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Scalable superhydrophobic coatings based on fluorinated diatomaceous earth: Abrasion resistance versus particle geometry

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ABSTRACT

Bio-inspired superhydrophobic surfaces were fabricated based on fossilized silica fresh water diatomaceous earth (DE) particles. These nanostructured silicified diatom frustules of cylindrical and circular structures were fluorinated to impart them with superhydrophobic properties. Substrates coated with superhydrophobic DE structures of varying size and shape were found to have water contact angles of approximately 170° and sliding angles of approximately 3°. The substrates were subjected to significant abrasion forces using a standard surface abrader. The ability to retain their superhydrophobic properties was observed to depend on the geometry and average size of the DE particles. The wettability of the abraded coatings was determined by their surface topology, and a transition from a non-wetted state to a partially wetted state was observed to occur and was dependent on the surface roughness. The proposed coatings are scalable, cost-effective, and can be applied on a variety of surfaces on critical infrastructures requiring protection from water saturation, ice formation and water based corrosion.

1. Introduction

Superhydrophobic materials have been the focus of increased scientific investigation in the past decade due to their unmatched ability to repel water. This remarkable water repellency is attributable to the low surface energy on what are typically nanostructured surfaces of superhydrophobic materials [1–5]. The contact angle of a water droplet on a structured surface is a function of the three interfacial free energies at the solid–water–vapor boundaries and of the surface topology. The synergistic effect of the surface roughness and surface functionalization with the low energy organic self-assembled monolayers has been shown to enhance hydrophobicity by creating surfaces with water contact angles well above 150°. Equilibrium and dynamic models have been proposed to describe the superhydrophobic states on structured surfaces. The equilibrium models are based on the early studies of Wenzel [6] and Cassie–Baxter [7]. In the Wenzel state, a water droplet is conformal with surface topology, i.e., it penetrates and wets grooves on the surface. In the Cassie state, a layer of air is trapped beneath the droplet, and this pinned air holds the droplet such that it is not conformal with the surface but instead touches only the tops of the protrusions of the rough surface, i.e., it makes a non-wetted contact with the surface. The dynamic behavior of a water drop is described by the sliding angle – the angle at which the water drop begins to roll along the surface under the influence of gravity. The sliding angle is a function of the contact angle hysteresis, and it has significantly lower values for patterned surfaces described by the Cassie state [8–11].

The fundamental principles governing the wettability of a surface have been studied extensively and several methods for fabricating superhydrophobic surfaces have been proposed [9,12–17]. The increasing demand for scalable superhydrophobic coatings necessitates the development of new methods that are durable, cost-effective and easy to apply. Herein, we present the results of studies on superhydrophobic surfaces based on fluorinated diatomaceous earth (DE) particles. DE particles are fossilized diatoms formed mainly of amorphous silicon dioxide ($SiO_2 \cdot nH_2O$). Their shape and morphology varies among different species of diatoms. Their nanoscale porous features and silica-rich structure provide a high surface area template with hydroxyl sites that can be functionalized with fluorosilanes. The resulting particles were found to exhibit excellent water repellent properties. Methods to functionalize DE particles [18,19] and particularly to prepare superhydrophobic DE powder [20,21] have been previously reported. In this study, we investigate the wetting properties and abrasion resistance of coatings based on superhydrophobic DE particles with different geometries (cylindrical or circular) and sizes. DE is one of the most abundant minerals in nature and superhydrophobic coatings based on functionalized DE particles can be manufactured at low cost and the coatings can be utilized for anti-corrosion, anti-biofouling, anti-icing and smart grid applications.

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2. Experimental

2.1. Materials

Superhydrophobic powder was produced by suspending DE particles in a solution of hexane and tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (Gelest Inc.) [15]. The concentrations of the DE particles and fluorosilane in the hexane were 10 and 1 wt%, respectively. The fluorosilane groups were hydrolyzed and hydrogen bonded to the surface of the DE particles [22] through the adsorbed water on the particle's surface. To avoid condensation reactions among the silane groups, additional water was not added to the hexane-silane solution. The solution was in excess in silane to maximize the fluorocarbon coverage on the surface of the DE particles. After stirring the mixture for 24 h at room temperature, the powder was washed with hexane to remove non-bonded silane groups and then dried at 70 °C in air for 12 h.

2.2. Characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy analyses of the superhydrophobic powder were performed using a Zeiss Merlin VP SEM/STEM. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific Model K-Alpha XPS instrument. The instrument utilizes a monochromated, micro-focusing, Al K_{α} X-ray source (1486.6 eV) with a variable spot size, ranging from 30 to 400 μm. Analyses of the powders were all conducted with a 400 μm X-ray spot size for maximum signal and to obtain an average surface composition over the largest possible area. The instrument has a hemispherical electron energy analyzer equipped with a 128 multi-channel detector system. The base pressure in the analysis chamber is typically 2×10^{-9} mbar or lower. Samples were mounted with double-sided tape to the sample holder and introduced into the analysis chamber through a vacuum load-lock. Areas were chosen for analysis by viewing the samples with a digital optical camera with a magnification of approximately 60–200×. Survey spectra (0–1350 eV) were acquired for qualitative and quantitative analysis and high-resolution spectra were acquired for appropriate elements for chemical state characterization. All spectra were acquired with the charge neutralization flood gun turned on to maintain stable analysis conditions on the nominally insulating samples. The flood gun uses a combination of low energy electrons and argon ions for optimum charge compensation. The typical pressure in the analysis chamber with the flood gun operating is 2×10^{-7} mbar. Data were collected and processed using the Thermo Scientific Avantage XPS software package (v.4.61).

The particle size distribution was determined using dilute aqueous suspensions of non-functionalized particles in a Horiba LA 950 laser diffraction analyzer with a broad measurement range (30 nm to 3 mm). The suspensions were subjected to ultrasonic agitation prior to the measurements to separate the particle aggregates. The analyzer is equipped with two different wavelength light sources (650 and 405 nm) and an array of photodiodes to detect the scattered light over a wide range of angles. The errors in the accuracy and precision are ±0.6% and ±0.1%, respectively.

Water contact angle experiments were carried out on a computer controlled KSV Instruments Theta optical tensiometer equipped with a video camera. Still images of the sessile drops, 4 μL in volume, were captured and the static contact angle was obtained by fitting a Young–Laplace equation to the surface outline of the water drops.

The durability of the superhydrophobic coatings was tested using a Taber 5135 rotary platform abrasion tester. Abrasive wear experiments were performed on samples turning against two abrading CS10 wheels at 60 rpm. An illustration of the test configuration [23] is shown in the inset of Fig. 6. The load on each grinding wheel was 75 g. The samples were subjected to consecutive abrading cycles and the abraded dust-powder was continuously vacuumed away during the cycles. The coated plates were blown with dry air and the contact angle was measured on the abraded patterns at six locations.

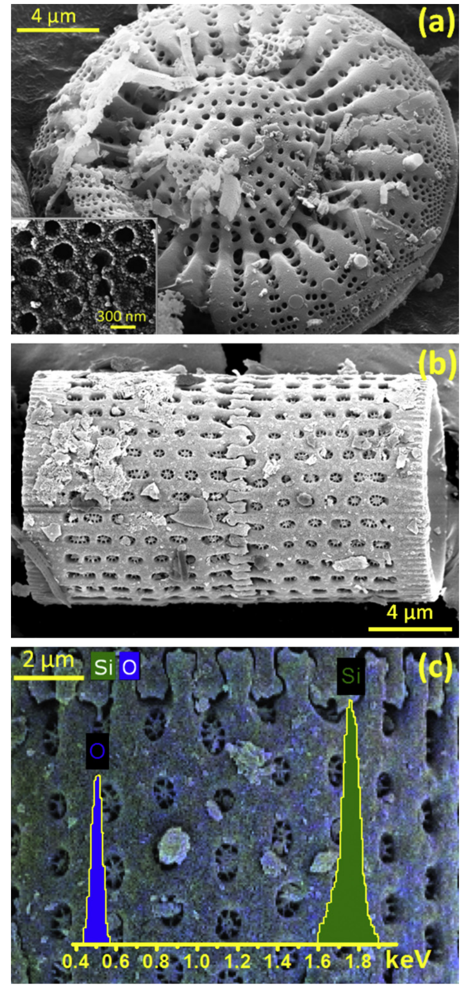

Fig. 1. Scanning electron microscopy images of a circular (a) and a cylindrical (b) diatom. The particles are characterized by micro and nanoscale surface features. (c) A representative energy dispersive X-ray spectrum on the surface of a cylindrical diatom. The spectrum is based on the background element map.

Surface profiles were collected using a Keyence VH-Z100UR optical profiler and digital microscope. Eight images were collected using bright field and dark field illumination modes at 4 different magnifications and the roughness (R_a) was calculated using the height data from the entire image.

3. Results and discussion

Diatoms are single-celled organisms encased within silicate frustules that consist of two shells (valves) pinned together. The fossilized (silicified) remains of the diatoms are recovered from sedimentary rocks and are classified by symmetry into two categories: pennate diatoms that are cylindrical with a bilateral plane of symmetry and centric or circular diatoms that are radially symmetric. The structures of fossilized cylindrical and circular diatoms are shown in the SEM images in Fig. 1a and b. Both structures contain nanopore cavities smaller than 400 nm in diameter. According to the element map analysis, the intricately shaped solid skeletons consist mainly of silicon dioxide that is uniformly distributed on the