Bio-inspired polydimethylsiloxane-functionalized silica particles - epoxy bilayer as a robust superhydrophobic surface coating

Aleksander Cholewinski [1], Josh Trinidad [1], Brendan McDonald, Boxin Zhao *

University of Waterloo, Department of Chemical Engineering and Waterloo Institute for Nanotechnology, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT

A robust superhydrophobic bilayer coating is developed containing polydimethylsiloxane (PDMS)-functionalized silica particles on top and an epoxy bonding layer at the base. It is fabricated with a facile dip-coating process that embeds micron-scale PDMS-functionalized silica particles with nano-scale roughness into an epoxy layer spin-coated onto a substrate. The dip-coating process uses multiple cycles to generate a repeatable and consistent coating onto a glass substrate. The resulting bilayer coating is able to be applied to multiple surfaces where the conventional epoxy coating is used. The concentration of silica particles was systematically varied, showing minimal influence on hydrophobicity and mechanical properties. The robustness of the coating is characterized by observing the wear properties and integrity of the rough surface as it is scratched with a stainless steel probe, while adhesive tape was applied repeatedly to the surface to observe any modification to the hydrophobicity. Additionally, a different substrate material, a transparent flexible polymer, has been successfully coated. This work demonstrates a facile dip-coating process using commercially available silica micro/nanoparticles to generate a robust superhydrophobic coating with the potential for a larger scale application to improve on the performance of conventional epoxy coatings.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the fabrication of superhydrophobic surfaces has become an interesting subject in many research activities to meet the increasing need of self-cleaning and waterproof advanced materials [1–13]. This subject draws inspiration from the natural example of the lotus leaf, a plant that possesses a waxy substance with low surface energy and a hierarchical surface structure at the micro- and nanoscopic levels [1–4]. The surface of the lotus leaf is composed of cilium-like nanostructures on top of micro-scale papillae [4–6], which has become the model for constructing superhydrophobic surfaces [2,3,7]. These structures have the ability to elicit a superhydrophobic effect, that is, a surface that exhibits water contact angles above 150° [4–6,8–12], as well as a contact angle hysteresis below 10° [5,8,13]. Superhydrophobic surfaces have a low adhesion to water, causing the beading of water droplets upon contact with the surface. This property can induce a self-cleaning effect [2,6,8,14,15] that allows the water droplet to carry away dirt and contaminants at low inclined angles [6,14].

The general process of producing a hydrophobic surface using micro/nano particles involves either (a) creating a rough surface by addition of particles via coating methods and then functionalizing the rough surface [7,9,15] or (b) producing hydrophobic particles first and then adding these particles onto the surface using coating methods [3]. Our work follows the latter method and aims to mitigate the inherent issue with synthetic superhydrophobic surfaces, that is, the weak mechanical properties that these surfaces exhibit [9,12]. This characteristic weak surface strength is also observed with the lotus leaf model, as light physical contact with the hierarchical structures of the lotus leaf leads to damage of the micro/nano-structures, resulting in a loss of surface properties [8,9,12,14].

In this work, we present the development of a robust superhydrophobic bilayer coating containing polydimethylsiloxane (PDMS)-functionalized silica particles on top and an epoxy bonding layer at the base. It is fabricated with a facile dip-coating process that embeds micron-scale PDMS-functionalized silica micro/nanoparticles into an epoxy layer spin-coated onto a substrate. Unlike some methods that are spray-based [16–18], the proposed method in this paper is designed to embed rough particles (to provide hydrophobicity) onto a conventional epoxy coating layer (to provide mechanical strength) which can be readily coated on a variety of substrates. The experimental results showed that this bilayer coating remains sturdy and functional when exposed to external stress so it will not require frequent re-applications,

* Corresponding author.
E-mail addresses: aacholew@uwaterloo.ca (A. Cholewinski), ejtrinid@uwaterloo.ca (J. Trinidad), brendan.mcdonald@uwaterloo.ca (B. McDonald), zhaob@uwaterloo.ca (B. Zhao).
[1] Equal contribution.

ultimately cutting costs and adding beneficial engineering properties to conventional epoxy coatings.

2. Materials and methods

2.1. Materials

The HDK H18 Wacker silica (PDMS modified/functionalized) hydrophobic nanoparticles were kindly donated by Wacker Chemie. The particle size of HDK H18 PDMS-silica particles is in the range of 0.1–1 μm in diameter, with an average diameter of 0.5 μm. These are made from individual silica spheres, 5–30 nm in size, which are fused together at high temperatures. These particles also form some agglomerates having a size of 1–250 μm. Dow epoxy resin, D.E.R. 331 (2,2-bis(p-(2,3-epoxypropoxy)phenyl)propane), and Dow epoxy curing agent, D.E.H. 24, were purchased from Dow Chemical Company. 99% tetrahydrofuran (THF) solvent, 99% HPLC methanol and 99% isopropanol (IPA) were purchased from Sigma Aldrich. All chemicals were used as received. Ultra-pure H_2O was dispensed from a Direct-Q Millipore Apparatus. The glass slides (Fisher Finest, Premium Plain Glass Microscope Slides 1″ × 3″) were purchased from Fisher Scientific. These were cut down to 1.5″ in length. The flexible substrate Xerox Removable Stripe Transparencies (referred to as flexible film), were purchased from Xerox. Both glass and flexible film substrates were pre-cleaned in a bath of methanol and dried by gentle wiping with Kim-wipes. The tape used for testing the surface of the coating was aluminum duct tape (which was determined to be hydrophobic with an average water contact angle of around 113°).

2.2. Dip-coating emulsion

A batch reactor was used to make the dip coating emulsion by adding a mixture of HDK H18 particles and THF into 70 mL of ultra-pure H_2O. The HDK H18 particles were mixed with THF in a 20 mL glass vial. Weight percentages of the particles in THF ranged from 0.5% to 4% w/w (used 20 mL of THF) and from 6% to 8% (used 10 mL of THF). The mixture was vortexed for 1 min to ensure a good dispersion which was then poured into ultra-pure water in the jar and vortexed again until the formation of a cloudy white emulsion. The emulsion contained in the open jar was placed onto a hotplate at 125 °C to allow the particles to move up to the top layer, which is necessary for the success of the coating.

2.3. Preparation of epoxy layer

Epoxy resin (D.E.R. 331) and curing agent (D.E.H. 24) were used in this procedure at a ratio of 13:1 resin to curing agent (as opposed to the fully-curing 100:13 ratio). This was to slow down the curing of the epoxy during the iterative procedure, allowing it to hold onto the particles during dip coating, while keeping the particles from sinking fully into the epoxy and losing surface roughness. To ensure a well-mixed epoxy solution, the resin was vortexed for at least 5 min upon addition of the curing agent. In order to have a uniform coating surface, the epoxy/curing agent solution was put in a desiccator to degas under vacuum for a minimum of 5 min. After degassing, the epoxy/curing agent was diluted with IPA at a ratio of 30 μL of IPA per gram of resin and vortexed for 2 min to reduce the viscosity. The diluted epoxy solution was then spin-coated onto the substrate at 3700 RPM for 40 s.

2.4. Fabrication of the superhydrophobic coating

After being spin-coated with epoxy, the substrate was dipped using tweezers into the heated emulsion in the jar placed on the hotplate. The substrate was swayed back and forth within the foam layer at the top of the jar, then slowly withdrawn at an approximate angle of 45° and placed onto the hotplate face-up. The glass jar was then removed from the hotplate to be vortexed until the liquid appeared to be cloudy white again (~20 s), then returned onto the hotplate. The coated substrate was placed into a glass Petri dish filled with THF with the coated side facing down; the back of the substrate was tapped with the tweezers. The sample was then swirled within the THF to get rid of the loose particles and was gently pulled out of the Petri dish. Afterwards, the coated substrate rested on a paper towel in a fume hood for ~30 s, and was then placed on the hotplate for ~20 s. After this, the previous steps were repeated for another two to three times. At the end of the final iteration, the sample was left on the hot plate for 20 min to cure the epoxy.

2.5. Characterization methods

The water contact angles were determined from silhouettes of static 30 μL droplets, using an elliptical best-fit model. The water contact angles were taken from the top-center, center-center, and right-center of the glass slide. Each snapshot contained two contact angles, giving six contact angles per sample. Static, advancing and receding contact angles were measured by placing 9 μL water on the surface, adding additional 9 μL water and then withdrawing the extra water using a syringe pump at 1.3 μL/s with the needle kept in the droplet. To determine the surface structure of the coated sample and obtain a topographical image of the surface, an optical profiler (Rtec Instruments) was used. Data from the topographical image was processed using the Gwyddion image analysis software in order to obtain RMS roughness values. Friction and wear tests were carried out using a Universal Material Tester (UMT) Tribological Test Equipment (CETR Campbell, CA, USA), with a hemispherical steel probe (R = 0.5 mm). For each friction test, the probe was slid over a 4 mm distance under a constant load for four half-cycles. The friction test was performed at varied loads in increments of 0.5 N over a range of 0.5 to 5 N on different sections of the surface.

3. Results and discussion

3.1. Coating PDMS-functionalized nanoparticles

Fig. 1 illustrates the coating process that utilizes PDMS-functionalized silica particles to generate a hierarchical roughness with a low surface energy material. Similar work in producing superhydrophobic surfaces via embedding of nanoparticles onto the surface is presented by C. Su et al., where they employed a method involving the spin coating of the epoxy and ethanol suspended silica nanoparticles, followed by a functionalization process [7]. Comparatively, our coating approach has two unique features. One is the use of an unstable emulsion of the PDMS-functionalized nanoparticles for coating process; the other is the use of wet epoxy pre-layer to enhance the bonding strength of the nanoparticles intended to be embedded on the surface.

It was experimentally determined that simply drop-coating a suspension of the HDK H18 particles in an organic solvent was not effective due to the aggregation of the hydrophobic particles during drying. Therefore, a dip-coating method was developed using an emulsion solution, which served as a batch reactor. Unlike emulsion solutions used for making latex particles [16], or spray-on solutions [16–18], this emulsion is unstable; a thick foamy top layer is formed when heated at 125 °C, which is able to prevent particle aggregation. The water has two roles: the first is to act as a medium to aid in the generation of foam, and the second is to ensure that the particles stay within the upper layer for easier dipping since the hydrophobic particles move away from the watery phase. THF serves as a good solvent for PDMS, allowing the functionalized particles to dissolve in the required weight percentage. Also, according to J. Lee et al., THF has the 7th highest swelling ratio for PDMS among the solvents they examined. Higher swelling indicates higher solubility (the solubility parameters of the two components are similar