

SYNTHESIS AND STUDY OF CORROSION PERFORMANCE OF EPOXY COATING CONTAINING MULTI-WALLED CARBON NANOTUBE / POLY ORTHO AMINOPHENOL NANOCOMPOSITE

N. Bahrami Panah* and N. Ajami

* bahramipanah@pnu.ac.ir

Received: August 2015

Accepted: January 2016

Department of Chemistry, Payame Noor University, Tehran, Iran.

Abstract: The epoxy coatings containing multi-walled carbon nanotube/ poly ortho aminophenol nanocomposite were prepared and used as anticorrosive coatings. The nanocomposites with different contents of carbon nanotube were synthesized in a solution of sodium dodecyl sulfate and ammonium peroxy disulfate as a surfactant and an oxidant, respectively. The morphology and structural properties were confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy methods. The mean size of nanocomposite particles was 20-35 nm determined by scanning electron microscopy. The epoxy coatings containing the nanocomposites were applied over mild steel panels and their corrosion performance was investigated using electrochemical impedance spectroscopy and potentiodynamic polarization measurements in a 3.5 % sodium chloride solution. The results showed that epoxy coatings consisting of nanocomposite with 1 wt.% multi-walled carbon nanotube exhibited higher anticorrosive properties than other prepared coatings of different carbon nanotube contents, which could be due to the strong interaction between the mild steel surface and the conjugated nanocomposite.

Keywords: Corrosion, Electrochemical impedance spectroscopy, Multi-walled carbon nanotube, Nanocomposite, Ortho aminophenol.

1. INTRODUCTION

The corrosion of metals is a serious problem for today industrial world. Mild steel is widely used in constructions and other applications because of its favorable properties and high speed of fabrication [1, 2]. Different methods are used for corrosion protection of steel in corrosive solution. The corrosion of mild steel can be controlled by organic compounds with a molecular structure of π -conjugation [3- 5], but the corrosion resistance does not increase significantly. Polymer coatings are largely used to improve corrosion resistance of steel [6- 10]. Among them, epoxies are widely used as the resin of different protective coatings since they show excellent adhesion, mechanical properties and chemical resistance in different media [11- 13]. However, long exposures to wet and humid conditions attenuate their barrier properties. Reinforcement of epoxy coatings by means of organic and inorganic pigments was a common way to prolong the duration of protection [14- 17]. Multi-walled carbon nanotubes (MWCNTs) as inorganic particles have a unique structure,

high surface to volume ratios, high chemical stability and mechanical strength. It has been demonstrated that the introduction of MWCNTs into a polymer matrix improves the redox properties as well as the mechanical properties of the original polymer [18- 22]. Khun et al. [18] evaluated the effects of multi-walled carbon nanotubes contents on the adhesion strength, wear and corrosion resistance of the epoxy composite coatings prepared on aluminum alloy (AA 2024-T3) substrates. It was reported that as the MWCNTs content is increased, the coating pore resistance also increases due to a decreased porosity density. Recently, using the intrinsically conducting polymers for protection of mild steel against corrosion and as organic pigments has been the subject of considerable research [23- 25]. Among those conducting polymers, poly ortho aminophenol (PoAP) is an interesting member of the class of substituted anilines and is a potential material for commercial applications resulted from its environmental stability, good processability and relatively low cost [26, 27]. Unfortunately, thin films of conducting polymers can provide protection only for a relatively short

time period. Therefore, it will be necessary to combine advantages of conducting polymers and classical organic coatings as epoxies to obtain better corrosion protection for common metals.

In this study, composites of poly ortho aminophenol and multi-wall carbon nanotubes (MWCNTs/ PoAP) with different contents of MWCNTs were synthesized by in-situ polymerization technique using ammonium peroxy disulfate (APS) oxidant and sodium dodecyl sulfate (SDS) surfactant. Then, the corrosion performance of epoxy coatings containing MWCNTs/ PoAP nanocomposites on mild steel was established by carrying out a series of electrochemical measurements in 3.5 % sodium chloride solution.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used in this work [ortho aminophenol, sodium dodecyl sulfate, ammonium peroxy disulfate, hydrochloric acid, nitric acid and methanol] were of Merck origin (Germany) and used without further purification. Doubly distilled water was used to prepare solutions. Epoxy resin based on bis-phenol A, having an epoxy equivalent weight of 450-500 (Ciba Geigy, Switzerland) and a polyamine hardner with amin value 210-230 mg KOH/g (symbol 115) was used. Typical MWCNTs were purchased commercially (Reinste Nano Ventures Private Limited, India) and they were uniform with outer diameter in the range of 20-35 nm and lengths up to several hundreds of nanometers.

2. 2. Synthesis of MWCNTs/ PoAP Nanocomposite

Chemical oxidative polymerization using ammonium peroxy disulfate as oxidant in aqueous HCl solution was used for the preparation of poly ortho aminophenol. The solution formed by APS agent (2.5 mmol) in 1.5 M HCl was added drop-wise (15-20 min. interval) under constant stirring (50 rpm) to a second 1.5 M HCl solution containing ortho aminophenol monomer (5 mmol) and sodium dodecyl sulfate (4 mmol) surfactant. The critical micelle concentration of the surfactant was determined by the electrochemical probe ($\text{Fe}^{2+}/\text{Fe}^{3+}$

response cyclic voltammograms) and found around 0.004 M. The reaction was allowed to proceed for 4 h. The PoAP was precipitated by adding the reaction mixture into the 500 ml of distilled water followed by filtration. The powdery substance was repeatedly washed with distilled water and then dried under vacuum at 60 °C for 24 h.

For the synthesis of MWCNTs/ PoAP nanocomposite, MWCNTs were purified by refluxing with 6 M nitric acid for 12 h, followed by washing with distilled water, and drying under vacuum for 8 h at 60 °C. A large number of purified MWCNTs were dispersed ultrasonically (Sigma-Aldrich-Bandelin Sonopuls ultrasonic homogenizer, Germany) in 15 ml of distilled water containing anionic surfactant SDS (4 mmol). Then, 5 mmol of ortho aminophenol was added and dispersed by ultrasonic method for 1 h. To this solution, 10 ml of an aqueous solution of 1.5 M hydrochloric acid and 2.5 mmol APS was added drop-wise (15-20 min. interval) and stirred constantly at 50 °C for 2 h. A dark brown precipitate was produced, which was separated by centrifuge (Rotofix 32A, Hettich, Germany) and washed three times with methanol and distilled water. The MWCNTs/ PoAP nanocomposite was dried under vacuum at 60 °C for 12 h.

2. 3. Preparation of Epoxy Coating Containing MWCNTs/ PoAP Nanocomposite

The epoxy resin solution was prepared by dissolving solid epoxy having an epoxy equivalent weight of 450- 500 and then stirred for 10 minutes. The MWCNTs/ PoAP nanocomposite synthesized with different contents of MWCNTs (1, 3, 5 and 7 wt.%), were completely dispersed in the resin by using attritor (Modern Machinery Manufacturing Company, India). For comparison, an epoxy coating without any nanocomposite was produced under similar conditions. All of the samples were cured with polyamine having an amine value of 210-230 mg. The surface of steel panel was mechanically abraded with different grades of emery paper and degreased with toluene and acetone. Then, the samples were applied over mild steel panels by a film applicator and evaluated after 10 days of curing at room temperature.

2. 4. Measurements

The morphology of the obtained nanocomposites was observed using a scanning electron microscope (SEM) model KYKY-EM3200, China made. The Fourier transform infrared (FTIR) spectrum of the poly ortho aminophenol was recorded at ambient temperature using a Shimadzu spectrometer (model 8400s, Japan). The thickness of dry coatings was measured with an Elcometer thickness gauge Phynix Surfix version: FNF 2.2, Germany. The dry film thickness was $80 \pm 5 \mu\text{m}$.

The protective properties of the coatings were investigated by electrochemical impedance spectroscopy (EIS) and Tafel polarization during the immersion time of the coatings in 3.5 % sodium chloride solution. Electrochemical studies were carried out in a one-compartment three-electrode cell powered by a Metrohm-Autolab potentiostat/ galvanostat (model 12/30/302, The Netherlands). Coated mild steel panels of 1 cm² area were employed as working electrodes (before each experiment, the bare mild steel was polished with emery paper of 1000 grit and finally rinsed with distilled water and acetone). Counter and reference electrodes were platinum and saturated Ag/AgCl electrode (Metrohm, The Netherlands), respectively. Polarization curves [$I = f(E)$] were recorded after 2 hours immersing the coatings in 3.5 % sodium chloride solution with a constant scan rate of 5 mV s⁻¹. The frequency range of 10 kHz to 10 mHz and modulation amplitude of 20 mV with respect to open circuit potential were employed for impedance studies. The fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was performed by Nova 1.8 software. Since MWCNTs are insoluble in most solvents, ultrasonication is required during preparation in order to effectively disperse the nanotubes. All the electrochemical experiments were carried out at $22 \pm 1^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3. 1. SEM Micrographs

Fig. 1 shows the SEM micrographs of

MWCNTs, epoxy coatings containing PoAP and MWCNTs/ PoAP nanocomposites with 1, 3, 5 and 7 wt.% carbon nanotubes. It is obvious, in Fig. 1a, that the tangled MWCNTs with diameters of 20-35 nm and lengths up to several hundreds of nanometers were distributed very well. The SEM image of epoxy coating containing PoAP exhibits a compact structure (Fig. 1b). The MWCNTs/ PoAP nanocomposites show both carbon nanotube and PoAP structures (Figs. 1c-f). The SEM of the nanocomposite containing 1 wt.% MWCNTs exhibits some porous structure of PoAP that has been wrapped on the surface of MWCNTs or MWCNTs have been dispersed in the polymer matrix (Fig. 1c). As the MWCNTs content was increased in the nanocomposite, one-dimensional nanostructures of roughly uniform size with diameters in the range of several hundreds of nanometers were observed (Figs. 1e and f).

3. 2. FTIR Spectrum

The FTIR spectrum of poly ortho aminophenol (Fig. 2) exhibits two peaks between 1600 and 1490 cm⁻¹, which are characteristics of the C=C stretching vibrations of the benzenoid and quinoid rings, respectively [26, 27]. The three bands appearing between 800 and 900 cm⁻¹ are attributed to an out-of plane C-H vibration. The band at 1121 cm⁻¹ is ascribed to the stretching of the C-O-C linkages and further support that the ortho aminophenol changed into PoAP [28]. The two peaks at 1320 and 1215 cm⁻¹ correspond to the C-N vibration. The doping of PoAP with SDS is confirmed by the appearance of a band at 1010 cm⁻¹, which is due to the adsorption of the -SO₃H from SDS [29]. The absorption peak appeared at 3480 cm⁻¹ corresponds to the characteristic band of the N-H stretching vibrations in the PoAP chain. The strong absorption peaks at 3000 and 1720 cm⁻¹ are ascribed to C-H vibration of aromatic structure and the C=N groups [30].

3. 3. Polarization Study

The corrosion performance of epoxy coatings containing PoAP particles and MWCNTs/ PoAP

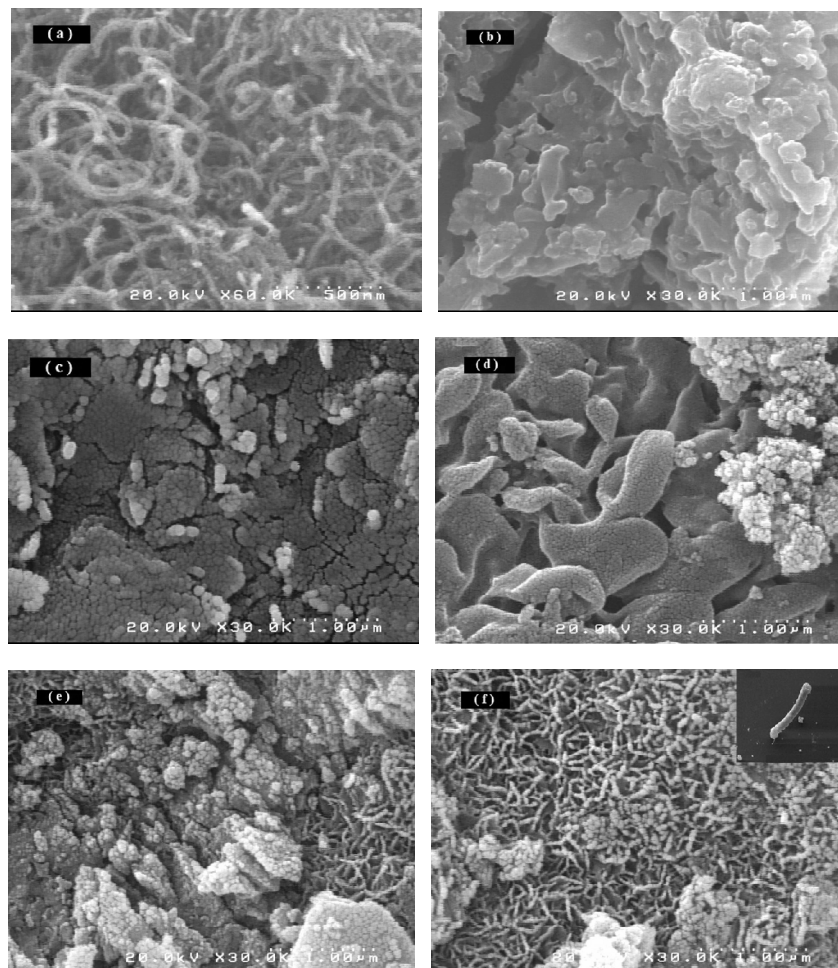


Fig. 1. SEM micrographs of (a) MWCNTs, (b-f) epoxy coating containing PoAP and MWCNTs/ PoAP nanocomposites with 1, 3, 5 and 7 wt.% MWCNTs, respectively. (The commercial MWCNTs have an outer diameter in the range of 20-35 nm and lengths up to several hundreds of nanometers.)

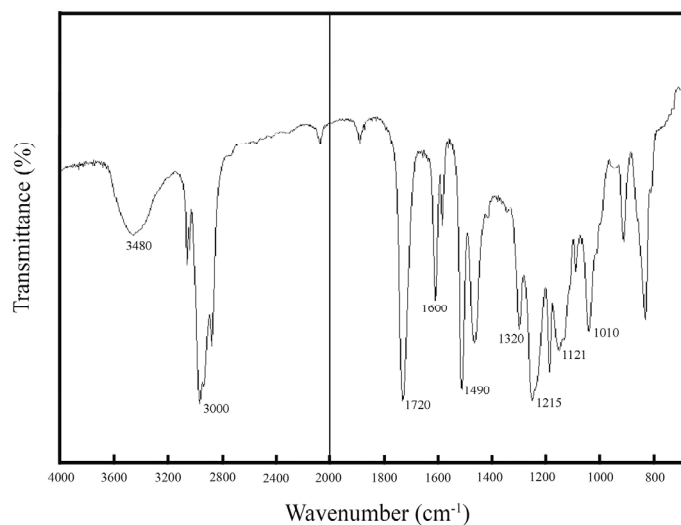


Fig. 2. FTIR spectrum of poly ortho aminophenol structure.

nanocomposite (with different contents of MWCNTs) was investigated after 2 hours immersion in 3.5 % sodium chloride solution via Tafel polarization (Fig. 3). According to the Tafel analysis shown in table 1, the corrosion current density of $1.40 \mu\text{A cm}^{-2}$ is obtained for epoxy coating containing PoAP particles and there is a substantial decrease in corrosion current density of the coatings containing MWCNTs. It seems that in the presence of MWCNTs, the permeation of the electrolyte in the composite coatings decreases due to the decreased porosity density and barrier properties of MWCNTs. Also, the water transport behavior of epoxy coatings containing MWCNTs decreases due to the higher surface hydrophobicity [18, 31]. The corrosion current density drops 95 % as the content of MWCNTs is decreased from 7 to 1 wt.% and a minimum value is obtained for the coating containing 1 wt.% MWCNTs. This leads the corrosion potential to move in the positive direction, indicating that the mild steel is nobler (The corrosion current density and potential of bare mild steel panel in a solution of 3.5 % sodium chloride is $35.45 \mu\text{A cm}^{-2}$ and -200 mV , respectively). However, it seems that the critical percent of MWCNT is 1 wt.% which is regarded as the maximum MWCNT percent where the corrosion potential decreases suddenly and the presence of higher amount of MWCNTs (1 wt.%<) in polymer matrix may cause loss of

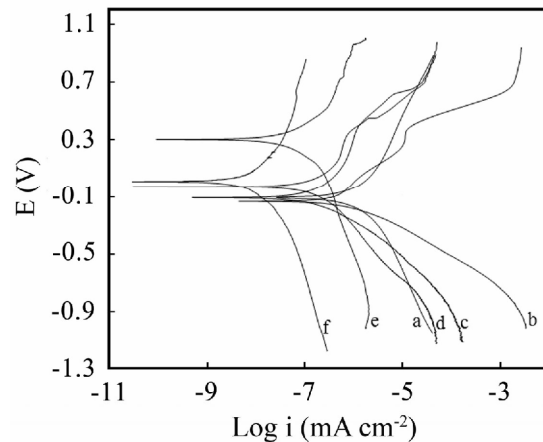


Fig. 3. Tafel plots of (a) epoxy in the absence of nanocomposite, (b) epoxy contained PoAP and (c-f) epoxy coating containing MWCNTs/ PoAP nanocomposite with different contents of MWCNTs 7, 5, 3 and 1 wt.% after 2 hours immersion in 3.5 % sodium chloride solution.

mechanical, adhesion properties of the coating and active behavior.

3. 4. EIS Studies

The impedance spectra were recorded at corrosion potential after various immersion times in a 3.5 % sodium chloride solution. Figures 4 and 5 illustrate Nyquist plots for epoxy coatings containing PoAP particles and MWCNTs/ PoAP

Table 1. Tafel parameters for epoxy coatings containing PoAP and MWCNTs/ PoAP nanocomposite with different contents of MWCNTs coated on mild steel in 3.5 % sodium chloride.

Sample	MWCNTs (wt.%)	$E_{\text{corr.}}$ (mV, vs. Ag/AgCl)	$I_{\text{corr.}}$ ($\mu\text{A cm}^{-2}$)
Epoxy	0	-115	2.30
PoAP/ Epoxy	0	-134	1.40
MWCNTs/ PoAP/ Epoxy	7	-107	0.19
MWCNTs/ PoAP/ Epoxy	5	-30	0.10
MWCNTs/ PoAP/ Epoxy	3	+7	0.05
MWCNTs/ PoAP/ Epoxy	1	+303	0.01

nanocomposite (with 1 wt.% MWCNTs) at corrosion potential after various immersion times (up to 40 days). For the coating containing PoAP particles, the impedance spectra exhibit a single time constant due to coating behavior and the absence of the second time constant indicates the absence of any corrosion reaction. An analogue circuit could be used as shown in Fig. 4, in which impedance (Z) depends on the coating resistance (R_c) and its capacitance (Q_c). The Nyquist plots of nanocomposite show a depressed semi-circle at high frequency range followed by a larger one at the low frequency side of the spectrum. The former is due to a parallel combination of coating resistance from the penetration of electrolyte under the coating (R_c) and the coating capacitance (Q_c). The latter represents the charge transfer resistance (R_{ct}) of the area at the metal/coating interface at which corrosion occurs and the double layer capacitance (Q_{dl}) in this interface. The equivalent circuit compatible with the Nyquist diagram of nanocomposite is depicted in Fig. 6 [32]. To obtain a satisfactory impedance simulation, it is necessary to replace the capacitor (C) with a constant phase element

(CPE) which is Q in the equivalent circuit.

In our previous study, it has been reported that the coating resistance of the epoxy in the absence of PoAP particles and MWCNTs/ PoAP nanocomposite has been estimated to be 100.03 kohm cm², but after 14 days epoxy coating lost its protective properties [9]. The results obtained from analyzing the impedance spectra of Fig. 4 by Nova 1.8 software indicate that the charge transfer resistance value in the presence of PoAP particles is initially 170.02 kohm cm² (table 2). After 40 days of immersion of coating containing PoAP particles, the charge transfer resistance decreases to 39.04 kohm cm² (resistance drop of 77 %) due to penetration of corrosive chloride ions from the corrosive solution on electrode surface. A comparison between the results of the electrochemical impedance data of the epoxy in the presence of PoAP and that in the presence of nanocomposite after immersion in corrosive solution demonstrates that the coating containing the nanocomposite has significantly higher anticorrosive performance compared to the one with the polymer. The charge transfer resistance of the coating containing nanocomposite

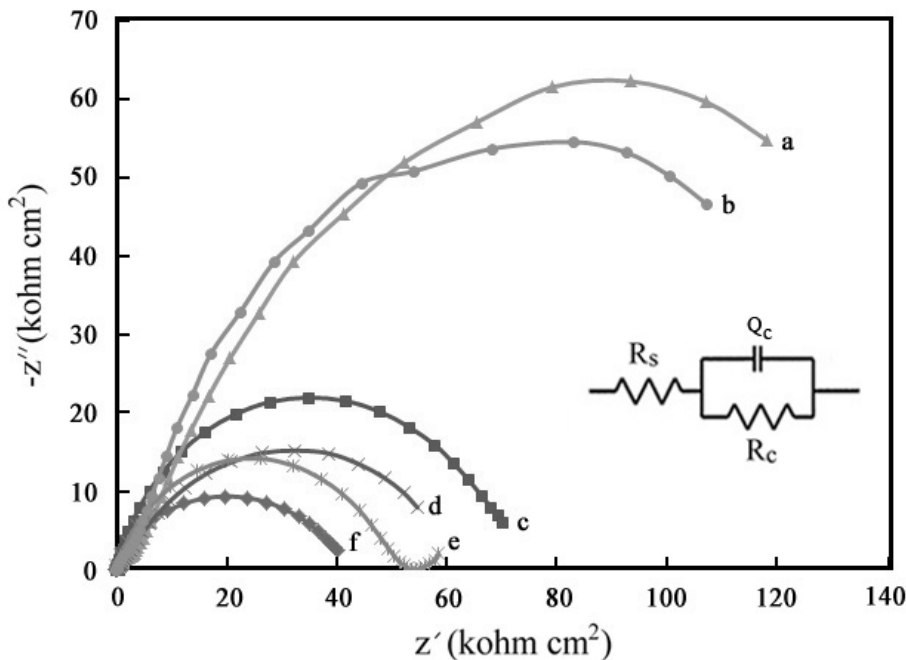


Fig. 4. Nyquist plots for epoxy coating containing PoAP particles as a function of immersion time at corrosion potential (a-f) 2 hours, 2, 10, 20, 30 and 40 days in 3.5 % sodium chloride solution.

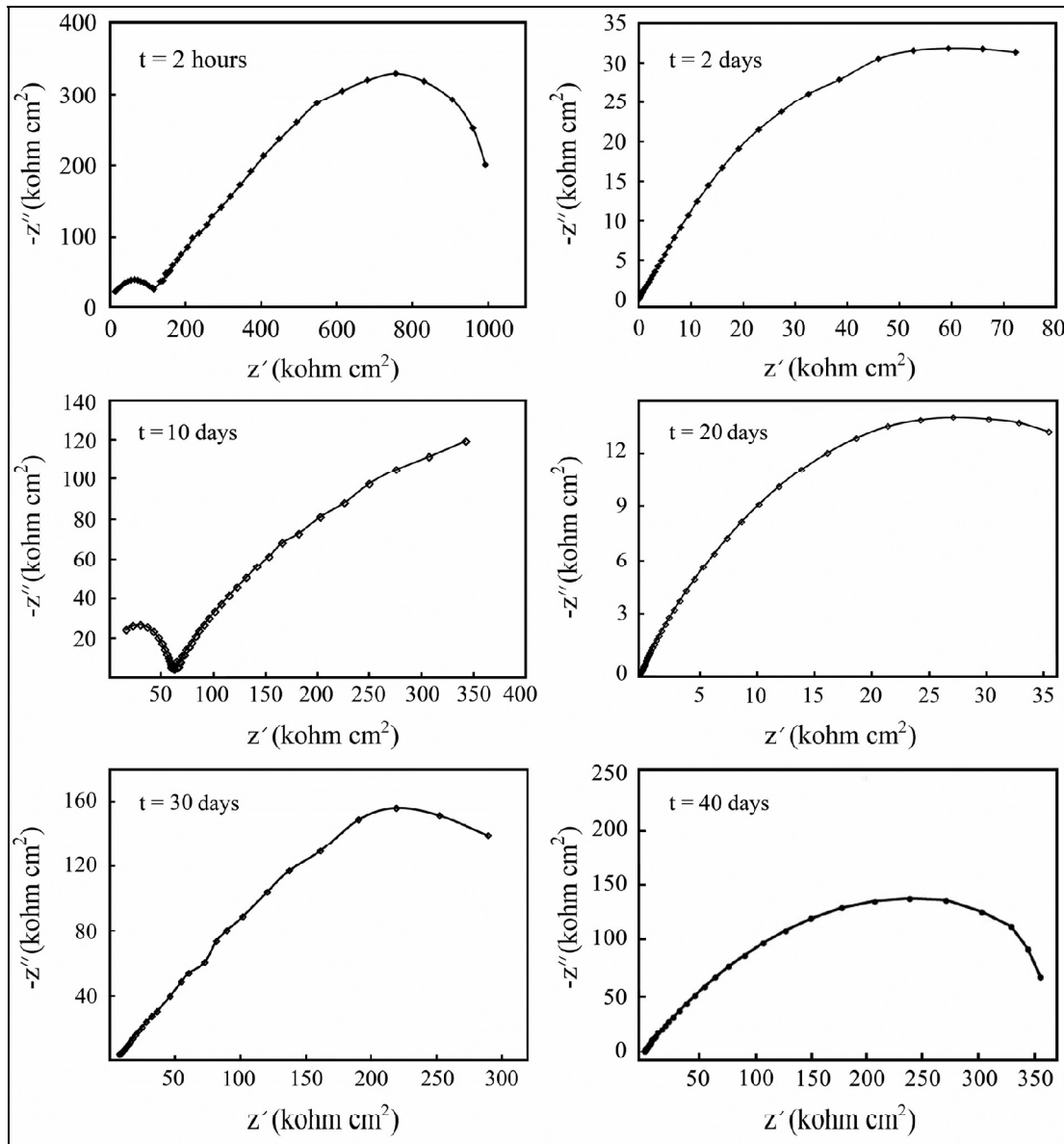


Fig. 5. Nyquist plots for epoxy coating containing MWCNTs/ PoAP nanocomposite (with 1 wt.% MWCNTs) as a function of immersion time at corrosion potential in 3.5 % sodium chloride solution.

decreases from 364.07 to 76.05 kohm cm² (resistance drop of 79 %) after 20 days of immersion in 3.5 % sodium chloride solution. Then, R_{ct} value increases during long immersion time due to corrosion product formation which acts as an anticorrosive coating. The high charge transfer resistance value after 40 days of immersion indicates that dissolution of iron under the film was negligible. The coating resistance value decreases as the immersion time

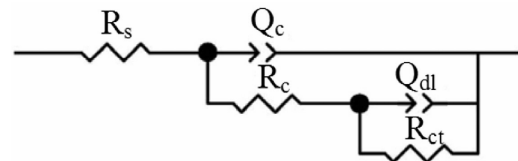


Fig. 6. The equivalent circuit compatible with the Nyquist diagram of Fig. 5.

Table 2. Values of equivalent circuit components revealed by fitting impedance data for epoxy coating containing (a) PoAP, (b) MWCNTs/ PoAP nanocomposite (1 wt.% MWCNTs) on mild steel in 3.5 % sodium chloride solution. Quality of fitting is judged by the estimated relative errors as given in the parentheses.

sample	Immersion time	2 hours	2 days	10 days	20 days	30 days	40 days
a	R_c (kohm cm ²)	170.02 (8.40%)	150.13 (7.54%)	71.55 (7.18%)	59.39 (11.76%)	50.97 (8.96%)	39.04 (12.51%)
	Q_c ($\mu\text{F cm}^{-2}$)	20.01 (8.84%)	30.05 (7.43%)	80.15 (9.19%)	100.30 (3.27%)	70.08 (8.83%)	90.10 (10.59%)
	Q_{cl} ($\mu\text{F cm}^{-2}$)	0.01 (13.18%)	0.12 (13.78%)	0.07 (15.06%)	1.08 (6.88%)	0.02 (10.63%)	5.90×10^{-3} (6.50%)
b	R_c (kohm cm ²)	863.16 (2.88%)	108.00 (2.12%)	77.18 (7.25%)	54.20 (0.67%)	53.32 (11.12%)	54.08 (9.29%)
	R_{ct} (kohm cm ²)	364.07 (9.17%)	239.66 (6.96%)	217.43 (6.61%)	76.05 (2.52%)	332.43 (6.21%)	259.72 (6.92%)
	Q_{dl} ($\mu\text{F cm}^{-2}$)	0.49 (6.10%)	2.04 (13.72%)	2.36 (12.44%)	7.01 (9.93%)	0.22 (11.93%)	0.57 (8.41%)

increases up to 20 days as a result of water and chloride ion uptake into the coating pores. Then, its value becomes constant. An increase in coating's capacitance values up to 20 days of immersion can be interpreted as consequence of continuous water uptake [33]. The capacitance values of the coating remain at very low values during the test period due to low permeation of water through the coating. Finally, the coating capacitance decreases to $5.90 \times 10^{-3} \mu\text{F cm}^{-2}$ after 40 days of immersion due to the occurrence of the corrosion process on the metal surface and protective property of the coating. Double layer capacitance values show that the coating containing nanocomposite has high performance as an inhibitor in corrosive media.

4. CONCLUSIONS

The synergetic effect of multi-walled carbon nanotube and poly ortho aminophenol on the anticorrosive properties of epoxy coating was investigated. The main objective of this study was to demonstrate that the addition of a composite of MWCNTs/ PoAP to a coating based on a classic polymer resulted in improved corrosion protection of mild steel. The composites of poly ortho aminophenol and MWCNTs with different contents were synthesized through in-situ polymerization technique. The SEM studies depicted that the nanocomposite containing 1 wt.% MWCNTs

shows some nano-porous morphology of PoAP that has been wrapped on the surface of MWCNTs or MWCNTs have been dispersed in the polymer matrix. The structure of poly ortho aminophenol was confirmed by FTIR spectroscopy. Potentiodynamic polarization studies showed that the critical percent of MWCNT is 1 wt.% which is regarded as the maximum MWCNT percent where the corrosion potential decreases suddenly. Based on the results obtained by EIS analysis, it was concluded that the epoxy coating containing 1 wt.% MWCNT/PoAP exhibited a significantly higher anticorrosive performance comparing to the epoxy coating without the composite in a solution of 3.5 % sodium chloride.

ACKNOWLEDGEMENTS

The support of this research by Payame Noor University is gratefully acknowledged.

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