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Hierarchically rough, mechanically durable and superhydrophobic epoxy coatings through rapid evaporation spray method

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ABSTRACT

A mechanically durable and scalable superhydrophobic coating was fabricated by combining the advantages of both bottom-up and top-down approaches into a one-pot, one-step application method. This is achieved by spray coating a solution consisting of silica nanoparticles, which are embedded within epoxy resin, onto a heated substrate to rapidly drive both solvent evaporation and curing simultaneously. By maintaining a high substrate temperature, the arrival of spray-delivered micrometer-sized droplets are rapidly cured onto the substrate to form surface microroughness, while simultaneously, rapid solvent evaporation within each droplet results in the formation of a nanoporous structure. SEM, dual-beam FIB, and cross-sectional TEM/EDAX elemental mapping were used to confirm both the chemistry and the requisite micro- and nano-porosity within the coating structure requisite for superhydrophobicity. The resultant coatings exhibit contact angles greater than 150° (153.8° ± 0.8°) and roll-off angles of 8° ± 2°, with a coating hardness of 6H on the pencil hardness scale, and a rating of 5 on an ASTM crosshatch test.

1. Introduction

Super water repellent surfaces arise from a combination of intrinsic chemical hydrophobicity and hierarchical surface roughness [1,2]. The superhydrophobic condition is defined by high water contact angles of $>150°$ and relatively small $<5°$ sliding angles [2]. Coatings with high hydrophobic characteristics give rise to inherent self-cleaning [1,3], non-stick properties that have been applied for use on windows and mirrors [1,3] to marine anti-fouling [4] and fabric protection [5,6].

Although the surface chemistry of coatings has been studied in depth [1,3,7,8], the challenge of designing hierarchical topography in the micro-scale and nano-scale, leading to high roughness, is a constant issue met with varying success [2,9,10]. Rough surface topography can be achieved in numerous ways [10–14] from controllable etching of silicon wafers to the scalable approach of templating polymers and the creation of sol–gel/nanoparticle hybrid coatings. The latter being a highly scalable approach that was first reported over 15 years ago [15]. One issue with creating micro and nano-rough surfaces is their inherent mechanical weakness due to the small feature size of protuberances on the surface coupled with the general brittleness of synthesized hydrophobic nanoparticles. One reported approach [12] to combat the fragility of coatings is to enhance the nano/micro hierarchy so that the large domains resist abrasive forces while the protected nano-features exhibit superhydrophobicity. With scalability in mind, research has developed bottom-up approaches with varying success due to the inherent weakness of weakly bonded nanoparticles [16]. Typically, for sol–gel methods, coating hardness enhancement was attempted through the use of cross-linking agents within continuous nanoparticle seeded sol–gels to strengthen the coating structure while maintaining a high degree of surface roughness. Polymer resins such as epoxy, when used correctly, can act as a moldable scaffold for micro and nano-rough coatings without the detrimental lack of adhesion of nanoparticles [2]. Epoxy is currently produced and used in a large range of industries. Applications range from metal coatings, to reinforced plastic materials and adhesives [17]. Usually created by reacting a di-epoxide with a curative agent to form a 3-dimensional polymer network, the hardened epoxy is strong, durable and chemically resistant [18].

Currently, there are numerous fabrication methods in literature that are distinctively divided between top-down and bottom-up approaches. Top-down approaches typically involves selective etching or photolithography produce superhydrophobic, hierarchically rough surfaces that are more durable, but at the cost of scalability, whereas bottom-up approaches are scalable, yet fragile.

This paper reports a novel fabrication method that merges the advantages of both top-down and bottom-up approach in a one-step application. The key to this method is to engineer the coating microstructure using a bottom-up approach, while incorporating a top-down mechanism within the microstructure to create the porous nanostructure that is theorized to aid non-wetting behavior through air layer stability [3, 4]. Combining this technique with the strength and versatility of epoxy chemistry, a scalable, durable, and versatile superhydrophobic coating is fabricated in a one-pot, one-step application.

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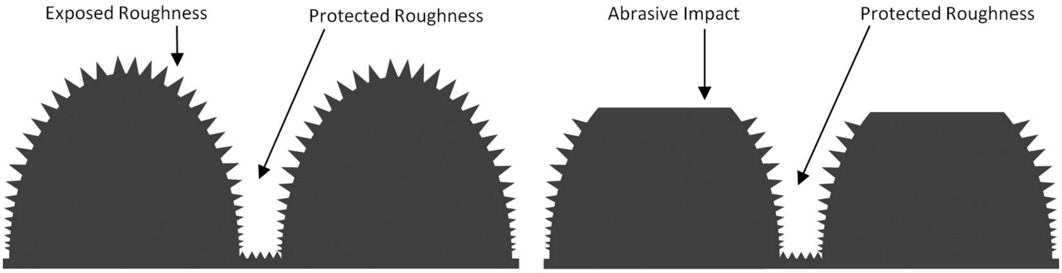

Fig. 1. Effect of abrasive force on hierarchically rough surfaces.

2. Experimental details

2.1. Materials

3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and hexamethylenediamine (98%) were obtained from Sigma Aldrich. Acetone LR grade was purchased from Chem-Supply. 12 nm Silica Nanoparticles Aerosil 200 were purchased from Aerosil. All reagents were used as received.

2.2. Epoxy resin preparation

3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (5 g) was dissolved in acetone (10 g) and heated under reflux at 60 °C for 10 min with continuous stirring. Thoroughly dissolved hexamethylenediamine (0.25 g) in acetone (2 g) was added dropwise (1 drop/s) with continued mixing for 30 min with reflux continuing for 2 h. Reflux was then suspended and silica nanoparticles (0.08 g) were added with continued heating at 70 °C with rigorous stirring until dispersed. Before spray coating, the mixture was topped up with acetone to the original volume.

2.3. Fabrication of epoxy superhydrophobic coating

The epoxy solution was maintained at above the boiling point of acetone (70–80 °C) while a glass slide was heated on a hotplate to 150 °C. The solution was then spray coated (Scorpion HVLP Spray Gun) intermittently onto the glass slide evenly, allowing all the acetone to evaporate between sprays. The slide was then cured at 130 °C for 24 h.

2.4. Measurement of coating durability

ASTM pencil hardness standard [19] test was adopted for coating hardness quantification. Varying pencil grades from 8B to 9H were used. The hardest pencil grading that did not scratch the surface was designated as the coating hardness. ASTM crosshatch tape test [20] was used to determine adhesion of coating to substrate.

2.5. Surface analysis

XPS data was acquired using a VG ESCALAB220i-XL spectrometer equipped with a hemispherical analyzer. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 220 W (22 mA and 10 kV). Survey (wide) scans were taken at analyzer pass energies of 100 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV step size and 100 ms dwell time. Base pressure in the analysis chamber was below 7.0×10^{-9} mbar. All data was processed using CasaXPS software and the energy calibration was referenced to the C 1s peak at 285 eV.

ATR-IR data was acquired using Bruker Tensor 27 Sample Compartment RT-DLaTGS Spectrometer with 2 cm^{-1} resolution with a range from 7500 cm^{-1} to 370 cm^{-1}. Data was analyzed using OPUS 6.5 software.

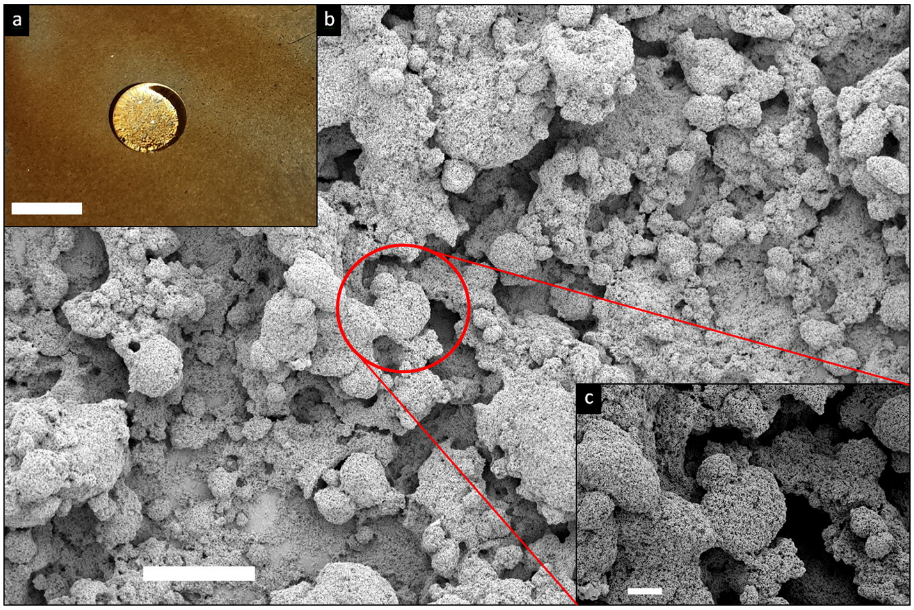

Fig. 2. Photograph of (a) water droplet on epoxy coating (scale bar = 3 mm) and an SEM image (b) of cured epoxy coating (scale bar = 25 μm) with enlarged inset (c) illustrating multiscale roughness (scale bar = 5 μm).