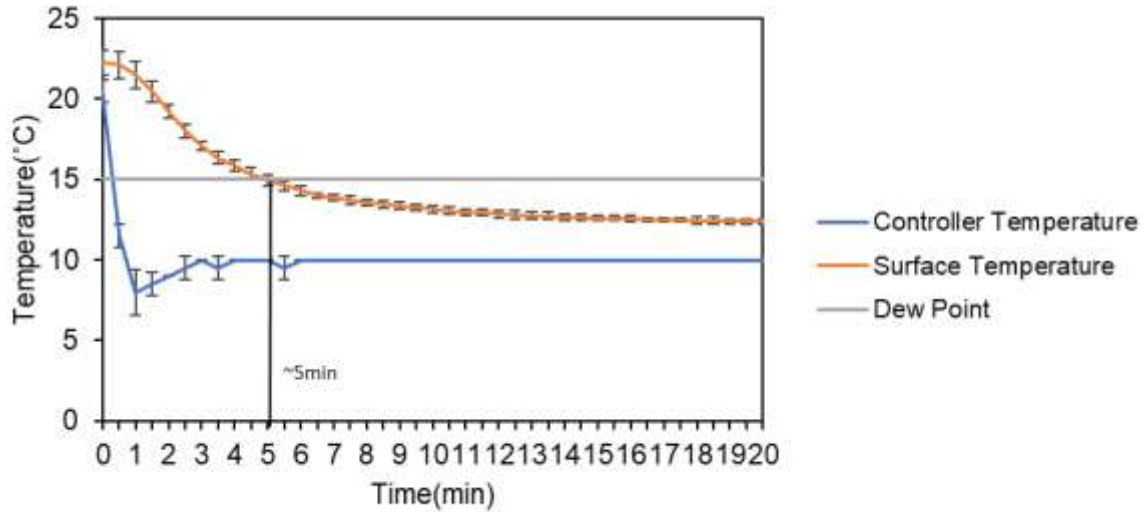


Figure 74: Temperature profile for the sample surface and the PID controlled base temperature.

6.4.6 Optical Microscopy

Optical micrographs of the antifog coatings were taken with a LEXT Laser OLS5100 microscope. The 5X objective lens was utilized for the images presented in this work to capture a large area of the surface.

6.4.7 Linear Stylus Profilometry

Surface roughness was measured via a Dektak 6M stylus profilometer (courtesy of Lurie Nanofabrication Facility). A 5mg stylus force, a segment length of 2000 μ m, and a raster time of 120 seconds was used for each measurement. At least 4 spatially separated segments were measured for each sample (abrased and unabraded).

Chapter 7 - Facile anti-frosting/anti-icing coating with enhanced longevity

In the final chapter we demonstrate a unique zwitterionic coating capable of absorbing water, forcing it in the ‘non-freezing’ state, and delaying ice-initiation for long durations of time. This work was done with Dr. Jun Li whom dedicated to designing a controlled freezing apparatus capable of reliably testing the ice-initiation time of a given surface. I focused on the creation, design, and characterization of the antifrost coatings. This work currently in progress.

7.1 Introduction

Ice and frost accretion is a serious problem affecting a wide range of industries which include but are not limited to: aircraft, ships, refrigerators, and heat exchangers^{155, 205-207}. Frost on climate controlling heat exchangers result in a decrease of heat transfer efficiency by up to 75%^{402, 403}. To combat this, recent efforts have sought various methods to suppress ice formation rather than facile removal of bulk ice. However, the performance of recent frost prevention innovations remained limited and are difficult to utilize in real world applications.

Ice formation and nucleation is relatively simple process, and becomes more complex when involving a surface. In homogeneous nucleation processes, supercooled water molecules will achieve hydrogen bonding for successively longer durations until a compact nucleus is formed. Once the ice nucleus reaches a point termed the critical radius, spontaneous crystallization occurs within the entire system⁴⁰⁴. In most industrial, transportation, and residential sectors, homogeneous nucleation does not occur, but instead heterogeneous ice nucleation. Heterogeneous

ice nucleation occurs when water freezes upon a surface at the solid/liquid interface. The presence of a solid/liquid interface reduces the energy barrier of ice nucleation, facilitating freezing to occur notably easier than in the homogeneous form ⁴⁰⁴. Therefore, surface design strategies which increase the thermodynamic barrier of ice nucleation to, or in some cases beyond that homogeneous ice nucleation, are necessary to prevent the icing of surfaces.

Initial surface design efforts included the reduction of surface energy and tuning of surface roughness and geometric structures. It was found that for a perfectly flat substrate, the free energy barrier of ice nucleation is reduced by a geometric factor compared with the free energy barrier of homogeneous nucleation⁴⁰⁴. This geometric factor scales with increasing water contact angle to limit of perfect nonwettability (ie 180°), whereby the homogeneous nucleation state is reached ⁴⁰⁴. Generally, the more nonwetting a substrate is, the lower the ice nucleation temperature. However, perfectly flat substrates are unrealistic, and surface features will facilitate nucleation. Although surface geometry and roughness tend to aid in ice nucleation, achieving sufficiently small features can reduce the ice nucleation temperature ^{163, 400}. Once features reach the size of the critical nucleation radius, the process reverts to that of homogeneous nucleation. Superhydrophobic surfaces alternatively have been shown to display an icing delay with liquid water, but this can be attributed to the reduced heat transfer across the composite interface in a Cassie-Baxter state ^{405, 406}. However superhydrophobic surfaces fail in condensation nucleation practices whereby water vapor has shown to condense within the structures of the superhydrophobic surfaces, leading to icing before droplets are large enough to be in the Cassie-Baxter state ¹².

Lubricant infused surfaces (LIS) have also yielded icing resistance. A notable study demonstrated anti-icing due to the LIS ultra-low contact angle hysteresis where the surfaces allowed water and ice droplets to easily slide off the surface on the lubricant layer ⁹. LIS and

superhydrophobic surfaces rely on shedding water or ice (applicable to freezing rain) rather than inhibiting frost growth from humid air. However LIS surfaces must be mounted at a given critical angle to dewet condensing water before freezing and suffer from deteriorating performance during icing/deicing cycles due to surface damage or lubricant depletion ^{225, 407, 408}. Magnetic slippery surfaces (MAGSS) combined the effects of superhydrophobic and LIS surfaces by generating liquid, low surface energy textured surfaces and have shown to significantly delay ice nucleation near to near homogeneous and with minimal cloaking/depletion ⁴⁰⁹. Yet the application of a magnetic field and usage of complex fluids yields difficulty for real-world application.

Recent advances have been made toward surface design that suppresses ice crystal formation and growth. Anti-freeze proteins have been of particular interest since the discovery of the mechanism in plants and fish to survive subzero temperatures ⁴¹⁰⁻⁴¹². These helical proteins bind to the crystal planes of ice and inhibit growth of the crystal ⁴¹³⁻⁴¹⁶. Proteins are susceptible to depletion, similar to the lubricated surfaces, as the surface goes through multiple ice/deice cycles, and performance decreases can be observed ¹⁹³. Polyelectrolyte brushes with a substituted counterion have shown to significantly inhibit ice formation ¹⁸⁸. The polyelectrolyte counterions migrate to the brush surface and disrupt the ice nucleation temperature and delay ice crystallization ^{188, 189}. The counterions can be reversibly exchanged to optimize the anti-icing properties; hydrophobic fluorinated counterions were found to yield the greatest anti icing properties ⁴¹⁷. Ionogels swollen with fluorinated ionic liquid demonstrated a unique anti-icing strategy. Instead of delaying freezing, droplets having frozen in relatively short time were internally melted by interfacial ions via colligative melting ⁴¹⁸. The usability of these brush surfaces and ionogels are limited by the complex process to create them, the toxic nature of fluorinated ionic species, and the inability to scale the thickness to further enhance anti-icing properties ^{189, 419}.

We have developed a simple, 2-step polyelectrolytic water absorbing, hydrogel coating that can easily be applied to surfaces, inhibits ice formation for longer than 4,000 seconds, and maintains its performance through multiple ice/deice cycles. Poly-zwitterionics contain side groups with spatially separated positive and negative charges, similar to polyelectrolytes, but without the mobile counterion. Unlike the previously mentioned strategies, these polyelectrolytic hydrogels delay freezing by absorbing large quantities of nonfreezing water^{420, 421}. The intramolecular zwitterionic charges yield no risk of depletion during freezing cycles, and retain no environmentally harmful fluorinated species.

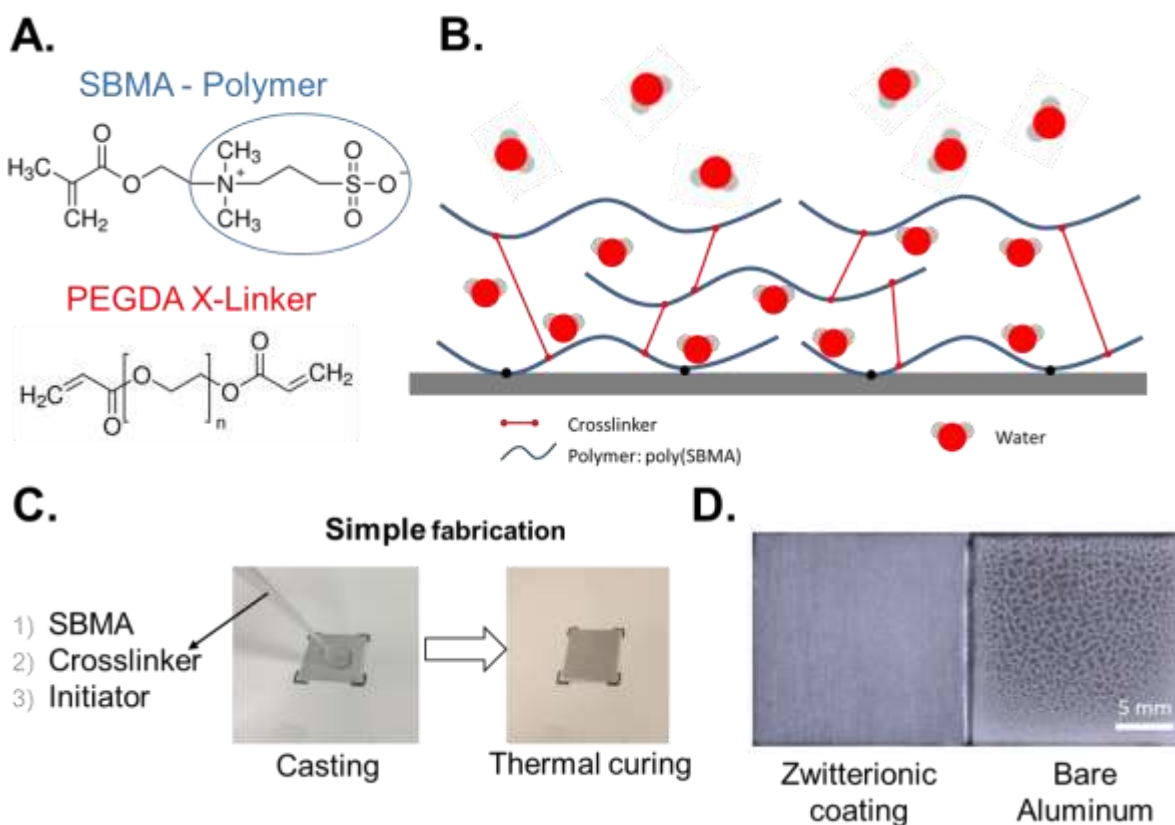


Figure 75: Formulation and fabrication process of SBMA anti-freezing coatings.

A) Chemistry of the coating B) general mechanism of water absorption and internal nonfreezing water C) Curing procedure D) ice-delay properties of the zwitterionic coating.

7.2 Results and Discussion

The controlled freezing of a substrate in a multiphase system is a complex problem as well as challenging to control and measure. Minimal groups measure the frosting phenomena for the three-phase process of vapor to liquid to solid (ice), and those who have, haven't done so for a water absorbing coating such as our SBMA-based coating. The SBMA coating was fabricated by thermally curing a resin composed of SBMA, water, PEGDA crosslinker, and thermal initiator. As the SBMA coating is cooled below 0 °C, the water absorbed within the network interacts with the highly charged zwitterionic groups and is forced into a metastable 'nonfreezing' state. This metastability poses a significant set of problems: the need to avoid freezing events caused by edge effects of dissimilar materials (ie aluminum edge, particles, foams), and the need to obtain consistent comparative measurement between samples. Here the former problem demands removing the ability to form ice on the sample edges, and requiring contacting materials to be highly thermally insulating. The consistency problem is addressed by introducing a reproducible thermal pathway between all samples tested. Failing to achieve either of these criterion for our system will lead to data with severe, and unacceptable data noise.

7.2.1 Chiller Apparatus

The first attempt in measuring the freezing delay time for the SBMA coatings was underwent utilizing a chiller system (See Materials & Methods). In short, the samples were pressed onto a copper stage with thermal paste. Surrounding the sample is insulation to prevent edge frosting, and an insulating Viton (McMaster) gasket was used as a contact point between the mounting plate and the testing surface. The gasket was fabricated to prevent extraneous heterogeneous ice nucleation. Before utilizing Viton, a foam was implemented, but this facilitated edge-freezing at the foam-SBMA interface. The use of Viton greatly minimized this phenomenon.

Once assembled, the sample mounting stage was placed into an environmental chamber for testing. The back end of the copper stage (mounted within the test section) was then cooled by circulating an ethylene glycol/water (50:50) coolant mixture, thereby reducing the surface temperature. The surface temperature, as a function of coolant temperature, was calibrated and is depicted in Figure 76 below. As shown, a -10 °C coolant temperature corresponds to a stabilized -7.2 °C surface temperature while a -20 °C coolant temperature corresponds to a stabilized -16.1 °C surface temperature.

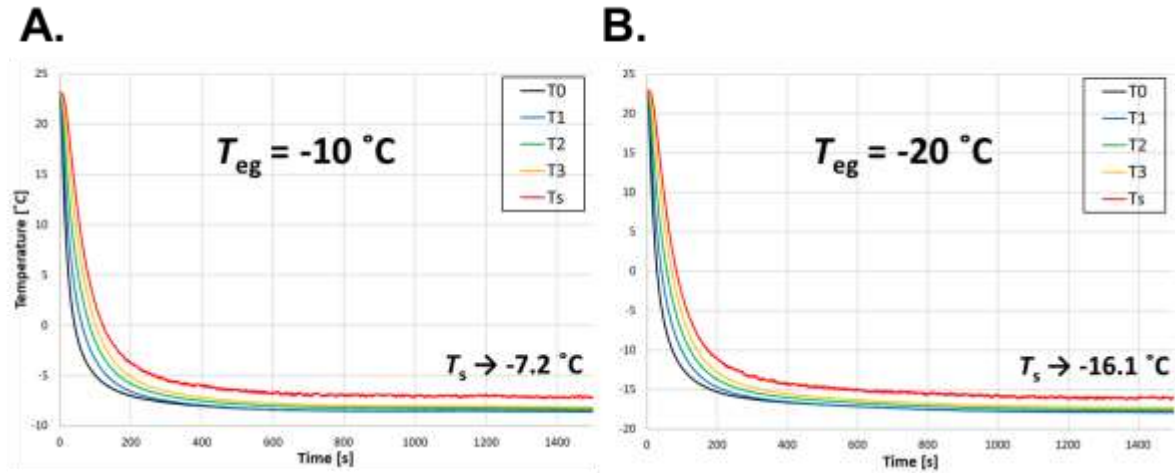


Figure 76: Chiller thermal profile for a given coolant temperature. A) Thermal profile for surface temperature (T_s) for -10 °C coolant and B) -20 °C coolant.

With a stable thermal profile confirmed, the tests were conducted at a -16.1 °C. The aluminum freezing baseline was first examined. The ambient air temperature (T_a) was 22-23 °C while the ambient relative humidity (RH) was 48-50%. As shown in Figure 77, the bare aluminum substrates yielded an average ice initiation time of 4min 35sec. Ice initiation is determined as the first qualitatively visible nucleate of ice that is observed before propagation. To examine our SBMA coating, a low crosslink density (0.25 wt%) sample was produced with a thickness of 150 μ m. The sample preparation details can be found in the materials & methods section. The ice

initiation time for the 150 μ m SBMA coating yielded an average time of 58min 51seconds; an almost 13X delay of freezing under the same conditions. The ice initiation time as a function of coating thickness was also evaluated. As the coating thickness was decreased to 100 μ m and 50 μ m, the ice initiation time reduced in a nearly linear fashion. The trend is demonstrated in Figure 78. This decrease in ice initiation time as a function of thickness indicates that the coating reaches a threshold capacity in absorbing nonfreezing water.

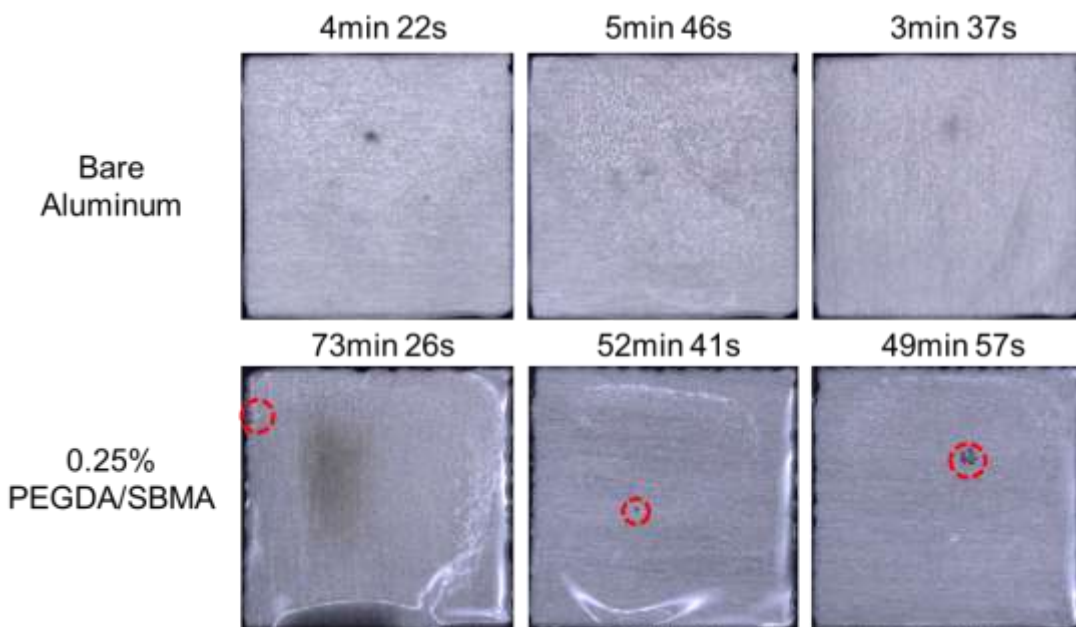


Figure 77: Frost delay testing of bare aluminum substrates and SBMA coated aluminum.

The SBMA coating is 150 μ m thick and the testing conditions were maintained at $T_s = -16^\circ\text{C}$, $T_a = 22^\circ\text{C}$, $\text{RH} = 48\%$

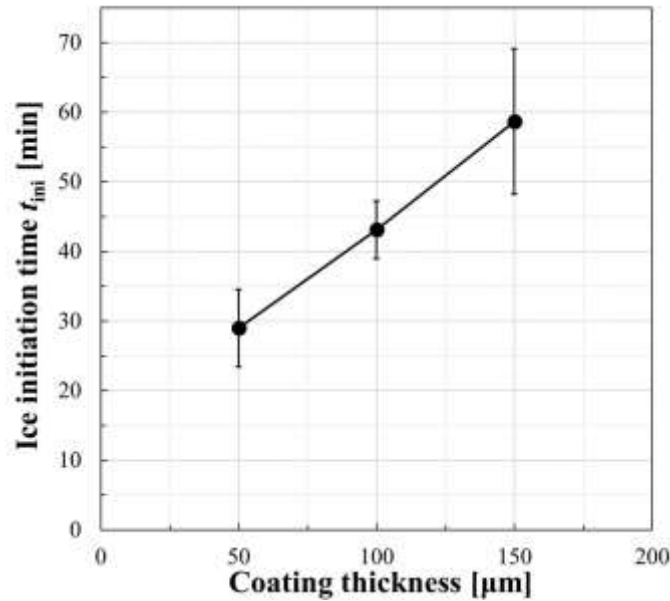


Figure 78: Ice initiation time for coating thickness of 150μm, 100μm, and 50μm.

$T_s = -16\text{ }^{\circ}\text{C}$, $T_a = 22\text{ }^{\circ}\text{C}$, $RH = 48\%$

7.2.2 Peltier Apparatus

Despite the ability of the chiller apparatus to test the three-phase frosting phenomena of the SBMA coatings, a few challenges remained. One challenging aspect of the chiller apparatus was the duration of time it took to conduct a single test (>3hrs). Another issue was the trenchant time of the cooling profile. To reach a nearly stable surface temperature, the process took 10 minutes (Figure 79A). This is problematic since as demonstrated in Figure 77, the aluminum baseline freezes at average of ~4.5minutes while the SBMA coating froze between roughly 30-60 minutes depending on the thickness, meaning that the samples freeze at different temperatures. Thus an apples-to-apples comparison between the SBMA coatings and the baseline are technically unfair. Lastly, due to the small volume of the testing chamber, it was difficult to adequately control the humidity once undesired condensation occurred onto chilled parts of the test section.

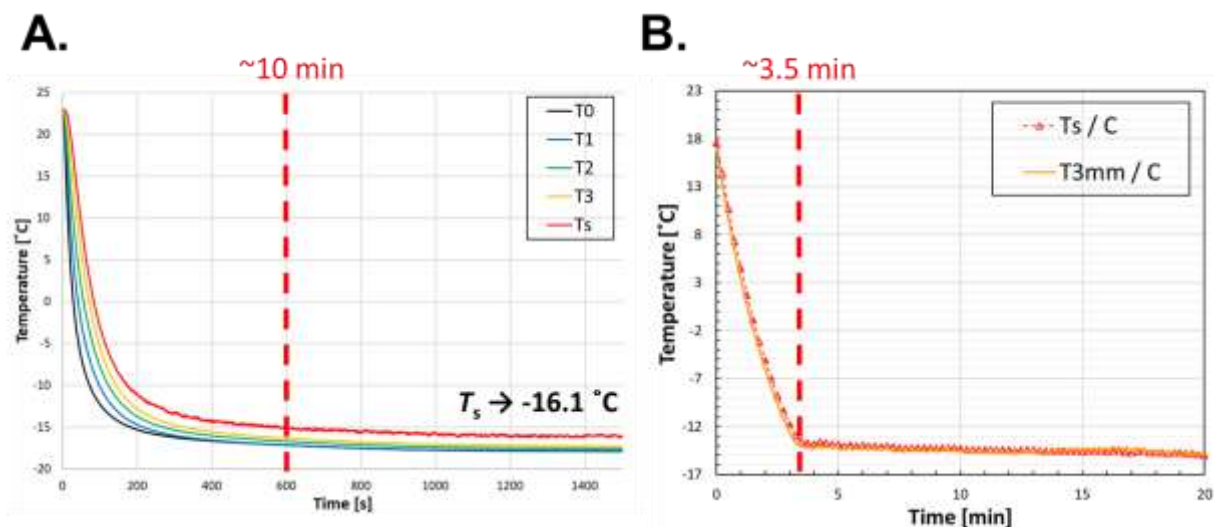


Figure 79: Temperature profile comparison between Chiller and Peltier apparatus.

A) 10 min and B) 3.5min trenchant time to for the chiller apparatus and the Peltier apparatus respectively.

To overcome the limitations of the chiller, a Peltier plate freezing apparatus was designed by Dr. Jun Li, and is shown in detail in the Materials & Methods section. The advantage of the Peltier plate apparatus shows in its ability to rapidly reduce the surface temperature. Unlike the chiller apparatus which relies solely on conduction of heat through the copper stage as a result of the cooling fluid, the Peltier plate setup is able effectively reduce the temperature within a few minutes and rapidly freeze the aluminum samples (Figure 79B). This is possible as a result of the PID controlled thermoelectric. The freezing time of the aluminum for the Peltier setup is now very close to the stabilization time. With the new Peltier setup, ice initiation times were collected for 100 μ m thick samples SBMA samples. To understand a preliminary effect of the crosslink density, a thermally cured pure polySBMA coating (0%PEGDA crosslinker) and a 0.25% PEGDA coating were tested for their ice initiation time. As demonstrated in Figure 81, the average freezing time is 56min 49 seconds for the uncrosslinked pure SBMA coating, while ice initiation time of the 0.25% PEGDA/SBMA coating is only slightly lower with an ice time of 53min 47 seconds. The result

indicates that the small amount of PEGDA crosslinker minimally effects the ice initiation time when compared to the pure, water-dissolvable SBMA coating. This preliminary data demonstrates the accuracy and precision of our testing apparatus and yields promising results for SBMA anti-frost coatings.

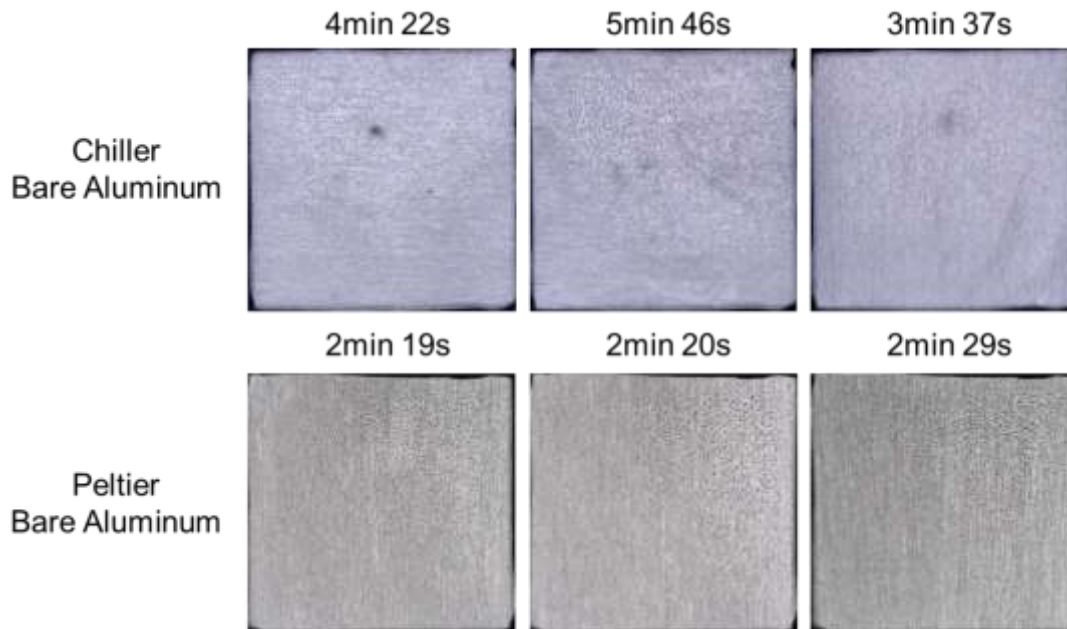


Figure 80: Frost formation time of bare aluminum utilizing different freezing apparatuses.

A) Chiller freezing conditions of $T_s = -16\text{ }^{\circ}\text{C}$, $T_a = 22\text{ }^{\circ}\text{C}$, $RH = 48\%$ and B) Peltier freezing with conditions of $T_s = -15\text{ }^{\circ}\text{C}$, $T_a = 23\text{ }^{\circ}\text{C}$, $RHa = 65\%$

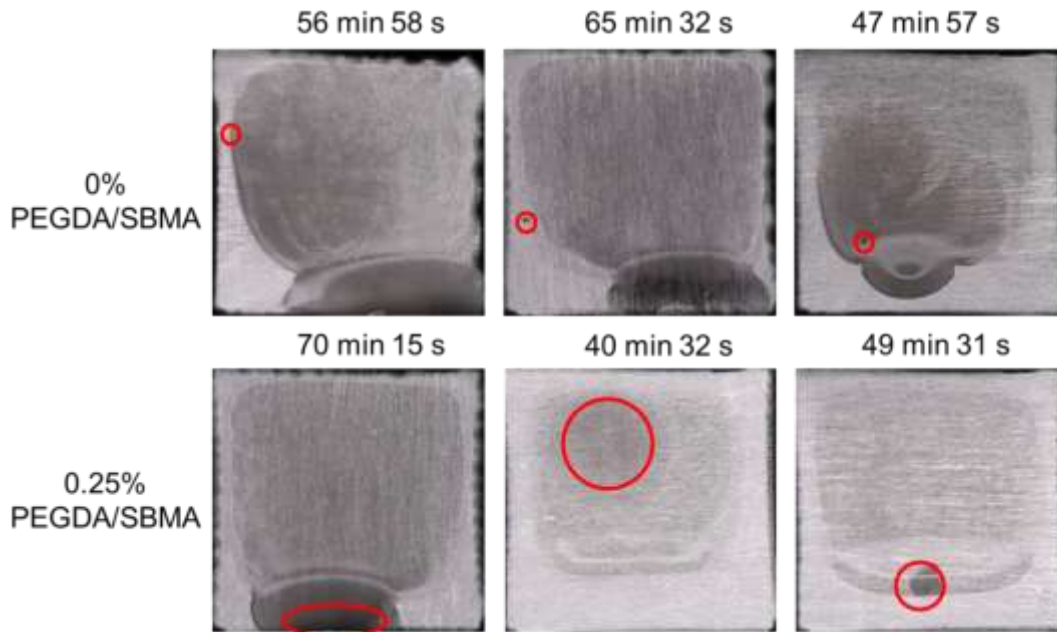


Figure 81: Ice initiation time of pure polySBMA (0%) and crosslinked 0.25% PEGDA/SBMA

Peltier freezing with conditions of $T_s = -15\text{ }^{\circ}\text{C}$, $T_a = 23\text{ }^{\circ}\text{C}$, $RHa = 65\%$

Lastly, water-absorbing coating compositional differences and their effects on ice initiation time was investigated. We hypothesized that the unique charged structure of polySBMA is needed to facilitate the formation of non-freezing water. To test this hypothesis, a more hydrophobic water absorbing coating was developed. A polyurethane-based coating was fabricated by blending a 1:1 mass ratio of Desmodur N3800: PEG 400. In the presence of catalyst and heat, these constituents can form the necessary isocyanate linkage of a polyurethane. 100 μm thick coatings were tested in order to fairly compare between the SBMA and Polyurethane coatings. The average ice nucleation time of for the PEG:PU coatings was 42min 1second. This is roughly 10 minutes shorter than the SBMA coating. Although our hypothesis was confirmed, the relatively long ice time of PEG-Polyurethane was surprising given the significantly increased degree of hydrophobic groups. One potential explanation is the formation of a self-stratified network, where the highly flexible PEG groups migrate to the surface to increase their conformational entropy. A top PEG layer if

sufficiently thick, could to a certain degree, facilitate water into the non-freezing bound state, but more work is necessary to verify.

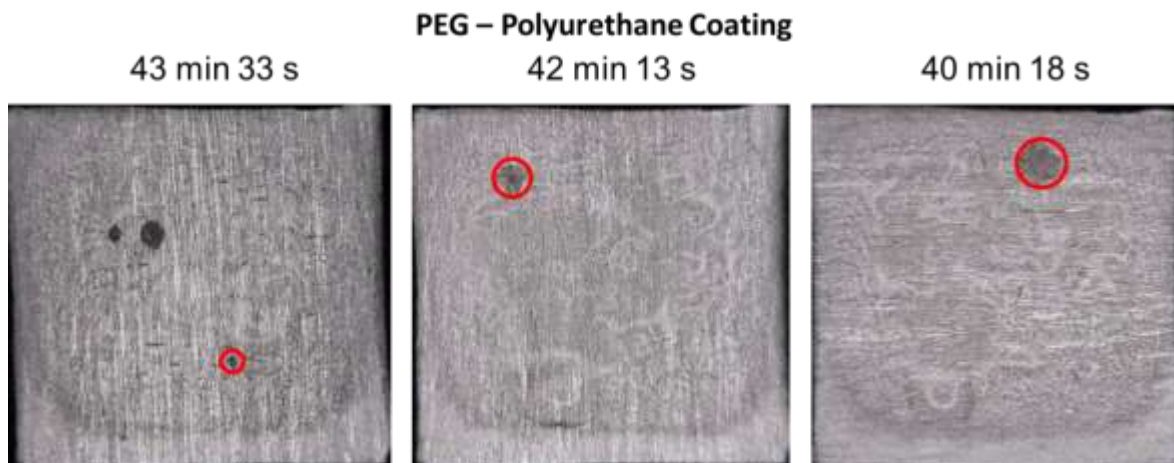


Figure 82: Ice initiation time for 100 μ m thick PEG-Polyurethane (1:1 mass ratio) coatings.

Peltier freezing with conditions of $T_s = -15\text{ }^{\circ}\text{C}$, $T_a = 23\text{ }^{\circ}\text{C}$, $RH_a = 65\%$.

7.3 Conclusion and Future Directions

To conclude, we have developed and preliminarily validated a polySBMA coating able to delay ice formation nearly 13X that of bare aluminum. In the process of developing the coating, we have uncovered the vacancy in research related to reproducible testing of three-phase frost formation from air, to solid ice on surfaces. This was achieved via a home built Peltier plate apparatus customized and finely tuned to promote coating and surface-dependent ice formation and thereby minimizing false negative results. We have proven that polySBMA coatings can greatly delay ice formation and is dependent on the coating thickness. Lastly we preliminarily demonstrated the ability of other hydrophilic coating's ability to delay ice nucleation and that their efficacy is to a degree tied to the ability to absorb water and facilitate the non-freezing bound water state.

Much more work is required for this project. Namely, the polySBMA coating ice initiation time dependency on coating thickness and crosslink density are needed for the Peltier plate setup. PEG-Polyurethane coatings also warrant further investigation and structural characterization is needed (self-stratifying coating confirmation). The ability of PEG-PU to delay ice formation is an exciting revelation due to the ubiquitous nature of polyurethanes in modern society, and potentially offers a new avenue for simple, durable, and easily deployable antifrost coatings. Lastly, the SBMA coatings (and PEG-PU) must be tested against the recent discoveries and innovations in frost delay and nucleation inhibiting coatings, such as SLIPS⁹ and polyelectrolyte¹⁸⁸ coatings.

7.4 Materials and Methods

7.4.1 Testing Apparatus and Conditions

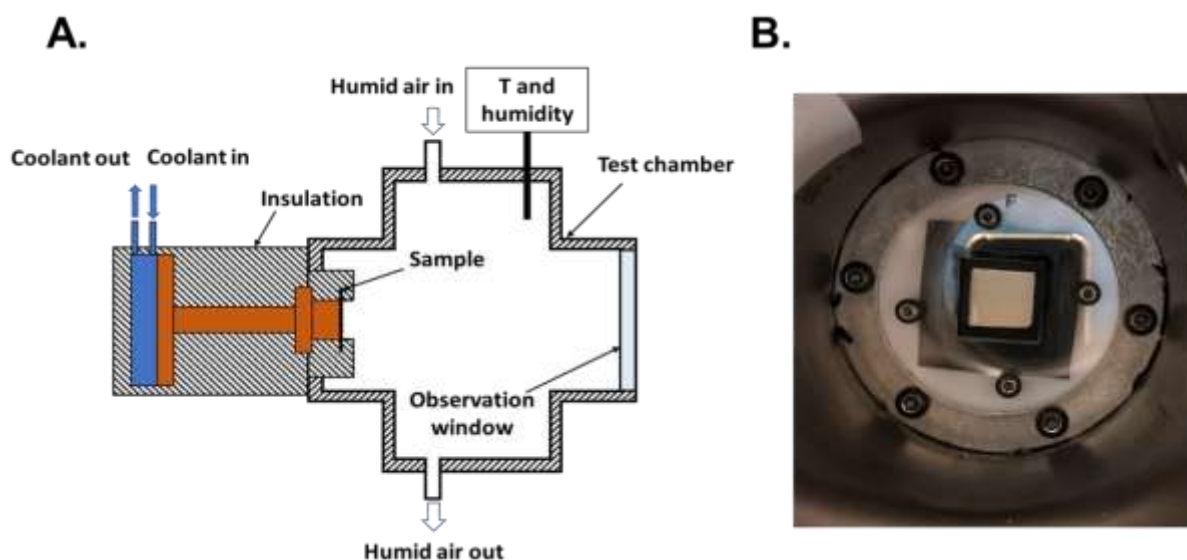


Figure 83: Schematic of chiller test section and image of secured sample for testing.

A) Schematic of the chiller freezing test section B) Image of sample secured within the test section and environmental chamber.

The chiller test section consists of chiller-cooled (Polyscience 15L) fluid which makes contact with a Teflon insulated copper rod whereby the sample is secured and further insulated.

The chamber temperature and humidity can be well controlled and everything is observable through a glass window. Imaging was taken with a single-lens camera D3200 (Nikon, Japan) with a 150 mm f/2.8 Macro 1:1 lens (Irix, Switzerland) and a 28 mm long spacer (Photo Plus, USA) at the rate of 1 frame per minute controlled by RC-N2II ShutterBoss II timer remote switch (Vello, USA) with a light source VM-160 LED macro ring light (Bolt, USA).

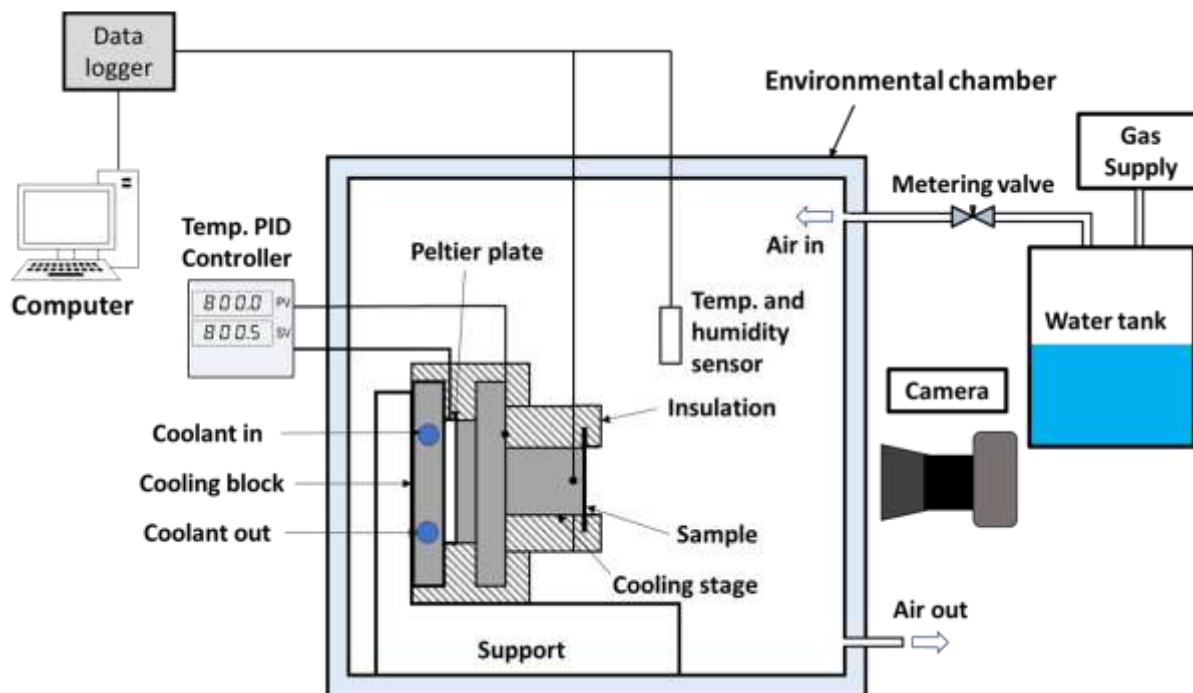


Figure 84: Peltier freezing test section.

A Peltier plate (Laird DL-060-12-00) is mounted sideways with an attached aluminum column/sample stage. Insulation covers the Peltier plate, aluminum column, and the edges of the sample. A mounting plate with a Viton gasket presses the sample into the stage. A PID controller (Auber instruments) was utilized to control the temperature setting. A small chiller (Yamato) was used to maintain a consistent cooling temp for the hot side of the Peltier plate and reduced to 5°C to ensure rapid surface cooling. The temperature data was collected with a data logger while images are gathered using the same camera as previously stated. Photographs of the test section presenting the aluminum stage and the fully constructed apparatus are shown in Figure 85 below.

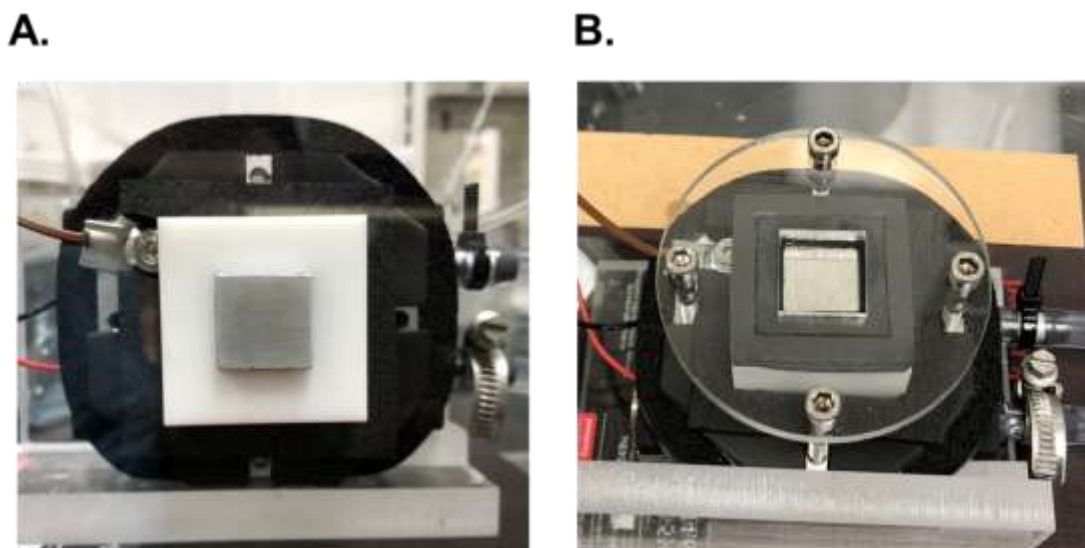


Figure 85: Photographs of Peltier plate test section. A) Aluminum test section with insulation and B) Fully constructed and insulated sample on the test section.

7.4.2 Coating Fabrication (redo)

1 gram of [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (TCI), was mixed into a 20ml glass scintillation vial containing 1.6 mL of deionized water. A 40mg/mL solution of thermoinitiator potassium persulfate (KPS) CAS# 7727-21-1 purchased from Sigma Aldrich, and deionized water was separately generated. 375 μ L was added to the SBMA solution. polyethylene glycol diacrylate (PEGDA) CAS# 26570-48-9, Mn: 250 was purchased from TCI were added to the SBMA solution in desired proportions. For low concentrations of 0.5% and 0.25% crosslinker, 20mg/ml (crosslinkers/water) were developed and added to the SBMA solutions. The aggregate solution was sonicated for 10minutes and gyrated for 20 minutes to fully solubilize all reagents.

7.4.3 Anti-Ice SBMA Network Coated Aluminum

The solubilized SBMA solution containing thermoinitiator KPS and crosslinker were dispensed onto the aluminum in the necessary amount to achieve 50 μm 100 μm and 150 μm thick. 32x32x0.5mm aluminum squares were sanded and sonicated for 10minutes in 2-Propanol, then 10minutes in acetone. Specific volumes of the solutions were spread across the entire area of the aluminum substrates. Once fully applied, the aluminum with SBMA solution was placed on top of a hotplate set to 35°C for 20 minutes, then 70°C for another 20 minutes, covered with a glass Corning petri dish with a 53mm diameter and 15mm height. Once cured, the samples were tested on the same day.

7.4.4 PEG-Polyurethane Coating Fabrication

0.66g of PEG 400 (Sigma-Aldrich) and 0.66g of Desmodure N3800, 2.85mL of toluene, and 0.150mL of 1wt% dibutyltin dilaurate (in toluene) were mixed in a 20mL scintillation vial for 10 minutes. The aluminum samples were prepared in the same manner as described in the above section. Specified volumes of the PEG-PU solutions were deposited on the aluminum, spread evenly, and cured for 10minutes at 50°C for 20 minutes, then 60°C.

Chapter 8 – Summery and Future Outlooks

The culmination of this work has aimed to advance the field of surface engineering by demonstrating multiple new surface design strategies which control the accretion of multiple states of matter with varying complexity. These works in many instances, push the boundary of applicability with regard to not only performance, but also durability. With the techniques and knowledge gained from this thesis, surfaces and coatings can be designed to be better suited within complex fouling processes, demonstrate robustness within harsh environments, and above all, achieve high levels of performance.

One of the most promising innovations for solid and liquid omniphobic surfaces highlighted within Chapter 2&3 of this thesis, has been PDMS liquid-like layers. These surfaces have proven to overcome the challenges of surface structures and their inability to thwart hard foulants such as ice, as well as their lack of durability. The liquid-like layers have also circumvented the issue of lubricant depletion, liquid-lubricant miscibility, and cloaking problem of lubricant-infused surfaces (LIS); where the tethered liquid-like layers demonstrate most of the beneficial features of LIS surfaces, but without the depletion of the active brush. The layers demonstrated significant liquid antifouling for broad ranging surface tensions, and solid antifouling for broad composition and size.

Chapter 4 demonstrated a new multi-combination bioinspired surface which prevents the settlement and facilitating the release of complex marine fouling. Prior to this work, to overcome

the toxic, environmentally destructive paints formerly used, fouling release coatings have been recently innovated. Silicones^{422, 423} and LIS²² surfaces, SBMA bushes^{167, 346}, and mechanical biocidal techniques³³², but have all fallen short due to the complexity of the marine fouling process. In our work, we attempted to bridge the gap between mechanical biocidal surfaces and the hydration layer generated by grafted SBMA polymers to effectively kill and remove small marine fouling species. We also utilized a complex algae-bacteria-protein system naturally found in Florida, unlike single species algae which is predominantly utilized for testing. Our work demonstrates that SBMA functionalized nanowires are able to both kill and release complex algae.

Multiphase vapor-liquid fouling control was investigated in chapters 5&6. Here we designed surfaces to combat the problem of fogging; a ubiquitous, yet challenging issue for many personal and industrial scenarios. The design of durable antifog coatings has generally been limited to glass substrates, which do not readily translate to plastic substrates. Thus polymer antifog coatings were investigated. Although numerous polymer antifog coatings have been developed as briefly mentioned in Chapter 5, only a few have investigated their durability, and none to our knowledge have done so in a systematic manor. In our work we offer two simple design avenues for engineering an abrasion resistant polymer antifog coating: The first includes the blending of miscible surfactant slip-additives, while the second (Chapter 6) involves the mixing of solid slip additives. In Chapter 5 we demonstrated that by finely tuning the miscibility parameter of the matrix-surfactant system, and the HLB value of the surfactant, not only can the durability be drastically enhanced (with respect to the matrix only), but the fogging properties could also be greatly improved. However due to the high HLB (hydrophilic) nature of the effective surfactants, gradual extraction of the slip-additives may occur with many fogging cycles and exposure to aqueous environments. Thus in Chapter 6, we demonstrated that the durability of a crosslinked

PVP film can be improved via the simple additions of solid slip additives such as graphite in low concentrations. However, unlike the former strategy, the strategy of Chapter 6 did not result in enhanced antifogging properties, but rather it maintained that of the base matrix. The durability and antifogging properties were both well maintained even after submerging into water for long durations of time. Also to our surprise, despite adding hydrophobic particles to the hydrophilic PVP network, the fogging did not proportionally increase, indicating that the PVP matrix yielded a dominant role in the fogging properties.

In Chapter 7 we developed a water absorbing, frost-delay polymer coating, as well as the challenges associated with measuring three-phase freezing phenomena on surfaces. Frost formation impacts a wide variety of industries, particularly for climate controlling heat exchangers which can result in a decrease of heat transfer efficiency by up to 75%^{402, 403}. To overcome this challenge, we developed a crosslinked SBMA coating able to absorb and engender water into the non-freezing, supercooled state for extended durations of time. However, the phenomenon itself is very difficult to measure without obtaining false negatives. The cooling rate, contact materials, and insulation, all play an important part in ensuring that only coating-based freezing phenomena are observed. Thus, as a result of the design and fabrication by Dr. Jun Li (a refrigeration expert), we developed a new method for the reliable testing of anti-frost coatings. With this system we were able to demonstrate a nearly 13X freezing delay time for our SBMA coating as opposed to bare aluminum, and a 10 minute delay increase compared to a PEG-Polyurethane (PU) coating of similar thickness. We also have some preliminary data that depicts a direct correlation between coating thickness and freezing delay time for the SBMA coatings.

In sum, this thesis has pushed the boundaries of surface science and engineering through various innovations which have proved able to control liquid and solid fouling. These innovations

included: a durable liquid-like surface technique able to control the accretion of liquids of varying surface tension and solids of various scale, combinatorial biomimetic hydration-layered nanowires which could limit and remove multi-species algae and proteins, an antifog coating that is both high performing and durable, and lastly, a facile and effective freezing delay polymer coating. These innovations aim to bridge the gaps between the existing surface design strategies that have typically proven to only narrowly control forms of material accretion. This thesis provides multiple examples of surfaces that control not only one, but two, or more foulants of various size, state of matter, composition, and/or scale; all while attempting to maintain or improve durability.

8.1 Future Directions

8.1.1 Solid and Liquid repellent Liquid-Like Layers

In Chapter 2 we demonstrated notable durability of the omniphobic PDMS liquid-like layers to multiple modes of wear which included: ice/de-ice cycles, heat, UV exposure, multiple solvents, and some abrasion. However, the biggest drawback in terms of durability is more severe abrasion resistance. In our work, we were able to prove that the liquid-like layers were abrasion resistant to a mild, felt-tip abradant. Yet it is not surprising for the layers to be wear resistant to this mode due to the interfacial slip nature of the chains, and their inherently low friction (Ratner-Lancaster Relation). Recent efforts by Zhao *et al.* have made notable strides in enhancing the durability of the liquid like layers by introducing fluorinated crosslinks between brush chains⁴²⁴. Yet despite their durability, these layers suffer the same fate as all silanes in that they lose their efficacy once the underlying substrate is removed; the silane is removed with it. Thus the maximum abrasion durability of the liquid-like layers are a function of the underlying substrate durability, rather than the layers themselves. Therefore, thicker, more damage tolerant coatings must be engineered which can continually produce these liquid-like layers after wear. One way to

potentially accomplish this would be the design of silicone materials that present a high density of PDMS chain ends at the air interface when cured. However an obvious challenge would be the ability to generate a high modulus, and tough material (wear resistant) that could produce such a liquid-like layer at its interface. To circumvent this dilemma, one could infuse silicone materials with nano or micro-particles that are functionalized with PDMS liquid-like layers. If the surface energy of the bulk matrix is tuned properly, and the fraction particles is optimized, these liquid-like particles could migrate to the surface and present the desired interfacial phenomenon. If a suitable liquid-like layer is presented, and the surface is harshly worn down (with subsequent removal of the functional particles), more particles could migrate to the surface to minimize the free energy; presenting a new liquid-like surface. Several groups have attempted to make coatings such as these, but rarely have made a fully functional, durable surface ⁴²⁵⁻⁴²⁸. Regardless of the design strategy implemented, the practical durability of the liquid-like layers must be addressed.

Liquid-like layers must be able to adhere to a larger variety of substrates. In most experiments including our own, silicon or glass was used as the underlying substrate for this process of grafting ^{194, 208, 230, 231, 238, 277, 279, 282-286}. It is not surprising that this is done as glass and silicon are nearly perfect substrates for silane reactions to occur (Si-O-Si bonds). However, the ability to react and present liquid-like layers less reactive surfaces such as most polymers (besides silicones), metals, and ceramics. To overcome this limitation, a pre-treatment, or linker must be developed to enhance the grafting density of PDMS chains reacted to the surface. One potential linker which has proven highly effective in adhesion to a multitude of substrates, and is utilized by mussels for adhesion, is DOPA⁴²⁹⁻⁴³¹. Through a more synthetic approach, if silicon oxide groups could be added to the DOPA compound, an adhesion layer could be formed which a subsequent PDMS silane reactions could occur. A properly thick adhesion layer of this kind could

also aid in preventing the corrosion of metal substrates by the HCl byproduct (from the vapor phase reaction). Although various attempts have been made to effectively bond PDMS liquid-like layers to various substrates, combining our rapid vapor phase technique with a protective adhesion promotor or linker would make this process more commercially viable.

8.1.2 Multifunctional Marine Antifouling Surfaces

Despite the success of the hydration-layer forming nanowire surfaces for mitigating marine fouling, further investigation is still warranted. First, it is important to push the limitations of the functionalized biocidal nanowire arrays. One thing we have not fully tested, is the long term performance and stability in a natural marine environment, and its efficacy to prevent the adhesion of large-scale marine foulants such as mussels and barnacles. As mentioned in Chapter 4, the nanowires were highly sensitive to bases and acidic and basic environments, which remains a concern regarding the complex environment of a natural body of water. To overcome this issue, relatively inert silica nanowires⁴³² could be grown. Silica also offers the advantage of being notably easier to modify with silanes (such as the surface initiator for ATRP) than alumina⁴³³. Using silica offers great promise in easily growing SBMA brushes on the structures, while increasing the resistance to chemical corrosion. However, one key problem with the nanowire structures is mechanical durability. Once lightly abraded, the nanowires are removed, which will lead to fouling. Thus one interesting possibility is the incorporation of functionalized nanowires into a strong elastic network. If the sufficiently blended into a polysilicone for example, within a marine environment, these high aspect ratio nanowires may to some degree protrude at the surface, offering mechanical biocidal properties as well as a hydration layer. Being within the elastomer network, they will be less susceptible to abrasion.

Another possible research path is influenced from insights of Chapter 3, and the ability of highly mobile PDMS chains to prevent the adsorption of polymers within solution. Unlike SBMA or PEG grafted surfaces, linear PDMS is ineffective in preventing protein adsorption. Despite the high degree of disorder of PDMS chains and the reduction in conformational entropy that is required for adsorption, the chains are too hydrophobic, thus allowing the metastable proteins to irreversibly attach to them^{90, 91}. However, another combination that has not been examined to our knowledge are the grafting of PDMS-SBMA copolymer brushes for marine fouling. A surface that presents a PDMS chain, with a terminal SBMA group would allow for a highly flexible base and a hydration-layer forming terminal segment. This may not only enhance protein resistance, but may also make it extremely difficult for larger species to absorb. If the hydration layer is able to remain in the event of a larger species attaching, the PDMS base layer will induce interfacial slippage upon a shear force; this allows for their facile release. Such a molecular design would include the chemical synthesis of a copolymer brush as well, as engineering the SBMA-PDMS segment lengths.

8.1.3 Durable Polymeric Antifog Coatings

Although we demonstrated some promising results, the solid-slip additive antifog coatings still require further efforts. The fogging properties of Boron Nitride, Nanoclay, and Graphene Oxide additive PVP coatings still require fog testing. The mechanically superior graphite additive PVP coating fogging must also be further examined with respect to a greater range of thickness and additive concentrations. The optical transparency is another factor that has not been quantitatively investigated. Therefore UV-Vis Haze measurements like those conducted in Chapter 5 are needed since the addition of solid additives may impact the visibility depending on the coating thickness, additive composition (and miscibility with matrix), as well as concentration.

These factors must be better understood in order to rationally develop a design framework for the antifog coatings.

Lastly, being that much of the polymer antifog coatings published in the literature do not evaluate the wear resistance, a broad, systematic examination of wear resistance for the prominent antifog strategies be helpful for the field in general. This would further aid in defining key methodologies that have fostered durable coatings as well as highlight the drawbacks and lack of real-world applicability of others.

8.1.4 Polymer Antifrost Coatings

Due to the long duration of time it took to develop a reproducible testing apparatus for this phenomenon, much work is still needed for this project. First, utilizing the new Peltier plate setup, the former data obtained on the chiller apparatus must be gathered. Icing as a function of coating thickness and PEGDA crosslink density, as well as contact angle data must also be gathered. The coating must also be compared to other state-of-the-art antifrost coatings such as polyelectrolyte brushes, SLIPS, and other hydrophilic polymer networks. Lastly, elucidating the interfacial phenomenon that facilitates frost delay for the SBMA and PEG-PU coatings are of importance. The latter work will be completed by Professor Zhan Chen's group via SFG.

One interesting discovery of this work was the degree to which the PEG-PU coatings were able to withstand freezing. This was very surprising due to the obvious increase in hydrophobicity of the PEG-PU coating compared to the SBMA coating. We hypothesized that the PEG-PU coating would have had a significantly faster freezing time than what was measured. Although this result is unexpected, it is also exciting as polyurethanes are wide-spread throughout modern society. If repeatable, this will potentially open up avenues of new mechanistic understandings of frost delay, and allow for a whole host of design parameters that are ubiquitous to polyurethanes. The chemical

functionality of the isocyanate, and the diol can be further modified toward a more hydrophilic nature. The molecular weight of PEG could also be greatly varied. In our brief exploration, we utilized low molecular weight PEG 400, but increasing the weight by orders of magnitude may enhance the water absorption and frost delay properties to an even greater extent.

Bibliography

1. Zhou, X.; Zhang, Z.; Xu, X.; Guo, F.; Zhu, X.; Men, X.; Ge, B., Robust and durable superhydrophobic cotton fabrics for oil/water separation. *ACS applied materials & interfaces* **2013**, 5 (15), 7208-7214.
2. Rajappan, A.; Golovin, K.; Tobelmann, B.; Pillutla, V.; Abhijeet; Choi, W.; Tuteja, A.; McKinley, G. H., Influence of textural statistics on drag reduction by scalable, randomly rough superhydrophobic surfaces in turbulent flow. *Physics of Fluids* **2019**, 31 (4), 042107.
3. Lu, Y.; Sathasivam, S.; Song, J.; Crick, C. R.; Carmalt, C. J.; Parkin, I. P., Robust self-cleaning surfaces that function when exposed to either air or oil. *Science* **2015**, 347 (6226), 1132-1135.
4. Pan, S.; Kota, A. K.; Mabry, J. M.; Tuteja, A., Superomniphobic Surfaces for Effective Chemical Shielding. *Journal of the American Chemical Society* **2013**, 135 (2), 578-581.
5. Kota, A. K.; Kwon, G.; Choi, W.; Mabry, J. M.; Tuteja, A., Hygro-responsive membranes for effective oil–water separation. *Nature communications* **2012**, 3 (1), 1-8.
6. Halvey, A. K.; Macdonald, B.; Dhyan, A.; Tuteja, A., Design of surfaces for controlling hard and soft fouling. *Philosophical Transactions of the Royal Society A* **2018**, 377 (2138).
7. Kim, S.; Kim, K. J., Dropwise condensation modeling suitable for superhydrophobic surfaces. *Journal of heat transfer* **2011**, 133 (8).
8. Dhillon, N. S.; Buongiorno, J.; Varanasi, K. K., Critical heat flux maxima during boiling crisis on textured surfaces. *Nature communications* **2015**, 6 (1), 1-12.
9. Kim, P.; Wong, T.-S.; Alvarenga, J.; Kreder, M. J.; Adorno-Martinez, W. E.; Aizenberg, J., Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance. *ACS nano* **2012**, 6 (8), 6569-6577.
10. Howarter, J. A.; Youngblood, J. P., Self-cleaning and anti-fog surfaces via stimuli-responsive polymer brushes. *Advanced materials* **2007**, 19 (22), 3838-3843.
11. Jung, S.; Tiwari, M. K.; Poulikakos, D., Frost halos from supercooled water droplets. *Proceedings of the National Academy of Sciences* **2012**, 109 (40), 16073-16078.
12. Varanasi, K. K.; Deng, T.; Smith, J. D.; Hsu, M.; Bhate, N., Frost formation and ice adhesion on superhydrophobic surfaces. *Applied Physics Letters* **2010**, 97 (23), 234102.
13. Meuler, A. J.; Smith, J. D.; Varanasi, K. K.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Relationships between Water Wettability and Ice Adhesion. *ACS Applied Materials & Interfaces* **2010**, 2 (11), 3100-3110.
14. Mishchenko, L.; Hatton, B.; Bahadur, V.; Taylor, J. A.; Krupenkin, T.; Aizenberg, J., Design of ice-free nanostructured surfaces based on repulsion of impacting water droplets. *ACS nano* **2010**, 4 (12), 7699-7707.

15. Farhadi, S.; Farzaneh, M.; Kulinich, S., Anti-icing performance of superhydrophobic surfaces. *Applied Surface Science* **2011**, 257 (14), 6264-6269.
16. Chen, J.; Liu, J.; He, M.; Li, K.; Cui, D.; Zhang, Q.; Zeng, X.; Zhang, Y.; Wang, J.; Song, Y., Superhydrophobic surfaces cannot reduce ice adhesion. *Applied Physics Letters* **2012**, 101 (11), 111603.
17. Halvey, A. K.; Macdonald, B.; Dhyani, A.; Tuteja, A., Design of surfaces for controlling hard and soft fouling. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2018**, 377 (2138).
18. Dhyani, A.; Wang, J.; Halvey, A. K.; Macdonald, B.; Mehta, G.; Tuteja, A., Design and applications of surfaces that control the accretion of matter. *Science* **2021**, 373 (6552).
19. Liu, Y.; Liu, Z.; Liu, Y.; Hu, H.; Li, Y.; Yan, P.; Yu, B.; Zhou, F., One-step modification of fabrics with bioinspired polydopamine@ octadecylamine nanocapsules for robust and healable self-cleaning performance. *Small* **2015**, 11 (4), 426-431.
20. Duran, I. R.; Laroche, G., Current trends, challenges, and perspectives of anti-fogging technology: Surface and material design, fabrication strategies, and beyond. *Progress in Materials Science* **2019**, 99, 106-186.
21. Golovin, K. B.; Gose, J. W.; Perlin, M.; Ceccio, S. L.; Tuteja, A., Bioinspired surfaces for turbulent drag reduction. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2016**, 374 (2073), 20160189.
22. Bhushan, B.; Jung, Y. C., Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-Cleaning, Low Adhesion, and Drag Reduction. *Progress in Materials Science* **2011**, 56 (1), 1-108.
23. Zhang, S.; Huang, J.; Chen, Z.; Lai, Y., Bioinspired special wettability surfaces: from fundamental research to water harvesting applications. *Small* **2017**, 13 (3), 1602992.
24. Young, T., III. An essay on the cohesion of fluids. *Philosophical transactions of the royal society of London* **1805**, (95), 65-87.
25. Yang, J.; Zhang, Z.; Xu, X.; Zhu, X.; Men, X.; Zhou, X., Superhydrophilic-superoleophobic coatings. *Journal of Materials Chemistry* **2012**, 22 (7), 2834-2837.
26. Dettre, R. H.; Johnson, R. E., Contact Angle Hysteresis. In *Contact Angle, Wettability, and Adhesion*, AMERICAN CHEMICAL SOCIETY: 1964; Vol. 43, pp 136-144.
27. Genzer, J.; Efimenko, K., Creating Long-Lived Superhydrophobic Polymer Surfaces Through Mechanically Assembled Monolayers. *Science* **2000**, 290 (5499), 2130-2133.
28. Gao, L.; McCarthy, T. J., A perfectly hydrophobic surface ($\theta_A/\theta_R = 180/180$). *Journal of the American Chemical Society* **2006**, 128 (28), 9052-9053.
29. Nosonovsky, M., Model for solid-liquid and solid-solid friction of rough surfaces with adhesion hysteresis. *The Journal of chemical physics* **2007**, 126 (22), 224701.
30. Barthlott, W.; Neinhuis, C., Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, 202 (1), 1-8.
31. 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 (8), 4114-4119.
32. Chen, H.; Zhang, P.; Zhang, L.; Liu, H.; Jiang, Y.; Zhang, D.; Han, Z.; Jiang, L., Continuous directional water transport on the peristome surface of *Nepenthes alata*. *Nature* **2016**, 532 (7597), 85-89.
33. Yun, G.-T.; Jung, W.-B.; Oh, M. S.; Jang, G. M.; Baek, J.; Kim, N. I.; Im, S. G.; Jung, H.-T., Springtail-inspired superomniphobic surface with extreme pressure resistance. *Science advances* **2018**, 4 (8), eaat4978.

34. Liu, T. L.; Kim, C.-J. C., Turning a surface superrepellent even to completely wetting liquids. *Science* **2014**, 346 (6213), 1096-1100.
35. Tuteja, A.; Choi, W.; Ma, M. L.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., Designing superoleophobic surfaces. *Science* **2007**, 318, 1618-1622.
36. Tuteja, A.; Choi, W.; McKinley, G. H.; Cohen, R. E.; Rubner, M. F., Design parameters for superhydrophobicity and superoleophobicity. *MRS bulletin* **2008**, 33 (8), 752-758.
37. Helbig, R.; Nickerl, J.; Neinhuis, C.; Werner, C., Smart skin patterns protect springtails. *PloS one* **2011**, 6 (9).
38. Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Robust omniphobic surfaces. *PNAS* **2008**, 105 (47), 18200–18205.
39. Marmur, A., From Hygrophilic to Superhygrophobic: Theoretical Conditions for Making High-Contact-Angle Surfaces from Low-Contact-Angle Materials. *Langmuir* **2008**, 24 (14), 7573-7579.
40. 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 (6), 4027-4035.
41. Kota, A. K.; Kwon, G.; Tuteja, A., The design and applications of superomniphobic surfaces. *NPG Asia Materials* **2014**, 6 (7), e109-e109.
42. Quéré, D., Non-sticking drops. *Reports on Progress in Physics* **2005**, 68 (11), 2495.
43. Wong, T.-S.; Kang, S. H.; Tang, S. K.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J., Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. *Nature* **2011**, 477 (7365), 443-447.
44. Lafuma, A.; Quéré, D., Slippery pre-suffused surfaces. *EPL (Europhysics Letters)* **2011**, 96 (5), 56001.
45. Smith, J. D.; Dhiman, R.; Anand, S.; Reza-Garduno, E.; Cohen, R. E.; McKinley, G. H.; Varanasi, K. K., Droplet Mobility on Lubricant-Impregnated Surfaces. *Soft Matter* **2013**, 9 (6), 1772-1780.
46. Zhang, L.; Guo, Z.; Sarma, J.; Dai, X., Passive Removal of Highly Wetting Liquids and Ice on Quasi-Liquid Surfaces. *ACS Applied Materials & Interfaces* **2020**.
47. Wang, L.; McCarthy, T. J., Covalently attached liquids: instant omniphobic surfaces with unprecedented repellency. *Angewandte Chemie* **2016**, 128 (1), 252-256.
48. Wexler, J. S.; Jacobi, I.; Stone, H. A., Shear-driven failure of liquid-infused surfaces. *Physical review letters* **2015**, 114 (16), 168301.
49. Schultz, M.; Bendick, J.; Holm, E.; Hertel, W., Economic impact of biofouling on a naval surface ship. *Biofouling* **2011**, 27 (1), 87-98.
50. Schultz, M.; Walker, J.; Steppe, C.; Flack, K., Impact of diatomaceous biofilms on the frictional drag of fouling-release coatings. *Biofouling* **2015**, 31 (9-10), 759-773.
51. Agency, E. P., Effluent limitation guidelines and new source performance standards for the airport deicing category. Federal Register, 2012; p 37.
52. Gent, R.; Dart, N.; Cansdale, J., Aircraft icing. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical Engineering Sciences* **2000**, 358 (1776), 2873-2911.
53. Laforte, J.; Allaire, M.; Laflamme, J., State-of-the-art on power line de-icing. *Atmospheric Research* **1998**, 46 (1-2), 143-158.

54. Aiyejina, A.; Chakrabarti, D. P.; Pilgrim, A.; Sastry, M., Wax formation in oil pipelines: A critical review. *International Journal of Multiphase Flow* **2011**, 37 (7), 671-694.
55. Leontaritis, K. J.; Mansoori, G. A., Asphaltene deposition: a survey of field experiences and research approaches. *Journal of Petroleum Science and Engineering* **1988**, 1 (3), 229-239.
56. Donlan, R. M., Biofilms and device-associated infections. *Emerging infectious diseases* **2001**, 7 (2), 277.
57. Percival, S. L.; Suleman, L.; Vuotto, C.; Donelli, G., Healthcare-associated infections, medical devices and biofilms: risk, tolerance and control. *Journal of Medical Microbiology* **2015**, 64 (4), 323-334.
58. Sojoudi, H.; Wang, M.; Boscher, N.; McKinley, G.; Gleason, K., Durable and scalable icephobic surfaces: similarities and distinctions from superhydrophobic surfaces. *Soft Matter* **2016**, 12 (7), 1938-1963.
59. Thomas, S. K.; Cassoni, R. P.; MacArthur, C. D., Aircraft anti-icing and de-icing techniques and modeling. *Journal of Aircraft* **1996**, 33 (5), 841-854.
60. Farzaneh, M.; Volat, C.; Leblond, A., Anti-icing and de-icing techniques for overhead lines. In *Atmospheric Icing of Power Networks*, Springer: 2008; pp 229-268.
61. Frankenstein, S.; Tuthill, A. M., Ice adhesion to locks and dams: past work; future directions? *Journal of Cold Regions Engineering* **2002**, 16 (2), 83-96.
62. Fillion, R.; Riahi, A.; Edrissy, A., A review of icing prevention in photovoltaic devices by surface engineering. *Renewable Sustainable Energy Reviews* **2014**, 32, 797-809.
63. Parent, O.; Ilinca, A., Anti-icing and de-icing techniques for wind turbines: Critical review. *Cold Regions Science Technology* **2011**, 65 (1), 88-96.
64. Petrenko, V. F.; Whitworth, R. W., *Physics of ice*. OUP Oxford: 1999.
65. Tatinclaux, J.-C.; Hirayama, K.-I., Determination of the flexural strength and elastic modulus of ice from in situ cantilever-beam tests. *Cold Regions Science Technology* **1982**, 6 (1), 37-47.
66. Eberle, P.; Tiwari, M. K.; Maitra, T.; Poulikakos, D., Rational nanostructuring of surfaces for extraordinary icephobicity. *Nanoscale* **2014**, 6 (9), 4874-4881.
67. Heydari, G.; Thormann, E.; Järn, M.; Tyrode, E.; Claesson, P. M., Hydrophobic surfaces: topography effects on wetting by supercooled water and freezing delay. *The Journal of Physical Chemistry C* **2013**, 117 (42), 21752-21762.
68. Jung, S.; Dorrestijn, M.; Raps, D.; Das, A.; Megaridis, C. M.; Poulikakos, D. J. L., Are superhydrophobic surfaces best for icephobicity? **2011**, 27 (6), 3059-3066.
69. Gbaruko, B.; Igwe, J.; Gbaruko, P.; Nwokeoma, R., Gas hydrates and clathrates: Flow assurance, environmental and economic perspectives and the Nigerian liquified natural gas project. *Journal of Petroleum Science and Engineering* **2007**, 56 (1-3), 192-198.
70. Sloan Jr, E. D.; Koh, C., *Clathrate hydrates of natural gases*. CRC press: 2007.
71. Sum, A. K.; Koh, C. A.; Sloan, E. D. J. I.; Research, E. C., Clathrate hydrates: from laboratory science to engineering practice. *Industrial Engineering Chemistry Research* **2009**, 48 (16), 7457-7465.
72. Devarakonda, S.; Groysman, A.; Myerson, A. S., THF–water hydrate crystallization: an experimental investigation. *Journal of Crystal Growth* **1999**, 204 (4), 525-538.
73. Koh, C.; Westacott, R.; Zhang, W.; Hirachand, K.; Creek, J.; Soper, A., Mechanisms of gas hydrate formation and inhibition. *Fluid Phase Equilibria* **2002**, 194, 143-151.
74. Sloan Jr, E. D., Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, 426 (6964), 353.

75. Azimi, G.; Cui, Y.; Sabanska, A.; Varanasi, K. K., Scale-resistant surfaces: Fundamental studies of the effect of surface energy on reducing scale formation. *Applied Surface Science* **2014**, *313*, 591-599.
76. Rankin, B.; Adamson, W., Scale formation as related to evaporator surface conditions. *Desalination* **1973**, *13* (1), 63-87.
77. Zhao, Q.; Liu, Y.; Wang, S., Surface modification of water treatment equipment for reducing CaSO₄ scale formation. *Desalination* **2005**, *180* (1-3), 133-138.
78. Alahmad, M., Factors affecting scale formation in sea water environments—an experimental approach. *Chemical Engineering Technology: Industrial Chemistry - Plant Equipment - Process Engineering - Biotechnology* **2008**, *31* (1), 149-156.
79. Müller-Steinhagen, H.; Zhao, Q., Investigation of low fouling surface alloys made by ion implantation technology. *Chemical Engineering Science* **1997**, *52* (19), 3321-3332.
80. Sanjay, M.; Simanta, B.; Kulwant, S., Paraffin problems in crude oil production and transportation: a review. *SPE Production & facilities* **1995**, *10* (01), 50-54.
81. Kelechukwu, E. M.; Al-Salim, H. S.; Saadi, A., Prediction of wax deposition problems of hydrocarbon production system. *Journal of Petroleum Science and Engineering* **2013**, *108*, 128-136.
82. Al-Yaari, M. In *Paraffin wax deposition: mitigation and removal techniques*, SPE Saudi Arabia section Young Professionals Technical Symposium, Society of Petroleum Engineers: 2011.
83. Wang, J.; Buckley, J. S.; Creek, J. L., Asphaltene deposition on metallic surfaces. *Journal of dispersion science and technology* **2004**, *25* (3), 287-298.
84. Patil, A. O.; Zushma, S.; Berluche, E.; Varma-Nair, M., Wax crystal modifiers (LAW657). Google Patents: 2002.
85. Pedersen, K. S.; Rønningsen, H. P., Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils. *Energy & fuels* **2003**, *17* (2), 321-328.
86. Kraiwattanawong, K.; Fogler, H. S.; Gharfeh, S. G.; Singh, P.; Thomason, W. H.; Chavadej, S., Effect of asphaltene dispersants on aggregate size distribution and growth. *Energy & Fuels* **2009**, *23* (3), 1575-1582.
87. Etoumi, A., Microbial treatment of waxy crude oils for mitigation of wax precipitation. *Journal of Petroleum Science and Engineering* **2007**, *55* (1-2), 111-121.
88. Brown, F. In *Microbes: The practical and environmental safe solution to production problems, enhanced production, and enhanced oil recovery*, Permian Basin Oil and Gas Recovery Conference, Society of Petroleum Engineers: 1992.
89. Paso, K.; Kompalla, T.; Aske, N.; Rønningsen, H. P.; Øye, G.; Sjöblom, J., Novel surfaces with applicability for preventing wax deposition: a review. *Journal of Dispersion Science and Technology* **2009**, *30* (6), 757-781.
90. Jeon, S.; Lee, J.; Andrade, J.; De Gennes, P., Protein—surface interactions in the presence of polyethylene oxide: I. Simplified theory. *Journal of Colloid Interface Science* **1991**, *142* (1), 149-158.
91. Gong, P.; Grainger, D. W., Nonfouling Surfaces. In *Microarrays*, Springer: 2007; pp 59-92.
92. Chambers, L. D.; Stokes, K. R.; Walsh, F. C.; Wood, R. J., Modern approaches to marine antifouling coatings. *Surface Coatings Technology* **2006**, *201* (6), 3642-3652.

93. Wahl, M., Marine epibiosis. I. Fouling and antifouling: some basic aspects. *Marine Ecology Progress Series* **1989**, 58, 175-189.
94. Magin, C. M.; Cooper, S. P.; Brennan, A. B., Non-toxic antifouling strategies. *Materials today* **2010**, 13 (4), 36-44.
95. Ji, B.; Gao, H., Mechanical properties of nanostructure of biological materials. *Journal of the Mechanics Physics of Solids* **2004**, 52 (9), 1963-1990.
96. Gosline, J.; Lillie, M.; Carrington, E.; Guerette, P.; Ortlepp, C.; Savage, K., Elastic proteins: biological roles and mechanical properties. *Philosophical Transactions of the Royal Society of London B: Biological Sciences* **2002**, 357 (1418), 121-132.
97. Saikhwan, P.; Chew, J. Y.; Paterson, W. R.; Wilson, D. I., Swelling and its suppression in the cleaning of polymer fouling layers. *Industrial Engineering Chemistry Research* **2007**, 46 (14), 4846-4855.
98. Metzger, U.; Le-Clech, P.; Stuetz, R. M.; Frimmel, F. H.; Chen, V., Characterisation of polymeric fouling in membrane bioreactors and the effect of different filtration modes. *J Journal of Membrane Science* **2007**, 301 (1-2), 180-189.
99. Watkinson, A. P., Chemical reaction fouling of organic fluids. *Chemical Engineering Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology* **1992**, 15 (2), 82-90.
100. Callow, M. E.; Callow, J. A., Marine biofouling: a sticky problem. *Biologist* **2002**, 49 (1), 1-5.
101. Bixler, G. D.; Bhushan, B., Biofouling: lessons from nature. *Phil. Trans. R. Soc. A* **2012**, 370 (1967), 2381-2417.
102. Engelsman, A. F.; Saldarriaga-Fernandez, I. C.; Nejadnik, M. R.; van Dam, G. M.; Francis, K. P.; Ploeg, R. J.; Busscher, H. J.; van der Mei, H. C., The risk of biomaterial-associated infection after revision surgery due to an experimental primary implant infection. *Biofouling* **2010**, 26 (7), 761-767.
103. Ward, W. K., A review of the foreign-body response to subcutaneously-implanted devices: the role of macrophages and cytokines in biofouling and fibrosis. SAGE Publications: 2008.
104. Wisniewski, N.; Reichert, M., Methods for reducing biosensor membrane biofouling. *Colloids Surfaces B: Biointerfaces* **2000**, 18 (3-4), 197-219.
105. Edmiston, C. E.; Seabrook, G. R.; Goheen, M. P.; Krepel, C. J.; Johnson, C. P.; Lewis, B. D.; Brown, K. R.; Towne, J. B., Bacterial adherence to surgical sutures: can antibacterial-coated sutures reduce the risk of microbial contamination? *Journal of the American College of Surgeons* **2006**, 203 (4), 481-489.
106. Kluge, R. M.; Calia, F. M.; McLaughlin, J. S.; Hornick, R. B., Sources of contamination in open heart surgery. *JAMA* **1974**, 230 (10), 1415-1418.
107. Schmalzried, T. P.; Amstutz, H. C.; Au, M.-K.; Dorey, F. J., Etiology of deep sepsis in total hip arthroplasty. The significance of hematogenous and recurrent infections. *Clinical Orthopaedics Related Research* **1992**, (280), 200-207.
108. Chan, J.; Wong, S., *Biofouling: types, Impact and Anti-Fouling*. Nova Science Publishers, Incorporated: 2010.

109. Chopra, V.; O'horo, J. C.; Rogers, M. A.; Maki, D. G.; Safdar, N., The risk of bloodstream infection associated with peripherally inserted central catheters compared with central venous catheters in adults: a systematic review and meta-analysis. *Infection Control Hospital Epidemiology* **2013**, *34* (9), 908-918.
110. Maki, D. G.; Tambyah, P. A., Engineering out the risk for infection with urinary catheters. *Emerging Infectious Diseases* **2001**, *7* (2), 342.
111. Peters, G.; Locci, R.; Pulverer, G., Adherence and growth of Coagulase-Negative Staphylococci on Surfaces of Intravenous Catheters. *Emerging Infectious Diseases* **1982**, *146* (4), 479-482.
112. Attaway III, H. H.; Fairey, S.; Steed, L. L.; Salgado, C. D.; Michels, H. T.; Schmidt, M. G., Intrinsic bacterial burden associated with intensive care unit hospital beds: effects of disinfection on population recovery and mitigation of potential infection risk. *American Journal of Infection Control* **2012**, *40* (10), 907-912.
113. Appendini, P.; Hotchkiss, J. H., Review of antimicrobial food packaging. *Innovative Food Science Emerging Technologies* **2002**, *3* (2), 113-126.
114. Han, J. H. J. N. f. p. t., Antimicrobial food packaging. *Novel Food Packaging Techniques* **2003**, *8*, 50-70.
115. Petersen, K.; Nielsen, P. V.; Bertelsen, G.; Lawther, M.; Olsen, M. B.; Nilsson, N. H.; Mortensen, G., Potential of biobased materials for food packaging. *Trends in Food Science Technology* **1999**, *10* (2), 52-68.
116. Quintavalla, S.; Vicini, L., Antimicrobial food packaging in meat industry. *Meat Science* **2002**, *62* (3), 373-380.
117. Flemming, H.-C., Reverse osmosis membrane biofouling. *Experimental Thermal Fluid Science* **1997**, *14* (4), 382-391.
118. Hyun, J.; Jang, H.; Kim, K.; Na, K.; Tak, T., Restriction of biofouling in membrane filtration using a brush-like polymer containing oligoethylene glycol side chains. *Journal of Membrane Science* **2006**, *282* (1-2), 52-59.
119. Lee, W.; Ahn, C. H.; Hong, S.; Kim, S.; Lee, S.; Baek, Y.; Yoon, J., Evaluation of surface properties of reverse osmosis membranes on the initial biofouling stages under no filtration condition. *Journal of Membrane Science* **2010**, *351* (1-2), 112-122.
120. Mansouri, J.; Harrison, S.; Chen, V., Strategies for controlling biofouling in membrane filtration systems: challenges and opportunities. *Journal of Materials Chemistry* **2010**, *20* (22), 4567-4586.
121. Potts, D.; Ahlert, R. C.; Wang, S. S., A critical review of fouling of reverse osmosis membranes. *Desalination* **1981**, *36* (3), 235-264.
122. Hellio, C.; Yebra, D., *Advances in marine antifouling coatings and technologies*. Woodhead Publishing 2009.
123. Townsin, R., The ship hull fouling penalty. *Biofouling* **2003**, *19* (S1), 9-15.
124. Edyvean, R.; Terry, L.; Picken, G., Marine fouling and its effects on offshore structures in the North Sea: A review. *International Biodeterioration* **1985**, *21* (4), 277-284.

125. Houghton, D., Marine fouling and offshore structures. *Ocean Management* **1978**, 4 (2-4), 347-352.
126. Hucknall, A.; Rangarajan, S.; Chilkoti, A., In pursuit of zero: polymer brushes that resist the adsorption of proteins. *Advanced Materials* **2009**, 21 (23), 2441-2446.
127. Banerjee, I.; Pangule, R. C.; Kane, R. S., Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. *Advanced materials* **2011**, 23 (6), 690-718.
128. Zhang, H.; Chiao, M., Anti-fouling coatings of poly (dimethylsiloxane) devices for biological and biomedical applications. *Journal of Medical Biological Engineering* **2015**, 35 (2), 143-155.
129. Amiji, M.; Park, K., Prevention of protein adsorption and platelet adhesion on surfaces by PEO/PPO/PEO triblock copolymers. *Biomaterials* **1992**, 13 (10), 682-692.
130. Schultz, M. P., Effects of coating roughness and biofouling on ship resistance and powering. *Biofouling* **2007**, 23 (5), 331-341.
131. Schultz, M. P.; Kavanagh, C. J.; Swain, G. W., Hydrodynamic forces on barnacles: Implications on detachment from fouling-release surfaces. *Biofouling* **1999**, 13 (4), 323-335.
132. Townsin, R. L., The ship hull fouling penalty. *Biofouling* **2003**, 19 Suppl, 9-15.
133. Alzieu, C.; Sanjuan, J.; Deltreil, J.; Borel, M., Tin contamination in Arcachon Bay: effects on oyster shell anomalies. *Marine pollution bulletin* **1986**, 17 (11), 494-498.
134. Smith, J. D.; Meuler, A. J.; Bralower, H. L.; Venkatesan, R.; Subramanian, S.; Cohen, R. E.; McKinley, G. H.; Varanasi, K. K., Hydrate-phobic surfaces: fundamental studies in clathrate hydrate adhesion reduction. *Physical Chemistry Chemical Physics* **2012**, 14 (17), 6013-6020.
135. Chen, Z.; Nosonovsky, M., Revisiting lowest possible surface energy of a solid. *Surface Topography: Metrology Properties* **2017**, 5 (4), 045001.
136. Chaudhury, M. K., Interfacial interaction between low-energy surfaces. *Materials Science Engineering: R: Reports* **1996**, 16 (3), 97-159.
137. Packham, D. E., Surface energy, surface topography and adhesion. *International Journal of Adhesion and Adhesives* **2003**, 23 (6), 437-448.
138. Golovin, K.; Kobaku, S. P. R.; Lee, D. H.; DiLoreto, E. T.; Mabry, J. M.; Tuteja, A., Designing durable icephobic surfaces. *Science Advances* **2016**, 2 (3).
139. Zhang, X.; Tian, J.; Wang, L.; Zhou, Z., Wettability effect of coatings on drag reduction and paraffin deposition prevention in oil. *Journal of Petroleum Science and Engineering* **2002**, 36 (1-2), 87-95.
140. Baier, R. E., *Surface properties influencing bacterial adhesion*. Academic Press Inc.: New York, 1970; p 15-48.
141. Baier, R. E., Surface behaviour of biomaterials: The theta surface for biocompatibility. *Journal of Materials Science: Materials in Medicine* **2006**, 17 (11), 1057-1062.
142. Chaudhury, M.; Kim, K., Shear-induced adhesive failure of a rigid slab in contact with a thin confined film. *The European Physical Journal E* **2007**, 23 (2), 175-183.
143. Kendall, K., The adhesion and surface energy of elastic solids. *Journal of Physics D: Applied Physics* **1971**, 4 (8), 1186.
144. Chaudhury, M. K.; Finlay, J. A.; Chung, J. Y.; Callow, M. E.; Callow, J. A., The influence of elastic modulus and thickness on the release of the soft-fouling green alga *Ulva linza* (syn. *Enteromorpha linza*) from poly(dimethylsiloxane) (PDMS) model networks. *Biofouling* **2004**, 21 (1), 41-48.

145. Chung, J. Y.; Chaudhury, M. K., Soft and Hard Adhesion. *The Journal of Adhesion* **2005**, *81* (10-11), 1119-1145
146. Epstein, A. K.; Wong, T.-S.; Belisle, R. A.; Boggs, E. M.; Aizenberg, J., Liquid-infused structured surfaces with exceptional anti-biofouling performance. *PNAS* **2012**, *109* (33), 13182-13187.
147. Xiao, L.; Li, J.; Mieszkina, S.; Fino, A. D.; Clare, A. S.; Callow, M. E.; Callow, J. A.; Grunze, M.; Rosenhahn, A.; Levkin, P. A., Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties. *ACS Appl. Mater. Interfaces* **2013**, *5* (20), 10074-10080.
148. Amini, S.; Kolle, S.; Petrone, L.; Ahanotu, O.; Sunny, S.; Sutanto, C. N.; Hoon, S.; Cohen, L.; Weaver, J. C.; Aizenberg, J.; Vogel, N.; Miserez, A., Preventing mussel adhesion using lubricant-infused materials. *Science* **2017**, *357* (6352).
149. Subramanyam, S. B.; Azimi, G.; Varanasi, K. K., Designing Lubricant-Impregnated Textured Surfaces to Resist Scale Formation. *Advanced Materials Interfaces* **2014**, *1* (2).
150. Wilson, P. W.; Lu, W.; Xu, H.; Kim, P.; Kreder, M. J.; Alvarenga, J.; Aizenberg, J., Inhibition of ice nucleation by slippery liquid-infused porous surfaces (SLIPS). *Physical Chemistry Chemical Physics* **2013**, *15* (2), 581-585.
151. Chen, D.; Gelenter, M. D.; Hong, M.; Cohen, R. E.; McKinley, G. H., Icephobic surfaces induced by interfacial nonfrozen water. *ACS applied materials & interfaces* **2017**, *9* (4), 4202-4214.
152. Dou, R.; Chen, J.; Zhang, Y.; Wang, X.; Cui, D.; Song, Y.; Jiang, L.; Wang, J., Anti-icing coating with an aqueous lubricating layer. *ACS applied materials & interfaces* **2014**, *6* (10), 6998-7003.
153. Zhang, S.; Huang, J.; Cheng, Y.; Yang, H.; Chen, Z.; Lai, Y., Bioinspired Surfaces with Superwettability for Anti-Icing and Ice-Phobic Application: Concept, Mechanism, and Design. *Small* **2017**, *13* (48), 1701867.
154. Chen, J.; Luo, Z.; Fan, Q.; Lv, J.; Wang, J., Anti-ice coating inspired by ice skating. *Small* **2014**, *10* (22), 4693-4699.
155. Kreder, M. J.; Alvarenga, J.; Kim, P.; Aizenberg, J., Design of anti-icing surfaces: smooth, textured or slippery? *Nature Reviews Materials* **2016**, *1* (1), 15003.
156. Urata, C.; Dunderdale, G. J.; England, M. W.; Hozumi, A., Self-lubricating organogels (SLUGs) with exceptional syneresis-induced anti-sticking properties against viscous emulsions and ices. *Journal of Materials Chemistry A* **2015**, *3* (24), 12626-12630.
157. Liu, Q.; Yang, Y.; Huang, M.; Zhou, Y.; Liu, Y.; Liang, X., Durability of a lubricant-infused Electrospray Silicon Rubber surface as an anti-icing coating. *Applied Surface Science* **2015**, *346*, 68-76.
158. Beemer, D. L.; Wang, W.; Kota, A. K., Durable gels with ultra-low adhesion to ice. *Journal of Materials Chemistry A* **2016**, *4* (47), 18253-18258.
159. Subramanyam, S. B.; Rykaczewski, K.; Varanasi, K. K., Ice adhesion on lubricant-impregnated textured surfaces. *Langmuir* **2013**, *29* (44), 13414-13418.
160. Rykaczewski, K.; Anand, S.; Subramanyam, S. B.; Varanasi, K. K., Mechanism of frost formation on lubricant-impregnated surfaces. *Langmuir* **2013**, *29* (17), 5230-5238.
161. Ivanova, E. P.; Hasan, J.; Webb, H. K.; Truong, V. K.; Watson, G. S.; Watson, J. A.; Baulin, V. A.; Pogodin, S.; Wang, J. Y.; Tobin, M. J.; Löbbe, C.; Crawford, R. J., Natural Bactericidal Surfaces: Mechanical Rupture of *Pseudomonas aeruginosa* Cells by Cicada Wings. *Small* **2012**, *8* (16), 2489-2494.

162. 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 (1), 55-62.
163. Cooper, S. J.; Nicholson, C. E.; Liu, J., A simple classical model for predicting onset crystallization temperatures on curved substrates and its implications for phase transitions in confined volumes. *The Journal of chemical physics* **2008**, 129 (12), 124715.
164. Cheng, G.; Zhang, Z.; Chen, S.; Bryers, J. D.; Jiang, S., Inhibition of bacterial adhesion and biofilm formation on zwitterionic surfaces. *Biomaterials* **2007**, 28 (29), 4192-4199.
165. Li, B.; Jain, P.; Ma, J.; Smith, J. K.; Yuan, Z.; Hung, H.-C.; He, Y.; Lin, X.; Wu, K.; Pfaendtner, J., Trimethylamine N-oxide-derived zwitterionic polymers: A new class of ultralow fouling bioinspired materials. *Science Advances* **2019**, 5 (6), eaaw9562.
166. He, Z.; Wu, C.; Hua, M.; Wu, S.; Wu, D.; Zhu, X.; Wang, J.; He, X., Bioinspired Multifunctional Anti-icing Hydrogel. *Matter* **2020**.
167. Zhang, Z.; Finlay, J. A.; Wang, L.; Gao, Y.; Callow, J. A.; Callow, M. E.; Jiang, S., Polysulfobetaine-grafted surfaces as environmentally benign ultralow fouling marine coatings. *Langmuir* **2009**, 25 (23), 13516-13521.
168. Jeon, S.; Lee, J.; Andrade, J.; De Gennes, P.; science, i., Protein—surface interactions in the presence of polyethylene oxide: I. Simplified theory. *Journal of Colloid Interface Science* **1991**, 142 (1), 149-158.
169. Prime, K. L.; Whitesides, G. M., Self-assembled organic monolayers: model systems for studying adsorption of proteins at surfaces. *Science* **1991**, 1164-1167.
170. Bearinger, J.; Terrettaz, S.; Michel, R.; Tirelli, N.; Vogel, H.; Textor, M.; Hubbell, J., Chemisorbed poly (propylene sulphide)-based copolymers resist biomolecular interactions. *Nature Materials* **2003**, 2 (4), 259.
171. Mrksich, M.; Whitesides, G. M., Using self-assembled monolayers to understand the interactions of man-made surfaces with proteins and cells. *Annual Review of Biophysics Biomolecular Structure* **1996**, 25 (1), 55-78.
172. Li, L.; Chen, S.; Zheng, J.; Ratner, B. D.; Jiang, S., Protein adsorption on oligo (ethylene glycol)-terminated alkanethiolate self-assembled monolayers: the molecular basis for nonfouling behavior. *The Journal of Physical Chemistry B* **2005**, 109 (7), 2934-2941.
173. Andrade, J.; Hlady, V.; Wei, A.; Ho, C.; Lea, A.; Jeon, S.; Lin, Y.; Stroup, E., Proteins at interfaces: principles, multivariate aspects, protein resistant surfaces, and direct imaging and manipulation of adsorbed proteins. In *Biologically Modified Polymeric Biomaterial Surfaces*, Springer: 1992; pp 67-84.
174. Jeon, S.; Andrade, J., Protein—surface interactions in the presence of polyethylene oxide: II. Effect of protein size. *Journal of Colloid Interface Science* **1991**, 142 (1), 159-166.
175. Sofia, S. J.; Premnath, V.; Merrill, E. W., Poly (ethylene oxide) grafted to silicon surfaces: grafting density and protein adsorption. *Macromolecules* **1998**, 31 (15), 5059-5070.
176. Tegoulia, V. A.; Rao, W.; Kalambur, A. T.; Rabolt, J. F.; Cooper, S. L., Surface properties, fibrinogen adsorption, and cellular interactions of a novel phosphorylcholine-containing self-assembled monolayer on gold. *Langmuir* **2001**, 17 (14), 4396-4404.

177. Holmlin, R. E.; Chen, X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M., Zwitterionic SAMs that resist nonspecific adsorption of protein from aqueous buffer. *Langmuir* **2001**, 17 (9), 2841-2850.
178. Chen, S.; Zheng, J.; Li, L.; Jiang, S., Strong resistance of phosphorylcholine self-assembled monolayers to protein adsorption: insights into nonfouling properties of zwitterionic materials. *Journal of the American Chemical Society* **2005**, 127 (41), 14473-14478.
179. He, Y.; Hower, J.; Chen, S.; Bernards, M. T.; Chang, Y.; Jiang, S., Molecular simulation studies of protein interactions with zwitterionic phosphorylcholine self-assembled monolayers in the presence of water. *Langmuir* **2008**, 24 (18), 10358-10364.
180. Chang, Y.; Liao, S.-C.; Higuchi, A.; Ruaan, R.-C.; Chu, C.-W.; Chen, W.-Y., A highly stable nonbiofouling surface with well-packed grafted zwitterionic polysulfobetaine for plasma protein repulsion. *Langmuir* **2008**, 24 (10), 5453-5458.
181. Keefe, A. J.; Jiang, S., Poly (zwitterionic) protein conjugates offer increased stability without sacrificing binding affinity or bioactivity. *Nature Chemistry* **2012**, 4 (1), 59.
182. Holmlin, R. E.; Chen, X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. J. L., Zwitterionic SAMs that resist nonspecific adsorption of protein from aqueous buffer. **2001**, 17 (9), 2841-2850.
183. Jiang, S.; Cao, Z., Ultralow-fouling, functionalizable, and hydrolyzable zwitterionic materials and their derivatives for biological applications. *Advanced materials* **2010**, 22 (9), 920-932.
184. Laughlin, R. G., Fundamentals of the zwitterionic hydrophilic group. *Langmuir* **1991**, 7 (5), 842-847.
185. Hsiao, S.-W.; Venault, A.; Yang, H.-S.; Chang, Y., Bacterial resistance of self-assembled surfaces using PPOM-b-PSBMA zwitterionic copolymer—Concomitant effects of surface topography and surface chemistry on attachment of live bacteria. *Colloids Surfaces B: Biointerfaces* **2014**, 118, 254-260.
186. Mi, L.; Jiang, S., Integrated antimicrobial and nonfouling zwitterionic polymers. *Angewandte Chemie International Edition* **2014**, 53 (7), 1746-1754.
187. Li, G.; Cheng, G.; Xue, H.; Chen, S.; Zhang, F.; Jiang, S., Ultra low fouling zwitterionic polymers with a biomimetic adhesive group. *Biomaterials* **2008**, 29 (35), 4592-4597.
188. He, Z.; Xie, W. J.; Liu, Z.; Liu, G.; Wang, Z.; Gao, Y. Q.; Wang, J., Tuning ice nucleation with counterions on polyelectrolyte brush surfaces. *Science advances* **2016**, 2 (6), e1600345.
189. Liu, Z.; He, Z.; Lv, J.; Jin, Y.; Wu, S.; Liu, G.; Zhou, F.; Wang, J., Ion-specific ice propagation behavior on polyelectrolyte brush surfaces. *RSC Advances* **2017**, 7 (2), 840-844.
190. Gavish, M.; Wang, J.; Eisenstein, M.; Lahav, M.; Leiserowitz, L., The role of crystal polarity in alpha-amino acid crystals for induced nucleation of ice. *Science* **1992**, 256 (5058), 815-818.
191. Ehre, D.; Lavert, E.; Lahav, M.; Lubomirsky, I., Water freezes differently on positively and negatively charged surfaces of pyroelectric materials. *Science* **2010**, 327 (5966), 672-675.
192. Liu, K.; Wang, C.; Ma, J.; Shi, G.; Yao, X.; Fang, H.; Song, Y.; Wang, J., Janus effect of antifreeze proteins on ice nucleation. *Proceedings of the National Academy of Sciences* **2016**, 113 (51), 14739-14744.

193. Esser-Kahn, A. P.; Trang, V.; Francis, M. B., Incorporation of Antifreeze Proteins into Polymer Coatings Using Site-Selective Bioconjugation. *Journal of the American Chemical Society* **2010**, 132 (38), 13264-13269.
194. Zhang, L.; Guo, Z.; Sarma, J.; Dai, X., Passive removal of highly wetting liquids and ice on quasi-liquid surfaces. *ACS Applied Materials & Interfaces* **2020**, 12 (17), 20084-20095.
195. Wang, L.; McCarthy, T. J., Covalently Attached Liquids: Instant Omniphobic Surfaces with Unprecedented Repellency. *Angewandte Chemie* **2015**, 55 (1), 244-248.
196. Zhao, H.; Deshpande, C. A.; Li, L.; Yan, X.; Hoque, M. J.; Kuntumalla, G.; Rajagopal, M. C.; Chang, H. C.; Meng, Y.; Sundar, S.; Ferreira, P.; Shao, C.; Salapaka, S.; Sinha, S.; Miljkovic, N., Extreme Antiscaling Performance of Slippery Omniphobic Covalently Attached Liquids. *ACS Applied Materials & Interfaces* **2020**, 12 (10), 12054-12067.
197. Jain, A.; Bhosle, N. B., Biochemical composition of the marine conditioning film: implications for bacterial adhesion. *Biofouling* **2009**, 25 (1), 13-19.
198. Cooksey, K.; Wigglesworth-Cooksey, B., Adhesion of bacteria and diatoms to surfaces in the sea: a review. *Aquatic Microbial Ecology* **1995**, 9 (1), 87-96.
199. Fletcher, R. L.; Callow, M. E., The settlement, attachment and establishment of marine algal spores. *British phycological journal* **1992**, 27 (3), 303-329.
200. Zhang, X.; He, J., Hydrogen-bonding-supported self-healing antifogging thin films. *Scientific reports* **2015**, 5, 9227.
201. Grube, S.; Siegmann, K.; Hirayama, M., A moisture-absorbing and abrasion-resistant transparent coating on polystyrene. *Journal of Coatings Technology and Research* **2015**, 12 (4), 669-680.
202. Howarter, J. A.; Youngblood, J. P., Self-Cleaning and Next Generation Anti-Fog Surfaces and Coatings. *Macromolecular Rapid Communications* **2008**, 29 (6), 455-466.
203. Ezzat, M.; Huang, C.-J., Zwitterionic polymer brush coatings with excellent anti-fog and anti-frost properties. *RSC advances* **2016**, 6 (66), 61695-61702.
204. Lee, H.; Alcaraz, M. L.; Rubner, M. F.; Cohen, R. E., Zwitter-wettability and antifogging coatings with frost-resisting capabilities. *ACS nano* **2013**, 7 (3), 2172-2185.
205. Boluk, Y., Adhesion of freezing precipitates to aircraft surfaces. **1996**.
206. Chang, Y.-S., Performance analysis of frostless heat exchanger by spreading antifreeze solution on heat exchanger surface. *Journal of Thermal Science and Technology* **2011**, 6 (1), 123-131.
207. Sayward, J. M., *Seeking low ice adhesion*. The Laboratory: 1979; Vol. 79.
208. Halvey, A. K.; Macdonald, B.; Golovin, K.; Boban, M.; Dhyani, A.; Lee, D. H.; Gose, J. W.; Ceccio, S. L.; Tuteja, A., Rapid and Robust Surface Treatment for Simultaneous Solid and Liquid Repellency. *ACS Applied Materials & Interfaces* **2021**, 13 (44), 53171-53180.
209. Schultz, M. P.; Walker, J. M.; Steppe, C. N.; Flack, K. A., Impact of diatomaceous biofilms on the frictional drag of fouling-release coatings. *Biofouling* **2015**, 31 (9-10), 759-773.
210. Kreder, M. J.; Alvarenga, J.; Kim, P.; Aizenberg, J., Design of anti-icing surfaces: smooth, textured or slippery? *Nature Reviews Materials* **2016**, 1, 15003-15003.
211. Kota, A. K.; Kwon, G.; Choi, W.; Mabry, J. M.; Tuteja, A., Hygro responsive membranes for effective oil-water separation. *Nat Commun* **2012**, 3, 1025-1025.
212. de Gennes, P. G.; Brochard-Wyart, F.; Quere, D., *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*. Springer: 2004.

213. Tuteja, A.; Choi, W.; McKinley, G. H.; Cohen, R. E.; Rubner, M. F., Design Parameters for Superhydrophobicity and Superoleophobicity. *MRS Bulletin* **2008**, 33 (8), 752-752.
214. Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Robust omniphobic surfaces. *Proceedings of the National Academy of Sciences* **2008**, 105 (47), 18200-18205.
215. Bixler, G. D.; Bhushan, B., Bioinspired micro/nanostructured surfaces for oil drag reduction in closed channel flow. *Soft Matter* **2013**, 9 (5), 1620-1635.
216. Chen, X.; Weibel, J. A.; Garimella, S. V., Water and Ethanol Droplet Wetting Transition during Evaporation on Omniphobic Surfaces. *Scientific Reports* **2015**, 5, 17110-17110.
217. Verho, T.; Bower, C.; Andrew, P.; Franssila, S.; Ikkala, O.; Ras, R. H., Mechanically Durable Superhydrophobic Surfaces. *Advanced Materials* **2011**, 23 (5), 673-678.
218. Kota, A. K.; Choi, W.; Tuteja, A., Superomniphobic surfaces: Design and durability. *MRS Bulletin* **2013**, 38 (05), 383-390.
219. Chen, J.; Liu, J.; He, M.; Li, K.; Cui, D.; Zhang, Q.; Zeng, X.; Zhang, Y.; Wang, J.; Song, Y., Superhydrophobic surfaces cannot reduce ice adhesion. *Applied Physics Letters* **2012**, 101 (11), 111603-111603.
220. Varanasi, K. K.; Deng, T.; Smith, J. D.; Hsu, M.; Bhate, N., Frost formation and ice adhesion on superhydrophobic surfaces. *Applied Physics Letters* **2010**, 97 (23), 234102-234102.
221. Nosonovsky, M.; Hejazi, V., Why Superhydrophobic Surfaces Are Not Always Icephobic. *ACS Nano* **2012**, 6 (10), 8488-8491.
222. Wong, T. S.; Kang, S. H.; Tang, S. K.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J., Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity. *Nature* **2011**, 477 (7365), 443-447.
223. Kim, P.; Wong, T. S.; Alvarenga, J.; Kreder, M. J.; Adorno-Martinez, W. E.; Aizenberg, J., Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance. *ACS Nano* **2012**, 6 (8), 6569-6577.
224. Boban, M.; Golovin, K.; Tobelmann, B.; Gupte, O.; Mabry, J. M.; Tuteja, A., Smooth, all-solid, low-hysteresis, omniphobic surfaces with enhanced mechanical durability. *ACS applied materials & interfaces* **2018**, 10 (14), 11406-11413.
225. Anand, S.; Paxson, A. T.; Dhiman, R.; Smith, J. D.; Varanasi, K. K., Enhanced condensation on lubricant-impregnated nanotextured surfaces. *ACS nano* **2012**, 6 (11), 10122-10129.
226. Wang, L.; McCarthy, T. J., Covalently attached liquids: instant omniphobic surfaces with unprecedented repellency. *Angewandte Chemie International Edition* **2016**, 55 (1), 244-248.
227. Cheng, D. F.; Urata, C.; Yagihashi, M.; Hozumi, A., A Statically Oleophilic but Dynamically Oleophobic Smooth Nonperfluorinated Surface. *Angewandte Chemie International Edition* **2012**, 51 (12), 2956-2959.
228. Gao, L.; McCarthy, T. J., Contact angle hysteresis explained. *Langmuir* **2006**, 22 (14), 6234-7.
229. Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J., Ultrahydrophobic and Ultralyophobic Surfaces: Some Comments and Examples. *Langmuir* **1999**, 15 (10), 3395-3399.
230. Zhao, X.; Khandoker, M. A. R.; Golovin, K., Non-Fluorinated Omniphobic Paper with Ultralow Contact Angle Hysteresis. *ACS Applied Materials & Interfaces* **2020**, 12 (13), 15748-15756.

231. Khatir, B.; Shabanian, S.; Golovin, K., Design and High-Resolution Characterization of Silicon Wafer-like Omniphobic Liquid Layers Applicable to Any Substrate. *ACS Applied Materials & Interfaces* **2020**, *12* (28), 31933-31939.
232. Zhao, X.; Khatir, B.; Mirshahidi, K.; Yu, K.; Kizhakkedathu, J. N.; Golovin, K., Macroscopic Evidence of the Liquidlike Nature of Nanoscale Polydimethylsiloxane Brushes. *ACS Nano* **2021**, *15* (8), 13559–13567.
233. Wooh, S.; Encinas, N.; Vollmer, D.; Butt, H.-J. r., Stable Hydrophobic Metal-Oxide Photocatalysts via Grafting Polydimethylsiloxane Brush. *Advanced Materials* **2017**, *29*, 1604637.
234. Liu, J.; Sun, Y.; Zhou, X.; Li, X.; Kappl, M.; Steffen, W.; Butt, H.-J. r., One-Step Synthesis of a Durable and Liquid-Repellent Poly(dimethylsiloxane) Coating. *Advanced Materials* **2021**, *33* (2100237), 2100237.
235. Flagg, D. H.; McCarthy, T. J., Rapid and Clean Covalent Attachment of Methylsiloxane Polymers and Oligomers to Silica Using B(C₆F₅)₃ Catalysis. *Langmuir* **2017**, *33* (33), 8129-8139.
236. Urata, C.; Masheder, B.; Cheng, D. F.; Hozumi, A., Unusual Dynamic Dewetting Behavior of Smooth Perfluorinated Hybrid Films: Potential Advantages over Conventional Textured and Liquid-Infused Perfluorinated Surfaces. *Langmuir* **2013**, *29* (40), 12472-12482.
237. Urata, C.; Masheder, B.; Cheng, D. F.; Miranda, D. F.; Dunderdale, G. J.; Miyamae, T.; Hozumi, A., Why Can Organic Liquids Move Easily on Smooth Alkyl-Terminated Surfaces? *Langmuir* **2014**, *30* (14), 4049-4055.
238. Wooh, S.; Vollmer, D., Silicone brushes: omniphobic surfaces with low sliding angles. *Angewandte Chemie International Edition* **2016**, *55* (24), 6822-6824.
239. Golovin, K.; Tuteja, A., A predictive framework for the design and fabrication of icephobic polymers. *Science Advances* **2017**, *3* (9).
240. Newby, B.-m. Z.; Chaudhury, M. K.; Brown, H. R., Macroscopic evidence of the effect of interfacial slippage on adhesion. *Science* **1995**, *269* (5229), 1407-1409.
241. Lee, J. N.; Park, C.; Whitesides, G. M., Solvent compatibility of poly(dimethylsiloxane)-based microfluidic devices. *Analytical chemistry* **2003**, *75* (23), 6544-6554.
242. Efimenko, K.; Wallace, W. E.; Genzer, J., Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment. *Journal of Colloid and Interface Science* **2002**, *254* (2), 306-315.
243. Schulman, F.; Zisman, W. A., The Spreading of Liquids on Low-Energy Surfaces. V. Perfluorodecanoic Acid Monolayers. *Journal of Colloid Science* **1952**, *7* (5), 465-481.
244. Barriet, D.; Lee, T. R., Fluorinated self-assembled monolayers: composition, structure and interfacial properties. *Current Opinion in Colloid & Interface Science* **2003**, *8* (3), 236-242.
245. Hansen, C. M., *Hansen solubility parameters : a user's handbook*. CRC Press: 2007; p 519-519.
246. Guenther, A. J.; Lamison, K. R.; Lubin, L. M.; Haddad, T. S.; Mabry, J. M., Hansen Solubility Parameters for Octahedral Oligomeric Silsesquioxanes. *Industrial & Engineering Chemistry Research* **2012**, *51* (38), 12282-12293.
247. Ostwald, W., Ueber die rechnerische Darstellung des Strukturgebietes der Viskosität. *Kolloid-Zeitschrift* **1929**, *47* (2), 176-187.
248. Navier, C. L. H. M., Memoire sur les lois du mouvement des fluides. *Mem. Acad. R. Sci. Inst. France* **1823**, *6*, 389-440.

249. Hadjistamov, D., Determination of the onset of shear thinning of polydimethylsiloxane. *Journal of Applied Polymer Science* **2008**, *108* (4), 2356-2364.
250. Mark, J. E., *Polymer data handbook*. Oxford University Press: 2009; p vii, 1250 p.-vii, 1250 p.
251. Owens, D. K.; Wendt, R. C., Estimation of the surface free energy of polymers. *Applied Polymer Science* **1969**, *13* (8), 1741-1747.
252. Singh, P.; Venkatesan, R.; Fogler, H. S.; Nagarajan, N., Morphological evolution of thick wax deposits during aging. *AIChE Journal* **2001**, *47* (1), 6-18.
253. Bauer, S.; Schmuki, P.; Von Der Mark, K.; Park, J., Engineering biocompatible implant surfaces: Part I: Materials and surfaces. *Progress in Materials Science* **2013**, *58* (3), 261-326.
254. Müller-Steinhagen, H.; Malayeri, M.; Watkinson, A., Heat exchanger fouling: mitigation and cleaning strategies. Taylor & Francis: 2011.
255. Gent, R.; Dart, N.; Cansdale, J., Aircraft icing. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* **2000**, *358* (1776), 2873-2911.
256. Halvey, A. K.; Macdonald, B.; Dhyani, A.; Tuteja, A., Design of surfaces for controlling hard and soft fouling. *Philosophical Transactions of the Royal Society A* **2019**, *377* (2138), 20180266.
257. Jellinek, H.; Kachi, H.; Kittaka, S.; Lee, M.; Yokota, R., Ice releasing block-copolymer coatings. *Colloid and Polymer Science* **1978**, *256* (6), 544-551.
258. Sun, Y.; Guo, S.; Walker, G. C.; Kavanagh, C. J.; Swain, G. W., Surface elastic modulus of barnacle adhesive and release characteristics from silicone surfaces. *Biofouling* **2004**, *20* (6), 279-289.
259. Chaudhury, M. K., Interfacial interaction between low-energy surfaces. *Materials Science and Engineering: R: Reports* **1996**, *16* (3), 97-159.
260. Chen, Z.; Nosonovsky, M., Revisiting lowest possible surface energy of a solid. *Surface Topography: Metrology and Properties* **2017**, *5* (4), 045001.
261. Callow, M. E.; Jennings, A. R.; Brennan, A.; Seegert, C.; Gibson, A.; Wilson, L.; Feinberg, A.; Baney, R.; Callow, J., Microtopographic cues for settlement of zoospores of the green fouling alga *Enteromorpha*. *Biofouling* **2002**, *18* (3), 229-236.
262. Petronis, Š.; Berntsson, K.; Gold, J.; Gatenholm, P., Design and microstructuring of PDMS surfaces for improved marine biofouling resistance. *Journal of biomaterials science, polymer edition* **2000**, *11* (10), 1051-1072.
263. Pu, X.; Li, G.; Huang, H., Preparation, anti-biofouling and drag-reduction properties of a biomimetic shark skin surface. *Biology Open* **2016**, *5* (4), 389-396.
264. Chapman, R. G.; Ostuni, E.; Liang, M. N.; Meluleni, G.; Kim, E.; Yan, L.; Pier, G.; Warren, H. S.; Whitesides, G. M., Polymeric thin films that resist the adsorption of proteins and the adhesion of bacteria. *Langmuir* **2001**, *17* (4), 1225-1233.
265. Venkatesan, R.; Nagarajan, N.; Paso, K.; Yi, Y.-B.; Sastry, A.; Fogler, H., The strength of paraffin gels formed under static and flow conditions. *Chemical Engineering Science* **2005**, *60* (13), 3587-3598.
266. Watkinson, A. P., Chemical reaction fouling of organic fluids. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology* **1992**, *15* (2), 82-90.

267. Saikhwan, P.; Chew, J. Y.; Paterson, W. R.; Wilson, D. I., Swelling and its suppression in the cleaning of polymer fouling layers. *Industrial & engineering chemistry research* **2007**, 46 (14), 4846-4855.
268. Saeda, S.; Suzaka, Y., Method for preventing fouling in the polymerization of olefins. Google Patents: 1976.
269. Leipert, J.; Tholey, A., Miniaturized sample preparation on a digital microfluidics device for sensitive bottom-up microproteomics of mammalian cells using magnetic beads and mass spectrometry-compatible surfactants. *Lab on a Chip* **2019**, 19 (20), 3490-3498.
270. Morris, R. E.; Hazlett, R. N.; McIlvaine III, C. L., The effects of stabilizer additives on the thermal stability of jet fuel. *Industrial & engineering chemistry research* **1988**, 27 (8), 1524-1528.
271. Szetela, E.; Giovanetti, A.; Cohen, S., Fuel deposit characteristics at low velocity. **1986**.
272. Wilson, D. I.; Watkinson, A. P., A study of autoxidation reaction fouling in heat exchangers. *The Canadian Journal of Chemical Engineering* **1996**, 74 (2), 236-246.
273. Dryer, C.; Lowry, C.; Morrell, J. C.; Egloff, G., Mechanism of Gum Formation in Cracked Gasoline-Formation of Peroxide, Aldehyde, and Acid in Storage. *Industrial & Engineering Chemistry* **1934**, 26 (8), 885-888.
274. Wang, Z.; Pujari, S. P.; van Lagen, B.; Smulders, M. M.; Zuilhof, H., Highly Polymer-Repellent yet Atomically Flat Surfaces Based on Organic Monolayers with a Single Fluorine Atom. *Advanced Materials Interfaces* **2016**, 3 (4), 1500514.
275. Wang, Z.; Zuilhof, H., Antifouling properties of fluoropolymer brushes toward organic polymers: the influence of composition, thickness, brush architecture, and annealing. *Langmuir* **2016**, 32 (26), 6571-6581.
276. Shabanian, S.; Khatir, B.; Nisar, A.; Golovin, K., Rational design of perfluorocarbon-free oleophobic textiles. *Nature Sustainability* **2020**, 3 (12), 1059-1066.
277. Zhao, X.; Khatir, B.; Mirshahidi, K.; Yu, K.; Kizhakkedathu, J. N.; Golovin, K., Macroscopic evidence of the liquidlike nature of nanoscale polydimethylsiloxane brushes. *ACS nano* **2021**, 15 (8), 13559-13567.
278. Wu, Q.; Yang, C.; Su, C.; Zhong, L.; Zhou, L.; Hang, T.; Lin, H.; Chen, W.; Li, L.; Xie, X., Slippery Liquid-Attached Surface for Robust Biofouling Resistance. *ACS Biomaterials Science & Engineering* **2019**, 6 (1), 358-366.
279. Zhao, H.; Deshpande, C. A.; Li, L.; Yan, X.; Hoque, M. J.; Kuntumalla, G.; Rajagopal, M. C.; Chang, H. C.; Meng, Y.; Sundar, S., Extreme Antiscaling Performance of Slippery Omniphobic Covalently Attached Liquids. *ACS Applied Materials & Interfaces* **2020**, 12 (10), 12054-12067.
280. Peppou-Chapman, S.; Hong, J. K.; Waterhouse, A.; Neto, C., Life and death of liquid-infused surfaces: a review on the choice, analysis and fate of the infused liquid layer. *Chemical Society Reviews* **2020**, 49 (11), 3688-3715.
281. Daniel, D.; Timonen, J. V.; Li, R.; Velling, S. J.; Kreder, M. J.; Tetreault, A.; Aizenberg, J., Origins of extreme liquid repellency on structured, flat, and lubricated hydrophobic surfaces. *Physical review letters* **2018**, 120 (24), 244503.
282. Zhao, X.; Bi, L.; Khatir, B.; Serles, P.; Filleter, T.; Wulff, J. E.; Golovin, K., Crosslinking Inert Liquidlike Polydimethylsiloxane Brushes using Bis-Diazirine Chemical Insertion for Enhanced Mechanical Durability. *Chemical Engineering Journal* **2022**, 136017.

283. Liu, J.; Sun, Y.; Zhou, X.; Li, X.; Kappl, M.; Steffen, W.; Butt, H. J., One-Step Synthesis of a Durable and Liquid-Repellent Poly (dimethylsiloxane) Coating. *Advanced Materials* **2021**, 33 (23), 2100237.
284. Wooh, S.; Encinas, N.; Vollmer, D.; Butt, H. J., Stable hydrophobic metal-oxide photocatalysts via grafting polydimethylsiloxane brush. *Advanced Materials* **2017**, 29 (16), 1604637.
285. Shang, B.; Chen, M.; Wu, L., One-step synthesis of statically amphiphilic/dynamically amphiphobic fluoride-free transparent coatings. *ACS applied materials & interfaces* **2018**, 10 (48), 41824-41830.
286. Cheng, D. F.; Urata, C.; Yagihashi, M.; Hozumi, A., A statically oleophilic but dynamically oleophobic smooth nonperfluorinated surface. *Angewandte Chemie* **2012**, 124 (12), 3010-3013.
287. Lopez, G.; Granado, L.; Coquil, G.; Lárez-Sosa, A.; Louvain, N.; Améduri, B., Perfluoropolyether (PFPE)-based vitrimers with ionic conductivity. *Macromolecules* **2019**, 52 (5), 2148-2155.
288. Lopez, G.; Ameduri, B.; Habas, J. P., A Versatile Strategy to Synthesize Perfluoropolyether-Based Thermoplastic Fluoropolymers by Alkyne-Azide Step-Growth Polymerization. *Macromolecular Rapid Communications* **2016**, 37 (8), 711-717.
289. Kahl, H.; Wadewitz, T.; Winkelmann, J., Surface tension of pure liquids and binary liquid mixtures. *Journal of Chemical & Engineering Data* **2003**, 48 (3), 580-586.
290. Wang, Z.; Zuilhof, H., Self-healing fluoropolymer brushes as highly polymer-repellent coatings. *Journal of Materials Chemistry A* **2016**, 4 (7), 2408-2412.
291. Johnson Jr, R. E.; Dettre, R. H., Contact angle hysteresis. III. Study of an idealized heterogeneous surface. *The journal of physical chemistry* **1964**, 68 (7), 1744-1750.
292. De Gennes, P.-G.; Gennes, P.-G., *Scaling concepts in polymer physics*. Cornell university press: 1979.
293. Gong, P.; Grainger, D. W., Nonfouling surfaces. *Microarrays* **2007**, 59-92.
294. Leng, C.; Hung, H.-C.; Sun, S.; Wang, D.; Li, Y.; Jiang, S.; Chen, Z., Probing the surface hydration of nonfouling zwitterionic and PEG materials in contact with proteins. *ACS applied materials & interfaces* **2015**, 7 (30), 16881-16888.
295. Leng, C.; Gibney, K. A.; Liu, Y.; Tew, G. N.; Chen, Z., In situ probing the surface restructuring of antibiofouling amphiphilic polybetaines in water. *ACS Macro Letters* **2013**, 2 (11), 1011-1015.
296. Hankett, J. M.; Liu, Y.; Zhang, X.; Zhang, C.; Chen, Z., Molecular level studies of polymer behaviors at the water interface using sum frequency generation vibrational spectroscopy. *Journal of Polymer Science Part B: Polymer Physics* **2013**, 51 (5), 311-328.
297. Yang, Z.; Li, Q.; Chou, K. C., Structures of water molecules at the interfaces of aqueous salt solutions and silica: Cation effects. *The Journal of Physical Chemistry C* **2009**, 113 (19), 8201-8205.
298. Myalitsin, A.; Urashima, S.-H.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T., Water structure at the buried silica/aqueous interface studied by heterodyne-detected vibrational sum-frequency generation. *The Journal of Physical Chemistry C* **2016**, 120 (17), 9357-9363.
299. Han, X.; Liu, Y.; Wu, F.-G.; Jansensky, J.; Kim, T.; Wang, Z.; Brooks III, C. L.; Wu, J.; Xi, C.; Mello, C. M., Different interfacial behaviors of peptides chemically immobilized on surfaces with different linker lengths and via different termini. *The Journal of Physical Chemistry B* **2014**, 118 (11), 2904-2912.

300. Ding, B.; Jasensky, J.; Li, Y.; Chen, Z., Engineering and characterization of peptides and proteins at surfaces and interfaces: a case study in surface-sensitive vibrational spectroscopy. *Accounts of chemical research* **2016**, 49 (6), 1149-1157.
301. Zuo, B.; Xu, Q.; Jin, T.; Xing, H.; Shi, J.; Hao, Z.; Zhang, L.; Tanaka, K.; Wang, X., Suppressed Surface Reorganization in a High-Density Poly (methyl methacrylate) Brush. *Langmuir* **2019**, 35 (46), 14890-14895.
302. Uchida, K.; Mita, K.; Yamamoto, S.; Tanaka, K., Local Orientation of Polystyrene at the Interface with Poly (methyl methacrylate) in Block Copolymer. *ACS Macro Letters* **2020**, 9 (11), 1576-1581.
303. Zuo, B.; Li, C.; Li, Y.; Qian, W.; Ye, X.; Zhang, L.; Wang, X., Toward Achieving Highly Ordered Fluorinated Surfaces of Spin-Coated Polymer Thin Films by Optimizing the Air/Liquid Interfacial Structure of the Casting Solutions. *Langmuir* **2018**, 34 (13), 3993-4003.
304. Hosseinpour, S.; Roeters, S. J.; Bonn, M.; Peukert, W.; Woutersen, S.; Weidner, T., Structure and dynamics of interfacial peptides and proteins from vibrational sum-frequency generation spectroscopy. *Chemical reviews* **2020**, 120 (7), 3420-3465.
305. Roy, S.; Covert, P. A.; FitzGerald, W. R.; Hore, D. K., Biomolecular structure at solid–liquid interfaces as revealed by nonlinear optical spectroscopy. *Chemical reviews* **2014**, 114 (17), 8388-8415.
306. Shen, Y., Surface properties probed by second-harmonic and sum-frequency generation. *Nature* **1989**, 337 (6207), 519-525.
307. Chen, C.; Wang, J.; Chen, Z., Surface restructuring behavior of various types of poly (dimethylsiloxane) in water detected by SFG. *Langmuir* **2004**, 20 (23), 10186-10193.
308. Cowie, J.; McEwen, I., Molecular motions in poly (dimethyl siloxane) oligomers and polymers. *Polymer* **1973**, 14 (9), 423-426.
309. Miranda, P.; Shen, Y., Liquid interfaces: A study by sum-frequency vibrational spectroscopy. *The Journal of Physical Chemistry B* **1999**, 103 (17), 3292-3307.
310. Zhang, C.; Chen, Z., Probing molecular structures of poly (dimethylsiloxane) at buried interfaces in situ. *The Journal of Physical Chemistry C* **2013**, 117 (8), 3903-3914.
311. Chen, S.; Yu, F.; Yu, Q.; He, Y.; Jiang, S., Strong resistance of a thin crystalline layer of balanced charged groups to protein adsorption. *Langmuir* **2006**, 22 (19), 8186-8191.
312. Liu, D.; Guo, J.; Zhang, J.-H., Chain mobility and film softness mediated protein antifouling at the solid–liquid interface. *Journal of Materials Chemistry B* **2016**, 4 (36), 6134-6142.
313. Shao, Q.; Jiang, S., Molecular understanding and design of zwitterionic materials. *Advanced Materials* **2015**, 27 (1), 15-26.
314. Leng, C.; Sun, S.; Zhang, K.; Jiang, S.; Chen, Z., Molecular level studies on interfacial hydration of zwitterionic and other antifouling polymers in situ. *Acta biomaterialia* **2016**, 40, 6-15.
315. Sheikh, S.; Blaszykowski, C.; Nolan, R.; Thompson, D.; Thompson, M., On the hydration of subnanometric antifouling organosilane adlayers: A molecular dynamics simulation. *Journal of colloid and interface science* **2015**, 437, 197-204.
316. Callow, J. A.; Callow, M. E., Trends in the development of environmentally friendly fouling-resistant marine coatings. *Nature Communications* **2011**, 2 (1), 1-10.
317. Jin, H.; Tian, L.; Bing, W.; Zhao, J.; Ren, L., Bioinspired marine antifouling coatings: Status, prospects, and future. *Progress in Materials Science* **2022**, 124, 100889.

318. Wang, X.-T.; Liu, H.; Lv, Z.-F.; Deng, F.-Y.; Xu, H.-L.; Qi, L.-J.; Shi, M.-S.; Zhao, J.-C.; Zheng, S.-X.; Man, H.-Y.; He, K.-B., Trade-linked shipping CO₂ emissions. *Nature Climate Change* **2021**, *11* (11), 945-951.
319. Tikhova, A.; Glukhareva, N.; Lebedeva, O., Oxidative degradation of polyglycols by the Ruff's system in the aqueous solutions. *Russian Journal of General Chemistry* **2014**, *84* (9), 1806-1809.
320. Gohad, N. V.; Aldred, N.; Hartshorn, C. M.; Jong Lee, Y.; Cicerone, M. T.; Orihuela, B.; Clare, A. S.; Rittschof, D.; Mount, A. S., Synergistic roles for lipids and proteins in the permanent adhesive of barnacle larvae. *Nature communications* **2014**, *5* (1), 1-9.
321. Bers, A. V.; Wahl, M., The influence of natural surface microtopographies on fouling. *Biofouling* **2004**, *20* (1), 43-51.
322. Schumacher, J. F.; Aldred, N.; Callow, M. E.; Finlay, J. A.; Callow, J. A.; Clare, A. S.; Brennan, A. B., Species-specific engineered antifouling topographies: correlations between the settlement of algal zoospores and barnacle cyprids. *Biofouling* **2007**, *23* (5), 307-317.
323. Lejars, M.; Margailan, A.; Bressy, C., Fouling release coatings: a nontoxic alternative to biocidal antifouling coatings. *Chemical reviews* **2012**, *112* (8), 4347-4390.
324. Cao, S.; Wang, J.; Chen, H.; Chen, D., Progress of marine biofouling and antifouling technologies. *Chinese Science Bulletin* **2011**, *56* (7), 598-612.
325. Leonardi, A. K.; Ober, C. K., Polymer-based marine antifouling and fouling release surfaces: Strategies for synthesis and modification. *Annual review of chemical and biomolecular engineering* **2019**, *10*, 241-264.
326. Gu, Y.; Yu, L.; Mou, J.; Wu, D.; Xu, M.; Zhou, P.; Ren, Y., Research strategies to develop environmentally friendly marine antifouling coatings. *Marine Drugs* **2020**, *18* (7), 371.
327. Ytreberg, E.; Bighiu, M. A.; Lundgren, L.; Eklund, B., XRF measurements of tin, copper and zinc in antifouling paints coated on leisure boats. *Environmental Pollution* **2016**, *213*, 594-599.
328. Maia, F.; Silva, A.; Fernandes, S.; Cunha, A.; Almeida, A.; Tedim, J.; Zheludkevich, M.; Ferreira, M., Incorporation of biocides in nanocapsules for protective coatings used in maritime applications. *Chemical Engineering Journal* **2015**, *270*, 150-157.
329. Amini, S.; Kolle, S.; Petrone, L.; Ahanotu, O.; Sunny, S.; Sutanto, C. N.; Hoon, S.; Cohen, L.; Weaver, J. C.; Aizenberg, J.; Vogel, N.; Miserez, A., Preventing mussel adhesion using lubricant-infused materials. *Science* **2017**, *357* (6352), 668-673.
330. Chen, L.; Qian, P.-Y., Review on molecular mechanisms of antifouling compounds: an update since 2012. *Marine drugs* **2017**, *15* (9), 264.
331. Feng, K.; Ni, C.; Yu, L.; Zhou, W.; Li, X., Synthesis and evaluation of acrylate resins suspending indole derivative structure in the side chain for marine antifouling. *Colloids and Surfaces B: Biointerfaces* **2019**, *184*, 110518.
332. Wang, J.; Lee, S.; Bielinski, A. R.; Meyer, K. A.; Dhyani, A.; Ortiz-Ortiz, A. M.; Tuteja, A.; Dasgupta, N. P., Rational Design of Transparent Nanowire Architectures with Tunable Geometries for Preventing Marine Fouling. *Advanced Materials Interfaces* **2020**, 2000672.
333. Ivanovich, U. A.; Nickolayevna, P. T.; Viktorovich, K. A., The effect of the loss of superhydrophobic surface properties on biofouling and flow around shipbuilding's steel plates. *Ocean Engineering* **2020**, *214*, 107801.

334. Wang, P.; Zhang, D.; Lu, Z., Slippery liquid-infused porous surface bio-inspired by pitcher plant for marine anti-biofouling application. *Colloids and Surfaces B: Biointerfaces* **2015**, *136*, 240-247.
335. Wang, P.; Zhang, D.; Sun, S.; Li, T.; Sun, Y., Fabrication of slippery lubricant-infused porous surface with high underwater transparency for the control of marine biofouling. *ACS applied materials & interfaces* **2017**, *9* (1), 972-982.
336. Yang, W. J.; Neoh, K.-G.; Kang, E.-T.; Teo, S. L.-M.; Rittschof, D., Polymer brush coatings for combating marine biofouling. *Progress in Polymer Science* **2014**, *39* (5), 1017-1042.
337. Leung, B. O.; Yang, Z.; Wu, S. S.; Chou, K. C., Role of interfacial water on protein adsorption at cross-linked polyethylene oxide interfaces. *Langmuir* **2012**, *28* (13), 5724-5728.
338. Chen, S.; Li, L.; Zhao, C.; Zheng, J., Surface hydration: Principles and applications toward low-fouling/nonfouling biomaterials. *Polymer* **2010**, *51* (23), 5283-5293.
339. Zheng, L.; Sundaram, H. S.; Wei, Z.; Li, C.; Yuan, Z., Applications of zwitterionic polymers. *Reactive and Functional Polymers* **2017**, *118*, 51-61.
340. Higaki, Y.; Kobayashi, M.; Murakami, D.; Takahara, A., Anti-fouling behavior of polymer brush immobilized surfaces. *Polymer Journal* **2016**, *48* (4), 325-331.
341. Bielinski, A. R.; Boban, M.; He, Y.; Kazyak, E.; Lee, D. H.; Wang, C.; Tuteja, A.; Dasgupta, N. P., Rational Design of Hyperbranched Nanowire Systems for Tunable Superomniphobic Surfaces Enabled by Atomic Layer Deposition. *ACS Nano* **2017**, *11* (1), 478-489.
342. Khung, Y. L.; Narducci, D., Surface modification strategies on mesoporous silica nanoparticles for anti-biofouling zwitterionic film grafting. *Advances in colloid and interface science* **2015**, *226*, 166-186.
343. Goux, A.; Pauporté, T.; Chivot, J.; Lincot, D., Temperature effects on ZnO electrodeposition. *Electrochimica Acta* **2005**, *50* (11), 2239-2248.
344. Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*. Elsevier: 2012.
345. Elbourne, A.; Crawford, R. J.; Ivanova, E. P., Nano-structured antimicrobial surfaces: From nature to synthetic analogues. *Journal of Colloid and Interface Science* **2017**, *508*, 603-616.
346. Cheng, G.; Liao, M.; Zhao, D.; Zhou, J., Molecular understanding on the underwater oleophobicity of self-assembled monolayers: zwitterionic versus nonionic. *Langmuir* **2017**, *33* (7), 1732-1741.
347. Wang, J.; Wu, B.; Dhyani, A.; Repetto, T.; Gayle, A. J.; Cho, T. H.; Dasgupta, N. P.; Tuteja, A., Durable Liquid- and Solid-Repellent Elastomeric Coatings Infused with Partially Crosslinked Lubricants. *ACS Applied Materials & Interfaces* **2022**, *14* (19), 22466-22475.
348. Chernyy, S.; Järn, M.; Shimizu, K.; Swerin, A.; Pedersen, S. U.; Daasbjerg, K.; Makkonen, L.; Claesson, P.; Iruthayaraj, J., Superhydrophilic polyelectrolyte brush layers with imparted anti-icing properties: effect of counter ions. *ACS applied materials & interfaces* **2014**, *6* (9), 6487-6496.
349. Kirkgöz, M. S.; Ardiçlioğlu, M., Velocity profiles of developing and developed open channel flow. *Journal of Hydraulic Engineering* **1997**, *123* (12), 1099-1105.
350. Guo, J.; Julien, P. Y., Shear stress in smooth rectangular open-channel flows. *Journal of hydraulic engineering* **2005**, *131* (1), 30-37.
351. Finlay, J. A.; Schultz, M. P.; Cone, G.; Callow, M. E.; Callow, J. A., A novel biofilm channel for evaluating the adhesion of diatoms to non-biocidal coatings. *Biofouling* **2013**, *29* (4), 401-411.

352. Gustave, A., Anti-fogging eyeglasses. Google Patents: 1964.
353. Dain, S. J.; Hoskin, A. K.; Winder, C.; Dingsdag, D. P., Assessment of fogging resistance of anti-fog personal eye protection. *Ophthalmic and Physiological Optics* **1999**, 19 (4), 357-361.
354. Crebolder, J. M.; Sloan, R. B., Determining the effects of eyewear fogging on visual task performance. *Applied ergonomics* **2004**, 35 (4), 371-381.
355. Margrain, T. H.; Owen, C., The misting characteristics of spectacle lenses. *Ophthalmic and Physiological Optics* **1996**, 16 (2), 108-114.
356. Sternberg, P., Practical Considerations for Management of Pediatric Victims during Hazmat Decontamination. *published in* **2005**.
357. Lu, X.; Wang, Z.; Yang, X.; Xu, X.; Zhang, L.; Zhao, N.; Xu, J., Antifogging and antireflective silica film and its application on solar modules. *Surface and Coatings Technology* **2011**, 206 (6), 1490-1494.
358. Lawrentschuk, N.; Fleshner, N. E.; Bolton, D. M., Laparoscopic lens fogging: a review of etiology and methods to maintain a clear visual field. *Journal of endourology* **2010**, 24 (6), 905-913.
359. Briscoe, B. J.; Galvin, K. P., The effect of surface fog on the transmittance of light. *Solar Energy* **1991**, 46 (4), 191-197.
360. Bhardwaj, R.; Agrawal, A., Tailoring surface wettability to reduce chances of infection of COVID-19 by a respiratory droplet and to improve the effectiveness of personal protection equipment. *Physics of Fluids* **2020**, 32 (8), 081702.
361. Patel, P.; Choi, C. K.; Meng, D. D., Superhydrophilic surfaces for antifogging and antifouling microfluidic devices. *JALA: Journal of the Association for Laboratory Automation* **2010**, 15 (2), 114-119.
362. Di Mundo, R.; d'Agostino, R.; Palumbo, F., Long-lasting antifog plasma modification of transparent plastics. *ACS applied materials & interfaces* **2014**, 6 (19), 17059-17066.
363. Chen, F.; Liu, J.; Cui, Y.; Huang, S.; Song, J.; Sun, J.; Xu, W.; Liu, X., Stability of plasma treated superhydrophobic surfaces under different ambient conditions. *Journal of colloid and interface science* **2016**, 470, 221-228.
364. Wenzel, R. N., Resistance of solid surfaces to wetting by water. *Industrial & Engineering Chemistry* **1936**, 28 (8), 988-994.
365. Park, K.-C.; Choi, H. J.; Chang, C.-H.; Cohen, R. E.; McKinley, G. H.; Barbastathis, G., Nanotextured silica surfaces with robust superhydrophobicity and omnidirectional broadband supertransmissivity. *ACS nano* **2012**, 6 (5), 3789-3799.
366. Xu, H.; Liu, L.; Wu, F.; Xu, D.; Lu, N., Fabrication of biomimetic patterns for high transmission and antifogging property. *RSC Advances* **2015**, 5 (35), 28014-28018.
367. Utech, S.; Bley, K.; Aizenberg, J.; Vogel, N., Tailoring re-entrant geometry in inverse colloidal monolayers to control surface wettability. *Journal of Materials Chemistry A* **2016**, 4 (18), 6853-6859.
368. da Silva, M. N.; Santilli, C. V.; Pulcinelli, S. H., Wettability and photodegradation activity of sol-gel dip-coated zinc oxide films. *Journal of sol-gel science and technology* **2012**, 63 (2), 230-234.
369. Maino, G.; Meroni, D.; Pifferi, V.; Falciola, L.; Soliveri, G.; Cappelletti, G.; Ardizzone, S., Electrochemically assisted deposition of transparent, mechanically robust TiO₂ films for advanced applications. *Journal of nanoparticle research* **2013**, 15 (11), 1-10.

370. Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T., Light-induced amphiphilic surfaces. *nature* **1997**, 388 (6641), 431-432.
371. Haga, M.; Onisawa, Y.; Shimizu, K., Plastic lenses and method of producing the same. Google Patents: 1999.
372. Lancaster, J., Abrasive wear of polymers. *Wear* **1969**, 14 (4), 223-239.
373. Shipway, P.; Ngao, N., Microscale abrasive wear of polymeric materials. *Wear* **2003**, 255 (1-6), 742-750.
374. Ton-That, C.; Teare, D.; Bradley, R., Friction, surface oxidation, and polar free energy for polymer surfaces by chemical force microscopy. *Chemistry of materials* **2000**, 12 (8), 2106-2111.
375. Myshkin, N.; Kovalev, A., Adhesion and surface forces in polymer tribology—A review. *Friction* **2018**, 6 (2), 143-155.
376. Nocita, D.; Critchlow, G.; Haworth, B.; Forte, G.; Hollingbery, L.; Kay, C., Novel super-hydrophilic coatings with enhanced adhesion on polyolefin substrate obtained by gravure deposition of true amphiphilic block co-polymer water dispersions. *International Journal of Adhesion and Adhesives* **2022**, 112, 103032.
377. Xiang, J.; Liu, X.; Liu, Y.; Wang, L.; He, Y.; Luo, L.; Yang, G.; Zhang, X.; Huang, C.; Zhang, Y., Synthesis of a novel anti-fog and high-transparent coating with high wear resistance inspired by dry rice fields. *Chemical Engineering Science* **2021**, 242, 116749.
378. Yuan, Y.; Liu, R.; Wang, C.; Luo, J.; Liu, X., Synthesis of UV-curable acrylate polymer containing sulfonic groups for anti-fog coatings. *Progress in Organic Coatings* **2014**, 77 (4), 785-789.
379. Zhu, X.; Lu, P.; Chen, W.; Dong, J., Studies of UV crosslinked poly (N-vinylpyrrolidone) hydrogels by FTIR, Raman and solid-state NMR spectroscopies. *Polymer* **2010**, 51 (14), 3054-3063.
380. Ramani, R.; Ranganathaiah, C., Degradation of acrylonitrile-butadiene-styrene and polycarbonate by UV irradiation. *Polymer degradation and stability* **2000**, 69 (3), 347-354.
381. Höfer, R., Processing and Performance Additives for Plastics. **2012**.
382. Cooper, I.; Tice, P. A., Migration studies on fatty acid amide slip additives from plastics into food simulants. *Food Additives & Contaminants* **1995**, 12 (2), 235-244.
383. Hansen, C. M., *Hansen solubility parameters: a user's handbook*. CRC press: 2007.
384. Golovin, K.; Boban, M.; Mabry, J. M.; Tuteja, A., Designing self-healing superhydrophobic surfaces with exceptional mechanical durability. *ACS applied materials & interfaces* **2017**, 9 (12), 11212-11223.
385. Griffin, W. C., Calculation of HLB values of non-ionic surfactants. *J. Soc. Cosmet. Chem.* **1954**, 5, 249-256.
386. Wypych, G., *Handbook of antiblocking, release, and slip additives*. Elsevier: 2021.
387. Kunwong, D.; Sumanochitraporn, N.; Kaewpirom, S., Curing behavior of a UV-curable coating based on urethane acrylate oligomer: the influence of reactive monomers. *Sonklanakarin Journal of Science and Technology* **2011**, 33 (2), 201.
388. Yang, D. K.; Chien, L. C.; Doane, J., Cholesteric liquid crystal/polymer dispersion for haze-free light shutters. *Applied physics letters* **1992**, 60 (25), 3102-3104.
389. Malik, O.; Joshi, T.; Goel, V.; Kapur, G. S.; Nebhani, L., Silica derived from variety of sources and its functionalized forms as an antiblock additive in polypropylene. *Journal of Thermoplastic Composite Materials* **2021**, 08927057211057114.

390. Patel, S. H., Surface property modifiers. *Functional fillers for plastics* **2005**, 339-366.
391. Xu, Z.; Yao, K.; Li, Z.; Fu, L.; Fu, H.; Li, J.; Cao, L.; Huang, J., Sulfur nanodots as MoS₂ antiblocking agent for stable sodium ion battery anodes. *Journal of Materials Chemistry A* **2018**, *6* (22), 10535-10542.
392. Chkhartishvili, L.; Tabatadze, G.; Nackebia, D.; Bzhalava, T.; Kalandadze, I., Hexagonal boron nitride as a solid lubricant additive (an overview). *Nano Stud* **2016**, *14*, 91-98.
393. Feneberger, K., Graphite: Solid Lubricant. *Industrial Lubrication and Tribology* **1973**, *25* (5), 176-178.
394. Greco, A.; Mistry, K.; Sista, V.; Eryilmaz, O.; Erdemir, A., Friction and wear behaviour of boron based surface treatment and nano-particle lubricant additives for wind turbine gearbox applications. *Wear* **2011**, *271* (9-10), 1754-1760.
395. Scharf, T.; Prasad, S., Solid lubricants: a review. *Journal of materials science* **2013**, *48* (2), 511-531.
396. Yasuda, H.; Sharma, A. K.; Yasuda, T., Effect of orientation and mobility of polymer molecules at surfaces on contact angle and its hysteresis. *Journal of Polymer Science: Polymer Physics Edition* **1981**, *19* (9), 1285-1291.
397. Haraguchi, K.; Li, H.-J.; Okumura, N., Hydrogels with hydrophobic surfaces: abnormally high contact angles for water on PNIPAA nanocomposite hydrogels. *Macromolecules* **2007**, *40* (7), 2299-2302.
398. Holly, F. J.; Refojo, M. F., Wettability of hydrogels I. Poly (2-hydroxyethyl methacrylate). *Journal of biomedical materials research* **1975**, *9* (3), 315-326.
399. Nouman, M.; Saunier, J.; Jubeli, E.; Yagoubi, N., Additive blooming in polymer materials: Consequences in the pharmaceutical and medical field. *Polymer Degradation and Stability* **2017**, *143*, 239-252.
400. Xu, D.; Johnson, W. L., Geometric model for the critical-value problem of nucleation phenomena containing the size effect of nucleating agent. *Physical Review B* **2005**, *72* (5), 052101.
401. Hummers Jr, W. S.; Offeman, R. E., Preparation of graphitic oxide. *Journal of the american chemical society* **1958**, *80* (6), 1339-1339.
402. Emery, A. F.; Siegel, B. L., Experimental measurements of the effects of frost formation on heat exchanger performance. In *Heat and mass transfer in frost and ice, packed beds, and environmental discharges*, 1990.
403. Huang, L.; Liu, Z.; Liu, Y.; Gou, Y.; Wang, J., Experimental study on frost release on fin-and-tube heat exchangers by use of a novel anti-frosting paint. *Experimental Thermal and Fluid Science* **2009**, *33* (7), 1049-1054.
404. Shen, Y.; Wu, X.; Tao, J.; Zhu, C.; Lai, Y.; Chen, Z., Icephobic materials: Fundamentals, performance evaluation, and applications. *Progress in Materials Science* **2019**, *103*, 509-557.
405. Cao, L.; Jones, A. K.; Sikka, V. K.; Wu, J.; Gao, D., Anti-icing superhydrophobic coatings. *Langmuir* **2009**, *25* (21), 12444-12448.
406. Cassie, A. B. D.; Baxter, S., Wettability of porous surfaces. *Transactions of the Faraday society* **1944**, *40*, 546-551.
407. Coady, M. J.; Wood, M.; Wallace, G. Q.; Nielsen, K. E.; Kietzig, A.-M.; Lagugné-Labarthe, F.; Ragonna, P. J., Icephobic Behavior of UV-Cured Polymer Networks Incorporated into Slippery Lubricant-Infused Porous Surfaces: Improving SLIPS Durability. *ACS Applied Materials & Interfaces* **2018**, *10* (3), 2890-2896.

408. Kulinich, S. A.; Farhadi, S.; Nose, K.; Du, X. W., Superhydrophobic surfaces: are they really ice-repellent? *Langmuir* **2011**, 27 (1), 25-29.
409. Irajizad, P.; Hasnain, M.; Farokhnia, N.; Sajadi, S. M.; Ghasemi, H., Magnetic slippery extreme icephobic surfaces. *Nature communications* **2016**, 7 (1), 1-7.
410. Devries, A. L., Glycoproteins as biological antifreeze agents in Antarctic fishes. *Science* **1971**, 172 (3988), 1152-1155.
411. Feeney, R. E.; Burcham, T. S.; Yeh, Y., Antifreeze glycoproteins from polar fish blood. *Annual review of biophysics and biophysical chemistry* **1986**, 15 (1), 59-78.
412. Zachariassen, K. E.; Kristiansen, E., Ice nucleation and antinucleation in nature. *Cryobiology* **2000**, 41 (4), 257-279.
413. Graether, S. P.; Kuiper, M. J.; Gagné, S. M.; Walker, V. K.; Jia, Z.; Sykes, B. D.; Davies, P. L., β -Helix structure and ice-binding properties of a hyperactive antifreeze protein from an insect. *Nature* **2000**, 406 (6793), 325-328.
414. Knight, C. A.; Cheng, C. C.; DeVries, A. L., Adsorption of alpha-helical antifreeze peptides on specific ice crystal surface planes. *Biophysical journal* **1991**, 59 (2), 409-418.
415. Liou, Y.-C.; Tocilj, A.; Davies, P. L.; Jia, Z., Mimicry of ice structure by surface hydroxyls and water of a β -helix antifreeze protein. *Nature* **2000**, 406 (6793), 322-324.
416. Zhang, W.; Laursen, R. A., Structure-function relationships in a type I antifreeze polypeptide the role of threonine methyl and hydroxyl groups in antifreeze activity. *Journal of Biological Chemistry* **1998**, 273 (52), 34806-34812.
417. Guo, Q.; He, Z.; Jin, Y.; Zhang, S.; Wu, S.; Bai, G.; Xue, H.; Liu, Z.; Jin, S.; Zhao, L.; Wang, J., Tuning Ice Nucleation and Propagation with Counterions on Multilayer Hydrogels. *Langmuir* **2018**, 34 (40), 11986-11991.
418. Zhuo, Y.; Xiao, S.; Håkonsen, V.; He, J.; Zhang, Z., Anti-icing Ionogel Surfaces: Inhibiting Ice Nucleation, Growth, and Adhesion. *ACS Materials Letters* **2020**, 2 (6), 616-623.
419. He, Z.; Wu, C.; Hua, M.; Wu, S.; Wu, D.; Zhu, X.; Wang, J.; He, X., Bioinspired Multifunctional Anti-icing Hydrogel. *Matter* **2020**, 2 (3), 723-734.
420. Nagura, M.; Saitoh, H.; Gotoh, Y.; Ohkoshi, Y., States of water in poly(vinyl alcohol)/poly(sodium l-glutamate) blend hydrogels. *Polymer* **1996**, 37 (25), 5649-5652.
421. Wolfe, J.; Bryant, G.; Koster, K. L., What is 'unfreezable water', how unfreezable is it and how much is there? *Cryoletters* **2002**, 23 (3), 157-166.
422. Hu, P.; Xie, Q.; Ma, C.; Zhang, G., Silicone-based fouling-release coatings for marine antifouling. *Langmuir* **2020**, 36 (9), 2170-2183.
423. Brady Jr, R. F.; Singer, I. L., Mechanical factors favoring release from fouling release coatings. *Biofouling* **2000**, 15 (1-3), 73-81.
424. Zhao, X.; Bi, L.; Khatir, B.; Serles, P.; Filleter, T.; Wulff, J. E.; Golovin, K., Crosslinking inert liquidlike polydimethylsiloxane brushes using bis-diazirine chemical insertion for enhanced mechanical durability. *Chemical Engineering Journal* **2022**, 442, 136017.
425. Green, D. L.; Mewis, J., Connecting the wetting and rheological behaviors of poly (dimethylsiloxane)-grafted silica spheres in poly (dimethylsiloxane) melts. *Langmuir* **2006**, 22 (23), 9546-9553.
426. Li, Y.; Tao, P.; Viswanath, A.; Benicewicz, B. C.; Schadler, L. S., Bimodal surface ligand engineering: the key to tunable nanocomposites. *Langmuir* **2013**, 29 (4), 1211-1220.
427. McEwan, M.; Green, D., Rheological impacts of particle softness on wetted polymer-grafted silica nanoparticles in polymer melts. *Soft Matter* **2009**, 5 (8), 1705-1716.

428. Peng, S.; Meng, W.; Guo, J.; Wang, B.; Wang, Z.; Xu, N.; Li, X.; Wang, J.; Xu, J., Photocatalytically stable superhydrophobic and translucent coatings generated from PDMS-grafted-SiO₂/TiO₂@ PDMS with multiple applications. *Langmuir* **2019**, *35* (7), 2760-2771.
429. Li, Y.; Cheng, J.; Delparastan, P.; Wang, H.; Sigg, S. J.; DeFrates, K. G.; Cao, Y.; Messersmith, P. B., Molecular design principles of Lysine-DOPA wet adhesion. *Nature communications* **2020**, *11* (1), 1-8.
430. Lee, H.; Scherer, N. F.; Messersmith, P. B., Single-molecule mechanics of mussel adhesion. *Proceedings of the National Academy of Sciences* **2006**, *103* (35), 12999-13003.
431. Nicklisch, S. C.; Waite, J. H., Mini-review: The role of redox in Dopa-mediated marine adhesion. *Biofouling* **2012**, *28* (8), 865-877.
432. Kaushik, A.; Kumar, R.; Huey, E.; Bhansali, S.; Nair, N.; Nair, M., Silica nanowires: growth, integration, and sensing applications. *Microchimica Acta* **2014**, *181* (15), 1759-1780.
433. Pujari, S. P.; Scheres, L.; Marcelis, A. T.; Zuilhof, H., Covalent surface modification of oxide surfaces. *Angewandte Chemie International Edition* **2014**, *53* (25), 6322-6356.