



Facile preparation of superamphiphobic epoxy resin/modified poly(vinylidene fluoride)/fluorinated ethylene propylene composite coating with corrosion/wear-resistance



Huaiyuan Wang*, Zhanjian Liu, Enqun Wang, Xiguang Zhang, Ruixia Yuan, Shiqi Wu, Yanji Zhu

College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, China

ARTICLE INFO

Article history:

Received 19 March 2015
Received in revised form 31 August 2015
Accepted 1 September 2015
Available online 3 September 2015

Keywords:

Epoxy resin
Poly(vinylidene fluoride)
Superamphiphobic
Reticulate papillae structures
Wear/corrosion-resistance

ABSTRACT

A robust superamphiphobic epoxy resin (EP)/modified poly(vinylidene fluoride) (MPVDF)/fluorinated ethylene propylene (FEP) composite coating has been prepared through the combination of chemical modification and spraying technique. Nanometer silica (SiO₂, 2.5 wt.%) and carbon nanotubes (CNTs, 2.5 wt.%) were added in the coating to construct the necessary reticulate papillae structures for superamphiphobic surface. The prepared EP composite coating demonstrated high static contact angles (166°, 155°) and low sliding angles (3°, 5°) to water and glycerol, respectively. Moreover, the prepared coating can also retain superhydrophobicity under strongly acidic and alkaline conditions. The brittleness of EP can be avoided by introducing the malleable MPVDF. The wear life of the EP composite coating with 25 wt.% FEP was improved to 18 times of the pure EP coating. The increased wear life of the coating can be attributed to the designed nano/micro structures, the self-lubrication of FEP and the chemical reaction between EP and MPVDF. The anti-corrosion performance of the coatings was investigated in 3.5% NaCl solution using potentiodynamic polarization. The results showed that the prepared superamphiphobic composite coating was most effective in corrosion resistance, primarily due to the barrier effect for the diffusion of O₂ and H₂O molecules. It is believed that this robust superamphiphobic EP/MPVDF/FEP composite coating prepared by the facile spray method can pave a way for the large-scale application in pipeline transport.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In nature, it is well known that lotus leaf exhibits self-cleaning property because of the excellent hydrophobicity [1]. Plenty of researchers were inspired to fabricate superhydrophobic surfaces with high static water contact angle (CA > 150°) and low sliding angle (SA < 10°) for industrial application [2,3]. However, with the rapid development of the petroleum industry, the pipeline surfaces with mere superhydrophobicity cannot solve the friction and corrosion problems caused by the internal oil–water fluid [4,5]. Therefore, the preparation of superamphiphobic surface with a CA greater than 150° to both water and oil fluids are an urgent demand. The essential elements of superamphiphobic surfaces are hierarchical structures and low surface energy materials [6]. Currently, various technologies have been applied to fabricate superamphiphobic surfaces, such as chemical etching [7], chemical vapor

deposition [8], electrospinning [9] and spraying [10]. Nevertheless, the real scale-up applications of the aforementioned coatings are scarce due to the unavoidable abrasion and corrosion in the presence of fluid with small solid particles or acidic/alkaline substances [11,12].

Recently, epoxy resin (EP) has been widely used to fabricate superhydrophobic coatings to reduce the abrasion and corrosion in many fields due to its high adhesion and chemical corrosion resistance [13,14]. For instance, Su [15] fabricated a superhydrophobic EP coating by grafting EP on the surface of microsilia and nanosilica, respectively. The prepared coating demonstrated a water CA as large as 165° and a SA as small as 2.5°, showing the same capability as lotus leaves. Yilgor et al. [16] developed multi-step spin-coating procedures to fabricate a superhydrophobic EP coating onto glass surface, which displayed WCA larger than 170° and very low contact angle hysteresis of less than 3°. Although EP is widely used to prepare superhydrophobic coatings, the large-scale applications of these surfaces are dramatically limited by the intrinsic brittleness and poor wear resistance of EP [17,18]. Therefore, there remains an urgent need to overcome the significant defects

* Corresponding author.

E-mail address: wanghyjji@163.com (H. Wang).

associated with EP. Traditional methods to overcome these drawbacks of EP are introducing reinforcing agents and fillers, such as various inorganic nanoparticles or fibers [19,20]. However, there are few reports about modifying EP by macromolecular polymer to prepare superhydrophobic coatings.

Poly(vinylidene fluoride) (PVDF) as a common membrane material possesses excellent ductility and corrosion/wear-resistance [21,22]. Recently, superhydrophobic PVDF composite coatings with excellent mechanical property, self-cleaning ability and high adhesion have been widely reported [23–25]. Moreover, PVDF has been proved that it can form hydroxyl groups on the molecular chain by means of dehydrofluorination under alkaline conditions [26,27]. Considering the hydrogen-bond interaction of the hydroxyl groups [28], the bonding force between EP and the modified PVDF (MPVDF) can be greatly enhanced. The frangibility of the EP coatings may be probably avoided by the introduction of MPVDF. Furthermore, the hydrophilicity of EP coating can be greatly reduced due to the intrinsic low surface energy of PVDF. Therefore, the superamphiphobic EP composite coating can be hopefully achieved by introducing more low surface energy materials and designing the multiscale structures.

In this work, we firstly introduce the macro-molecular cross-linking reaction between MPVDF and EP to prepare a robust superamphiphobic composite coating via simple spraying technique. Nanometer silica (SiO_2) and carbon nanotubes (CNTs) were used to fabricate the requisite multilayer structures for the superamphiphobicity and fluorinated ethylene propylene (FEP) was added to further decrease the surface energy of the composite coating. The prepared coating demonstrated excellent superamphiphobicity to both water ($\text{CA}=166^\circ$, $\text{SA}=3^\circ$) and glycerol ($\text{CA}=155^\circ$, $\text{SA}=5^\circ$), respectively. The wear/corrosion-resistance properties and bending properties of the prepared coating were investigated in detail. It is believed that this work will provide a new-type of robust superamphiphobic EP/MPVDF/FEP composite coating on the oil pipeline and related outdoor equipments.

2. Experimental

2.1. Materials

Commercial PVDF powders (FR904) were supplied by Shanghai 3F Co. Ltd. (China). Fluorinated ethylene propylene (FEP) was purchased from DuPont, USA. EP (E-44) was provided by Nanjing Huntsman Advanced Materials Company (China). Nanometer silica (SiO_2) was provided by Nanjing hydratight nano materials Co. Ltd. (China). Carbon nanotubes (CNTs) were provided by Beijing Boyu New Material Technology Co. Ltd. The ethyl acetate was bought from Huadong Reagent Factory, Shenyang, China. Glycerol, with surface energy close to the oil/water mixture, was selected to test the oleophobic property of the prepared coating.

2.2. Preparation of EP composite coatings

0.5 g PVDF powders were added into 20 mL alkaline solution (5 wt.% NaOH) with magnetic stirring for 12 h at room temperature. After filtration and drying, the modified PVDF powders were obtained.

50 wt.% g EP, 5 wt.% curing agent (ethanediamine), 25 wt.% MPVDF powders, FEP powders (0 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.% and 25 wt.%), 2.5 wt.% SiO_2 and 2.5 wt.% CNTs were ultrasonically dispersed in 500 wt.% ethyl acetate solvent for 30 min. The coatings were prepared by spraying the above solution on the as-treated aluminum plates (type=1100 grade, 80 mm \times 80 mm \times 1 mm) with 0.6 MPa and curing at 180 $^\circ\text{C}$ for 1.5 h.

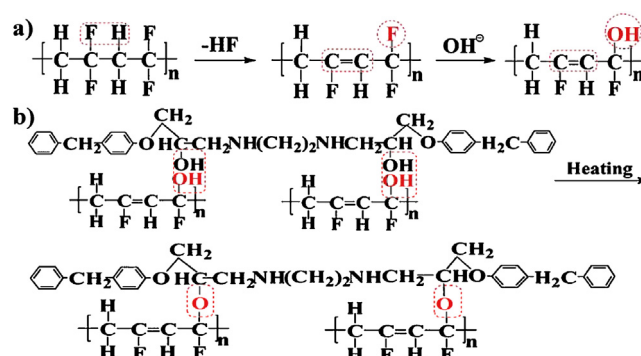


Fig. 1. The modification mechanisms of PVDF (a) and the EP composite coating (b).

2.3. Characterization

The functional groups of the prepared coating samples were characterized by Tensor27 infrared spectrometer (FT-IR). X-ray diffraction (XRD) (D/max2200) was used to obtain the crystal structure of the coating samples. The surface morphologies of the coatings were observed by scanning electron microscopy (SEM) (Quanta 200). Contact angles were measured by Contact Angle Meter (JGW-360A, Chengdeshi Shipeng Detection Equipment Co. Ltd.) with a droplet (5 μL) of distilled water at ambient temperature. The wear resistance tests were carried out on a pin-on-disk friction and wear tester (MPX-2000, Xuanhua Testing Factory, China). The bending properties of the prepared coating were measured using a universal testing machine at the speed of 2 mm/min and the test time is 5 min. The corrosion resistance was evaluated by using the electrochemical workstation (LK 2010) in 3.5 wt.% NaCl solution.

3. Results and discussion

3.1. The modification mechanisms and FT-IR analysis

The chemical modification mechanisms of PVDF and EP are schematically illustrated in Fig. 1. The neighboring hydrogen and fluoride atom in PVDF macromolecules can be removed in the form of hydrogen fluoride molecules under strongly alkaline conditions ($\text{pH} > 14$) [29]. After PVDF dehydrofluorination, the electron-withdrawing inductive effects of the formed $\text{C}=\text{C}$ can promote the nucleophilic substitution of low-activity groups $-\text{F}$ with high-activity hydroxyl groups (Fig. 1a). Afterwards, the cross-linking effect among MPVDF and EP macromolecule chains may be induced by intermolecular dehydration condensation of hydroxyl groups under high temperatures [30]. The significant high bond energy of the generated covalent bonds $-\text{C}-\text{O}-\text{C}-$ can potentially play an important role in enhancing the mechanical properties of the composite coating (Fig. 1b). Furthermore, the introduction of nano- SiO_2 /CNTs and FEP with $-\text{CF}_3$ groups can contribute to the following surface roughness with low surface energy. Accordingly, the superamphiphobic coating with high wear-resistance can be obtained.

To confirm the abovementioned mechanisms, the FT-IR spectra of the pure PVDF, MPVDF, pure EP and the EP composite coating were investigated (Fig. 2). From the spectrum of MPVDF, the new absorption band of $\text{C}=\text{C}$ at 1633 cm^{-1} is generated from the dehydrofluorination of PVDF (Fig. 1a). The significant enhanced band of 3435 cm^{-1} is related to the stretching vibration of $-\text{OH}$, which is consistent with a substitution reaction involving $-\text{F}$. The peaks at 1157 and 874 cm^{-1} indicate the stretching vibration of $-\text{CF}_2$ and the amorphous phase of the PVDF, respectively. For the spectrum

Download English Version:

<https://daneshyari.com/en/article/5348323>

Download Persian Version:

<https://daneshyari.com/article/5348323>

[Daneshyari.com](https://daneshyari.com)