



Investigation of Corrosion Properties of Modified Epoxy and Polyurethane Organic Coating on Steel Substrate

M. Mirzaei¹, M. Rezaei Abadchi^{2*}, A. Fateh³, A. Zolriasatein²

¹ University of Tehran, Faculty of Engineering, School of Metallurgy and Materials Engineering, P.O. Box: 11155-4563, Tehran, Iran.

² Non-metallic Materials Research Group, Niroo Research Institute, P.O. Box: 14665517, Tehran, Iran.

³ Department of Materials Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran.

ARTICLE INFO

Article history:

Received: 25 Oct 2020

Final Revised: 02 Jan 2021

Accepted: 03 Jan 2021

Available online: 28 Feb 2021

Keywords:

Epoxy

Polyurethane

Zinc-chromate

Corrosion Resistance

ABSTRACT

In this study, the organic coating of epoxy zinc-chromate (E) and the two-layer coating of epoxy zinc-chromate-polyurethane (PU-E) was coated on the steel substrate using the spraying method. Then, their corrosion resistance was compared using electrochemical impedance spectroscopy (EIS) and dynamic polarization tests. Comparison of corrosion properties using parameters of, phase angle at a maximum frequency (100kHz), and breakpoint frequency (f_b) were performed during 2, 4, and 8 weeks. A comparison of these three parameters showed that the corrosion resistance of the PU-E coating was higher than the E coating due to the behavior of the polyurethane coating barrier as well as the active protective behavior induced by the chromate pigments which was distributed on the epoxy coating. According to the test results, E and PU-E coatings had good hardness and scratch resistance and were resistant to pencil scratches with H and F hardness, respectively. The salt spray test for the two-layer coating showed no qualitative change, damaged area, blistering/delamination, or corrosion products on the coated sample. The results showed that both coatings were suitable candidates for use in various industries, including marine and power industries, and other industries that suffered from corrosion problems. Prog. Color Colorants Coat. 15 (2022), 25-36 © Institute for Color Science and Technology.

1. Introduction

The annual cost of corrosion in the United States and the European Union is estimated at 3 to 5 percent of the GDP. Corrosion of metals in the oil and gas industry, power plants, shipping and aviation industries, drinking water systems, pipelines, bridges, and public buildings make up the bulk of corrosion costs [1-3]. Many electrical industry structures are made of carbon steels and low-alloy steels, which have advantages such as excellent mechanical properties, ease of construction and welding, and low initial cost, which can cause significant corrosion problems in aggressive

environments [4, 5]. Organic coatings and paints are mainly used to protect metal structures in aggressive atmospheres. Organic coatings act as a barrier between corrosive environments and metal structures and are among the most effective and inexpensive methods of corrosion protection [6-10].

Epoxy resins have led to significant advances in color technology. Epoxies are used to paint structures in and out of the water, because their coatings have excellent adhesion, low cost, and good resistance to chemical agents, marine environments, solvents and water [11-13]. But they are not very flexible because

*Corresponding author: * mrezaei@nri.ac.ir

the binder evaporates under the sun's ultraviolet light and the pigments remain on the surface, creating a brittle surface [14]. The curing of epoxy resins is based on the opening of the epoxy chains by the active hydrogen atoms in the amine curing agent. Although alkaline cyclone amines have been widely used as a curing agent for epoxy resins because they provide high corrosion resistance, these curing agents are no longer used in the commercial market. Instead, polyamides are often used in mixtures to control the process of coating and create coatings with desirable properties [7]. Urethane resins are other types of polymers with cross-links that can withstand air erosion and are more flexible than epoxy [15-17].

Polyurethane coatings are unique because they can be modified for using in both humid and icy conditions. Other properties of polyurethanes include good chemical resistance, higher resistance to acids compared to epoxy, applicability in various conditions, and resistance to UV radiation. Although the top coating of polyurethane does not exhibit corrosion and real barrier protection, it does protect the integrity of the coating system. Therefore, polyurethane coatings are often used as top coatings in cases where they are exposed to ultraviolet radiation. Of course, polyurethane coatings are also used as primer coatings and intermediate coatings [18, 19].

One of the problems with polyurethanes is their sensitivity to water. So, their transportation and storage must be done under special conditions according to the manufacturer's instructions [7, 20]. Epoxies are more stable in alkalis than polyurethanes. The final coatings of polyurethane are robust and have an excellent shine. But in some cases, they are challenging to repaint after they are worn out, and the surfaces must be thoroughly clean so that polyurethane paints adhere well to the base.

Although different methods of preventing corrosion are being used, it is still necessary to increase the lifetime of consumables. One of the novel methods used to increase the adhesion and corrosion resistance of polymer coatings is nanocomposite coatings [21]. Nanoscale pigments and fillers have recently been used in coating systems to solve these problems and improve the properties and performance of coatings. In this method, many coating problems are tried using nanotechnology. Eliminate them and improve their performance [22]. Due to their nanoscale, nanomaterials exhibit unique properties and can be used to produce multi-purpose coatings. Nanoparticles

with dimensions less than 100 nm can strengthen the polymer field without compromising transparency and other coating properties. Also, the concentration of nanoparticles required to modify the properties of coatings is much lower than the concentration of microparticles used in coatings [22]. Zinc oxide and chromate [23] are used to increase corrosion resistance and increase the stability of epoxy coatings to ultraviolet radiation. For example, Dhoke and Khanna showed that ZnO nanoparticles could improve the corrosion resistance of alkyd coatings. Research has also shown that ZnO nanoparticles are non-toxic nanoparticles hence can be used to synthesize environmentally friendly coatings. In a study by Ramazanzadeh and Attar [27], epoxy nanocomposites containing different amounts of zinc nanoparticles (2, 3.5, 5, and 6.5 % by weight of ZnO) were prepared for 60 years. The tests was examined in 3.5 wt% NaCl solution. Their results showed that nanoparticle-free samples were rapidly degraded after being placed in corrosive environments, but the corrosion resistance of nanoparticle-containing samples increased dramatically. The results indicated that zinc oxide nanoparticles significantly increase the resistance of the coating to hydrolytic degradation [22, 24].

In a study by Bastos et al. [25], the evaluation of electrochemical parameters for comparing two pigments of zinc phosphate and zinc chromate in 0.1 M NaCl solution showed that the corrosion resistance of the solution containing zinc chromate inhibitor was higher. Over a more extended period, the protective layer of pigments formed under the coating, and the lamination rate for the sample containing zinc chromate was lower. Amirudin et al. showed that zinc chromate performs well on cold-rolled and galvanized steel [26]. Immersion tests and salt spray tests showed that zinc chromate barrier properties were not degraded and good corrosion inhibitory performance was obtained [27]. In another study, stable oxidation was observed in parts of defects in chromate-coated epoxy-containing steel (after the initial delay), resulting in a continuous oxide/hydroxide composite film with high strength properties in exposure to corrosive agents. For steel, continuous oxidation in the presence of chromate leads to the formation of a passive film that may be more resistant than the film formed in the absence of chromate [28].

In this study, first, the corrosion properties of epoxy coating containing zinc-chromate were investigated,

and then polyurethane coating was applied as the top layer on the epoxy coating. Its corrosion and mechanical properties were compared using EIS, dynamic polarization, adhesion, scratch resistance, and salt spray tests.

2. Experimental

2.1. Chemicals and synthesis of coating

St37 steel sheets used for coating and corrosion tests were prepared in the dimensions of $1 \times 25 \times 50$ and $1 \times 100 \times 100$ mm³. The steel specimens were mechanically polished with 100, 220, 400, 600, and 800 sandpapers to remove the oxide layers, and then washed with deionized water. Before coating, the surface of the specimens was degreased and cleaned by acetone and ethanol followed by air-drying. Spray method was used to apply different coatings. In this regard, the coating mixture was transferred to the spray chamber. The coating was applied at the angle of 45°. Then the samples were dried for 24 h at room temperature. Finally, the samples were stored in a desiccator with a dry environment.

2.2. Preparation of organic coating for electrochemical characterization

For each of the defined coatings, the resin and the hardener were first mixed at a certain weight ratio. Resins and hardeners were purchased from Khuzestan Petrochemical Co. The purchased epoxy grade was EP06SPL. Stirring was done using mechanical stirrer, and dilution was done to reach 20% of the total weight using a thinner. The weight ratio of resin to hardener for mixing is as follows:

1) Zinc chromate Epoxy /hardener resin (E) ratio: 10:3.5

2) Polyurethane/Hardener Resin (PU) ratio: 10:2.7

The thickness of the E and PU-E coatings was 43.3 and 134.8 μm in the dry state, respectively. The wetting angle was measured using a contact angle analyzer (Krüss DSA100) equipped with droplet shape analysis software. For this purpose, 20 μL of water is dropped on both organic coatings, and after 30 seconds, the contact angle was measured.

2.3. Electrochemical and mechanical characterization

Electrochemical impedance spectroscopy and open

circuit potential (OCP) was performed using a potentiostat/galvanostat electrochemical analysis device. The EIS test was used to check the resistance of the coating and its protective properties. The cell in this test consisted of a platinum electrode with an area of 2 cm² as a counter electrode, an Ag/AgCl as a reference electrode. A prepared steel sample (with and without the above coatings with dimensions of $1 \times 25 \times 50$ mm³) was used as a working electrode, and the electrolyte used in this test was 3.5 wt.% NaCl. Only 1 cm² of the surface of the coating was exposed to the corrosive environment, and the rest of the sample surface (the areas inside the corrosive solution) was sealed by beeswax. The EIS test was done for two, four, and eight weeks of immersion. The EIS test was performed in open circuit potential (OCP) with a frequency range of 100 kHz to 10 mHz and a sinusoidal voltage range of 10 mV. The E and PU-E samples were immersed in 40 ml salt electrolyte (3.5% NaCl solution) and tested using EIS over time. All EIS experiments were performed at ambient temperature. EIS data was measured using Ivium software, and data were adjusted with ZSimDemo software. Electrochemical polarization tests were performed to measure the corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarization resistance (R_p), and corrosion rate (C.R) of the steel substrate and coated substrate. First, the open circuit potential (OCP) was recorded in the system equilibrium as corrosion potential. Then, the Tafel charts were scanned with a potential scan in the range of -250 mV to 250 mV of the corrosion potential at a scan rate of 10 mV/min. After drawing the Tafel diagram, the density of corrosion current was determined by extrapolation.

Salt spraying test, according to the ASTM B-117 standard, was used to check the performance of the coating in corrosive environments. Humidity test (ASTM D 4585-07), the degree of delamination (ASTM D-610), and the degree of blistering (ASTM D-714) were also investigated. For this purpose, an artificial damage with the dimensions of 2 cm \times 2 mm was created in the coated specimens using a surgical knife.

The pull-off test was used according to the ASTM D4541 standard to check the adhesion strength, and the adhesion was reported based on the force required to separate the coating from the substrate.

Scratch or pencil hardeners were used to determine the hardness and scratch-resistance of the coating applied on the steel substrate by ASTM D3363 standard. The pencil hardness test is qualitative and

uses hardness scale from 6B as the lowest hardness to 9H as the highest hardness. ASTM D3363 standard allowed the analysis to be performed manually without a retainer, but a pencil hardener was used to ensure that the test results are repeatable.

3. Results and Discussion

3.1. Coatings analysis

3.1.1. OCP and EIS measurement

The protective performance of the coated steel specimens immersed in a corrosive solution was assessed during immersion time with the OCP method (Figure 1). The OCP for modified epoxy coating in the first two weeks was -0.452 V. As the immersion time increases, the potential value reached -0.403, which was more positive than first two weeks due to the formation of a protective film at the steel /coating interface. By the penetration of the electrolyte into the interface, the zinc chromate pigments were dissolved. The cations Cr^{3+} and Zn^{2+} were released and penetrated to the metal/coating interface. As the immersion time increased, the amount of open circuit potential became more negative due to the penetration of corrosive substances into the coating. The behavior of the PU-E coating was similar to the epoxy coating. The more positive OCP was due to the active protection caused by chromate pigments and barrier behavior of polyurethane.

The EIS test was performed for steel panels coated

with E coating immersed in a saline solution (3.5 wt% NaCl) after 2, 4, and 8 weeks immersion. The resulting bode graphs are presented in Figure 2a and b. Investigating the value of phase analysis at high frequencies and the value of the total impedance at low frequencies helped to clearly understand the corrosion protection performance of the system under study. Low-frequency range and high-frequency range were assigned to charge transfer resistance and zinc-chromate epoxy coating resistance, respectively. To interpret bode diagrams, three parameters, including the total resistance at the minimum frequency ($|Z|_{10mHz}$), the phase angle at the maximum frequency ($-\theta_{100kHz}$) and the breakpoint frequency (f_b), must be studied. Generally, the value of $|Z|_{10mHz}$ indicated the protective properties of the coating against corrosion [29-31].

As shown in Figure 2 a and Table 1, the value of $\log(|Z|_{10mHz})$ for sample E2, relating to the immersion of epoxy chromate coating for two weeks, was 8.2532. With increasing the immersion time to 4h, the value for sample E2 slightly increased to 8.6134. Then, as the immersion time increased for sample E8, the value of $\log(|Z|_{10mHz})$ decreased slightly to 8.4723. Previous research showed that when the immersion time increased for epoxy coatings without protective additives (pigment and nanoparticles containing active ingredients, etc.), the total resistance of the coating reduced due to the penetration of electrolyte into the coating/substrate interface [1, 2].

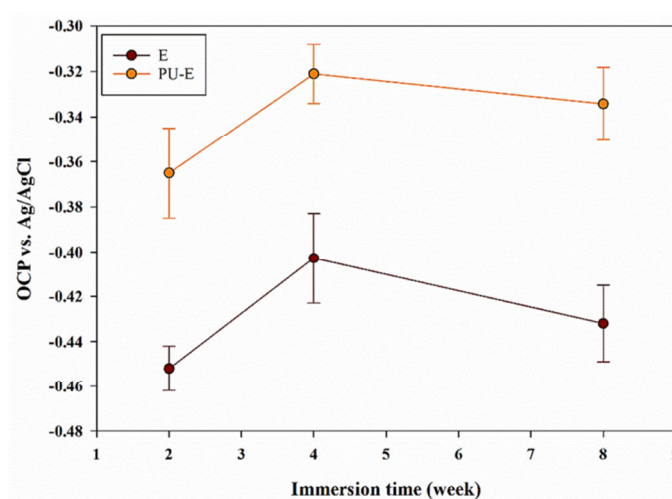


Figure 1: Open circuit potential for E and PU-E coatings within 2, 4, and 8 weeks.

In other words, for pure epoxy, the total resistance of the coating was only related to the resistance of the barrier, and the protective effect of the coating reduced by increasing the immersion time and the presence of more corrosive components. But as the results of this study show, with increasing the immersion time from 2 weeks to 4 weeks, not only the overall resistance of the epoxy chromate coating did not decrease, but also the total resistance increased due to the presence of zinc-chromate pigments in the coating. This phenomenon was related to the formation of a protective film on the steel surface and at the coating/substrate interface. With the penetration of electrolyte into the interface, the chromate pigments were dissolved in it and Cr^{3+} and Zn^{2+} cations were released through the existing penetration pathways [3]. According to the results reported by other researchers, Cr^{3+} and Zn^{2+} ions can form a very thin nanometer-size layer on a steel substrate (and at the coating/metal interface). Therefore, the overall resistance of the epoxy chromate coating increased due to the formation of a protective film in the interface of the coating/substrate at time intervals of 2 to 4 weeks.

$\theta_{100 \text{ kHz}}$, i.e. the phase angle at the maximum frequency of 100 kHz, was another parameter used to study the corrosion properties of the coating. A significant reduction in the phase angle value at high frequencies confirms a significant reduction in the adhesion and protective properties of the coating [4-6]. Studies have shown that by increasing the immersion time of non-additive epoxy coatings in corrosive solutions, the coating adhesion to the substrate decreases due to the penetration of electrolyte into the interface of coating/substrate and the occurrence of the corrosion process. These events manifested themselves as a decrease in the value of the phase angle at the maximum frequency in the frequency-phase diagram.

Figure 2 b and Table 1 showed that $\Theta_{100 \text{ kHz}}$ did not change significantly during the immersion time, and

the coating had excellent adhesion during this period. $\theta_{100 \text{ kHz}}$ after two and four weeks were 75.67 and 81.36, respectively. This increase in the phase angle value at the maximum frequency was attributed to the formation of protective films with barrier capability by chromium cations at the coating/substrate interface within 2 to 4 weeks of immersion. Due to the stability and adhesion of the top layer of the protective layer, the phase angle remained constant up to 8 weeks. As a result, the adhesion of the coating did not change, indicating the promising corrosion resistance of the coating.

A critical parameter that can be considered at higher frequencies was the breakpoint frequency (f_b) which is a reliable measure for the coverage of the coating. Less failure frequency indicated less delamination of coating and better barrier protection performance [6]. The frequency at which a sharp drop occurred in the phase angle values, or in other words, the frequency at which the phase angle was equal to 45° , can be considered as a criterion for the breakpoint frequency. It was generally believed that there was a direct relationship between the breakpoint frequency and the delamination region in the common sublayer and coating interface. Thus, the lower the breakpoint frequency, the less is the destruction of the coating and its separation from the substrate. $\log(f_b)$ is obtained by drawing a horizontal line from the angle of 45° in Figure 2 b which is 0.6, 0.4, and for E2, E4, and E8 samples, respectively. According to the results shown in Table 1, the increase in immersion time from 2 weeks to 4 weeks decreased the breakpoint frequency while it increased up to 8 weeks. The reduction in the failure frequency between two and four weeks was attributed to the formation of protective layers, whereas within eight weeks, the corrosion mechanisms prevailed in the interface and the breakpoint frequency increased to some extent [2, 7].

Table 1: Total impedance values $|Z|_{10mHz}$, phase angle at maximum frequency ($-\theta_{100kHz}$ ($^\circ$)), and breakpoint frequency (f_b) obtained from EIS test for epoxy chromate coatings immersed for 2, 4 and 8 weeks.

Sample	$\log(Z _{10mHz}/\Omega \cdot \text{cm}^2)$	$-\theta_{100kHz}$ ($^\circ$)	f_b
E2	8.21	75.67	0.6
E4	8.61	81.36	0.4
E8	8.47	81.12	1

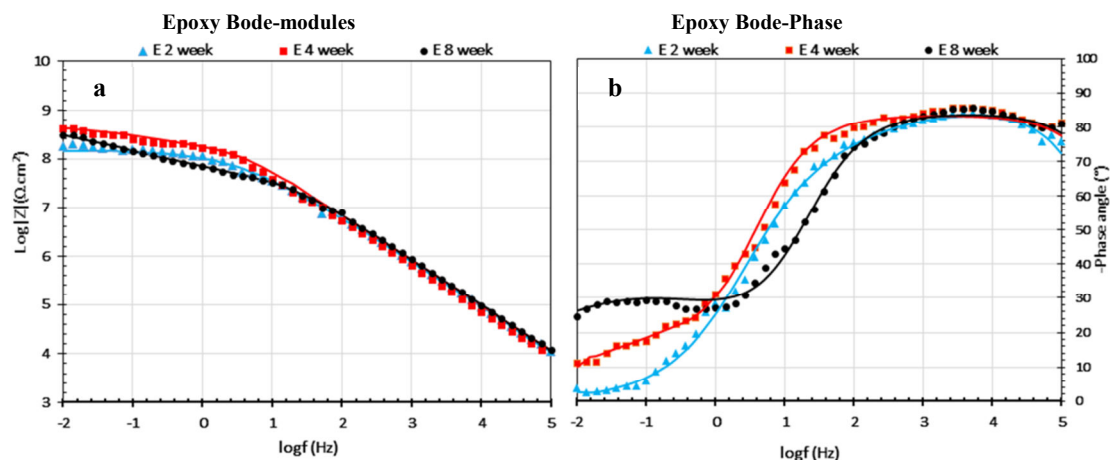


Figure 2: (a) Bode plots, and (b) Phase diagrams for the steel sample coated with epoxy chromate immersed for 2, 4, and 8 weeks in 3.5% NaCl solution.

Figure 3 and Table 1 show that this coating has excellent resistance to electrolyte and the penetration of corrosive ions. Zinc chromate pigments in the coating provided self-healing properties and active protection for the coating.

Steel samples coated with a two-layer epoxy chromate-polyurethane (PU-E) and immersed in corrosive saline solution (3.5 wt% NaCl) were subjected to EIS test after 2, 4 and 8 weeks. The results are presented in the form of Bode-Phase diagrams in Figures 3 and Table 2. As shown in Figure 3(b), the results of the EIS test for two-layer epoxy-polyurethane coating were associated with a significant amount of noise, which was directly related to the very high barrier strength of the coating and its impermeability after eight weeks of immersion [8]. To interpret the graphs of PU coatings, parameters of $|Z|_{10\text{mHz}}$ and $-\theta_{100\text{kHz}}$ were discussed, and the breakpoint frequency (f_b) was extracted compared to single-layer epoxy chromate coatings. As mentioned earlier, the value of $|Z|_{10\text{mHz}}$, was referred to as corrosion resistance. As shown in Figure 3a and Table 2, the value of $\text{log}(|Z|_{10\text{mHz}})$ for the PU2 sample (immersion of epoxy chromate-polyurethane coating for two weeks) was 9.6 $\Omega.\text{cm}^2$. As the immersion time increased to 4 weeks, the amount of $\text{log}(|Z|_{10\text{mHz}})$ increased slightly and reached 9.99 $\Omega.\text{cm}^2$, and then with the increase in immersion time to 8 weeks, $\text{log}(|Z|_{10\text{mHz}})$ decreased slightly and reached 9.72 $\Omega.\text{cm}^2$. As the results of $|Z|_{10\text{mHz}}$ for PU coatings showed, the overall resistance during eight weeks of immersion was

very high and almost unchanged. Also, an increasing trend and then a continuation of the decrease in resistance that was observed in epoxy chromate coatings due to self-healing was also observed in PU coatings. Examination of the results related to $-\theta_{100\text{kHz}}$ PU coating, which was presented in Figure 3a and Table 2, showed that this parameter did not significantly decrease during two months of immersion in corrosive solution. Within a specific range, it underwent minor changes. Further study of the changes in $-\theta_{100\text{kHz}}$ showed that the value of this parameter in the two-layer PU coating at the beginning and the interval of 2 to 4 weeks of immersion in corrosive solution, increased from 73 to 79.81 and with increasing immersion time by eight weeks, the variance decreased to 75.26. It seemed that the trend of changes in $-\theta_{100\text{kHz}}$ of this coating was similar to the increasing and then decreasing trend observed in single-layer epoxy chromate coatings, which was also due to the very high barrier resistance of this coating. Over time, even with the penetration of corrosive electrolyte into the substrate, this coating system maintains its protective function with active protection by chromium pigments and does not suffer from severe degradation. As a result, it can be concluded that the corrosion resistance of this coating system against corrosive solution depends on the barrier behavior of the polyurethane coating as well as the actual protection behavior induced in the coating system, which was the active protection of zinc chromate pigments distributed in the epoxy coating.

Table 2: Total impedance values $|Z|_{10mHz}$, phase angle at a maximum frequency ($-\theta_{100kHz}$ (°)), and breakpoint frequency (f_b) resulting from EIS test for two-layer epoxy chromate-polyurethane (PU) coatings at different immersion times.

Sample	$\log (Z _{10mHz}/\Omega . cm^2)$	$-\theta_{100kHz}$ (°)	$\log (f_b/Hz)$
PU2	9.6	73	0.6
PU4	9.99	79.81	0.4
PU8	9.72	75.26	1.0

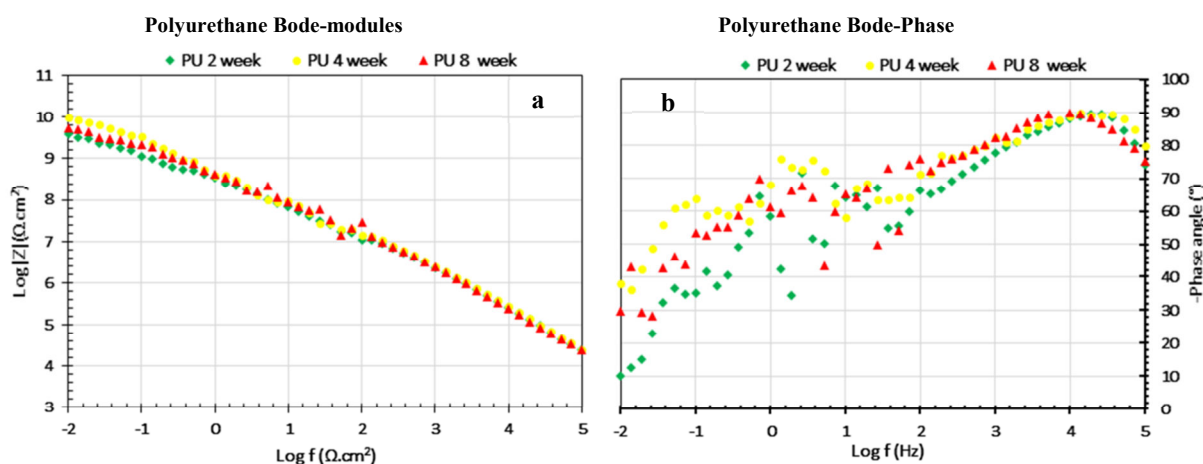


Figure 3: (a) Bode and (b) Phase diagrams for steel specimens with a two-layer epoxy-chromate-polyurethane coating immersed in NaCl solution for 2, 4, and 8 weeks.

In connection with the breakpoint frequency (f_b), since the two-layer coating of epoxy chromate-polyurethane (PU) had very high resistance, it showed a barrier behavior. It means that with decreasing the frequency, its overall resistance increased and no breakpoints were observed in the diagram. Also, due to the very high resistance of this coating (PU), there was a lot of noise in the bode-phase diagram, which made it impossible to use the 45° angle criterion to determine the frequency of the breakpoint. Thus, with increasing the immersion time, the breakpoint frequency decreased from 2 to 4 weeks and increased after up to 8 weeks, which can be attributed to the formation of protective layers within 2 to 4 weeks. Then, the corrosion mechanisms, to some extent, prevailed in the interface, and the breakpoint frequency somewhat increased [9].

3.1.2. Polarization curves

Figure 4 showed the polarization curves of the bare steel substrate and coated substrates with E and PU-E

after eight weeks of immersion in a corrosive saline solution (3.5 wt. % NaCl).

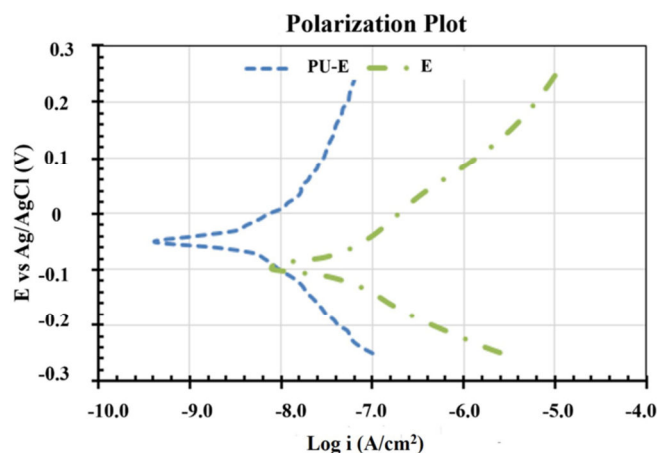
The open-circuit potential (OCP) was considered in terms of corrosion potential (E_{corr}), and the density of corrosion (i_{corr}) was obtained by extrapolation of the linear area of the polarization curve (Tafel) to the E_{corr} diagram. Tafel constants, including anode (β_a) and cathode (β_c) slopes, were measured for anode and cathode areas of polarization curves (in Tafel area), respectively. Also, the corrosion rate (CR) was obtained in millimeters per year (mm/year) according to the following equation (Eq. 1) [10]:

$$CR = 3.27 \times \frac{i_{corr}}{\rho} \times E_w \quad (1)$$

In this equation, i_{corr} , ρ , and E_w are the current density (mA/cm^2), the density of steel ($7.87 g/cm^3$), and the equivalent mass of carbon steel ($27.93 g$), respectively [10]. The parameters obtained from the polarization curves are presented in Table 3.

Table 3: The parameters obtained from the polarization test for the substrate coated with E and PU-E coatings immersed in 3.5 wt. % of NaCl solution.

Samples	E_{corr} (V vs. Ag/AgCl)	i_{corr} (mA/cm ²)	β_a (V/dec)	$-\beta_c$ (V/dec)	C.R (mm/year)
PU-E	-0.05±0.006	$6.31 \times 10^{-7} \pm 0.06 \times 10^{-7}$	0.26±0.013	0.18±0.011	$7.3 \times 10^{-6} \pm 0.04 \times 10^{-6}$
E	-0.95±0.009	$3.16 \times 10^{-6} \pm 0.03 \times 10^{-6}$	0.12±0.009	0.09±0.006	$3.6 \times 10^{-5} \pm 0.08 \times 10^{-5}$

**Figure 4:** PU-E and E coating polarization curves in corrosive saline solution (3.5 wt.% NaCl) after eight weeks.

As it is clear from the results, the corrosion rate of steel samples covered with E and PU was equal to 3.6×10^{-5} and 7.3×10^{-6} mm/year, respectively. To better understand the protective performance of coatings, the corrosion rate of uncoated st37 steel in the same corrosive environment (3.5 wt.% NaCl) was 0.27 mm/year [11, 12]. Comparing the corrosion rate of the noncoated st37 steel with those coated by E and PU-E showed that these coatings significantly reduced the corrosion rate of the steel in corrosive environments and protected it well. Therefore, it can be concluded that with E and PU-E coatings, the life of the steel increased significantly. As can be seen from Figures 2 and 3, and Tables 1 and 2, although the samples coated with E and PU-E had been immersed in the saline corrosive solution for eight weeks, they retain their protective properties well. According to the results of research, the corrosion rate of steel coated with pure epoxy was 0.1705 mm/year [13], which was a very weak protective function for the steel substrate. The reason for this poor performance of the pure epoxy coating against corrosion can be attributed to the fact that this coating protects the steel substrate only through barrier protection. If penetrating paths are created in the coating and the corrosive ions can reach the metal/coating interface, the protective barrier of the coating will be disrupted, and by

forming an electrolyte layer in the interface, the steel will be exposed to the electrolyte followed by intensified corrosion process [13, 14]. But as the results of the PU-E and E coating polarization test showed, even after two months of immersion of the samples in the corrosive solution, the corrosion rate of the steel substrate was still low. The reason for this can be attributed to the active protection combined with the barrier protection of the coatings used in this research. For example, if due to the long-term proximity of the epoxy chromate (E) coating to the corrosive solution, the electrolyte and corrosive ions disrupt the protection of the coating barrier and reach the interface, the chromate-zinc pigments in the electrolyte will decompose. The interface was dissolved and, by producing zinc and chromium cations, protective films are formed in the interface and provided protection for the steel substrate in the presence of corrosive electrolytes. Therefore, the induction of active protection in the E and PU-E coatings used in this research provided long-term durability of the steel substrate against uniform corrosion in corrosive salt environments [15]. Comparing the corrosion life of E and PU-E according to Figure 4 and Table 3 shows that the corrosion rate of steel coated with PU-E was lower than that of the steel coated with E. In addition, the corrosion potential of the PU-E sample had lower negative values

than the E sample. In other words, it was nobler against corrosion, so it can be concluded that the PU-E coating provided better protection than E coating for steel substrate.

E and PU-E coating's contact angle was 53 ± 3 and $82\pm 5^\circ$, respectively, which showed that the two-layer coating surface has more hydrophobic nature, which was in agreement with the EIS and polarization tests. The more hydrophobic nature of the PU-E coating compared to the E coating caused less corrosive agent penetration into the coating surface, resulting in higher impedance of the two-layer coating, as shown in Figures 1 and 2.

3.2. Mechanical properties of the coating

3.2.1. Adhesion test

The adhesion of E and PU coatings to the steel substrate was evaluated by the Pull-off method [16, 17]; their adhesion strength was 3.45 and 2.07 MPa, respectively (Figure 5). Previous studies had reported the adhesion strength of epoxy coatings containing zinc chromate pigments in the range of 5 MPa [18]. They concluded that the chromate pigments in coatings increase the adhesion strength of coatings compared to non-pigmented epoxy coatings [19]. The adhesive strength of the two-layer epoxy-chromate coating had significant decrease compared to the single-layer epoxy chromate coating (40%). This was also consistent with

the results of the high-frequency phase angle at the impedance charts (Tables 1 and 2), because the high-frequency phase angle, as a criterion for the adhesion of the coating to the substrate, was more for single-layer epoxy chromate (E) coating compared to the two-layer epoxy chromate-polyurethane coating (PU-E). Also, the thickness of dry E and PU-E coatings was 43.3 and 134.8 μm , respectively. On the other hand, the decrease in the adhesion strength of PU coatings compared to E coatings can be attributed to the much higher thickness of this coating. Either increasing the coating thickness or the use of multilayer coatings reduces the adhesion strength of the coating.

3.2.2. Hardness and scratch resistance test

scratch or pencil hardness tester in accordance with the ASTM D3363 standard was used to determine the hardness and scratch resistance [20, 21]. The pencil hardness test is a standard method used for many years in the industry to determine the wear resistance of scratches and dents [22]. The hardness measurement of this test was qualitative and used a scale with a range of 6B for the lowest hardness up to 9H for the highest hardness. The results of this test are presented in Table 4 according to which E and PU-E coatings had good hardness and were resistant to pencil scratches with H and F hardness, respectively.

Table 4: Hardness of coatings by scratch or pencil hardness tester.

Sample	degree of hardness	Hardness range
PU-E	F	Resistant
E	H	Resistant

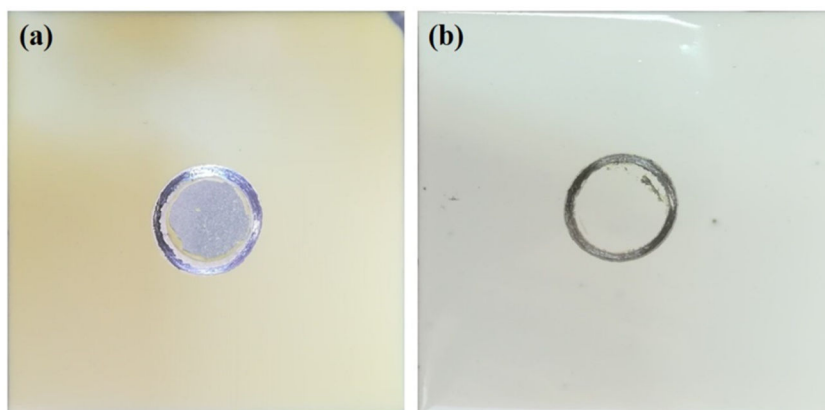


Figure 5: Adhesion test for steel substrates coated with (a) E, and (b) PU-E.

3.2.3. Salt spray test

Salt spraying test, according to ASTM B-117 standard, is a way to check the performance of the coating in corrosive environments [23]. For this purpose, the coated samples with artificial damage are subjected to salt mist created by spraying corrosive saline solution with high humidity in the enclosure of the device. The salt spraying test was a qualitative acceleration corrosion test in which the protective performance of the coating (with or without artificial defect) is determined by the dimensions and distribution of the damaged areas on the surface of the coated sample. Protective performance of the coated sample was evaluated with first signs of discontinuity and separation of the coating [20, 24]. The reason for the separation of the coating from the substrate is attributed to the reduction of the adhesion strength of coating to the substrate. The reduction of the adhesion during the test is also directly related to the volume of salt electrolyte containing corrosive components. It penetrates and corrodes steel in the interface. Corrosion products formed on the samples (created around artificial defects), the presence of blisters covered by the corrosion products, and the blisters distribution are good criteria for comparing the protective performance of the samples [3, 25]. In this study, a steel sample with a PU-E coating was placed in a simulated corrosive salt spray medium for 5 days (120 h). In order to investigate the damaged areas, the coated steel specimens were visually inspected after the salt spraying test. After the mentioned period, no qualitative changes, damaged area, blister/delamination of the coating, or corrosion products were observed on the coated sample, indicating the appropriate protective and active protection of the coating during the test period (Figure 6).



Figure 6: Salt Spray test for steel substrate coated with PU-E within 120 days.

4. Conclusion

In this study, single-layer epoxy-chromate composite coatings and two-layer epoxy-chromate-polyurethane coatings were coated on the metal substrate to increase the corrosion resistance and lifetime of the coating systems. Both coatings retained their protective performance during the immersion period and did not experience a sharp drop in the overall resistance and adhesion of the coating. During different periods of immersion in the saline corrosive solution, the epoxy-polyurethane coating had a total coating resistance and higher barrier protection than the single-layer epoxy coating. Total coating resistance of single-layer and double-layer coatings were 2.95×10^8 and 5.24×10^9 , respectively, and the percentage of resistance reduction after eight weeks for both coatings was 2.8 and 1.25 %, respectively. Due to the high cost spent annually on the maintenance, repair, and inspection of metal surfaces in the marine and power industry, The results of article can reduce these problems by creating coatings with mechanical properties and proper adhesion to steel substrates.

5. References

1. G. H. Koch, M. P. Brongers, N. G. Thompson, Y.P. Virmani, J.H. Payer, Corrosion cost and preventive strategies in the United States, United States. Federal Highway Administration, 2002.
2. A. Krishnamurthy, V. Gadhamshetty, R. Mukherjee, Z. Chen, W. Ren, H. Cheng, N. Koratkar, Passivation of microbial corrosion using a graphene coating, *Carbon*, 56 (2013) 45-49.
3. ISO, Paints and Varnishes-Corrosion Protection of Steel Structures by Protective Paint Systems-Part 2: Classification of Environments, (1998).
4. B. Phull, R. Kain, Corrosion and protection of structures in marine atmospheres, *Str. Mag.*, (2004) 18-20.
5. C. Gerwick, Construction of marine and offshore structures, CRC press 2002.
6. W. I. Hung, J. M. Yeh, K. C. Chang, Y. H. Chang, Advanced anticorrosive coatings prepared from polymer-clay nanocomposite materials, INTECH Open Access Publisher, 2011.
7. J. P. Ault, The use of coatings for corrosion control on

- offshore oil structures, *J. Protect. Coat. Lin.*, 23(2006), 33-42.
8. K. I. Aly, O. Younis, M. H. Mahross, E. A. Orabi, M. Abdel-Hakim, O. Tsutsumi, M.G. Mohamed, M. M. Sayed, Conducting copolymers nanocomposite coatings with aggregation-controlled luminescence and efficient corrosion inhibition properties, *Prog. Org. Coat.*, 135(2019), 525-535.
 9. K. I. Aly, M. G. Mohamed, O. Younis, M. H. Mahross, M. Abdel-Hakim, M.M. Sayed, Salicylaldehyde azine-functionalized polybenzoxazine: Synthesis, characterization, and its nanocomposites as coatings for inhibiting the mild steel corrosion, *Prog. Org. Coat.*, 138(2020), 105385.
 10. M. G. Mohamed, S. W. Kuo, A. Mahdy, I. M. Ghayd, K. I. Aly, Bisbenzylidene cyclopentanone and cyclohexanone-functionalized polybenzoxazine nanocomposites: Synthesis, characterization, and use for corrosion protection on mild steel, *Mater. Today Commun.*, 25(2020), 101418.
 11. Y. Xia, Y. He, C. Chen, Y. Wu, F. Zhong, J. Chen, Co-modification of polydopamine and KH560 on g-C₃N₄ nanosheets for enhancing the corrosion protection property of waterborne epoxy coating, *React. Funct. Polym.*, 146(2020), 104405.
 12. Y. Yao, H. Sun, Y. Zhang, Z. Yin, Corrosion protection of epoxy coatings containing 2-hydroxyphosphonocarboxylic acid doped polyaniline nanofibers, *Prog. Org. Coat.*, 139(2020), 105470.
 13. C. Shi, Y. Shao, Y. Wang, G. Meng, B. Liu, Influence of submicro-sheet zinc phosphate modified by urea-formaldehyde on the corrosion protection of epoxy coating, *Surf. Interfaces*, 18(2020), 100403.
 14. M. Toorani, M. Aliofkhaezrai, M. Mahdavian, R. Naderi, Effective PEO/Silane pretreatment of epoxy coating applied on AZ31B Mg alloy for corrosion protection, *Corros. Sci.*, (2020), 108608.
 15. J. Guo, C. Wang, H. Yu, X. Li, Preparation of a wear-resistant, superhydrophobic SiO₂/silicone-modified polyurethane composite coating through a two-step spraying method, *Prog. Org. Coat.*, 146(2020), 105710.
 16. H. Zhang, C. Su, X. Bu, Y. Zhang, Y. Gao, M. Huang, Laboratory investigation on the properties of polyurethane/unsaturated polyester resin modified bituminous mixture, *Constr. Build. Mater.*, 260(2020), 119865.
 17. S. Li, Z. Liu, L. Hou, Y. Chen, T. Xu, Effect of polyether/polyester polyol ratio on properties of waterborne two-component polyurethane coatings, *Prog. Org. Coat.*, 141(2020), 105545.
 18. Y. Zhou, B. Rossi, Q. Zhou, L. Hihara, A. Dhinojwala, M.D. Foster, Thin plasma-polymerized coatings as a primer with polyurethane topcoat for improved corrosion resistance, *Langmuir*, 36 (2020), 837-843.
 19. Y. Ma, R. Yuling, Y. Dai, J. Zhang, L. Zhu, Aluminium-zinc hot-plated steel plate having excellent weather resistance, corrosion resistance and alkali resistance, and manufacturing method and surface treating agent therefor, Google Patents, 2020.
 20. S. K. Dhoke, A. Khanna, Electrochemical impedance spectroscopy (EIS) study of nano-alumina modified alkyd based waterborne coatings, *Prog. Org. Coat.*, 74(2012), 92-99.
 21. B. M. Yoo, H. J. Shin, H. W. Yoon, H. B. Park, Graphene and graphene oxide and their uses in barrier polymers, *J. Appl. Poly. Sci.*, 131(2014), 22-36.
 22. Y. Dong, Fillers, Wiley Encyclopedia of Composites, (2011), 1-17.
 23. R. Twite, G.P. Bierwagen, Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys, *Prog. Org. Coat.*, 33(1998), 91-100.
 24. B. Ramezanzadeh, M. Attar, Studying the corrosion resistance and hydrolytic degradation of an epoxy coating containing ZnO nanoparticles, *Mater. Chem. Phys.*, 130(2011), 1208-1219.
 25. A. Bastos, M. Ferreira, A. Simoes, Comparative electrochemical studies of zinc chromate and zinc phosphate as corrosion inhibitors for zinc, *Prog. Org. Coat.*, 52(2005), 339-350.
 26. A. Amirudin, D. Thierry, Application of electrochemical impedance spectroscopy to study efficiency of anticorrosive pigments in epoxy-polyamide resin, *British Corr. J.*, 30(1995) 128-134.
 27. P. de Lima-Neto, A.P. de Araújo, W.S. Araújo, A.N. Correia, Study of the anticorrosive behaviour of epoxy binders containing non-toxic inorganic corrosion inhibitor pigments, *Prog. Org. Coat.*, 62(2008), 344-350.
 28. J. He, V.J. Gelling, D.E. Tallman, G.P. Bierwagen, A scanning vibrating electrode study of chromated-epoxy primer on steel and aluminum, *J. Electrochem. Soc.*, 147(2000), 3661.
 29. Y. Zuo, R. Pang, W. Li, J. Xiong, Y. Tang, The evaluation of coating performance by the variations of phase angles in middle and high frequency domains of EIS, *Corr. Sci.*, 50(2008), 3322-3328.
 30. M. Mahdavian, M. Attar, Another approach in analysis of paint coatings with EIS measurement: phase angle at high frequencies, *Corros. Sci.*, 48(2006), 4152-4157.
 31. M. Izadi, T. Shahrabi, B. Ramezanzadeh, Active corrosion protection performance of an epoxy coating applied on the mild steel modified with an eco-friendly sol-gel film impregnated with green corrosion inhibitor loaded nanocontainers, *Appl. Surf. Sci.*, 440(2018), 491-505.
 32. I. Mohammadi, M. Izadi, T. Shahrabi, D. Fathi, A. Fateh, Enhanced epoxy coating based on cerium loaded Na-montmorillonite as active anti-corrosive nanoreservoirs for corrosion protection of mild steel: synthesis, characterization, and electrochemical behavior, *Prog. Org. Coat.*, 131(2019), 119-130.
 33. R. Naderi, B. Ramezanzadeh, Promotion of the active/barrier protection function of epoxy ester coating/steel system utilizing differently synthesized hybrid pigment through zinc acetylacetonate tailored with green inhibitor molecules, *Prog. Org. Coat.*, 138(2020), 105380.
 34. M. T. Majd, T. Shahrabi, B. Ramezanzadeh, The role of

- neodymium based thin film on the epoxy/steel interfacial adhesion and corrosion protection promotion, *Appl. Surf. Sci.*, 464(2019), 516-533.
35. A. Ghazi, E. Ghasemi, M. Mahdavian, B. Ramezanzadeh, M. Rostami, The application of benzimidazole and zinc cations intercalated sodium montmorillonite as smart ion exchange inhibiting pigments in the epoxy ester coating, *Corros. Sci.*, 94(2015), 207-217.
 36. M. Rostami, S. Rasouli, B. Ramezanzadeh, A. Askari, Electrochemical investigation of the properties of Co doped ZnO nanoparticle as a corrosion inhibitive pigment for modifying corrosion resistance of the epoxy coating, *Corros. Sci.*, 88(2014), 387-399.
 37. J. R. Scully, Electrochemical impedance of organic-coated steel: correlation of impedance parameters with long-term coating deterioration, *J. Electrochem. Soc.*, 136(1989), 979-983.
 38. W. Li, Z. Fan, X. Li, B. Jiang, F. Yan, Z. Zhang, X. Wang, Improved anti-corrosion performance of epoxy zinc rich coating on rusted steel surface with aluminum triphosphate as rust converter, *Prog. Org. Coat.*, 135(2019), 483-489.
 39. H. Yang, Q. Mo, W. Li, F. Gu, Preparation and properties of self-healing and self-lubricating epoxy coatings with polyurethane microcapsules containing Bifunctional linseed oil, *Polymers*, 11(2019), 1578.
 40. I. Šoić, S. Martinez, M. Dubravić, Gel-Electrolyte EIS setup used for probing of IR Dried/Cured industrial coatings, *Prog. Org. Coat.*, 137(2019), 105331.
 41. Y. Singhababu, B. Sivakumar, J. Singh, H. Bapari, A. Pramanick, R.K. Sahu, Efficient anti-corrosive coating of cold-rolled steel in a seawater environment using an oil-based graphene oxide ink, *Nanoscale*, 7(2015), 8035-8047.
 42. M. Heydarpour, A. Zarrabi, M. Attar, B. Ramezanzadeh, Studying the corrosion protection properties of an epoxy coating containing different mixtures of strontium aluminum polyphosphate (SAPP) and zinc aluminum phosphate (ZPA) pigments, *Prog. Org. Coat.*, 77(2014), 160-167.
 43. C. Tassin, F. Laroudie, M. Pons, L. Lelait, Improvement of the wear resistance of 316L stainless steel by laser surface alloying, *Surf. Coat. Technol.*, 80(1996), 207-210.
 44. S. Pourhashem, M.R. Vaezi, A. Rashidi, Investigating the effect of SiO₂-graphene oxide hybrid as inorganic nanofiller on corrosion protection properties of epoxy coatings, *Surf. Coat. Technol.*, 311(2017), 282-294.
 45. M. T. Majd, M. Davoudi, M. Ramezanzadeh, E. Ghasemi, B. Ramezanzadeh, M. Mahdavian, Construction of a smart active/barrier anti-corrosion system based on epoxy-ester/zinc intercalated kaolin nanocontainer for steel substrate, *Constr. Build. Mater.*, 247(2020), 118555.
 46. S. B. Ulaeto, R. Rajan, J.K. Pancrecius, T. Rajan, B. Pai, Developments in smart anticorrosive coatings with multifunctional characteristics, *Prog. Org. Coat.*, 111(2017), 294-314.
 47. Y. Tsuji, Y. Kitamura, M. Someya, T. Takano, M. Yaginuma, K. Nakanishi, K. Yoshizawa, Adhesion of epoxy resin with hexagonal boron nitride and graphite, *ACS Omega*, 4(2019), 4491-4504.
 48. B. Fathi, M. Foruzanmehr, S. Elkoun, M. Robert, Novel approach for silane treatment of flax fiber to improve the interfacial adhesion in flax/bio epoxy composites, *J. Compos. Mater.*, 53(2019), 2229-2238.
 49. J. Bajat, O. Dedić, Adhesion and corrosion resistance of epoxy primers used in the automotive industry, *J. Adhes. Sci. Technol.*, 21(2007), 819-831.
 50. D. Quan, B. Deegan, R. Alderliesten, C. Dransfeld, N. Murphy, A. Ivanković, R. Benedictus, The influence of interlayer/epoxy adhesion on the mode-I and mode-II fracture response of carbon fibre/epoxy composites interleaved with thermoplastic veils, *Mater. Des.*, 36(2020), 108781.
 51. Ł. Byczyński, M. Dutkiewicz, R. Januszewski, P. Wrona, B. Pilch-Pitera, Epoxy coatings with increased hydrophobicity modified by isocyanurate containing siloxane, *Mater. Today Commun.*, 24(2020), 101001.
 52. M. Ridzuan, M.A. Majid, A. Khasri, E. Gan, Z. Razlan, S. Syahrullail, Effect of pineapple leaf (PALF), napier, and hemp fibres as filler on the scratch resistance of epoxy composites, *J. Mater. Res. Technol.*, 8(2019), 5384-5395.
 53. N. N. Taheri, B. Ramezanzadeh, M. Mahdavian, Application of layer-by-layer assembled graphene oxide nanosheets/polyaniline/zinc cations for construction of an effective epoxy coating anti-corrosion system, *J. Alloys. Compd.*, 800(2019), 532-549.
 54. Y. He, C. Chen, G. Xiao, F. Zhong, Y. Wu, Z. He, Improved corrosion protection of waterborne epoxy/graphene coating by combining non-covalent and covalent bonds, *React. Funct. Polym.*, 137(2019), 104-115.
 55. S. Ralkhal, B. Ramezanzadeh, T. Shahrabi, Studying dual active/barrier and self-healing reinforcing effects of the Neodymium (III)-Benzimidazole hybrid complex in the epoxy coating/mild steel system, *J. Alloys. Compd.*, 790(2019), 141-155.

How to cite this article:

M. Mirzaee, M. Rezaei Abadchi, A. Fateh, A. Zolriasatein, Investigation of Corrosion Properties of Modified Epoxy and Polyurethane Organic Coating on Steel Substrate. *Prog. Color Colorants Coat.*, 15 (2022), 25-36.

