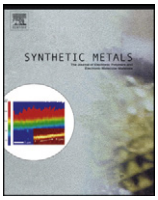
Synthetic Metals 162 (2012) 176–185

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

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



A promising copolymer of *p*-phenylendiamine and *o*-aminophenol: Chemical and electrochemical synthesis, characterization and its corrosion protection aspect on mild steel

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ARTICLE INFO

Article history:
Received 30 July 2011
Received in revised form
18 November 2011
Accepted 28 November 2011
Available online 20 December 2011

Keywords:
Anticorrosion
Mild steel
AFM
^{1}H NMR
EIS
Polymer coatings

ABSTRACT

The poly (*p*-phenylendiamine-co-*o*-amino phenol) has been synthesised by chemical and electrochemical polymerisation method for corrosion protection of mild steel (MS) in acidic medium. The copolymer structure was confirmed by ^{1}H NMR, FT-IR spectroscopy and its thermal stability was observed by TGA. The surface of copolymer coated MS revealed that uniform and relatively less porous morphology. The corrosion protection performance of copolymer coated MS were evaluated using potentiodynamic polarisation and EIS measurements. The copolymer coated MS by electropolymerisation exhibit a higher corrosion protection efficiency than homo polymers and copolymer prepared by chemical polymerisation, which can be due to strong interaction between the mild steel surface and conjugated copolymer.

1. Introduction

Mild steel (MS) continues to be the prime construction material for a wide range of structures, as it has favourable properties and high speed of fabrication [1]. However, its corrosion resistance is highly weakened when it is exposed to acid environment [2–4]. Corrosion of MS will result in the loss of its mechanical properties and structural integrity [5]. At this juncture, there is necessary to protect it from corrosion when it is designed for long term service.

A generic way to protect the material from corrosion is to apply protective coatings [6,7]. Among the various types of protective coatings that are in use, organic polymer coatings play an important role in the prevention of corrosion of MS [8–12]. Conducting polymers that are either chemically or electrochemically deposited on the metal substrate have now been used as corrosion protection coatings [13–16]. Among the family of conducting polymers, polyaniline (PANI) has been received a significant share of attention owing to its inherently excellent versatility including high stability, novel electronic, electrochemical properties and simple reversible acid–base doping–dedoping chemistry. It has been reported that PANI containing coatings are able to protect steel in acid, chloride and alkaline environments [17–19].

Recently, we have reported that the corrosion protection properties of electrochemically synthesised copolymers of aniline and its derivatives on MS in acidic medium [20]. It also attempted to compare the protection efficiency of these copolymers with PANI. However, PANI has some inherent limitations such as poor solubility and poor process ability [21]. To circumvent this limitation, a great deal of attention has been paid to synthesise aniline-based copolymers in recent years. A possible reason is probably attributed to great difficulty to synthesise new conducting polymers with electric properties and stability better than PANI. The copolymerisation of aniline and its derivatives with other monomers offers a possibility to prepare a new type of copolymer that not only retains the good properties of PANI itself but also possesses new properties.

The aromatic diamine and amino phenol based copolymers are more applicable and attractive one since they exhibit more novel multifunctionality due to free amino group present in the repeating unit of the polymers chain than PANI. Nevertheless, there have been a few attempts for their use in anticorrosive applications. The protection of metal surface against corrosion by aromatic diamine and amino phenol based polymers were reported on iron [22], copper [23] mild steel [24] and stainless steel [25]. In addition, it has been suggested that a derivative of aniline such as phenylendiamine and *o*-amino phenol polymers exhibits excellent anticorrosion properties [26,27]. To the best of our knowledge, there was no report in

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doi:10.1016/j.synthmet.2011.11.028

the literature dealing with the corrosion protection behaviour of poly (*p*-phenylendiamine-co-*o*-amino phenol) on MS and on other active metals.

In this present work, an attempt has been made to investigate the corrosion protection behaviour of newly synthesised poly (*p*-phenylendiamine-co-*o*-aminophenol) over MS in acidic environment using potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS).

2. Experimental procedure

2.1. Materials

P-phenylendiamine (*p*PD), *o*-amino phenol (*o*AP), sodium dodecyl sulphate (SDS) and ammonium persulphate (APS), oxalic acid were purchased from Sigma–Aldrich. All the analytical grade chemicals were used as received. Aqueous electrolytes used for the synthesis of the polymer films were prepared using double distilled water. All experiments were carried out at room temperature.

The chemical composition of MS was given in wt% as 0.040 C, 0.350 Mn, 0.022 P, 0.036 S and balance Fe. The MS specimens (size ≈1 cm × 1.5 cm and 0.5 mm thick) were mechanically grinded with different grit size of SiC papers from 400 to 1200. Further, they were degreased with acetone in an ultrasonic bath to remove the impurities, rinsed thoroughly with double distilled water and finally dried in air. Prior to each experiment, the specimens were treated as described and freshly used with no further storage.

2.2. Synthesis of poly (p-phenylendiamine-co-o-amino phenol) by emulsion polymerisation

The emulsion was prepared by SDS (0.2 M) in water and chloroform with vigorous stirring. A pre-cooled aqueous solution of monomers viz., *p*PD (0.25 M) and *o*AP (0.25 M) in 0.1 M HCl solution were prepared separately and added to the emulsion with constant stirring. Then, the contents were kept in an ice bath. To initiate the polymerisation, the acidic aqueous solution (0.1 M HCl) of APS (0.25 M) was added drop wise with constant stirring. The polymer reaction was continued for 24 h at room temperature. Then the polymerisation was terminated by pouring the reaction mixture into acetone, whereupon the copolymer precipitated out. The resulting product was thoroughly washed with deionised water to remove the impurities, unreacted monomers and finally washed with acetone. The product was dried in vacuum oven at 60 °C for 24 h.

The homopolymers such as poly (*p*-phenylendiamine) P*p*DA, poly (*o*-aminophenol) P*o*AP were also synthesised using ammonium persulfate in aqueous acid medium [28,29]. The homo and copolymers were coated on MS by dip coating method with a withdrawal speed of 1 cm min^{-1}. The polymer coatings thus obtained on MS substrates were then allowed to dry for 10 min in air. Finally, the film was allowed to dry at 80 °C in a vacuum oven for 2 h. The average thickness of the homo and copolymer coatings was about 10–30 μm. The structure of synthesised homo and copolymer [30] is shown in Fig. 1a–c.

2.3. Synthesis of poly (p-phenylendiamine-co-o-amino phenol) by electro polymerisation

Poly (*p*-phenylendiamine-co-*o*-aminophenol), poly (*p*-phenylendiamine) and poly (*o*-aminophenol) was electrochemically synthesised by cycling the working electrode potential between −200 and 1200 mV at a scan rate of 50 mV s^{-1} from an aqueous 0.5 M oxalic acid solution containing 0.25 M *p*PD + 0.25 M *o*AP, 0.25 M *p*PD and 0.25 M *o*AP, respectively. After electrodeposition of the films, polymer coated electrodes were removed from the polymerisation medium and rinsed with deionised water to remove unreacted monomer molecules before being dried in air.

2.4. Characterisations

FT-IR spectra of the homo and copolymer were recorded in the range of 400–4000 cm^{-1} by Perkin Elmer FT-IR spectrophotometer with KBr pressed pellet. The thermo gravimetric analysis (TGA) was carried out using Mettler TA 3000 thermal analyser with 5–10 mg of samples from ambient temperature up to 1400 °C, at a heating rate of 20 °C min^{-1} in nitrogen atmosphere to determine the degradation rate of polymer. The proton NMR spectrum of the polymers was recorded on a 600 MHz Bruker spectrometer at 303.1 K in dimethyl sulfoxide-d6 (DMSO-d6) in a 5 mm diameter NMR tube and TMS as an internal reference. The surface topography was taken using AFM, Seiko instruments (SII), Japan. The images were acquired by non-contact mode using Au coated silicon cantilevers with a spring constant of 1.6 N/m at a resonance frequency of 26 kHz under air atmosphere at room temperature. The surface morphology of homo and copolymer films was observed using Field emission scanning electron microscopy (Hitachi S4800).

The standard three electrode cell assembly was used, the polymer coated mild steel act as working electrode, platinum wire act as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrochemical corrosion studies of the homo and copolymer coated mild steel were investigated in 0.5 M HCl solution by potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) measurements. The potentiostat (model PGSTAT 12, Autolab, The Netherlands B.V.) was controlled by a personal computer with dedicated software (GPES version 4.9.005).

Impedance spectra were acquired in the frequency range of 40 kHz–0.001 Hz with a 10 mV amplitude sine wave. In order to test the reproducibility of the results, the experiments were performed in triplicate.

3. Results and discussion

3.1. Electro polymerisation of poly (p-phenylendiamine-co-o-amino phenol)

The cyclic voltagrams (CVs) corresponding to the electropolymerization of homo and copolymers at the MS are shown in Fig. 2a–c. In all cases, mild steel surface is passivated by applying a single forward scan from −200 to +300 mV in 0.5 M oxalic acid solution at the scan rate of 4 mV s^{-1} [31]. As can be seen from Fig. 2a, CV exhibits two oxidation peaks at +280 mV and +800 mV repetitely. The first oxidation peak corresponds to removing one electron from nitrogen atom of one of the amino groups to give radical cation [32]. The formed radical attacks other monomer molecule that leads to the formation of semiquinone radical cation (polaron state). Conversely, the second oxidation peak at 800 mV is attributed to oxidation of the formed semiquinone to the quinone imine (bipolaran state) [33]. On reverse scan, the anodic current is very small indicating the presence of polymer layer adhered to the electrode surface, since a blue-colour uniform film is deposited on the mild steel. Beyond +200 mV, one cathodic peak observed could be ascribed to the reduction of the bipolaron state to polaron state. On repetitive cycling, the voltammograms identical to that of the second scan are obtained. However, the current density corresponding to the oxidation peak increases gradually with the number of scans. This suggests that the electrochemical polymerisation of *p*-phenylendiamine takes place on the mild steel electrode in aqueous oxalic acid solution.