



A biomimetic spherical cactus superhydrophobic coating with durable and multiple anti-corrosion effects

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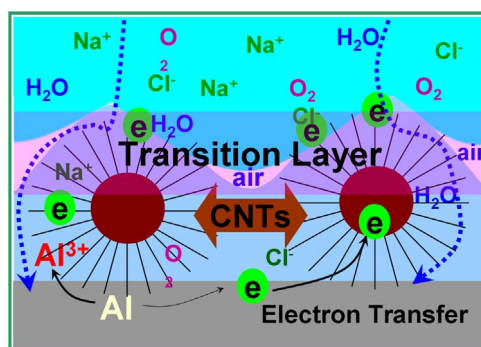
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HIGHLIGHTS

- The superhydrophobic PCFn coating at different substrates was fabricated.
- The PCFn coating showed excellent self-cleaning and corrosion-resistant properties.
- It promises a wide applicability of the PCFn coating in different engineering process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Biomimetic structure
Polysulfone nanocomposite coating
Carbon nanotube
Superhydrophobic
Multiple corrosion resistance
Durability

ABSTRACT

Superhydrophobic polysulfone (PSU)/carbon nanotubes (CNTs) nanocomposite coating with biomimetic golden spherical cactus surface structure (with micro-sphere and nano-thorns) was fabricated by electrostatic powder-spraying method. The superhydrophobic PSU-CNTs-FEP nanocomposite (PCFn) coating can be applied to different substrates such as aluminum plate, steel plate, glass plate, and steel pipe, which exhibited a maximum water contact angle all beyond $164 \pm 1.5^\circ$ and low slide angle of less than $5 \pm 0.5^\circ$. The morphology, chemical composition and spherical cactus structure formation of the coatings were investigated. The electrostatic spraying and micro-phase separation promise a synergistic effect on promoting the superhydrophobicity, self-cleaning and high durability of PCFn coating. Moreover, the PCFn coating demonstrated unique multiple anti-corrosion effects, providing with air bubble corrosion protection, physical shielding and decreasing interfacial electronic agglomeration effect, which promises the wide applicability of the PCFn coatings in different engineering processes.

1. Introduction

Inspired by natural lotus leaves [1,2], superhydrophobic coatings

have gained tremendous research interests for their wide range of applications in different fields [3,4] such as petroleum pipeline industry [5], metal corrosion protection [6], biomedical engineering [7], and

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etc. The unique anti-fouling, self-cleaning and anti-corrosion properties of the superhydrophobic coatings promise excellent material performance in above-mentioned applications [8]. It is desirable and actually in huge demand to combine different functions into one single coating. Jiang et al. [9] proposed a facile method to fabricate a foam with superhydrophobicity and superoleophilicity. Sharma et al. [10] reported a novel superhydrophobic film with exceptional thermal, corrosive and environmental stability. While in reality, superhydrophobicity often sacrifices other properties such as mechanical strength of a coating and durability of surface microstructure [11,12]. It is true that coatings fabricated by convention spraying methods are not able to provide all the mentioned properties simultaneously while exist the problem of surface hydrophobicity degrades quickly over the time of operation [13,14]. Compared with the traditional solvent and paint spraying method, powder coating method acquires obvious advantage of environmental friendliness since solvent usage can be avoided during the spraying process [15,16]. As a facile processing technology, electrostatic powder spraying has already been widely adopted in industry for fabricating functional coatings [17]. This technique has the capability to paint charged nanoparticles [18], like CNTs [19,20], onto the surface of substrate uniformly [21]. The coulombic attraction between charged particles and oppositely charged substrate allows fast movement of particles and polymer powders onto substrate, and generates a large impact force that facilitates the formation of a thin and compact coating.

Over the past decades, researchers have developed versatile methods to fabricate surfaces or coatings with superhydrophobic properties. Rao et al. [22] demonstrated a simple dip coating method for the preparation of thermally stable, transparent superhydrophobic silica films on glass substrates at room temperature. Rutledge et al. [23] produced superhydrophobic fabrics by combining electrospinning and initiated chemical vapor deposition. Ramasamy et al. [24] fabricated superhydrophobic silicon nanostructures by anisotropic etching of silicon coated with a thin hydrophobic layer. The coating exhibited outstanding superhydrophobic properties. However, several other factors have not been considered in this work such as heat-resistance and corrosion-resistance, which may cause a weak boundary layer on the metal surface and the poor interfacial adhesion under crucial working conditions. Recently, electrostatic powder spraying technology has been adopted by Lin et al. [25] to fabricate superhydrophobic fabric with remarkable self-healing capability against both physical and chemical damages. Even though electrostatic powder spraying is widely adopted as a mature coating technique in this field, it still remains a great challenge to enable a durable superhydrophobic coating with multiple functionalities [26,27].

As a member of thermoplastic polymers, polysulfones (PSU) have found wide applications in the coating materials for their resistance to high temperatures and hydrolysis stability [28]. However, the polysulfones coating has low resistance to some solvents and weathering instability, which can be offset by adding other materials into the polymer [29]. Owing to the high aspect ratio, high conductivity coupling with good mechanical strength and thermal stability, carbon nanotubes (CNTs) are considered as ideal reinforcement materials for polymer coatings [30]. Predictably, the combined application of PSU and CNTs in coating materials will achieve a good general performance. It is generally known that the rough surfaces and low surface energy materials are important elements in fabricating a superhydrophobic surface [31]. To get pure carbon-fluorine structure or fully fluorinated, fluorinated ethylene propylene (FEP) has been used in superhydrophobic coating [32].

In this paper, PSU-CNTs-FEP nanocomposite (PCFn) coatings are prepared on different substrates via electrostatic powder spraying technique. The prepared PCFn coating combines the advantages of PSU, CNTs and FEP that exhibits golden spherical cactus structure, which possesses excellent superhydrophobic, self-cleaning, durability and corrosion-resistant properties. The PCFn coating demonstrated

excellent superhydrophobicity ($158 \pm 1.5^\circ$) and high oleophobicity ($148 \pm 1.5^\circ$). The surface properties can be remained even after heat treatment at 500°C and sands impacting test. Furthermore, the PCFn coating shows outstanding anti-corrosion property in harsh corrosive environments by providing with air bubble corrosion protection, physical shielding and decreasing interfacial electronic agglomeration effect. The fabricating method of PCFn coating is simple, cost-effective and environmentally benign. The PCFn coatings are expected to be widely used in industrial applications such as liquid transportation, drag reduction and corrosion resistance.

2. Experimental

2.1. Materials

Polysulfone power (PSU 3010, $15\ \mu\text{m}$) was obtained from Polyplastics Company (Japan). Epoxy resin (EP, E44) was purchased from Miller-Stephenson (USA). Fluorinated ethylene propylene (FEP, $6.5\ \mu\text{m}$) was purchased from DuPont (USA). Multiwall carbon nanotubes (CNTs) with $10\text{--}25\ \text{nm}$ diameter and $1\text{--}5\ \mu\text{m}$ length were provided by Beijing Boyu New Material Technology Co. Ltd. The anhydrous alcohol was provided by Quan Rui Reagent Co. Ltd of Liaoning (China). The ethyl acetate was purchased from Huadong Reagent Factory Shenyang (China).

2.2. Preparation of coatings

The superhydrophobic coating was prepared by electrostatic powder spraying method. The substrate was firstly polished with 1000 grade waterproof abrasive paper to remove surface impurities, and then washed with anhydrous alcohol. After sonication in water for 10 min and dried in air at room temperature, the substrate was ready for coating. EP was firstly sprayed on the substrate as a transition layer between functional coating and substrate. A mixture of PSU, 1 wt% FEP and 5 wt% CNTs was stirred at 1500 rpm for 5 min, after that, the mixture powder was processed by COLO-900T electrostatic spraying system under the voltage of 80 kV and air flow of $4\ \text{m}^3/\text{h}$. The samples were grounded as the positive electrode. There was an electric discharge at the outlet of the spray gun, and the negative pressure generated by the gun could produce a corona discharge. The resultant powder was electrostatically sprayed on different substrate (such as aluminum (Al), glass, steel plate and steel pipe) surfaces forming functional coatings, and then these coatings were cured at 220°C for 30 min. By using the same method, the PSU coating, the CNTs coating, and the coatings without FEP (PSU-1%CNTs and PSU-5%CNTs) were also produced and cured at 220°C for 30 min in order to compare with the PSU-CNTs-FEP composite coating. The corresponding performance of samples that prepared by electrostatic powder spraying without curing at 220°C had been carried out.

2.3. Characterization

The surface wettability of the coatings was measured by contact angles (CAs) and sliding angles (SAs) with $5\ \mu\text{L}$ liquid droplets using a contact-angle meter (JGW-360A, Chengdeshi Shipeng Detection Equipment Co. Ltd) at room temperature. The average value was reported by taking at least five measurements in different regions of the coating. In order to evaluate the hydrophobicity and oleophobicity of the coatings, the CAs of both water and glycol were measured. The sliding performance was investigated by blue ink (that can be availed from a stationery shop) and glycol on the surface of the prepared coatings. The morphology of the coating was characterized by scanning electron microscopy (SEM) (Quanta 200). Tensor 27 infrared spectrometer (FT-IR) and X-ray diffraction (XRD) (D-max 2200) were used to study the chemical composition and crystalline structure of the prepared coatings, respectively. The self-cleaning and anti-fouling

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