SUPERHYDROPHOBIC SURFACES TO RESIST DROPLET
SPRAYS, SIMULATED RAIN, AND WATER JETS

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Abstract

With anti-wetting properties such as contact angles greater than 150° and sliding angles less than 10° , low-cost superhydrophobic coatings hold great promise in reducing fouling and icing. However, these coatings must also resist saturation and erosion caused by water droplet impact. The first experimental study investigates the performance of a polyurethane/organoclay superhydrophobic nanocomposite modified with perfluoroalkyl methacrylic copolymer (PMC) in the presence of a high pressure air-water spray which simulates an icing cloud impact. Superhydrophobic samples were exposed at 25, 45, and 65 cm from the spray nozzle. The velocities of droplets impacting the superhydrophobic samples were estimated computationally for each of these distances to be 14.5, 4.5, and 3.4 m/s, respectively. It was found that liquid saturation did not occur immediately, but over time, the high mass flow rate of water led to anti-wetting performance degradation. Upon evaporation through heating, contact angle returned to pre-test values, indicating little mechanical erosion. This was consistent with scanning electron microscopy (SEM) which showed that the nano- and micro-structure was preserved, as well as with energy-dispersive X-ray spectroscopy (EDXS), which showed no surface chemistry change after testing. However, sliding angle showed stronger degradation, especially at higher impact velocities.

The objective of the second study was to test the mechanical durability of a polyurethane/organoclay/PMC nanocomposite coating in conditions that replicate extended rain impact. Samples were impacted with 1.4 mm droplets at a velocity of 25 m/s and a flow rate of 0.78 gpm for a period of 5 hours by an axial full cone nozzle. The cases of normal and angled 40° droplet impact were examined. After the spray period, samples were heated at 100°C to allow saturated liquid to evaporate from the surface. Contact angle and sliding angle of the superhydrophobic surfaces were measured before and after the spray period. A decrease in performance for both samples was observed, with the vertically sprayed sample showing greater degradation. After

refunctionalizing the vertically sprayed surface with PMC, an increase in performance was observed. Microscopy of the superhydrophobic samples before and after spray impact revealed a change in surface morphology which, along with leaching of the fluoroacrylic copolymer, was the likely cause of the decrease in performance.

In the third study, a novel superhydrophobic surface composed of a PTFE binder and flame-generated carbonaceous soot was created. Importantly, unlike previous surfaces created from flame-generated material, the produced surface showed good adhesive properties. Owing to the natural hydrophobicity of carbon and nanostructure of the deposited soot, surfaces displayed extreme resistance to saturation by an impinging high pressure water jet. Surfaces were found to saturate more easily as they were tilted to the impinging water jet. However, the anti-wetting properties of samples that were tilted to the impinging water jet returned closer to pre-test values after saturated water was allowed to evaporate. Before testing, SEM of the surface revealed a “fuzziness” of carbon aggregates that appeared similar to grass. After testing, the surface was more akin to molded clay with honeycomb-like structures. EDXS also showed a decrease in carbon on the surface after testing, and a larger signal of the underlying fluorine.

In the final section, a method to reduce the surface roughness of a spray-casted polyurethane/silica/PMC superhydrophobic coating was demonstrated. Through changing the main slurry carrier fluid, fluoropolymer medium, surface pre-treatment, and spray parameters such as distance and pressure, the arithmetic surface roughness was reduced from $5.4\ \mu\text{m}$ to $1.4\ \mu\text{m}$. In addition, general homogeneity of the film was improved, with roughness and cracking in the film decreased. Importantly, anti-wetting performance was largely maintained with a decrease in roughness. The ability to create superhydrophobic coatings with a smooth finish consistent with conventional polyurethane coatings is an important step in their ability to find real world applications.

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Nomenclature

Abbreviations

CA	Contact Angle
CFD	Computational Fluid Dynamics
CVD	Chemical Vapor Deposition
DRW	Discrete Random Walk
EDXS	Energy Dispersive X-Ray Spectroscopy
GPM	Gallons Per Minute
MCPU	Moisture Cured Polyurethane
MVD	Mean Volume Diameter
PCBTF	parachlorobenzotrifluoride
PDMS	Polydimethylsiloxane
PMC	Perfluoroalkyl Methacrylic Copolymer
PTFE	Polytetrafluorethylene
PU	Polyurethane
SA	Sliding Angle
SEM	Scanning Electron Microscope
SiO ₂	Silicon Dioxide
TFA	Trifluoroacetic Acid
TiO ₂	Titanium Dioxide

Symbols

C_{Df}	Skin Friction Drag Coefficient
p	Dynamic Pressure
u_x	Gas Phase Axial Velocity
$u_{x,CL}$	Gas Phase Axial Velocity Taken at the Centerline
v_x	Droplet Axial Velocity
$v_{x,impact}$	Axial Velocity of Impacting Droplet at the Wall
We	Weber Number
S_a	Arithmetic Mean Surface Roughness
S_{kur}	Kurtosis
S_{sk}	Skewness

1 Motivation

1.1 Aerodynamic Icing

Two of the harshest applications for icing are wind turbines and aircraft. In the case of wind turbines, icing brings aerodynamic, structural, and safety issues. Aerodynamic problems arise from accreted ice increasing roughness. An increased roughness can induce a transition from a laminar to turbulent boundary layer, increasing the skin friction drag coefficient, C_{Df} . Accreted ice can cause large scale vibrations due to increased weight, especially if ice is distributed unevenly. Ice that is thrown from a wind turbine poses a safety risk for any surrounding structures or people.

Figure 1.1.1: An aircraft being sprayed with freezing point depressant to melt ice

Several ways to either prevent icing or shed ice from an aerodynamic surface once it has accreted have been investigated. Freezing point depressant can be sprayed onto aircraft to melt ice that has accreted during flight, shown in Figure 1.1.1. A way to shed ice is a flexible pneumatic boot that inflates during flight and cracks ice. Aerodynamic surfaces can also simply be heated to prevent icing. However, most anti-icing or de-icing systems require extra weight and energy themselves, so a cheap and passive solution is desired. An ideal solution would be an anti-wetting coating

that would be able to deflect impacting icing clouds

1.2 Superhydrophobic Surfaces

A surface is defined as superhydrophobic if it satisfies two criteria:

- 1 Contact angle greater than 150°
- 2 Low sliding angle and contact angle hysteresis (generally taken to be $<10^\circ$)

Contact angle (CA) is defined as the angle that a water droplet makes with the surface at the three-phase contact line (where water, the solid surface, and vapor are all in contact). Sliding angle (SA) is the angle at which a water droplet will slide off of a surface when tilted. Contact angle hysteresis (CAH) is the difference between advancing and receding contact angles of the liquid droplet while it is sliding on the tilted surface.

There are many anti-wetting surfaces in nature, notably the lotus leaf, cicada wings, and water-strider legs. In fact the extreme anti-wetting effect of superhydrophobic surfaces is called the lotus effect. It has been seen in these natural phenomena that their anti-wetting property comes from two sources. First is micro- and nano-scale surface texture that reduces liquid-solid contact area. Second, anti-wetting comes from low-surface energy chemical functionality on these surfaces (e.g. lotus leaves have a layer of paraffin wax, similar to car polish that causes water to bead up and roll off).

Three analytical models have been made to predict what contact angle a droplet will have, shown in Figure 1.2.1. The first model, Young's equation, assumes a liquid droplet sitting on a completely flat surface. This equation comes from a force balance

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}} \quad \text{Young's Equation}$$

at the three phase contact line and predicts that contact angle, θ is simply a function of

surface tensions. The Wenzel model recognizes that no surface is completely flat and predicts that the apparent contact angle of the droplet, θ^* , is affected by a roughness factor of the surface, r . The Cassie-Baxter model recognizes surface roughness as

$$\cos \theta^* = r \cos \theta \quad \text{Wenzel Model}$$

well, with a vapor layer trapped underneath the liquid, creating a composite interface of solid and vapor. In this case, the smaller the fraction of liquid-solid contact,

$$\cos \theta^* = -1 + \phi_s(1 + \cos \theta) \quad \text{Cassie-Baxter Model}$$

ϕ_s , the higher the apparent CA will be. This is the situation needed to create a superhydrophobic surface.

Many different methods to create superhydrophobic surfaces have been explored in the past. Nanocomposite coatings have shown promise as surfaces capable of real-world use because of:

- High mechanical durability
- Inexpensive to fabricate
- Adaptable to substrates
- Do not require functionalization

In this thesis, four important factors for a superhydrophobic nanocomposites real-world applicability were investigated. In Section 1, the mechanical and functional resistance of a superhydrophobic nanocomposite was investigated when exposed to an icing-cloud sized droplet spray. In Section 2, erosion resistance of a nanocomposite was investigated when exposed to rain-sized droplet impact. In Section 3, the resistance of a novel flame soot-based superhydrophobic surface to an impinging water jet was investigated. Finally, in Section 4, a method to decrease the surface roughness of a superhydrophobic nanocomposite, while still maintaining superhydrophobicity, was investigated.

Figure 1.2.1: a) Young's equation for predicting contact angle, b) the Wenzel model, and c) the Cassie-Baxter model.

2 Icing Cloud Impact Resistance

2.1 Introduction

Up to 50% of a wind turbines annual power production can be lost due to inefficiencies caused by icing.¹ A promising way to alleviate this problem is through the use of anti-wetting coatings. Inspired by lotus leaves, recent novel techniques combine micro- and nano-scale surface structure with low surface energy to create superhydrophobic synthetic surfaces (contact angle greater than 150° and sliding angle less than 10°).²⁻⁵ These techniques include template synthesis, pulse electron deposition, electrochemical deposition, crystallization control, plasma treatment, Langmuir-Blodgett deposition, nanotube arrays, electro-spinning, and chemical vapor deposition (CVD).⁶ Most of these techniques require some combination of vacuum processing (e.g. plasma treatment) and expensive or restricting fabrication tools which limit application to surfaces on the order of square centimeters. Thus, for large scale industrial applications a different solution is desired.

The mechanical durability and preservation of anti-wetting performance when subjected to mechanical abrasion has been explored for several types of superhydrophobic surfaces. Steele et al.⁷ found that contact angles above 160° and contact angle hysteresis below 10° was maintained for a polyurethane/organoclay nanocomposite when subjected to a 1750 N/m adhesion strength tape test, and a 3850 N/m test did not noticeably remove any coating. A superamphiphobic surface was recently made from fluorosurfactant-modified silica aerogel that stayed superamphiphobic when rubbed 100 times with 600 grit sandpaper under 450 Pa pressure.⁸ Superhydrophobicity of micro-molded polypropylene remained intact when pressed with 500 kPa pressure.⁹ When tested under 32 kPa linear abrasion, polyethylene sheets that had been laminated over steel mesh remained superhydrophobic for over 5500 cycles.¹⁰

A major challenge for these superhydrophobic coatings is the ability to perform

under droplet impact. This is especially a concern for the increasing number of wind turbines being constructed offshore. One source of droplet impact on a wind turbine blade is impacting fog droplets. Droplet impact could cause erosion of the superhydrophobic coatings surface structure, reducing performance. Another danger of droplet impact is it could, even without mechanically wearing the surface, cause a transition from the non-wetting Cassie state to the wetting Wenzel state. This transition, known herein as saturation, occurs when it becomes thermodynamically favorable for the asperities on a superhydrophobic surface to become penetrated with water.¹¹ Saturation has been induced in the past through the application of force or pressure to the droplet,¹² electric voltage,^{13,14} light for a photocatalytic texture,¹⁵ and vibration.¹⁶ Other studies have investigated this transition when it is caused by prolonged liquid contact.¹⁷⁻¹⁹

Work has been done in the past to study the low velocity impact (<3 m/s) and immediate rebound of single ~ 1 mm diameter droplets on superhydrophobic surfaces.²⁰⁻²³ However, to date, investigations have been limited to single droplets where no erosion is expected. This experimental study investigates the performance of a novel polyurethane/organoclay superhydrophobic nanocomposite coating against a high pressure air-water spray to simulate fog impact. Superhydrophobic samples were impacted with an air jet laden with droplets representative of an icing cloud at three different impacting velocities. A computational fluid dynamics (CFD) study was performed to find the velocities of the impacting droplets. The anti-wetting performance was examined immediately after spraying intervals as well as after water trapped in the textured surfaces was allowed to evaporate.

2.2 Experimental

2.2.1 Sample Preparation

The process for sample preparation was the same as used by Steele, et al.⁷ Precursor solutions were first created, followed by spray casting and then thermosetting to produce the final nanocomposite coatings. Alcohols are common solvents for epoxy and polyurethane formulations. A recent study found that alcohols can have a strong tendency to adsorb on layered silicate surfaces rendering the surfaces functional for many applications including polymer reinforcement.²⁴ Thus, as-received dimethyl dialkyl C14-C18 amine functionalized montmorillonite clay particles (Nanoclay, Nanocor Inc., USA) were first dispersed in ethyl alcohol at room temperature and then waterborne perfluoroalkyl methacrylic copolymer (PMC) (30% wt polymer, 70% wt water; Dupont) was added slowly to the solution and blended with vortex mixing. Fluorinated polymers are of interest due to their extremely low surface energies, while an organoclay-based nanocomposite coating is desirable because it is both compatible with fluoroacrylics and environmentally friendly unlike some other nanofiller materials e.g. carbon nanotubes.²⁵⁻²⁷ Separately, moisture cured polyurethane (MCPU) was also dispersed in ethyl alcohol. The MCPU was a one-component liquid formula comprising 25% diphenylmethane-diisocyanate and 75% polyurethane pre-polymer (hexanedioic acid, polymer with 1,6-hexanediol and 1,1-methylenebis 4-isocyanatobenzene). Its viscosity was measured to be 4200mPas at 25C. This type of polyurethane formula is commonly found in many commercially available adhesives such as Titebond and Gorilla. Finally, the alcohol/organoclay/PMC suspension was blended into the MCPU solution, creating a Pickering emulsion. The final blend was stirred using a vortex mixer for 15 minutes until the mixture was in a homogenous and stable state.

The ethyl alcohol solvent concentration can also be tailored to suit the spray

applicator if necessary in order to obtain a dry spray coating and counteract the coffee stain effect.²⁸ To create the nanocomposite coatings from this precursor solution, the slurries were spray cast onto aluminum substrates using an internal mix, double-action airbrush atomizer (model VL-SET, Paasche). The substrates were coated with a single spray application and then heat cured at 100° C overnight.

Figure 2.2.1: Schematic of the spray test setup.

2.2.2 Spray Test Setup

The test design was centered around a set of MOD-1 air-assist nozzles supplied by the NASA Glenn Research Center Icing Research Tunnel (IRT). These nozzles were chosen because of their well-known correlation between inlet air and water pressures and resulting droplet sizes produced. The nozzles were also desirable because of the extensive work done in the past by Bulzan et al.²⁹ to both numerically and experimentally validate the nozzles radial and axial profiles of velocity and turbulent kinetic energy.

The test setup consisted of a MOD-1 nozzle pointed vertically down towards a test

sample. The nozzle was enclosed inside of a brass adapter with inlets for water and air. The design of the nozzle and adapter allowed for the distinct air-water mixtures to be created. Tap water entered the adapter from the back inlet and flows unobstructed through the nozzle. Air entered the adapter from the side inlet and into a cavity around the nozzle. The air could then circulate freely around the nozzle and enter the stream through a series of holes drilled around the outer surface of the nozzle. Unlike other air-assist nozzles, it did not use swirling for atomization. The adapter had extensions on either side with screw holes. These extensions were attached to stationary aluminum struts on either side with mounting holes 5 centimeters apart and allowed for a maximum of 65 centimeters of distance between the nozzle and the superhydrophobic sample. The sample was mounted on a lab jack that allows for micrometer height adjustments that total less than 2.5 centimeters. A schematic of the setup is shown in Figure 2.2.1.

The nozzle was supplied with a water pressure of 50 psi and air pressure 20 psi to create a spray of 25 micron mean volume diameter (MVD) droplets. The air and water mass flow rates were approximately 2.3 and 0.5 g/s, respectively.²⁹ For three different test runs, the nozzle was placed at distances of 25, 45, and 65 cm from the superhydrophobic sample.

2.2.3 Nanocomposite Characterization

A sample was made for each of the spray distances. Droplets were sprayed onto each sample in 10 second time intervals. After each spray interval, the sample was shaken by hand for 2 minutes to clear any large droplets from the surface. Compressed air was then blown on the surface for 10 seconds from a distance of approximately 3 inches to clear off remaining droplets. A CMOS camera (Canon T2i, Canon, USA) with a macro lens (MP-E 65mm f/2.8 1-5xm Canon, USA) was used to capture static and dynamic water droplet images on a custom tilt stage for wettability measure-

ments. ImageJ was then used to process the images with a Java plugin (Drop Shape Analysis, Aurlen Stalder)³⁰ to calculate the static and dynamic contact angles. Contact angles were measured at three different points on the surface after each spray interval, with the average reported. After 5 time intervals, equaling a total of 50 seconds, the sample was heated at 100° C for 30 minutes to let any water inside the asperities of the surface evaporate. Scanning electron micrographs (SEM) were taken of superhydrophobic samples after being sprayed from 45 and 65 cm to compare surface morphology before and after testing. Energy dispersive X-ray spectroscopy (EDXS) was also performed before and after testing using a PGT IMIX-SPIRIT detector.

2.3 Computational Modeling

To estimate the velocities of impacting droplets, numerical predictions were obtained from a density-based Reynolds Average Navier-Stokes (RANS) approach using the FLUENT software package. The discretization scheme, governing equations, and turbulence model for free jet calculations (i.e. without a downstream wall) were the same as used by Clark, et al.³¹ The temporal discretization of the RANS equations employed a second-order upwind scheme for the momentum, turbulence, and dissipation conservation equations. The two equation $k-\omega$ Menter-SST was chosen for the turbulence model. The mesh used was 2-D, axisymmetric, and contained about 16,000 nodes. Mass flow was assumed to be choked at the nozzle exit, with a Mach number equal to 1. CFD was first done to find the downstream characteristics of pure airflow coming from a MOD-1 nozzle with no obstructions downstream. An injection of water droplets was then released 10 cm from the nozzle exit. The initial droplet velocities were set to the axial velocities found experimentally by Bulzan et al.²⁹ at this downstream distance from the nozzle exit. Experimental data was found using a two-component phase/Doppler instrument.

Figure 2.3.1: Distribution of droplet size bins used in computational study.

The water droplet sizes were based off of a cumulative distribution function tabulated from experimental data³² obtained within the NASA Glenn IRT. The experimental data had a range of water droplet sizes with a MVD of 21 μm . The experimental data were fitted with a Rosin-Rammler distribution using the equation seen below,

$$C(d) = 1 - \exp \left[- \left(\frac{d}{d_{rr}} \right)^{\frac{1}{h_{rr}}} \right]$$

In this expression $C(d)$ is the cumulative droplet distribution, d is the droplet diameter, d_{rr} is the reference diameter and corresponds to $C(d) = 0.63$, and h_{rr} is the spread parameter.³³ For the current Rosin-Rammler fit, $d_{rr} = 24 \mu\text{m}$ and $h_{rr} = 2.4$. This cumulative distribution function was converted into a probability density function and ten droplet bin sizes were determined by keeping the integral of the Rosin-Rammler fit equal between each droplet size which can be seen by the black lines in Figure 2.3.1. Ten different droplet diameters were chosen to give an adequate range of droplet sizes and using the Rosin-Rammler fit allows the MVD to stay at 21 μm and to match with experiments.

The droplet trajectories were computed with a Lagrangian discrete-phase model with a particle time step of $100 \mu\text{s}$. For improvement in the predictive ability of turbulent droplet diffusion, a Discrete Random Walk (DRW) model was used. In the DRW model, a Gaussian random number generator is used to describe instantaneous fluid velocity perturbation so that information for the mean particle diffusion can be subsequently obtained. The droplet force-balance equation implemented a sphere drag law³⁴ but neglected lift forces, droplet-droplet interactions and droplet break-up. The airflow was analyzed from simulations with droplets with two way coupling. The cases of a wall 25, 45, and 65 cm from the nozzle exit were then investigated. A stationary wall with a no-slip boundary condition was placed at these downstream distances. Trajectory calculations of droplets were set to terminate if they came into contact with the wall. A sample of droplets was taken at the downstream wall to find the axial velocities upon impact.

2.4 Results and Discussion

2.4.1 Computational Results

Figure 2.3.2 shows the flow characteristics of an unobstructed free jet exiting the MOD-1 nozzle determined by the current study along with a comparison to Bulzan's previous study.²⁹ Figure 2.3.2a and Figure 2.3.2b show the radial variation of u_x , defined as gas phase axial velocity, and v_x , defined as droplet axial velocity, at distances of 20 and 30 cm downstream of the nozzle exit. For both phases and downstream distances, the present computational study gives higher axial velocities than Bulzan's, but more closely matches Bulzan's experiments, indicating the present computational results can be used to predict experimental results. u_x reaches a velocity of about 25 m/s at the centerline 20 cm downstream of the nozzle exit, and tapers off to zero at a radial distance of 4 cm from the centerline. At 30 cm downstream of the nozzle, u_x is 16 m/s at the centerline, and positive velocity is found up to 7 cm away from the

(a) Radial variation of gas phase axial velocity at 20 cm (top) and 30 cm (bottom) downstream of nozzle.

(b) Radial variation of droplet phase axial velocity at 20 cm (top) and 30 cm (bottom) downstream of nozzle.

Figure 2.3.2: Radial flow characteristics for (a) gas phase phase and (b) droplet phase

centerline. v_x values are slightly than u_x values at 20 cm from the nozzle, but the two more closely match at 30 cm. Figure 2.4.1 shows the axial variation of $u_{x,CL}$, or u_x taken at the centerline, for the present free jet and comparison to Bulzan et al. Also shown are the axial velocities in the cases of an impinging wall. Once again, the axial velocities from the present study are higher than Bulzan found numerically, but match Bulzan's experimental results. In the cases of an impinging wall u_x decelerates to 0 m/s at the wall as is required. As the impinging wall moves closer to the nozzle exit (i.e. from 65 to 25 cm), the deceleration of the jet to zero occurs closer to the wall. For example, when the wall is 65 cm from the nozzle exit deceleration starts about 10 cm upstream of the wall. Whereas when the wall is 25 cm from the exit, deceleration starts about 6 cm ahead of the wall.

Figure 2.4.1: Axial variation of gas phase centerline axial velocity.

Figure 2.4.2 shows a scatter plot of droplets downstream of the MOD-1 nozzle in all three wall cases, as well as $v_{x,impact}$, the axial velocities of impacting droplets at the walls. As mentioned above, droplets were injected 10 cm downstream of the nozzle exit. In the cases of walls 45 and 65 cm downstream, $v_{x,impact}$ tend to $u_{x,CL}$ at those downstream distances, shown in a dashed gray line. However, for a 25 cm

Figure 2.4.2: Scatter plot of droplets (colored by axial velocity) and axial velocity of impacting droplets (colored by droplet size) for a wall 65 cm (top), 45 cm (middle), and 25 cm (bottom) away from nozzle exit. Freejet gas phase axial velocity at those downstream distances are shown in a dashed gray line.

Figure 2.4.3: Average droplet impact velocity and fraction of all impacting droplets that impact within a 1 inch of the centerline as a function of downstream wall distance

downstream wall, some impacting droplets have a higher axial velocity than $u_{x,CL}$ at that distance. Bulzan et al. also found that droplets have higher velocities than the gas phase through the first ~ 30 cm. Figure 2.4.3 shows the average $v_{x,impact}$ within 2.5 centimeters of the centerline, corresponding to the area that a superhydrophobic sample would be exposed to during testing. Also shown is "Impact %", defined as the fraction of droplets that impact within 2.5 centimeters of the centerline. Average $v_{x,impact}$ decreases from 14.5 m/s at 25 cm, to 4.5 m/s at 45 cm, to 3.4 m/s at 65 cm. For a total number of 1500 droplets sampled in each case, Impact % also decreases as wall distance increases. Impact % decreases from 46% at 25 cm, to 19% at 45 cm, to 7 % at 65 cm.

2.4.2 Experimental Results

Figure 2.4.5 shows the effect of droplet impact on the contact angle of each superhydrophobic sample immediately after each spraying interval. Before spraying, each of the samples produced a contact angle of $150 \pm 2^\circ$. All three samples lost about the same amount of performance after being sprayed for 10 seconds. After that point, the difference in impacting velocities became clear. While the 65 cm and 45 cm samples again lost some performance after 30 seconds, the 25 cm sample saw a substantial loss in contact angle. At the conclusion of spraying at 50 seconds, the 65 cm and 45 cm samples produced a contact angle measurement of 99° and 94° , respectively, while the 25 cm sample produced a contact angle of 70° . Upon heating the samples after spraying, the contact angle for each sample returned to its original value. This suggests that the loss in performance during spraying was not due to mechanical erosion or a change in surface morphology, but rather due to liquid saturation of the micro-textured surface. This saturation effectively changed the surface from the superhydrophobic Cassie state to the wetted Wenzel state. Once the liquid was allowed to evaporate from the asperities on the surface, the non-wetting

performance returned.

(a) Contact angle.

(b) Sliding angle.

Figure 2.4.4: (a) Contact angle and (b) sliding angle of samples before spray tests and after surface moisture evaporation.

Saturation most likely came from two sources. First, as can be seen in , the distance between large asperities on the surface can be as large as 50-100 microns. This is enough space for individual droplets to get inside of the micro-texture and wet asperities. Second, as is noted by Deng et al.,²² the stagnation pressure of impacting droplets was likely large enough to overpower the capillary pressure of the asperities, causing droplets to penetrate the micro-texture. The hypothesis that no mechanical

erosion occurred and that all loss in performance was due to saturation is supported by the SEM images shown in Figure 2.4.6. There does not appear to be a major difference in the surface morphology when comparing superhydrophobic samples before and after 45 cm and 25 cm impact.

The performance of the samples before spraying and after surface moisture evaporation is shown in Figure 2.4.4. It is clear that contact angle (Figure 2.4.4a) was unaffected by the droplet impact, as these values returned to their original state after each of the samples was dried. However, sliding angles (Figure 2.4.4b) increased significantly for the highest impact velocity even after water was allowed to evaporate. One possible cause of this increase involves recognizing that contact angle and sliding angle are not necessarily coupled. For example, an improvement in contact angle does not necessarily bring an improvement in sliding angle. It has been shown that increased roughness, which is critical for an increased contact angle and superhydrophobicity in general, can actually lead to a higher sliding angle.³⁵ EDXS, shown in Figure 4.4.3, did not reveal a change in surface chemistry. Carbon and fluorine (components of PMC) and aluminum, silicon, and titanium (components of montmorillonite clay) were all detected as much before testing as after. It is important to note that EDXS detects elements in the bulk of a tested sample, several microns within the surface. Thus, a change in the surface chemistry of the superhydrophobic sample might not have been detected. Another possible reason for the degradation in sliding angle is that the fluoropolymer chains present on the surface rearranged while being exposed to water for extended periods of time. A change in the orientation of the polymer would not have been detected through EDXS. Elements present in tap water used in the experiment might have also contaminated the surface.

Figure 2.4.5: Variation of contact angle with spray time for different spray distances.

2.5 Conclusion

In this experimental study, polyurethane/organoclay superhydrophobic nanocomposite coated aluminum samples were sprayed with 25 micron droplets impacting at 25, 45, and 65 cm to simulate fog droplet impact. It was shown that anti-wetting performance degraded as a function of spray time and impact velocity. Contact angle returned to pre-test values after the water that had penetrated the surfaces microtexture was allowed to evaporate. However, sliding angle increased with increasing droplet impact velocity. Maintaining mechanical structure while being impacted with fog-sized droplets is an important step in bringing superhydrophobic nanocomposites to real world use. Based on the results of this study, future work will include increasing droplet size and impact velocity to simulate rain impact and higher wind turbine tip speeds, as well as tailoring nanocomposite surfaces to improve saturation resistance to such conditions.

Figure 2.4.6: SEM images of superhydrophobic surface before testing and after testing

(a) Before testing.

(b) After 25 cm spray impact.

Figure 2.4.7: EDXS of superhydrophobic samples (a) before testing and (b) after 25 cm spray impact

3 Simulated Rain Impact Resistance

Mechanical durability of superhydrophobic surfaces has to date been a limiting factor for their widespread industrial application. Wear mechanisms that have been explored include sand impingement,³⁶ frictional abrasion,^{10,37} and adhesive peel tests.³⁸ An area of interest for wind turbines and other mobile outdoor systems is the durability of superhydrophobic coatings to extended periods of rain. In such a case, drops may impact with large diameters (1 - 2 mm) and high speeds (e.g. 5 - 50 m/s). However, there has been little investigation into the durability of a superhydrophobic surface in the presence of a continuous, high flow rate, high velocity impacting water spray where erosion might occur. For example, previous studies of ~ 1 mm droplets interacting with superhydrophobic molded polydimethylsiloxane (PDMS) and carbon nanofiber surfaces were conducting with single droplets impacting at less than 0.4 m/s.²⁰ Grazing impact of many drops at 10 - 20 m/s but with diameters of < 50 μm has also been examined.²¹ As such, no previous study has examined durability to rain-sized drops (1 mm diameter) with high impact speeds (greater than 1 m/s) for extended periods (e.g. for at least several minutes).

This experimental study investigates the performance of a polyurethane/organoclay superhydrophobic nanocomposite coating against a simulated rain impact. Superhydrophobic samples were impacted with 1.4 mm droplets at a speed of 25 m/s for a period of 5 hours. While saturation occurred, the anti-wetting performance was examined after water trapped in the textured surfaces was allowed to evaporate. Surface morphology of the surfaces was also inspected before and after testing using SEM to determine overall impact resistance.

3.1 Spray Test Setup

An axial full cone nozzle (model 1/8G-3007, Spraying Systems) was supplied with a water pressure of 50 psi, creating a spray of 1.4 mm MVD droplets at a flow rate of 0.78 GPM ($180 \text{ in}^3/\text{min.}$). The nozzle was pointed down towards superhydrophobic samples from a distance of 1 foot for a period of 5 hours. A schematic of the test setup is shown in Figure 3.1.1 and a photo of the setup is shown in Figure 3.1.2. With a spray angle of 30° , the spray cone impacted with a diameter of 6.4 in. consistent with an impact area of 32 in^2 . Based on the water volumetric flowrate, this yields a deposition rate of $5.6 \text{ in}^3/\text{min.}$ of water over the impacted surface area. Based on the mean annual rainfall of Virginia of 44 inches,³⁹ the simulated rain test was consistent with about 38 years of rainfall.

With a nozzle orifice diameter of 0.063 inches, the nozzle flow rate corresponded to a droplet velocity of about 25 m/s . Due to the high inertia of the droplets, their impacting velocity was assumed to be the same as their exit velocity from the nozzle. The terminal velocity of a 1.4 mm rain droplet is in the range of $4 - 5 \text{ m/s}$, so this impact velocity was comparable to what could be expected for rain impacting an about 5 MW wind turbine near the middle of the blade. This droplet velocity is also akin to a car driving through rain, or rain impacting a stationary structure while being driven by high-speed storm winds. The cases of normal ($\theta = 90^\circ$) and angled ($\theta = 40^\circ$) droplet impact were examined to study the effect of impact inclination (θ) as noted in Figure 3.1.1.

3.2 Performance Characterization

After the 5 hour test period, samples were heated at 100°C for 1 hour to allow all moisture trapped in the asperities of the surface texture to evaporate. After the surfaces cooled, a CMOS camera (Canon T2i, Canon, USA) with a macro lens (MP-E 65mm f/2.8 1-5xm Canon, USA) was then used to capture static water droplet images

Figure 3.1.1: Schematic of the spray impact setup used to investigate of superhydrophobic surfaces

and a goniometer was used to measure sliding angle. ImageJ was then used to process the images with a Java plugin (Drop Shape Analysis, Aurlien Stalder) to calculate the static contact angle. SEM images were also taken of superhydrophobic samples before and after testing to compare surface morphology.

3.3 Results

The impacting dynamic pressure, p , of individual water drops was calculated to be 312 kPa, where

$$p = \frac{1}{2}\rho v^2$$

In this expression, ρ is the density of water (1000 kg/m^3), and v is the velocity of individual drops. Weber number, We , a dimensionless ratio of droplet inertial forces

Figure 3.1.2: Photo of the spray impact setup used to investigate of superhydrophobic surfaces

to surface tension forces, is defined as

$$We = \frac{\rho v^2 d}{\sigma}$$

where d is the diameter of a droplet and σ is the surface tension of water, 72 mN/m . We was calculated to be 1.2×10^4 for drops in this study.

The impacting droplets were able to penetrate the asperities of the superhydrophobic samples, causing a rapid transition of the surfaces from the non-wetting Cassie-Baxter state to the wetting Wenzel state (saturation). The hydrophobic performance of the samples before and after spray testing is shown in Table 1. After the spray impact and after evaporation through heating, the surfaces were hydrophobic did not fully return to their pre-test performance. In particular, a small reduction in static contact angle but more problematic was an increase in sliding angle. The sample that was subjected to normal impact showed a larger decrease in performance than the tilted sample. Higher degradation in a sample that was subject to normal impact is similar to a result that was seen for water jets as discussed in Section 4. A tilted sample resulted in a larger shearing force and thus different wear physics than the direct

Superhydrophobic Surface	Static Contact Angle (deg.)	Sliding Angle (deg.)
Before Spray	154	11
After 40° Spray	148	24
After 90° Spray	144	33
After 90° Spray and Refluorination	151	24

Table 1: Antiwetting performance of the baseline sample, tested samples, and refluorinated sample

spray, thus the normal component may play a more significant role in degradation compared to the shear component.

To understand the mechanism for performance decay, both surface topology and chemical topology effects were considered. SEM images of the surfaces are shown in Figure 3.3.1 to examine surface morphology. It was immediately noticed that a large number of circular indentations were apparent on the samples that experienced droplet impact. These indentations, approximately 20 microns in diameter, were initially believed to be micro-scale craters caused by the impacting droplets. However because of the large size disparity between these indentations and the impacting droplets this result was deemed unlikely. Rather, it was thought more likely that through the duration of the spray test, the silicate layers of the montmorillonite clay particles were continuously exfoliated by the saturated liquid inside the surface asperities. This is believed to have led to turgid clay particles bursting, causing the marks shown in Figure 3.3.1. Figure 3.3.2 shows higher magnification images of the region shown in Figure 3.3.1. Striations around what is thought to be a bursted clay particle is particularly visible in Figure 3.3.2, indicating the polyurethane binder had been stretched and plastically deformed.

Nonetheless, it was apparent after these spray tests that a change in surface morphology occurred. However, leaching of the fluoroacrylic copolymer from the surface throughout testing may have also increased surface energy and thus decreased superhydrophobic performance. To test this hypothesis, the surface subjected to normal spray impact was subsequently refluorinated by spray casting a thin layer of PMC

in ethanol solution onto the surface and cured at 100°C for 2 hours. An increase in performance was subsequently observed, as shown in Table 1. However, even after refluorination the sample did not perform as well as it had before droplet impact testing. This indicates that the loss in performance seen after testing was not only caused by mechanical surface morphology degradation, but also by fluoropolymer leaching.

3.4 Conclusion

In this experimental study, polyurethane/organoclay superhydrophobic nanocomposites were impacted by a spray of 1.4 mm water droplets at a speed of 25 m/s for a period of 5 hours in an effort to simulate the real world rain conditions experienced by a wind turbine blade. The surfaces were immediately saturated by the spray, but no macro-scale mechanical degradation occurred. After trapped water was allowed to evaporate from the surface, a decrease in anti-wetting performance was observed, with a larger decrease observed for a sample tested under direct spray impact than one at a 40° angle to impacting droplets. SEM images of the impacted samples revealed the likely remnants of over-exfoliated silicate layers of clay nanoparticles. A sample was refluorinized to assess the relative effects of changes in surface morphology and chemistry. Performance increased but did not return to pre-test values, indicating both changes in surface morphology and chemistry contributed to performance degradation. This set of tests serves as a benchmark for future improvements in superhydrophobic nanocomposite performance during extended rain-sized droplet impact.

Figure 3.3.1: SEM images of surfaces (a,b) before exposure to rain-sized droplets, (c,d) after normal-impact exposure, and (e,f) after 40 degree exposure.

Figure 3.3.2: Higher magnification of images of bursted clay particle after direct exposure.

4 Soot-based Superhydrophobic Surface Water Jet Resistance

4.1 Introduction

Previous work has investigated carbonaceous flame soot to make superhydrophobic nanostructures.^{40–44} While showing amazing anti-wetting properties when adhered to a substrate, surfaces created from flame generated materials typically have very low substrate adhesion and durability, with a small amount of touching, blowing, or water flow being able to carry away loosely adhered particles. Recently, candle soot was used as a template for hollow silica shells, which were then treated with a semi-fluorinated silane by chemical vapor deposition to create a robust superamphiphobic surface.³⁶ While impressive, this process is both costly and time consuming. An electrically conductive superhydrophobic surface was recently created through impinging a diffusion flame onto a film of fluorinated acrylic modified with multi-walled carbon nanotubes, thus melting the acrylic and producing surface texture.⁴⁵ In this work, a much simpler and quicker process was used to make robust flame-generated surfaces. Of particular note, the process is completely "dry", requiring no solvent for either substrate polishing,⁹ spray casting,^{7,26,28} hydrophobic functionalization,⁴⁶ solutions for electro-spinning,⁴⁷ or as a precursor for chemical vapor deposition.⁸

4.2 Surface Preparation

Polytetrafluoroethylene powder (PTFE, Sigma Aldrich) was brushed onto P500 aluminum oxide sandpaper using a polyurethane foam paint brush. Due to the friction of brushing and strong electronegativity of fluorine, the powder was able to stick to the sandpaper through a buildup of static charge. SEM images of the as-received sandpaper and brushed-on PTFE are shown in Figure 4.2.1. The underlying texture

Figure 4.2.1: SEM images of (a) P500 sandpaper and (b) brushed-on PTFE. (c) and (d) are higher magnification images of brushed-on PTFE.

of the sandpaper, shown in Figure 4.2.1a, also provided grooves into which PTFE could adhere. Brushed-on PTFE masked much of this texture, as can be seen in Figure 4.2.1b. Higher magnification images of the PTFE, Figure 4.2.1c and 4.2.1d, reveal that individual particles have a width in the range of 100 - 200 nm. The surface exhibited highly hydrophobic performance at this step in the process with contact angle = 135° and sliding angle = 18° .

The process for depositing soot onto the PTFE layer is illustrated in Figure 4.2.2. The surface was held above the diffusion flame of a handheld butane lighter, as shown in Figure 4.2.2a. For a period of 5 seconds, the surface was held at a distance just beyond the lean blue region of the flame (Figure 4.2.2b). With a temperature of $\sim 1500^\circ\text{C}$, the flame was able to melt the brushed-on PTFE, creating a binder for

deposited soot. The surface was then exposed to the yellow, soot-rich region of the flame for a period of 10 seconds. As shown in Figure 4.2.2c, soot was deposited not only onto the melted PTFE region, but much of the surrounding area. Next, when compressed air was blown over the surface, soot particles in the PTFE binder region adhered to the surface, while those on the periphery were blown away (Figure 4.2.2d). After soot was deposited into the PTFE binder, the surface exhibited superhydrophobic behavior, with $CA = 164^\circ$ and $SA = 2^\circ$. A photograph of water impacting and flowing over a representative surface is shown in Figure 4.2.3. Water can be seen to bead up and bounce off the surface.

Figure 4.2.2: (a) photograph of flame treatment, (b) melted PTFE, (c) soot deposited onto surface, and (d) air blown over surface to remove loosely adhered soot

Figure 4.2.3: Photograph of water impacting and flowing over a surface composed of flame generated material

4.3 Experiment

To test the robustness of the surface with respect to an impacting water jet, samples were exposed to a water jet with varying dynamic pressures, calculated in the same way as in Section 3. v was found by first connecting the water nozzle to a flowmeter to find the volumetric flowrate, Q . Then,

$$v = \frac{Q}{A}$$

where A is the area of the water jet. With a diameter of $1/8''$, the water jet had an area of $7.9 \times 10^{-6} \text{ m}^2$. Samples were exposed until a $10 \mu\text{L}$ droplet would not slide off the samples (“pinned” state). To find the effect of impact angle, β , samples were also tilted when exposed to the water jet. A schematic of the experimental setup is shown in Figure 4.3.1.

Figure 4.3.2 illustrates the importance of the PTFE binder in creating a robust surface. Two samples, one created through the method described above (i.e. soot deposited into a PTFE binder), and one created through simply holding P500 sand-

Figure 4.3.1: Schematic of the water jet experimental setup

paper above a flame and allowing soot to deposit, were exposed to a 10 kPa water jet impacting at $\beta = 0^\circ$, with contact angle recorded in 10 second increments. The surface containing a PTFE binder maintained a high contact angle, displaying its robust nature. The surface composed of only soot deposited onto sandpaper initially showed superhydrophobic performance, with a $CA = 160^\circ$. However, when it was exposed to a relatively gentle water jet, soot quickly washed off of the surface. Contact angle steadily decreased as the surface deteriorated.

To find the reference time for which samples would be exposed to jet impact, samples were subjected to a 40 kPa water jet impacting at $\beta = 0^\circ$ for exposure times increasing in 2 minute increments. The results of this test, shown in Figure 4.3.3, revealed that the contact angle of the exposed samples stayed nearly constant through 6 minutes. However, after 8 minutes, contact angle degraded to 125° , and thus below superhydrophobicity. A minor degradation in SA occurred through 2 minutes, from 2° to 4° . Increasing exposure times produced a more dramatic degradation in performance, with a pinned state occurring after 8 minutes.

Figure 4.3.2: Comparison of robustness of surface comprised of only soot deposited onto sandpaper, and surface comprised of soot deposited into PTFE binder.

4.4 Results

Anti-wetting performance after being exposed to the water jet for 2 minutes as a function of dynamic pressure and impact angle is shown in Figure 4.4.1. Three clear trends were apparent. First, as β increased, the dynamic pressure required to degrade superhydrophobic performance. For example, contact angle performance, shown in Figure 4.4.1a, degraded when exposed to $p = 60$ kPa and when the sample was normal to the jet ($\beta = 0^\circ$). However, when tilted to $\beta = 20^\circ$, performance degraded when exposed to only $p = 40$ kPa. When tilted to $\beta = 80^\circ$, contact angle degraded when exposed to just 10 kPa. The same trend was observed in sliding angle (Figure 4.4.1b). Maintained below 5° through 50 kPa when subjected to normal impact, in the case of $\beta = 80^\circ$, a pinned state was observed after being impacted by just a $p = 10$ kPa water jet.

The second trend seen was that as β increased, the amount of degradation in contact angle done by the water jet increased. For example, once it entered the pinned state, the sample that was exposed normal to the water jet saw its contact

Figure 4.3.3: CA and SA of samples as a function of exposure time when exposed to 40 kPa water jet

angle degrade to just 15° . In contrast, even when water droplets were pinned to the sample that had been tilted to $\beta = 80^\circ$, its contact angle degraded to 119° .

The third trend observed was that anti-wetting performance did not degrade until a clear threshold in dynamic pressure had been reached. It might have been expected that decrease in CA and SA would be a linear or exponential function of p . However, performance was maintained at a constant β for varying p until a sudden degradation occurred. The importance of the deposited soot layer is also shown in Figure 4.4.1b. A sample composed of only PTFE was exposed to a normal water jet and entered the pinned state when subjected to only a 20 kPa water jet. Interestingly in this case though, the trend of a "sudden" degradation was not observed, with sliding angle increasing $\sim 7^\circ$ when exposed to a 10 kPa jet.

SEM images of surface morphology before testing and after being exposed to a $p = 60$ kPa water jet at $\beta = 0^\circ$ revealed a stark difference (Figure 4.4.2). Before testing the surface exhibited a "fuzzy" or "grassy" morphology of carbon aggregates. After failure the surface looked more akin to molded clay, with a high magnification image

(a) Contact angle

(b) Sliding angle

Figure 4.4.1: Anti-wetting performance of samples as a function of water jet dynamic pressure and impact angle

(Figure 4.4.2d) showing a honeycomb-like structure. EDS, shown in Figure 4.4.3, also revealed a large difference in surface chemistry before and after testing. Before testing, Figure 4.4.3a showed a large peak of carbon, indicating the presence of the soot layer that had been deposited. A smaller fluorine peak was also detected as part of the underlying PTFE. Figure 4.4.3b showed that after testing, a much smaller carbon peak was detected, along with more fluorine. This indicated that carbonaceous soot had been washed away, and more PTFE was detected.

A relationship was also observed between the impact angle, β , and the region of a sample that was degraded. For example, optical microscope images taken immediately after testing revealed that the spot that the water jet impacted upon, as well as two bands to either side of this point, had been affected when a sample was tilted to $\beta = 60^\circ$ (Figures 4.4.4a and 4.4.4c). These regions were covered with either a film or drops of water, indicating that they had degraded and were no longer superhydrophobic. Likewise, images of a sample that was tilted to $\beta = 80^\circ$ during testing showed one continuous degraded region (Figures 4.4.4b and 4.4.4d).

4.5 Conclusion

In this study, a novel superhydrophobic surface was created by holding a sheet of PTFE microparticles above the diffusion flame of a handheld butane lighter. The heat of the flame was able to melt the PTFE, creating a binder for deposited soot particles. Surfaces displayed very high water repellancy and resistance to saturation by high-pressure water jets. Unlike other methods for creating superhydrophobic surfaces from flame generated material, a robust surface was created through a quick and simple process.

Figure 4.4.2: SEM images of a soot-based superhydrophobic surface (a) before, and (b) after being exposed to a $p = 60$ kPa water jet at $\beta = 0^\circ$. $\beta = 0^\circ$. Higher magnification images are shown in (c) and (d).

Figure 4.4.3: EDXS of flame-generated surface (a) before, and (b) after water jet exposure.

Figure 4.4.4: Optical microscope images of a soot-based superhydrophobic surface immediately after testing when tilted at (a) $\beta = 60^\circ$ and (b) $\beta = 80^\circ$. (c) and (d) highlight degraded regions (gray) and non-degraded regions (blue).

5 Reducing Surface Roughness for Icing Resistance

5.1 Introduction

Superhydrophobic coatings have drawn great interest as an energy independent technique to delay ice accretion and lower ice adhesion on power lines, aircraft, and wind turbines. Meuler et al.⁴⁸ found that the introduction of surface texture was able to decrease ice adhesion strength to less than what was achievable just through chemical modification. Coatings that can be applied through one-step spray casting are particularly desirable because of their relatively low cost and ease of application. Yeong et al.⁴⁹ showed that a polyurethane/silica/PMC superhydrophobic surface was able to deflect supercooled droplets and prevent icing. However, a superhydrophobic surface created through spray casting can have significant arithmetic mean surface roughness, S_a , where

$$S_a = \frac{1}{n} \sum_{i=1}^n |y_i|$$

where y_i are the vertical distances from the mean height and n is the total number of points sampled on the surface. From an aerodynamic perspective, skin friction drag coefficient, C_{Df} is independent of roughness for laminar flow over a flat plate. However, C_{Df} increases as roughness increases for a turbulent boundary layer, the regime most likely to be found in a wind turbine or aircraft application. Surface roughness can also trip a laminar boundary layer into turbulence, bringing an increase in C_{Df} .⁵⁰ Large scale surface roughness on a superhydrophobic surface can also allow the surface to become saturated, and problematically provides additional surface area onto which ice can adhere. For example, the delay time of ice accretion onto a superhydrophobic surface with nanoscale roughness was observed to be higher than one with microscale roughness when tested in an icing wind tunnel.⁵¹ Another study found that ice adhesion strength decreased as the surface area of textured PDMS was decreased.⁵²

Although work has been done in the past to control the roughness features of surfaces created through micro-molded polymers,⁹ plasma treatment,^{37,53} electrodeposition,⁵⁴ and electrospinning,⁵⁵ there has not been, to the author's knowledge, a similar detailed study for a spray casted superhydrophobic coating. Instead, the focus for spray casted surfaces has been on other performance aspects (e.g. coating adhesion, omniphobicity, durability, etc.) and typical nanocomposite surfaces have had arithmetic roughness on the order of 10 microns.⁷ Developing smoother superhydrophobic surfaces (less than 10 μm) is critical for tuning surfaces for specific anti-wetting properties, such as high contact angle or high water pressure resistance.⁵⁶

The objective of this work was to refine the process to create smoother spray-casted polyurethane/fluoropolymer/silica superhydrophobic coatings by removing finish defects and changing the self-assembly process. The main pre-cursor slurry solvent, fluoropolymer medium, surface pre-treatment, and spray parameters were varied to produce nanocomposite coatings, and anti-wetting performance and surface roughness were then measured.

5.2 Surface Preparation

After several trials, three different superhydrophobic coating formulations were developed with arithmetic mean surface roughness values of about 5 μm (SH-5), 3 μm (SH-3), and 1 μm (SH-1). These formulations are listed in Table 2. All samples were sprayed with the same spray casting process described by Yeong,⁵⁷ with the aluminum substrates lying on a motorized platform traversing longitudinally and laterally, while the spray gun was held stationary. A photo of the setup is shown in Figure 5.2.1. SH-5 was the initial surface formulation and consisted of a single stage two component urethane paint (Dupont) mixed in a vial with silica nanopowder (Sigma-Aldrich), acetone, and waterborne perfluoroalkyl methacrylic copolymer (PMC, Dupont, ~ 80 wt.% H_2O). This emulsion was vortex mixed for several minutes and then sprayed

	SH-5	SH-3	SH-1
PU wt%	24	24	25
PCBTF	0	29	33
Acetone	58	29	33
Water	12	12	0
PMC	3	3	5
Silica	3	3	3
Mixing	Vortex	Vortex	Sonication
Surface Cleaning	No	No	Yes
Spray Distance	3.5 in.	4.5 in.	6.0 in.
Air Pressure	30 psi	30 psi	50 psi

Table 2: Surface formulations and their preparation procedure

onto aluminum (320-grit sanded to promote mechanical adhesion between coating and substrate) using a conventional siphon atomizing spray nozzle (1/4JCO series, Spray Systems Co., USA) at an air pressure of 30 psi and spray distance of 3.5 in. The coating was then immediately heat cured at 100°C for 6 hours.

The formulation of SH-3 employed changes that successfully reduced the surface roughness. The same urethane paint, silica nanopowder, and waterborne PMC were vortex mixed. Instead of dispersing in acetone, a commercial urethane reducer (Dupont), consisting of a $\sim$ 50/50 blend of acetone and parachlorobenzotrifluoride, was used as the solvent. SH-3 was vortex mixed and spray casted with the same air pressure as SH-5, and was also immediately heat cured. However, the spray distance was increased to 4.5 in. for SH-3. This change was made because at closer spray distances, atomizing air tended to deform the still-wet film.

The most successful formulation to reduce surface roughness was SH-1. In this case, urethane paint and silica nanopowder were dispersed in the previously mentioned urethane reducer. In a separate vial, equal volumes of trifluoroacetic acid (TFA) and waterborne PMC were mixed, causing fluoropolymer to come out of solution. While the as-received waterborne PMC solution had a slightly hazy orange color, when out of solution, the orange color of the polymer as well as white surfactants that stabilize the as-received latex became clearly visible. The elastic nature of the

acrylic polymer was also clear. The solid fluoropolymer was then re-dispersed in the urethane reducer and vortex mixed into the PU/silica/reducer emulsion. The entire mixture was sonicated at 35% amplitude and a frequency of 20 khz for two minutes with an ultrasonicator (Model VC750, Sonics & Materials, Inc., USA). Viscosity was measured to be 15 seconds using a Zahn #2 cup (Gardco EZ Cup). The stability of SH-1 was also better than the other two formulations; the surfactants present in the as-received fluoropolymer were not compatible with acetone, so agitation was required to keep SH-5 and SH-3 from separating into two phases within a few seconds. Without surfactants present, SH-1 remained stable without agitation.

In addition to sanding, the aluminum substrate was washed with isopropyl alcohol to remove any contaminants such as wax or grease from the surface. The mixture was then sprayed using the same nozzle as mentioned above except at an air pressure of 50 psi and spray distance of 6 in. This larger distance and higher pressure allowed for smaller drops and more evaporation.²⁸ SH-1, unlike SH-5 and SH-3, was allowed to flash off (all of the solvent left on the substrate after spray-coating evaporated after a period of 40 minutes) before being heat cured.

5.2.1 Surface Characterization

A CMOS camera (Canon T2i, Canon, USA) with a macro lens (MP-E 65mm f/2.8 1-5xm Canon, USA) was used to capture static water droplet images, and a goniometer was used to measure sliding angle. ImageJ was then used to process the contact angle images with a Java plugin (Drop Shape Analysis, Aurlien Stalder).³⁰

For surface morphology visualization, samples were coated with a 12 nm thick layer of Au/Pd to reduce surface charging and scanning electron microscope (SEM) images were taken of superhydrophobic samples using a JEOL 6700F FESEM. Samples were tilted at 30 degrees to greater bring out differences in morphology. Confocal laser scanning microscope scans (CLSM) of the surfaces were also done using a Zeiss LSM

Figure 5.2.1: Schematic of the automated spray-coating setup.

510. After initial scans, a robust gaussian filter with an $8\ \mu\text{m}$ cutoff was applied with the MountainsMap topography software (Digital Surf) to separate waviness from roughness. S_a , was then calculated from the waviness features.

5.3 Results

5.3.1 Surface Roughness

CLSM scans of the superhydrophobic samples are shown in Figure 5.3.1. The surface height distribution of SH-5 is shown in Figure 5.3.1a and has significant peaks and valleys. This formulation used a solvent of pure acetone with a very high vapor pressure (184 mm Hg at 20°C). The acetone evaporated quickly when atomized while creating SH-5, resulting in a rough surface without much leveling. As noted in Table 3, the measured S_a was found to be $5.4\ \mu\text{m}$. Significant cracking in the film was also apparent as seen in Figure 5.3.2a and 5.3.2b. Not only does this contribute to surface roughness and integrity of the film, cracks in the coating provide surface area for accreted ice to adhere. It is even possible for a crack in the coating to expose bare substrate, nullifying the the effectiveness of the anti-icing coating.

For SH-3, the solvent was changed to a commercial urethane reducer that included parachlorobenzotrifluoride (vapor pressure = 5 mm Hg at 20 °C), and much less carrier liquid evaporated during spray casting. This resulted in a more level surface and a roughness of 3.2 μm . Surface SH-3 showed a slight qualitative reduction in roughness, but more noticeably, the amount of cracking in the film was greatly reduced, as can be seen in Figure 5.3.2c and 5.3.2d.

For SH-1, the PMC/reducer solution resulted in a much lower surface tension (25 dyne/cm) than water (72 dyne/cm). This allowed for better substrate wetting and a more unified film with cracking in the film decreased. Washing the aluminum substrate with isopropyl alcohol before spraying also eliminated "craters" on the surface that are caused by contaminants that create uneven areas of surface tension. In addition, allowing the sprayed surface to flash off before heat curing allowed the surface to level as much as possible and S_a was reduced to 1.4 μm . Images of SH-1, shown in Figure 5.3.2e and Figure 5.3.2f, show a much more uniform and homogenous film, brought about by using a carrier fluid that allowed for leveling of the coating and wetting of the substrate before evaporation.

The distribution of surface heights from the mean plane (e.g. a height of 5 μm corresponds to 5 μm above mean plane, a height of -5 μm corresponds to 5 μm below mean plane) were also calculated, with a probability density function (PDF) of these heights shown in Figure 5.3.3. It is clear that as S_a decreases, the distribution becomes more tightly bound around the mean height, as expected. It is also interesting to note that the shape of the PDF is approximately preserved as Gaussian for all three cases. Skewness, defined as

$$S_{sk} = \frac{1}{nR_q^3} \sum_{i=1}^n y_i^3$$

where

$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$$

is the nondimensional measure of assymetry of surface heights around the mean height. For example, a surface with positive skewness would be composed of "hills", while negtive skewness corresponds to "valleys". Kurtosis, defined as

$$S_{\text{kur}} = \frac{1}{nR_q^4} \sum_{i=1}^n y_i^4$$

is the nondimensional measure of peakedness of surface heights. A surface with high kurtosis would exhibit spiky features, while a surface with low kurtosis would show more blunt topography. Skewness and kurtosis values remain fairly constant for the surfaces produced, indicating that all three surfaces share similar asymmetry and peakedness, but at different length scales. Kulinich et al.⁵⁸ found that spin coated surfaces with high skewness and kurtosis, corresponing to a morphology akin to spiky mountains, was conducive to high contact angle and low sliding angle. Whereas spray coated surfaces with negative skewness and low kurtosis, with morphology similar to rounded valleys, displayed high contact angle but high sliding angle.

Figure 5.3.1: Confocal microscopy scans of (a) SH-5, (b) SH-3, and (c) SH-1 superhydrophobic coatings

Figure 5.3.2: SEM images of (a) SH-5, (b) SH-3, and (c) SH-1. (d-f) are higher magnification images

5.3.2 Hydrophobicity and Chemical Topology

With the largest S_a , SH-5 exhibited the highest contact angle and lowest sliding angle, 159° and 9° , respectively. However, superhydrophobicity was not greatly reduced with the decrease in surface roughness; contact angles were only slightly lower

Figure 5.3.3: Probability density function of surface heights from the mean plane.

	SH-5	SH-3	SH-1	Kulinich Spin-Coated ⁵⁸	Kulinich Spray-Coated
S_a	5.4 μm	3.2 μm	1.4 μm	419.1 nm	257.8 nm
Skewness	.615	.668	.813	5.02	-1.27
Kurtosis	3.44	4.05	4.3	25.13	7.36
CA(deg.)	159	152	153	> 150	> 150
SA (deg.)	9	11	12	5	80

Table 3: Surface texture measurements and wetting characteristics of superhydrophobic coatings

for SH-3 and SH-1 and sliding angles were both within uncertainty of the measurement. Higher magnification images of SH-1, shown in Figure 5.3.4, reveal the two particles present in the coating. Largest are titanium dioxide (TiO_2) pigments that are present in the as-received urethane paint. These pigments give the coating a white hue and also serve as UV protection. Smaller are the dispersed silica nanoparticles. Figure 5.3.5 shows the approximate diameters of each of these particles. TiO_2 pigments were measured to have a diameter in the range of 200 - 400 nm, while SiO_2 particles had diameters in the range of 20 - 60 nm. The particles were identified by their size as well as EDXS, shown in Figure 5.3.6. When focused on a group of presumed TiO_2 pigments, EDXS revealed large peaks at ~ 4.5 and 4.9 keV, corre-

sponding to the K_α and K_β absorption energies of titanium. Similarly, a peak at 1.7 keV appeared when the detector focused on suspected SiO_2 particles, corresponding to silicon's K_α absorption energy. Three scales of roughness are then found in the coating: 1) The microscale roughness of the film itself that has been explored in this study, 2) that of the TiO_2 pigments, and 3) that of the SiO_2 particles.

5.4 Conclusions

In this experimental study, the surface roughness of a spray casted superhydrophobic coating was systematically reduced. The initial coating (SH-1), using acetone and water as co-solvents and no surface cleaning, produced an S_a of $5.4\ \mu\text{m}$ and significant film heterogeneity. SH-3 achieved a decrease in S_a to $3.2\ \mu\text{m}$ and an improvement in film quality was achieved by changing the main solvent to a commercial urethane reducer that included a slower evaporating solvent. For SH-1, water was replaced as the PMC medium by the urethane reducer, giving a further decrease in S_a . Skewness and kurtosis were similar for all three surfaces as were sliding angle and contact angle. While generally not mentioned when describing superhydrophobic surface topology, the lack of a major effect of S_a on superhydrophobicity indicates that S_{sk} and S_{kur} may be factors that require greater consideration when designing superhydrophobic surfaces.

(a) 5000x image of surface SH-1

(b) 15000x image of surface SH-1. SiO₂ agglomerates are circled

Figure 5.3.4: Higher magnification images of silica-based superhydrophobic surface

(a) TiO_2 pigments

(b) SiO_2 powder

Figure 5.3.5: Annotation of diameters of (a) TiO_2 pigments and (b) SiO_2 powder

(a) TiO₂ pigments

(b) SiO₂ powder

Figure 5.3.6: EDXS of (a) TiO₂ pigments and (b) SiO₂ powder

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