



One pot fabrication of superhydrophobic anticorrosive coating without fluoro compounds and inhibitive pigments

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ABSTRACT

We report the successful fabrication of fluorine free superhydrophobic coating involving silicone binder, pigments like nanosilica, nanotitania and magnesium silicate and aluminium stearate as additive. The pristine resin with no pigments and additives show hydrophobic behaviour with water contact angle (WCA) of 93.5° and tilting angle (TA) of 60°. The WCA increased to 152.5° and TA to 20° with incorporation of pigments and additives. The introduction of pigments/additives created micro/nano roughness through agglomeration of pigments used in the coating. The as prepared superhydrophobic coating also exhibited excellent corrosion resistance property without using any inhibitive / sacrificial pigments in it. To the best of our knowledge this is the first work towards preparation of superhydrophobic coating with excellent corrosion protection without fluoro compounds and inhibitive pigments.

1. Introduction

Superhydrophobicity is a state at which the surface emanates extreme water repellency over which water droplets attain spherical shape and the contact angle (CA) exceeds 150° with low contact angle hysteresis (CAH). [1] Wetting phenomenon is accustomed in many industrial processes and plays a crucial role in many processes like coating, heat transfer, pesticide application and cleaning [2,3]. The basic equation for wetting phenomenon dates back 200 years which was formulated by Young [4]. The degree of wetting by a liquid is reflected in the CA it makes with the solid surface. CA of water on the solid surface is entailed by the specific surface energies of solid – gas, liquid – gas and solid – liquid interfaces. CA relies on the surface chemistry and surface roughness of the solid surface. The limiting factor for chemical hydrophobicity is circumscribed to 120° and it cannot be outnumbered without substantial surface roughness. [5–7] Surface roughness has a profound influence on wetting. Superhydrophobicity culminates when the hydrophobicity of a substrate is amplified by roughness [8]. Therefore, superhydrophobic surfaces always possess appropriate surface roughness at micro/nanometer scale.

With their unparalleled properties and growing demand superhydrophobic surface is an active area of research for the past few decades. Diversified approaches have been made so far, to fabricate superhydrophobic surfaces using a vast number of materials over a

wide number of surfaces. Most methods involve strict and harsh chemical treatment, sophisticated and time consuming processing procedures and expensive materials. There is thrive for the development of simple, nontoxic, economically affordable and viable application procedure and chemical method to fabricate superhydrophobic surfaces for practical use over a large surface area. Coating provides an efficient platform for scaling up superhydrophobic surfaces and it is more advantageous than many other methods. It is more practical, convenient, inexpensive and easy to apply in large scale. Traditionally, coating comprise of binder, pigment, additives and solvent. Depending on the coating thickness we need to build, volume solids (VS) and pigment volume concentration (PVC) are fixed. VS is the amount of non-volatile solids left after drying/curing of the coating which includes resin, pigment and additive and PVC is the ratio of the volume of pigment to the total VS. Based on the refractive index (RI) pigments are classified as main pigments and extender pigments. The role of main pigment is to provide hiding to the coating which should have a RI \geq 3.7. Extender pigments are comparatively less expensive than main pigment which are used to bring down the cost and to alter the properties of the coating.

Mostly, superhydrophobic coating is prepared from fluorinated polymers or polydimethylsiloxane (PDMS). The intrinsic low surface energy of fluorinated polymers [9,10] and PDMS [11] generate superhydrophobicity readily but they have many disadvantages in terms of

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Table 1
Composition of pigment in the prepared coating.

System	Nanosilica (%)	Nanotitania (%)	Magnesium silicate (%)	Aluminium stearate (%)
1.	Pristine resin			
2.	10	10	70	10
3.	20	10	60	10
4.	30	10	50	10
5.	40	10	40	10
6.	50	10	30	10
7.	60	10	20	10
8.	70	10	10	10
9.	100	–	–	–
10.	–	100	–	–

expenditure and ecological footprint. In spite of its incredibly low surface energy, fluoro compounds pose serious threat to environment and human health. Conversely, nature has flaunted superhydrophobic surface with wide range of topographical variations which mainly comprise hydrocarbons with CH₂ groups rather than low surface energy fluoro materials. Therefore, extreme low surface energy is not demanded in all cases to prepare superhydrophobic surface. [12] In addition many research groups have also fabricated fluorine free superhydrophobic surfaces [13,14]. In this study, silicone resin is used as the binder, nanotitania as the main pigment, nanosilica and magnesium silicate as the extender pigment, aluminium stearate as the additive and xylene as the solvent. Silicone resin has many propitious characteristics like high resistance to temperature [15], water repellency [16] and environmentally benign nature. Hierarchical roughness in the coating is imparted by utilizing nanoparticles and introduction of nanoparticles produces the micro/nano dual roughness through agglomeration. The resulted agglomerated structures increase the surface roughness of the coating which in turn induces superhydrophobic nature to the coating. Our method is simple and applicable under practical condition since it does not involve any sophisticated instrumentation or expensive materials. In this paper we elucidate a simple one step spraying process, for preparing superhydrophobic coating and the coating is free from fluoro compound which makes this process more eco-friendly.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Nanosilica (20–50 nm), nanotitania (20–50 nm) were purchased from nanoshel. Silicone resin was procured from Wacker silicones of molecular weight Mn ~ 165,000. Commercial grade xylene, magnesium silicate, aluminium stearate were used. The chemicals were used as such without further purification.

2.1.2. Method for the preparation of coating

The coating was formulated with a volume solid (VS) of 36% and pigment volume concentration (PVC) of 15%. The contribution of VS from resin part was 30.6% and pigment part was 5.4%. Various pigments were used which included nanotitania nanosilica, magnesium silicate and aluminium stearate. Oil absorption value of the various pigments used in the coating were evaluated and given in Table S1. The different composition of the pigments used to formulate the coating is given in Table 1. Silicone resin, xylene and pigments as per the composition in Table 1 were weighed and dispersed using a high speed homogenizer for 20 min/till the degree of dispersion value reaches 8–9 in Hegmann gauge. Coating was applied to the mild steel panels prepared as per ASTM G1 using air spray at an atomizing air pressure ranging from 2 to 3 kg/cm². The coating was cured at room temperature and the panels were subjected to various evaluations for the coating performance after seven days of curing. Dry film thickness of

Table 2
Concentration of nanosilica* with their CA, TA, W and f₁.

System	Nanosilica (%)	CA (°)	TA (°)	W (mN/m)	f ₁
1.	Pristine resin	93.5	60	68.4	1
2.	10	111.3	55	46.36	0.6778
3.	20	121.8	48	34.43	0.5034
4.	30	126.3	45	29.69	0.434
5.	40	131.3	42	24.73	0.3616
6.	50	144.4	30	13.58	0.1985
7.	60	152.5	20	8.20	0.1198
8.	70	154.7	18	6.95	0.1017
9.	100	141.6	25	15.72	0.2298
10.	–	81.2	52	84.01	1.228

*Composition of other pigments are as same as in Table 1.

the coating was measured using magnetic thickness gauge meter as per ASTM D7091 and the thickness was 70 ± 5 μm.

2.2. Characterizations

Static water contact angle measurements were carried out by goniometer (OCA 35 Data Physics) with water droplet volume of 5 μl. The measurements were made using Laplace-Young fitting mode and the values given were the average of five measurements with a variance of ± 2°. Morphology of the coating was characterized by field emission scanning electron microscope images, elemental mapping and surface profile of the coated samples were analysed utilizing energy dispersive X-ray analysis using field emission scanning electron microscope, Carl Zeiss AG (Supra 55 VP) with an acceleration voltage of 5–30 kV. In addition morphology of the coating was analysed by atomic force microscopy using Agilent SPM 5500.

3. Results and discussion

3.1. Superhydrophobicity, fractional surface of solid and work of adhesion of the coating

CA for the pristine resin was 93.5° and the CA was increased after incorporating nanosized pigments like titania, silica and micron sized pigments like magnesium silicate and aluminium stearate. The relation between CA and TA are given in Fig. 4.1. The coating composition in extender pigments nanosilica and magnesium silica were interplayed and the micro/nano roughness were fine tuned to achieve superhydrophobicity. The observed CA for the coating with different concentration of pigment where given in Table 2.

From Fig. 1 and Table 2 it was observed that CA increased gradually and the tilting angle decreased with increase in nanosilica concentration till 60% and after that there was physical impairment i.e. the coating was powdery. Superhydrophobicity was attributed by the roughness in the coatings with 60% nanosilica loading. The increased CA and the attainment of superhydrophobicity can be explained by the well-known Wenzel and Cassie-Baxter model [17,18]. The coating without any pigment was in Wenzel state, where addition of pigment induced roughness and with increase in nanosilica concentration increased the roughness and there occurred transition from Wenzel to Cassie-Baxter state [19]. The pigment had self-organised / agglomerated with increase in nanosilica concentration and are shown Scheme 1. The homogeneous Wenzel state was transformed via intermediate Cassie impregnated wetting state to heterogeneous Cassie-Baxter wetting state. The homogeneous wetting state was given by Wenzel, $\cos \theta = r \cos \theta_s$, where r is the roughness factor. Here, it was assumed that the water filled the grooves of the rough surface.

Since the composite Cassie – Baxter state was followed, the following equation was used $\cos \theta = f_1 (\cos \theta_s + 1) - 1$ (where f_1 is the fractional surface area of solid, θ and θ_s is the CA for rough surface and smooth surface of the coating with and without pigments, respectively)

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