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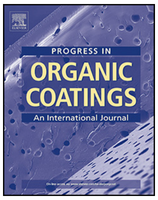

Epoxy/polyaniline–ZnO nanorods hybrid nanocomposite coatings: Synthesis, characterization and corrosion protection performance of conducting paints

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ABSTRACT

The objective of this research is the production of an epoxy coating blended with organic–inorganic hybrid nanocomposite as a corrosion inhibiting pigment applied over carbon steel grade ST37. A series of conducting polyaniline (PANI)–ZnO nanocomposites materials has been successfully prepared by an in situ chemical oxidative method of aniline monomers in the presence of ZnO nanorods with camphorsulfonic acid (CSA) and ammonium peroxydisulfate (APS) as surfactant and initiator, respectively. The synthesized polymers were characterized by X-ray diffraction pattern (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA) and electrical conductivity techniques. Synthesized nanocomposites were solved in tetraethylenpentamine (TEPA), and then prepared solution was mixed with epoxy and then was applied as a protective coating on carbon steel plates. The anti-corrosion behavior of the epoxy binder blended with PANI–ZnO nanocomposites were studied in 3.5% NaCl solution at a temperature of 25 °C by electrochemical techniques including electrochemical impedance spectroscopy (EIS) and chronopotentiometry at open circuit potential (OCP). It was observed that the epoxy coating containing conducting PANI–ZnO nanocomposites exhibited higher corrosion resistance and provided better barrier properties in the paint film in comparison with pure epoxy and epoxy/PANI coatings. In the case of conducting coatings, the OCP was shifted to the noble region due to presence of PANI pigments. Additionally, the possibility of formation of a passive film in the presence of PANI was reinforced at the substrate–coating interface. SEM studies taken from surface of the coatings showed that epoxy/PANI–ZnO hybrid nanocomposite coating systems (EPZ) are crack free, uniform and compact. Furthermore, it was found that the presence of ZnO nanorods beside PANI can significantly improve the barrier and corrosion protection performance of the epoxy coating due to the flaky shaped structure of the PANI–ZnO nanocomposites.

1. Introduction

Recently, substantially conducting polymers (ICPs) such as polypyrrole (PPy), polyaniline (PANI) and their derivations have been studied due to their electrical conductivity, reversible electrochemical behavior, electrical and optical properties and so forth. Polyaniline is a p-type semiconductor which can be synthesized by both electrochemical and chemical methods [1–3]. This conducting polymer has attracted considerable industrial interest and also has potential applications in a wide range of applications due to its versatility and useful characteristics including physical, chemical and mechanical properties, safety and low costs. Several applications of conducting polymers have been known like in sensors [4,5], electronic devices [6], batteries [7,8], and as anti-corrosive additive in organic coatings [9–12].

In recent decades, several studies have been carried out to enhance polyaniline–metal oxide hybrid nanocomposites materials [13]. The electrical property of polyaniline is an important factor which could be modified by the addition of inorganic fillers such as metal oxide nanostructures with dimensions in the nano-scale. Also, it was reported that the electrical conductivity of polyaniline can be influenced by dopant ions used in the synthesis of polyaniline polymer [14–16]. Unfortunately, thin layer of conducting polymers can provide protection of the substrate only for a short period of time. Thus, it will be crucial to combine benefits of organic coating and conducting polymer to gain practical and long-term corrosion resistance for common metallic substrates such as iron and its derivations [11]. There are numerous coating

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Table 1
Quantity of used materials and content of ZnO nanorods in nanocomposites.

Sample	Aniline (gr)	Nano ZnO (gr)	ZnO% in aniline	Nanocomposite yield (gr)	ZnO% in product[a]
PANI	4.5	–	–	3.227	0
PANI–ZnO 1 wt.%	4.5	0.045	1	3.392	1.327
PANI–ZnO 2 wt.%	4.5	0.090	2	3.468	2.595
PANI–ZnO 4 wt.%	4.5	0.180	4	3.635	4.952

[a] (gr ZnO/gr composite) × 100.

systems based on epoxy resin however they have not been completely emerged in field of application in which high corrosion resistance was required. Therefore, use of an appropriate compound blended into epoxy resin is necessary. Several reports have been mentioned that organic–inorganic hybrid nanocomposite coatings can increase the corrosion resistance of metallic substrates such as iron [11,17–22], aluminum [11] and Magnesium [10,23].

It is also reported that coatings containing metal oxide nanoparticles such as ZnO [3,18,20,21], TiO_2 [10] and Fe_2O_3 [24] have better corrosion protection abilities due to uniform distribution of PANI and possibility of formation of uniform passive layers on the surface of metallic substrate. Thus, PANI–metal oxide nanocomposite materials are the potential candidates to add into organic coatings as advanced anti-corrosion additives.

In this paper, a novel hybrid conducting nanocomposite comprising polyaniline and ZnO nanorods were synthesized and then were characterized by different methods such as XRD, FT-IR, SEM, TEM, TGA and electrical conductivity measurement. Additionally, the corrosion protection performance of epoxy/PANI–ZnO nanocomposite coating applied on low carbon steel was investigated by the electrochemical methods. ZnO with rod-like morphology was chosen due to its improved electrical property [25,26]. At the end, possible corrosion protection mechanism of iron at the presence of PANI and ZnO nanorods in the paint film was proposed.

2. Materials and methods

2.1. Reagents and materials

Tetraethylenpentamine (TEPA, Merck, purity 99%) was used as received without any purification. Ammonium peroxydisulfate (APS, Merck) and camphorsulfonic acid (CSA, Merck) were used as the oxidant and the acid dopant, respectively. Aniline (Fluka, Purity 99.5%) was distilled under reduced pressure. Epoxy resin was purchased from Ciba (MY 720) with an epoxy equivalent weight (EEW) of 117–134 and a viscosity of about 10,000 mPas.

In order to synthesize ZnO nanorods, zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and NaOH (Merck) were purchased. ZnO nanorods were synthesized according to the method proposed by Wu et al. [27]. The phase and morphological characterization of ZnO nanorods were studied using X-ray diffraction (XRD-D8 Advance-Bruckers AXS diffractometer) and transmission electron microscopy (TEM-Ziess 100 kV).

2.2. Synthesis of PANI and PANI–ZnO nanocomposites

Polyaniline (PANI) was synthesized through in situ emulsion polymerization. A typical procedure for synthesize of CSA-doped PANI is given as follows: Initially, 0.003 moles (0.704 g) of CSA were mixed with 0.05 moles (4.5 g) of aniline monomer in 200 mL of distilled water and the solution was stirred for 2 h. Then, the mixture was pre-cooled to ~0 °C in an ice bath, to form a homogeneous dispersion of aniline–CSA complex. Afterwards, 50 mL of aqueous solution containing 0.04 moles (9 g) of APS was added drop wisely into the emulsion while it was stirred at the temperature of 0 °C. After 4 h, precipitates were collected on a Buchner funnel and repeatedly washed with distilled water. Then, the products were then dried in an oven for 12 h. The obtained green color of all four samples was the first evidence of the formation of polyaniline in its conducting form, emeraldine salt (ES).

To prepare PANI–ZnO nanocomposites with different ratio of ZnO nanorods, the following steps were carried out: 0.045, 0.090 and 0.180 g of ZnO nanorods were mixed with 0.05 moles (4.5 g) of aniline monomer in 200 mL of distilled water in a set of reaction vessels. The mixtures were stirred with magnetic stirrers in ice water baths for 4 h to get a uniform suspension. The work-up procedure was the same as described above. On the basis of these reactions, pure PANI and PANI–ZnO nanocomposites were obtained with compositions summarized in Table 1.

2.3. Preparation of PANI and PANI–ZnO composite containing paint

Since this study is our continuous work on synthesis, characterization and application of metal-oxide nanocomposite materials in organic coatings, optimum ratio of nanocomposite-hardener to epoxy binder was achieved based on the previous experimental researches [28–30]. In order to prepare paint, a certain amount (0.306 g) of the synthesized powder of PANI or PANI–ZnO nanocomposite was suspended in 3 mL tetraethylenpentamine (TEPA), followed by proper mixing using a magnetic stirrer, with a speed of 400 rpm for about 12 h. TEPA acts as a hardener and solvent for epoxy resin. One gram of epoxy was mixed with 0.2 g of suspension mixture and then solution was stirred again for 5 min. Epoxy resin acts as a binder for the nanocomposites in order to obtain a thick and uniform coating on steel. After stirring, a homogeneous composite was obtained. Low carbon steel grade ST37 plates (Table 2) were grinded, polished using 320, 600, 800, 1200, 1500, 2000 and 2500 grade emery papers and used as substrate coated with the developed paint. All the carbon steel samples were pretreated in acetone and ethanol solution to degrease prior to coating and surface of all samples were smooth and shiny after polishing. The liquid paints were coated on the substrate by dipping and then were dried in the temperature of 50 °C for 24 h. The composition of the prepared epoxy (E), epoxy/PANI (EP) and epoxy/PANI–ZnO (EPZX which $X = 1$, 2, and 4) paints are given in Table 3. In general, the amount of conducting materials content in the epoxy binder was 2 wt.%. The dry film thickness (DFT) of all coatings is about 120 ± 10 μm (Table 4). Since a coating thickness of 120 μm or more is generally employed for protection of marine structures, this coating thickness was chosen in this study. In order to

Table 2
Chemical composition of the iron samples.

Element	Percent (wt.%)	Element	Percent (wt.%)
Fe	96.117	P	0.041
C	0.132	S	0.034
Si	0.415	Ni	0.307
Mn	1.580	Cr	0.305
Mo	0.743	Cu	0.326

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