Durability of a Superhydrophobic Nanocomposite Coating Under Extended Replicated Rain Impact

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ABSTRACT

The objective of this study was to test the mechanical durability of a polyurethane/organoclay nanocomposite modified with perfluoroalkyl methacrylic copolymer (PMC) in conditions that replicate extended rain impact. Samples were impacted with 1.4 mm droplets at a velocity of 24 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 imaging of the superhydrophobic samples before and after spray impact revealed a change in surface morphology which, along with leaching of the fluoroacrylic copolymer, were the likely causes of the decrease in performance.

Keywords: superhydrophobicity, durability, droplet impact, nanocomposites, wetting

1 INTRODUCTION

Up to 50% of a wind turbine's annual power production can be lost due to inefficiencies caused by icing in extreme cases [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 hysteresis less than 10˚). 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) [2]. 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.

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 [3], frictional abrasion [4-6], and adhesive peel tests [7]. While studies have been conducted to understand the physics of low velocity impact (< 3 m/s) and immediate rebound of a single droplet upon an anti-wetting surface [8-14], 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.

This experimental study investigates the performance of a polyurethane/organoclay superhydrophobic nanocomposite coating against an impacting spray simulating rain impact. Superhydrophobic samples were impacted with 1.4 mm droplets at a speed of 25 m/s for a period of 5 hours. The anti-wetting performance was examined after water trapped in the textured surfaces was allowed to evaporate. Surface morphology of the surfaces was inspected before and after testing using scanning electron microscopy (SEM).

2 EXPERIMENT

2.1 Surface Fabrication

Polyurethane was initially dispersed in acetone. Dimethyl dialkyl C14–C18 amine functionalized (35 – 45wt%) montmorillonite clay particles (Sigma-Aldrich) were then dispersed and blended with vortex mixing. Recent studies have shown that polyurethane–organoclay nanocomposites can have improved thermal stability and barrier properties compared to pristine polyurethane elastomers [15]. The main reason for the improved performance originates from the nanoscale dispersion of organoclay, and from the strong interactions between exfoliated silicate layers and the polyurethane matrix [16]. Organoclay has also shown strong compatibility with rubber and fluoroacrylic superhydrophobic approaches [17]. Waterborne perfluoroalkyl methacrylic copolymer (20% wt polymer, 80% wt water; Dupont) was blended in, creating a Pickering emulsion. 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 from a distance of 3.5 inches above the substrate and then heat cured at 100ºC for 7 hours. No post-surface treatment was needed to render them superhydrophobic.

2.2 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. Assuming a mean annual rainfall of 48.87 inches as in Charlottesville, VA [18] and a standard NOAA 8" diameter rain gauge to measure rainfall, the volume of water equalling 20 years of rain could be produced with this nozzle in a time of ~5 hours. Thus, a test time of 5 hours was chosen. With a nozzle orifice diameter of 0.063 inches, the nozzle flow rate corresponded to a droplet velocity of ~25 m/s. This impact velocity was comparable to what could be expected for rain impacting a ~5 MW wind turbine near the middle of the blade. The nozzle was pointed down onto superhydrophobic samples from a distance of 1 foot. 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 cases of normal and angled 40° droplet impact were examined.

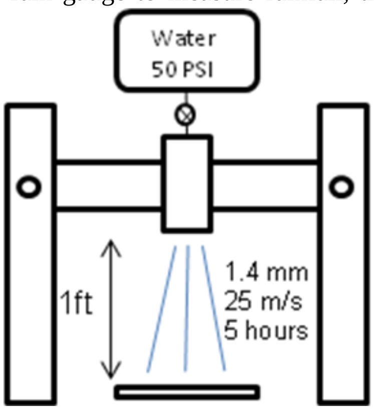


Figure 1. Schematic of the spray impact setup used to investigate of superhydrophobic surfaces.

2.3 Performance Characterization

After the 5 hour test period, samples were heated at 100ºC for 1 hour to allow for moisture trapped in the asperities of the surface texture to evaporate. 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 on a custom tilt stage for wettability measurements. ImageJ was then used to process the images with a Java plugin (Drop Shape Analysis, Aurélien Stalder) to calculate the static contact angle. SEM images were taken of superhydrophobic samples before and after testing to compare surface morphology.

3 RESULTS

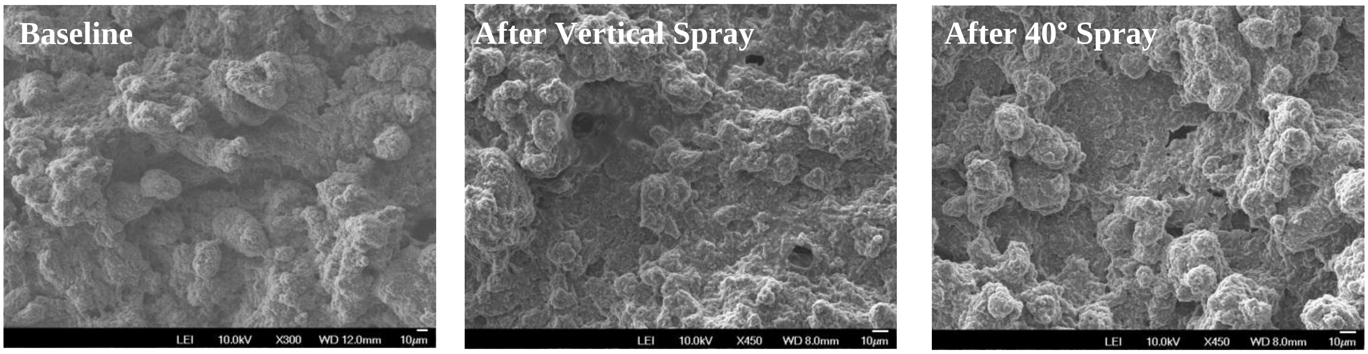
With an impacting dynamic pressure of 312 kPa, the impacting droplets were able to penetrate the asperities of the superhydrophobic samples. This caused a virtually instantaneous transition, known herein as saturation, of the surfaces from the non-wetting Cassie-Baxter state to the wetting Wenzel state. Saturation has been induced in the past through the application of force or pressure to a droplet [19], electric voltage [20,21], light for a photocatylitic texture [22], and vibration [23]. Other studies have investigated this transition when it is caused by prolonged liquid contact [24-26]. The performance of the samples before and after spray testing is shown in Table 1. It was seen that even after water that had penetrated the surface texture was allowed to evaporate through heating, the surfaces did not return to their pre-test performance. The sample that was subjected to normal impact showed a larger decrease in performance than the angled sample. An angled spray resulted in a larger shearing force and thus different wear physics than the direct spray, thus the normal component plays a more significant role in mechanical degradation compared to the shear component.

SEM images of the surfaces are show in Fig. 2. 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 indiameter, 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 particle bursting, causing the marks shown in the SEM images.

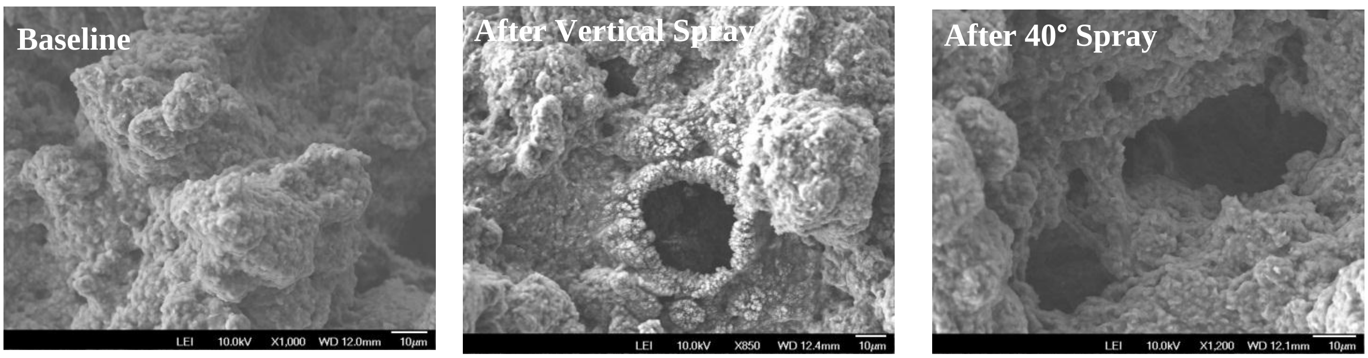
Nonetheless, it was apparent after these spray tests that a change in surface morphology occurred. However, leaching of the fluoroacrylic copolymer from the surface

Superhydrophobic Surface	Contact Angle	Sliding Angle
Baseline	154.1	11.1
40° Spray	147.5	23.7
Vertical Spray	144.2	33.3
Vertical Spray after Refluorination	150.7	24.1

Table 1. Antiwetting performance of the baseline sample, sprayed samples, and refluorinated sample.



a) Lower magnification



b) Higher magnification

Figure 2. SEM images of surface morphology for a) lower magnification and b) higher magnification.

throughout testing may have also increased surface energy and thus decreased superhydrophobic performance. To test this hypothesis, the surface under normal spray impact was 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 caused by a combination of mechanical surface morphology degradation and fluoropolymer leaching.

4 CONCLUSIONS

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.

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