Cumhuriyet Üniversitesi Fen Fakültesi
Fen Bilimleri Dergisi (CFD), Cilt:36, No: 3 Özel Sayı (2015)
ISSN: 1300-1949

Cumhuriyet University Faculty of Science
Science Journal (CSJ), Vol. 36, No: 3 Special Issue (2015)
ISSN: 1300-1949

# Effect of HCl-doped polyaniline nanoparticles on the corrosion protection properties of epoxy coating

Ghasem EBRAHİMİ[1], Fereshteh REZAEİ[1,*], Jaber NESHATİ[2]

[1] *Corrosion Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran*

[2] *Coating Research Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163, Tehran, Iran*

Received: 01.02.2015; Accepted: 05.05.2015

**Abstract.** Corrosion protection of epoxy novalac coatings containing HCl-doped polyaniline nanoparticles (PANs) on carbon steel were studied by EIS test. SEM image showed that the size of PANs was less than 50 nm. FT-IR analysis characterized polyaniline. TEM micrograph proved uniform dispersion of PANs in epoxy matrix. The results indicated that, addition of PANs could improve the corrosion resistance of epoxy coating. The epoxy coating containing 1wt% HCl-doped PANs had the best performance of corrosion protection among three systems under investigation. The variations in EIS results indicated that the protective layers had been formed under the coating.

**Keywords**: Epoxy novalac Coating, Polyaniline Nanparticles, HCl-Doped, Corrosion resistance, TEM, EIS

## 1. INTRODUCTION

Conductive polymers had been the topic of the large number of investigations during last decades because of their unique properties such as mechanical strength, electrical conductivity, corrosion protection, stability and possibility of both oxidative and electrochemical synthesis [1]. For the corrosion protection, several mechanisms have been proposed; include barrier protection, corrosion inhibition, anodic protection, and shift of electrochemical interface. On the barrier effect, the polymer coating works as a barrier against the penetration of oxidants and aggressive anions, protecting the substrate metals. This effect is similar to paint coating which inhibits the substances from penetrating to the substrate steel. The ability of the conducting polymer to oxidize the substrate steels allows potential of steels to be shifted to the passive state, in which the steels are protected by the passive oxide formed beneath the conducting polymer [2]. It has been postulated that conducting polymers stabilizes the potential of the metal in a passive regime, maintaining a protective oxide layer on the metal. Oxygen reduction on the polymer film is thought to replenish the polymer charge consumed by metal dissolution, thereby stabilizing the potential of the exposed metal in the passive regime and minimizing the rate of metal dissolution [3]. In recent years, it has been established that the presence of PANs in organic coating on steel is able to passivate the pinholes and coating defects by passivation of iron exposed [4].

The inception of Nitrogen hetero atom between Phenyl rings of Polyaniline backbone chain results the significant properties of PANI .The polymer can be prepared by chemical and electrochemical methods from aqueous or organic media. The electrolytic species can participate as dopant and incorporate into the polymeric films [5]. The anions are indispensable to compensate the conducting polymer charges. The structure and the concentration of these anions affect the conductivity, the stability and the morphology of the PAN films [4, 6].

In the present paper, the effect of PAN in epoxy coating on the corrosion protection of carbon steel was observed, and the protective mechanism imparted by PAN was discussed.

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* Corresponding author. *Email address: rezaeif@ripi.ir*

*Special Issue:* The Second National Conference on Applied Research in Science and Technology

## 2. MATERIALS AND METHODS

### 2.1. Materials

The studied samples were formulated with an epoxy polymeric binder. Epoxy (EP) novalac D.E.N 431 (Equivalent Weight (EEW): 175), and polyamine D.E.H (EEW: 24) hardener were used. The weight mixing ratio of resin to hardener was 13:1. Aniline (Ani) (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), HCl acid (37 wt%, Merck) were used.

### 2.2. Synthesis of PANs

Chemical oxidative polymerization of aniline has been carried out in aqueous solution at 0° C by dissolving aniline in a strong acidic solution 1M HCl. The polymerization is initiated by drop wise adding of aqueous Ammonium perdisulphate solution. The reaction is highly exothermic, hence the addition rate of oxidant is properly controlled. At the time of polymerization pH of solution should be controlled to 3 to get emaraldine form of polyaniline. After complete addition of oxidant, this mixture is stirred for 30 min and then the solution was ultrasonicated for 10 min with a UIP 1000 HD ultrasonic instrument from Hielscher Ultrasound Technology Co. After that, the solution was located in refrigerator at 0-4° C for 6 and 24 h. Afterward the deep green mixture is filtered by gravity filtration method and washed with doubly ionized $H_2O$ and dilute HCl until the filtrate become colorless. Further addition of protonic acid, i.e., HCl doping, convert the Emaraldine base form into Emaraldine salt form. Finally the Polyaniline has been sintered in an oven at 50°C for 5 h to get PANs powder. A Vega Tescan Scanning Electron Microscope (SEM) was used to observe the PANs.

### 2.3. Preparation of nanocomposite coating

PANs was added to the resin and the mixture was stirred for 2 h in 2000 rpm. Prior to the application of the coatings, the sharp edges of mild steel panels of size 10 cm×7. 5 cm were filed down. The panel surface was then polished by sand blast and cleaned with acetone. The hardener added to the mixture of resin and PAN. The mixture were then applied on the panels by air spraying and cured at room temperature for 10 days. There was no pinhole on the specimens selected for corrosion measurement. The transmission electron micrographs of polyaniline-epoxy nanocomposite films were obtained using a CM 30, Philips Co. Transmission Electron Microscope (TEM) instrument.

### 2.4. EIS Measurements

Glass tubes were attached to the paint-coated panels to form the electrochemical cells, in order to limit the measurable areas to 7.065 $cm^2$ . The cells were then filled with a 3.5% NaCl solution which acts as a corrosion medium. The test cells were maintained at ambient temperature and the NaCl solution was refreshed regularly during the whole test period. EIS data were collected using a Potentiostat/ Galvanostat Autolab 84165 with Nova 1.6 software, after immersion time in 3.5%wt NaCl. The EIS measurements were performed in 3-electrode mode, using a saturated calomel reference electrode (SCE) and a graphite counter electrode. All measurements were carried out on open-circuit potential (OCP), using 10 mV rms amplitude sinusoidal voltage, over a frequency range of $10^5$–$10^{-2}$ Hz. Prior to each experiment, the open circuit potential was monitored for 30 seconds. The impedance spectra were collected as a function of the exposure time. The times required to perform this test varied between 0 to 2500 h for different samples. Three samples were investigated that were neat epoxy (EP), 0.5 wt%

polyaniline HCl-doped nanoparticles (PAN5) and 1 wt% polyaniline HCl-doped nanoparticle (PAN10).

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the PANs powders

Fig.1 shows the FT-IR absorption spectroscopy of the synthesized PANs powder. For the FT-IR absorption spectroscopy of the synthesized emeraldine base PANs, the vibration at 1578 $cm^{-1}$ is for the quinoid ring, while the vibration at 1496 $cm^{-1}$ depicts the presence of benzenoid ring unit [7]. Furthermore, the peak at 1298 $cm^{-1}$ is related to the C–N stretching of a secondary aromatic amine. The peak at 1160 $cm^{-1}$ is assigned to vibrations associated with the C–H of N=Q=N (Q= quinoid ring). These results suggest that the synthesized powder was PAN in emeraldine state [8].

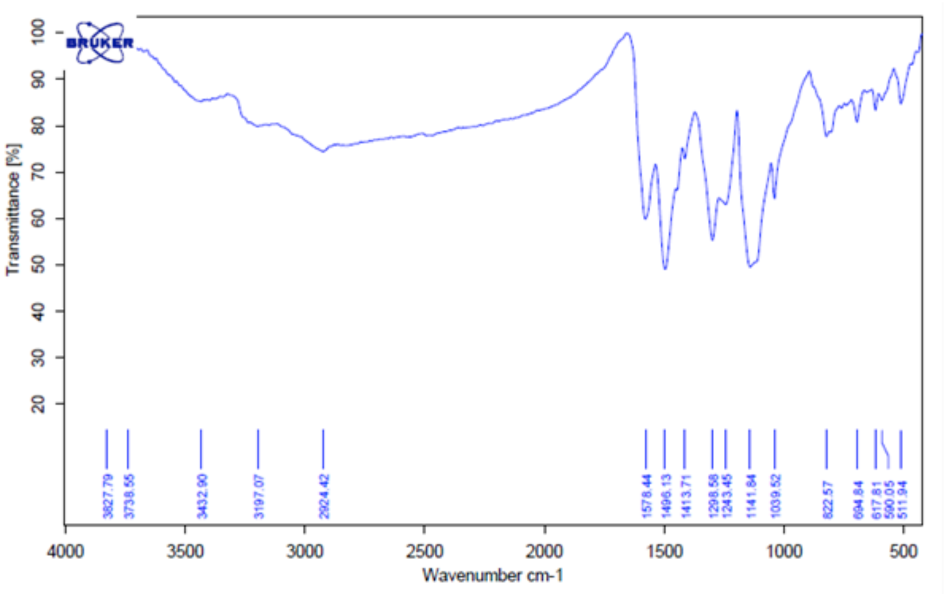


**Figure 1.** FT-IR spectra of synthesized polyaniline

### 3.2. Characterizations of the PANs

SEM images (Figure 2) are used to illustrate the morphology and size of the PANs. Fig. 2(a) and 2(b) showed PANs that were kept in refrigerator for 24 h and 6 h, respectively. Fig. 2(a) showed that the polymerization in solution was finished and then PANs attached to each other wich led to agglomeration. In Fig 2(b) time of polymerization were decreased in order to prevent agglomeration of PANs. Fig. 2(b) showed uniform and nice synthesis PANs with the size less than 50 nm. After adding PANs to epoxy resin, the TEM image (Figure 3) shows the uniform dispersion of the PANs in epoxy cured matrix.

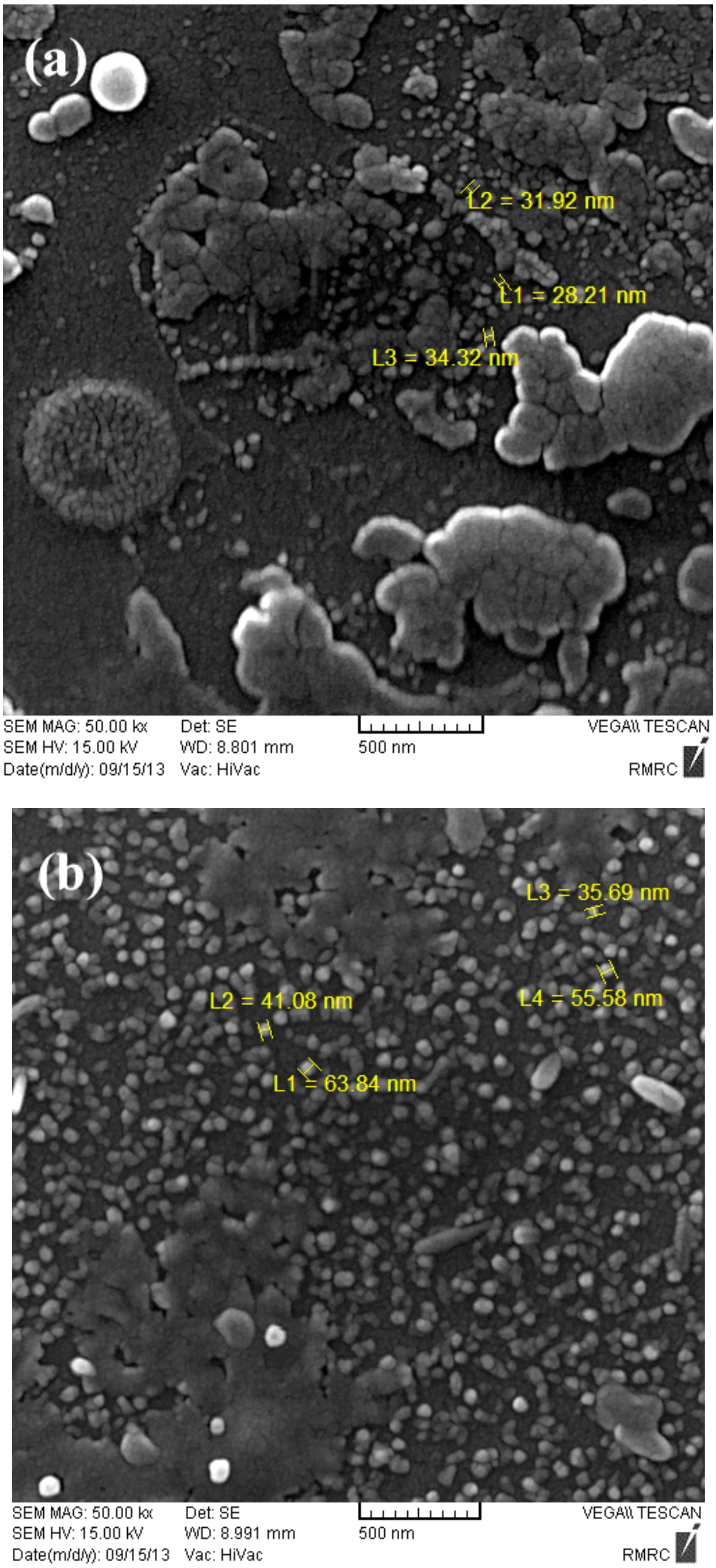


**Figure 2.** SEM micrograph of synthesized polyaniline nanoparticles after 24 h (a) and 6 h (b) of polymerization.

### 3.3. EIS Evaluation

Electrochemical impedance spectroscopy (EIS) has been used with moderate success to monitor and predict the degradation of paint coatings [9-11]. EIS has been used widely and successfully to evaluate the corrosion resistance of the coatings. EIS results for EP coating and PAN5 and PAN10 coatings are presented in the Bode plot and Nyquist formats as a function of immersion time, as shown in Fig. 4-6. The impedance modulus at low frequency (|Z|0.01 Hz)is an appropriate parameter for characterization of the corrosion protection of coatings [12]. In the initial period of immersion, the value of |Z|0.01 Hz of EP coating was $10^8\Omega.cm^2$ (Fig. 4(a)). After 72 h immersion, the value of |Z|0.01 Hz gradually decreased to $10^3$ $\Omega.cm^2$ until the end of immersion period. The Nyquist plots turned to the semicircle shape after 24 h that indicated the diffusion of corrosive agent had been started. Also, after 150 h of immersion the Nyquist plots turned to the semicircle shape with the line by diagnose 45° (Fig. 4(b)). This line indicated that Warburg effect had been revealed in this coating. Warburg element showed an acceleration in EP coating degradation wich led to limiting metal ions generation. Increasing of corrosive products did not allow the metal ions easily to move that so that Warburg element emerged. For PAN5 coating, the value of |Z|0.01 Hz was constant 1MOhm.cm$^2$ up to150 h of immersion (Fig. 5(a)), then it increased slightly to 110MOhm.cm$^2$ until 2000 h immersion, and finally decreased to 10 KOhm.cm$^2$ after 2500 h. This resistance increase and then decrease in long period of immersion indicated protective layer formation on the metal surface behind the coating. The Nyquist plots showed the Warburg element after 150 h immersion (Fig. 5(b)). Warburg element would be emerged because of limiting the corrosive agents diffusion. In PAN5 the impedance increased that is related to the protective layer wich limited corrosive ions. After 2500 h ingress of water and ions increased and led to lose the effect of protective layer and degradation of PAN5 coating. The value of |Z|0.01 Hz of PAN10 coating showed 1GOhm.cm$^2$ (Fig. 6(a)) initially, then smoothly decreased to 100KOhm.cm$^2$ after 300 h of immersion, afterwards it increased to 1MOhm.cm$^2$ until 2000 h. The value of |Z|0.01 Hz of PAN10 coating was more than 5 orders of magnitude higher and 2 orders of magnitude higher than those of EP coating and PAN5 coating, respectively. The EIS results indicated that the corrosion protection of PAN5 coating and that of PAN10 coating were more protective than that of EP coating. Furthermore, PAN10 coating has the highest protective property among three kinds of coatings under investigation.

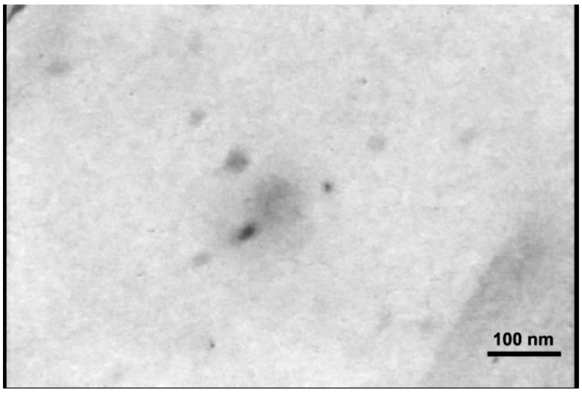


**Figure 3.** TEM micrograph of homogeneous PAN in epoxy coating.

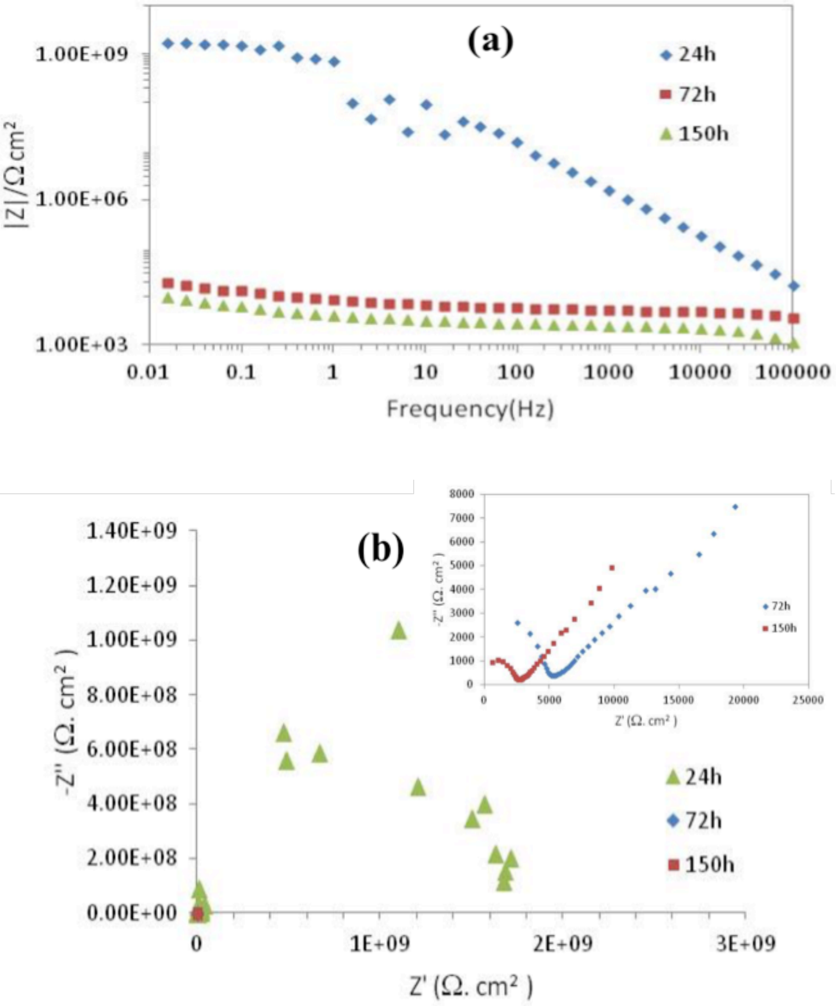
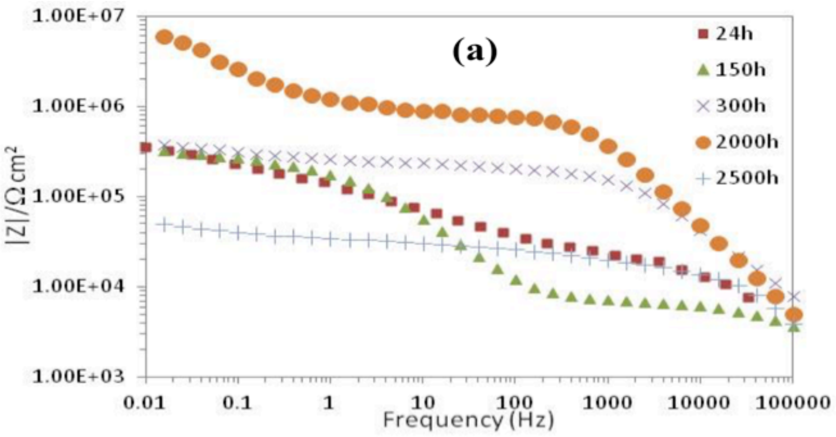


**Figure 4.** The Bode (a) and Nyquist (b) plots of the EP coating at different immersion times in 3.5% NaCl solution.



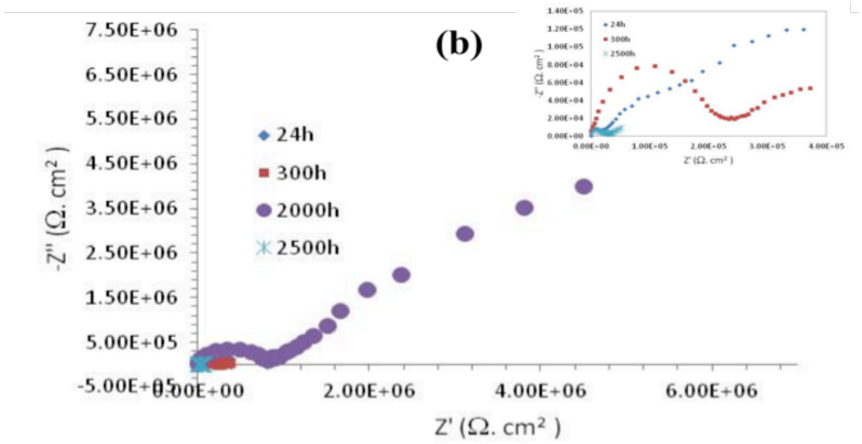


**Figure 5.** The Bode (a) and Nyquist (b) plots of the PAN5 coating at different immersion times in 3.5% NaCl solution.

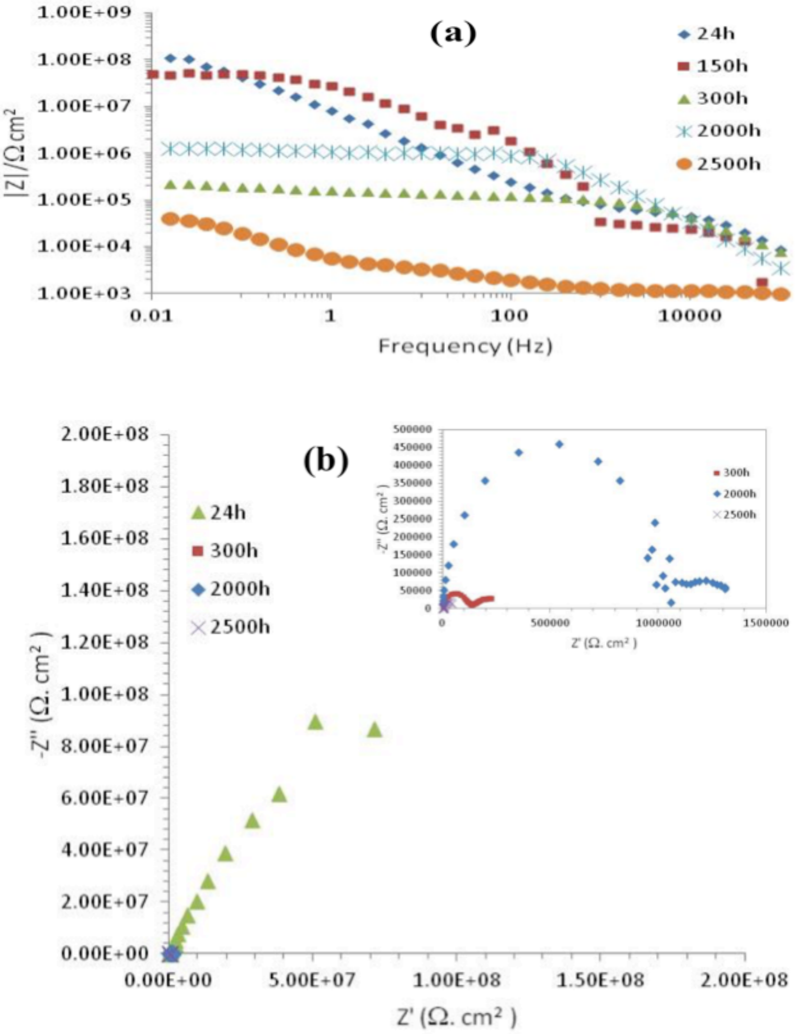


**Figure 6.** The Bode (a) and Nyquist (b) plots of the PAN10 coating at different immersion times in 3.5% NaCl solution.

### 3.4. Mechanism of corrosion resistance of PANs in coating

It has been stated that PANs containing coatings can protect metals by several kinds of possible mechanisms such as barrier protection, corrosion inhibition, anodic protection, and formation of an insoluble counter-anion salt, the inhibitory properties of the counter-anion, etc. [5]. In the following section the mechanisms of PANs coatings were discussed. One of the important functions of coating was barrier protection for aggressive ions. According to the above analysis, the polyaniline coating impedance had higher values than EP coating. The diffusion process of the electrolyte into the PANs coating would be more difficult than into the EP coating. The better barrier property of PANs coating could impede the penetration of the corrosive ions to the interface of the coating/carbon steel substrate and improve the protective properties of the coating on the surface of carbon steel. Hence, mechanism of the inhibition of polyaniline by protective layer to corrosion had been proposed by some researchers [13]. In general, the corrosion protection ability is mainly attributed to the passivating effect of polyaniline due to the oxidizing ability of its emeraldine state. The emeraldine base polyaniline in the coating was reduced to reductive polyaniline (Leuco base), and then the reduced PAN (Leuco base) was again oxidized to its original form (emeraldine base polyaniline) by the oxygen reduction reaction occurring in polyaniline [13]. Results of EIS showed that the impedance after initial immersion times increased that indicated passive layer formation. So the protective film was formed on the surface of carbon steel beneath the PAN5 coating and the PAN10 coating due to redox reaction with emeraldine base of PAN. Therefore, PAN5 coating and PAN10 coating had better protective corrosion ability than EP coating.

## 4. CONCLUSION

In the present work, effect of HCl-doped polyaniline nanoparticles on corrosion protection abilities of epoxy coatings on carbon steel plates were studied by using EIS technique. SEM micrograph showed a nice synthesis polyaniline nanoparticles with the size less than 50 nm. For investigation dispersion of polyaniline nanoparticles, TEM proved a uniform dispersion in the epoxy matrix. EIS results revealed that the coating contain polyaniline nanoparticles had better corrosion resistance than neat epoxy. In addition increasing impedance to corrosion after initial times indicated protective layer generation beneath PANs containing Epoxy coating.

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