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Full Length Article

A sturdy self-cleaning and anti-corrosion superhydrophobic coating assembled by amino silicon oil modifying potassium titanate whisker-silica particles

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ABSTRACT

A sturdy self-cleaning and anticorrosion superhydrophobic coating based on poly(phenylene sulfide) (PPS) matrix has been successfully fabricated by combination of sol-gel and spraying technology without using any fluorine materials. The prepared coating possessed excellent superhydrophobicity with the water contact angle (WCA) $(161 \pm 1.2)^{\circ}$ and slide angle (SA) $(2 \pm 1.5)^{\circ}$, which was ascribed to the synergistic effect of low-surface energy material amino silicon oil (ASO) and the binary potassium titanate whisker-silica (PTW-SiO_2) composite particles formed by in-situ growth of SiO_2 on modified PTW via sol-gel. Moreover, The PPS/ASO/PTW-SiO_2 superhydrophobic coating exhibited decent self-cleaning property with clean surface even after 100 times immersion in muddy solution. The abrasion test demonstrated that the mechanical stability of prepared coating was about 2 times of the pure PPS coating. Simultaneously, the potentiodynamic polarization and electrochemical impedance spectroscopy testified the excellent corrosion resistance of prepared coating with the performance of lower corrosion current (1.289×10^{-10} A/cm^2) and high protection efficiency (99.999%) even after immersion in 3.5 wt.% NaCl solution for 28 days. It is believed that this sturdy self-cleaning and anti-corrosion superhydrophobic coating might have a promising application prospect in industry.

1. Introduction

A superhydrophobic surface with water contact angle (WCA) beyond 150° and slide angle (SA) under 10° has received much attention in recent years [1]. The special surface makes it successfully applied in the area of water repellency [2], self-cleaning [3], drag reduction [4], anti-icing [5], anti-bio-fouling [6], anti-corrosion [7], oil/water separation [8] and so on. In common, the resulting superhydrophobic surface is ascribed to the combination of the low-surface-energy materials and hierarchical surface structure [9], which can be prepared by various methods such as chemical vapor deposition (CVD) [10], template-based extrusion [11], electrospinning [12], self-assembly extrusion [13], plasma etching [14], sol-gel process [15], layer by layer deposition [16], and lithographic methods [17]. At present, spraying hydrophobic nanoparticles deposition is considered to be one of most potential methods used in preparing superhydrophobic surface [18,19]. The method mentioned above can not only be used for large-scale preparation, but also be used in repairing the degradation superhydrophobic coating by respraying. For low surface energy materials, fluorocarbons are usually employed to fabricate superhydrophobic products. For instance, Wang et al. fabricated a superhydrophobic and superoleophobic fabrics modified with a hydrolysis product from fluorinated alkyl silane (FAS) and fluorinated-decyl polyhedral oligomeric silsesquioxane (FD–POSS) [20]. Privett et al. have synthesized a superhydrophobic xerogel coating by mixing nanostructured fluorinated silica colloids and fluoroalkoxysilane, whose WCA could reach to 167° [21]. However, any further using of the fluorocarbons, not only increases the preparation costs, but also leads a matter of concern to the environment. Fortunately, some fluorine-free interface materials with low surface energy have been discovered as modifier to construct superhydrophobic surface due to their low-cost and innocuous to the environment. For example, a fluorine-free superhydrophobic coating has been prepared by Wu et al. with low-cost method of spray-coating metal alkylcarboxylates onto virtually substrates [22]. Zhao et al. reported a water-based and non-fluorinated sol-gel method for ambient healing superhydrophobic fabric coatings [23]. A robust

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superhydrophobic coating was fabricated on various substrates using polydimethylsiloxane (PDMS), tetrahydrofuran (THF) and water as raw materials via phase-separation method [24]. However, the studies concentrating on key performance of coating for the practical application, such as corrosion resistance and mechanical stability, were rare. Therefore, the further studies and developments are necessary for preparing excellent fluorine-free superhydrophobic coatings.

As a semi-crystalline engineering thermoplastic material, the molecular structure alternated by para-substituted phenylene rings and sulphur atoms, poly(phenylene sulphide) (PPS) possesses excellent high stiffness, modulus and thermal stability, good chemical and anti-aging, fatigue resistance as well as easy processability [25,26]. So far, commercial PPS powder in the market has solved its poor physical properties such as brittleness and easy to crack, becoming a very promising matrix applied in anti-corrosion coating fields. Thus, it is a great option for us to use the polymer as film-forming substance for fabricating sturdy superhydrophobic coatings.

In comparison with the general fiber such as glass fiber, carbon fibers, etc, potassium titanate whisker (PTW) with the size of tiny fibrous sub-nanometer is especially suitable for enhancing the microstructure of superhydrophobic coatings due to its excellent chemical stability, abrasion resistance, mechanical reliability and the high ratio of performance to price [27,28]. It is widely known that the hierarchical structure on the superhydrophobic coating shows better hydrophobicity and abrasion resistant than any single structure. The construction of nano-micro structure can be achieved by grafting SiO_2 on the surface of PTW in sol-gel method. However, it is not effective to modify whisker surface by using ordinary fiber grafting method on account of its smooth surface and stable chemical properties [29]. In nature, marine mussels can firmly adhere to solid surfaces even under rigorous conditions by secreting a layer of adhesive proteins. Researches have revealed that the strong adhesion of mussels is attributed to dopamine and its analogues contained in 3,4-dihydroxyphenylalanine (DOPA) [30,31]. Therefore, adhesion between PTW and nano-SiO_2 can be enhanced by selecting dopamine. Due to the polarity of amino, environmentally-friendly amino silicone oil (ASO) can interact and bring forth very strong orientation and adsorption with the hydroxyl and carboxyl groups on the surface of fiber, methyls of which are repelling to the water molecules [32,33]. Thus, the ASO can act as low-surface free energy for preparing a superhydrophobic coating [34,35].

In this work, we have successfully fabricated a sturdy superhydrophobic coating by adding PTW-SiO_2 modified with ASO into PPS matrix via a simple spraying method. Under optimal condition, the prepared coatings exhibit excellent superhydrophobic ability with WCA $(161 \pm 1.5)^{\circ}$ and SA $(2 \pm 1.2)^{\circ}$, respectively. Compared with others' work, dopamine was first used as interface binder for stable loading silica nanoparticles on the surface of PTW, and more detailed elaborations of the wettability on the composite coating filled with PTW-SiO_2 were described. It has a certain guiding significance for other functional coatings fabrication. Meanwhile, the sample was experienced a series of characterization to investigate their chemical properties and surface morphology. The results of self-cleaning and friction test indicated that the final coating possessed excellent mechanical stability, being capable of remaining long-term hydrophobic ability under harsh environment. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) results obtained by electrochemical workstation were discussed in detail, suggesting that the final coating had the superior anti-corrosion performance. Thus, it is believed that the PPS/ASO/PTW-SiO_2 superhydrophobic coating has huge potential in industrial applications.

2. Materials and methods

2.1. Materials

Poly(phenylene sulfide) (PPS, Mn: 4×10^3 to 5×10^3, yellow color) with a diameter of approximately 30 μm was supplied by Yuyao Degao Plastic Technology Co. Ltd, China. Potassium titanate whisker (PTW, $K_2Ti_6O_{13}$) in average diameter and length of 1 and 20 μm respectively was manufactured by Shenyang Jinjian short fiber Co. Ltd (China). Dopamine and tris(hydroxymethyl) aminomethane hydrochloride (Tris–HCl) were purchased from Suzhou Tianke Trade Co. Ltd (China). Tetraethylorthosilicate (TEOS) was obtained from Aladdin. The absolute ethanol, ethyl acetate and ammonium hydroxide ($NH_3 \cdot H_2O$) were bought from Huadong Reagent Factory, Shenyang, China. Amino Silicon Oil (ASO) was provided by Jinan Guobang chemical Co. Ltd (China). All reagents were used as received. Deionized water was applied in all experimental process.

2.2. Methods

2.2.1. The hydrophobic modification of PTW

The modification process of PTW was mainly divided into three steps:I. 0.2 g PTW was dispersed in 100 ml distilled water with ultrasonic treatment for 10 min. Then 0.12 g Tris–HCl and dopamine were added into above solution with magnetic stirring for 24 h to promote the self-polymerization of dopamine. The activated PTW can be obtained by filtration and drying. II. 0.2 g activated PTW was ultrasonically dispraised in 10 ml absolute ethanol for 30 min. 1 ml $NH_3 \cdot H_2O$ was then added into above solution with continuous magnetic stirring to form an uniform solution A. 1 ml TEOS was dissolved in 2.5 ml of ethanol to form a solution B. The activated PTW was grafted with SiO_2 nano particles by adding dropwise solution B into solution A about 10 min. After the magnetic stirring for 24 h, the nano-SiO_2 structures were formed on the PTW surface by the hydrolization of TEOS. III. 0.005 g ASO in 1 ml ethyl acetate was drop slowly into 0.2 g PTW-SiO_2 in 9 ml of ethanol with magnetic stirring. The modification of the PTW covered by nano-SiO_2 was proceeded with the water bath heating in 80 ° until the solvent volatilization completely. The resulting product was abbreviated as ASO/PTW-SiO_2. In order to investigate the effect of grafted SiO_2 on the wettability property of samples, the ASO/PTW was also obtained by the same step III.

2.2.2. The preparation of PPS composite superhydrophobic coatings

Before spraying, the aluminum (1100 grades, $50 \times 50 \times 1\ mm^3$) plate was polished with 1000 mesh sandpaper to remove surface oxide film and get relatively surface roughness. The polished Aluminum was then cleaned in absolute ethanol solution with the ultrasonic for 10 min to remove the grease on the surface. After being dried under 80 ° in an oven for 30 min, the pre-treatment of base plate was accomplished.

0.1 g ASO/PTW-SiO_2 and 0.9 g PPS was ultrasonically dispersed in 15 ml ethanol for 30 min. Whereafter, the superhydrophobic coating was prepared by spraying the above solution onto the pretreated aluminum plate using a spraying gun with the heat-treatment in 320 ° for 60 min. The distance between the substrate and gun was 20 cm and the type of gas was air. The time of spraying was about 5 min. Optimal operating conditions have been discussed in the previous experiments (Fig. S1 ESI†).

2.3. Characterization

To evaluate the wettability on the surface of the samples, the WCAs and SAs of a droplet (5 μL) were measured by contact angle