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Investigation of anti-corrosive properties of poly(aniline-co-2-pyridylamine-co-2,3-xylidine) and its nanocomposite poly(aniline-co-2-pyridylamine-co-2,3-xylidine)/ZnO on mild steel in 0.1 M HCl

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ABSTRACT

A soluble terpolymer of aniline (AN), 2-pyridylamine (PA) and 2,3-xylidine (XY), poly(AN-co-PA-co-XY) and its nanocomposite with ZnO nanoparticles namely, poly(AN-co-PA-co-XY)/ZnO were synthesized by chemical oxidative polymerization employing ammonium persulfate as an oxidant. Nanocomposites of homopolymers, polyaniline/ZnO, poly(XY)/ZnO and poly(PA)/ZnO were also synthesized by following similar synthesis route. FTIR, XRD and SEM techniques were used to characterize the synthesized compounds. The synthesized compounds were chemically deposited on mild steel specimens by solvent evaporation method using N-methyl-2-pyrrolidone (NMP) as solvent and 10% epoxy resin (by weight) as binder. Anticorrosive properties of homopolymer nanocomposites, terpolymer and its nanocomposite coatings were studied in 0.1 M HCl by subjecting them to various corrosion tests which includes: free corrosion potential measurement (OCP), weight loss measurements, potentiodynamic polarization, and AC impedance technique. The surface morphology of the corroded and uncorroded coated steel specimens was evaluated using SEM. The corrosion protection performance of terpolymer nanocomposite coating was compared to the terpolymer and individual homopolymers nanocomposites coatings after 30 days immersion in corrosive medium.

1. Introduction

Ever since the discovery of the metal, corrosion has not only impacted the daily-life of the people but also hindered their technical progress. It involves issues pertaining to public safety, huge economic and environmental impact and conservation of materials. Various techniques have been used to overcome the effect of corrosion, among which coating of the active metal surface by conducting polymer is most widely used method in the recent past [1–4]. However, conducting polymers have some limitations, e.g., difficulty in their processing, poor stability at elevated temperatures, poor adhesion to metal surface, limited availability of conjugated π-electrons containing monomers, lack of fusibility and solubility. In order to overcome these limitations a number of conducting co-polymers and terpolymers were synthesized in which a combination of monomers with specific properties have been used to change the physical–chemical properties of resultant polymers [5–9]. For example, a particular monomer may improve the stability and adhesion, whereas the other may provide excellent barrier property and lower the water up taking rate. The coatings of co- or terpolymer were found to show better corrosion protection performance than the constituent's homopolymer coatings. The co- or terpolymers have been synthesized either electrochemically or by chemical oxidization polymerization. Owing to extensive application area further studies are required to improve the properties and quality of conducting polymer coatings.

In this context, the synthesis of a previously reported conducting terpolymer poly(AN-co-PA-co-XY) was done by chemical oxidative polarization technique using aniline (AN), 2-pyridylamine (PA), 2,3-xylidine (XY) as monomers [10]. Its nanocomposite poly(AN-co-PA-co-XY)/Zno with ZnO nanoparticles was also synthesized in situ by following the identical synthesis route. Three homopolymers nanocomposites namely, polyaniline/ZnO, poly(2-pyridylamine)/ZnO and poly(2,3-xylidine)/ZnO were also synthesized by following the identical synthesis route. The resultant homopolymer nanocomposites, terpolymer and its

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nanocomposite were characterized by FTIR, XRD and SEM techniques, deposited on mild steel and subjected to various corrosion tests in 0.1 M HCl.

2. Experimental procedure

2.1. Chemicals

Aniline, 2,3-xylidine, 2-pyridylamine, HCl, and NMP were all Merck products. Ammonium persulfate and other organic reagents were of AR grade and used without further purification. Double distilled water was used throughout the experimental procedure.

2.2. Preparation of metal specimen

The mild steel coupons of dimension 40.0 mm × 15.0 mm × 1.3 mm having chemical composition (wt%) 0.049% C, 0.028% P, 0.081% Mo, 0.723% Mn, 0.051% Cr, 0.01% Al, 0.033% V and balance Fe. The surface of mild steel coupons were polished mechanically by series of emery papers, degreased and rinsed with acetone and distilled water, respectively, and dried prior to coating with homopolymer nanocomposite, terpolymer and its nanocomposite.

2.3. Synthesis and characterization of poly(AN-co-PA-co-XY), poly(AN-co-PA-co-XY)/ZnO, polyaniline/ZnO, poly(2-pyridylamine)/ZnO and poly(2,3-xylidine)/ZnO

Terpolymer poly(AN-co-PY-co-XY) with monomer ratio 80:10:10 was synthesized by chemical oxidative polymerization following previously reported method [10]. ZnO nanoparticles were synthesized by the procedure reported elsewhere [11]. The nanocomposites poly(AN-co-PA-co-XY)/ZnO, polyaniline/ZnO, poly(PA)/ZnO and poly(XY)/ZnO were also synthesized in situ by dispersing 10% ZnO (by weight) nanoparticles in the reaction mixture, the synthesis was further proceeded following the identical procedure as prescribed for the synthesis of the terpolymer. The resultant homopolymer nanocomposites, terpolymer and its nanocomposite were characterized by FTIR, XRD and SEM techniques. X-ray diffraction (XRD) studies were done in the 2θ range of 20–80° using Shimadzu 6100X X-ray diffractometer. Fourier Transform Infra-Red (FTIR) spectroscopy (Model: Perkin Elmer) was studied in the frequency range of 500–4000 cm^{-1}. The morphological study of the terpolymer and its nanocomposite were carried out using Scanning Electron Microscopy (SEM) (Model: JEOL JSM- 6510LV).

2.4. Preparation of coating of poly(AN-co-PA-co-XY), poly(AN-co-PA-co-XY)/ZnO, polyaniline/ZnO, poly(2-pyridylamine)/ZnO and poly(2,3-xylidine)/ZnO on mild steel

The coatings of resultant polymers were obtained on previously polished mild steel using NMP (N-methyl-2-pyrrolidone) as solvent. 10% epoxy resin by weight, which was previously synthesized [12], was used to increase the adhesive property of the polymers. Saturated solution of polymers were separately prepared and spread on the steel surface with the help of dropper, which was followed by evaporation of solvent at temperature 85–90 °C. The solution was poured on the steel surface till a thick and near uniform strongly adherent coating was obtained. Following identical procedure more coated samples were obtained. The coating thickness was measured using Elcometer (Model: 456) and found to be in the range of 11.05–13.30 μm. The thickness of the coatings was controlled by monitoring the weight of the deposited coating per unit area.

2.5. Evaluation of corrosion protection performance of poly(AN-co-PA-co-XY), poly(AN-co-PA-co-XY)/ZnO, polyaniline/ZnO, poly(2-pyridylamine)/ZnO and poly(2,3-xylidine)/ZnO coating on mild steel

The coated and uncoated samples were subjected to free corrosion potential (OCP), weight loss, potentiodynamic polarization, and AC impedance measurements in 0.1 M HCl as a corrosive medium at room temperature (30 °C). The micrographs of coated mild steel samples prior and after 30 days immersion were obtained by SEM analysis.

2.5.1. Immersion test

The uncoated and coated mild steel samples were weighed and immersed in 0.1 M HCl solution using a nylon thread. The immersion tests were performed on triplicate samples for the duration of 30 days under the static condition at room temperature. After 30 days of immersion the mild steel specimens were taken out from the test solution, thoroughly washed with distilled water, dried with warm air and then weighed again. The corrosion rate in mills per year (mpy) and %PE (protection efficiency) was calculated by using the procedure reported elsewhere [13]. The integrity of the coating after immersion in uninhibited and inhibited acid solution was visually examined.

2.5.2. Free corrosion potential measurements

The uncoated and coated steel specimens were electrically connected with a wire having an alligator clip on both the ends. One end of the alligator clip was connected to a multimeter, whereas the other end was connected to the steel specimen and placed into the test solution. Saturated calomel electrode (SCE) was used as reference electrode to measure change in voltage which was plotted vs. time. The measurement of OCP was continued till a steady state was obtained.

2.5.3. Potentiodynamic polarization and AC impedance measurements

The electrochemical measurements were carried out using a corrosion cell with Ag/AgCl electrode (saturated KCl) as reference electrode, steel samples with exposed surface area of 1 cm^2 as working electrode and Pt wire as counter electrode. To minimize IR drop a Luggin–Haber capillary was also used and the tip of the capillary was kept very close to the surface of the working electrode. The polarization studies were carried out by sweeping the potential between −250 and 250 mV with respect to the steady-state potential at a scan rate of 0.001 V/s. Prior to measurements, the specimens were left for 30 min to attain a steady state. All the experiments were carried out at room temperature (30 ± 1 °C) under static condition. The linear segments of the anodic and cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current densities (i_{corr}). The % PE was calculated from the measured i_{corr} values using the following equation:

$$\%PE = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current density of uncoated and coated sample.

Impedance measurements were carried out at OCP within frequency range of 10^{-2}–10^5 Hz with 10 mV perturbation. The values of charge transfer resistance (R_{ct}) were used to calculate the % PE.

$$(\%PE) = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \quad (2)$$

where R_{ct} and R^0_{ct} are the charge transfer resistance of coated and uncoated samples.