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Influence of particle size in fluorine free corrosion resistance superhydrophobic coating - Optimization and stabilization of interface by multiscale roughness

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ABSTRACT

Fluorine free superhydrophobic coatings with stabilized air-water interface had been fabricated by utilising different particle sized silica. Coatings were formulated with various composition of different sized nanosilica's along with nanotitania and aluminium stearate embedded in a matrix of silicone resin of Mn ~1,65,000. The as-prepared coating exhibited higher contact angle (CA) 152.5° along with high mechanical properties like abrasion, adhesion and impact resistance. As particles with different sizes were incorporated in the coating, the interface was stabilized during immersion in water uptake study. In addition most of these coatings also exhibited exceptional corrosion resistance withstanding upto 1000 h of salt spray.

1. Introduction

Superhydrophobicity had sprouted in later 1970's and extended its branches in both experimental as well as theoretical research. In the recent decades superhydrophobic surfaces with surpassed CA (contact angle) of 150° and lower tilting angle (TA) are being explored in different arenas like self-cleaning [1] wind shields for automobiles, stain resistant textiles [2], anti-soiling architectural coatings [3] and so on. Mostly, these surfaces are fabricated by using low surface energy fluoro materials with appropriate surface roughness [4–6]. Besides their low surface energy, the shortcomings associated with fluoro compounds are their intoxication to human beings [7] and environment along with high price. Superhydrophobic coatings that are free of fluorine [8–10] are an active area of research whereas in this study we had fabricated fluorine free superhydrophobic coatings with stabilized interface with the help of different particle sized nanosilica. In our previous work we had produced superhydrophobic coating using silicone resin and nanosilica and tuned the micro/nano roughness by changing the concentration of nanosilica. As a continuation of our previous work, where nanosilica of size 50 nm alone were used whereas here combination of nanosilica with different sizes were used to increase the hierarchical roughness which endow stability to Cassie–Baxter state (CB).

Customarily, superhydrophobic surfaces are elucidated by two states, namely sticky Wenzel state and easy roll off CB state. Wenzel state is a homogenous state where there is no entrapped air but in CB state air is entrapped and exists in heterogeneous state. CB composite state is preferred and desirable for many practical applications because the entrapped air acts as a cushion and induce collateral self-cleaning property [11,12]. Downside being the CB state is metastable and collapse into Wenzel on external perturbations [13], gravitational force, capillary force [14], critical hydrostatic pressure [15] and nucleation/condensation of water [16] within the micro/nano roughness [17]. CB impalement take place more readily because it is also energetically more favourable. Sustaining the stability of the CB state is a major challenge which can be done by taking advantage of nature's resourcefulness.

Mostly superhydrophobic structures observed in nature are

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found to have hierarchical micro/nano roughness. Lotus leaf, the epitome of superhydrophobicity have microroughness with nano level asperities [18]. Mostly the transition between CB state and Wenzel are irreversible because of the energy barrier in between where CB state rest at a higher energy state [19]. Many theoretical and experimental studies were carried out with different structural shapes and sizes to study the stability of SA (sliding angle) interface of CB state. With increased pillar height and decreased distance between adjacent pillars the SA interface was stabilized [20]. Thus, to effectively resist the impalement of less stable CB interface and to hamper the transition, multiscale hierarchical roughness is needed [21]. Mostly, CB interface was studied on a microscopic scale with few microliter of water droplet with the aid of external stimuli. In this study in addition to FESEM analysis, the as-prepared coatings were studied by water uptake and water vapour permeation studies in a macroscale. It is noteworthy that these coatings also possessed markedly high corrosion resistance behaviour in salt spray. This process of creating superhydrophobicity has a vital significance in industrialization on account of the advantages associated with them like low cost, easy to construct in the field and can be applied over large area.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Nanosilica (50 nm), Nanosilica (250 nm), Nanosilica (500 nm), nanotitania (20 nm) were procured from nanoshell. Silicone resin of molecular weight Mn ~165000 was purchased from Wacker silicones. Xylene, magnesium silicate and aluminium stearate of LR grade were used. All chemicals were utilized as such without further purification.

2.1.2. Preparation of coating

Coatings with varying composition of pigments were prepared accordingly as given in Table 1. Silicone resin of molecular weight Mn ~165000 was used as the binder. Pigment volume concentration (PVC) of the coating was fixed as 15% with 36% volume solids (VS) and the concentration of nanosilica in the 15% PVC was fixed as 60%. Calculated amount of pigments were dispersed in the silicone matrix with intended amount of solvent (Xylene) in a high speed homogenizer for 20 min. After the fineness of coating was checked in tapered Hegman gauge, the prepared coatings were coated over precleaned mild steel panels using a spray gun with an air pressure of 2.5 kg/cm^2. The coatings were dried at room temperature and evaluated after seven days of curing.

2.2. Characterizations

Static water contact angle measurements for the coatings were made by OCA 35 Data Physics goniometer with Millipore water by Laplace–Young fitting. CA were measured at five different places. Morphology of the coatings were analysed by field emission scanning electron microscope Carl Zeiss AG (Supra 55VP) with an acceleration voltage of 5–30 kV. The physical properties of the pigments like density and oil absorption were performed according to ASTM standards, ASTM D153 and ASTM D1483 which were given in supplementary information. Physical properties of the coatings in wet as well as in dry state were studied as per ASTM standards. The resistance of the coating to abrasion was examined by ASTM D4060. The coated specimen was mounted on a rotating disc with constant weight of 1 kg and an abrading wheel of CS 10. The test panels were weighed before and after testing and wear index (WI) was calculated.

$$\boldsymbol{WI} = \frac{\text{Weight of specimen } (\textbf{\textit{before}} - \textbf{\textit{after}}) \text{ abrasion } X \text{ 1000}}{\text{Number of abrasion cycles}}$$

Adhesive tensile strength of the coating was determined by ASTM 4541. A dolly was fixed normal to the substrate with coating using an epoxy adhesive and allowed to cure for 7 days. The testing apparatus was aligned with the dolly fixed on the substrate and force normal to the coating was applied gradually. The force necessary to detach the dolly from the surface gave the tensile strength of the coating. Adhesion strength of the coating was also assessed by tape test as per ASTM D3359, where a cross hatch cut was made with 6 cuts at 2 mm apart on a substrate. Then, an adhesive tape was applied and peeled off at 180° angle and the area was inspected after removal of tape. It was then indexed according to the damage in the coating. The thickness of the coating was measured by using magnetic pull-off gauges as per ASTM D7091. The dry film thickness of nonmagnetic coatings over ferrous metal base is based on the attraction forces and a static magnetic field. The force required to pull a permanent magnet from a coated ferrous metal surface was correlated with the thickness of nonmagnetic coating.

Flexibility of coating was determined by mandrel bend test as per ASTM D522. The coated sample was clamped in between mandrel and the drawbar. The lever was then moved to 180° at a uniform velocity, kept for one second and the coated sample was visually examined for cracks along the bent. Impact resistance of the coating was evaluated by ASTM D6905. A standard weight (1.8 Kg) was indented from different height over coated sample and visually observed for damage in the coating on the other side. Salt spray, an accelerated test to evaluate the corrosion resistance of the

Table 1
Composition of pigment in the prepared coating.

System	SiO_2 50 nm (%)	SiO_2 250 nm (%)	SiO_2 500 nm (%)	TiO_2 20 nm (%)	Magnesium silicate (%)	Aluminium stearate (%)
1.			Pristine	resin		
2.	60	–	–	10	10	10
3.	40	20	–	10	10	10
4.	35	25	–	10	10	10
5.	30	30	–	10	10	10
6.	25	35	–	10	10	10
7.	20	40	–	10	10	10
8	–	60	–	10	10	10
9.	40	–	20	10	10	10
10.	35	–	25	10	10	10
11.	30	–	30	10	10	10
12.	25	–	35	10	10	10
13.	20	–	40	10	10	10
14.	–	–	60	10	10	10