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Corrosion protection of steel by epoxy nanocomposite coatings containing various combinations of clay and nanoparticulate zirconia

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ABSTRACT

Epoxy-based nanocomposite coatings containing various amounts of nano-clay and aminopropyltrimethoxy silane (APS) treated zirconia nanoparticles were prepared via slurry method. Morphology and dispersion of nanoparticles within the nanocomposites were evaluated using XRD and TEM analyses. Corrosion performance of mild steel coated specimens was investigated using EIS and EN techniques. The results showed that the simultaneous addition of the spherical ZrO_2 and layered clay nanoparticles promotes the exfoliation of the clay nanoparticles and in so doing improves the corrosion performance of nanocomposite coatings via enhancing the barrier properties and ohmic resistance.

1. Introduction

Polymeric coatings are usually used to protect metals against corrosion and this is most likely achieved by means of barrier properties against water, oxygen or/and corrosive ions such as; Cl^- and H^+ [1]. However, all polymeric coatings are permeable to oxygen and water during their service life and in some cases the diffusion of water and oxygen through the polymeric film is several times greater than the minimum amount required to initiate the corrosion of metallic substrate [2]. Application of inorganic fillers is one the methods to enhance anti-corrosion property of organic coatings [3]. Smaller filler particles may increase polymer–filler interactions and also improve barrier properties of the host polymeric coating. Hence, nano-sized particles with very fine grain size and high boundary volume, provide enhanced barrier properties in comparison with conventional fillers [4]. Nanoparticles containing coatings are well known for their outstanding physical, mechanical and thermal properties [5]. Among the various available nanoparticles, nanoclay and its derivatives are widely used [6]. Because of plate-like shape and aspect ratio, clay nanoparticles embedded nanocomposites combine different valuable properties such as; excellent barrier to moisture and gases [7,8], appropriate mechanical properties [9] and thermal stability [10], and improved flame retardancy [11]. These unique properties, together with relatively low material cost, provide a great attraction in polymer science and technology toward the commercialization of the clay-based nanocomposites [12].

It has been shown [13,14] that the inclusion of clay nanoparticles can improve the corrosion resistance of the coating film via enhancing barrier properties. The extent of the improvement; however, greatly depends on the nanoparticles content and the quality of the dispersion and, the best results are reported with the exfoliated systems [15].

In our previous study, the effect of ZrO_2 nanoparticles addition on the mechanical properties of clay nanoparticles embedded epoxy coatings was reported [16]. It was found that the addition of spherical ZrO_2 nanoparticles can facilitate the exfoliation process of the clay layers and in so doing can affect the barrier properties of the coating. In another work, the authors have studied the effect of zirconia nanoparticles on the corrosion performance of an epoxy coating and have observed an increase in the ohmic resistance of the coating film [17]. Considering the properties observed with individual nanoparticles, the aim of this study is to evaluate the effect of simultaneous use of these nanoparticles on the corrosion performance of an epoxy coating.

2. Experimental

2.1. Materials

Epoxy resin, Epon 828, based on diglycidyl ether of bisphenol A (DGEBA) and amine hardener (Epikure F205) were purchased from Shell Chemicals. ZrO_2 nanoparticles (Zircox™15) with an average particle size of 15 nm were provided by IBU-tec advanced materials

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AG. Aminopropyltrimethoxy silane, APS, (99.5%) was purchased from Merck Chemicals. Montmorillonite nano-clay, Cloisite 30B, with an average dry product size of less than 13 μm, modified with a ternary ammonium salt, was obtained from Southern Clay Products, Inc. (USA). All other chemicals were analytical grade and used as-received.

2.2. Preparation of epoxy based nanocomposites

ZrO_2 nanoparticles were treated by APS coupling agent via a two-stage method. The procedure details are reported elsewhere [16]. In brief, ZrO_2 nanoparticles were dried in a low pressure oven for 2 h at 100 °C. One gram of nanoparticles were dispersed in 30 mL acetone via stirring at 300 rpm for 1 h at 23 ± 2 °C and then sonicated (Bandelin, SONO PULS-UW 2200) for 20 min under power of 70 W, 20 kHz frequency, 0.7 s pulse on, and 0.3 s pulse off. In the next step, 50 wt% (0.5 g) APS was drop wise added to the above-mentioned dispersion and stirred for additional 24 h at 23 ± 2 °C. Finally, it was centrifuged (6000 rpm) and the residue was washed with acetone solvent. The washing process was repeated for three times and the remained precipitated powder was dried in a low pressure oven at 50 °C for about 48 h.

Because of relatively high viscosity of Epon 828 resin, 13,000 cP, the dispersion of nanoparticles into the resin was carried out using acetone as the dispersion media. To prepare the dispersion, various amounts of clay nanoparticles and different combinations of zirconia and clay nanoparticles, were added directly to the acetone with a concentration of 1 g in 30 mL and sonicated (Bandelin, SONO PULS-UW 2200) for 30 min. To avoid heat generation during sonication process, the sample's container was placed in an ice-water bath. The dispersion was added gradually to the epoxy resin while stirring (Heidolph RZR 2102 stirrer) at speed of 2000 rpm for 6 h at 60 °C. Then it was degassed for 3 h in a low pressure oven at 60 °C, to remove residual acetone and trapped air during the mixing process. Finally, a stoichiometric amount of the hardener, with a weight ratio of 58:100, was added to the mixture and stirred for 5 min. Various formulations of the prepared nanocomposites are tabulated in Table 1.

Prior to coatings' application, the mild steel plates (Q-Panel size) were ground with two different sandpaper sheets (400 grit and then 800 grit), followed by degreasing in acetone and drying at ambient temperature. The coating samples with a wet film thickness of 120 μm were then applied on the substrate using a film applicator blade (Model 352, Erichsen Co.).

2.3. Evaluation of nanoparticles dispersion

X-ray diffraction, XRD, patterns of clay nanoparticles, and EC1, EC2 and EC3 nanocomposites samples were recorded on a Siemens D5000 using Cu Kα1 radiation ($\lambda = 0.1541$ nm), with 50 mA flow intensity and voltage of 30 kV, in a range (2θ) of 2–10°. Transmission electron micrographs, TEM, of EC2 and EC1Z1 nanocomposite films were obtained using a TEM instrument (Model EM 208, Philips Co.). Thin section, ca 70 nm, of the specimens was prepared by microtome with a diamond knife. The filament voltage was set at 100 kV.

2.4. Corrosion performance studies

To verify the effect of nanoparticles inclusion on the corrosion performance of epoxy coated mild steel substrate, electrochemical impedance spectroscopy (EIS) and electrochemical noise (ECN) techniques were employed. Back and the edges of the samples were sealed by hot melt mixture of beeswax and colophony resin, and then a defined area of each specimen was exposed to the electrolyte. EIS measurements were performed on a PGSTAT 30 Autolab instrument (Metrohm) using FRA software. A three-electrode arrangement was used, including an Ag/AgCl reference electrode, a platinum counter electrode and the exposed sample (area of 2 cm × 2 cm, with a coating thickness of 85 ± 5 μm) as the working electrode, immersed in a 3.5% NaCl solution. All EIS measurements were carried out in a period of 120 days immersion, at open circuit potential (OCP) and at the frequency range of 10 mHz to 10 kHz, with an AC signals of amplitude 10 mV around OCP, peak to peak. At least three individual replicates for each sample were tested, for statistical accuracy. EIS spectrum was also collected for bare mild steel specimen within 30 min exposure time.

ECN data were obtained for nanocomposite coating samples using a PGSTAT 30 Autolab instrument (Metrohm) for a period of 30 days immersion in a 3.5% NaCl electrolyte. A three-electrode cell arrangement, including two nominally identical panels with an exposed area of (1 cm × 1 cm, with a film thickness of 45 ± 5 μm) for each sample as the dual working electrodes and a saturated reference Ag/AgCl electrode, was used [18,19]. Electrochemical current noise was collected between the dual working electrodes and simultaneously, the potential fluctuations of two short circuited working electrodes were also measured with respect to the standard calomel electrode (SCE) for a period of 1024 s with sampling rate of 1 point s^{-1}.

3. Results and discussion

3.1. XRD

XRD technique was used for the characterization of clay-filled nanocomposites. This technique allows determining the spaces between the silicate layers by using Bragg's equation:

$$\sin\theta = n\lambda/2d \quad (1)$$

where λ represents wavelength of X-ray radiation used in the diffraction experiment, d is the distance between diffractional lattice planes and θ stands for the diffraction angle or glancing.

XRD pattern of pristine clay, Cloisite 30B, nanoparticles is shown in Fig. 1a. An intense single reflection peak is observed at

Table 1
Formulation of various samples for preparation of nanocomposite coatings.

Sample coding[a]	ZrO_2 (wt%)	Cloisite 30B (wt%)	Epon 828 (wt%)	Epikure F205 (wt%)
NE	0	0	66.70	33.30
EC1	0	1	66.00	33.00
EC2	0	2	65.33	32.67
EC3	0	3	64.67	32.33
EC1Z1	1	1	65.33	32.67
EC1Z2	2	1	64.67	32.33
EC2Z1	1	2	64.67	32.33

[a] NE, stands for neat epoxy sample, E, C and Z represent; epoxy resin, clay and zirconia nanoparticles, respectively, and first number shows clay nanoparticles wt% and second number illustrates zirconia nanoparticles wt%.

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