



## Aqueous epoxy-based superhydrophobic coatings: Fabrication and stability in water



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### ABSTRACT

Superhydrophobic (SH) surfaces have numerous application forms; however, perhaps the most commonly used form is as coatings. Most of coatings apply organic compound as solvents thus are not environment-friendly. In this study, we successfully fabricated SH coatings using waterborne epoxy resin emulsion. Such coatings possess an excellent adhesive strength with substrates and a high surface hardness; however, their SH properties were less durable when immersed in water, e.g. a Cassie-Wenzel transition occurred. Although this phenomenon is reversible following surface drying, it seriously limits the application of SH surface in areas such as anti-icing, self-cleaning, drag reduction, etc. XPS and SEM characterizations confirmed that this instability or transition was caused by an increase in the number of exposed hydrophilic groups embedded within the coating surface, but not by changes associated with the surface microstructure. By enhancing the macromolecular weight of the epoxy resins, for example, by reducing their epoxy value and reducing the number of cross-linking agents, the number of exposed hydrophilic groups such as hydroxyl (-OH) and amidocyanogen (-NH) functionalities decreased, which increased the SH stability in submerged conditions. This study will be helpful in improving the practical application of SH coatings.

### 1. Introduction

Superhydrophobic (SH) surfaces have been investigated for 20 years since 1997 due to their unique properties and potential applications [1–5]. However, to date, no practical applications have been commercialized besides water splashing resistant reagents being applied to textile surfaces [6]. The main reasons for such limited application do not arise from cost or difficulty of production on a large scale, but from its poor stability [7–10]. For example, many SH surfaces are not resistant to abrasion [7], water impaction [8], or vapor condensation [9,10]. In earlier studies, much research was directed towards improving the stability of SH surfaces [11], e.g. enhancing its scratch resistance by developing 3D [12], elastic [13] and super-hard [14] SH surfaces. However, little attention was paid to the stability of SH surfaces to long term water contacting, i.e. their changes in wettability after being immersed in water or subjected to rain [15–17].

SH surfaces are most widely used as coatings [18]. Among coating families, those based on waterborne resins have attracted much attention [19–22]. However, due to the native properties of waterborne resins, e.g., the presence of hydrophilic groups or surfactants, coatings based on such resins generally suffer from poor water resistance, resulting in bubbling or even shedding from substrates. In this study, we

successfully fabricated a SH coating using a waterborne epoxy resin emulsion. Such a coating had excellent substrate adhesive strength and high surface hardness. However, it had less durable SH properties when it was immersed in water for a certain period of time, which seriously limits the application of SH surfaces in many fields such as anti-icing, self-cleaning, drag reduction, etc.

The mechanism responsible for the poor durability of SH coatings based on the waterborne epoxy resin emulsion was investigated. We found that a number of hydrophilic groups were present on the water-exposed face, but no changes in surface microstructure were observed; this caused Cassie-Wenzel transition of the coating surface when it was immersed in water for several hours or days. Although this phenomenon could be reversed after the surface was dried again, the SH surface could be easily contaminated by miry water. SH surfaces possessing significantly enhanced durability in water could be prepared by optimization of the coating formula, i.e. by decreasing the number of hydrophilic groups in the coating. This study will aid the development and application of SH surfaces in areas that require the coating to be immersed in water for a long period of time.

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## 2. Experimental

### 2.1. Materials

SiO<sub>2</sub> nanoparticles (SP-30) were purchased from Wanjiang New Material Ltd (Hangzhou, China); 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS-17) was purchased from Sicong New Material Ltd (Quanzhou, China). 3-Aminopropyltriethoxysilane (KH-550) was obtained from Aladdin Reagent Ltd (Shanghai, China). Waterborne epoxy emulsion (EP-51) and its curing agent (HGA), waterborne epoxy emulsion (EP-20) and its curing agent (HGA-50), were all purchased from Zhejiang Anbang New Material Ltd. These EP resins have poly(ethylene glycol) (PEG) short side chains for self-emulsion. Other agents such as ethanol were purchased from general companies.

### 2.2. Preparation of superhydrophobic coatings

The SH coatings were prepared via a simple and rapid spraying method. Briefly, 2.5 g nano SiO<sub>2</sub> was first dispersed in a mixture of 60 mL H<sub>2</sub>O and 10 mL ethanol by magnetic stirring for 10 min and further ultrasonic treatment for 20 min. Then 1 mL KH-550 and 0.8 mL FAS-17 were quickly added into the above mentioned nano SiO<sub>2</sub> suspension at stirring state and the mixture was continuously stirred for 1.5 h to form nano SiO<sub>2</sub>/fluorine silicon sol. Simultaneously, 7 g EP-51 and 5.6 g HGA were mixed homogeneously with 5 mL water; 2.94 g EP-20 and 0.84 g HGA-50 were mixed homogeneously with 5 mL water, too. These two types of epoxy emulsion/curing agent mixtures were further mixed homogeneously with the above mentioned nano SiO<sub>2</sub>/fluorine silicon sol, respectively. The resulting coats were sprayed onto glass slides and dried at 120 °C for 30 min. As a parallel study, the coatings containing no nano SiO<sub>2</sub> fillings, herein named as “smooth coating”, were prepared simultaneously. Scheme 1 shows the preparation process for epoxy-based SH coatings. The synthetic principle of fluorine silicon sol and its reaction with waterborne epoxy net to form double net system is shown in Scheme 2.

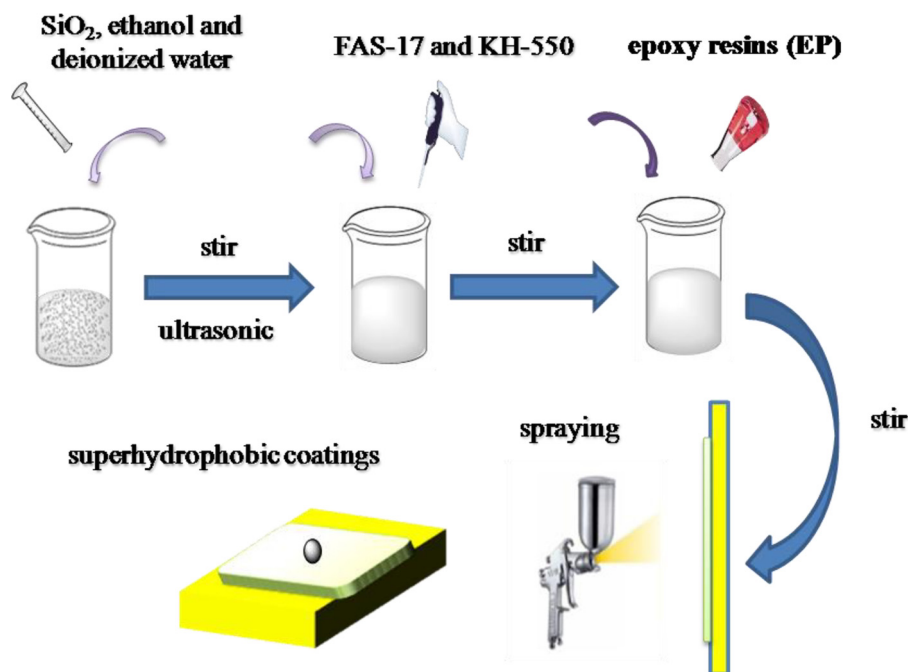
### 2.3. Characterization techniques

The morphologies of the as-prepared coatings were characterized by

field emission scanning electron microscopy (FE-SEM, S4700, Hitachi, Japan). The apparent water contact angles (CAs) and slide angles (SAs) were measured using a Data physics OCA35 contact-angle system with 4 μL deionized water droplets at room temperature. Either apparent CAs or SAs, they were the averaged value of five different measuring points on each surface. For studying the mechanism for the formation of the SH coating, the contents of the coating (smooth) surface elements, such as F, O, N and their distribution along the depth of coating, were characterized by X-ray Photoelectron Spectroscopy (XPS, Kratos AXIS Ultra DLD, Shimadzu, Japan) at different measuring angles. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR, Nicolet 6700, Thermo Nicolet Corporation, USA) spectra were recorded to characterize surface chemical groups of the as-prepared coatings. For samples with water immersion, they were dried with a N<sub>2</sub> gas flow before ATR-FTIR recording.

The stabilities of the SH coatings were monitored by immersing the coatings in deionized water, taking out them at different time intervals and then measuring their apparent CAs, SAs and CA hysteresis after drying with N<sub>2</sub> gas flow. In CA hysteresis testing, a 2 μL deionized water droplet was dropped on the surface, then 8 μL deionized water was infused into the 2 μL droplet and then absorbed back both at a speed of 1 μL/s with 1 min interval between infusing and back drinking. By this method, advancing CAs and receding CAs of the samples were obtained and their difference was just CA hysteresis. To more accurately investigate the stabilities, the coatings were placed in a humid and transparent box and a 10 μL deionized water droplet was placed on the SH coating and changes in the apparent CA were continuously monitored. As a parallel study, the smooth coatings without filling nano SiO<sub>2</sub> were immersed downwards in deionized water and 8 μL air was bubbled onto the coatings and changes in the CA were measured.

To explore the instability mechanism of the SH coating in water, changes in the morphology of the SH coatings were observed by FE-SEM after being immersed in water for 7 days. Changes in the amounts of elements (F, O, N) present on the coating surface after the coatings had been immersed in water for different lengths of time (1, 4, 7 days) were measured by XPS as soon as the coatings were removed from the water and dried with a N<sub>2</sub> gas flow. To confirm the source of the instability, the wetted SH coatings were dried at 120 °C for 1 h and then changes in apparent CA, SA and the content of elements on the surface



Scheme 1. Preparation process of waterborne EP based SH coatings.

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