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Bifunctional CuO/TiO_2 nanocomposite as nanofiller for improved corrosion resistance and antibacterial protection

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ABSTRACT

The capability to improve the performance of polymer coatings with the inclusion of nanomaterial is a vital factor for mitigating corrosion and reducing bacterial growth caused by micro-organisms in marine environment. Herein, we report the usage of TiO_2-CuO nanocomposite as nanofillers for epoxy coatings to protect the surface of steel against corrosion and bacterial growth. A novel TiO_2-CuO nanocomposite was synthesized using oxalate method and the composite was characterized for its phase composition and morphology using different techniques such as X-Ray diffraction, Raman spectral studies and scanning electron microscopy with energy dispersive X-ray (EDX) analysis. Surface characterization of synthesized nanocomposite revealed the shape and uniform distribution of CuO and TiO_2 nanoparticles. The results of electrochemical measurements conducted in 3.5% NaCl solution exhibited enhanced corrosion-protective properties of epoxy coatings with synthesized TiO_2-CuO nanocomposites compared with the pure epoxy coating. In addition, the coated mild steel (MS) substrates tested for their antibacterial performance against the Gram-negative bacterium, Escherichia coli, showed that the nanocomposite coatings presented strong antimicrobial activity against Escherichia coli.

1. Introduction

Based on the recent report, the international trade in paints and coatings extended $129 billion in 2015 and it is estimated to raise from almost $132.2 billion in 2016 to $164.1 billion in 2021 at a complex yearly growing percentage of 4.4% from 2016 to 2021. This number have confirmed the increasing the application of protective coatings. It has been estimated that the paint/coating industries are nearly 40% of the total direct expenditures, and the major part of this cost (88%) is ascribed to organic coatings which are employed to protect structural materials in marine environment against corrosion and fouling. In general, the integration of inhibitive pigments in nanometric size into organic coatings delivers remarkable ability for constructing hybrid coatings with multifunctional characteristics rising from the distinctive features of the starting nanomaterials which further alter their protective performance.

Titanium dioxide (TiO_2) nanoparticles, in particular, have drawn considerable attention in the past decades as an inhibitive element with a strong oxidation power, being considered one of the best white pigments in protective coatings and it has almost completely replaced the other white pigments from the coating sector [1]. Saeed et al. have recently evaluated the effects of nano TiO_2 inclusion on thermal, mechanical and corrosion resistance of epoxy coatings [2]. Xiuzhi Zhang et al. have confirmed the improved corrosion performance of the epoxy coatings with TiO_2 nanoparticles due to the lowest diffusion coefficient for the interior passage of aggressive species through the coating in the given system [3]. Ultimately, significant improvement was achieved for the progress of TiO_2-based nanocomposites with other metal oxide nanoparticles such as ZrO_2, ZnO, Nb_2O_5 and CuO to improve and attain the required properties.

On the other hand, copper (Cu) is evidently considered as a marked biocide, and together Cu ions and its nanoparticles have already proved their antibacterial behavior against a wide series of bacteriological organisms [4,5]. Furthermore, CuO nanoparticles are reasonably harmless to living beings. However, they exhibit effective toxicity against a wide-ranging microbes [6]. Shaswat Barua et al. have fabricated the epoxy nanocomposite coatings with CuO nanoparticles and proved its ability to prevent bacterial, fungal and microalgae fouling

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against the tested strains [7]. It has already been reported that epoxy nanocomposites with the inclusion of 5% nano CuO displayed the improved thermal performance owing to the uniform distribution of nanoparticles [8]. In addition, it has been reported that the corrosion resistance of the carbon steel coated by epoxy coating containing Fe_3O_4/CNTs nanocomposite was considerably higher than that of carbon steel coated by pure epoxy coating and epoxy coating containing CNTs [9].

Recently, nanocomposite of CNTs and CeO_2 nanoparticles was utilized as nanofillers in polyurethane coatings and the results revealed improved corrosion protection performance in marine environment than that of the coatings developed without it [10]. Navarchian et al. prepared polyaniline/clay nanocomposite and utilized as nanofillers in epoxy coatings and their results specified that the incorporation of PANI/clay nanocomposite into epoxy paint effects in improved anticorrosion properties on steel in comparison with pure epoxy [11]. Mostafaei et al. have also prepared PANI/ZnO nanocomposites and studied the anti-corrosion behavior of the epoxy binder blended with PANI–ZnO nanocomposites. The obtained results revealed that the existence of ZnO nanorods beside PANI can considerably increase the barrier and corrosion protection performance of the epoxy coating due to the flaky shaped structure of the PANI–ZnO nanocomposites [12].

Considering the synergistic properties of TiO_2 and CuO nanoparticles, combining the two certainly broadens their application potential as nanofillers in protective coatings with improved corrosion and antibacterial performance. George et al. and McDonald et al. have recently fabricated the nanostructured titania-copper composites that combine the photocatalytic activity of TiO_2 and the bactericidal properties of copper [13]. Although CuO-titania nanocomposites have been reported to be advantageous for photocatalytic hydrogen production and gas sensor applications, there is no report dedicated to the use of nanofillers in organic coatings. To our knowledge this multifunctional coating is distinctive in presenting two functionalities; TiO_2 nanoparticles protecting against corrosion and an effective antibacterial performance result from the CuO nanoparticles. The effect of incorporation of these nanocomposites into the epoxy coating on its corrosion protection properties was evaluated using electrochemical impedance spectroscopic measurements in 3.5% NaCl solution.

2. Experimental

2.1. Reagents and chemicals

Titanium dioxide powders (< 25 nm, 99.7%, spec. surface area 45–55 m^2/g), Copper acetate and oxalic acid were procured from sigma Aldrich. Ethanol, was obtained from Alfa Aesar. Epoxy resin (diglycidyl ether of bisphenol A) and polyamide hardener were used to prepare epoxy coatings. MS substrates used as base substrate with weight compositions of 0.040C, 0.350 Mn, 0.022 P, 0.036 S and balance Fe. All the experimental solutions were prepared with deionized water (> 18.2 MΩ-cm) purified using a reverse osmosis and ultrapure water system (Branstead-Thermo scientific).

2.2. Synthesis of cuO-titania nanocomposites

For the synthesis of TiO_2-CuO nanocomposites, 46 mg of Cu (II) acetate (17.0 mM) was dissolved in 15 mL absolute ethanol to make a clear solution. Anatase TiO_2 powder (80 mg) was suspended in resulting solution under stirring. Oxalic acid (5 mL, 24 mM) was added dropwise to the suspension while kept on stirring. The molar ratio of Cu (II) acetate to oxalic acid was kept 1:2 in total volume (20 mL). The mixture was dried in ambient air under fume hood.

The TiO_2-CuO nanocomposite was synthesized in a programmed temperature quartz tubular furnace by heating the dried powder particles in gaseous O_2 atmosphere. The sample was heated at 400 °C for 4 h under continuous flow of O_2 with 25 mL/min. After reaction, the reactor was cooled to room temperature while maintaining O_2 flow at 25 mL/min. The brown color TiO_2-CuO powder was collected and used as such for further study.

2.3. CuO-titania nanocomposites coating on MS substrates

Before coating, all the MS substrates were regularly ground from 400 to 2400 grits emery papers and washed with deionized water and then ultrasonically cleaned in acetone for about 10 min and finally dried in air. Epoxy resin and hardener with a ratio of 1:3 were utilized to prepare epoxy coatings. Firstly, different weight percentage of TiO_2-CuO nanocomposites (5, 10 and 20%) was ultrasonically dispersed in acetone for about 1 h which leads to TiO_2-CuO suspension. The suspension was then transferred to hardener; subsequent dispersion was done by probe sonicator for 10 min followed by warming at 50 °C to gradually vaporize the solvent. Lastly, the TiO_2CuO-hardener mixture was added into the stoichiometric quantity of epoxy resin and stirred using the laboratory mixer. The prepared coatings were applied on MS substrates using bar coater at constant speed and then permitted to dry at room temperature for about 24 h. This led to the formation of a uniform coating with thickness in the range of 40 ± 5 μm. However, epoxy with above 20% of TiO_2-CuO exhibited adhesion issues on the steel surface. Hence, the experiments were conducted up to 20 mass% of nanocomposites in the epoxy coatings. For the sake of comparison, pure epoxy (PE) without nanocomposites were also prepared in the same condition as mentioned above. The prepared epoxy coatings without and with the inclusion of 5, 10, and 20% of TiO_2-CuO nanocomposites were denoted as PE, PE5CTN, PE10CTN and PE20CTN, respectively. The transparency of the epoxy coatings was decreased with increasing the nanocomposite inclusions, whereas the color of epoxy coatings turns light brown with increasing the nanocomposite inclusions. Further, the adhesion between the steel and coatings was checked using the ASTM D 3359 standard tape adhesion test. The results revealed that the adhesion remaining (AR%) values of all the coatings exhibited above 95% without any failed regions, 5B, which suggests good adhesive strength of epoxy coatings towards steel substrates.

2.4. Characterization

Systematic characterization of the synthesized samples was carried out using standard analytical techniques. X-ray Diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 0.15406 Å) with operating voltage of 40 kV and current of 30 mA was employed to examine the phase and crystal structure identification in a 2θ range from 10 to 80°. Field emission scanning electron microscope (FE-SEM, Tescan Lyra-3), was used to examine the surface morphological features of the synthesized nanocomposites with the composition investigation using EDS analyzer. Raman spectrometer were also used to characterizing the Cu content in synthesized nanocomposites. X-ray photoelectron spectroscopy (XPS) was performed using ESCALAB-250Xi (AlKα radiation, 1486.6 eV) to identify the surface elemental composition of the synthesized nanocomposites.

2.5. Electrochemical corrosion evaluations

Electrochemical corrosion test were performed using a Gamry potentiostat with a three-electrode assembly. The coated MS substrates with exposure area of 1.766 cm^2 served as the working electrode, while an Ag/AgCl electrode and a graphite rod were employed as the reference and counter electrode respectively. Electrochemical corrosion measurements were studied through electrochemical impedance spectroscopic (EIS) in short and long term immersion in 3.5% NaCl aqueous solutions. Coated MS substrates were exposed for 30 min to confirm the steady-state earlier to each measurements. The electrochemical impedance spectrum was acquired in a frequency range from 10^5 Hz–10^{-2} Hz in logarithmic increments with 0.01 V amplitude,