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A fluorine-free superhydrophobic PPS composite coating with high thermal stability, wear resistance, corrosion resistance

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ABSTRACT

A simple spraying method was used for fabricating stability and wear-resistance fluorine-free superhydrophobic coatings by introducing the silicone rubber (SR) particles and carbon nanotubes (CNTs) into poly(phenylene sulfide) (PPS) matrix. When the weight content of PPS:SR:CNTs = 0.7:0.3:0.015, the water contact angle (WCA) and the slide angle (SA) of the prepared coating were (164 ± 1.5)° and (1 ± 0.8)°, respectively. The WCA of the prepared coating also possessed good durability, which could maintain (141 ± 1)° after 10,000 times of abrasion. It was mainly ascribed to the internal micro/nano-structure designed by combining SR particles with CNTs and low surface free energy groups Si-CH_3 of SR. Moreover, the prepared coating exhibited excellent wear resistance, which was 2 times higher than pure PPS coating. The adhesive ability of the prepared coating corresponded with Grade 4 according to ASTM D3359 due to the synergy of SR particles and CNTs. The test results of thermogravimetric (TG) indicated the outstanding thermal stability of the prepared coating with weight loss less than 10% under 478 °C. Furthermore, the corrosion resistance of the aluminum could be effectively enhanced by the prepared superhydrophobic coating with performance of higher corrosion potential −756.69 mV and lower corrosion current 4.97×10^{-8} A/m^2 after 15 days immersion in 3.5 wt.% NaCl solution. Therefore, it is believed that the prepared coating with excellent thermal-stability, wear-resistance and corrosion-resistance might have a huge potential in large-scale industrial application.

1. Introduction

A highly hydrophobic surface, on which the water drop has static contact angles (WCAs) larger than 150° and the slide angles (SAs) less than 10°, is commonly called a superhydrophobic surface [1]. It is inspired by lots of plants and animals in nature [2–5], and the most representative is the "lotus effect" [6]. The superhydrophobic surface with special performance has vast foreground in applications and can be applied to water proof [7], anti-fog [8], self-cleaning [9], oil/water separation [10], fluid drag reduction [11]. Previous researches have shown that the micro-nano binary structure and low surface energy materials are vital for fabricating a superhydrophobic surface [12]. Various methods have been developed for preparing superhydrophobic surfaces [13–19]. The spraying deposition of fillers is considered to be one of most potential methods used in preparing large-scale superhydrophobic surfaces [20,21], with the advantage of stronger applicability and controllability, simple operation and cost-effectiveness.

In previous studies, many researchers chose fluorine chemical as the lowest surface energy material to prepare superhydrophobic surfaces [22,23]. In spite of this, the fluorine chemical materials still have a limited application because of high-cost and environmentally hazardous nature. Thus, more and more researchers have begun to adopt the way of fluorine-free materials to fabricate superhydrophobic coating via introducing liquid siloxane polymer or long-chain fatty acids. For example, Wu et al. prepared a low-cost non-fluorine superhydrophobic coating by spraying metal alkylcarboxylates onto any substrates [24]. Wang et al. fabricated a hierarchical structured copper mesh film, which attained the superhydrophobic ability with the modification of the long-chain fatty acid mono-layer [25]. A water soluble siloxane emulsion mixed with silica nanoparticles (7 nm) possessing excellent hydrophobicity was manufactured by Dimitra et al. for protecting the large surface, without using any of organic solvent [26,27]. Panagiotis et al. produced superhydrophboic composites films by spraying suspensions mixing SiO_2 nanoparticles in solutions of poly(methyl methacrylate) and poly(alkyl siloxane), respectively, on glass surfaces [20]. Ioannis et al. sprayed the suspensions, which were the commercial hydrophobic poly(alkyl siloxane) enriched with hydrophilic Al_2O_3 nanoparticles in different concentrations, on the glass surfaces to obtain a surface WCA 160° [28]. The existing reports were mainly aim at using fillers (microparticles, nanoparticles and other) for fabricating super-

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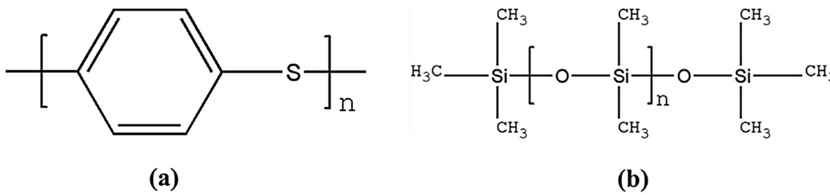

Fig. 1. The structures of PPS (a) and SR particle (b).

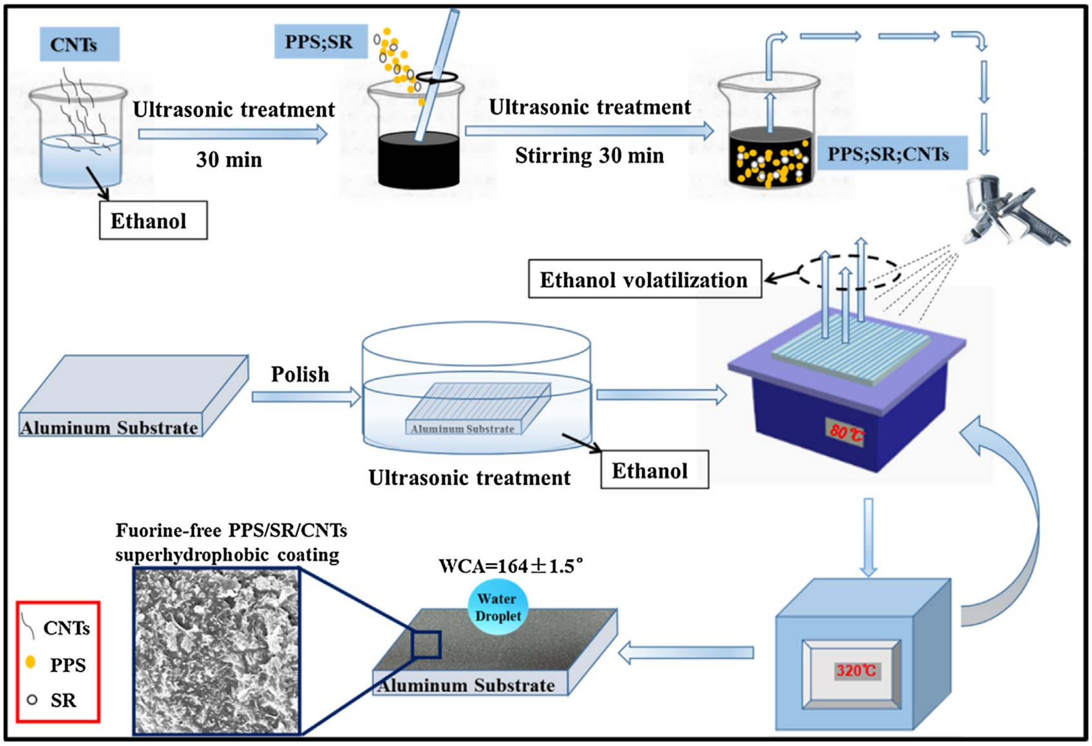

Fig. 2. Schematic illustration of the fabrication process for superhydrophobic coating with a dual nano/micro scaled two-tier roughness.

hydrophobic coatings and had made a great contribution to the effect of microscopic particles on the wettability of coatings. Nevertheless, there was rare detailed exploration on some key performances of prepared coatings for practical application, such as anti-corrosion property, mechanical stability. We can't judge whether these coatings could be used in industry under harsh conditions. Therefore, fluorine-free superhydrophobic coatings with excellent integrated performance still need to be further studied and developed.

As a high performance engineering plastics with an ordered alternating arrangement of phenylene and sulfide atoms (Fig. 1a), poly (phenylene sulfide) (PPS) has unique properties. It not only has the performance of general engineering plastics but also possesses high thermal stability, excellent chemical corrosion resistance, good flame resistance, and non-toxic [29]. Thus, PPS can be used into film forming substance with the superb ability of bonding with various metal, nonmetal materials and polymers, widely applied in many fields such as heat sensor, filter in chemical engineering and industrial facilities, automobile and aerospace industry [30]. Silicone rubber (SR) particle is a macro-molecular elastomer material with a main chain of Si-O units and side chains of organic groups (primarily methyl) (Fig. 1b). It has many excellent properties, such as heat-resistance, flexibility and chemical stability [31,32]. Due to the low energy surface, the SR particles exhibit good water repellent property and hold back continuous water spreading on the surface. Momen et al. elaborated a nanostructured superhydrophobic surface by applying RTV silicone rubber coating on the anodised aluminum substrates [33]. Hence, the SR particles are capable of applying in superhydrophobic coating as low surface energy fillers. Carbon nanotubes (CNTs) is a kind of nanomaterials with great aspect ratio, lightweight and perfect hexagon structure connection, which has unique physical properties, superior toughness and strength [34]. Therefore, CNTs is widely applied to enhance strength, elasticity, fatigue resistance and isotropic of composites materials with the suitable capacity [35].

In this paper, we have successfully fabricated a fluorine-free superhydrophobic coating through a simple spraying method by introducing SR particles and CNTs into PPS matrix. The prepared coating showed great wettability with higher WCA (164 ± 1.5)° and lower SA (1 ± 0.8)°, and exhibited good abrasion resistance with half weight loss and lower friction coefficient than pure PPS coating. In particular, the produced coating was subjected to chemical analysis (FT-IR and XRD analysis), thermal analysis (DSC and TG analysis) and its adhesive ability and corrosion-resistance were evaluated in detail. It is believed that the PPS/SR/CNTs superhydrophobic coating has broad application prospects. It's worth noting that the described procedures and interesting results presented in this article are full of guiding significance to practical applications.

2. Materials and methods

2.1. Materials

Commercial SR (silicon rubber) particles GM300 with average diameter of about 41 μm were supplied by Tianjin Mingji Jintai Plastic Technology Co. Ltd, (China). Poly(phenylene sulfide) (PPS,

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