Progress in Organic Coatings 101 (2016) 149–160

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Electrochemical evaluation and surface study of magnetite/PANI nanocomposite for carbon steel protection in 3.5% NaCl

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ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 5 June 2016
Accepted 9 August 2016

Keywords:
Corrosion
Polyaniline
Fe_3O_4 nanoparticles
Nanocomposite
3.5% NaCl
EIS

ABSTRACT

Herein, a nanocomposite of polyaniline and magnetite (Fe_3O_4) nanoparticles (Fe_3O_4/PANI) was prepared through a two-step oxidative polymerization in different mass ratio as 1:1, 1:2 and 2:1. Prepared Fe_3O_4/PANI nanocomposites were characterized by FT-IR, XRD, TEM, SEM and EDXA. A thin layer of the Fe_3O_4/PANI nanocomposites was used to coating carbon steel as corrosion protector film in NaCl 3.5%. Anti-corrosion performance of the Fe_3O_4/PANI nanocomposites was investigated through electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS). Observed results showed a dramatic shift in corrosion potential and a decrease in cathodic and anodic reactions rate in Tafel plots. Also, EIS data showed charge transfer resistance was increase after coating the carbon steel with Fe_3O_4/PANI nanocomposite. Affecting parameters like mass ratio, amount of nanocomposite, and film formation time, were optimized. Our electrochemical results showed that 100 mg/L of Fe_3O_4/PANI (1:1) nanocomposite in 60 mine can achieved to protection efficiency of 96.8% in 3.5% NaCl. Finally ability of proposed coating as an anticorrosive layer was further proofed by using surface methods i.e. SEM and EDXA. Observed results are presented and discussed.

1. Introduction

A number of methods for the protection of metals against corrosion are known, but looking for new method of corrosion control continues to be subject of intensive research. The conducting polymers, which possess the electronic properties of semiconductors and processing advantages of conventional polymers, have widely been studied for corrosion protection during the last few years. Since the first reported work on the corrosion protection of metals using conducting polymers in 1981, a large number of studies with focus mainly on polyaniline (PANI) [1–5] and polypyrrole [6,7] have been carried out. Nevertheless, the PANI is more challengeable due to low cost of aniline monomers as compared to pyrrole, its environmental stability, the easy solution processing, low specific mass, controllable conductivity, and excellent physical and chemical properties including thermal stability and readily available raw material [8]. Conversely combination of PANI with nanomaterials to form the composites could enhance the mechanical and also donate other unique properties depending to the additive type. Nanomaterials have been employed to reduce the impact of corrosive environments through the alternation of the matal/electrolyte interface [9]. Also, the application of nanomaterials in the corrosion protection of metals has recently gained momentum and environmental impact can improved by utilizing nanostructure particulates in corrosion inhibition [10–12]. Magnetite (Fe_3O_4), that recently has attracted more attention in material and analytical chemistry [13–17], is one of the most promising nanoparticles, as a one of the corrosion products, that can employ in anticorrosion coatings [18,19].

However, two synthetic routes have been established to achieve composite materials composed of conducting polymers and Fe_3O_4 nanoparticles. The first type of method relies on the in-situ formation of Fe_3O_4 magnetic nanoparticles in the presence of conducting polymer upon chemical reactions, such as hydrolysis of Fe (II) and Fe (III) ions, while the second type of method is based on the polymerization of monomers in the presence of Fe_3O_4 magnetic nanoparticles. In comparison with the first type of synthetic routes, the second one offers better control over the magnetic properties of the resultant hybrid materials [20]. PANI is commonly synthesized by oxidizing aniline monomer in acid solution via either chemical or electrochemical method. In comparison with electrochemical method, the chemical synthesis of PANI is widely used for mass

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http://dx.doi.org/10.1016/j.porgcoat.2016.08.011
0300-9440/

production [21]. Moreover, as a conventional microwave absorbing material, Fe_3O_4 has also been frequently used as a promoter for microwave absorption enhancement of conductive polymers due to its excellent magnetic properties and easy preparation [20,22]. Consequently, a composite of Fe_3O_4 and PANI shall have unique properties of each one of them plus protective properties against corrosion environments and microwave irradiations.

In the present work, firstly a nanocomposite of PANI and Fe_3O_4 nanoparticles (Fe_3O_4/PANI) was prepared in different mass ratio as 1:1, 1:2 and 2:1. Prepared Fe_3O_4/PANI nanocomposites were characterized by FT-IR, XRD, TEM, SEM and EDXA. Then a thin layer of the Fe_3O_4/PANI nanocomposites was used to coating carbon steel as corrosion protector in NaCl 3.5%. Anticorrosion performance of the Fe_3O_4/PANI nanocomposites was investigated through electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS). Affecting parameters like mass ratio, amount of nanocomposite and film formation time, were optimized. And finally ability of proposed coating as an anticorrosive layer was further studied by using surface methods like SEM and EDXA. Observed results are presented and discussed here.

2. Material and experimental methods

2.1. Material

All reagents were of analytical reagent-grade and used as supplied. Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), hydrochloric acid (HCl), sodium hydroxid (NaOH), ammonium persulfate (APS), aniline monomer and sodium chloride were purchased from Merck®. All solutions were prepared with purified water (18 MΩ cm, Millipore-MilliQ, Millipore Inc.).

2.2. Apparatuses and methods

Fourier-transform infrared (FTIR) spectroscopy analysis was performed with Nicolet 400D model. The structure of the prepared samples was studied by X-ray diffractometer (XRD, Philips PW 1800 model). The surface morphology of the samples was observed by scanning electron microscopy, SEM equipped with EDXA, (Philips XL30 model). TEM images were obtained using transmission electron microscopy (EM 208 S 100KW model).

A piece of carbon steel, its composition is summarized in Table 1, was cut to $0.2 \times 0.5 \times 1\ cm^3$ dimensions for surface studies. All electrochemical measurements including open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were carried out using an Autolab PGSTAT300N Potentiostat/Galvanostat equipped with a NOVA software (Eco Chemie, Utrecht, The Netherlands). A three-electrode cell including an Ag/AgCl reference electrode, a Pt electrode as the counter electrode, and a carbon steel, 0.2×0.5 cm ($0.1\ cm^2$), as a working electrode was used for electrochemical measurements. Anticorrosion performance was evaluated by using different electrochemical testing techniques during immersion in NaCl 3.5% corrosive solution. All the electrochemical measurements were repeated three times.

For the EIS measurements, a sine wave potential with 10 mV amplitude superimposed on OCP was applied, a wide frequency range from 10 kHz to 100 mHz was scanned, and the impedances were recorded. The EIS data analysis was performed using Zview 2® software and the complex nonlinear least square (CNLS) approximation method. A modified Randles' model in which double layer capacitance (C_{dl}) was replaced by a constant phase element (CPE), was enough to explain the impedances obtained in the whole frequency range, from which kinetic information were extracted [23–29]. The polarization curves were measured by scanning rate $10\ mV\ s^{-1}$ in range ±200 mV around OCP. All experiments were carried out at atmospheric pressure and room temperature and performed at least thrice to ensure repeatability.

2.3. Synthesis of Fe_3O_4 nanoparticles

The Fe_3O_4 nanoparticles were prepared by chemical co-precipitation methods [14]. Briefly, 5.2 g of $FeCl_3{\cdot}6H_2O$, 2.0 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 25 mL 1 M of HCl (degassed with nitrogen gas before use for 20 min). Then, the solution was added drop wise into 250 mL of 1.5 M NaOH solution under vigorous stirring using magnetic stirrer at 80 °C. The obtained Fe_3O_4 nanoparticles were separated from the reaction medium by magnetic field, and washed with 200 mL deionized water four times, then resuspended in 100 mL deionized water and used for next section.

2.4. Synthesis of Fe_3O_4/PANI nanocomposites

1.0 g of Fe_3O_4 nanoparticles were dispersed into 100 mL of stock solution containing 0.25 M $FeCl_3$ and 0.02 M HCl, and then (0.98 mL) of aniline monomer was added. The solution was mechanically stirred in an ice-water bath for 10 h before adding pre-cooled ammonium persulfate (APS) aqueous solution for oxidative polymerization for another 12 h. The mass ratio of Fe_3O_4 to PANI was 1:1, 2:1, and 1:2 by varying the proportion of aniline monomer to suspended Fe_3O_4 nanoparticles and the resulted nanocomposites specified as Fe_3O_4/PANI (1:1), Fe_3O_4/PANI (2:1), and Fe_3O_4/PANI (1:2), respectively. The precipitated powder was separated from the reaction medium by magnetic field and washed with distilled water and ethanol until became colorless and then dried in a vacuum drying cabinet at 70 °C. Throughout the experiment, the total mass of Fe_3O_4 nanoparticles and aniline monomer was 2.0 g, and the molar ratios of aniline to APS were fixed at 0.4 [22].

2.5. Electrode pretreatment and preparation

The working electrode with a surface area of $0.1\ cm^2$ was prepared from carbon steel alloy. A copper wire was attached to one side of a $0.1\ cm^2$ piece of alloy. Then, the assembly was embedded in epoxy resin, leaving the smooth side exposed. This electrode was gradually ground with different grade of emery paper, and placed in an ultrasonic bath to the water-ethanol-water for 5 min each, then washed with distilled water and dried with nitrogen gas. All experiments were performed using the carbon steel electrode with freshly prepared surface. Finally surface covering was donned via immersion of the electrode into a Fe_3O_4/PANI suspension having different mass ratio (1:1, 2:1, and 1:2) and amount (50–250 mg/L).

Table 1
Chemical composition of carbon steel sample used in this work other than Fe.

Composition of used carbon steel sample, elements other than Fe															
Element	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Nb	Ti	V	Sn	As	Ca	B
%	0.180	0.0828	0.459	0.0108	0.0210	0.0402	0.0032	0.0341	0.0566	0.0023	0.0017	0.0035	0.0022	0.0021	0.00092	0.00025