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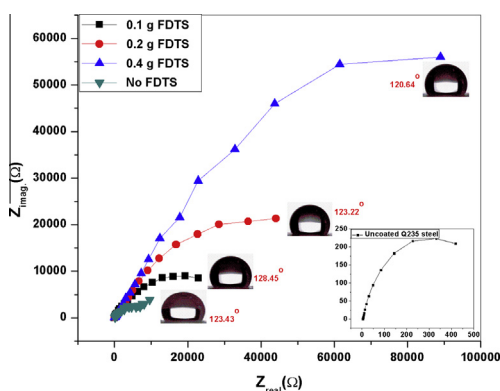
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Regular Article

Fabrication of FDTS-modified PDMS-ZnO nanocomposite hydrophobic coating with anti-fouling capability for corrosion protection of Q235 steel

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GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorodecyltrichlorosilane-based poly(dimethylsiloxane)-ZnO (FDTS-based PDMS-ZnO) nanocomposite coating with anti-corrosion and anti-fouling capabilities has been prepared using a one-step fabrication technique. XPS analysis and contact angle measurements showed the fluorine content to increase, while the hydrophobicity of the coatings decreased with addition of FDTS. XRD analysis revealed existence of ZnO nanoparticles of dimensions ranging from 11.45 to 93.01 nm on the surface of coatings, with the mean particle size decreasing with FDTS addition, and was confirmed by SEM and TEM observations. Interestingly, the anti-corrosion performance and mechanical properties of the coatings increased remarkably on addition of FDTS. Indeed, the observed low adhesion strength, surface energies and the outstanding anti-corrosive properties imply that the obtained coating would be useful in anti-fouling applications.

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1. Introduction

Corrosion and bio-fouling are major problems of underwater structures used in the marine industry mainly due to interactions

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with water and marine organisms [1–3]. Such interactions could be minimized by lowering the surface or interfacial energy of the substrates using appropriate micro- or nano-structured low surface energy coatings [4,5]. The coatings render the substrate surfaces hydrophobic or superhydrophobic, as well as make settlement and attachment of bio-foulers difficult. Both effects and appropriate surface topography cause substrate surfaces to become anti-corrosive and anti-fouling [6–11]. Coating surface adhesion has been related to the number of attachment points of marine organism on surfaces [12,13]. Indeed, some siloxane non-stick fouling-release coatings possess low adhesive surfaces, which have been shown impart anti-fouling activity under hydrodynamic conditions [14–16].

It has been suggested that bio-adhesion capacity has no definite correlation with the surface energy of a substrate, although surface energy window (20–30 mN/m) was identified, within which bio-adhesion would be minimal [17,18]. Again, the surface chemistry of coatings has been shown to be directly correlated with bio-adhesion capacity [19,20], with adhesion onto hydrophilic substrates favored when the bacterial surface is more hydrophilic than the suspending liquid, whereas adhesion onto hydrophobic surfaces is promoted when the bacterial surface is more hydrophobic [19,20]. These differences in settlement and attachment behavior have necessitated the development of composite surfaces that present both hydrophilic and hydrophobic domains to settlement and attachment of cells and organisms [21]. To this end, addition of zinc oxide nanoparticles (which possess hydrophilic character as well as provide anti-microbial, UV resistant and catalytic effects) to antifouling coatings is generating considerable interests [22]. Liang et al. [23] fabricated a novel anti-irreversible fouling polyvinylidene fluoride membrane using a non-solvent induced phase separation (NIPS) technique, wherein nano-ZnO was added to modify the internal surfaces of the membrane pores. In a related study, Li et al. [24] used nano ZnO-modified polyvinylidene fluoride (PVDF) to address fouling of polysaccharide, by means of atomic layer deposition (ALD). Furthermore, the effect of nano-ZnO on the mechanical properties, hydrophobicity, surface morphology and roughness, impact resistant as well as gloss properties of coatings based on FEVE copolymer was highlighted by Zhang et al. [25]. While Yong et al. [26] used ZnO as pigment in the formulation of ZnO nanopaint for marine anti-fouling applications.

In the present study, we aim to prepare a low adhesive strength, FDTS based hydrophobic PDMS-ZnO nanocomposite coatings with surface energies within 20–30 mN/m for possible anti-fouling and anti-corrosion applications on Q235 steel, using a simple, one-step fabrication technique. The ZnO nanoparticle was chosen to exploit the anti-microbial property, particulate nature and hydrophilic character, so as to impart anti-fouling, surface roughness and reduce the hydrophobicity of the coating. The FDTS was selected to modify the surface energy of the resulting coating in order to keep it within the Baier's surface energy window (20–30 mN/m) for anti-fouling application. The resultant coatings have been assessed for both antifouling and anti-corrosion efficacy.

2. Experimental procedure

2.1. Materials

A two-part poly(dimethylsiloxane) (PDMS) (Sylgard 184 silicone elastomer) with accompanying curing agent from Dow Corning Chemicals, USA was used as a coating resin, while ethyl acetate (analytical grade) from Sinopharm Chemical Reagent Co. Ltd. was used as diluent. Perfluorodecyltrichlorosilane (FDTS) from Tokyo Chemical Ind. Co. Ltd. Japan was used as a surface modifying additive. Hexadecyltrimethoxysilane (HDTMS) and Zinc oxide (ZnO)

nanoparticles (90 ± 10 nm) were purchased from Aladdin Industrial Corporation, Shanghai, China. All reagents were used as received without further treatment. Glass slides and Q235 steel were used as substrates on which the coatings were applied.

2.2. Preparation of coating

Firstly, 5 g of ZnO was ultrasonically dispersed in 20 g of ethyl acetate for 15 min. On the other hand, 20 g of ethyl acetate was added into the vessel containing 10 g of PDMS in order to reduce the viscosity of PDMS. This was achieved by magnetic stirring for about 5 min. Thereafter, 0.1 g of FDTS was added into the PDMS solution and allowed for another 5 min of stirring, followed by addition of 0.5 g of hexadecyltrimethoxysilane (HDTMS). The dispersed ZnO solution was added and the resulting mixture was allowed for 10 min stirring after which 1.0 g of curing agent was added. The entire mixture was allowed for homogenous mixing for more 10 min. This coating preparation was carried out at a heating temperature of 35 °C. Similar procedure was repeated for other coating formulations containing 0.2 g FDTS and 0.4 g of FDTS addition. Again, for comparative analysis, another coating preparation was carried out at 35 °C without FDTS addition. Consequently, four different coating formulations were obtained and applied on glass and Q235 steel substrates by spin coating technique. Then the coatings were cured in oven set at 40 °C for 7 days to allow for sufficient curing. The average thickness of the coating on steel was measured using the Positest thickness gauge, while that on the non-conducting glass substrate was measured with a vernier caliper.

2.3. Coating characterization

2.3.1. Adhesion strength test

Quantitative adhesion strength test was carried out on the steel substrates using a Defelsko Positest pull-off adhesion tester. This is to evaluate the basic adhesion capability of the coatings. A loading fixture, commonly called a dolly or stub, was affixed by an adhesive to the coated Q235 steel substrates and was allowed for 24 h to ensure proper adhesion. By use of a portable pull-off adhesion tester, a load was increasingly applied to the surface until the dolly was pulled off. The force required to pull the dolly off the coated substrates yielded the adhesion strength in mega Pascals (MPa).

2.3.2. Surface wettability measurement

Contact angle measurement which is a measure of wettability was undertaken to assess the hydrophobicity of the obtained coatings. An automatic contact angle goniometer, model JCY series from Shanghai Fangrui Instrument Company Ltd. was used to record the static water contact angle. The measurements were conducted with a 6 μ L droplet size. Immediately the water droplet rested on the coating surface, the CCD camera captured the curvature profile and with the help of the in-built software, the static water contact angle, work of adhesion and surface energy of the coating were measured. The final values of static water contact angle, work of adhesion and surface energy of the coating reported are based on average of five measurements conducted on a given sample.

2.3.3. Surface morphology and chemical composition analyses

The surface morphologies of the coatings were obtained by a scanning electron microscope (SEM) INSPECT F50 model under an operating voltage of 25 kV. The X-ray photoelectron spectroscopy analysis was conducted using Escalab 250 Thermo Fisher XPS system with 150-W Al K α radiation at 1486.6 eV. The C1s, Si2p, F1s, Zn2p, Cl2p, and O1s core level spectra were obtained at

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