Research Article

Polyaniline/Palm Oil Blend for Anticorrosion of Mild Steel in Saline Environment

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The corrosion protective performance of polyaniline/palm oil (PANI-PO) blend coated on mild steel in 3% NaCl aqueous solutions has been evaluated by electrochemical methods, namely, open circuit potential (ocp), potentiodynamic polarization, and EIS spectroscopy. The surface of mild steel was covered by a dark green protective layer due to the physical interaction between the coating and steel. The permanent shifts of ocp and potentiodynamic polarization towards higher positive value of oxidation potential by about 800 mV and by a decrease in corrosion current density by sixfold in magnitude and an increase of 10 orders of magnitude in charge transfer resistance are due to protective coating.

1. Introduction

Polyaniline has been widely studied as being the most conducting and efficient corrosion inhibitor containing π -bond molecular structure under conjugation [1]. The pioneer work of DeBerry [2] had studied the electrolysis of polyaniline on mild steel in a strong acid environment and observed the passivation of pure iron by a layer of polyaniline; the corrosion potential was shifted towards the more noble metal. The corrosion current density was significantly reduced at the corrosion potential. The conducting polymers have been the good candidates for protection for metals against corrosion [3–5]. Polyaniline (PANI) is probably the most vital industrial conducting polymer due to its ease of synthesis, high processability, low-synthetic cost, and environmentally stable behavior. Many papers have been published on the corrosion protection of carbon steel by polyaniline-based material [6–25]. The formation of oxide layer by passivation of iron and the reactions sequence were reported by Wessling [19]. Yao et al. [20] reported the corrosion inhibition of carbon steel by polyaniline nanofibres prepared by interfacial polymerization. The polyaniline is highly insoluble in most of the conventional organic solvents and water, restricting its use as a coating material. Sathiyarayanan et al. [21] studied that

soluble poly(ethoxyaniline) behaved as a corrosion inhibitor of iron in acidic medium. Polyaniline solutions are more effective in corrosion protection than aniline at 75–100 ppm for mild steel. Thompson et al. [22, 23] reported significant corrosion inhibition of mild steel exposed to saline (3.5% NaCl) and acidic environment; the working electrode was coated by polyaniline. Wessling reported that the dispersions of doped polyaniline acted as corrosion inhibitor for mild steel, stainless steel, and copper were passivated by repeatedly dipping clean surfaces of the metals conditions. Polyaniline induces the formation of an oxide layer on mild steel and led the passivation of metal surface [7]. These fascinating results of Thompson and Wessling encourage us to investigate the corrosion protection of mild steel provided by palm oil based coating of polyaniline in saline (3% NaCl) solution. The anticorrosion property of polyaniline/palm oil blend has never been reported in the literature to the best of our knowledge. In this paper polyaniline/palm oil blend coatings were applied without using any solvent or resin.

2. Materials and Methods

Aniline (analytical grade) was used without further purification as received from BDH, England. NaCl used was used

as received from Aldrich. Ammonium persulfate was used as received from R&M Chemicals; U.K. Aqueous solutions were prepared from the ultrapure double-distilled water. Palm oil was procured from super market Tesco (Penang Malaysia).

2.1. Synthesis of Polyaniline/Palm Oil Coatings. The typical procedure involved in the synthesis of polyaniline/palm oil based coating is as follows: 5 mL of aniline (0.05 M, 0.1 M, and 0.2 M) was dissolved in 100 mL of 0.1 M HCl in three conical flasks and 2 mL of palm oil was added to each solution and stirred for some time to get three different blends (PAni-PO-1, PAni-PO-2, and PAni-PO-3) separately for the coating. To initiate the polymerization, 20 mL freshly prepared solution of ammonium persulfate (0.1 M) dissolved in 0.1 M HCl was slowly added with continuous stirring on a magnetic stirrer at room temperature of 22–24°C for 30 minutes. The transition in color change was observed for the reaction mixture which indicated the onset of polymerization reaction. There was an appearance of light green color within minutes and it gradually changes from green to dark green in color within 15 minutes. Finally, the dark green colored dispersion of polyaniline was obtained. The precipitate was collected after 48 hr by filtration using filter paper number 42 and washed with distilled water, acetone and followed by drying under vacuum at room temperature. The double-distilled water was used throughout the experiment. The polyaniline/palm oil based composite (jelly-like) as synthesized by above mentioned procedure was applied physically on the mild steel sample with solvent free coatings of uniform thickness of approx. 250 μm and allowed to dry in the oven at 50°C for proper adhesion.

2.2. Electrochemical Studies. The experiments were designed with conventional three electrodes cell assembly using Potentiostat/Galvanostat/ZRA (Gamry, Reference 600). The working electrode was a mild steel sample of radius 1 cm with the rest being covered with araldite epoxy and the platinum wire was used as a counter electrode and SCE as a reference electrode. The polishing of working electrode was carried out by different grades emery papers and subsequently washed and degreased by distilled water and acetone, respectively. The working electrode has been coated with as-synthesized polyaniline/palm oil based composite having different concentration of polyaniline. The open circuit, electrochemical impedance, and potentiodynamic measurement were carried out in 3% NaCl solution after the open circuit potential of the system was stabilized in half an hour. The polarization was carried out at cathodic potential of -0.3 V to an anodic potential of $+0.3\text{ V}$ with respect to the corrosion potential at a sweep rate of 1 mV s^{-1} . The Tafel plots of anodic and cathodic curves were extrapolated to corrosion potential to get the values of corrosion current, I_{corr} . Electrochemical impedance measurements were carried out at open circuit potential after immersing the mild steel specimen in experimental solution in the frequency range 10 KHz to 0.1 Hz. Applied voltage of sinusoidal wave was 10 mV.

FIGURE 1: FTIR spectrum of as-synthesized palm oil based polyaniline in 0.1 M hydrochloric acid.

3. Results and Discussion

3.1. IR Spectroscopy. The polymer was characterised by recording Fourier Transform Infrared Spectroscopy (FTIR) spectrum using Perkin-Elmer-2000 system (USA) with KBr pellet. Figure 1 shows the FTIR spectrum of the polymer; the major absorption peak at 1588 cm^{-1} is attributed to nitrogen-quinoid unit in the ring structure and peak observed at 1501 cm^{-1} corresponds to benzenoid unit in the structure. The bands appear at 1298 cm^{-1} attributed to the stretching of C–N. The C–H out-of-plane bending mode has been a key to identify the type of substituted benzene. The characteristic band at 824 cm^{-1} is observed as a single band in polyaniline salt [21, 26]. A broad and weak peak at 3237 cm^{-1} is assigned to the free N–H stretching. In addition, it is observed that some peaks are also visible in the frequency range $2800\text{--}3000\text{ cm}^{-1}$, assigned to the absorbance of methylene asymmetric and symmetric stretching vibrations, which confirm that the palm oil has chemical bond formation with PAni. A characteristic peak at 1744 cm^{-1} is observed for carbonyls stretching vibration of C=O group present in palm oil.

3.2. Open Circuit Potential Measurement. Figure 2 (dash lines) shows the open circuit potential of mild steel electrode with and without the presence of corrosion inhibitor exposed to 3.0% NaCl solution for 30 mins. The corrosion is controlled by monitoring the oxidation or passivation of the metal surface. The shifting of open circuit potential towards the more positive potential value indicates that increasing the thickness of coating of PAni-PO-1, PAni-PO-2, and PAni-PO-3, on top of the sample and makes it more passivated and it behaves predominantly as an anodic inhibitor.

3.3. Potentiodynamic Study. Figure 3 shows the potentiodynamic polarization curves for three different coatings on mild steel in contact with 3% NaCl aqueous solution saturated with air. The formation of a passive oxide layer on mild steel in the curves is formed clearly with coating containing PAni-PO-1, PAni-PO-2, and PAni-PO-3 while there is no tendency for passivation without PAni-PO. It is clear that the formation of the oxide layer results in the decrease

FIGURE 2: Potential-time curve of PANi-PO coating on mild steel as function of concentration and time.

of corrosion rates by many folds. Both active and passive behaviors are more pronounced in saline environment of NaCl. The mild steel coated with PANi-PO did not show active/passive behavior. However, the mild steel with PANi-PO exhibits a very significant reduction in corrosion current density. These results showed very clear evidence of the significant corrosion protection exhibited to bare mild steel sample mechanically coupled to PANi-PO coatings [7]. The corrosion kinetics parameters extrapolated from these curves are given in Table 1. There is shift in the corrosion potential towards the direction of noble metal from -750 to -400 mV and the redox current density was decreased by about five orders of magnitude as compared to mild steel. A significant difference was observed for the two coatings with different PANi-Palm oil compositions.

3.4. Impedance Measurements. Figures 4(a)–4(c) show the Nyquist representation of the impedance values for mild steel in 3.0% NaCl in the presence of different concentrations of polymer. Impedance measurement that provides various parameters such as charge-transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) is shown in Table 2. The R_{ct} values are calculated from the difference in impedance at lower and higher frequency as reported by Haruyama and Tsuru [27]. The Randles circuit (Figure 5) is used as an equivalent circuit where R_s is the solution resistance, C_{dl} is the double layer capacitance, and R_{ct} is the charge transfer resistance using ZSimp Win Demo 3.2 d Software. The values extrapolated from Nyquist plots are listed in Table 2. It is clear from the observed data that the R_{ct} decreased from the value of 336.8 to $3542 \Omega \text{ cm}^2$ and C_{dl} values decrease from 1.201×10^{-3} to $8.986 \times 10^{-6} \text{ F cm}^{-2}$. The slightly depressed

FIGURE 3: Potentiodynamic polarization curves for carbon steel without and with PANi-PO coating, in the presence of 3% NaCl aqueous solution.

semi-circle and decrease in the length of the diameter of the semicircle with coating of palm oil/polyaniline blend of different composition indicated lower rates of corrosion. The centre of the semicircle below the x -axis signifies the existence of microroughness at the surface of metal during the corrosion process [22, 23, 28–30]. Single semicircle predicts the occurrence of single charge transfer in the process and further increase or change in concentration of polyaniline in the blend does not affect the corrosion inhibition. The diameter of semicircle in the Nyquist plot tends to increase with the increase of polyaniline up to a certain limit and further addition of polyaniline coating on the top of the mild steel has no effect in the protection of the sample. Similar shape of semicircles predicted that inhibition of corrosion followed the same mechanism of corrosion inhibition. Bode plot are shown in Figures 4(a')–4(c') the presence of one phase maximum was observed at intermediate frequencies, which indicated the presence of one time constant corresponding to the impedance of the formed protective coating [31]. The values of CPE decrease with the increase of in PANi-PO composition, which consequently may decrease the electrical capacity and/or increase the thickness of the electrical double layer [32].

4. Conclusion

The coatings containing polyaniline/palm oil blend could provide excellent protection for very thin layer when coated onto mild steel which clearly indicates that it can provide significant corrosion protection to mild steel exposed to the saline environment of NaCl. The data assessed from results of potentiodynamic study predicts that the protection is mainly due to anodic polarization and EIS measurement clearly confirms that the potentiodynamic measurements are in good agreement with EIS spectroscopy data simulated. This coating formulation is more advantageous and easy as it does not involve the use of any organic solvent or supporting

FIGURE 4: ((a)–(c)) and ((a')–(c')) show the Nyquist and Bode plot of mild steel, without and with coating of palm oil/polyaniline blend in 3% NaCl solution, respectively.

TABLE 1: Corrosion kinetics parameters derived from the potentiodynamic curves of mild steel in 3% NaCl coated with PANi-PO.

	I_{corr} $\mu\text{A cm}^{-2}$	E_{corr} mV versus SCE	b_a mV dec^{-1}	b_c mV dec^{-1}	Rate _{corr}
Blank	34.16	-721.0	101.7	382.8	15.21
PAni-PO ($\times 10^{-1}$ M)					
0.5	10.34	-491.5	60.41	133.0	4.72
1.0	6.0	-417.0	60.0	382.0	2.74
1.5	5.28	-623.0	100.8	272.0	2.41

TABLE 2: Electrochemical impedance data deduced from Nyquist plots by fitting to an equivalent circuit in Figure 5.

	R_{ct} $\Omega \text{ cm}^2$	C_{dl} F cm^{-2}	R_s $\Omega \text{ cm}^2$
Blank	336.8	1.201×10^{-3}	5.2
PAni/PO ($\times 10^{-1}$ M)			
0.5	521.5	1.643×10^{-5}	11.5
1.0	1713.0	1.659×10^{-5}	11.8
1.5	3542	8.986×10^{-6}	195.6

FIGURE 5: Randles circuit used for polyaniline/palm/oil blend coating on mild steel electrode.

resin. The results of open circuit potentials indicate that the blend has more positive oxidation potential than polyaniline reported in the literature. More studies are needed for elucidating the mechanism of protection.

Conflict of Interests

The authors do not have direct financial relation with the commercial identities mentioned in the paper despite using the Potentiostat/Galvanostat/ZRA (Gamry, Reference 600), Perkin Elmer Spectrophotometer. Therefore, the authors declare that there is no conflict of interest regarding the publication of this paper.

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