

# An Electrolytic Reaction to Resist Saturation on Conductive Superhydrophobic Nanocomposites

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## ABSTRACT

Achieving saturation resistance is a critical obstacle preventing the application of superhydrophobic surface coatings to potential industrial applications including drag reduction, anti-icing, and anti-fouling. In the current study, saturation characterization and saturation resistance are investigated for superhydrophobic nanocomposite coatings. Until recently, there has been little investigation of continuous submersion in water and the effects on superhydrophobic performance. Thus, quantitative characterizations of superhydrophobic performance loss periods under continuous surface contact with water were developed with a novel diagnostic method. Additionally, results have shown for the first time that electrolytic reactions on synthetic conductive nanocomposites can extend superhydrophobic performance and resist saturation by as much as 400% in duration.

**Keywords:** superhydrophobicity, nanocomposite, electrolysis, saturation, submersion

## 1 INTRODUCTION

Surfaces that possess anti-wetting properties are considered superhydrophobic if the apparent contact angle of water droplets exceeds  $150^\circ$  and the contact angle hysteresis is below  $10^\circ$  (known as the Cassie state) [1]. Superhydrophobic surfaces have a unique wetting behavior -- they are ultra-water repellent and are characterized by a reduced water-surface contact area created by a textured surface morphology. Such surfaces that exhibit the Cassie state while submerged in water maintain a visible air layer trapped between the surface and the water [2-4].

The presence of a trapped air layer on a statically submerged superhydrophobic nanocomposite can be visually observed as a reflective sheen shown in Figure 1.

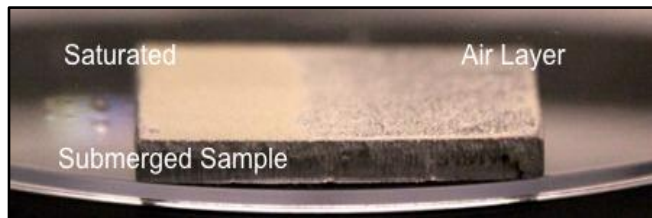


Figure 1: Superhydrophobic surface that depicts the visual difference of a saturated surface and a surface in the reflective Cassie state under static submersion.

Until recently, there has been little analysis of superhydrophobic surfaces and their critical air layers under continuous contact with water [5]. The loss of superhydrophobic performance under continuous submersion, which is characterized by the degradation of the trapped air layer, is herein defined as saturation. This is also referred to as the transition from the Cassie state to the Wenzel state, which is the penetration of water into surface structures [1, 6]. Previously, experimental methods only attempted to confirm the existence of the air layer, but neglected to examine air layer saturation behavior with respect to submersion time [3]. This performance behavior is of critical importance in many anti-wetting applications that experience prolonged liquid contact and is a remaining barrier toward realizing the benefits of superhydrophobic surfaces in industry [7, 8].

Artificial superhydrophobic surfaces are biologically inspired by several natural anti-wetting phenomenon, but the condition is often referred to as the Lotus effect [1]. Aquatic insects that submerge themselves in water retain an air layer on their superhydrophobic exterior that behaves as a physical gill, providing oxygen to the insect under submerged conditions [2]. Currently, prolonged resistance to saturation of superhydrophobic surfaces has only been known to occur on natural surfaces, including the floating water fern, *Salvinia molesta*, and the water strider insect, *Gerris lacustris* [2,4]. Generally, the transition from Cassie state to Wenzel state on synthetic surfaces is irreversible until the surface is dried. Increasing the stability and retention of an air layer will allow for increased functionality and applicability of superhydrophobic surface, since repeated drying is impractical in most applications.

Compared to their biological counterparts under complete submersion in water, current synthetic superhydrophobic nanocomposites maintain superhydrophobicity for a significantly shorter time period [2]. Thus, in the current study saturation characterization and saturation resistance are investigated for superhydrophobic nanocomposite coatings.

## 2 EXPERIMENT

### 2.1 Nanocomposite Fabrication

The process involved creating a conductive nanocomposite slurry, which is spray cast onto a fiberglass substrate and ultimately cured in an oven where the formulation self-assembles to produce a low surface free

energy with both nano- and micro-scale roughness. As-received silver paint (Flash-Dry Silver Paint #04998-AB, SPI Supplies) was first dispersed into acetone and formic acid (53.3% wt silver, 26.7% wt acetone, 20% wt formic acid). Separately, a solution of as-received fatty amine/amino-silane surface modified montmorillonite clay nanofiller (organoclay, Sigma Aldrich), acetone, waterborne perfluoroalkyl methacrylic copolymer (Capstone ST-110, DuPont), and formic acid was created (2.3% wt organoclay, 60.2% wt acetone, 33.8% wt PMC, 3.7% wt formic acid). Finally, the silver/acetone/formic acid and organoclay/acetone/PMC/formic acid suspensions were blended via vortex mixing. The final weight percentage of each component was as follows: 19.2% wt silver, 1.5% wt organoclay, 21.6% wt PMC, 48.1% wt acetone, 9.6% wt formic acid). It is important to note that vortex mixing was used during each chemical addition to the slurry.

The slurry was spray cast onto fiberglass substrates using an internal mix, double-action airbrush atomizer (model VL-SET, Paasche). The substrates are coated with a single spray application from a distance of approximately 25 cm above the substrate at 30 psi and then heat cured at 100 °C for 7 hours.

## 2.2 Quantifying Saturation

The presence and saturation of the trapped air layer was quantitatively measured by focusing a laser on the surface and measuring the illuminance of the reflected light with a light meter as a function of the incident angle. The diagnostic setup, depicted in Figure 2, allowed for the dynamics of saturation to be investigated for the first time to the author's knowledge and can show a significant variation in performance when comparing a range of surface coating formulations.

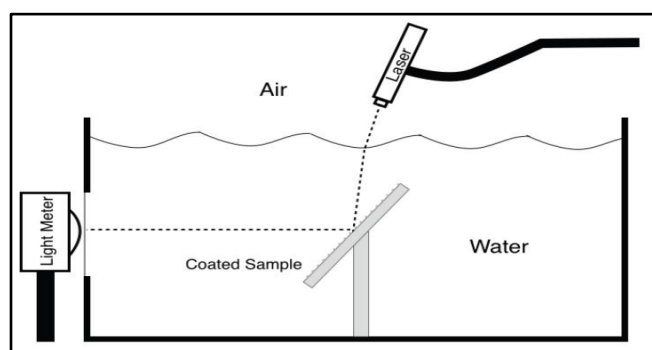


Figure 2: Schematic of saturation diagnostic capable of quantifying saturation of a statically submerged superhydrophobic surface over time.

The presence and reduction of an air layer was measured by focusing a constant power HeNe gas laser on the surface and measuring the illuminance of the reflected light as a function of the incident angle with a light meter

(catalog number 21800-014, VWR). The angle of incidence of the laser on the surface must be greater than 48.6° (the critical angle for water-air interfaces) so as to ensure total internal reflection of the light off the water-air interface. As the surface gas layer was saturated by water, the reflected illuminance consequently diminished toward zero illuminance. This approach produced significantly more detail compared to past investigative methods [3, 9]. This methodology was inspired in part by a similar procedure used to confirm and verify the presence of a trapped air layer on a submerged superhydrophobic surface [3].

In order to analyze the anti-wetting performance of the nanocomposite, the apparent contact angle and sliding angle of 10 µL water droplets were measured with a goniometer (model CAM 200, KSV Instruments). 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 [10]. We assume that sliding angle measurements of droplets on the surface is a temporary rough substitute for dynamic advancing and receding contact angle measurements (hysteresis angle).

## 2.3 Resisting Performance Loss

Considering that the saturation of superhydrophobic surfaces is merely water penetrating the porous nanocomposite, it is possible to eradicate that water from the surface by decomposing water into its respective gases, hydrogen and oxygen. This can be achieved by inducing a continuous electrolytic reaction on the surface as it is submerged underwater [11]. Increasing the stability and retention of an air layer will allow for increased applicability of superhydrophobic surfaces [11]. Resisting saturation on a conductive surface was accomplished with the following experimental setup illustrated in Figure 3.

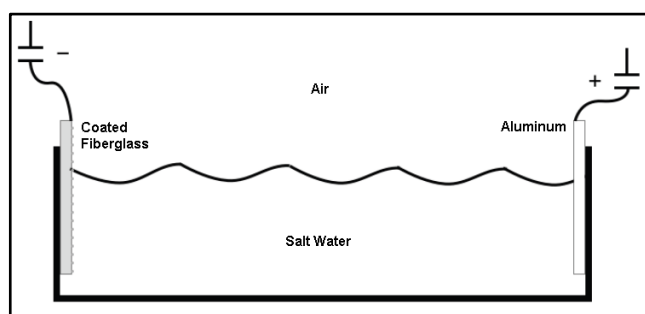


Figure 3: Electrolysis experimental schematic designed to resist saturation and prolong superhydrophobic performance periods.

The superhydrophobic surface was connected as the cathode in the circuit, which allowed hydrogen gas to form

on the nanocomposite. We selected the cathode as the electrode for the nanocomposite because two times the volume of hydrogen gas was generated during the reaction as compared to oxygen gas. The reaction for saturation resistance purposes was generated at a total voltage of 2 V and an electrical current of 0.225 mA. Power consumption was 0.45 mW, which is considerably less than other performance revitalization techniques [11].

Low electrical currents are ideal and were selected because of the low total power consumption and the potential for non-destructive electrolytic reactions that do not eject the coating material from the surface with the generated gases. Additionally, this process may make it possible to completely recharge the gas layer on a surface in the future. For illustrative effect, Figure 4 represents an exaggerated gas generation experiment on a conductive superhydrophobic nanocomposite. This gas generation was developed at a total voltage of 8 V and an electrical current of 70 mA. Uniform bubble generation was clearly visible over the entire surface area. It was easily noticeable on the edges where bubbles can be observed ejecting from the surface.

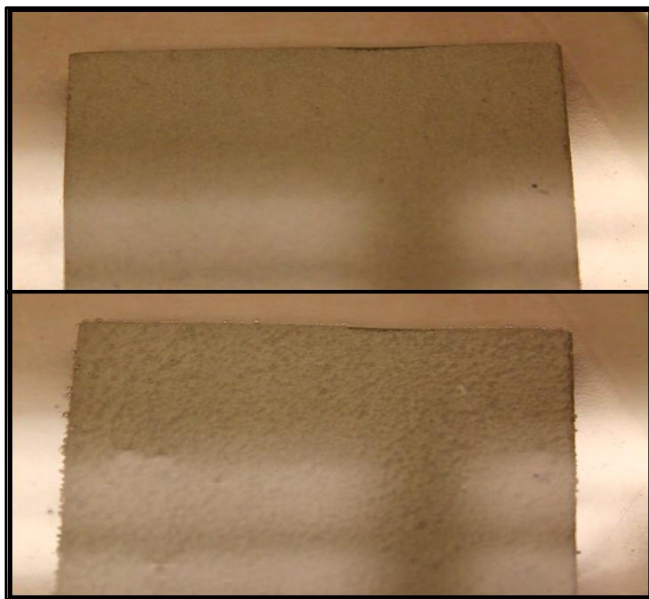


Figure 4: Electrically conductive nanocomposite statically submerged illustrating *before* and *after* an exaggerated gas generation effect on the surface at 8 V and 70 mA.

### 3 RESULTS & DISCUSSION

#### 3.1 Saturation Detection

The decrease in superhydrophobic performance was correlated with the depletion of the surface gas layer, which was monitored by recording the reflected light intensity with respect to time. Figure 5 represents saturation periods of three nanocomposites that have progressively increased their performance longevity based on formulation

improvements. Air layer retention periods for the most recent nanoclay/polyurethane/PMC formulation reached approximately two days. This was a major improvement from the past formulation, which used a different type of polyurethane and only achieved several hours of air layer retention. This wide range of performance clearly demonstrated the high sensitivity to coating formulation.

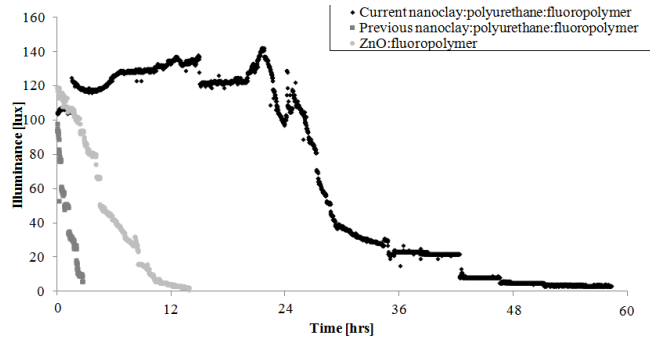


Figure 5: Time until saturation for three formulations illustrating formulation sensitivity to saturation performance.

#### 3.2 Superhydrophobic Performance

It was experimentally observed that superhydrophobic performance of the nanocomposite was lost long before the trapped air layer was entirely saturated, which rendered the reflected light intensity analysis less useful for superhydrophobic purposes. For this reason, a new metric was developed to monitor superhydrophobicity over time.

This new method involved submerging a surface underwater and removing it every five minutes to measure apparent contact angles and sliding angles of droplets on the surface. After the apparent contact and sliding angle measurements crossed the superhydrophobic thresholds ( $>150^\circ$  contact and  $<10^\circ$  sliding), the surface was considered to have transitioned from the Cassie state to the Wenzel state [1]. It was determined experimentally that this method did not disrupt or affect saturation periods and did not damage the surface coating.

#### 3.3 Electrolytic Reaction

In order to resist saturation and extend superhydrophobic performance, an electrolytic reaction was induced on a conductive nanocomposite. As shown in Figure 6, a baseline performance loss period was determined by measuring apparent contact angles of a submerged surface every 5 minutes. The surface retained superhydrophobic performance for a total of 5 minutes before the superhydrophobicity thresholds were crossed. At this point, the surface was considered to be no longer superhydrophobically functional.

Next, 2 V and 0.225 mA were applied across the electrolytic cell with a second conductive nanocomposite,

which generated a superhydrophobic performance period of 20 minutes. This result, although a relatively small time period, suggests that an electrolytic reaction can extend superhydrophobic performance by as much as 400% in duration. This proof-of-concept result demonstrates the potential for active saturation resistance on nanocomposite surfaces. For comparison, the most recent non-conducting nanocomposite formulation with two day air-layer retention observed in Figure 5 is also shown in Figure 6.

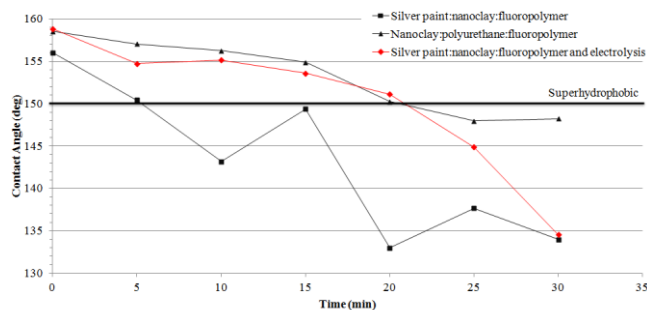


Figure 6: Extension of superhydrophobic performance on electrically conductive nanocomposites as a consequence of an electrolytic reaction on the surface.

## 4 CONCLUSIONS

Saturation characterization and resistance were experimentally investigated for conductive superhydrophobic surface coatings. Superhydrophobic performance is characterized by an observable reflective air layer. Although total air layer depletion was not indicative of superhydrophobic performance loss, periodic measurements of apparent contact and sliding angles were found to be a suitable and more relevant replacement metric. Performance loss occurs after apparent contact and sliding angle measurements cross superhydrophobic thresholds.

It was also found that a conductive nanocomposite formulation containing silver, montmorillonite clay nanofiller, and a fluoropolymer had significantly increased superhydrophobic performance periods underwater via continuous electrolytic reactions. At a total voltage of 2 V and a low electrical current of 0.225 mA, it was shown that performance longevity increased by as much as 400% in duration.

Future work will involve conductive formulation improvements and performance revivals of completely saturated surface coatings.

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