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Study on the wetting behavior and theoretical models of polydimethylsiloxane/silica coating

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ABSTRACT

The hydrophobic coatings were successfully fabricated through spraying via mixing the hydrophobic silica (SiO_2) and the cross-linked polydimethylsiloxane (PDMS) which was cured by tetraethoxysilane (TEOS) under the catalysis of dibutyltin dilaurate (DBTDL). The effects of SiO_2 content on the surface morphology and wettability, as well as the water at different temperatures on the hydrophobic behavior were investigated. When the mass ratio of SiO_2 to PDMS-TEOS is 0.3, the micromorphology of coating shows random micro/nanostructure and the water contact angle (WCA) of the coating reaches 153.4° with a sliding angle (SA) lower than 5°. However, with the increase of temperature of water droplet over 50 °C, the WCA falls below 130.4° and the SA significantly increases to nearly 180°, which implies that the state of water droplet on superhydrophobic surface has changed from Cassie–Baxter (CB) model to Wenzel model. Meanwhile, on the basis of the variant WAC of water at different temperatures on the same surfaces, a revised model is proposed to explain the state of water droplet on the hydrophobic surface. Thus, the effective way to increase the WCA is to capture more air in the grooves. Finally, based on the models, the relationship between hydrophobicity and superhydrophobicity is explained.

1. Introduction

Recently, superhydrophobic surfaces [1–3], with a water contact angle (WCA) higher than 150° and a sliding angle (SA) lower than 5°, have gained much attention due to their potential applications in self-cleaning coating [4], liquid transportation [5], waterproof and stain resistant textiles [6]. The superhydrophobicity can be achieved by the combination of low surface energy materials and hierarchical micro/nanostructures on the surfaces [7]. Although many methods to fabricate superhydrophobic surfaces have been reported [8,9], lots of them need special equipment and expensive materials [10–12], some even only applicable to particular surfaces [13,14], which may limit their developments in practical application. Therefore, it is necessary to put forward a simple and facile way to construct superhydrophobic surface, which is suitable for different substrates. Furthermore, the study of theory about surface wettability is also important, and it will have guiding significance for the fabrication of hydrophobic coatings.

Currently, there are two classical theoretical models to study the wetting behavior of the surfaces – the Wenzel model and the Cassie–Baxter (CB) model [15,16]. In Wenzel model, the water droplet fills up the grooves and is pinned on the solid surfaces. In contrast, in CB model, the water droplets only contact the top of the grooves and the air pockets are trapped inside the grooves, which results in a composite interface (air–liquid–solid) on the surfaces. Enormous progress has been made on the study of the two models which provide theoretical model for designing a rough substrate with superhydrophobicity [17]. Generally, the water droplets on hydrophobic surfaces are thought to be in Wenzel model and the water droplets on superhydrophobic surfaces prefer to CB model [18]. There is an energy barrier between the two models, which prevents spontaneous transition from one model to another. But the transitions between Wenzel and CB model on superhydrophobic surfaces can be induced under certain conditions, such as temperature [19], electricity [20] and pressure [21]. Nosonovsky and Bhushan [22] found that the energy barrier for the transition from Wenzel to CB model was much smaller than that of the opposite transition, which meant that the Wenzel–CB transition was easier to be induced. However, the fundamental mechanisms of wetting still need to be improved. Most of the researches are focused on the study of models on superhydrophobic surface, while less attention is paid to the hydrophobic models which are important for the understanding of wetting behavior on the solid surface. Meanwhile, the relationship between superhydrophobic model and hydrophobic model is seldom mentioned.

Herein, by mixing the commercial hydrophobic silica (SiO_2), hydroxyl-terminated poly(dimethylsiloxanes) (PDMS), dibutyltin dilaurate (DBTDL) and tetraethoxysilane (TEOS), the

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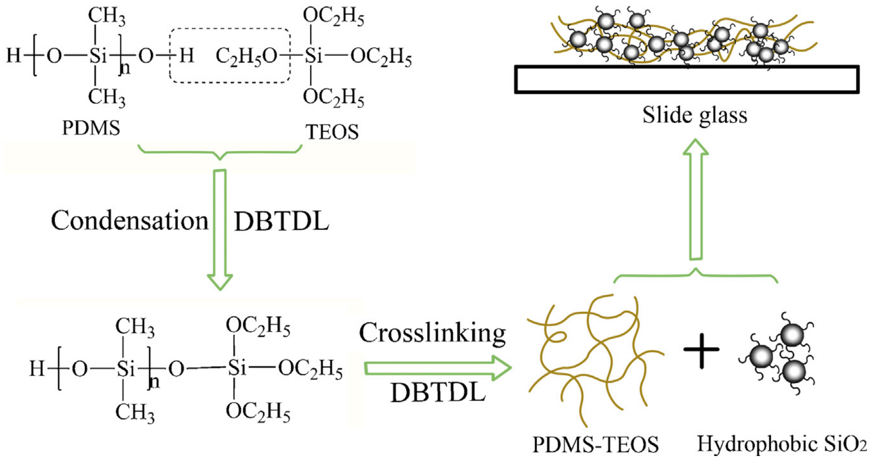

Fig. 1. Schematic diagram of fabrication process of PDMS/SiO_2 coating.

superhydrophobic coating was fabricated via spraying. In the study, the low surface energy material hydroxyl-terminated PDMS was cross-linked by TEOS under the catalysis of DBTDL, and the roughness was controlled by SiO_2. This is a facile and practical method and it can be applied to different substrates [23]. On the superhydrophobic surface, the CB–Wenzel transition was induced when the temperature of water increased. For the understanding of the wetting behavior on the surfaces, the effect of water at different temperatures on WCAs of composite coating with different SiO_2 contents was investigated. Moreover, the relationship between hydrophobicity and superhydrophobicity was illustrated based on models.

2. Experimental

2.1. Materials

Hydrogen-terminated poly(dimethyl siloxane) (PDMS) (Sylgard 107) was purchased from Jiangxi Xinghuo Organic Silicone Plant (China). Tetraethoxysilane (TEOS) was obtained from Guangzhou Chemical Reagent Factory (China). Dibutyltin dilaurate (DBTDL) was acquired from Shanghai Reagent Factory (China). Ethanol and n-hexane were got from Sinopharm Chemical Reagent Limited Company. Hydrophobic nano-SiO_2 (H15) was provided by Wacker Company (Germany). All of the reagents were used as received.

2.2. Fabrication of PDMS/SiO_2 coating

Firstly, the slide glasses were immersed into 50 mL ethanol–water solution with the help of ultrasonic for 10 min, and washed with water for three times, then dried in a clean oven at 60 °C. Subsequently, 0.5 g PDMS, 0.01 g DBTDL, 0.1 g TEOS and a certain amount of SiO_2 were mixed in 15 mL n-hexane under ultrasonic condition. Then, the mixture was magnetic stirred for another 1 h. Finally, the composite coating was fabricated on the slide glass via spraying, and the coating was cured at 45 °C for 30 min. The fabrication process of PDMS/SiO_2 coating was shown in Fig. 1.

2.3. Characterization

The microscopic morphologies of the coating surfaces were characterized by the field-emission scanning electron microscopy (SEM, FEI NOVA NANOSEM 430, Netherlands) under an acceleration voltage of 15 kV. The coatings were sprayed by a thin gold layer to improve electrical conductivity before testing. The WCA (a water droplet of 5 μL) and SA (a water droplet of 10 μL) were determined on a contact angle analyzer (DSA100, Germany) with distilled water at ambient temperature. The water droplet at different temperatures was placed on the composite coatings by a pipettor (WKYIII-2, China). All of the samples were measured at least five times on the different places of the surfaces to get the mean values of the WCA and SA.

3. Results and discussion

3.1. Surface morphology and wettability

The SiO_2 content had a great effect on the microstructure and the WCA of the composite coating. Fig. 2 shows the surface morphologies and the WCAs of PDMS-TEOS/SiO_2 coatings with different SiO_2 contents. In Fig. 2(a), the surface of the pure PDMS-TEOS coating was flat, without any obvious bumps, and the intrinsic WCA was about 104.5°. From Fig. 2(b) and (c), with the increase of mass ratio from 0 to 0.2, the surface of coating gradually became rough and the WCA varied from 104.5° to 119.6°. When the mass ratio was 0.3, the surface of the coating became rougher, similar to some nanoparticle aggregates. Meanwhile, the composite coating exhibited superhydrophobicity and the WCA reached as high as 153.4° with a SA lower than 5°. The high magnification of superhydrophobic coating was shown in Fig. 2(e), there were many irregular protrusions randomly distributing on the surface in nano scale. Hence, the random micro/nanostructure morphology on the surface resulted in the superhydrophobic behavior, which was always regarded as the “lotus effect” [24]. With further addition of SiO_2 up to the mass ratio of 0.6, the coating kept superhydrophobicity and there were no cracks on the surface determined by naked eye. But the SEM image of Fig. 2(f) shows that cracks could be found on the surface when the ratio was 0.6, indicating that the excessive SiO_2 was unfavorable for the perfect film forming. Hence, the microstructure and the wetting behavior could be adjusted by the SiO_2 content.

3.2. Transition between CB model and Wenzel model on superhydrophbic surface

As shown in Fig. 3, the WCA and SA changed little when the temperature of water was lower than 40 °C. However, when the temperature of water rose to 50 °C, the WCA declined to 130.4° and the SA remarkably increased to nearly 180°, indicating that the water droplet had changed from CB model to Wenzel model. The difference between the two models was often considered as that the CB model had low SA while the Wenzel model had high SA [19].