Anti-corrosion performance of PANI and POEA coatings applied into 13% Cr stainless steel at 3.5% NaCl solution with neutral pH

Nacer Mounir, Malha Nazef, Zakaria Baka, and Hamid Yousfi

Abstract−The doped PANI and POEA polymers were incorporated into a commercial epoxy resin with xylene solvent to develop effective anticorrosion coatings applied to 13% Cr stainless steel. The produced epoxy resin coatings were systematically characterized by FTIR, XRD, SEM, AFM, and immersion tests. The corrosion resistance performance of the ZP, PANI, and POEA coatings was evaluated through potentiodynamic polarization, electrical impedance spectroscopy, open circuit potential (OCP), and linear polarization resistance (LPR) measurements in a long-term exposure to a 3.5% NaCl solution at pH 6.5. The corrosion resistance of the commercial ZP coating was significantly improved by the PANI and POEA coatings, and their performance was correlated with the highly enhanced protection of the passivation barrier provided. The higher corrosion resistance observed in POEA coatings in acidic ambient conditions is explained by the auxiliary cathodic reaction between the conducting emeraldine PANI and the non-conducting leuco-PANI. The suggested manufacturing method for storage tanks can be used to simultaneously replace the substrate (carbon steel) and the conventional anticorrosion coating based on zinc phosphate.

***Keywords*−Conducting polymers, PANI Coating, POEA coating, ZP Coating, 3.5% NaCl solution.**

NOMENCLATURE

PANI	Polyaniline.
POEA	Poly(Ortho-Ethoxyaniline).
ZP	Zinc Phosphate.
SS	Stainless Steel.

I. INTRODUCTION

Comparative research into two types of steel substrates holds significant importance in the field of materials science, as it enables a thorough exploration of the properties, performance, and potential applications of different steel grades. Steel, being a fundamental material across numerous industries, offers diverse compositions and characteristics to cater to specific requirements. Consequently, this study aims to underscore the distinctions between two highly significant steel types: AISI 1010 carbon steel and AISI 420 martensitic stainless steel.

On one hand, AISI 1010 carbon steel, primarily composed of iron and carbon, finds widespread usage in a variety of industrial and structural applications, as documented by Mirmohseni in 2000 [1] and Ebrahimi in 2017 [2]. On the other hand, AISI 420 martensitic stainless steel, characterized by its elevated chromium (13% Cr) and carbon content, offers unique features such as increased corrosion resistance and the ability to harden through heat treatment, as noted by Zhong in 2006 [3]. This thorough comparison aims to investigate the advantages and limitations of each steel type, taking into account criteria like mechanical strength, corrosion resistance, and durability. The research focuses on the specific properties of these steels and aims to provide essential information for well-informed material selection across various sectors, including manufacturing, construction, marine engineering, and aerospace. The ultimate goal is to aid designers and engineers in selecting the most suitable material for each application, thereby enhancing efficiency, durability, and overall performance in diverse industrial contexts, including the oil and technology sectors.

The study is particularly interested in evaluating the effectiveness of coatings on AISI 1010 carbon steel and AISI 420 martensitic stainless steel, as it relates to materials protection. Coatings play a pivotal role in enhancing the performance and longevity of these substrates, especially in demanding environments where corrosion, abrasion, and other forms of deterioration are primary concerns, as observed by Xu in 2016 [4]. Protective coatings serve as an effective shield against corrosive agents for AISI 1010 carbon steel, which is more susceptible to corrosion due to its carbon content. Coatings such as epoxy paints, oxide-reinforced polymers, and zinc-based anticorrosion coatings have demonstrated their ability to safeguard carbon steel by isolating it from external elements that may cause harm, as evidenced by Sazou in 2007 and Ozyilmaz in 2010 [5, 6]. These coatings not only delay the corrosion process but can also enhance abrasion resistance, thereby improving durability in challenging environments.

In the case of AISI 420 martensitic stainless steel, which already possesses corrosion resistance due to its chromium content, coatings can further augment this resistance, particularly under aggressive conditions, as highlighted by

Manuscript received October 20, 2024; revised July 9, 2025.

N. Mounir (Corresponding author) is with the laboratories LSGM, Department of Metallurgy and laboratory LSTE, Department of Quality, Health, Safety, Environment and Industrial Risk Management, Ecole Nationale Polytechnique, El Harrach 16200 Algiers, ALGERIA (e-mail:nacer.mounir@g.enp.edu.dz).

M. Nazef is with the laboratory of Corrosion, Department of Corrosion, Division Laboratories Exploration and Production SONATRACH (Ex CRD), Boumerdes, ALGERIA (e-mail:malha.allaoua@sonatrach.dz).

Z. Baka is with the laboratory of Green and Mechanical Development (LGMD), Department of Mechanical Engineering, Ecole Nationale Polytechnique, El Harrach 16200 Algiers, ALGERIA (e-mail: zakaria.baka@g.end.edu.dz).

H. Yousfi is with the LSTE, Laboratory of Quality, Health, Safety, Environment and Industrial Risk Management, Ecole Nationale Polytechnique, El Harrach 16200 Algiers, ALGERIA (e-mail: hamid.yousfi@g.enp.edu.dz).

Digital Object Identifier (DOI): 10.53907/enpesj.v5i1.296

Mrad in 2009 [7]. Epoxy coatings offer additional protection by forming a barrier against corrosive agents while preserving the innate characteristics of martensitic stainless steel. In summary, the effectiveness of coatings on AISI 1010 carbon steel and AISI 420 martensitic stainless steel lies in their ability to extend the operational lifespan of these materials, reduce maintenance costs, and ensure long-lasting performance in environments where corrosion and abrasion challenges are prevalent. Customizing coatings to the properties of each steel type maximizes the benefits of each material while overcoming its limitations, thereby creating comprehensive and effective protective solutions.

Our study aims to conduct an in-depth comparative assessment of the effectiveness of coatings applied to two distinct substrates: AISI 1010 carbon steel and 420SS martensitic stainless steel. Our primary objective is to differentiate the performance of specific coatings and evaluate the impact of the stainless steel substrate on the performance of epoxy coatings. Additionally, we aim to anticipate the potential advantages of using low-chromium (13%) stainless steels in oil installations exposed to saline environments (saturated with NaCl) and aggressive acidic pH levels. This study's purpose is to provide essential information to guide material selection and optimize coating practices in conditions where corrosion and hostile environments are major considerations.

II. Materials and Methods

A. Materials

1. Products used

In our quest to develop innovative coatings, we ventured beyond the traditional realm of anti-corrosion elements by replacing zinc phosphate with highly conductive polymers: Polyaniline (PANI) and Poly (ortho-ethoxyaniline) (POEA).

To formulate our coatings, we harnessed the potential of two distinct semi-conducting polymer powders: PANI-EB (Polyaniline doped with an acid) and POEA (Poly(ortho-ethoxyaniline)). These polymers exhibit remarkable conductivity and corrosion resistance properties.

We carefully applied three unique coatings onto stainless steel surfaces, each incorporating a specific anti-corrosion agent:

- Coating N°1: Epoxamine in a commercial white shade (referred to as ZP), fortified with a 7.5wt.% by zinc phosphate anti-corrosion agent.
- Coating N°2: A captivating pearly green epoxy, enriched with a 3wt.% by PANI-doped anti-corrosion agent.
- Coating N°3: An elegant navy-blue epoxy, fortified with a 3wt.% by POEA anti-corrosion agent.

These coatings were meticulously formulated, taking into account the desired properties and optimal concentrations of the PANI and POEA agents. The composition details can be found in Section *A.1.4*.

For a comprehensive understanding of the substrate, we conducted XRF analysis, providing valuable insights into the chemical composition of the stainless steel. The results are presented in Table I, aiding in the evaluation of the coating's compatibility and performance.

Through our innovative approach, we aim to revolutionize the field of corrosion protection, offering coatings that not only safeguard against degradation but also harness the unique properties of conductive polymers to enhance the overall durability and longevity of the coated surfaces.

Table.I
Chemical composition of 13% Cr stainless steel substrate by XRF.

Chemical elements	C	Mn	Si	Cu	Ni	Cr	Fe
Massfraction (%)	0.38	0.49	0.43	0.19	0.21	13.08	85.22

2. Doped PANI and POEA synthesis

To prepare the doped Polyaniline (PANI), we followed a polymerization procedure utilizing a chemical oxidizing solution as described in previous studies[8-13]. The synthesis involved gradually adding the oxidizing solution, consisting of 400ml of 1M HCl, to a solution containing 0.2 moles of the monomer aniline. This reaction mixture was stirred slowly for 4 hours.

After the reaction, the resulting PANI-ES salt was washed with acetone. Subsequently, 0.1M NH_2OH was added to the salt with vigorous stirring for 2 hours. The obtained product, PANI-EB, was then rinsed with distilled water and filtered. To remove any remaining moisture, it was dried in a vacuum oven at 40°C for 48 hours [11].

To facilitate the doping of Polyaniline, the salt obtained from the previous step was dissolved in a solution of 4M concentrated sulfo-5-salicylic acid [14]. The solubilization process involved stirring the mixture for 12 hours to ensure thorough doping. Subsequently, the mixture was dried in a vacuum oven at 40°C for 48 hours to remove any residual moisture. The resulting doped PANI was then carefully stored in an airtight bottle to maintain its properties.

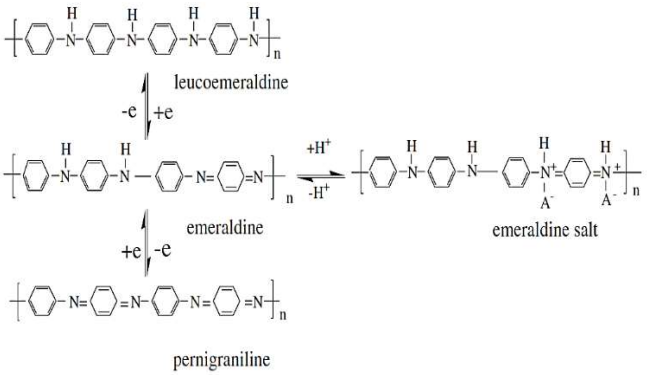

Fig.1: The PANI transformation forms [3, 15].

The doping mechanism used to obtain PANI is illustrated in Figure 1, providing a visual representation of the process.

The synthesis of Poly(o-ethoxyaniline) was carried out following a method described in previous works [16, 17]. In a reaction vessel, 0.6 moles of ethoxyaniline monomer (ORMECON, Germany) were combined with 400ml of 1M HCl and stirred for 2 hours. Then, 0.4 moles of ammonium peroxy-disulphate were carefully added to the mixture under a vacuum atmosphere, maintaining a temperature of 28°C.

To ensure adequate electrical conductivity, the solution's pH was adjusted to 8 by adding 1M NaOH. The resulting product was then mixed with concentrated sulfo-5-salicylic acid [14] and stirred for 24 hours, as depicted in Fig.2. Finally, the mixture was dried in a vacuum oven at room temperature for 48 hours [11]. This procedure allowed for the successful synthesis of Poly(o-ethoxyaniline) (POEA), a crucial component in our research, with desired properties for the development of our innovative coatings.

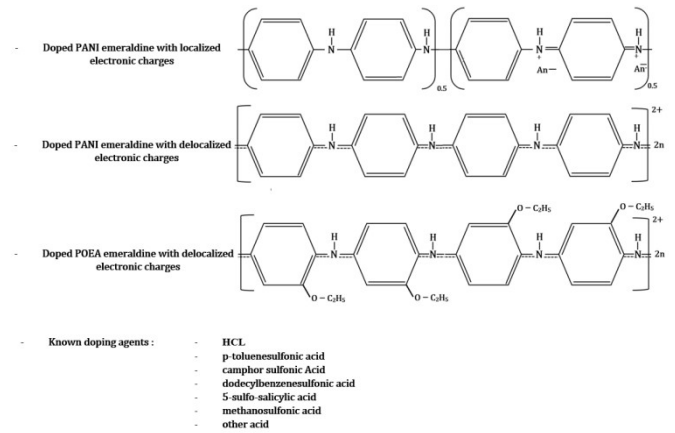

Fig. 2: The Polyaniline and Poly (O-Ethoxyaniline) doped with acid [18-21].

3. *Powder Grinding*

Following the synthesis of the two polymers, additional steps were taken to achieve the desired fineness required for the development of primer paints, adhering to standards such as ISO 2808, ASTM D4414, and D1212. For instance, in the case of the white Epoxamine commercial paint (ZP), the typical acceptable fineness falls within the range of 5 to 7 on the Hegman scale, as determined by a grinding fineness gauge (ERICHSEN Model 232 ASTM D 1210 ISO 1524, ENAP ALGERIE).

To meet these specifications, a mechanical grinding process was initially employed, followed by an automatic grinding process. Through these grinding procedures, we were able to achieve a caliber rating of 4 to 5 on the Hegman scale, corresponding to particle sizes ranging from 40 to 30 µm.

By attaining the desired particle size distribution, we ensured that the resulting powders were suitable for the formulation of primer paints, meeting the required industry standards.

4. *Formulation and Development of Epoxy Coatings*

4.1. Formulation of Epoxy Coatings

In order to assess the corrosion resistance properties of the epoxy coatings, we developed three distinct coatings. To carry out this formulation, we collaborated with the main physicochemical laboratory at the national paint company (ENAP, Algeria). The following protocol was followed:

- Preparation of the commercial coating (referred to as ZP). We formulated a white Epoxamine coating containing 7.5% of zinc phosphate ($Zn_3(PO_4)_2$) [21].
- Formulation of two other coatings: These coatings were developed by replacing the anti-corrosion agent of the commercial formula with two different agents known as PANI-EB and POEA. The PANI-EB coating contained 3 wt.% of PANI-EB, while the POEA coating contained 3 wt.% of POEA. Detailed formulation parameters can be found in Table II [21].

During the formulation process, great care was taken to ensure accurate measurements of the ingredients. Precise weighing was carried out using an analytical balance with a 4-digit decimal scale (SARTORIUS 220g, ENAP ALGERIA).

By adhering to rigorous formulation procedures, we aimed to create epoxy coatings with specific anti-corrosion properties, enabling comprehensive evaluation of their performance against corrosion in subsequent testing and analysis [21].

The followingtable presents the specific formulation details for the anti-corrosion epoxy coatings developed in this study.

Table.II
Formulation of Anti-Corrosion Epoxy Coatings [21].

Components	Commercial paint (ZP)	PANI coating	POEA coating
	$Zn_3(PO_4)_2$) (wt.%)	PANI-ES (wt.%)	POEA (wt.%)
Epoxy resin	30.50	30.50	30.50
Anti-corrosion agent	7.50	3.00	3.00
Additives	5.70	5.70	5.70
Fillers	19.50	23.50	23.50
Pigments	21.00	21.00	21.00
Solvents & Xylene	7.00 + 8.800	7.00 + 9.300	7.00 + 9.30
Total	100	100	100

4.2. Coating Elaboration (Operating Procedure)

Prior to initiating the preparation of the primer coatings, compatibility tests were conducted between the components and the two conductive polymers, PANI-ES and POEA. Solubility tests were performed using Xylene [22], while also considering the strong solubility of the polymers in DMF, DMSO, and alcohols [14, 23-25].

To formulate 100g of paint, a metal paint can with a capacity of 250g was utilized. The required mass of the anti-corrosion agent (zinc phosphate or conductive polymers) was accurately weighed using a KERN ABS 220-4N balance. This agent was then dissolved in 50 wt.% xylene solvent. Subsequently, the epoxy resin, additives, fillers, pigments, and remaining solvents were gradually added to the mixture with moderate stirring using a RAKUTEN 2100W mixer [21].

To ensure proper grinding, mixing, and achieve the desired fineness of the final product, 50 wt.% glass beads were incorporated into the mixture. The entire mixture was then placed in an automatic grinder (VM2 RED DEVIL5400 vibrator, ENAP Algeria) for a duration of 90 minutes. Following the grinding process, the mixture was filtered, and a Versamid 115/70-type hardener was added at a paint-to-hardener ratio of 93:7 [21].

Subsequently, the metal substrates, in disc form with a radius of 3.5 cm, were prepared using the stainless steel material specified in Table I. The preparation involved primary pickling. Secondary stripping was performed using a mixture of two acids (0.1N H_2SO_4 and 0.1N HCl), and the surface of the samples was degreased with acetone. For this comprehensive coating elaboration procedure, we ensured the preparation of well-formulated coatings and properly prepared metal substrates for subsequent testing and analysis of corrosion behavior [21].

Lastly, the three paints were applied onto the metal substrates using a manual projection torch. After the application, wet coatings with a thickness ranging from 100 to 150 µm were obtained and measured using a thickness gauge (ATQC ISO 2808, ENP Algeria). Once dried, the coatings reached a thickness of approximately 40 to 70 µm, as measured by a thickness gauge (POSITECTOR 600 ISO 2178, ENAP Algeria).

B. Methods for Coating Characterization

1. Surface Characterization

The surface of the coatings was subjected to three different types of observation to gain comprehensive insights. Initially, an optical microscope was employed to evaluate the overall quality of the surface obtained. Subsequently, more detailed observations were conducted using scanning electron microscopy (SEM) to identify the finest particles present on the coating surface. Additionally, atomic force microscopy (AFM) mappings were performed using specific types and brands of AFM equipment to assess the roughness of the coatings. These characterization methods provided valuable information about the surface properties and morphology of the coatings.

2. Structural and Micrographical Characterization

The composition of the three coatings was analyzed using non-destructive experimental methods, including infrared Fourier-transform attenuated total reflection spectroscopy (FTIR-ATR) and SEM observation. This characterization process involved analyzing both the initially doped PANI and POEA powders, as well as the final coatings. These methods provided valuable insights into the structural and micrographical properties of the coatings, allowing for a comprehensive understanding of their composition and characteristics.

3. Electrochemical Measurements

To evaluate the corrosion resistance of the coatings, electrochemical measurements were performed. The sample preparation involved cutting a coated sample into a small disc with a diameter of 1.25 cm. This diameter was chosen to fit inside a flat specimen holder kit specifically designed for conducting electrochemical immersion tests. The disc's surface area in contact with the 3.5% NaCl electrolyte was approximately 1 cm², providing a defined attack surface for corrosion assessment.

The electrochemical corrosion measurements were conducted using a VersaSTAT 3 potential stat (Princeton Applied Research, ENP Alger). The electrolyte solutions were prepared to simulate seawater, consisting of 3.5 wt.% NaCl [10, 11, 26, 27], with a pH 6.5.

The measurements were taken at a room temperature of 25 ±1°C. A Reference electrode (Ag, AgCl/KCl (3.5M)) with a standard potential of E_0 = +0.205V [28] and a pH controller (HANNA Instruments 2211 pH/ORP meter, ENP Algiers) were used.

The obtained results, highlighting the variations in iron concentration over the immersion period, are presented in Table III.

Prior to each electrochemical impedance spectroscopy (EIS) measurement, open potentials (OCP) and linear polarization resistance (LRP) were measured. EIS measurements were performed within the frequency range of 0.05 Hz to 50 kHz, with an alternating amplitude potential of 50 mV [26, 29]. All tests were conducted on a minimum of five samples, and the results demonstrated good reproducibility.

In addition, potential dynamic corrosion polarization tests (Tafel tests) were performed to assess the protective behavior of the coatings. These tests involved observing the anodic displacement of the corrosion potential, current density, and determining the corrosion rate (E corrosion) of the coatings [11].

4. Immersion Test

In our study, we conducted an immersion test to investigate the performance of samples coated with three different paints: POEA, PANI, and ZP. The samples had dimensions of 40×20×0.01cm^3. They were submerged in a 3.5% NaCl solution with a pH of 6.5 for a total duration of 60 days.

To conduct the immersion tests, we implemented a systematic approach. At specific time intervals (5, 10, 15, 20, 30, 45, 60, 90, 120, 180, and 240 days), the samples were carefully weighed (KERN ABS 220-4N) to monitor any changes (Fig.3b). Additionally, after each sampling session, 30 ml vials were collected (Fig.3a). These vials were crucial for analyzing the progressive loss of iron concentration in the solution (Fe^{+2} and Fe^{+3}) as the immersion time increased. The analysis of iron concentration was carried out using two instruments: the PerkinElmer Optima8000 for ECP Test and the HACH DR 1900 for UV-visible Test.

Fig. 3: (a) The solution collection vial 30ml, (b) the electronic scale.

III. Results and Discussions

A. Physical and Chemical Results

We measured the contact angle (CA) of the electrolyte on the surface of the substrate coated with the three types of epoxy: ZP, PANI, and POEA (see Fig.4). It was observed that this angle decreases rapidly for ZP, while it remains more stable for PANI and POEA during immersion tests in a 3.5% NaCl solution. This indicates the degradation of the ZP coating surface, which is initially smooth and hydrophobic but becomes hydrophilic after 60 days of immersion (around 63°). In contrast, the stability of the CA (at 78°) for PANI (even with a hydrophilic surface) and POEA (smooth and hydrophobic surface) is maintained (approximately 83°). The results show that the ZP coating degrades (from 96° to 62°) due to the removal of zinc (sacrificial electrode), while the PANI and POEA coatings serve as excellent anticorrosion barriers against the aggressive electrolyte.

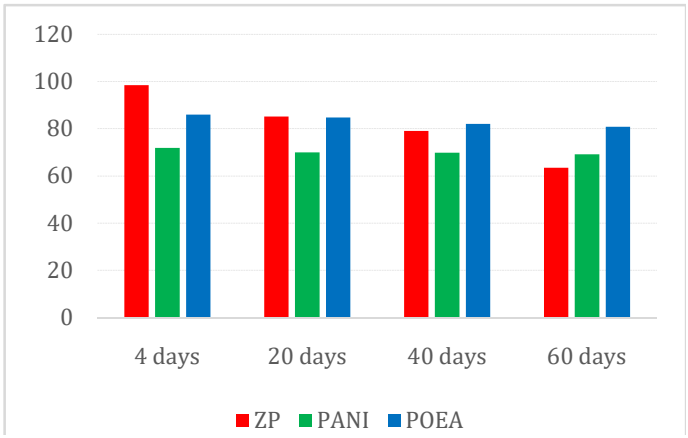

Fig.4: Variation in contact angle of ZP, PANI and POEA epoxy coatings as a function of immersion time in 3.5 wt.% NaCl solution.

B. Corrosion Studies Effects

1. Open Circuit (OCP) and Linear Polarization Resistance (R_P)

The equilibrium potential (OCP) of ZP, PANI, and POEA epoxy coatings varies with immersion time (see Fig. 5). It is observed that the ZP coating undergoes a gradual decrease, from -250 mV after 4 days of immersion to -480 mV after 15 days in the saline solution. Similarly, the potential of PANI decreases from -120 mV (after 4 days) to -380 mV after 40 days in the marine solution. In contrast, the POEA shows an increase from -160 mV (after 4 days) to -50 mV after 40 days, followed by a slow decrease to -220 mV by the end of the test.

The polarization resistance results for the epoxy coatings (see Fig. 6) show that ZP experiences a significant drop, from 1 MΩ (after 4 days of immersion) to 100 kΩ after just 15 days in a 3.5% NaCl solution. However, the PANI and POEA coatings maintain stable resistance after 40 days of immersion (approximately 2.5 MΩ and 1.2 MΩ, respectively), before gradually decreasing to 830 kΩ after 200 days of exposure to an aggressive marine solution.

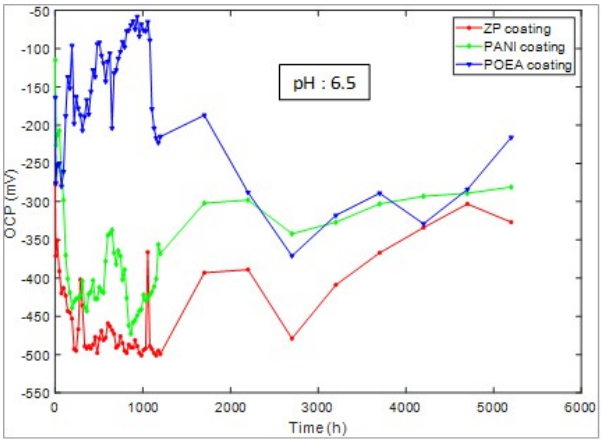

Fig.5: Open circuit potential of ZP, PANI and POEA epoxy coatings applied into 420SS with immersion time in 3.5 wt.% NaCl solution.

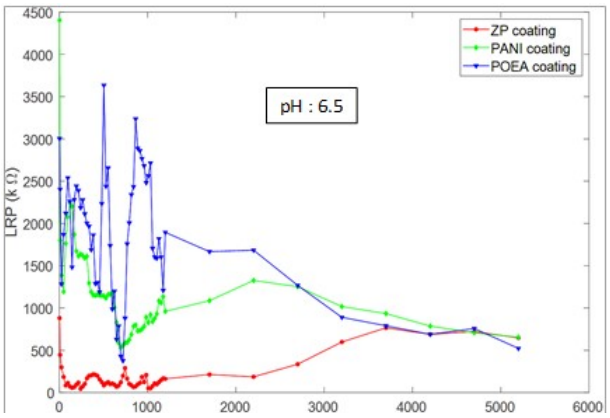

Fig.6: R_P evolution of ZP, PANI and POEA epoxy coatings applied into 420SS with immersion time in 3.5 wt.% NaCl solution.

2. The Potential Dynamic Polarization of Corrosion

The ZP, PANI, and POEA coatings are carefully applied onto a 13% Cr stainless steel surface, and they are subjected continuous immersion in 3.5% NaCl solutions with a pH of 6.5. The insightful results obtained from this experiment are vividly depicted in Fig.7. Notably, both the PANI and POEA coatings exhibit remarkable capabilities in safeguarding and reinforcing the formation of a passivation layer, specifically in the form of chromium oxide [3].

At the beginning of the test (after 4 days' immersion), the corrosion rates of PANI and POEA are much higher than those of ZP, and the corrosion current density of POEA and PANI is much lower than that of the ZP coating: -52 and -72 to -178mV, 1.8×10^{-11} and 1.23×10^{-10} to 33.71×10^{-9} A.cm^{-2} respectively (see Table III and Fig.7). It can be affirmed that, initially, both POEA and PANI coatings have stronger protective characteristics than ZP coatings.

However, after a duration of 60 days immersed in a 3.5% NaCl solution with a pH of 6.5 and at ambient temperature, all three coatings experienced substantial attack by the solution. This led to notable degradation in the intrinsic characteristics of each coating, particularly in the case of the ZP coating, which exhibited a significant decrease of -350mV compared to its initial immersion state. On the contrary, the POEA and PANI coatings demonstrated a relatively lower corrosion potential decrease, with values of -80mV and -180mV (respectively) compared to their initial potentials. Furthermore, the corrosion current density witnessed an increase to 4.60×10^{-7}, 3.10×10^{-8}, and 1.1×10^{-9}A.cm^{-2}for the ZP, PANI, and POEA coatings, respectively.

Based on the findings, it can be concluded that the POEA, PANI, and ZP coatings, when applied to 13% Cr stainless steel and immersed in a marine solution, exhibit varying levels of anti-corrosion performance. The POEA coating demonstrates a strong resistance to corrosion, the PANI coating exhibits a moderate level of protection, while the ZP coating shows a relatively weaker ability to prevent corrosion.

The evaluation of anti-corrosion performance involves the calculation of coating efficiency known as GAP (η). This calculation serves a dual purpose: firstly, to measure the corrosion rate of uncoated stainless steel immersed in a salt solution, and secondly, to assess the anti-corrosion effectiveness of our coatings [3]. The efficiency factor is determined by comparing the corrosion potential difference between the substrate with and without the coating, as defined

by the following formula (see equation 1) [3]:

$$\eta = (1 - \frac{I_{corr}}{I^0_{corr}}) \times 100\% \quad (1)$$

I_{Corr} andI^0_{Corr} represents the corrosion current density values for the working electrodes (uncoated stainless steel) and (coated stainless steelwith ZP, PANI and POEA), respectively. The results are shown in Table III.

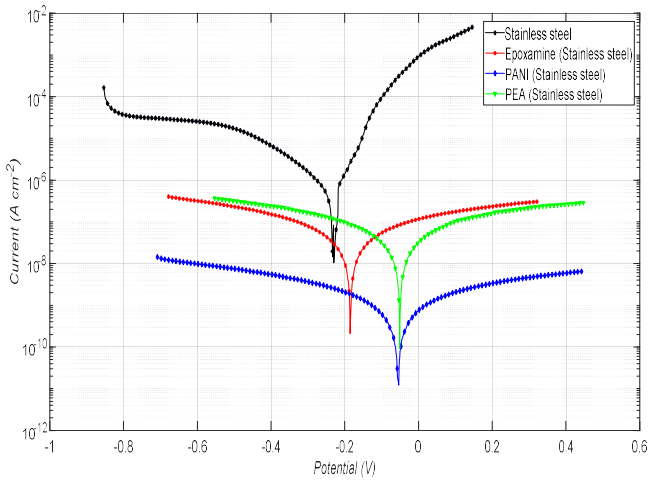

Fig.7: Tafel curves (a) after 4 days of immersion in 3.5% NaCl solution.

Table. III
Electrochemical parameters of MS, ZP, PANI, POEA Coating onto stainless steel in 3.5%NaCl solution.

Electrode	Immersion (days)	$E_{Corr.}$ (mV)	$i_{Corr.}$ (ACm^{-2})	β_a ($Vdec^{-1}$)	β_c ($Vdec^{-1}$)	η (%)
MS	4	-297.62	76.62×10^{-8}	0.088	0.157	-
	60	-414.51	5.87×10^{-6}	0.176	0.323	-
ZP	4	-178.38	19.23×10^{-9}	0.181	0.181	97.49
	60	-438	96.73×10^{-9}	0.137	0.137	87.37
PANI	4	-137.81	1.68×10^{-10}	0.225	0.225	99.98
	60	-247.81	1.31×10^{-9}	0.354	0.354	99.82
POEA	4	-80.63	0.18×10^{-10}	0.161	0.161	99.99
	60	-107.91	1.11×10^{-10}	0.081	0.081	99.98

3. *Electrochemical Impedance Spectroscopies*

The anti-corrosion properties of the coatings (POEA, PANI, andZP) were characterized experimentally by EIS measurements. The Nyquist curves to the various coatings during immersion of 60 days in a 3.5% NaCl solution at pH 4.5 are shown in Fig.6. The results obtained by EIS test reveal that, at low frequencies (0.05 Hz), $|Z|_{0.05Hz}$ (or R_P) values are very high [30-32]. After 2 days immersion, the POEA and PANI coatings show $|Z|_{0.05Hz}$ values of the order to but it is in opposition to the ZP coating, which is in the order to 8.92×10^5 Ω. This value of $|Z|_{0.05Hz}$ is used as a quantitative classification index for the performance of coatings against the passage of electronic charges from a steel to the corrosive solution. This high impedance value implies that the barrier of coatings against corrosion is very effective [32, 33]. The plots observed were predominantly characterized by a depressed semicircular shape, with the resistance value corresponding to the diameter of this semicircle being equivalent to the polarization resistance (R_P).

In addition, the coatings have same appearance in the immersion test, which proves that they have the same R_P behavior towards the solution with different POEA and PANI coatings produced very high values, compared to the ZP-based coating, which proves the electron exchange process between steel and solution is so complex and negligible.

After 60 days of immersion in 3.5% NaCl solution (Fig.8), we can see the difference between POEA, PANI and ZP-based coatings with a significant decrease in R_P for ZP unlike the POEA coating, and the appearance of second half-arc, larger than the first day of immersion. The obtained results from the EIS curves measured are presented in Table IV. At this time of immersion, the impedance values for POEA $5.6\times10^6\Omega$) and PANI ($5.1\times10^6\Omega$) remain high compared with ZP ($8.3\times10^5\Omega$). This may explain their anti-corrosion performance due to their excellent barrier effect [28, 34, and 35]. On the other hand, the barrier effect of ZP coatings has been degraded by electron migration from the surface by a reaction of Zn with Zn^{2+} as the coating progresses in depth [36].

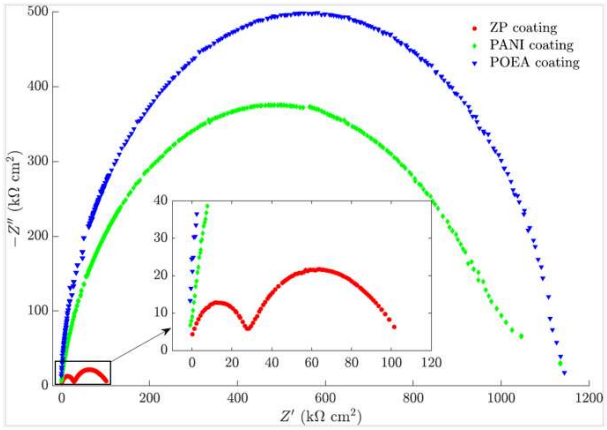

Fig.8: Nyquist plots (EIS curves) of ZP, PANI and POEA coatings after 60.days of immersion in 3.5% NaCl.

The electrical impedance of PANI coating is high compared to that of commercial coating, and it always remains at the same pace; which explains the resistance of the coating to degradation as a function of immersion time. The real and imaginary impedances of the PANI and POEA coatings remain very high during the immersion time, contrary to the commercial coating.

According to Fig.6, after adjustment with Zsimpwin soft word, the obtained equivalent circuits are shown in Fig.9. In the circuits presented, R_S, R_{pore}, C_C, C_{dl} and R_{ct} signify such as solution resistance, coating pore resistance, capacitance of the coating, double layer capacitance resulting from the corrosion reaction at interface of the carbon steel substrate and charge transfer resistance,respectively.

Table. IV
Calculated electrochemical parameters for ZP,PANI and POEA coatings after 60 days of immersion in 3.5% NaCl solution with a pH6.5.

Epoxy	RS (Ω cm^2)	R_{pore} (kΩ cm^2)	C_{PE} (μF cm^{-2}) Y0	N0	C_{dlE} (μF cm^{-2}) Y1	N1	R_{ct} (Ω cm^2)	R_P (Ω cm^2)
ZP	0.0122	15.97	12.34	0.96	1.48	0.91	1.71×10^4	1.72×10^4
PANI	0.0118	158.62	1.3×10^{-4}	0.98	1.1×10^{-3}	0.88	8.59×10^5	8.60×10^5
POEA	0.0120	238.74	1.1×10^{-4}	0.92	3.8×10^{-4}	0.94	1.11×10^6	1.12×10^6

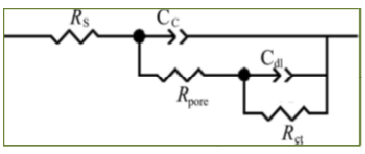

Fig.9: Equivalent circuits of the coatings, ZP, PANI and POEA after 60 days of immersion in 3.5% NaCl.

C. Micrographic Corrosion Analysis of Coating

Microstructural observations by SEM reveal that the effect of corrosion on the three coatings (ZP, PANI, and POEA) is inversely proportional in a significant manner (see Fig. 10). It is observed that corrosion heavily affects the ZP coating, while this effect is less on PANI and almost negligible on the POEA film. This highlights the superior anticorrosion barrier performance of the PANI and POEA coatings compared to the ZP coating.

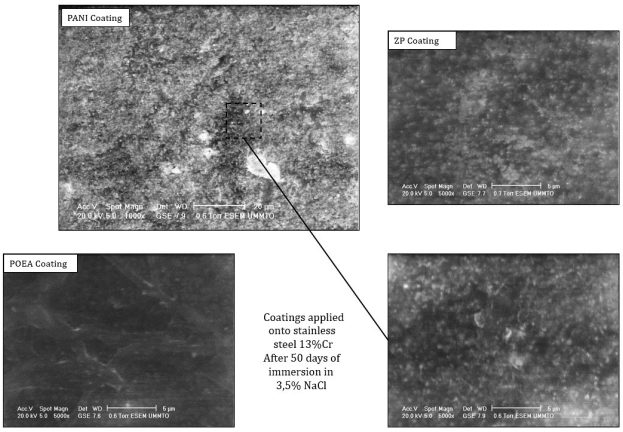

Fig.10: SEM images of the facial-section of ZP, PANI and POEA epoxy.coatings after 50 days of immersion in 3.5% NaCl.

D. Immersion Test and the Fe Dissolutions Analyzing

The specimens, cut in 40×80×0.1mm rectangles, are immersed in a 3.5% NaCl solution with a neutral pH while the immersion time is growing. The solutions are sampled after 10, 15, 20, 30, 40, 60 and 75 days. Optical observations on the samples showed that there was no trace of rust on the substrates coated with ZP, PANI and POEA. The 30ml solutions taken from each stage were analyzed to determine the total mass of iron in saline solution. The results obtained after OCP and Uv-visible analysis are shown in the following table:

Table. V
Fe dissolved after immersion in 3.5 wt.% NaCl with pH 6.5.

	Total concentration of Fe dissolved ($\times 10^{-6}$ g l^{-3})							
Days	10	15	20	30	40	50	60	75
ZP	0.011	0.016	0.019	0.021	0.026	0.031	0.036	0.042
PANI	0.003	0.007	0.009	0.013	0.018	0.022	0.026	0.034
POEA	0.002	0.005	0.007	0.010	0.015	0.018	0.021	0.028

Total solute iron content in solution is very high for uncoated 13% Cr stainless steel. In coated samples, on the other hand, the mass of iron is very negligible. The POEA coating provides a strong protective barrier against salt solution, with the lowest mass of iron in solution compared with the ZP and PANI coatings.

The iron content of all three coatings decreases with increasing immersion time, due to the formation of a passivation layer that counteracts the aggressive nature of the solution (corrosion).

In our immersion experiment, given the small difference in iron dissolution rate in 3.5% NaCl and in order to classify the best coating, it is preferable to continue the test at extended immersion times other than 120 days, and also to try another test outright (such as salt spray).

IV. Conclusion

In this article, we successfully prepared two organic acid (SSA)-doped conducting polymers based on simple polyaniline and an ortho-ethoxy-conjugated derivative. These polymers exhibit high electrochemical activity and good solubility in common organic solvents such as xylene, making them ideal candidates as anticorrosion agents for epoxy coatings. Among them, POEA shows the best dispersion within the epoxy matrix, resulting in a homogeneous and smooth surface (contact angle around 90°), whereas PANI exhibits agglomeration and porosity defects (contact angle below 70°), as confirmed by scanning electron microscopy. Electrochemical impedance spectroscopy (EIS) results revealed that corrosion protection of the coatings containing 3 wt.% of PANI and POEA is significantly improved compared to the conventional zinc phosphate (ZP) coating system. Notably, the POEA-based coating system exhibited the highest resistance (over 2 MΩ) after 60 days of immersion in a 3.5 wt.% NaCl solution, as indicated by the EIS measurements. This superior protection is attributed to the formation of a stable passive layer composed of Cr_2O_3, reinforced by Fe_2O_3 and Fe_3O_4 compounds [21]. Ultimately, coatings based on PANI and POEA show strong potential for protecting oil installations in aggressive environments, particularly for long-term applications.

Acknowledgment

The authors gratefully acknowledge the financial support provided by the Directorate-General for Scientific Research and Technological Development (DG-RSDT) of the Algerian government through a research grant. Sincere thanks are also extended to the Laboratoire des Sciences et Techniques de l'Environnement (LSTE),Laboratoire de Génie Minier (LGM) and the Laboratory of Green and Mechanical Development (LGMD) at the National Polytechnic School (ENP). Laboratory Division (formerly CRD SONATRACH Boumerdes) and the Central Laboratory of ENAP Lakhdaria, Bouira, are also acknowledged for providing essential resources and technical support throughout this work.

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Nacer Mounir received his Engineering degree in Materials Engineering from the École Nationale Polytechnique (ENP), Algiers, Algeria, in 2011, a Master's degree in Mechanics, Materials, and Processes from ENSAM ParisTech, Paris, France, in 2013, and a Ph.D. in Materials Engineering from ENP in 2025. He is currently conducting research at the laboratory of Quality, Health, Safety, Environment and Industrial Risk Management. His research interests include corrosion, thin films and coatings, electrochemical characterization, and electrochemical hydrogen conversion.

Malha Nazef is a Corrosion Manager, working at the laboratory of Corrosion, Department of Corrosion, Division Laboratories Exploration and Production SONATRACH (Ex CRD), Boumerdes, Algeria. Her main research interests include corrosion, thin films and coatings, synthesis and characterization of conductive polymers.

Zakaria Baka received his Engineering, Master's, and Ph.D. degrees in Mechanical Engineering from the Ecole Nationale Polytechnique, Algiers, Algeria, in 2013, 2014, and 2024, respectively. He is currently conducting research at the Laboratory of Green and Mechanical Development, ENP. His research interests include engineering mechanics, solid mechanics, heat transfer, elasticity, and thermo-elasticity.

Hamid Yousfi is a full Professor at Laboratory of Quality, Health, Safety, Environment and Industrial Risk Management at the Ecole Nationale Polytechnique, Algiers, Algeria. His main research interests include corrosion, thin films and coatings, synthesis and characterization of aluminum alloys.