# Durable Superhydrophobic Coatings for Icephobic Applications

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## ABSTRACT

Recent studies related to the application of superhydrophobic surfaces for anti-ice properties demonstrated that ice adhesion strength is reduced significantly compared to bare aluminum surfaces, but these surfaces lack durability. In this work, bottom up cost-effective and durable coatings were synthesized using silica nanoparticles for roughness control, flourosilane for hydrophobic chemistry, and three binding polymers: urethane acrylate, ethyl 2-cyanoacrylate, and epoxy. The polymer-to-silica nanoparticle ratio was studied to optimize coating's roughness for all the three polymers. The effect of substrate wetting 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 the tape test (ASTM D3359). Wetting these novel coatings under freezing conditions for different periods of time exhibited measured contact angles of > 160° and sliding angles of < 1°, indicating that the coatings were icephobic.

## 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. Superhydrophobic surfaces have static contact angles above $150^0$ and sliding angles below $10^0$ allowing easy rolling of water droplets along the surface. Superhydrophobicity can be achieved with surfaces comprising of hydrophobic chemistry (fluorine, alkane, or silicone based moieties) and hierarchical surface topography (both nanometer and micrometer-sized) mimicking the lotus leaf.

The relationship between water wetting and ice adhesion was studied by Dotan et al. [9]. It was found that superhydrophobic surfaces reduce ice adhesion 18 times compared to bare aluminum. More recently, Wang et al.[12] showed that ice adhesion to superhydrophobic surfaces was ~163.8 times less than that for the bare aluminum samples. Alizadeh et al.[13] demonstrated that ice nucleation under low-humidity conditions can be delayed through control of surface chemistry and texture.

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 effects 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.

## CHARACTERIZATION

The contact angle 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 (Quanta FEG) 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 Standard. 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 pressed into place by a finger and tighten with the eraser on the end of a pencil to ensure good contact of the tape. Then, the tape was removed rapidly at an angle of 180°. The rating of the adhesion was in accordance with the ASTM standard scale.

## EXPERIMENTAL

### Formulation

Three types of formulations were prepared using three different adhesives; ethyl cyanoacrylate, epoxy, and urethane acrylate. For each formulation 0.375 gr fumed silica NPs were dispersed in fluoroalkylsilane and stirred at room temperature for 10 min. Polymer adhesives at 5, 10, 15, 20 and 25 wt% were dissolved in acetone and stirred for 10 min under 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 ranging from 2:1 to 10:1 (5 wt% to 25 wt% adhesive respectively). Total 15 formulations were studied.

### Coating

Microscope glass slides (hydrophilic) and PC sheets (hydrophobic) were used as substrates for the coating and cut to 1x1" squares. The substrates were rinsed with ethanol and dried under air pressure. 1 ml solution was spin coated (Specialty Coating Systems, Inc, SCS G3 Spin Coater) to enable homogenous distribution of the polymer and NPs layers. Spin coating was done at 1250 rpm for 1 minute. Ethyl cyanoacrylate and epoxy formulations were cured at $110^0$C for 2 hours. Urethane acrylate was cured under UV radiation for 2 minutes.

## 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 $70^0$, $100^0$, and $63^0$ respectively.
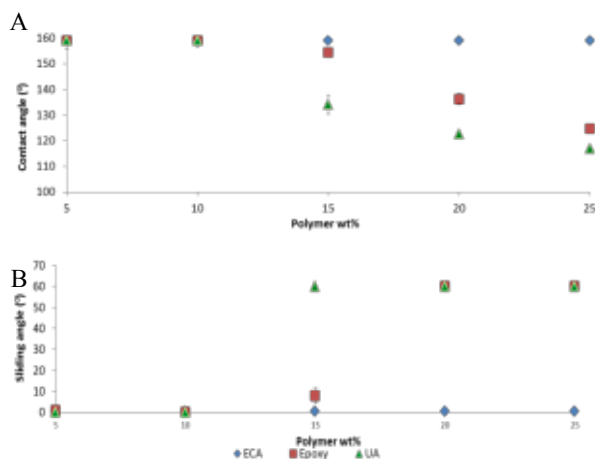


**Figure 1:** A) Contact angle B) Sliding angle for ethyl cyanoacrylate, epoxy, and urethane acrylate formulations on glass substrate.

As can be seen, ethyl cyanoacrylate formulation shows superhydrophobicity (CA>$160^0$ and SA<$10^0$) for all adhesive to nanoparticles ratios compared to epoxy and urethane formulations. In order to understand the distinct behavior of cyanoacrylate, coating topographies were studied using SEM and are shown in Fig. 2.
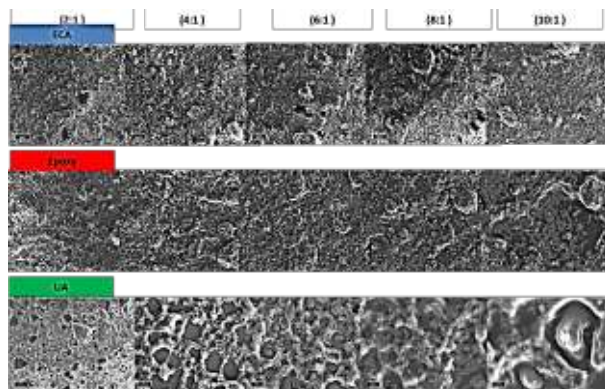


**Figure 2.** SEM images of ethyl cyanoacrylate, epoxy and urethane acrylate formulations on glass substrate with different adhesive to nanoparticle ratio.

SEM images show different surface structure for each type of adhesive used. In ECA formulation, for all the polymer concentrations, the hydrophobic nanoparticles remained on the top-most layer of coating and thus creating the nano-roughness required for superhydrophobicity. On the contrary, in epoxy and urethane acrylate formulations, with increase in the polymer wt%, the hydrophobic particles penetrated into the adhesive resulting in loss of nano-roughness and hence decreasing the contact angle values. The greater decrease in contact angle for urethane acrylate is probably due to lower contact angle of the neat adhesive compared to epoxy and ethyl cyanoacrylate.

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 3.
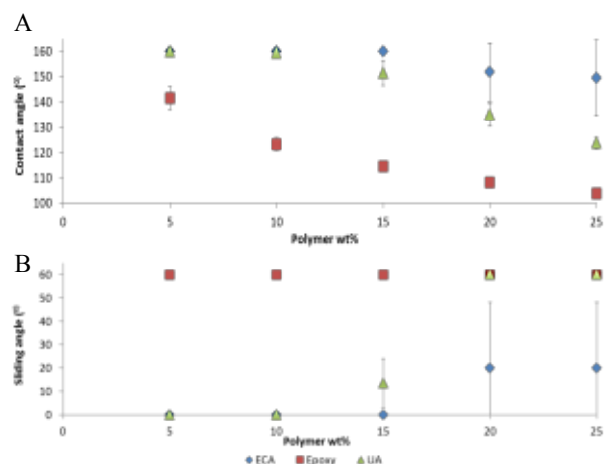
**Figure 3:** A) Contact angle B) Sliding angle for ethyl cyanoacrylate, epoxy, and urethane acrylate formulations on PC.

Contact angle measurement shows different wetting behavior on PC compared to 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, in the case of PC with increasing adhesive wt%, some areas showed superhydrophobicity and some did not which explain the high standard deviations in Figure 3. Similar trends were observed in urethane acrylate formulations showing superhydrophobicity only at lower polymer concentrations. Whereas for epoxy, none of the formulations were superhydrophobic when PC was used as a substrate.

The change in surface topography was evaluated using SEM and is shown in Fig. 4
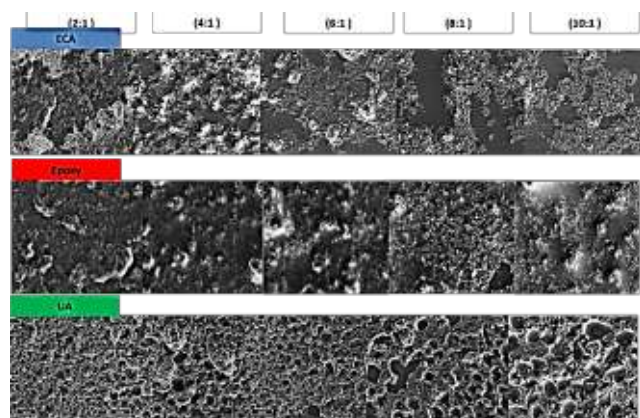


**Figure 4.** SEM images of ethyl cyanoacrylate, epoxy and urethane acrylate formulations on PC substrate with different adhesive:nanoparticle ratio.

It can be clearly seen that all formulations on PC showed a change in surface structure compared to the glass substrate. This may be due to the compatibility between wetting properties of PC (CA=90$^0$) and the adhesives. This similarity contributes to more homogenous distribution of the adhesive over the substrate and as a consequence nanoparticles are also distributed evenly which ultimately

cause decrease in roughness. With the increase in adhesive wt%, the superhydrophobicity was reduced as the surface was less rough. For cyanoacrylate, hydrophobic nanoparticles were on the top most layer of the coating and did not penetrate as in epoxy and urethane acrylate with increasing adhesive wt%. Hence, although the total roughness was lower with increasing adhesive wt%, the nano-roughness was still maintained by the nanoparticles on the top most layer of the coating resulting in higher contact angle and lower sliding angle for higher adhesive to nanoparticle ratio. To summarize, cyanoacrylate showed better results on PC substrate as compared to epoxy and urethane.

Wetting these novel coatings under freezing conditions for different periods of time exhibited measured contact angles of > 160° and sliding angles of < 1°, indicating that the coatings were icephobic.

## 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 substrates were used to study the role of surface energy on the superhydrophobic properties of the coatings. The results show that 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 thermodynamics between the substrate and the adhesive, as well as the adhesive concentration, have to be controlled to ensure high surface roughness.

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