Reducing Surface Roughness of a Spray-Coated Superhydrophobic Nanocomposite

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ABSTRACT

In this study, we demonstrate a method to reduce the surface roughness of a spray-casted polyurethane/fluoropolymer/silica superhydrophobic coating. 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 μm to 1.4 μm. In addition, general homogeneity of the film was improved, with seediness 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.

Keywords: superhydrophobic, surface roughness, nanocomposites, spray-casting

1 INTRODUCTION

Superhydrophobic coatings have drawn great interest as a passive way to delay ice accretion and lower ice adhesion on power lines, aircraft, and wind turbines. Coatings that can be applied through one-step spray casting are particularly desirable because of their relatively low cost and ease of application. However, unlike other techniques, a surface created through spray casting can be susceptible to common finish defects such as orange peel, fish eye, seediness (undissolved solid particles), or cracking in the film. These defects could affect surface roughness and thus the anti-wetting properties of the film. [1, 2] Of particular interest is the effect of roughness on a coating's anti-icing effect. [3–6]

Although work has been done in the past to control the roughness features of surfaces created through micro-molded polymers [7], plasma treatment [8,9], electrodeposition [10], and electrospinning [11], there has not been to the author's knowledge any study on the parameters needed to control the surface roughness of a spray casted superhydrophobic coating. While surfaces with excellent adhesion performance have been created based on functionalized nanoclay, they have had roughness on the order of 10 microns. [12] Understanding this is critical for tuning surfaces for specific anti-wetting properties, such as high contact angle or high water pressure resistance. [1] The objective of this work was to refine the process to create spray-casted polyurethane/fluoropolymer/silica superhydrophobic coatings in order to remove finish defects and produce a smooth finish. The main pre-cursor slurry solvent, fluoropolymer medium, surface pre-treatment, and spray parameters were varied to produce superhydrophobic coatings, and anti-wetting performance and surface roughness were then measured.

2 SURFACE PREPARATION

Three different superhydrophobic samples were made, known herein as SH-5, SH-3, and SH-1. These samples displayed arithmetic mean surface roughness values, S_a, values of about 5μm, 3μm, and 1μm, respectively. SH-5 was the inital surface created. A single stage two component urethane paint (Dupont) was mixed in a vial with silica nanopowder (Sigma-Aldrich), acetone, and waterborne perfluoroalkyl methacrylic copolymer (PMC, Dupont, $\sim$80 wt.% H_2O). This emulsion was vortex mixed for several minutes and then sprayed 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.

In the case of SH-3, an effort was made to reduce 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 was able to deform the still-wet film.

More effort was made to reduce surface roughness when making SH-1. UIn the case of SH-1, urethane paint and silica nanopowder were dispersed in the previously mentioned urethane reducer. In a separate vial, equal volumes of trifluoroacetic acid (TFA) and water-

Surface	Carrier Fluid	PMC Medium	Surface Cleaning	Spray Distance	Air Pressure	S_a	CA	ROA
SH-5	Acetone	Water	No	3.5 in.	30 psi	5.4 μm	159 °	9 °
SH-3	Reducer	Water	No	4.5 in.	30 psi	3.2 μm	152 °	11 °
SH-1	Reducer	Reducer	Yes	6.0 in.	50 psi	1.4 μm	153 °	12 °

Table 1: Surfaces made and their wetting characteristics

borne 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). 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. SH-1 was sprayed from an even larger distance to account for atomizing air affecting the film. Also, unlike SH-5 and SH-3, SH-1 was allowed to flash off (all of the solvent left on the substrate after spray-coating evaporated) before being heat cured. The preparation procedure for all surfaces and their wetting characteristics are shown in Table 1. All samples were sprayed with the same spray casting process described by Yeong [13], 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 ??.

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 and dynamic water droplet images on a custom tilt stage for wettability measurements. ImageJ was then used to process the images with a Java plugin (Drop Shape Analysis, Aurlien Stalder) [14] to calculate the static and dynamic contact angles. 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. Confocal laser scanning microscope scans (CLSM) of the surfaces were also done using a Zeiss LSM 510. After initial scans, a robust gaussian filter with an 8 μm cutoff was applied with the MountainsMap topography software (Digital Surf) to separate waviness from roughness. S_a, was then calculated from the waviness features.

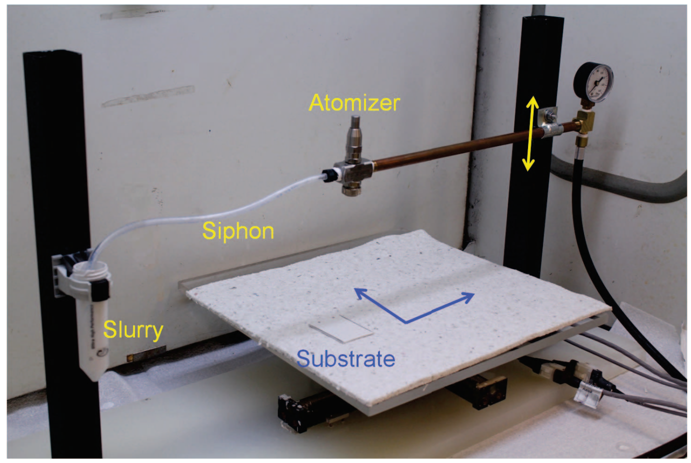

Figure 1: Schematic of the automated spray-coating setup.

3 SURFACE ROUGHNESS

CLSM scans of the superhydrophobic samples are shown in Figure 2. With a very high vapor pressure (184 mm Hg at 20 °C), acetone evaporated quickly when atomized while creating SH-5, resulting in a rough surface without much leveling and an S_a of 5.4 μm. Significant cracking in the film was also apparent. When the solvent was changed to a commercial urethane reducer that included parachlorobenzotrifluoride (vapor pressure = 5 mm Hg at 20 °C for SH-3, much less carrier liquid evaporated during spray casting resulting in a more level surface and a roughness of 3.2 μm was achieved. As noted above, SH-3 was sprayed from a farther distance than SH-5. Even lower roughness was seen in SH-1. With a much lower surface tension (25 dyne/cm) than water (72 dyne/cm), the PMC/reducer solution 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.

SEM images, shown in Figure 3, reveal the qualitative differences in surface texture. Samples were tilted at 30 degrees to greater bring out differences in morphol-

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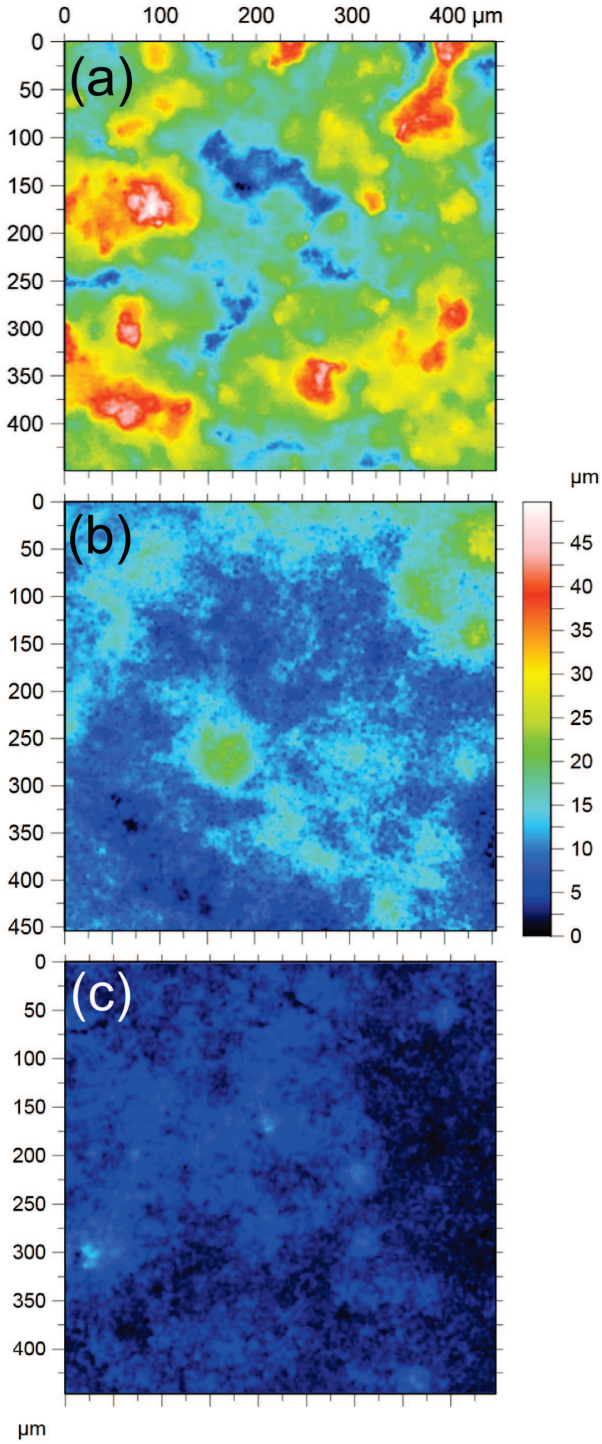

Figure 2: Confocal microscopy scans of (a) SH-5, (b) SH-3, and (c) SH-1 superhydrophobic coatings

ogy. Figure 3a reveals the large amount of cracking in the film of SH-5. 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

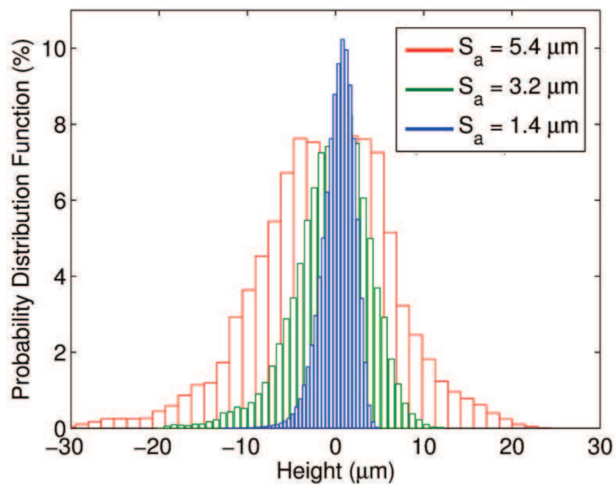

Figure 3: Probability density function of surface heights from the mean plane.

coating. Surface SH-3 (Figure 3b) shows a slight qualitative reduction in roughness, but more noticeably, the amount of cracking in the film was greatly reduced. An image of SH-1, shown in Figure 3c, shows 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. Higher magnification images of the surfaces (Figures 3c and 3d) also reveal the large scale protrusions of SH-5 compared to the flatness of SH-1.

The distribution of surface heights from the mean plane (e.g. a height of 5 μm corresponds to 5μm above mean plane, a height of -5 μm corresponds to 5μm below mean plane) were also calculated, with a probability density function of these heights shown in Figure 4. It is clear that as S_a decreases, the distribution becomes more tightly bound around the mean plane, as would be expected. It also interesting to note that while the width of height distribution, quantified by S_a is different for all three surfaces, the asymmetry and peakedness of the distributions, quantified by skewness and kurtosis, respectively, are fairly similar.

	SH-1	SH-3	SH-5
Skewness	.813	.668	.615
Kurtosis	4.3	4.05	3.44

Table 2: Skewness and kurtosis of superhydrophobic coatings

4 CONCLUSION

In this experimental study, the surface roughness of a spray casted superhydrophobic coating was systematically reduced. The initial coating, using acetone and

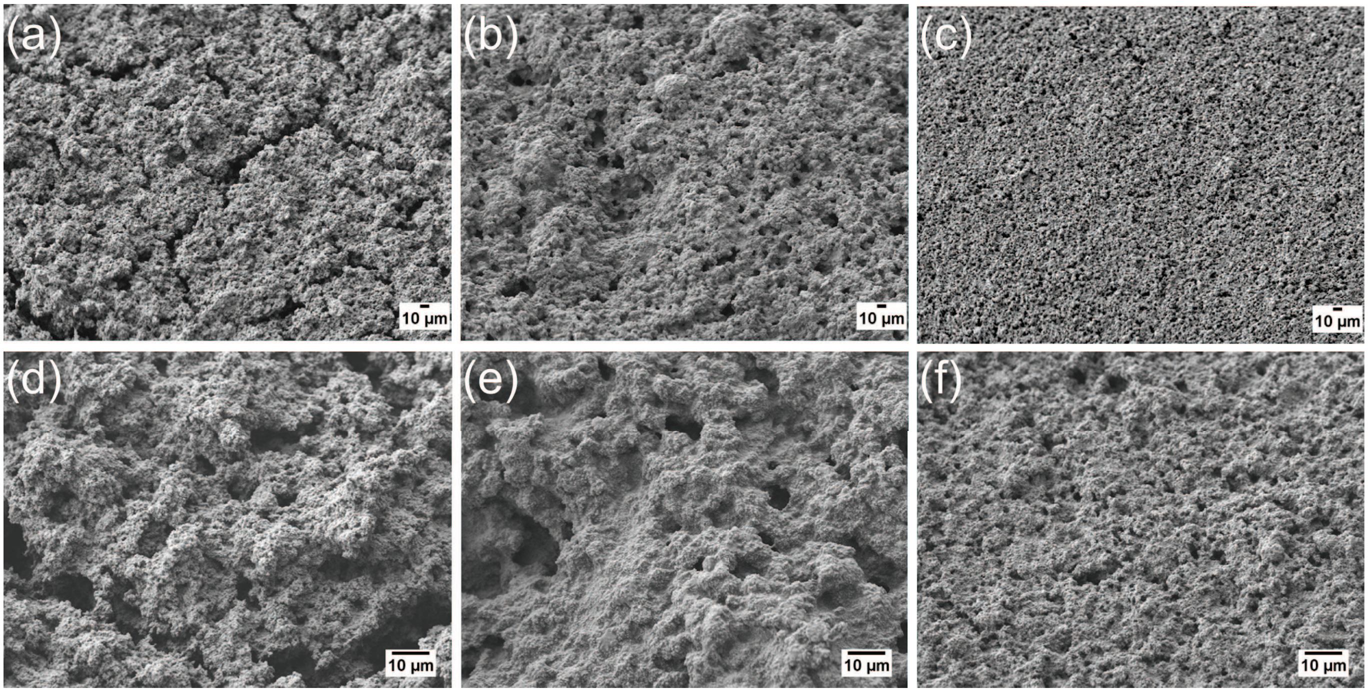

Figure 4: SEM images of (a) SH-5, (b) SH-3, and (c) SH-1. (d-f) are higher magnification images

water as co-solvents and no surface cleaning, produced an S_a of 5.4 μm and significant film heterogeneity. A decrease to 3.2 μm and an improvement in film quality was achieved by simply changing the main carrier of the slurry to a commercial urethane reducer that included a slower evaporating solvent. When water was removed as a solvent and replaced with reducer a further decrease in S_a was achieved. Not only was a decreased surface roughness achieved, but skewness and kurtosis were maintained, as well as low roll-off angle and high contact angle consistent with superhydrophobicity.

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