Polyaniline-Epoxy Coatings for Corrosion Protection of Carbon Steel in Acidic Soil Solution

N. A. Rahman¹, M.C. Ismail², and Z. Man³

¹Mechanical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

²Centre for Corrosion Research, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

³Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

mokhtis@petronas.com

Abstract

This article is providing the information on properties of Polyaniline (PANI)-epoxy as an external coating in acidic soil environment (pH 3 and 5). Epoxy incorporating with PANI at varied weight percentages. The corrosion assessment on coated carbon steel was evaluated by salt spray, cathodic disbonding test, and immersion test. The impedance properties of the coated substrate are estimated by electrochemical impedance spectroscopy (EIS). The increasing of corrosion protection of PANI-epoxy coating was obtained shown that 1.5 wt.% PANI content in epoxy provides an acceptable protection against corrosion in acidic NS4 soil solution. The cross section images by SEM were clearly shows that addition of PANI is able to increase the porosity own by neat epoxy coating which supported well that PANI played an important role in anti-corrosion performance for carbon steel in acidic media.

Keywords: PANI-epoxy coating, NS4 soil solution, corrosion

Introduction

In general, the external coating primarily functions as a protection barrier against corrosive environment. Coating systems are formulated based on both environmental conditions and desired life of the structure [1]. A foremost application of external coatings is to protect the metal structure from corrosion attack. Further innovation and coating technology development is important since corrosion attack still remains a serious problem with a multiple of governing factors. In underground conditions, the pH plays an important role

and affects the corrosion potential of the pipelines. In underground environment, the pH of soil sometimes was fall in acidic range, depends on the surroundings factors. The acidic pH was produced from industrial waste, human activities such as agriculture, acid rains, mineral leaching and microbiological activity will lead to a serious corrosion risk to buried structure such as steel, cast, iron and even zinc [2]. To date, most studies on corrosion of steel was carried out in soil environment with an average pH of 3.5 to 6 [3]–[8] but focusing on the bare carbon steel substrate. However, the performance of coated carbon steel structure subject to underground corrosion in acidic soil condition is important to be obtained.

For buried pipeline structure, the external coating provides an extra protection against corrosion in corrosive soil media. Epoxy materials are known to be the most conventional and superior coating in many aspects when compares to regular paints [9]. However, over the time, the barrier of the epoxy coating can fail due to surrounding factors that can influence the integrity of the pipeline protection system. The combination of epoxy and PANI is given better performance over prolonged exposure compared to neat epoxy paint system [10]-[14]. PANI also has studied for multiple types of development including flameretardant additives [15], [16], bio corrosion [17], catalyst [18] and recognizable protecting properties against corrosion on metal surfaces in the different types of media [9], [19]-[22]. Since PANI has an excellent chemical stability and environmentally friendly properties, it has been emerging as one of the most promising conducting polymer as a coating against corrosion. To date, there have been extensive researches, studies on the performance of PANI as a coating to investigate pipeline corrosion occurring under a different type of corrosive media. The mechanism protection by external coating is still in debate. Some authors say that the barrier coating can block the passage of oxygen and water reaching the metal surface and others think that the protection offered by the organic coating which offers the high electrical resistance thus preventing current flow between anodic and cathodic side [13], [20], [23], [24]. Other researchers [10], [22], [25] were demonstrated the ability of PANI, acts as a self-healing coatings and improved the corrosion resistance of carbon steel in corrosive media. Among all the proposed mechanism, the most accepted possible corrosion protection mechanisms of PANI are the combination of the electrochemical inhibitor and cathodic protection systems [20].

To the best of our knowledge, no previous work has been done on the corrosion resistant assessments of PANI-epoxy coating in acidic of NS4 soil solution media. Since the carbon steel structure which in contact with soil has the risk to be corroded, the performance of PANI should also be assessed in this condition. This work aims to use PANI in epoxy paint system as external coating and to study its anticorrosive properties in the acidic NS4 soil

solution, with pH 3 and 5. The anticorrosion behavior of the PANI–epoxy coating over carbon steel substrate was examined via salt spray, immersion, and cathodic disbonding tests. In addition, the electrochemical impedance spectroscopy (EIS) also was performed in order to investigate the impedance properties of the system during immersion test. EIS is a powerful technique in order to understand the electrical properties of coating on the substrate. The cross–section of PANI–epoxy coatings adhere on the carbon steel substrate was studied by a scanning electron microscopy (SEM).

Experimental

Substrate and test solution

Carbon steel of composition (weight %): C: 0.07, Si: 0.25, Mn: 1.54, P: 0.013, S: 0.001, Mo: 0.007, Cr: 0.05, Ni: 0.04, Al: 0.041 and Fe remainder was embedded in epoxy cold mounting, with an exposed surface area of 1.5 cm² for immersion and cathodic disbondment test. The substrates were connected to the copper wire in order to establish the electrical connection during tests (Figure 1) prior to the mounting process. Meanwhile, for the salt spray test, the substrates with dimension 8.5 cm x 5 cm x 0.8 cm were used. The substrates were grit blasted to achieve the required surface finish prior to the application of the coating.



Figure 1. Schematic represent the coated sample for electrochemical measurement

The corrosive environment employed was NS4 soil solution which is widely used as reference solution to simulate the condition under disbonded pipeline coating in many types of research [4][26]–[28]. The soil solution was prepared by dissolving analytic grade reagents in distilled water with following composition (g/L): 0.122 potassium chloride (KCl), 0.483 sodium bicarbonate (NaOHCO3), 0.181 calcium chloride (CaCl2.2H2O), and 0.131 magnesium sulfate (MgSO4.7H2O). The pH of NS4 soil solution is ranged from pH 8 to 8.5 while 0.1 M of Hydrochloric acid (HCl) was used to achieve soil solution pH of 3 and 5 for

comparison purpose. The conductivity of the solution was measured by digital conductivity meter model EC600 from Extech Instruments and is shown in Table 1.

Table 1. Conductivity data of test soil solution at ambient temperature

Soil solution	рН	Conductivity, (X 10-6 S cm-1)
NS4 + 1M HCl	5	1250
NS4 + 1M HCl	3	1568

Coating formulation

PANI-epoxy paint was prepared by direct mixing of PANI into epoxy resin liquefied. PANI in powder form with a particle size range of 0.3 to 100 µm was commercially obtained from Sigma-Aldrich. PANI was dissolved in the epoxy resin at different weight percentages which are tabulated in Table 2. The diglycidyl ether of bisphenol-A epoxy resin (EPIKOTE 828) was used in this work. The mixture was stirred for 1 hour to obtain a homogeneous solution. The dispersion of PANI in epoxy coating also was increased by more than 90% by addition of aromatic solvent into the mixture, in this case, toluene. The rotary evaporator at temperature 44 °C and 100 RPM rotation was used to remove the solvent from the mixture. Finally, an aromatic amine hardener was added to the mixture with an epoxy/hardener ratio of 2:1. The paint was applied on a blasted substrate by using a brush and dried at room temperature for 24 hours. The dry film thickness (DFT) of the coating was in the range of 165 to 200 µm were measured by coating thickness gauge, model Elcometer 456. In addition, cross–section morphology of coating on the substrate was observed by Scanning Electron Microscopy (SEM) once the coating was completely cured.

Table 2. Weight percentages of epoxy resin and PANI

Coating designation	PANI (wt.%)	Epoxy resin (wt%)
EP	0	100
0.5 EP	0.5	99.5
1.0 EP	1.0	99.0
1.5 EP	1.5	98.5

Corrosion testing

Cathodic disbondment (CD)

An artificial defect was made in the middle of exposed surface area of the coated substrates prior to the test. The defect was drilled until the angular cone point of the drill was fully entered the panels where the cylindrical portion of the drill meets the steel surface. The coated substrate was drilled by using a 3 mm diameter drill bit. The defect was prepared at the last moment before cell assembly.

Subsequently, the substrates were immersed for 24 hours in NS4 soil solution at 65 \pm 2 °C and maintained at a -3.5 volt (V) potential with respect to a silver/silver chloride reference electrode (Ag/AgCl). The potential of the system was controlled by potentiostatic procedure equipped by Autolab Metrohm potentiostat/galvanostat instrument using NOVA 1.10 software. An examination is performed immediately at the end of the test. A sharp, thin knife was used to cut a star pattern onto the coated substrate. An attempt was then made to peel easily the disbonded coating from the substrate which delaminated radially outward from the defect site. The CD test was recorded in terms of the radial disbondment (RD) (in accordance with ASTM G8 [29]).

Salt-spray exposure

This test provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information of coated metals exposed in a salt spray chamber. Every coating system has a pair of coated substrate. The scribed in the form of 'X' was made across one of the coated substrates by using a sharp knife. It served as an artificial designed to accelerate the corrosion process. The coated substrates were supported between 15° to 30° from the vertical and parallel, respectively, to the principal direction of flow of fog through the chamber. The test solution was 5 wt. % NaCl prepared with deionized water with the pH of the solution in the range from 6.5 to 7.2. The temperature was maintained at 35 \pm 2 °C in salt spray chamber for 720 hours according to ASTM B117 [30]. The salt solution was sprayed by an atomizer, using compressed air supply, at 0.085 MPa with humidifier temperature at 47 \pm 2 $^{\circ}\text{C}.$ The inspection was done for every week and the photo of test panels was recorded. The coated substrate was carefully removed from the chamber at the end of the test before it was gently washed with clean running water to remove salt deposits from their surface, and immediately dried. Evaluation of rust creepage for scribed coated substrate was done and the rating was given in accordance with Procedure A, ASTM D1654-08 [31].

Immersion test

The anticorrosion properties of the coatings were also evaluated by immersion test in the NS4 soil solution for a period of 30 days according to ASTM G31. The impedance properties of each coated substrate were measured by EIS, on day 3 and day 30 of immersion period by ACM Gill AC potentiostat/ galvanostat equipped with (Ag/AgCl) reference electrode and graphite as the auxiliary electrode.

RESULT AND DISCUSSION

Coating morphology

As noted from the cross-section images, PANI-epoxy coating was able to reduce the porosity of EP coating. We identified that the compact layer produced by the coating content PANI acts as a barrier to protect underlying substrate shown in Figure 2. The content of PANI in the coating has increased the ability to reduce the entry of corrosive species. This can be attributed by a completely incorporated between PANI and epoxy.

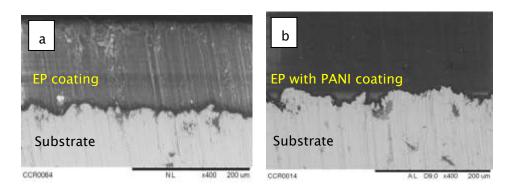


Figure 2. A micrograph of a cross-section coating (a) EP coating and (b) PANI-epoxy coating

Cathodic disbondment (CD) test

The magnitude of RD value in CD test indicates the disbondment area around the holiday. The coating with a lower RD is better toward CD failure. In both test solution, the average radial disbondment (RD) value for tested substrate was found to be less than 3.9 mm, 2.9 mm, 2.6 mm, and 2.1 mm for EP, 0.5EP, 1.0EP, and 1.5EP respectively in NS4 of pH 3. Meanwhile the substrate exposed in NS4 of pH 5 having a lower RD value which are 3.8 mm, 2.6 mm, 2.4 mm, and 2.0 mm 1 mm for EP, 0.5EP, 1.0EP, and 1.5EP respectively. The greatest disbondment was observed on the EP substrate as shown in Figure 3.

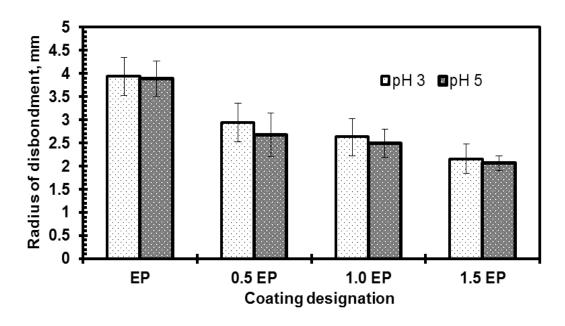


Figure 3. The RD values on different pH of NS4 soil solution

They are less disbondment of substrate coated was found on the coated substrate with increasing PANI amount in the paint system. This implies that PANI and epoxy work together to reduce the water entry during CD test while improving the performance of the coating in acidic soil solution. It is notice that the effect becomes minimal when reducing the PANI concentration, since the differences in PANI content in epoxy paint system were minimal to each other. Theoretically, the disbondment was low resistance against water penetration from the artificial defect. 1.5 EP showing the lowest RD value compared to others. The different performance of coating system was due to how fast PANI reduction starting from the defect site will progress into the intact coating. Obviously, in a good coating system,

PANI in the vicinity of the defect can be activated and stop corrosion [32]. Hence, based on CD test, it is hypothesized that 1.5 EP was given an outstanding coating system for corrosion protection coating with reduction in almost 50% and 46 % of RD value in pH 3 and 5 respectively compared to EP. In the absence of PANI (EP coating), a low interdiffusion bonding causes molecules to migrate easily across the interface. The reason for the different corrosion protection provided is complicated by the reaction between epoxy and PANI. Generally, PANI affects the nature of the oxide layer forming at the coating/metal interface and at the exposed defect. Sathiyanarayanan [33] was successfully demonstrated the effectiveness of PANI pigmented coating to protect steel in acidic media by passivation mechanism of pin holes. In these cases, it is believed that more PANI loaded in epoxy based system was found to be more resist to CD.

Salt spray test

The scribed and unscribed test panels are shown in Figure 4 (a) and (b) respectively. Basically, all test panels clearly show the sign of corrosion after 30 days of ASTM B117 exposure. It can be seen that the performance of a developing coating system was limited. EP test panel corroded the most compared to the other test panels. The delamination and rusting phenomena on EP test panel are worst compared with the condition of the coated test panel in the presence of PANI. 1.5 EP test panels showed the least corroded, delaminated and rusted areas.





Figure 4. Test panels images after exposed in ASTM B117 condition (a) scribed test panel coated by EP, 0.5 EP, 1.0 EP, and 1.5 EP coating system in order and (b) unscribed test panel coated by coated by EP, 0.5 EP, 1.0 EP, and 1.5 EP in order

Other than the visual analysis, evaluation of rust creepage for scribed test panel was done and the rating was given in accordance with Procedure A, ASTM D1654-08. The rating values are tabulated in Table 3.

Table 3. Salt spray test evaluation

Coating Designation	Creepage Size (mm)	Rating
EP	Over 5 to 7	4
0.5 EP	Over 2 to 3	6
1.0 EP	Over 2 to 3	6
1.5 EP	Over 1 to 2	7

According to Protective coatings and lining, QP-CS1[34], the acceptance criteria for passing the salt spray exposure belong to the coated substrate which was rated at more than 4-5. Based on this standard, all test panels were passing the acceptance criteria except the test panels coated with EP coating system. In accelerated corrosive environment, the creepage was spread which evidently confirm there are none of the self-healing reaction on the coated substrate. There were a significant amount of rusts and blistering on all the tested panels. The corrosion products formed during the corrosion process are mainly localized in the scribe. However, the presence of PANI was able to reduce the delamination of coating, up to 43% compared to EP. For unscribed test panels, after 30 days exposure, the conditions for every test panels were observed to be almost the same. It has been found that the coating is intact with a lesser degree of blister or delamination. No apparent change in gloss or texture was observed except the discoloration of the coating after long exposure in the salt spray chamber. In this test, the ability of all coated test panels to withstand in the corrosive-humid atmosphere can be acquired. According to available results obtained in this test, it can be proposed that the test panels coated with PANI-epoxy coating provide better corrosion protection than EP. Basically, the relationship between the spreading of creepage and adhesion between coating/substrate is a reversible relationship. If the adhesion strength between coating/substrate is high, supposedly there will be less delamination and damage. However, the delamination could be due to the low hydrolysis of the bonds in wet conditions, experienced by the test panels in the salt spray chamber.

Electrochemical Impedance Spectroscopy (EIS) measurements

The coated substrates were evaluated based on the EIS measurement during immersion test, is expressed graphically by Nyquist plot and Bode plot as shown in Figure 6 and Figure 7 respectively.

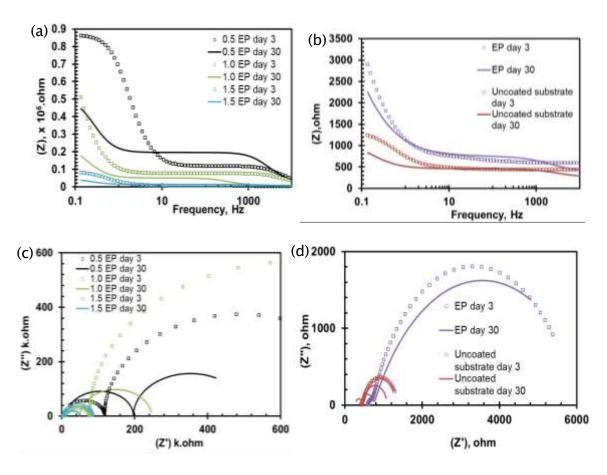
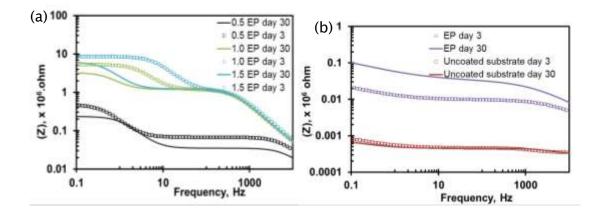


Figure 6. EIS data for coated substrate immersed in NS4 soil solution of pH 3 shows as Bode plot for; (a) 0.5 EP, 1.0 EP and 1.5 EP, (b) EP and uncoated substrate, and Nyquist plot for; (c) 0.5 EP, 1.0 EP and 1.5 EP, and (d) EP and uncoated substrate



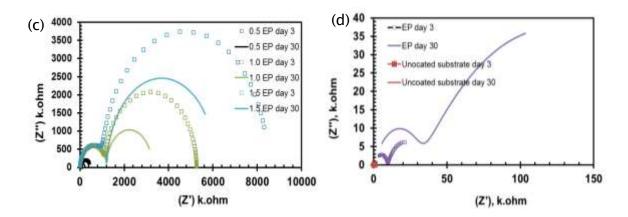


Figure 7. EIS data for coated substrate immersed in NS4 soil solution of pH 5 shows as Bode plot for; (a) 0.5 EP, 1.0 EP and 1.5 EP, (b) EP and uncoated substrate, and Nyquist plot for; (c) 0.5 EP, 1.0 EP and 1.5 EP, and (d) EP and uncoated substrate

Changes in impedance parameters were monitored when corrosion began and subsequently coating properties become degraded [35]. The Nyquist plots are characterized by a semicircle inductive loop which attributed to the adsorption of an intermediate product in the corrosion reaction [9]. The higher diameter of semicircle arc, representing the lower of the charge transfer resistance (the corrosion rate). In Bode plots, the impedance spectrum exhibited two–time constants. The first time constant, which is at higher frequencies, HF was associated with the properties of the coating, while the second at lower frequencies, LF was related to the degree of delamination and/or corrosion[36] . The coating behaves like capacitance at HF while resistance at LF [37]. According to the literature [38]–[42], the impedance modulus at 0.1 Hz ($|Z|_{0.1Hz}$) is an appropriate parameter for characterization of the protective properties of the coatings. The high values of $|Z|_{0.1Hz}$ are associated with a high resistance behavior of the coating.

The output data from EIS spectra were analyzed using NOVA 1.0 software from Metrohm Autolab, using the fitting procedure to a Rs (Qc [R_{pore} (Q_{dl} Rp)]) model circuit for uncoated substrate and EP coating system and a Rs (Cc [R_{pore} (C_{dl} Rp)]) model circuit for PANI in epoxy coating systems. Rs was the solution resistance, Rp coating resistance, R_{pore} pore resistance, C_{dl} the capacitance at the area under the coating, and Cc was related to the coating capacitance. Instead of capacitance (C), a constant phase element (Q) combine with resistance, R was used to represent the non-ideal behavior of the coating which gave a better fitted model for uncoated substrate and EP coating system. The components in the equivalent circuit are divided into certain regions to represent the process occurred on each of the layers. For example 'the coating regions' labeled in the schematic diagram shown in Figure 5a and b, both equivalent circuits represent the activity denoted by the coating,

particularly during immersion period. Furthermore, the RpC_{dl} or RpQ_{dl} combinations which are in series to R_{pore} represented the electrochemical corrosion process at the metal interface. In addition, Rp is considered to be due to the formation of ionically conducting paths in the polymer [43]. The impedance values consist of Rs, Q_{dl} , Q_{cl} , Q_{cl

Table 4. Electrical properties for substrate immersed in NS4 soil solution of pH 3

Immersion	Coating system	Q _c		Cc	R _{pore}	R_{ρ}	Q_{dI}		C _{dl}
time		Y	п	(pF)	(kΩ)	(kΩ)	Y	n	(µF)
		(µMho)					(µMho)		
	Uncoated substrate	256.0	0.8	-	0.1	0.7	253.4	0.8	-
Day 3	EP	0.96	0.7	-	0.2	5.6	269.2	0.7	-
,	0.5 EP	-	-	3.32	11.1	748	-	-	0.16
	1.0 EP	_	-	15.3	63.7	1140	-	-	2.26
	1.5 EP	_	-	86.2	93.4	3910	-	-	5.15
Day 30	Uncoated substrate	1.24	0.8	-	0.2	0.6	1688	0.8	-
	EP	0.9	0.8	-	0.3	5.1	550	0.6	-
	0.5 EP	_	-	0.4	18.2	313	_	-	2.33
	1.0 EP	-	-	0.5	42.1	195	-	-	6.16
	1.5 EP	-	-	64.1	45.1	1360	-	-	0.28

Table 5. Electrical properties of substrate immersed in NS4 soil solution of pH 5

Immersion Coating		Qc		Cc	R _{pore}	R_{ρ}	Q dI		Cdl
time	system	Y	п	(pF)	(kΩ)	(kΩ)	Y	п	(μF)
		(µMho)					(µMho)		
	Uncoated substrate	1.2	0.9	-	0.1	0.6	39.5	0.6	-
Day 3	EP	0.05	0.7	-	8.2	23.1	0.6	0.6	-
,	0.5 EP	-	_	0.6	54	400	-	_	0.9
	1.0 EP	-	=	0.3	1170	4070	-	_	0.01
	1.5 EP	-	-	0.2	1210	7260	-	_	0.003
Day 30	Uncoated substrate	0.4	0.9	-	0.1	0.3	31.6	0.7	-
	EP	0.04	0.7	-	6.3	35.8	0.4	0.5	-
	0.5 EP	-	=	1.0	25.9	200	-	_	0.7
	1.0 EP	-	-	0.3	1170	2070	-	-	0.1
	1.5 EP	-	-	0.3	1230	4900	-	-	0.007

Immersion in NS4 soil solution of pH3

The Nyquist plots recorded in Figure 6 (b and d), shows the diameter of the semicircles arc for 30 days immersion is smaller than 3 days of immersion. This suggests the water adsorption could be the reason behind this response. However, the higher semicircle arc for EP and uncoated substrate were much smaller than those obtained for 0.5 EP, 1.0 EP and 1.5 EP. Unfortunately, the higher the semicircle arc is found on the substrate which having a reducing amount of PANI content in the epoxy coating system. According to the Bode plots, every substrate immersed in NS4 with pH 3 exhibit an obvious decreasing of $|Z|_{0.1Hz}$ values from days 3 to days 30 in the range of 3% to 68%. Initially, the 0.5 EP exhibits lower metal dissolution followed by 1.0 EP, 1.5 EP, EP and finally the uncoated substrate. However, as the immersion period was up to day 30, the value of |Z| decreased sharply for all substrates. The decreasing value of $|Z|_{0.1Hz}$ for PANI in the epoxy coating was higher at the end of the test compared to EP and the uncoated substrate. However, a comparison of the overall impedance, the $|Z|_{0.1Hz}$ values are still higher in magnitude for PANI in the epoxy coating system, especially for 1.5 EP. Such behavior can be further explained with the increasing of the resistance (R_{pore}). It evolves with immersion time for all substrates with 1.5 EP exhibited the highest value compared to the others. The resistance found to increase in the presence of corrosion product. In addition, a significant decreasing of R_p value is observed for all substrate. For example, the R_p values of the uncoated substrate and 0.5 EP are 0.7 k Ω and 748 k Ω on day 3, decreased to 0.6 k Ω and 313 k Ω respectively at the end of immersion period. These results indicate that the poor barrier property owns by the EP coating can be drastically increased up to 98% when added 0.5% concentration of PANI on it. The degree of protection is increased in addition higher concentration of PANI in EP coating system.

Immersion in NS4 soil solution of pH5

Figure 7 depicts the Nyquist plot and Bode plot of the substrates immersed in NS4 soil solution at pH 5. All the impedance spectra exhibit two depressed semicircles arc for substrate 0.5 EP, 1.0 EP and 1.5 EP. The resistive behavior with high impedance is decreased towards the end of immersion period for all substrates. However, the corresponding Nyquist plot for 1.5 EP exhibits the higher impedance compare to the others. Such behavior is shown that PANI-epoxy coating act as an effective physical barrier against the penetration of corrosive ions and protect the underlying metal surface in this particular media In addition, the impedance values at LF denote that the 1.5 EP own the best corrosion protection as it had the highest $|Z|_{0.1Hz}$ values throughout the immersion period. The less corrosion protection was carried out by the coating consists of lower PANI content. At the end of immersion period, $|Z|_{0.1Hz}$ values of all coated substrate were decreased in less than one order of magnitude compare to their initial |Z|0.1Hz values except for uncoated substrate. Such behavior is consistent with the decreasing of R_{pore} values throughout the immersion test. As the time elapsed, the solutions gradually penetrated to the coating system and consequently decrease the impedance value due to porosity especially on the EP coating. However in the presence of PANI a lower porosity was obtained resulted a higher R_{pore} values at the end of immersion period. Furthermore, R_p values of all substrate also decreased rapidly at the end of immersion period. Besides, the C_c values are lower about 10-10 F cm², indicative of purely capacitive coating and low ion permeation owned by the coating systems. The corrosion resistance of these coating enhanced by synergistic interaction between PANI and epoxy. In fact, the coating resistance was increased in the increasing of the PANI content in the coating.

Summary and conclusions

Following conclusions were drawn from this study. The presence of PANI in epoxy resin act as an effective physical barrier against the penetration of corrosive ions and protect the underlying metal surface regardless the pH of the NS4 soil solution. In addition to this, PANI in powder form is able to provide the mechanical integrity to the epoxy coating by filling up the porous characteristics of epoxy. The homogenous dispersion of PANI in epoxy mixture was successfully reducing the porosity of EP coating. This behavior was clearly observed in the cross–section images, discussed previously. Therefore, PANI–epoxy coating delays the start of corrosion on the underlying surface, and the optimum protection is increased by increasing the amount of PANI in the coating.

Accelerated corrosion studies such as immersion, CD, and salt spray test was successfully adopted in this work. PANI-epoxy coating is able to improve the overall anticorrosion performance of the coating in comparison with the neat epoxy coating. Furthermore, EIS showed that the effective physical barrier against the penetration of corrosive ions and protect the underlying metal surface with 1.5 wt. % of PANI content. In addition, the coating properties demonstrate excellent performance in terms of resistant against long-term immersion period. In CD test, it was found that the coating is intact with a lesser degree of blister or delamination when increasing the PANI content in the epoxy coating.

References

- [1] J. K. Saha, P. K. Mitra, S. Paul, and D. D. N. Singh, "Performance of different organic coatings on steel substrate by accelerated and in atmospheric exposure tests," *Indian J. Chem. Technol.*, vol. 17, pp. 102–110, 2010.
- [2] S. R. A. Saupi, M. A. Sulaiman, and M. N. Masri, "Effects of Soil Properties to Corrosion of Underground Pipelines: A Review," *J. Trop. Resour. Sustain. Sci.*, vol. 3, no. May, pp. 14–18, 2015.
- [3] L. Mejfa, "Effect ofprotective coatings on the stress corrrosion cracking of API 5L-X52 low carbon steel in soil and NS4 solution," *Corrosion*, no. Paper No. 03526, pp. 1-14, 2003.
- [4] D. Mendoza, R. Perez, and A. Aguilar, "Cathodic protection behavior of API X-52 and API X-65 steels buried in natural soil," *Corrosion*, no. NACE, paper NO: 11052, pp. 1-15, 2011.
- [5] X. Xu, L. Xu, W. Liu, and M. Lu, "study of AC corrosion on coated pipeline steel in simulated soil solution," *NACE*, *Corros.*, no. 11343, pp. 1–20, 2011.
- [6] A. Benmoussat and M. Traisnel, "Corrosion Study of API 5L X60 Gas Pipelines Steels in NS 4 Simulated Soil," *Integr. pipelines Transp. hydrocrbons, Springer Sci. Bus. media*, pp. 167–179, 2011.
- [7] Z. Y. Liu, X. G. Li, C. W. Du, G. L. Zhai, and Y. F. Cheng, "Stress corrosion cracking behavior of X70 pipe steel in an acidic soil environment," *Corros. Sci.*, vol. 50, no. 8, pp. 2251–2257, Aug. 2008.
- [8] Y. H. Wu, T. M. Liu, C. Sun, J. Xu, and C. K. Yu, "Effects of simulated acid rain on corrosion behaviour of Q235 steel in acidic soil," *Corros. Eng. Sci. Technol.*, vol. 45,

- no. 2, pp. 136-141, 2010.
- [9] A. H. Navarchian, M. Joulazadeh, and F. Karimi, "Investigation of corrosion protection performance of epoxy coatings modified by polyaniline/clay nanocomposites on steel surfaces," *Prog. Org. Coatings*, vol. 77, no. 2, pp. 347-353, 2014.
- [10] A. Mostafaei and F. Nasirpouri, "Epoxy / polyaniline ZnO nanorods hybrid nanocomposite coatings: Synthesis, characterization and corrosion protection performance of conducting paints," *Prog. Org. Coatings*, vol. 77, no. 1, pp. 146-159, 2014.
- [11] S. Radhakrishnan, N. Sonawane, and C. R. Siju, "Epoxy powder coatings containing polyaniline for enhanced corrosion protection," *Prog. Org. Coatings*, vol. 64, pp. 383-386, 2009.
- [12] A. Talo, O. Forsen, and S. Ylasaari, "Corrosion protective polyaniline epoxy blend coatings on mild steel," *Synth. Met.*, vol. 102, no. 1-3, pp. 1394-1395, 1999.
- [13] Y. Li, L. Yang, X. Gao, and Z. Zeng, "Polyaniline / Epoxy Composite Emulsion Coatings for Anticorrosion to Mild Steel," *Adv. Mater. Res.*, vol. 153, pp. 132-133, 2010.
- [14] M. Pelíšková, J. Vilčáková, R. Moučka, P. Sáha, J. Stejskal, and O. Quadrat, "Effect of coating of graphite particles with polyaniline base on charge transport in epoxy-resin composites," *J. Mater. Sci.*, vol. 42, no. 13, pp. 4942-4946, 2007.
- [15] X. Zhang, Q. He, H. Gu, H. A. Colorado, S. Wei, and Z. Guo, "Flame-retardant electrical conductive nanopolymers based on bisphenol F epoxy resin reinforced with nano polyanilines," *ACS Appl. Mater. Interfaces*, vol. 5, no. 3, pp. 898-910, 2013.
- [16] H. Gu, J. Guo, Q. He, S. Tadakamalla, X. Zhang, X. Yan, Y. Huang, H. A. Colorado, S. Wei, and Z. Guo, "Flame-retardant epoxy resin nanocomposites reinforced with polyaniline-stabilized silica nanoparticles," *Ind. Eng. Chem. Res.*, vol. 52, no. 23, pp. 7718-7728, 2013.
- [17] S. Yuan, S. Tang, L. Lv, B. Liang, C. Choong, and S. O. Pehkonen, "Poly(4-vinylaniline) Polyaniline bilayer-modified stainless steels for the mitigation of biocorrosion by sulfate-reducing bacteria (SRB) in seawater," *Ind. Eng. Chem. Res.*, vol. 51, no. 45, pp. 14738–14751, 2012.
- [18] G. Gnana, C. J. Kirubaharan, S. Udhayakumar, C. Karthikeyan, and K. S. Nahm,

- "Conductive Polymer / Graphene Supported Platinum Nanoparticles as Anode Catalysts for the Extended Power Generation of Microbial Fuel Cells," 2014.
- [19] A. Olad, M. Barati, and S. Behboudi, "Preparation of PANI / epoxy / Zn nanocomposite using Zn nanoparticles and epoxy resin as additives and investigation of its corrosion protection behavior on iron," *Prog. Org. Coatings*, vol. 74, no. 1, pp. 221–227, 2012.
- [20] E. Armelin, R. Pla, F. Liesa, X. Ramis, and C. Alema, "Corrosion protection with polyaniline and polypyrrole as anticorrosive additives for epoxy paint," *Corros. Sci.*, vol. 50, pp. 721-728, 2008.
- [21] G. Tansuğ, T. Tüken, a. T. Özyılmaz, M. Erbil, and B. Yazıcı, "Mild steel protection with epoxy top coated polypyrrole and polyaniline in 3.5% NaCl," *Curr. Appl. Phys.*, vol. 7, no. 4, pp. 440-445, May 2007.
- [22] H. Zhang, J. Wang, X. Liu, Z. Wang, and S. Wang, "High performance self-healing epoxy/polyamide protective coating containing epoxy microcapsules and polyaniline nanofibers for mild carbon steel," *Ind. Eng. Chem. Res.*, vol. 52, no. 30, pp. 10172–10180, 2013.
- [23] A. A. A. Al-dulaimi, S. Hashim, and M. I. Khan, "Corrosion Protection of Carbon Steel Using Polyaniline Composite with Aluminium Oxide," *Petranika J. Sci.*, vol. 19, no. April 2010, pp. 329–337, 2011.
- [24] T. Mousavinejad, M. R. Bagherzadeh, E. Akbarinezhad, M. Ahmadi, and M. J.-F. Guinel, "A novel water-based epoxy coating using self-doped polyaniline-clay synthesized under supercritical CO2 condition for the protection of carbon steel against corrosion," *Prog. Org. Coatings*, vol. 79, pp. 90-97, 2015.
- [25] T. Siva, K. Kamaraj, and S. Sathiyanarayanan, "Epoxy curing by polyaniline (PANI) Characterization and self-healing evaluation," *Prog. Org. Coatings*, vol. 77, no. 6, pp. 1095–1103, 2014.
- [26] A. H. S. Bueno, E. D. Moreira, P. Siqueira, and J. a. C. P. Gomes, "Effect of cathodic potential on hydrogen permeation of API grade steels in modified NS4 solution," *Mater. Sci. Eng. A*, vol. 597, pp. 117–121, Mar. 2014.
- [27] D. X. He, W. Chen, and J. L. Luo, "Effect of cathodic potential on hydrogen content in a pipeline steel exposed to NS4 near-neutral pH soil solution," *Corros. Eng. Sect.*, vol. 60, No. 8, no. August, pp. 778-786, 2004.

- [28] I. M. Gadala and A. Alfantazi, "Electrochemical behavior of API-X100 pipeline steel in NS4, near-neutral, and mildly alkaline pH simulated soil solutions," *Corros. Sci.*, vol. 82, pp. 45-57, 2014.
- [29] G.-96 ASTM, "Standard test method for cathodic disbonding of pipeline coating," *ASTM Int.*, vol. 88, pp. 4-6, 2010.
- [30] C. Coatings, R. C. Products, and G. Electrode, "ASTM B117: Standard Practice for Operating Salt Spray (Fog)," *ASTM Stand.*, pp. 1-12, 2011.
- [31] S. Surfaces, R. Coatings, U. W. Immersion, U. Water, F. Apparatus, S. Con-, U. C. Condensation, and B. Nomenclature, "ASTM D1564-08 Standard Test Method for evaluation of painted or coated specimens subjected to corrosive environments," *ASTM Stand.*, no. C, pp. 1-4, 2011.
- [32] M. Rohwerder and A. Michalik, "Conducting polymers for corrosion protection: What makes the difference between failure and success?," *Electrochim. Acta*, vol. 53, pp. 1300–1313, 2007.
- [33] S. Sathiyanarayanan, S. Muthukrishnan, G. Venkatachari, and D. C. Trivedi, "Corrosion protection of steel by polyaniline (PANI) pigmented paint coating," *Prog. Org. Coatings*, vol. 53, pp. 297–301, 2005.
- [34] Protective coatings and lining, QP-CS1:Procedure for qualification and testing of coating system, CORAL Malaysia. 2001.
- [35] Z. Sharer and J. Sykes, "Insight into protection mechanisms of organic coatings from thermal testing with EIS," *Prog. Org. Coatings*, vol. 74, pp. 405–409, 2012.
- [36] F. Mansfeld and C. H. Tsai, "Determination of coating deterioration with EIS: Part I. Basic relationships," *Corrosion*, vol. 47, no. 12, pp. 958-963, 1991.
- [37] S. Duval, V. Sauvant-Moynot, and F. Ropital, "EIS: A powerful tool for in-situ monitoring of coating performance," *Corrosion*, vol. Paper No: , pp. 1-15, 2003.
- [38] Y. Chen, X. H. Wang, J. Li, J. L. Lu, and F. S. Wang, "Long-term anticorrosion behaviour of polyaniline on mild Steel," *Corros. Sci.*, vol. 49, no. 7, pp. 3052-3063, Jul. 2007.
- [39] A. Shi, S. Koka, and J. Ullett, "Performance evaluation on the weathering resistance of two USAF coating systems (standard 85285 topcoat versus fluorinated APC topcoat) via electrochemical impedance spectroscopy," *Prog. Org. Coatings*, vol. 52, no. 3, pp.

- 196-209, 2005.
- [40] D. T. A. Amirudin, A. Amirudin, and D. Thierry, "Application of electrochemical impedance spectroscopy to study the degradation of polymer-coated metals," *Prog. Org. Coatings*, vol. 26, no. 3, pp. 1-28, 1995.
- [41] J. N. Murray, "Electrochemical test methods for evaluating organic coatings on metals: an update. Part III: Multiple test parameter measurements," *Prog. Org. Coatings*, vol. 31, no. 4, pp. 375–391, 1997.
- [42] J. . Park, G. . Lee, a Nishikata, and T. Tsuru, "Anticorrosive behavior of hydroxyapatite as an environmentally friendly pigment," *Corros. Sci.*, vol. 44, no. 5, pp. 1087–1095, 2002.
- [43] G. Grundmeier, W. Schmidt, and M. Stratmann, "Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation," *Electrochim. Acta*, vol. 45, no. 15-16, pp. 2515-2533, 2000.