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Review

Corrosion-resistance, robust and wear-durable highly amphiphobic polymer based composite coating via a simple spraying approach

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ABSTRACT

This study successfully developed a simple spray approach to fabricate a robust highly amphiphobic poly(phenylene sulfide) (PPS)/fluorinated ethylene propylene (FEP)/poly(dimethylsiloxane) (PDMS) composite coating with high-performance in corrosion-resistance, wear-durable through designing the nano/micro two-tier roughness and fluorinating with materials of the low surface free energy. The highly amphiphobic and tribological properties of the coatings were measured by the contact angle meter and the pin-on-disc tribometer, respectively. It was interested to observe that the composite coating showed superhydrophobic and highly oleophobic simultaneously, with the highest contact angles of water, glycerine and ethylene glycol up to $173 \pm 2.1^{\circ}$, $142 \pm 2.2^{\circ}$ and $139 \pm 2.1^{\circ}$, respectively. Moreover, the surfaces of the PPS/FEP composite coatings were investigated by means of Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometry (XRD) and energy-dispersive X-ray spectroscopic (EDS). The robust highly amphiphobic coating also showed remarkable durability against strong acid and strong alkali in the pH range from 1 to 14. After 47 h sliding wear test, no failure sign on the PPS/45%FEP/PDMS composite coating was observed. Such unique characteristics were attributed to the synergistic effect of the nano/micro two-tier roughness and fluorinating with low surface free energy groups ($-CF_2-$, $-CF_3-$).

Contents

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1. Introduction

Amphiphobic coatings, which show a high contact angle (CA) for both water and oil, have attracted great attention in recent research owing to their broad application prospect [1–3], including self-cleaning surfaces [4], anti-adhesion films [5], stain resistant coatings, and water–oil repellent fabrics [6–9]. Usually, the amphiphobic coatings can be achieved by one of two general ways: they can be fabricated directly by creating nano/micro two-tier roughness structure or re-entrant geometries and overhang structures on the hydrophobic substrates [10–13]. Moreover, they can be produced by modifying rough structures with materials that have a low surface free energy [14–17].

Up to now, many strategies and techniques have developed to achieve hydrophobic and oleophobic coatings, including: chemical vapor deposition [18], electro spinning [19,20], template etching [21], lithography [22], spraying [23,24], sol–gel method [25] or self-assembly [26,27]. However, most of aforementioned methods require some special equipment, complex process, costly materials or long period. By contrast, spraying is an efficient and low-priced method for making amphiphobic coatings. There are very few artificial highly amphiphobic surfaces that have been fabricated by spray coating.

As an engineering plastic, poly(phenylene sulfide) (PPS) is an appropriate matrix for fabricating coatings with hydrophobic properties due to the outstanding thermally stabilization, solvent resistance, adhesion [28]. Fluorinated ethylene propylene (FEP) behaves unique properties for self-lubricate, low surface energy and high chemical inertness, which is widely used to improve the tribological properties of coatings [29]. Polydimethylsiloxane (PDMS) possesses excellent properties such as chemical inertness, low surface energy, and weatherability [30]. However, it is rare for them to be used fabricating coatings with amphiphobic performance.

It has important significance to improve the surface hydrophobic and oleophobic properties of oil pipeline coatings for the purposes of saving energy, enhancing the corrosive and friction wear resistance [31]. Nevertheless, because of harsh conditions, it is difficult for coating in petroleum pipeline to hold its amphiphobic for a long time due to wear problem. Thus, seeking a right way to solve mechanical damage and oil pollution problems of amphiphobic coatings has become an insistent demand.

In this work, a simple spraying technique is used to fabricate the above mentioned PPS–matrix composite coating with good performances in corrosion-resistance and wear-durable by nano/micro two-tier roughness design and modification of the lowest surface free energy groups (–CF2–, $-CF_3-$). The whole procedures are simple to carry out and environmentally friendly. The corrosion-resistance and wear-durable performance of the PPS/FEP/PDMS composite coatings are investigated and corresponding mechanisms are discussed. Our research provides a new approach to extending the life span of amphiphobic coatings for petroleum pipeline. It is believed that the work is of great interest to researchers, particularly in the fields of multi-functional nanocomposites and amphiphobic polymer coatings.

2. Experimental

2.1. Materials

Aluminum plates (80 mm × 80 mm × 1.27 mm, purity ≥99.9 wt%) are obtained from the Jiayun aluminium product Co. Ltd, China. Poly(phenylene sulfide) (PPS, M_n: 4×10^3 to 5×10^3) in a diameter of approximately 30 μm is obtained from Yuyao Degao Plastic Technology Co. Ltd, China. Fluorinated ethylene propylene (FEP, average diameter of 6.5 μm) is purchased from DuPont, America. Polydimethylsiloxane (PDMS, reagent grade, purity ≥98 wt%) is purchased from Jinan Hailan Reagent Factory of China. The nano-scale SiO_2 particles are supplied by Nanjing Hi-Tech Reagent Factory, China. And ethanol (ET, reagent grade, purity ≥98 wt%) is purchased from Shenyang Huadong Reagent Factory, China.

2.2. Characterization techniques

The morphology of the coatings with one- and two-tier roughness is examined by SEM (Quanta 200). A contact-angle meter (JC2000A) is adopted to measure the CA of liquid droplets on the prepared surfaces. The volume of the individual droplet used for the CA measurement is controlled at around 5 μL. Each CA value is repeated at least in five different positions on the same coating, and the average value is obtained. Composition of the coating was acquired by FT-IR (Tensor27), XRD (D/max2200) data and EDS (2000-4T0300G).

An MPX-2000 pin-on-disc friction and wear tester (Xuanhua Testing Factory, China) is used to evaluate the tribological behaviors of the PPS/FEP/PDMS composite coating. Before each test, the steel pin in a diameter of 3 mm is polished with 1000 grade water proof abrasive paper and then washed with anhydrous ethanol, followed by drying in air. All the tribological tests are operated at standard loading of 1.4 MPa, sliding speeds of 0.47 m/s, ambient temperature of 20–25 °C and a relative humidity of 40–60%. The frictional data is recorded in the current work at a rate of one data per second.

2.3. Sample preparation

The schematic of the fabrication process for amphiphobic coating with a dual nano/micro scaled two-tier roughness is shown in Fig. 1. As the substrate, the aluminum plates are polished with the 1000 grade water proof abrasive paper to remove surface impurities and washed with anhydrous ethanol in an ultrasound bath for 10 min, followed by drying in air at room temperature. PPS and SiO_2 nano-particles, which dispersed in the anhydrous ethanol solvent, are used as starting materials for their low cost and easy manipulation by spraying and then anneal at 320 °C. The powder of PPS/FEP with 3 wt% PDMS as the finished coating is dispersed in the anhydrous ethanol solvent and ultrasonic stirring for 30 min to allow the formation of coating precursors. The above precursors is poured into a spray gun and sprayed onto the starting coating with 0.5 MPa air gas at a distance of L = 20–30 cm. Finally, the samples are calcined at 320 °C for 1.5 h. The thickness of the coatings is about 0.15 mm.

3. Results and discussions

3.1. Surface wettability

Fig. 2 shows the CA and SA measurement results for water of the PPS/FEP composite coating with PDMS or not. It can be observed that the CA of both PPS/FEP and PPS/FEP/PDMS composite coating increases gradually whereas the SA decreases with the increasing FEP content. The measured CA for water on the PPS/45%FEP/PDMS coating reaches a maximum value of about 173 ± 2.1° and the SA reach a value of about 1°, while the CA and SA of PPS/FEP coating is 158 ± 2.2° and 4° to the highest, respectively.

Previous studies have pointed out that the CA for water on the coatings with PPS alone is 96 ± 2.1° because the lack of low surface free energy composite [32]. In this research, the CA reaches 112 ± 2.2° when the content of FEP up to 8%, and the CA is up to 150 ± 2.1° when the content of FEP is 39 wt% as can be seen in Fig. 3, which indicates that the coatings have higher hydrophobicity due to the high concentration of $-CF_2$ and $-CF_3$ groups. It also can be