



# Durability of hydrophobic coatings for superhydrophobic aluminum oxide



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## ABSTRACT

Robust and easily produced superhydrophobic surfaces are of great interest for mechanical applications, including drag reduction and MEMS. We produce novel superhydrophobic surfaces with several different coatings and tested the durability of each of these coatings with respect to long term immersion in water in order to determine the most long-lasting surface preparation. A pair of combinations of spin on polymers, surface features, and adhesion promoters was found that provide long term durability.

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## 1. Introduction

Hydrophobicity is the tendency of a surface to repel water. It is typically measured in terms of two angles: contact angle, the interior angle at the point where a liquid/vapor interface meets a solid surface, and rolling angle, the angle from horizontal to which a sample must be tipped to start a drop placed on its surface rolling. In general, contact angles above 150° are considered superhydrophobic [1]. On a superhydrophobic material, water does not spread, remaining in a stable drop which is typically able to roll almost freely along the surface.

Superhydrophobicity is of increasing interest for its usefulness in a variety of applications, including drag reduction [2,3], and MEMS [4,5]. The production of such surfaces is often difficult, requiring multiple steps and materials. One approach involves combining hydrophilic structures with a hydrophobic coating [6,7]. Many such surfaces are prone to degradation, in particular when immersed in liquids for extended periods [8]. However, there is little data concerning the behavior of coatings on aluminum oxide, as is reported here.

We have developed a simple method utilizing porous anodized aluminum oxide (PAA) to produce a superhydrophobic surface. PAA is well understood, is highly durable, and can easily be used

to create a variety of nano-structural shapes via anodization and etching [9–11]. It naturally forms a hexagonally ordered vertical pore structure [12,13], and this structure is commonly used as a template for producing spiked or columnar structures in other materials [6,14]. We use it to create a superhydrophobic surface with minimal processing, by creating a large array of micro-scale spikes in a hexagonal arrangement. Furthermore, this process has the unique feature that the surface structure is always oriented normal to the original aluminum surface, even if the surface is curved. Thus, it is straightforward to make complex machined aluminum parts superhydrophobic, which may not be practical with other methods involving lithography or imprinting [6,15–17]. Without chemical surface alteration, microscopic spikes would tend to increase liquid adhesion [18]. However, when this structured surface is conformally coated with a hydrophobic layer, it becomes superhydrophobic [19].

We describe our fabrication method, and examine several coatings to determine the optimal one for long term use when immersed in water.

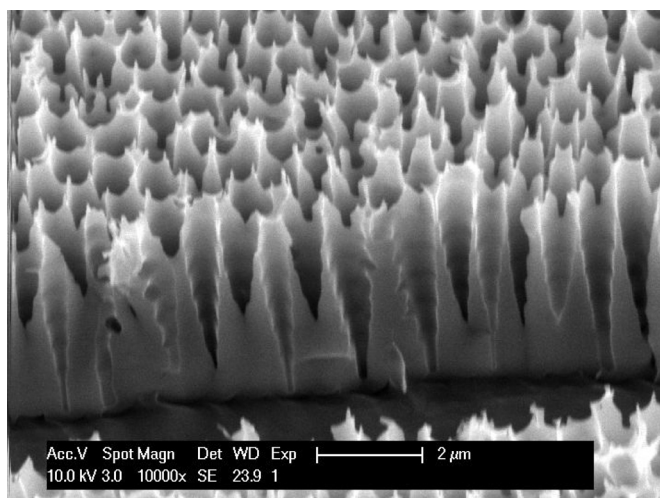
## 2. Material and methods

### 2.1. Fabrication

We utilize 50 mm diameter, 99.999% pure aluminum discs, 0.5 mm thick (Goodfellow AL000650). Utilizing a single point diamond turning machine, we flatten our samples to less than 10 nm surface roughness and remove all native oxide from our

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**Fig. 1.** SEM image of a spiked PAA surface in cross section at 20° inclination, thickness 4 μm. Note the visible steps made by alternation of 8 anodization and 7 etching steps.

substrate, leaving a pure aluminum surface. Since a thick native oxide layer may interfere with further processing, we quickly place our samples in an evacuated bell jar so the diamond turned surface experiences minimal regrowth.

PAA grown via anodization forms hexagonal pores, if produced within current, temperature, and voltage limits that depend on the anodizing acid used. We convert this natural vertical pore structure into a spiked surface by alternating anodizing growth with chemical etching steps, as illustrated in the graphical abstract. The older oxide is etched back further with each etching step, while newer material is grown underneath at each anodization step, creating a stepped spike array, as shown in Fig. 1. Anodization is performed in 0.1175 molar citric acid at 320 V, at a current density limit of 0.051 A/m<sup>2</sup> and a temperature of 18–20 °C, which produces 750 nm spike separation [12]. Etching is performed in 2% tetramethylammonium hydroxide (TMAH) at 18 °C. The thickness of the oxide and aspect ratio of the spikes are easily controlled by choosing the total charge passed through the sample during anodization and the etching times, within certain limits [12]. A similar technique that is used to create molds for anti-reflection coatings, with different choices of chemical and voltage, has been described in detail [11,14].

After anodization and etching, the disc is cut with a knife blade into smaller samples. All samples are cleaned with isopropyl alcohol and baked at 200 °C for 90 min to drive off any remaining surface liquids prior to coating.

Our primary surface coating is Solvay Plastics Hyflon AD-60, a hydrophobic fluoropolymer [21] (similar to Teflon AF [22]). We examine multiple coatings of this material and the use of underlying adhesion promoters to find the optimal combination for long term water immersion. Two types of self assembled mono-layers (SAM), (tridecafluoro 1,1,2,2, tetrahydrooctyl) trichlorosilane (TTTS), which is also used in the production of hydrophobic surfaces, and ethyltrichlorosilane (ETS), used in adhesion promotion, are examined. Hexamethyldisilazane (HMDS), a common adhesion promoter with hydrophobic properties [7,23], is also studied. Coating combinations we examined are shown in Table 1.

Sample F2 was coated by submerging it for 30 min in a solution of 9.9 mL hexane and 0.1 mL of ETS, F3 and F4 were treated likewise with 0.1 mL of TTTS. F0 and F1 were submerged in 10 mL hexane for the same duration to ensure minimal variation in processing history. F0–F4 were then baked for 15 min at 150 °C, and ultrasonically cleaned in isopropanol individually to remove residue, blown

**Table 1**  
List of coatings tested.

F0	Single layer Hyflon
F1	Double layer Hyflon
F2	ETS +Hyflon
F3	TTTS
F4	TTTS +Hyflon
F5	HMDS +Hyflon

dry with compressed air, and then all but F3 were spin coated at 1000 RPM with 2% (w/w) Hyflon in 3M Fluorinert FC-40.

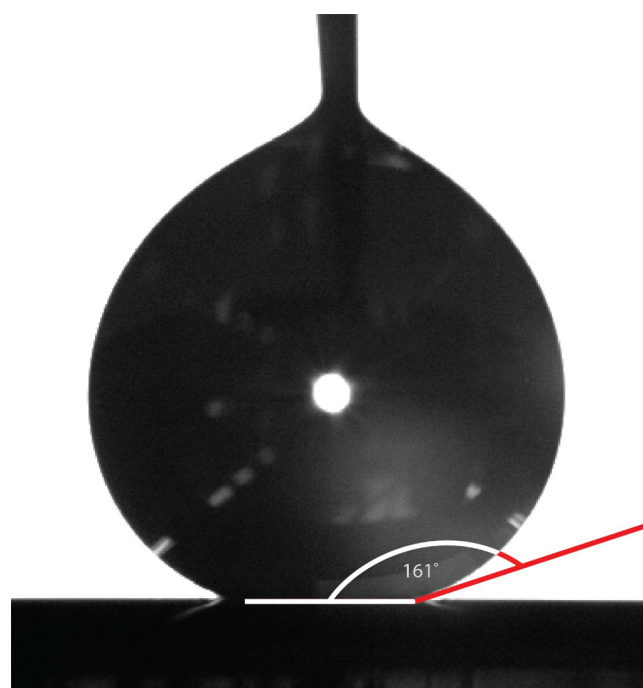
F5 was taken directly from the initial bake, allowed to cool, and then spin coated with a propylene glycol monomethyl ether acetate (PGMEA):HMDS in 4:1 solution at 4000 RPM. This was followed immediately by a coating of the Hyflon solution at 1000 RPM (without being allowed to dry between coatings).

Following individual coating, all samples were baked together at 75 °C for 30 min, then ramped to 150 °C (heating the Hyflon above its glass transition temperature) and baked for 3 h. Samples were allowed to cool, then a second coating of Hyflon was applied to F1 and all samples were subjected to the same bake cycle again to eliminate thermal history as a variable.

## 2.2. Experimental method

At the conclusion of fabrication, samples were photographed in profile with a drop of deionized water (held in place using a needle suspended above the surface) to determine static contact angles. Static contact angles of  $161 \pm 1^\circ$  were seen for all samples, as shown in Fig. 2, indicating that they were initially superhydrophobic and very uniform in character. Numerical fitting was used to model the outline of the drops and determine contact angles.

To test long term sample durability in water, samples were immersed for an extended period, and periodically extracted for testing (samples were allowed to air dry if any water adhered). A



**Fig. 2.** Profile image showing contact angle of a drop of water on the material before full immersion in water was undertaken. Drop is held in place with a needle suspended above the surface.

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