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Superhydrophobic organic and inorganic clay nanocomposites for epoxy steel coatings

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ABSTRACT

A new exfoliated superhydrophobic nanocomposite based on the modification of hydrophobic montmorillonite clay (HMT) was obtained by using hydrophobic silver and iron oxides nanoparticles. The modified HMT nanocomposites were blended with the epoxy resin and cured with polyamine hardener and easily sprayed on the rough steel surface through a facile and effective one-step spraying method. The highest seawater contact angles above 150° obtained for iron oxides/HMT blended with epoxy coating matrix. The atomic force microscope and scanning electron microscope images elucidate that the exfoliation of HMT and the production of rough surface coatings that responsible for the superhydrophobic hierarchical microstructure of iron oxides/HMT epoxy coatings. Furthermore, the porosity and agglomeration of Ag/HMT epoxy composites were responsible for the failure of their superhydrophobicity. The superhydrophobic epoxy nanocomposites were endowed with extraordinary adhesion, mechanical, chemical and abrasion resistivity via salt spray resistance to the high saline seawater environment.

1. Introduction

Steel substrate is widely used in several industrial applications domains due to its outstanding mechanical performance and relatively low cost compared to other alloys substrates although it has some critical issues owing to its high corrosion rate under aggressive conditions [1]. Although the organic epoxy coatings inhibited the steel corrosion but the water diffusion through micro-cracks of epoxy surfaces was identified as epoxy coatings failure [2]. Modification of epoxy with the superhydrophobic surfaces has received considerable attention in the field of anticorrosive, self-cleaning and smart surface technology coatings for the different corrosive substrates over the last twenty years [3,4]. The advanced superhydrophobic surfaces should have two coexistence properties based on a chemical modification to produce solid surfaces having low surface energy and physical property created a hierarchical roughness to alter the wetting characteristics of the organic coatings. There are several nanomaterials proposed to produce superhydrophobic coatings with controlled roughness [5–8]. They applied on different substrate surfaces by using different coating techniques such as spin, spray, dip and layer by layer deposition coatings techniques. The poor wear resistance and mechanical durability [9], porous and lower adhesion of the superhydrophobic films limited their applications as real-world anticorrosive coatings for different substrates. There are numerous techniques reported to control the surface hierarchical microstructure such as chemical etching [10], templating [11], sol-gel [12], and anodization [13]. Moreover, the chemical reactions of superhydrophobic nanomaterials with the epoxy resins facilitated the fabrications of durable superhydrophobic epoxy coatings for the steel substrates [14–16].

The blending of epoxidized fatty acid calcium carbonate nanomaterials during the curing of epoxy resins produced adhered superhydrophobic epoxy coatings with steel substrate [14]. The electroactive epoxy fabricated by replicating the microstructure of lotus, and Xanthosoma sagittifolium leaves were reported as superhydrophobic coatings [16]. Clay is one of the most important cheap filler used to modify the mechanical properties of the epoxy coatings used as anticorrosive coatings in marine aggressive environmental conditions of the steel substrate [17]. There are some drawbacks produced from lower dispersion and agglomeration of clay into epoxy coatings that affected the mechanical properties and anticorrosive characteristics as protective coatings that solved by exfoliation of layered clay nanoparticles [18–20]. It is proposed that the presence of ZrO_2 nanoparticle enhances

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the exfoliation, barrier properties and ohmic resistance of clay silicate layers into epoxy coatings [18]. The encapsulation of two-layered alumino-silicate nano-tubular structure halloysite clay was an effective technique to produce smart, self-healing and superhydrophobic coatings [19]. Spray coating of the modified clay mineral with hydrophobic silane derivatives into epoxy coatings produced superhydrophobic epoxy coatings with superior anticorrosive characteristics for different substrates [20]. The present work aims to modify and exfoliate the montmorillonite hydrophobic clay layer, HMT, to superhydrophobic by interaction with hydrophobic iron oxides and Ag nanoparticles. The prepared nanocomposites were blended with different weights to the epoxy matrix to improve their coatings and anticorrosive properties as a primer for steel substrate. Moreover, the wetting characteristics of the modified epoxy HMT nanocomposite were evaluated to investigate their superhydrophobicity, anticorrosive, protective and self-healing coatings for the steel substrate.

2. Experimental

2.1. Materials

Hydrophobic nanoclay (HMT; nanomer 1–34 TCN) montmorillonite modified with quaternary ammonium (hydrogenated tallow)bis(hydroxyethyl)methyl chloride, ammonium solution (ammonia 28 Wt. %), oleic acid (OA), oleylamine (OAm), ethylene glycol, $AgNO_3$, $Fe(NO_3)_3,9H_2O$, $FeCl_3.6H_2O$, and $FeCl_2.4H_2O$ were purchased from Aldrich-Sigma Co. and used as received. The commercial epoxy resin, SigmaGuard ™ CSF 650 solvent-free; purchased from SigmaKalon Group, was cured with its polyamine hardener and mixed at a volume ratio of 4:1 Wt. % (epoxy resin / hardener). The steel panels having a chemical composition (in wt.%) of 0.14 % C, 0.57 % Mn, 0.21 % P, 0.15 % S, 0.37 % Si, 0.06 % V, 0.03 % Ni, 0.03 % Cr and Fe as balance were used as the substrate. The steel panels were cleaned from oil by washing with xylene, soap, and water followed by the formation of rough surfaces (35 μm) using the blasting machine. The blasted steel panels were finally cleaned with acetone and air-dried before coatings.

2.2. Preparation procedure

a) Iron oxide/HMT composite: Iron cations were prepared by dissolving $FeCl_3.6H_2O$ (1.352 g; 5 mmol) and $FeCl_2.4H_2O$ (0.45 g; 2.5 mmol) in ethylene glycol (60 mL) under vigorous stirring at room temperature. The HMT (2.16 g) was dispersed into ethylene glycol (50 mL) and mixed with iron cation solution under a nitrogen atmosphere and heating up to 70 °C. Ammonia solution (3.8 mL; 50 mmol) was added dropwise to the reaction mixture under heating and the reaction temperature maintained for 6 h. The product was collected by centrifuge at 8000 rpm and washed several times with ethanol and dried at 30 °C under vacuum.

b) Ag/HMT composite [21]: $AgNO_3$ (1.36 g; 8 mmol), $Fe(NO_3)_3,9H_2O$ (0.32 g; 0.8 mmol), and HMT (1 g) were dispersed into OA(80 mL) and OAm (80 mL) solution under vigorous stirring for 2 h. The temperature of the reaction mixture increased up to 150 oC under a nitrogen atmosphere and vigorous stirring. The reaction temperature maintained at 150 °C for 1 h. The product was separated by ultracentrifuge at 20,000 rpm and washed several times with ethanol. The final Ag/HMT composite was dried at 30 °C under vacuum.

2.3. Characterization

The morphology of the modified HMT composites was estimated using a transmission electron microscope instrument (TEM; JEOL JEM-2100 with an acceleration voltage of 200 kV). Their surface morphology evaluated by scanning electron microscope (SEM; JEOL 6510 LA) The diffraction patterns of the modified HMT composites were performed using X-ray powder diffractometer (XRD; Bruker D230 kV, 10 mA) using Cu anode (k = 0.15406 nm) at 25 °C. The wide-angle x-ray diffraction (WAXRD) was performed on a Rigaku D/MAX-3C OD-2988 N X-ray diffractometer with Ni filter and copper target at a scanning rate of $2^{\circ}.min^{-1}$ to evaluate the exfoliation and intercalation of HMT composites. The particle sizes and polydispersity index (PDI) of HMT composites were determined in heptane pH using Laser Zeta meter Malvern Instruments (Model Zetasizer 2000). The contact angles of seawater droplet measurements on the coated steel and glass substrates were evaluated by drop shape analyzer (DSA-100) at room temperature. The surface roughness of the coatings was evaluated by atomic force microscope images (AFM; Agilent5500). The salt spray resistance of the coated steel panels toward seawater was evaluated using salt spray cabinet (manufactured by CW Specialist Equipment Ltd. model SF/450) at a humidity above 99 % and temperature of 35 °C.

2.4. Coatings of the steel substrate

The modified HMT, iron oxide/HMT or Ag / HMT composites were mixed in the presence of acetone (25 Wt. % based on epoxy resin) with commercial epoxy resin with the help of planetary centrifugal mixer (AR-100). The different weight ratios of modified HMT composites were ranged from 1 to 10 Wt. % (based on the total weight of both epoxy resin and hardener). The epoxy HMT composites were mixed with the recommended polyamine hardener. The mixture was then sprayed onto blasted and clean steel panels (roughness 35 μm) with the average dry film thickness of 50 μm. The curing procedure of the modified epoxy HMT composites completed at room temperature for 7 days or at 120 °C for 4 h in the oven to form epoxy nanocomposite on the steel substrate. The same procedure was repeated without using HMT composites to produce blank cured epoxy coatings on the steel substrate.

2.5. Mechanical, chemicals and salt spray resistance of modified epoxy coatings

The mechanical tests such as adhesion (pull-off), hardness and impact were evaluated according to ASTM of organic coatings. The adhesion of epoxy coatings with the steel substrate was determined by using a hydraulic pull-off adhesion tester in the range of 0–25 MPa. Erichsen pencil, model 318S, scratching force in the range of 0.5–20 N was used to determine the hardness of cured epoxy composite films. The abrasion resistance of the cured epoxy films was evaluated according to ASTM D4060-07 for 5000 cycles with 1000 g load.

The salt spray cabinet was used to investigate the salt spray resistance of the epoxy-coated steel panels according to the ASTM B117 procedure using seawater. The chemical resistance of the cured epoxy resins was tested by heating the coated panels at 90 °C for 24 h against aqueous solutions of HCl and NaOH (10 M) different pHs.

3. Results and discussion

The formation of the iron oxides in the presence of ethylene glycol in the presence of ammonium salts was previously reported [22]. The Fe (III) is used only and the Fe (II) was produced from the oxidation of Fe (III) in the presence of ethylene glycol, dehydrated to acetaldehyde [22], to form ferrous hydroxide in the green colloid as following:

$$2OH-CH_2-CH_2-OH \leftrightarrow 2CH_3CHO + 2H_2O \tag{1}$$

$$2CH_3CHO + 2\,Fe\,(III) \leftrightarrow CH_3CO-COCH_3 + 2\,Fe(II) + 2H^+ \tag{2}$$

$$NH_3 + H_2O \leftrightarrow NH4^+ + OH^- \tag{3}$$

$$Fe(III) + 3OH^- \leftrightarrow Fe(OH)_3 \tag{4}$$

$$Fe(II) + 2OH^- \leftrightarrow Fe(OH)_2 \tag{5}$$

The iron oxides expected to form in the following reaction are: