



Influence of the coating method on the formation of superhydrophobic silicone–urea surfaces modified with fumed silica nanoparticles



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ARTICLE INFO

Article history:

Received 18 December 2014
Received in revised form 10 March 2015
Accepted 11 March 2015
Available online 7 April 2015

Keywords:

Superhydrophobic surfaces
Fumed silica
Spray coating
Spin coating

ABSTRACT

Effect of the coating method on the formation of superhydrophobic polydimethylsiloxane–urea copolymer (TPSC) surfaces, modified by the incorporation of hydrophobic fumed silica nanoparticles was investigated. Four different coating methods employed were: (i) layer-by-layer spin-coating of hydrophobic fumed silica dispersed in an organic solvent onto TPSC films, (ii) spin-coating of silica–polymer mixture onto a glass substrate, (iii) spray coating of silica/polymer mixture by an air-brush onto a glass substrate, and (iv) direct coating of silica–polymer mixture by a doctor blade onto a glass substrate. Influence of the coating method, composition of the polymer/silica mixture and the number of silica layers applied on the topography and wetting behavior of the surfaces were determined. Surfaces obtained were characterized by scanning electron microscopy (SEM), white light interferometry (WLI) and advancing and receding water contact angle measurements. It was demonstrated that superhydrophobic surfaces could be obtained by all methods. Surfaces obtained displayed hierarchical micro-nano structures and superhydrophobic behavior with static and advancing water contact angles well above 150° and fairly low contact angle hysteresis values.

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1. Introduction

Preparation and characterization of superhydrophobic polymeric surfaces and coatings have been investigated extensively during the past 15 years, following the detailed description of the surface structures and hierarchical micro and nano topographies of a large number of natural plant leaves [1,2]. A major reason for such a remarkable interest in superhydrophobic coatings and surfaces has been their interesting combination of properties, such as the self-cleaning, anti-fouling, stain-resistant and ice-repellant behaviors [3–5], which enable potential applications in a variety of fields, which include paints and coatings, textiles, exterior glass windows, rooftops, windshields, solar panels, aircraft wings and wind turbine blades [3,4,6,7]. As well documented in the literature, wetting behavior of a surface is mainly controlled by two parameters, which are; (i) the surface chemical structure and composition, and (ii) the surface topography or roughness [8–10]. When naturally occurring superhydrophobic plant surfaces, such as a lotus leaf surface is examined under a scanning electron microscope, it is seen that the

surface is covered by irregularly distributed, micron-sized protrusions called *papilla*, which also display a fine nanoscale roughness [1,2,10]. When such a micro-nano dual surface roughness is combined with the inherent hydrophobicity of the waxy layer on the leaf, they provide the lotus leaf its superhydrophobicity, with static water contact angle values above 150° and contact angle hysteresis values below 10° [11–17]. Similar superhydrophobic surfaces with micro-nano hierarchical structures are also observed in various insects, such as the butterfly wings, which display two key periodic structures [18–21]. The individual shingle-like epidermal scales which comprise the wings of butterflies are about 40 × 80 μm each and the micro-relief of the raised ridges covering each wing scale, each between 1.0 and 1.5 μm [22]. The contact angles of the water droplets on the butterfly wing surface are measured to be higher than 150° [23], which rolls freely when the inclining angle is larger than 3°, thus keeping the butterfly wing surface clean of dust and other debris. A wide range of synthetic materials with superhydrophobic surfaces, based on polymers, ceramics, metals or hybrid composite systems have been prepared by templating the natural systems such as lotus leaf, rice leaf, butterfly wings [18,19] and others [24,25].

Theoretical treatment of the effect of the topography on the wetting behavior of surfaces has been provided by Wenzel [26]

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and Cassie and Baxter [27]. Wenzel assumed complete wetting of a rough surface by the droplet and modified the contact angle measured by introducing a roughness factor (r), defined as the ratio of the actual area of a rough surface to its projected geometric area, which has a value greater than 1. Cassie and Baxter assumed the apparent contact angle on a rough surface to be the weighted average of the contact angles on the solid and air surfaces. They defined (f) to be the surface fraction on top of the protrusions and ($1-f$) on air pockets [28]. When Cassie–Baxter and Wenzel relationships are combined, a general equation given below, which provides the apparent contact angles measured on a rough surface (θ_R) as a function of the contact angle measured on a smooth surface (θ), roughness (r) and surface void fraction (f) is obtained. This equation clearly indicates that for an inherently hydrophobic and flat surface with a contact angle greater than 90° , increased surface roughness will lead to much higher contact angles. Modified versions of this equation explaining the contact angle behavior of rough surfaces have also been reported [29–32].

$$\cos \theta_R = r \cdot f \cdot \cos \theta + f - 1$$

As a result of the remarkable academic and industrial interest in the superhydrophobicity, a large number of methods and processes have been developed for the preparation of superhydrophobic polymer surfaces showing hierarchical micro/nano roughnesses. These include layer-by-layer deposition [33], electrospinning [34], microphase separation [28,35,36], etching [37,38], spin-coating or dip-coating [28,39,40], sol–gel synthesis [10,41], templating [20,21,28,36,42], spraying [5,43] and many others [10,16,28,37,38,44]. Although a wide range of approaches have been proposed for the preparation of superhydrophobic polymer surfaces, most of them are polymer specific, fairly complex and involve several steps. Recently we reported a fairly simple method, which was based on the spin coating of fumed silica dispersions in an organic solvent onto polymer surfaces for the preparation of polymeric materials with controlled wettability, from superhydrophilic to superhydrophobic [39,40]. The method was applicable to a wide range of polymeric materials, thermoplastic or thermoset.

In this study we investigated the utilization of more practical coating methods for the preparation of superhydrophobic silicone–urea copolymer surfaces, which included spray coating using an airbrush and direct coating using a doctor blade, in addition to the spin-coating process. Topography and the average roughness of the superhydrophobic polymer surfaces obtained were characterized by field emission scanning electron microscopy (FESEM) and white light interferometry (WLI). Static, advancing and receding water contact angle (CA) measurements were also performed to demonstrate the formation of superhydrophobic surfaces. Our results indicate that: (i) the extent of surface silica coverage and the distance between silica particles, (ii) average sizes of the silica particles or agglomerates, (iii) presence of micro–nano hierarchical structures, and (iv) the average surface roughness, play critical roles in obtaining superhydrophobic surfaces.

2. Experimental

2.1. Materials

Segmented thermoplastic polydimethylsiloxane–urea copolymer (Geniomer TPSC 140) (TPSC) with a PDMS content of about 92% by weight and the hydrophobic fumed silica (HDK H2000) were supplied by Wacker Chemie, Munich, Germany [45]. Primary particle size for the hydrophobic silica is reported to be 5–30 nm, which increases to 100–250 nm after aggregation. The specific surface area is 170–230 m²/g [45]. Reagent grade isopropanol (IPA),

tetrahydrofuran (THF) and toluene were obtained from Merck and were used as received.

2.2. Preparation of superhydrophobic silicone–urea copolymer surfaces

Methods used for the preparation of superhydrophobic polymer surfaces through the use of hydrophobic fumed silica (HDK H2000) are explained in detail below.

2.2.1. Spin coating of silica dispersed in THF onto the TPSC surface

The first method was layer-by-layer spin coating of silica particles onto TPSC surface from a dispersion in THF, which was explained in detail previously [39,40]. TPSC was dissolved in IPA (15% by weight), whereas the hydrophobic silica was dispersed in THF at a concentration of 0.5% by weight and was subjected to ultrasound sonication at a frequency of 35 kHz on a Sonorex RK 255H type bath for 10 h. Dynamic light scattering (DLS) measurements on hydrophobic silica suspensions in THF (10 mg/mL) indicated fairly homogeneous distribution of the silica nanoparticles, with a number average size distribution of 44 ± 9 nm. Spin coating was applied on a Model 7600 Spin Coater by Specialty Coating Systems, Inc., Indianapolis, IN, USA.

Glass slides ($20 \times 20 \times 0.15$ mm), cleaned by wiping with IPA and THF were used as the substrate for spin coated TPSC films, which had a thickness of about 20–30 μ m. 8–10 drops of 0.5% by weight silica dispersion in THF were then placed onto the polymer film and spin coated after waiting for 1 min to allow the surface wetting and efficient penetration of silica particles into the polymer film. This step was repeated several times to achieve optimum coverage. To improve the durability, the silica containing surfaces were finally spin coated with a thin layer of TPSC film. Spin coating was performed at 1000 rpm for 70 s. All samples were dried at room temperature overnight and then in a vacuum oven at room temperature until constant weight and were kept in sealed containers until further testing.

2.2.2. Spin coating of TPSC/silica dispersions on a glass substrate

TPSC was dissolved in IPA at a concentration of 0.5% by weight. To this polymer solution silica particles were added at different amounts to obtain TPSC/silica ratios of 1/4, 1/7 and 1/10 (by weight). Mixtures were stirred vigorously for 30 min by a magnetic stirrer and then were sonicated for 30 min to obtain homogeneous dispersions. DLS measurements on TPSC/silica (1/10) mixtures containing 40 mg/mL silica indicated number average particle size distribution of 272.0 ± 24.7 nm, which was stable for several hours. TPSC/silica dispersions were spin coated onto glass slides at 1000 rpm. Spin coating step was repeated to apply successive layers. Samples were dried at room temperature overnight and then in a vacuum oven at 40°C for 24 h.

2.2.3. Coating of TPSC/silica dispersions on a glass substrate using a doctor blade

TPSC/silica (1/10) (by weight) dispersion prepared in IPA as described before was coated on a glass substrate using a doctor blade with a gauge thickness of 200 μ m. Coating was dried overnight at room temperature and then in a vacuum oven at 40°C for 24 h.

2.2.4. Spray coating of TPSC/silica dispersions with an airbrush

Spray coating was applied by using a Max H2000 model Cora airbrush painter with a nozzle diameter of 0.8 mm, pressurized by a Black and Decker compressor. TPSC/silica (1/10) (by weight) mixture prepared in IPA was transferred into the tank of the airbrush and the mixture was sprayed onto the glass slides under different conditions. The coating parameters included the tank pressure,

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