



Influence of the average surface roughness on the formation of superhydrophobic polymer surfaces through spin-coating with hydrophobic fumed silica



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ABSTRACT

Formation of superhydrophobic polymer surfaces were investigated through successive spin-coating of hydrophobic fumed silica dispersed in an organic solvent onto polymer films. Two different polymers, a hydrophobic segmented silicone-urea copolymer (TPSC) and hydrophilic poly(methyl methacrylate) (PMMA) were used as model substrates. Influence of the polymer type and structure, silica concentration and the number of silica layers applied on the topography, average roughness and the wetting behavior of the surfaces were determined. Polymer surfaces obtained were characterized by scanning electron microscopy, white light interferometry, atomic force microscopy and advancing and receding water contact angle measurements. It was possible to obtain superhydrophobic surfaces displaying hierarchical micro/nano features both for TPSC and PMMA. A close correlation was observed between the number of silica layers applied and average surface roughness obtained. It was demonstrated that an average surface roughness value of 125–150 nm was necessary for the formation of superhydrophobic surfaces, both for TPSC and PMMA. Chemical structure and nature of the polymeric substrate seem to play a significant role on the topography and average roughness of the silica coated surfaces formed. Superhydrophobic surfaces displayed static and advancing water contact angles well above 150° and fairly small contact angle hysteresis.

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1. Introduction

Preparation and characterization of polymeric materials with superhydrophobic surfaces have been extensively investigated during the last 15 years, after the detailed description of the surface structure of various natural plant leaves, including the lotus leaf by Barthlott and Neinhuis in 1997 [1,2]. One of the main reasons for such a remarkable interest in superhydrophobic surfaces is their very interesting behavior, which include, self-cleaning, anti-fouling, stain-resistant and ice-repellant properties [3–5]. Such properties make these materials applicable in a wide range of diversified fields, including paints and coatings, textiles, exterior glass windows, rooftops, windshields, solar panels, aircraft wings and wind turbine blades [3,4,6,7]. It is well documented that the wetting behavior of a surface is controlled both by its chemical structure and the surface topography or roughness [8–10]. One of

the best known examples of a superhydrophobic surface in nature is the lotus leaf [1,2,10]. As clearly shown by scanning electron microscopy (SEM) studies, the surface of the lotus leaf is covered by irregularly distributed, micron-sized protrusions called *papilla*, which have further nanoscale roughness [1,2]. Combined with the inherent hydrophobicity of the waxy layer on the leaf, these irregularly dispersed surface structures with dual-scale roughnesses give the plant its superhydrophobicity, with static water contact angle values above 150° and fairly small contact angle hysteresis [11–17].

Theoretical explanation of the effect of surface roughness on wetting behavior has been provided by Wenzel [18] and Cassie and Baxter [19]. Wenzel assumed complete wetting of the rough surface by the liquid droplet and modified the contact angle measured on a rough surface ($\cos\theta_W$) by introducing a roughness factor (r) as shown in Eqn. 1. (r) is defined as the ratio of the actual area of a rough surface to its projected geometric area and therefore its value is always greater than 1.

$$\cos\theta_W = r \cdot \cos\theta \quad (1)$$

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Cassie–Baxter correlated the apparent contact angle (θ_{CB}) on a rough surface to the weighted average of the cosines of the contact angles on the solid and air surfaces (Eqn. 2), where (f) is defined as the fraction of the surface on top of the protrusions, ($1 - f$) the fraction of air pockets and (θ_g) the contact angle on the air in the valleys [20]. When the contact angle of air pockets is taken as 180° , the Cassie–Baxter relationship is given by Eqn. 3.

$$\cos\theta_{CB} = f \cdot \cos\theta + (1 - f) \cdot \cos\theta_g \quad (2)$$

$$\cos\theta_{CB} = f \cdot \cos\theta + f - 1 \quad (3)$$

By combining the Cassie–Baxter and Wenzel relationships, a general equation is obtained for the apparent contact angles measured on a rough surface (θ_R).

$$\cos\theta_R = r \cdot f \cdot \cos\theta + f - 1 \quad (4)$$

As can be easily deduced from Eqn. 4, increased surface roughness will lead to much higher contact angles for hydrophobic surfaces that have a contact angle $>90^\circ$ on flat surfaces. There are various reports, where modified versions of these equations were developed to better explain the contact angle behavior of rough surfaces [21–24].

Due to the remarkable interest in superhydrophobicity, there have been intense efforts on developing new methods and processes for the preparation of superhydrophobic surfaces that display dual micro/nano roughness by employing a wide variety of techniques, which include; layer by layer (LBL) deposition [25], electrospinning [26], microphase separation [20,27,28], etching [29,30], spin-coating or dip-coating [20,31,32], sol–gel synthesis [10,33], surface modified silica deposition [34–36], templating [20,28,37], spraying [5,38,39] and others [10,16,20,29,30,40]. However, most of the methods described in the literature are fairly complex and may involve many steps and in general can only be applied to specific polymers. Recently we reported a fairly simple method for the preparation of polymeric materials with controlled wettability [31,32]. The method is based on spin coating of a fumed silica dispersion on a wide range of polymeric materials, thermoplastic or thermoset. It has been shown that with this simple process it was possible to prepare superhydrophobic polymer surfaces with static water contact angles greater than 170° [32]. Very interestingly, although the dramatic effects of the particle geometry or feature shape and size and distribution of protrusions on surface roughness and superhydrophobicity have been extensively discussed, no direct correlation between the experimental values of the average surface roughness and values of water contact angles or contact angle hysteresis were provided in the literature [20,30,41,42].

One of the main goals of this study was to investigate the effect of the layer-by-layer spin coating of hydrophobic fumed silica on the surface coverage, particle size and distribution, surface topography and average roughness of the surfaces obtained. Furthermore, we were especially interested in finding out if there was a critical or threshold value for the average surface roughness in order to obtain superhydrophobic surfaces. For this purpose two polymers different in nature, an inherently hydrophobic segmented silicone-urea copolymer (TPSC) and hydrophilic PMMA were chosen as the polymeric substrates. Polymer surfaces obtained were characterized by a wide range of complementary techniques which included, field emission scanning electron microscopy (FESEM), white light interferometry (WLI), static, advancing and receding water contact angle (CA) measurements, in order to gain a better understanding on the formation of 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 kindly provided by Wacker Chemie, Munich, Germany [43]. Poly(methyl methacrylate) (PMMA) ($M_n = 190,000$ g/mol) was synthesized in our laboratories. 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 m^2/g [43]. Reagent grade isopropanol (IPA), tetrahydrofuran (THF) and toluene were obtained from Merck and were used as received.

2.2. Sample preparation

Samples were prepared through a successive or multi-step spin-coating process, which was explained in detail previously [31,32]. TPSC solution was prepared in IPA, whereas the PMMA solution was prepared in toluene at concentrations of 15% and 10% by weight respectively. Silica was dispersed in THF or THF/toluene (5/2 by volume) mixture at a concentration of 0.5% and 1.0% by weight respectively. To obtain a homogeneous distribution, the dispersion was subjected to ultrasound sonication at a frequency of 35 kHz on a Sonorex RK 255H type ultrasonic bath (Bandelin, Berlin, Germany) for 10 h. Dynamic light scattering (DLS) measurements on hydrophobic silica suspensions in THF indicated fairly homogeneous distribution of the nanoparticles, with a number average size distribution of 44 ± 9 nm, which is in very good agreement with the supplier's specifications.

Glass slides ($20 \times 20 \times 0.15$ mm) were used as the substrate for spincoated films. Coating procedure was as follows: Glass slide surfaces were cleaned by wiping with IPA and THF successively several times and the parent polymer solution (TPSC or PMMA) was spincoated to obtain a film with a thickness of 20–30 μm . TPSC surfaces were coated using the silica dispersion in THF at a concentration of 0.5% by weight, while PMMA was coated by using a 1% by weight silica dispersion in THF/toluene (5/2 by volume) mixture. In each case 8 drops of silica dispersion were placed onto the base polymer film and were allowed to wet the film surface for 1 min in order to achieve efficient penetration of silica particles into the polymer during the spin coating process. Spin coating process was performed at 1000 rpm for 70 s. Before applying the subsequent layer, the coating was dried under a mild air flow at room temperature for 3 min. These steps were repeated until the desired number of silica coatings were achieved. To improve the durability of the surfaces formed, a final silica coating was applied which also contained the parent polymer. The ratio of the parent polymer to the silica in dispersion was 1/10 by weight. All samples were first dried in the hood for several hours and then in a vacuum oven at room temperature overnight. Table 1 provides the description of the sample preparation and the coding of the samples obtained, where the first four letters indicate the base polymer and (X) the number of silica layers spin coated on the film. For example TPSC-7

Table 1
Description of process parameters used for sample preparation.

Sample code	Solvent for polymer	Conc. polymer soln. (wt %)	Solvent for silica dispersion	Conc. silica dispersion (wt %)
TPSC-X	IPA	15	THF	0.5
PMMA-X	Toluene	10	THF/Toluene (5/2 by wt)	1.0

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