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Full Paper

Effect of Chloride-Doped Polyaniline Content on the Adhesion, Barrier Property and Corrosion Behaviour of Zinc Phosphate Epoxy Primer in 3 wt% NaCl Solution

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Abstract- In the present work, HCl doped polyaniline (Pani-Cl) was chemically synthesized. Chemical structure of Pani-Cl powder was confirmed using UV-visible, infrared spectroscopy and electrical conductivity measurements. Synthesized Pani was added to commercial zinc phosphate primer paint (ZP) to enhance its anticorrosion properties. The anticorrosion performance of coatings containing 0.1- 0.4 wt% polyaniline on carbon steel was evaluated in 3.0 wt% NaCl solution by open circuit potential (OCP), polarization curves and electrochemical impedance spectroscopy (EIS) measurements. The experimental results showed that the coating with 0.2 wt% of Pani-Cl (ZP-Pani0.2) provides higher anticorrosion properties and offers better barrier characteristics in the paint film, as compared with original primer. After a period of 600 hours, carbon steel coated with ZP-Pani0.2 showed good resistance against corrosion (low corrosion rate and high resistance). Besides, the OCP value was higher than that of ZP-coated steel due to the barrier effects of Pani-Cl. However, the use of more than 0.2 wt% Pani-Cl additives reduced the coating's protection efficiency. Paints adhesion was evaluated by cross cut test. It was found that paints containing 0.3 and 0.4 wt% of polyaniline present lower adhesion, as compared with the reference paint.

Keywords- Corrosion; Coatings; Polyaniline; Carbon steel; Electrochemical methods

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1. INTRODUCTION

Corrosion is the destruction of materials, *especially a metal*, by chemical reactions with their environment. It is one of the major processes that cause huge economic losses and damage in many industrial sectors. The annual expenses on corrosion globally are more than 3% of gross domestic product (GDP) [1,2].

One of the most effective ways to prevent metallic structures from corrosion is to apply organic protective coatings that contain anticorrosion pigments. These coatings act as a barrier to prevent the diffusion of aggressive substances to the steel surface. However, all organic coatings are not ideal barriers. The addition of anticorrosive pigments can reduce the corrosion rate at coating defects and decrease the rates of anodic corrosion [3,4].

For its relative environmental protection, zinc phosphate pigment attracted much attention [5-7]. There are various arguments regarding its inhibition mechanism in the corrosion process. Some authors noted that the addition of zinc phosphate pigments to the paints enhances their barrier properties [8,9]. Many researchers considered that the protective action of zinc phosphate was due to phosphatization or passivation of the metal surface with the formation of complex substances [6,10,11].

In recent years, several types of research have focused on the use of conductive polymers as anticorrosive pigments in paint formulations [12-15]. Due to its environmental stability and excellent chemical stability and corrosion inhibition, polyaniline (Pani) has been widely investigated [13,16-18]. *P*aints containing polyaniline or combinations of pigments offer more corrosion resistance to steel surfaces [19-21].

Several reports described the corrosion protection mechanism of polyaniline in paints. It was reported by Sathiyanarayanan [22] and Gonçalves [23] that the coating pigmented with polyaniline offers more corrosion resistance to steel by the formation of layers of iron oxides. XPS and Raman spectroscopy analysis revealed the formation of a protective layer of oxides beneath the coating. Diniz et al. [24] found that the addition of dodecylbenzene sulfonic acid (*DBSA*) doped PANI, as a pigment; in epoxy coatings increases its barrier effect in a salt spray medium. Yang et al. [25] studied the corrosion resistance of steels coated with zinc-rich epoxy paint, containing *o*-amino benzene sulfonic acid-doped polyaniline, in a saline solution. PAni-salt was found to offer good corrosion resistance by both barrier and electrochemical passivation effects.

Due to the redox property of polyaniline, Wessling [26,27] suggests that organic coatings, containing polyaniline (ES) salt, protect exposed areas of steel by an anodic shift in corrosion potential, which leads to passivation and anodic protection. Other authors [28,29] attribute the effect to the formation of a complex between iron and the dopant anion associated with polyaniline.

Generally, the Anticorrosion mechanism of Pani-based coatings depends on dopant acid, substrate, aggressive medium, and paint formulation.

In the present work, the corrosion behaviour of a commercial zinc phosphate paint (ZP paint) was studied with different chloride-doped Pani (Pani-Cl) contents in the range of 0- 0.4 wt%. Firstly, polyaniline salt powder was prepared and characterized by UV-Visible, FTIR, and conductivity measurements. Then, the influence of Pani-Cl content on the anticorrosion performance of the coatings was studied in 3 wt% NaCl by electrochemical techniques, including open circuit potential (OCP), potentiodynamic polarization, and impedance spectroscopy (EIS).

2. EXPERIMENTAL SECTION

2.1. Synthesis of Pani-Cl

Doped polyaniline was prepared by oxidative polymerization of aniline (98.5 pur. from VWR Prolabo Chemical, Figure 1), at a low temperature (0–5 °C), using ammonium persulfate (APS, from Biochem Chemopharma) as an oxidant in a hydrochloric acid medium (37% pur. from VWR Prolabo Chemical). Initially, 0.025 mol of aniline monomer (2.328 g) was dissolved in 50 ml of HCl (1 M). Then, the solution was cooled in an ice bath. After, 50 mL of chloridric acid solution (1 M), containing 0.025 mol of APS (5.71 g) was added slowly to the monomer solution. The final solution was stirred for 5 hours. The resulting Pani precipitate was filtered and washed with distilled water and acetone and dried at 60 °C under vacuum for 24 hours.

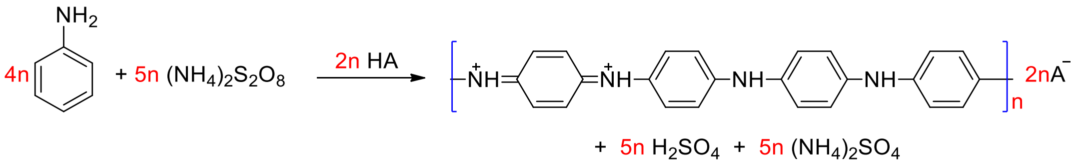

Figure 1. Scheme of the oxidation reaction of aniline. HA is the doping acid [30]

2.2. Preparation of paint and coated samples

The substrate used for coating purposes is a carbon steel sheet of the composition, C=0.24%, Mn=0.9%, P=0.035%, Cu=0.2, S=0.04%, Si=0.4%, and Fe=balance, with 1.5 cm^2 of exposure area used for the corrosion analysis. All samples were ground using 800 grit emery papers, degreased in ethanol, rinsed with water, and dried in the air before the coating was applied.

A commercial zinc phosphate epoxy primer (supplied by the Algerian national company of paints ENAP) was used as a reference paint to prepare various coating compositions. The ZP paint was constituted of epoxy resin and polyaminoamide hardener, with a ratio of paint/hardener 93/7 in weight, zinc phosphate as an anti-corrosion agent, additives, and solvent. To prepare the Pani-modified ZP coating, different weight percentages of Pani-Cl powder were added to the original ZP paint. Four different contents, 0.1%, 0.2%, 0.3%, and 0.4%, were selected for the incorporation of additives. The obtained paints were noted as ZP-Pani0.1, ZP-Pani0.2, ZP-Pani0.3, and ZP-Pani0.4, respectively.

The coatings were applied onto steel panels using a paintbrush. The samples were dried in the air for five days. The paint thickness was 80±5 µm.

The samples were cut into plates of dimensions 60 x 60 x 4 mm for the adhesion test. These latter were ground using 800 grit emery papers before being covered with the studied paints.

2.3. Characterization of Pani-Cl pigment

The prepared Pani-Cl was characterized with UV–vis spectra in the 300-800 nm wavelength range, using Cary 60 UV-Vis spectrophotometer and Fourier-transform infrared spectroscopy (Perkin-Elmer FTIR 1720-X model). The conductivity measurement of polyaniline was carried out under laboratory conditions, using Jandel four-point probe connected with a Keithley 2400 sourceMeter. For UV- visible and conductivity tests, pre-treated glass slides were placed in the beaker, during the polymerization reaction, for film deposition. The optical microscopy image of the formed film and the polyaniline powder, dispersed in distilled water, was performed using Primo Star microscope.

2.4. Characterization of coatings

2.4.1. Adhesion

The adhesion strength is an important target to evaluate the quality of paint layers. It was qualitatively determined by the cross-cut method according to ASTM D3359.

2.4.2. Barrier effect and anticorrosion performance of the coatings

To investigate the barrier effect and the anticorrosive performance of the studied coatings, OCP, potentiodynamic polarization, and EIS experiments were performed in 3 wt% NaCl solution at room temperature, using an AUTOLAB model PGSTAT 302 N. Electrochemical tests were conducted in a conventional three-electrode cell, in which the reference electrode was Ag/AgCl (in a saturated KCl solution), the counter electrode was Platinium, and the coated steel served as the working electrode (1.5 cm^2 exposure area). The EIS measurements were carried out in the range from 10^5 Hz to 10^{-1} Hz, with a 10-mV sinusoidal signal perturbation. The fitting parameters for the EIS spectra and the simulation of electrical circuit analogs were performed with the software Nova 2.1.4. Open circuit potentials (OCP) were measured prior to each impedance measurement.

3. RESULTS AND DISCUSSION

3.1. UV- visible and FTIR spectra of Pani-Cl

Figure 2 shows UV-Vis and FTIR spectra of hydrochloric acid-doped polyaniline (Pani-Cl) prepared by chemical oxidation. Three bonds characteristic of the polymer are observed at 355, 435, and 775 nm. The first (355 nm) corresponds to the π-π^*transition of the benzenoid rings. The bonds at 435 and 775 nm are assigned to the polaron band transition [31]. The presence of these three absorption bands confirms that polyaniline is in the doped form.

The FTIR spectrum of the synthesized polyaniline shows the typical peaks of protonated Pani-Cl. The absorption peaks at 1476 and 1570 cm^{-1} are assigned to the stretching vibrations of the benzenoid and quinoid rings, respectively [32]. Stretching vibration of aromatic C–H in-plane bending is found at 1116. The peaks at 1235 and 1279 cm^{-1} are corresponding to the C–N vibrating mode of secondary aromatic amine [33]. The C–H out-of- plane bending mode appears at 790 cm^{-1}.

The optical microscopy image of the film formed on the glass slide and the polyaniline particles, dispersed in distilled water, are shown in Figure 3.

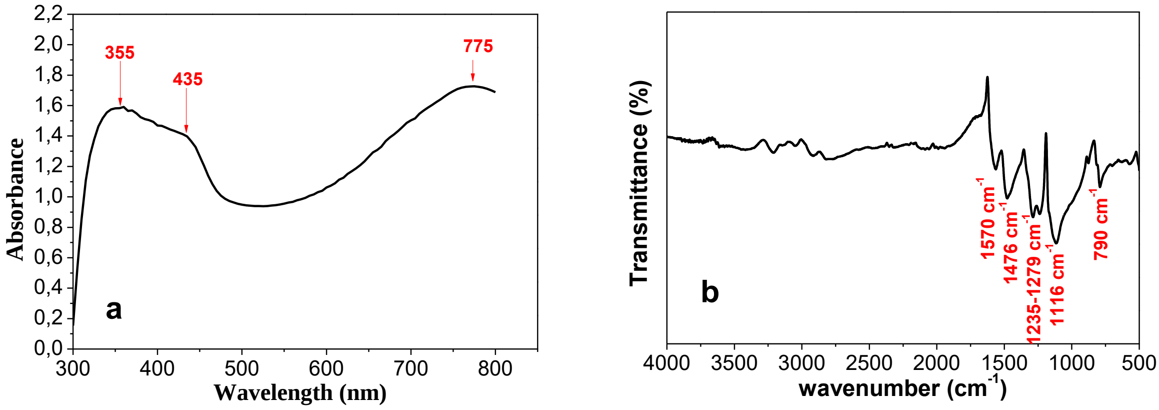

Figure 2. Pani-Cl absorption spectra: (a) UV–visible and (b) infrared spectroscopy

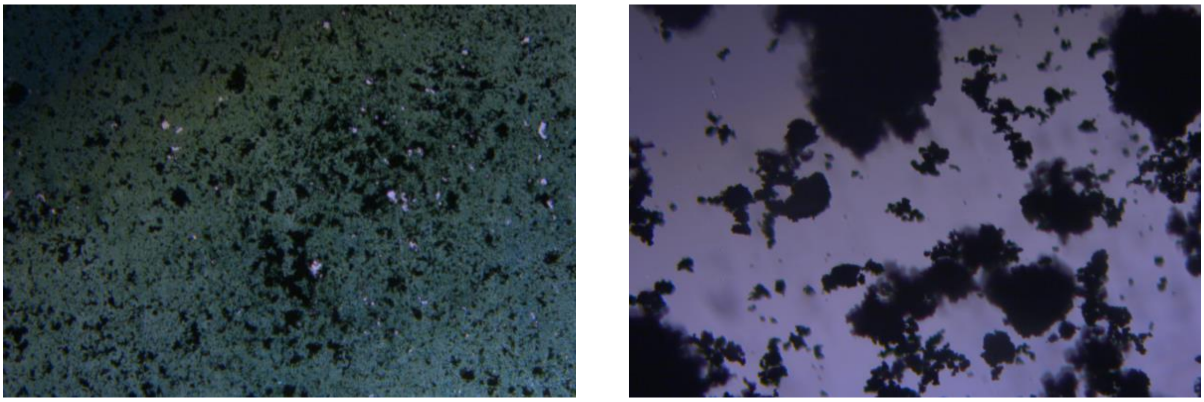
(a) (b)

Figure 3. Optical microscopy image of film formed on the glass slide (a) and the polyaniline powder dispersed in distilled water (b)

3.2. Conductivity

The conductivity of polyaniline doped with HCl was measured according to four-point method and were recorded 0.48 S/cm. This value is significantly higher than those of common polymer, which is 10^{-9} S.cm^{-1} but lower than that of typical metals (>10^4 S.cm^{-1}) [34].

3.3. Adherence strength

The adherence strength between the coating system and the steel surface is an important parameter influencing the anticorrosion efficiency of paints. Table 1 compares the adhesion properties of the investigated coatings before immersion in NaCl solution. Zinc phosphate coating (ZP) and Zinc phosphate-Pani coatings (ZP-Pani0.1 and ZP-Pani0.2) exhibited a good adhesion to their steel surface, where less than 5% of the paint was affected. The removed area percent increases with the increase in polyaniline content. The adhesion of ZP-Pani0.3 and ZP-Pani0.4 are lower than that of the reference paint.

Table 1. Adhesion test classification for coatings according to ASTM D3359

	Percent area removed	**Classification (5B = 0% removed area and 0B = more than 65% of removed area**
ZP	Less than 5%	4B
ZP-Pani0.1	Less than 5%	4B
ZP-Pani0.2	Less than 5%	4B
ZP-Pani0.3	5–15%	3B
ZP-Pani0.4	5–15%	3B

3.4. OCP measurements

The variation in OCP with time indicates the coating's stability when exposed to an aggressive medium. Figure 4 shows the OCP plots as a function of immersion time, in 3 wt% NaCl solution, during 25 days, for the different systems investigated.

The OCP values of ZP/steel changed slowly in a negative direction and reached a level of -0.056 V after 25 days of exposure. ZP-Pani0.1 and ZP-Pani0.2 coatings are able to maintain higher noble and stable potential values, as compared with ZP coating (at around -0.033 and 0.015 V, respectively), which indicates an improved barrier property and a stable coating/ surface metal interface. In other words, polyaniline slows down the diffusion of water and aggressive species and creates an active electronic barrier in the paint [24]. The corrosion potential of steel coated with ZP-Pani0.3 and ZP-Pani0.4 is more negative than that of the ZP paint. The OCP values of these coatings decrease gradually with the immersion time, indicating the penetration of the electrolyte into the film [35].

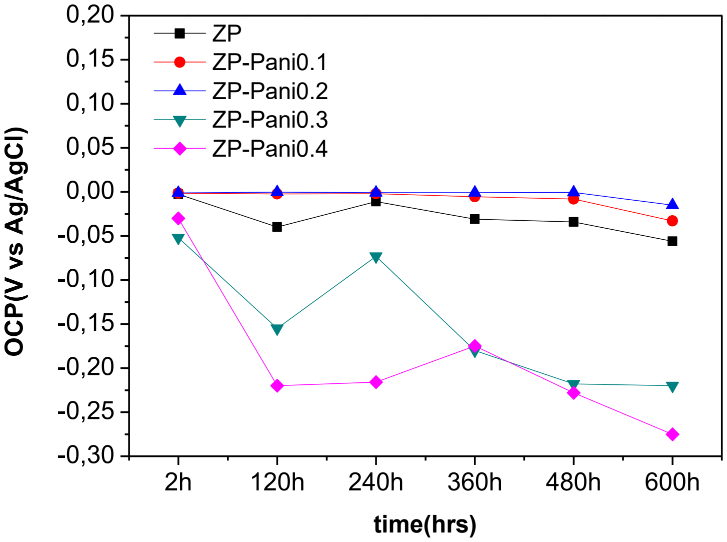

Figure 4. OCP versus time of exposure in NaCl 3 wt % of different coatings.

3.5. Potentiodynamic measurements

The polarization curves of the coated steel samples were made after 600 hrs of immersion in 3 wt% NaCl solution. The intersection of the corresponding anodic and cathodic polarizations was used to calculate the electrochemical parameters [36,37].

Figure 5 presents the Tafel polarization plots of ZP and ZP-Pani coatings. The corrosion parameters (corrosion current (I_{corr}) and corrosion potential (E_{corr})) of these curves are given in Table 2.

All of the curves are the same shape, with a cathodic and anodic part. This latter shows an approximate passive behaviour with a nearly low current density.

Table 2. Parameters obtained from polarization curves of different studied coatings

	E_{corr} (mV/AgCl) ±5 mV	**I_{corr} (nA/cm^2) ±0.2**	**Corrosion rate (10^{-5} mm/year) ±0.4**
ZP	-188	5.1	5.92
ZP-Pani0.1	-142	3.5	4.07
ZP-Pani0.2	-124	2.9	3.43
ZP-Pani0.3	-227	8.14	9.46
ZP-Pani0.4	- 248	12.5	14.53

Compared with ZP paint, the E_{corr} values of ZP-Pani0.1 and ZP-Pani0.2 coatings positively shifted to -142 and -124 mV, respectively. Accordingly, the values of I_{corr} decreased to 3.5 and 2.9 nA/cm^2, respectively. Potentiodynamic results showed that the corrosion rates of ZP-

Pani0.1 and ZP-Pani0.2 were lower than those of ZP. However, the electrochemical tests performed in samples coated with ZP-Pani0.3 and ZP-Pani0.4 showed different behaviour. Figure 5 shows that the potential was more negative for these both coatings (-227 and -248 mV, respectively). Corrosion rates and corrosion currents were higher, as compared with the reference one. The good anticorrosive properties of the coating are associated with its lower porosity [35]. This gives a preliminary idea that the presence of Pani in a small amount improves the protective efficiency of ZP coating by barrier effect. And the increase in polyaniline contents leads to an increase in the coating's porosity, resulting in a low barrier effect.

ZP-Pani0.2 coating has the lowest I_{corr} and most positive E_{corr}. This means that this coating provides the best anti-corrosion performance. The obtained results are in good agreement with OCP measurement.

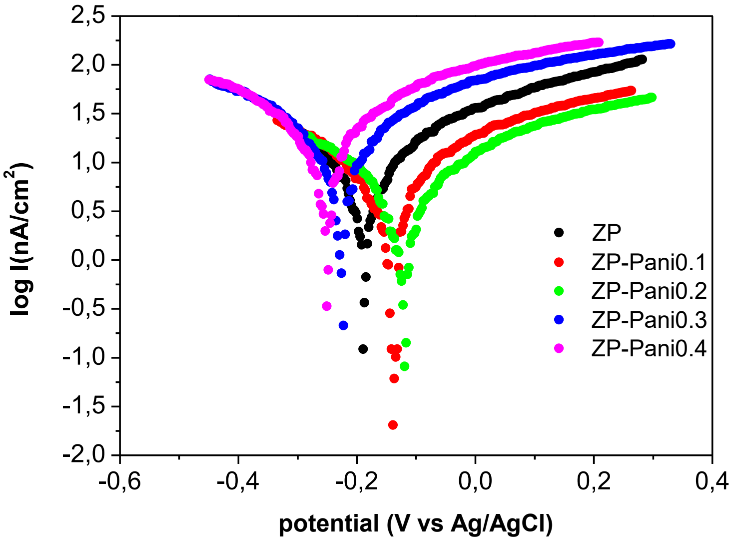

Figure 5. Tafel polarization curves measured in 3 wt% aqueous NaCl solution of the different investigated coatings

3.6. EIS measurements

The EIS analysis has been frequently used to evaluate the anticorrosion efficiency of coatings [38-43]. EIS data were used to represent the corrosion protection behaviour of carbon steel electrodes, coated with zinc phosphate paint, with different content of Pani-Cl. Figure 6 displays Nyquist plots as a function of exposure time. The diagrams of the reference coating show a single capacitance loop over the whole exposure time, which is attributed to the coating characteristics. The diameter of the semicircle in the Nyquist plots decreased gradually with exposure time, indicating that the electrolyte penetrated into the film, but did not reach the coating/substrate interface. The coatings with 0.1, 0.2, and 0.3 wt% Pani exhibit similar features as the reference coating, indicating a capacitive behaviour and barrier protection. The

ZP-Pani0.4 coating plots show one capacitance loop during 480 hours of immersion. After 600 hrs, a second-time constant appeared in the low frequencies region, which can be attributed to the processes occurring underneath the film [42,43], suggesting that water and corrosive agents penetrated into the coating and that the metal surface was reached.

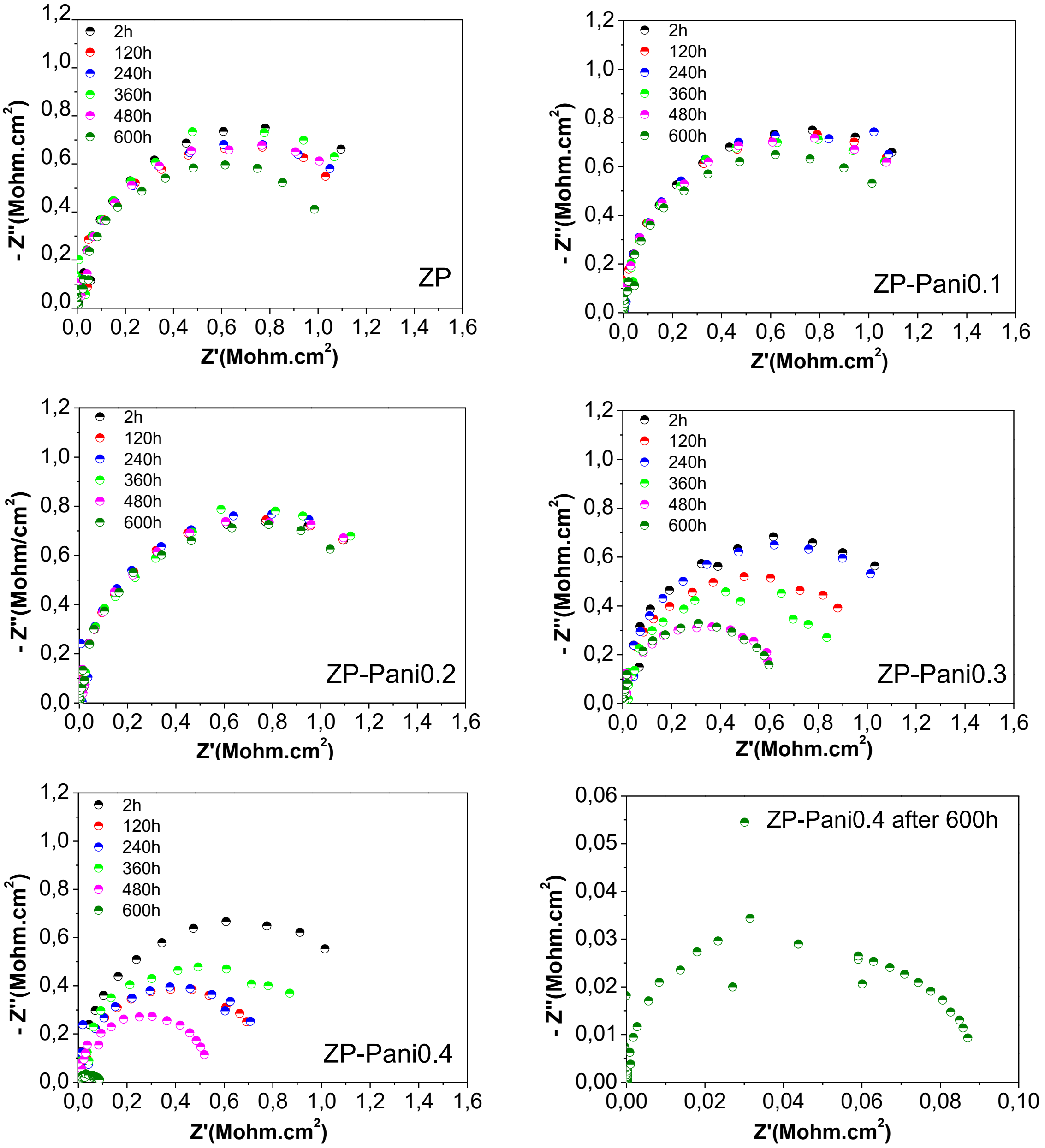

Figure 6. Nyquist plots of coated steel with ZP and ZP-Pani paints, at different immersion times, in 3% NaCl for 600 hrs

The equivalent circuit in Figure 7 was selected to fit the EIS data. A parallel RC circuit in series with solution resistance (Figure 7a) was selected for data fitting, during the whole immersion test period, when there is only one capacitive arc in the Nyquist plots of the coating.

The model consists of solution resistance (R_s), coating resistance (R_c) and coating capacitance (C_c).

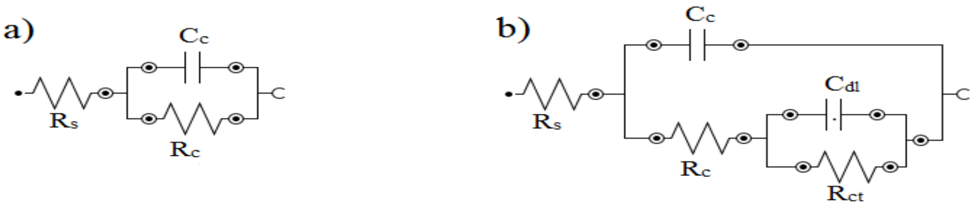

Figure 7. Equivalent electrical circuit for impedance measurements: (a) with one time constant, and (b) with two times constant

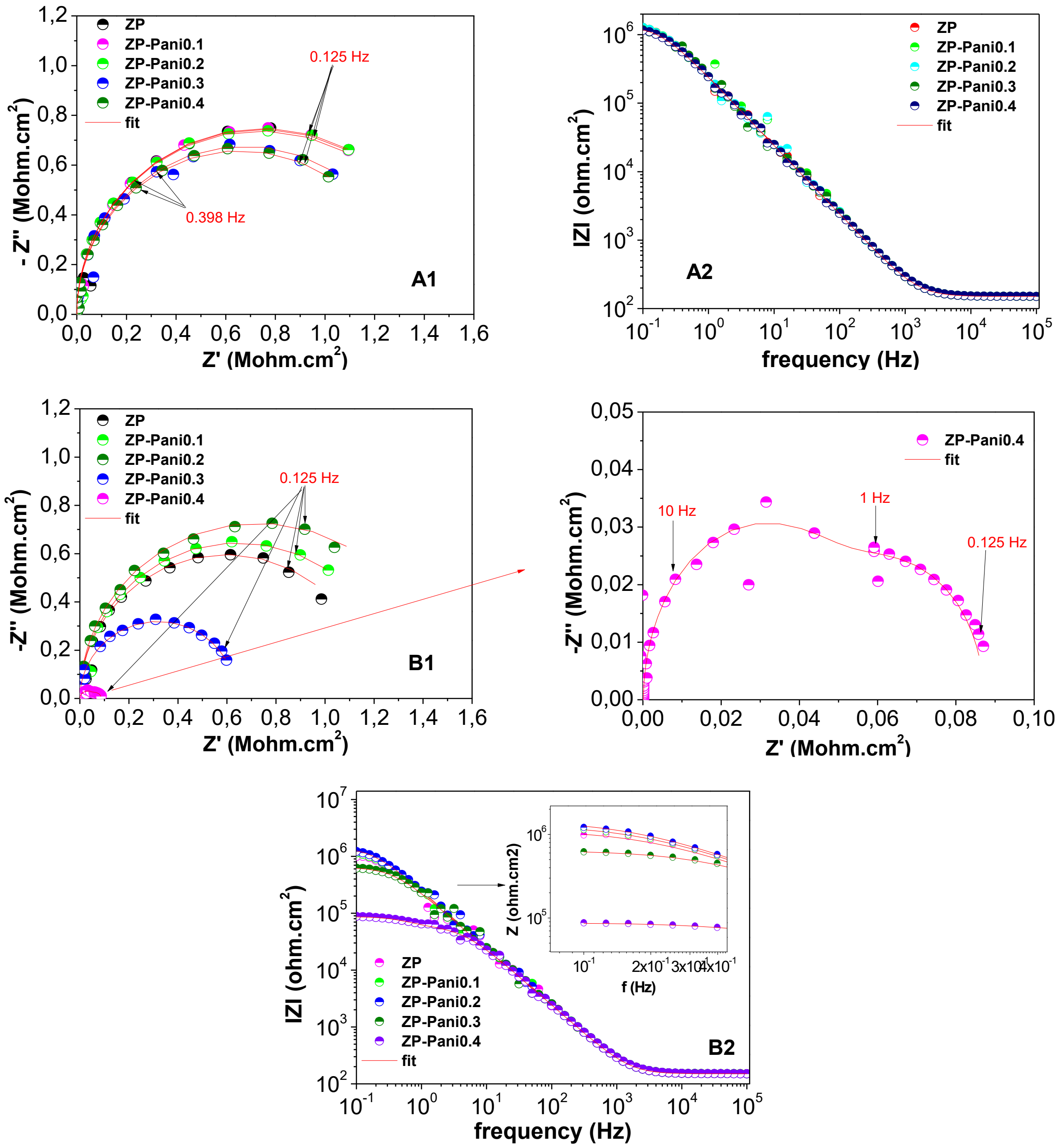

Figure 8. Experimental and fitted Nyquist and Bode plots of different studied paints after 2 hrs (A) and 600 hrs (B) of immersion in 3 wt% NaCl

The equivalent circuit in Figure 7b shows that there are two-time constants and it was chosen for data fitting of ZP-Pani0.4 coating spectra, after 600 hrs of exposure in 3 wt% NaCl.

It consists of a solution resistance (Rs), coating resistance (R_c), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), and coating capacitance (C_c). Experimental and fitted Nyquist and Bode plots of different studied paints are shown in Figure 8, after 2 and 600 hrs of immersion. The detailed EIS parameters fitted with Nova software are shown in Table 3.

The barrier capacity of the coating is directly related to coating resistance (R_c) and coating capacitance (C_c) [44-46]. Coating resistance reflects the anti-permeability effect of the coating on the electrolyte solution, and coating capacitance is closely related to the diffusion behavior of the electrolyte solution into the film paint.

The evolution of the fitted values of R_c and C_c of all coating systems is shown in Figure 9. The coating resistance of ZP paint was initially 1.47 MΩ.cm^2. After 600 hrs of immersion, the resistance of the film decreased to 1.11 MΩ.cm^2. The resistance of the coatings with 0.1 and 0.2 wt% of Pani-Cl, as determined by the EIS data fitting, was initially at around 1.49 MΩ.cm^2. It decreased to 1.29 MΩ.cm^2 for ZP-Pani0.1 and 1.45 MΩ.cm^2 for ZP-Pani0.2, after 600 hrs of exposure time. The R_c of the ZP-Pani0.2 paint changed negligibly during the whole immersion period. Besides, during the entire immersion time, the C_c values of ZP-Pani0.1 and ZP-Pani0.2 coatings are lower than that of ZP coating, due to low permeation of water through the paint film, indicating that the addition of a little amount of polyaniline can improve the barrier effect of coating. These results show that the addition of polyaniline improved the resistance of coatings. The coating with 0.2 wt% Pani-Cl showed the best corrosion performance.

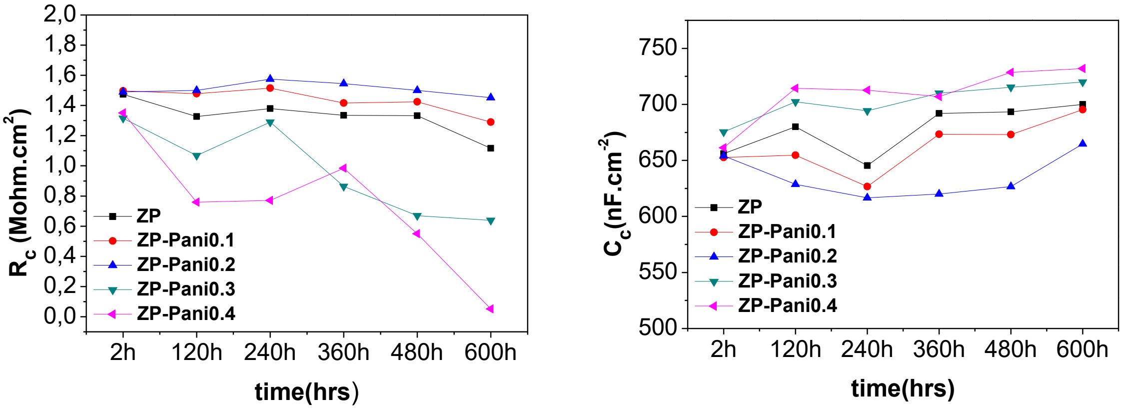

Figure 9. Evolution of R_c and C_c with time derived from EIS data

However, the increase in Pani-Cl pigment induced a rapid decrease in the resistance, which reached 0.63 and 0.052 MΩ.cm^2 for coatings containing 0.3 wt% and 0.4 wt% Pani-Cl, respectively, after 600 hrs of immersion time. Figure 9 shows a quick increase in C_c of paints containing 0.3 and 0.4 wt% of Pani-Cl, indicating that water passed rapidly through the film paint to reach the steel surface.

Table 3. EIS parameters of different coatings investigated

	OCP(V vs Ag/AgCl)	**R$_s$** (Ω.cm^2)	**R$_c$** (MΩ.cm^2)	**C$_c$** (nFcm^{-2})	**R$_{ct}$** (Ω.cm^2)	**C$_{dl}$** µF.cm^{-2}	**IZI$_{0.1Hz}$** (kΩ.cm^2)
ZP							
2h	-0.0025	150.69	1.474	656	-	-	1279.89
120h	-0.040	150.34	1.327	680	-	-	1168.55
240h	-0.011	150.52	1.38	645.33	-	-	1199.62
360h	-0.031	150.67	1.335	692	-	-	1240.38
480h	-0.034	150.61	1.332	693.33	-	-	1177.16
600h	-0.056	150.75	1.117	700	-	-	985.62
Z-Pani0.1							
2h	-0.0015	150.6	1.497	652.67	-	-	1277.40
120h	-0.0023	150.34	1.479	654.67	-	-	1247.16
240h	-0.002	150.54	1.515	626.67	-	-	1261.59
360h	-0.0055	150.43	1.416	673.33	-	-	1232.60
480h	-0.008	150.34	1.425	673	-	-	1237.02
600h	-0.033	150.52	1.29	695.33	-	-	1144.8
Z-Pani0.2							
2h	-0.0012	150.64	1.49	654	-	-	1279.54
120h	-0.0003	150.57	1.5	628. 67	-	-	1278.1
240h	-0.0008	150.61	1.575	616.67	-	-	1275.06
360h	-0.00075	150.49	1.545	620	-	-	1312.72
480h	-0.00071	150.58	1.5	626.67	-	-	1284.17
600h	-0.015	150.39	1.452	664.67	-	-	1212.86
Z-Pani0.3							
2h	-0.052	150.33	1.315	675.33	-	-	1175.43
120h	-0.155	150.49	1.068	702.33	-	-	963
240h	-0.073	150.52	1.29	694.33	-	-	1144.8
360h	-0.18	150.45	0.864	710	-	-	877.96
480h	-0.218	150,58	0.67	715.33	-	-	618.68
600h	-0.220	150.57	0.639	720	-	-	618.9
Z-Pani0.4							
2h	-0.030	150.66	1.351	661.33	-	-	1155.47
120h	-0.220	150.52	0.759	714.33	-	-	736.39
240h	-0.216	150.46	0.771	712.67	-	-	751.26
360h	-0.175	150.3	0.984	707	-	-	945.08
480h	-0.228	150	0.55	728.67	-	-	530.61
600h	-0.275	150.21	0.052	732	0.034	8.93×10^3	87.53

The increase in water absorption can be assigned to the poor distribution of the Pani particles in the ZP matrix and to the increase in the pigment volume in the coating, which leads to the formation of fine pores in the paint film [47].

After 600 hrs, the ZP-Pani0.4 paint lost its barrier properties. ZP, ZP-Pani0.1, ZP-Pani0.2, and ZP-Pani0.3 coatings maintained a good barrier effect.

ZP-Pani0.2 coating had the lowest C_c value and highest R_c value, suggesting that it has the best penetration barrier aptitude after long-term exposure.

According to the literature [48,49], the impedance modulus at low frequency ($|Z|_{0.1\ Hz}$) can be used to measure the protective efficiency of the coatings.

At the initial stage of immersion, $|Z|_{0.1Hz}$ of ZP coating in NaCl solution was 1279.89 $k\Omega.cm^2$ and it decreased to 985.62 $k\Omega.cm^2$ (Figure 10). After 600 hrs of immersion, indicating the continuous permeation of electrolyte. As a comparison, $|Z|_{0.1Hz}$ of coatings containing 0.1 and 0.2 wt% of Pani, in the same solution, decreased slightly. After 2 hours of immersion, it was 1277.40 $k\Omega.cm^2$ and 1279.54 $k\Omega.cm^2$ for ZP-Pani0.1 and ZP-Pani0.2 coating, respectively. The final $|Z|_{0.1\ Hz}$ of these two coatings were 1144.8 and 1212.86 $k\Omega.cm^2$, respectively. The impedance modulus of coatings containing 0.3 and 0.4 wt% of polyaniline at low frequency decreased quickly with exposure time. It reached 618.9 and 87.53 $k\Omega.cm^2$, respectively, after 600 hrs. This means a rapid penetration of the electrolyte through the paints film. The barrier property of the ZP-Pani0.4 coating was not stable and failed after 600 hours of exposure.

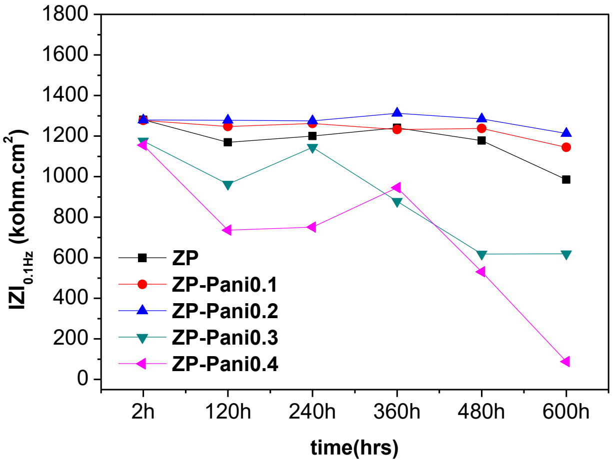

Figure 10. Evolution of $|Z|_{0.1\ Hz}$ with immersion times of different studied coatings

In summary, the impedance data showed that the addition of 0.2 wt% of Pani-Cl pigment enhanced the anticorrosion performance of ZP paint.

4. CONCLUSION

In this work, polyaniline particles (Pani) were chemically prepared in the presence of HCl as a dopant. Conductivity UV-vis and Infrared spectroscopy results confirm that polyaniline is in the doped form. The corrosion resistance of the commercial zinc phosphate coating and the zinc phosphate coating, containing polyaniline, in 3 wt% NaCl solution, was investigated by the electrochemical methods. The OCP and EIS results revealed that the coating with 0.2 wt% of Pani-Cl offered a higher corrosion protection than the zinc phosphate coating. This could be attributed to the barrier ability of polyaniline and its good dispersion in epoxy matrix. The coatings with 0.3 and 0.4 wt% Pani contents showed a lower anticorrosion efficiency, as compared with the other coatings. This poor performance could be attributed to the high porosity of the coating. The potentiondynamic measurements also pointed in the same direction.

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