Durable Superhydrophobic Coatings

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ABSTRACT

Recent studies about the application of superhydrophobic surfaces have found these surfaces have lack durability. In this work, bottom up cost-effective and durable coatings were created using silica nanoparticles for roughness control, fluorosilane for hydrophobic chemistry, and three polymers: urethane acrylate, ethyl 2-cyanoacrylate, and epoxy. The polymer-to-silica nanoparticle ratio was studied to obtain the optimized coating's roughness for all the three polymers. The effect of substrate wetting behavior on the superhydrophobic characteristics of the coatings was also investigated. Morphology was examined using scanning electron microscopy and contact profilometry, whereas durability was evaluated using a tape test (ASTM D3359) as well as subsonic wind tunnel and supersonic wind tunnel tests.

INTRODUCTION

Superhydrophobic surfaces have been studied for a variety of applications such as: self-cleaning [1-2], anticorrosion [3], antipollution [4], oil/water separation [5-6], self-healing [7] and ice repellant [7–11] surfaces. These surfaces have static contact angles above 150° and sliding angles below 10°, allowing easy rolling of water droplets along the surface. Superhydrophobicity can be achieved with surfaces comprising of hydrophobic chemistry (e.g., fluorine, alkane, or silicone-based moieties) and hierarchical surface topography (both nanometer and micrometer-sized structures) that mimick the lotus leaf.

Most superhydrophobic surfaces lose their rough topography under harsh conditions and thus are unsuitable for long term applications. As the stability and durability are important for commercial applications, recent studies have addressed the mechanical robustness under environmental and UV radiation conditions [14], exposure to variety of chemicals [15], and in water environments [16]. Most of the assemblies possess weak bonding and it still remains a challenge to prepare a robust superhydrophobic surface to endure harsh environments.

In the present work, three superhydrophobic formulations were produced using three types of adhesives; ethyl cyanoacrylate, epoxy, and urethane acrylate. The effect of adhesive type, adhesive concentration, and substrate wetting properties on the durability of the coating was studied. For each formulation, the weight ratio between adhesive and the nanoparticle was optimized to achieve superhydrophobic coating with the best durability. Since the adhesion between the coating and the substrate is of key importance to achieve durability, two types of substrates - namely glass and polycarbonate (PC) - with hydrophilic chemistry and hydrophobic chemistry, respectively, were examined.

EXPERIMENTAL

Formulation

Three types of formulation were prepared using three different adhesives: ethyl cyanoacrylate, epoxy, and urethane acrylate. For each formulation 0.375 g fumed silica nanoparticles (NPs) were dispersed in fluoroalkylsilane and stirred at room temperature for 10 min. The adhesives at 5, 10, 15, 20 and 25 wt% were dissolved in acetone and stirred for 10 min at room temperature. Then the two solutions were mixed and stirred for another 10 min. For each formulation, the weight ratio between the adhesive and the silica nanoparticles was optimized with ratios ranging from 2:1 to 10:1 (5 wt% to 25 wt% adhesive, respectively). In total, 15 formulations were studied.

Coating

Microscope glass slides (hydrophilic) and polycarbonate (PC) sheets (hydrophobic) were used as substrates for the coating. These substrates were cut to 25 mm squares, rinsed with ethanol, and dried under air pressure. A 1 ml solution of each coating was spin coated on the substrate at 1250 rpm for 1 minute using a spin coater (Specialty Coating Systems, Inc, SCS G3 Spin Coater). Ethyl cyanoacrylate and epoxy formulations were cured at 110°C for 2 hours. Urethane acrylate coatings were cured under UV radiation for 2 minutes.

For subsonic wind tunnel testing, coatings with 10 wt% epoxy were spray coated onto an aluminum substrate. Al-2024 with thermal treatment T-351 was chosen because this alloy currently is used for airplane wings. Prior to coating, a primer layer was applied to the Al plates. In contrast, a brass wedge was the substrate used in supersonic wind tunnel tests. The wedge was first treated with a self-etching primer and then spray coated with the 10 wt% epoxy coating.

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Characterization

The contact angle of the coated substrates was measured according to the sessile controlled, contact angle analyzer (Drop Shape Analyzer – DSA100, KRUSS GmbH, Germany). The sliding angle was incorporated into the contact angle analyzer. A drop was deposited on the horizontal substrate and after equilibrium the substrate plane was tilted until the onset of drop motion. The contact angle was measured using a 5 µl water drop. Field-emission scanning electron microscope (FE-SEM) images were taken using 15 kV accelerating voltage and 10 µA emission field. All samples were coated with gold.

The adhesion of the coatings to the substrates was measured using Tape Test (ASTM D3359). Sharp razor blade was used to create 1 mm space cuts through the coating and the substrate. The center of the tape was placed over the coating and smooth into place by a finger and tighten with the eraser on the end of a pencil to ensure good contact the tape. Then, the tape was removed rapidly back upon itself at as close to an angle of 180° as possible. The rate of the adhesion was in accordance with the ASTM standard scale. Subsonic and supersonic wind tunnels were used to evaluate superhydrophobicity at different air velocities. In subsonic wind tunnel, the samples were mounted on a fixture while air moves past by a powerful fan system. Measurement of the dynamic pressure, the static pressure, and temperature rise in the airflow were taken as well. In supersonic wind tunnel test, high pressure chamber was used to store high-pressure air which was then accelerated through a nozzle to provide supersonic flow.

RESULTS AND DISCUSSION

The wetting behavior of all the formulations on glass substrate was studied using contact angle and sliding angle measurements. Three samples were made for each formulation and the average values are shown in Fig 1. The contact angles for neat ethyl cyanoacrylate, epoxy, and urethane acrylate on glass substrate were 70°, 100°, and 63°, respectively. As shown in Fig. 1a, the ethyl cyanoacrylate formulations showed superhydrophobicity (CA >160° and SA <10°) for all adhesive-to-nanoparticle ratios. In contrast, the epoxy and urethane formulations only exhibited superhydrophobic behavior at low adhesive loadings (5 and 10 wt%).

All the formulations were also studied in detail for PC as well in order to understand how the substrate wetting behavior could affect the coating's structure. Three samples were made for each formulation and the average values are shown in Fig 2. Contact angle measurements showed different behavior on PC compared to the glass substrate, indicating the effect of substrate type on the surface wetting properties. While on glass, ethyl cyanoacrylate formulation was superhydrophobic for all adhesive to nanoparticle ratios, on PC with increasing adhesive wt%, some areas showed superhydrophobicity and some did not; this behavior explain the high standard deviation values in Figure 2. Similar trends were observed in urethane acrylate formulations as well showing superhydrophobicity only at lower polymer concentrations. For epoxy, none of the formulation were superhydrophobic when PC was used as a substrate.

A

B

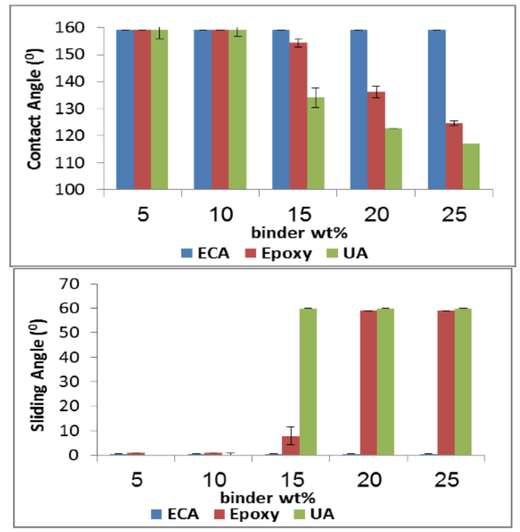

Figure 1: A) Contact angle B) Sliding angle for ethyl cyanoacrylate, epoxy, and urethane acrylate formulations on glass substrate.

A

B

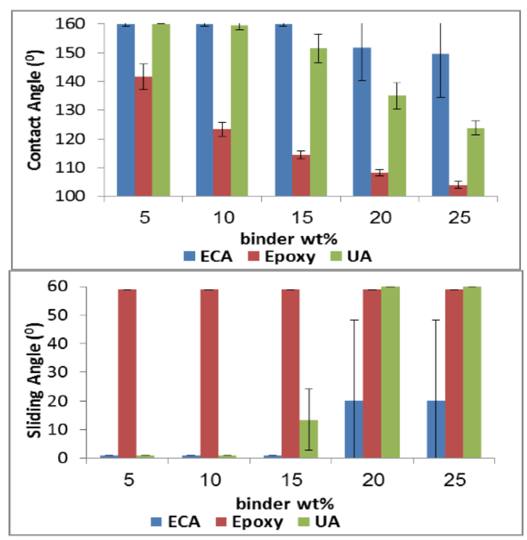

Figure 2: A) Contact angle B) Sliding angle for ethyl cyanoacrylate, epoxy, and urethane acrylate formulations on PC.

As mentioned earlier, most superhydrophobic surfaces lose their rough topography under harsh conditions. To evaluate durability, first all samples were tested using the Tape Test. The results showed best durability for epoxy formulations where both superhydrophobic and non-superhydrophobic surfaces kept their contact angles and sliding angles after the tape test. Since superhydrophobicity was the goal of this work, 10 wt% epoxy formulation with highest binder wt% was chosen to be tested further.

First, the 10 wt% epoxy superhydrophobic coating was tested in a subsonic wind tunnel test. As mentioned earlier, Al-2024 with thermal treatment T-351 was chosen as the substrate as this alloy is used for airplane wings. The plates were mounted in a wind tunnel and tested at five different air velocities. For each velocity, three plates were mounted at the same time; a total of 15 plates were tested. To insure laminar flow while testing, the Reynolds number (Re) at each velocity was calculated; the calculated values are listed in Table 1. For flat plates, Re_L< 500,000 provides laminar flow. The wetting characteristic of the coated plates was measured after wind tunnel testing and results are shown in Table 1. The results showed that the epoxy coating was durable and superhydrophobic, with the coated aluminum plates retaining their superhydrophobicity after all air velocities.

Table 1: Subsonic Wind Tunnel Test Results

Test Number	Wind Tunnel Velocity (mph)	Air Density (Kg/m^3)	Reynolds Number	Results
1	**82**	1.1913	2.57E+05	**Superhydrophobic**
2	**105**	1.1889	3.22E+05	**Superhydrophobic**
3	**118**	1.1938	3.64E+05	**Superhydrophobic**
4	**140**	1.1871	4.15E+05	**Superhydrophobic**
5	**157**	1.1923	4.70E+05	**Superhydrophobic**

Lastly, supersonic wind tunnel testing was performed to insure durability under harsh conditions. Here, a brass wedge model was used as the substrate; this model was chosen because it is more difficult to achieve good adhesion to brass surfaces compared to aluminum surfaces. The coated wedge was mounted and live camera recorded the shock waves as shown in Figure 3. The same wedge was tested at three speeds (Mach 2, 2.3 and 3). The results are shown in Table 2.

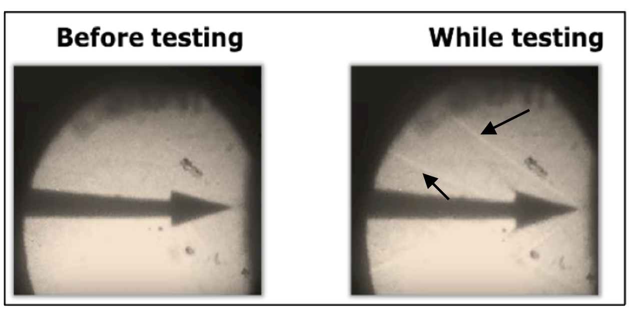

Figure 3: Mounted coated wedge before and while testing. Arrows show shock waves

Supersonic wind tunnel test results (Table 2) showed that coated wedge retained its superhydrophobicity at all Mach numbers tested. This results confirmed high durability of 10 wt% epoxy formulation.

Table 2: Supersonic Wind Tunnel Test Results

Test Number	Mach Number	Results
1	**2**	**Superhydrophobic**
2	**2.3**	**Superhydrophobic**
3	**3**	**Superhydrophobic**

CONCLUSIONS

A facile and cost effective method to prepare three different types of superhydrophobic surfaces was presented using three different adhesives: ethyl cyanoacrylate, epoxy and urethane acrylate. Two different substrates - one hydrophilic glass and second hydrophobic polycarbonate substrate - were used to study the role of surface energy on the superhydrophobic properties of the coatings. The results show how the chemistry between the adhesive and substrate affects the nanoparticles distribution and as a consequence surface structure. It can be concluded that in order to achieve superhydrophobicity the chemistry between the substrate and the adhesive, as well as the adhesive quantity, have to be controlled to ensure high surface roughness. Superhydrophobic formulation comprising epoxy 10 wt% showed high durability, retaining its superhydrophobicity after three different durability tests: starting from tape test, going to subsonic wind tunnel test with air velocity up to 157 mph, and at last supersonic wind tunnel test with Mach 3 speed. These results indorse the potential application of superhydrophobic coatings in commercial applications.

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