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Electrochemical study of the polymer behavior of an epoxy coating on carbon steel in 3% NaCl using polarization curves and SIE

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Abstract

In this paper, authors studied the impact of carbon steel coatings by functional epoxy resin TGEDA. The thickness of the deposited film on the substrate is estimated at 170 ± 10 µm. Firstly, to evaluate this impact of coating, the authors used two electrochemical methods: the stationary method using the polarization curve, the transient method based on the electrochemical impedance spectroscopy, and scanning electronic microscopy (SEM) were used in this study. The obtained results of this study showed that the corrosion current (i_{corr}) is equal to 0, 07 µcm^{-2} and the polarization resistance (R_p) is equal to KΩ.cm^2.This shows that the effect of the investigated coating of carbon steel by the resin is more effective in 3 % NaCl compared to the uncoated one in the same medium. Subsequently, we conducted a new formulation by adding a series of inorganic fillers in the matrix of protection TGEDA/hardener (MDA), TEDA/MDA/load. The nature of the charges was 5% of zinc, 5% of trisodium phosphate and their mixtures. The stationary and transient electrochemical studies are very interest in according to their stationary efficiency 90%, 94%, 99, 6 % and 99,7% and the transient 93%, 95 %, 99,5 % and 99,7 %concerning respectively the formulations MP_1 (TGEDA/ MDA), MP_2 (TGEDA/ MDA/ Zinc), MP_3 (TGEDA/ MDA/ trisodium phosphate) and MP_4 (TGEDA/MDA/Zinc/ trisodium phosphate).

Keywords: C-steel; coating; 3% NaCl; formulation; epoxy resin; hardener; polarization curve; electrochemical impedance

1. Introduction

Today, steel is a material used in our lives due to its various applications in various competitive fields: marine, nuclear energy, fossil fuel power stations, transportation, chemical industry, production and oil refining, pipelines, mines and construction, etc. [1-3].

However, carbon steel is subject to corrosion problems, given its use in areas that are not inert, which means that its protection by different conventional methods, namely protection inhibitors based on organic, mineral, and micellar [4-7].The best way to protect metals against corrosion is to apply protective coatings [8, 9]using organic polymers.

The way those methods protect metals by acting as a physical barrier between a corrosive electrolyte and the metallic substrate. The coating parameters are the number of pores, the ionic resistance of the coating against the diffusion of the electrolyte, and the crosslink density of the coating, which may affect the stationary as well as the transient efficiencies [10].

The coating method by the cross-linked epoxy resins with hardening amines agents remains a very effective approach because of its good adhesion, good resistance to acid / alkali and its high crosslinked density, which is due to hydrophilic chemical groups present in the hardened resin structure [11-16].

Furthermore, many coating systems based on conventional epoxy resin (DGEBA) were not tested in increased corrosive environments. This allowed us to test our formulations based on epoxy resin synthesized and optimized in standard or formulated forms with an aim to develop an appropriate coating in industrial and natural corrosive environments such as our case. The choice of charges was carefully chosen by substituting toxic zinc chromate with a green environmental-friend additive, which is zinc phosphate. The toxicity of this compound is 50 times lower than that of chromates [17-21].

In this study, corrosion performance for four formulations MP_1, MP_2, MP_3 and MP_4 on carbon steel in 3% NaCl solution were characterized by different methods such as polarization curve, the electrochemical impedance spectroscopy and scanning electronic microscopy were used in this study.

2. Experimental

2.1. Materials and methods.

All basic chemicals were purchased from Aldrich and then stored at a temperature between 4 and 7 °C, and used without any further purification. Our formulations are made from matrix constituted of TGEDA, crosslinked with methylene dianiline (MDA), on the one hand, and by inorganic charges on the other hand. The formulations contain powder-like charges in the form of very fine particles of zinc and /or trisodium phosphate in order to improve the anticorrosion properties.

2.1. 1. Synthesis of TGEDA.

TGEDA is obtained by condensing the epichlorohydrin and 4,4'-ethylene dianiline in the presence of triethylamine (Figure 1) [22-23].

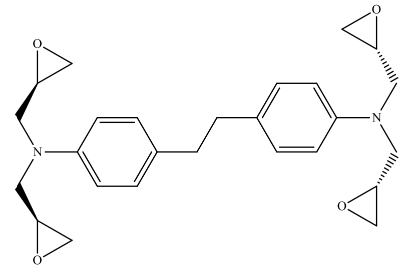


Figure 1: Chemical structure of TGEDA.

2.2. Hardening of TGEDA

Epoxy resins can be processed into thermally cured polymers through many chemical compounds acting as bridging agent or hardeners during the implementation [22]. Among the curing polyepoxide systems, there are two broad classes: the amines and acid anhydrides. We limited ourselves to one hardener class: aromatic diamine. According to their chemical structure, the aromatic compounds provide a very good thermal stability and good mechanical properties to the resin. Therefore, they are often used for high-tech applications.

The hardener that we used is methylene dianiline (MDA) whose chemical formula is as follows (Figure 2) [24]:

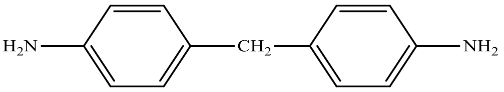


Figure 2: Chemical structures of 4, 4'-Methylene Dianiline (MDA) using as curing epoxy resins.

The reaction between epoxide and diamine is a bi-molecular reaction of addition of the primary amine functions on the epoxide cycles by the opening of oxirane cycles (Figure 3). Polymer networks are formed from functional precursors by reactions between their functional groups resulting in bond formation. The crosslinked branched structures are generally formed by this method. The system consisting of a tetra functional epoxy and a bi-functional diamine remains a typical example. Primary amine sites in this system act as chain extenders while secondary amines produce branches (Figures 4).

The action 4, 4'-ethylene dianiline on the epoxide is described by the following reaction [25-26]:

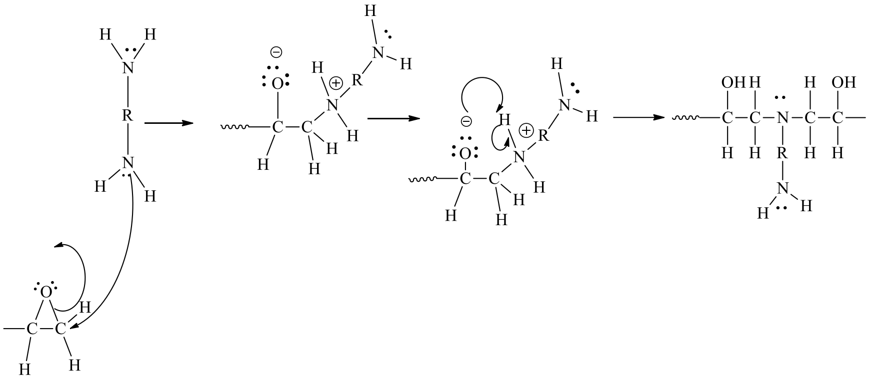


Figure 3: The proposed mechanism for the reaction of an epoxy resin and a primary diamine as a hardener.

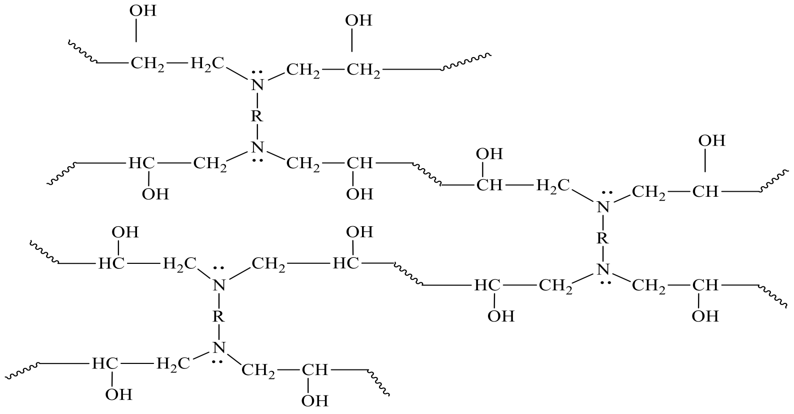


Figure 4: Structure of idealized epoxy resins and primary diamines as hardening agent.

Mixing the epoxy resin with the hardener prior to crosslinking is performed differently depending on the used hardening agent. With the methylene dianiline (MDA), the protocol that is adopted by Levan[26], methylene dianiline crystallized at room temperature is placed in an oven at 120 °C (a temperature above its melting point) while the resin is carried out at 60 °C. Once melted, the curing agent (MDA) is mixed with the epoxy resin to provide a single fluid phase being then at 70 °C.

In order to harden the TGEDA by the MDA, the epoxy equivalent (EE) of the TGEDA must be 109 g/eq and the amine equivalent (EA) of the MDA must be 49, 56 g/eq. The amount of the required MDA then for the hardening of 100g TGEDA is 45,46g.

2.2.1. Preparation of epoxy resin synthesized formulations

In our study, we proposed new formulations applied on carbon steel which consists of an epoxy resin TGEDA synthesized with stoichiometric amounts of the hardening agent (MDA), and two charges the first of which is zinc-based powder and the second is trisodium phosphate (Na_3PO_4) in the presence of epichlorohydrin as a solvent.

The different formulations were homogenized in a beaker by mechanical stirring to evaporate the solvent existing in our samples before each experiment on carbon steel (Table 1). The latter has the following composition:

Table 1: Chemical composition of carbon steel substrate.

C	Mn	Si	Al	Cr	Mo	Ni	Cu	Co	V	Fe
0.11	0.47	0.24	0.03	0.12	0.02	0.1	0.14	<0.001	<0.003	Balance

The formulations were applied to carbon steel using a stick that deposits a thickness that varies between 170 ± 10 µm. We deposite the coati substrats in an oven for an over night at a temperature of 70 ° C.

2.3 Electrochemical Techniques

2.3.1 Electrochemical cell

The experimental device used for the electrochemical study of the behavior of carbon steel vis-a-vis the corrosive medium consists of a test cell and a device for the electrochemical characteristics (Figure 5).

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the carbon steel specimen as working electrode (WE), platinum mesh as counter electrode (CE), and (Ag/AgCl) (3M KCl) is used as the reference electrode.

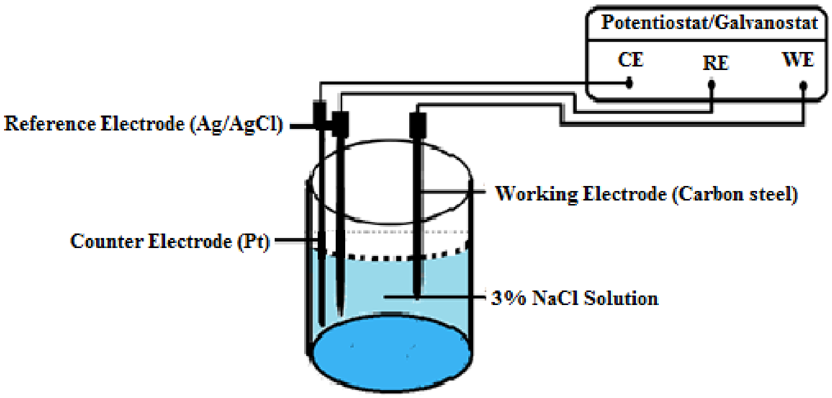


Figure 5: Plan of the experimental setup

2.3.2 Polarization measurements

The polarization curves plot was carried out using a potentiostat / galvanostat (PGZ100) controlled by a software application "master VoltaLab 4.0. Before each manipulation, the electrode is maintained immersed for 30 min to the corrosion potential to soften the electrochemical system into a stationary state. These polarization curves (i=f(E)) are obtained in a potentiodynamic mode with a potential scanning speed equal to of 1 mV/s, departing from the corrosion potential E_{corr} and reaching more and more negative potentials, and then from the E_{corr} to more and more positive potentials. The value of the efficiency of protection is determined by the equation (1):

$$\eta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

where i^0_{corr} and i_{corr} are respectively the current densities of the corrosion of the steel tempered in the corrosive medium with and without a coating of various formulations, which are obtained by the extrapolation of cathodic and anodic Tafel right to the corrosion potential.

In this work, the determination of electrochemical parameters (E_{corr}, i_{corr}, b_a and b_c) from the polarization curves is made by a nonlinear regression by using the software "Origin 6.0" according to Stern-Geary equation [27]:

$$i = i_c + i_a$$

$$i = i_{corr} \times \left\{ \exp\left[b_a \times \left(E - E_{corr} \right) - \exp\left[b_c \times \left(E - E_{corr} \right) \right] \right] \right\} \quad (2)$$

where i_{corr} is the corrosion current density (A cm^{-2}), b_a and b_c are respectively the Tafel constant of anodic and cathodic reactions (V^{-1}). These constants are related to the slope of β (V dec^{-1}) on a logarithmic scale by:

$$\beta = \frac{\ln(10)}{b} = \frac{2,303}{b} \quad (3)$$

However, for this calculation, the applied potential range was limited to ± 100 mV / Ag / AgCl. Besides, a systematic difference was observed for both anodic and cathodic branches.

2.3.3 Spectroscopy of electrochemical impedance (SIE) measurements

Electrochemical impedance spectroscopy measurements were performed with low amplitudes of 10 mV signals in a frequency ranging from 100 kHz to 0.1 Hz, to 10 points per decade.

The impedance data were then analyzed by an equivalent electric circuit using the simulation program bouckamp [28]. The efficiency of protection is evaluated from R_p which is obtained from the diameter of the semi-circle in the Nyquist representation that was found by using equation (4):

$$\eta = \frac{R_p - R_p^0}{R_p} \times 100 \quad (4)$$

Where R_p and R_p^0 are respectively the resistance with and without a coating

2.4. Scanning electron microscopy (SEM)

The observation and examination of these new formulations applied on carbon steel were performed on a scanning electron microscope of JEOL-JSM-5500 type. The analysis is performed with an acceleration voltage of 0.5-30 kV.

3. Results and discussion

3.1. The polarization curves

Figure 6 includes the potentiodynamic polarization curves that describe the carbon steel protective effect in the corrosive 3% NaCl solution by the pair (TGEDA/MDA) at different formulations.

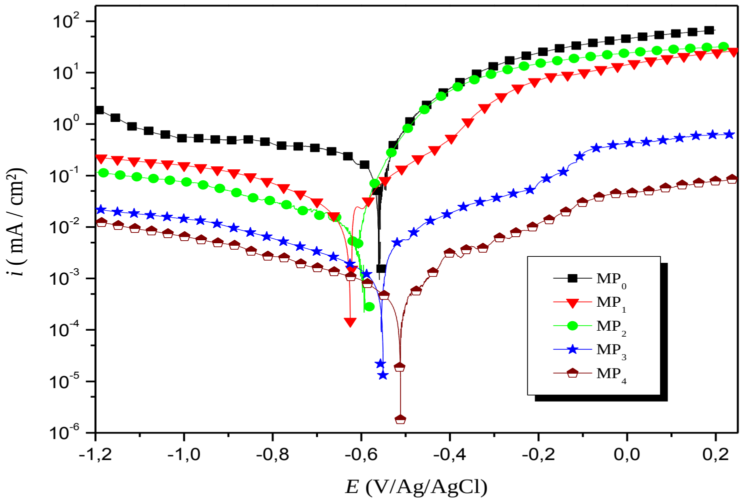


Figure 6: Carbon steel polarization curves in 3% NaCl at different matrices after 30 min immersion at 298 K.

The corrosion protection settings for the four formulations based on TGEDA/MDA from the polarization curve measurements at 298 K in 3% NaCl are summarized in Table 2.

Table 2 summarizes the different electrochemical parameters associated with carbon steel polarization curves in 3% NaCl at different matrices.

Plates	E_{corr} (mV/Ag/AgCl)	i_{corr} (µA/cm²)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	η%
MP_0	-559	280	121	121	-
MP_1	-624	28	460	200	90
MP_2	-593	17	54	209	94
MP_3	-550	1	287	60	99.6
MP_4	-510	0.07	230	53	99.7

The protection mechanism is studied according to the protective matrices (MP_0, MP_1, MP_2, MP_3 and MP_4), which are constituted by the standard polymeric epoxy resin (TGEDA), the hardener (MDA) and both zinc and inorganic charges trisodium phosphate as additive. The interpretation of the results according to the constitution of the matrix is given as follows and regrouped in figures 7, 8 and 9.

a) Coating by matrix MP_0

In the matrix MP_0 as a witness which is constituted without a substrate coating (carbon steel), anions Cl^- and OH^- from the corrosive environment directly attack the substrate which indicates a direct and increased corrosion.

b) Coating by matrix MP_1

Through the MP_1 matrix (TGEDA / MDA), we expect that there is a relatively large diffusion of chloride ions and hydroxide through the protective film which may present micropores, while inducing a primary corrosion formulated as $i_{corr} = 28\ \mu A/cm^2$ and η = 90 %. This would lead to an acceleration of the anodic dissolution of the metal (Figure 7) [29].

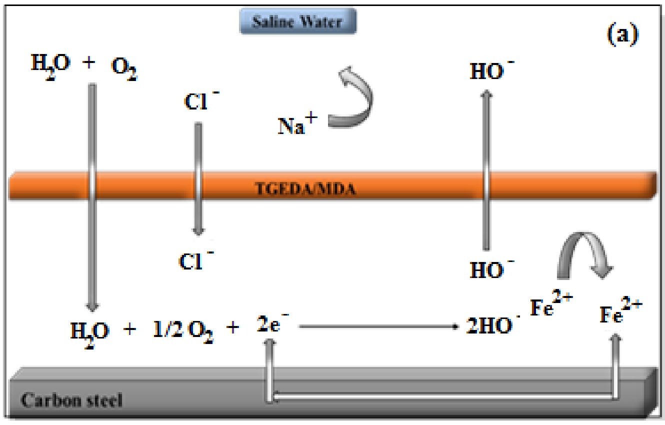


Figure 7: Mechanism proposed for the protective matrix MP_1 (TGEDA/MDA) between the metal substrate and the film after the immersion in 3% NaCl.

c) Coating by matrix MP_2

When applying the matrix MP_2 (TGEDA/MDA/Zn) the diffusion of corrosive species (Cl^- and OH^-)is slowed by the coating of passivation [30] from the couple Zn/Zn^{2+} according to equations 5 and 6 (Figure 8).

In this case, the corrosion electrochemical parameters are $i_{corr} = 17\ \mu A/cm^2$ and η = 94 %.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \longrightarrow ZnO + H_2O \quad (5)$$

$$Zn^{2+} + 2Cl^- \longrightarrow Zn(Cl)_2 \quad (6)$$

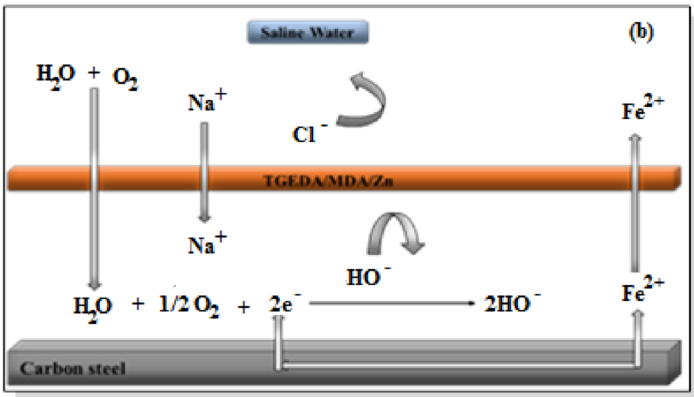


Figure 8: mechanism of formation of the passivation coating at the interface between the metal substrate and the film after the immersion in 3% NaCl.

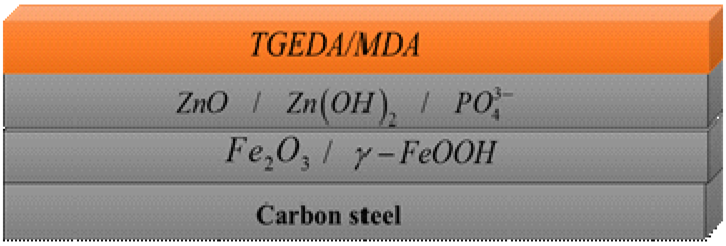
d) Coating by matrix MP_3

However, the coating of the substrate by the matrix MP_3 ($TGEDA/MDA/Na_3PO_4$) gives the following corrosion parameters $i_{corr} = 1\ \mu A/cm^2$ and η = 99, 6 %. This could be due to the inhibiting character of the phosphorus present in the molecule of trisodium phosphate (Na^{2+}, PO_4^{3-}) [31]. Indeed, there would be a competition of the ion PO_4^{3-}

and the corrosion species (Cl^- and OH^-), which minimize the degradation of the substrate based on the carbon steel.

e) Coating by the matrix MP_4

In the end, the application of the matrix allowed us to have the most important electrochemical parameters namely i_{corr} = 0, 07 µA/cm^2 and η = 99, 7%. This is explained by a synergistic effect provided by the passivation layer [31-34] issued from (Zn/Zn^{2+}) and the inhibitory nature of Na_3PO_4 (Figure 9).



(c)

Figure 9: Diagram of the passivation coating induced by the presence of zinc phosphate pigments [30].

The resulting coating could be explained by electrochemical reactions at the level of metal surface according to the mechanism of the dissolution/precipitation of phosphates that cause a reduction in oxygen eletrons (eq.7) helping to reduce the degradation of the coating [35].

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad (7)$$

3.2. Electrochemical impedance spectroscopy measurements

To confirm the results obtained by potentiodynamic polarization curves and to study the coating mechanism in more details, we achieved the electrochemical impedance spectroscopy.

The results of this method are shown as Nyquist plots. These carbon steel impedance diagrams which are immersed for 30 minutes before each measurement in an open circuit in the corrosive solution 3% NaCl vis-a-vis all matrices (MP_0, MP_1, MP_2, MP_3 and MP_4) are grouped in Figure 10.

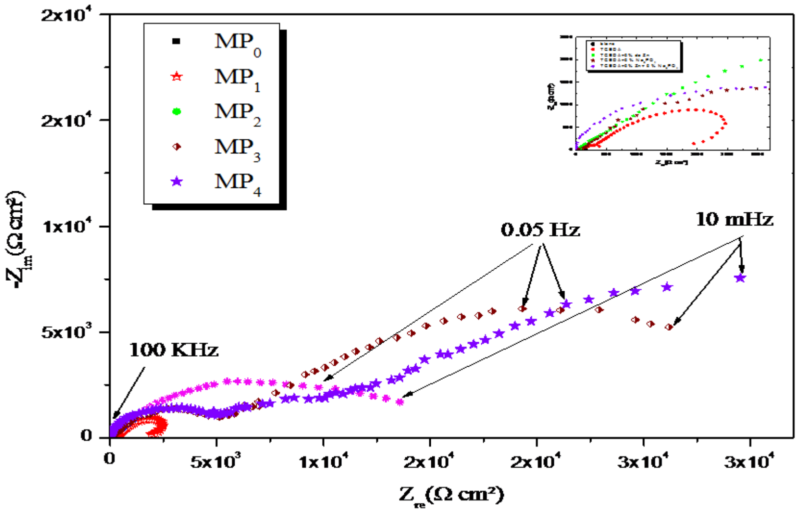


Figure 10: Electrochemical impedance diagrams with open circuit after 30 min of immersion for carbon steel in 3% NaCl in the presence of matrices (MP_0, MP_1, MP_2, MP_3 and MP_4) (Transition Method) at 298 K.

The analysis of the different diagrams (D_0, D_1, D_2, D_3 and D_4)corresponding respectively to the protective matrices (MP_0, MP_1, MP_2, MP_3 and MP_4) shows that the latter are formed by two capacitive loops: one with high frequency (HF) assigned to the film effect and the other with low frequency (LF) which is generally attributed to the charge

transfer process. This is due to the phenomenon of diffusion. Indeed, the larger the diameter of semicircle longer increases, the better will be the corrosion resistance of the protective film [36].
This study confirms the results obtained by the stationary method.
For the electrochemical impedance spectroscopy results, we based our study on the equivalent circuit established in figure 11 which we chose to reasonably adapt to the experimental results. This circuit is composed of: R_s which is the resistance of the electrolyte (Ω.cm²) ; R_{pf} which is the resistance of the coating pores (Ω.cm²) having a certain ionic strength ; R_{pf} which corresponds to the diameter of the first semi-circle at high frequencies of the diagram Nyquist; R_{ct} which is the charge transfer resistance (Ω.cm²) ; C_f which is the di-electric capacity of the coating film (F/m) ; and C_{dl} which is the double layer capacity (capacity of polarization) of the substrate (F/m).

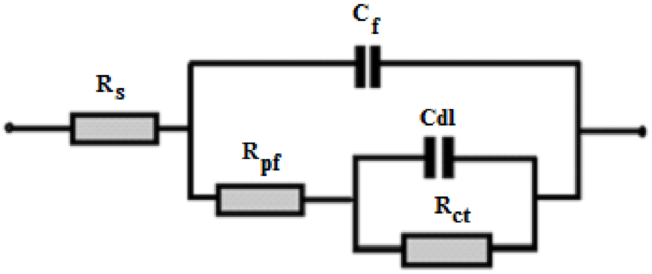


Figure 11: Equivalent circuit provided for the adjustment of dies for spectra of impedance obtained in the presence of different matrices for carbon steel in 3% NaCl.

The values of electrochemical impedance and the protective efficiency résulting from each matrice of protection (MP_0, MP_1, MP_2, MP_3 and MP_4) are summarized in Table 3.

Table 3 summarizes the various electrochemical parameters obtained from the impedance diagrams.

(MP)	R_s (Ω.cm²)	C_{cf} (µF/cm²)	R_{pf} (Ω.cm²)	C_{dl} (µF/m²)	R_{ct} (Ω.cm²)	R_p (Ω.cm²)	η %
MP_0	10	201	175	-	-	165	-
MP_1	47	150	450	82	2200	2603	93
MP_2	48	3	9847	50	7265	17064	95
MP_3	161	5	7183	19	27905	35026	99.5
MP_4	186	8	5520	25	50189	55625	99.7

This table shows that the values of the polarization resistance (R_p) for the four coating matrices are evaluated between 10^3 and 10^4 Ω.cm². This confirms the results of parameters issued from the potentiodynamic polarization curves.

Table 4 summarizes the results of stationary and transient method.

	Polarization curves		Electrochemical impedance spectroscopy	
	i_{corr} (µA/cm²)	η %	R_p (Ω.cm²)	η %
MP_0	280	-	165	-
MP_1	28	90	2603	93
MP_2	17	94	17064	95
MP_3	1	99.6	35026	99.5
MP_4	0.07	99.7	55625	99.7

In fact, the behavior correlates with a very small barrier effect issued from the existence of pores and defects in the coating and / or a poor adhesion between the coating and the metal substrate. The absence of adhesion of non-pigmented coatings are suggested by the resistance of transfer of low obtained charge, and the rapid formation of bubbles on the whole coating surface, where a significant corrosion occurs [37].

On this basis, the largest semi-circle in the Nyquist diagram of MP_4 coating system indicates a better corrosion resistance (see table 4), which can be explained by the presence of the ZP responsible for higher corrosion resistance [38-40].

3.3. Observations of Surface condition by SEM.

To confirm the results obtained by the electrochemical measures for the four matrices without (MP_0), with standard coating (MP_1) and loaded (MP_2 and MP_4) by zinc (Zn) and zinc phosphate (ZP), we used as a means of analysis the coating surface on carbon steel in 3% NaCl after the immersion for 48 hours at 298 K.

Figure 12 shows the SEM morphologies of the state of carbon steel surface immersed in 3% NaCl for 48 h at 298 K for four samples with and without coating.

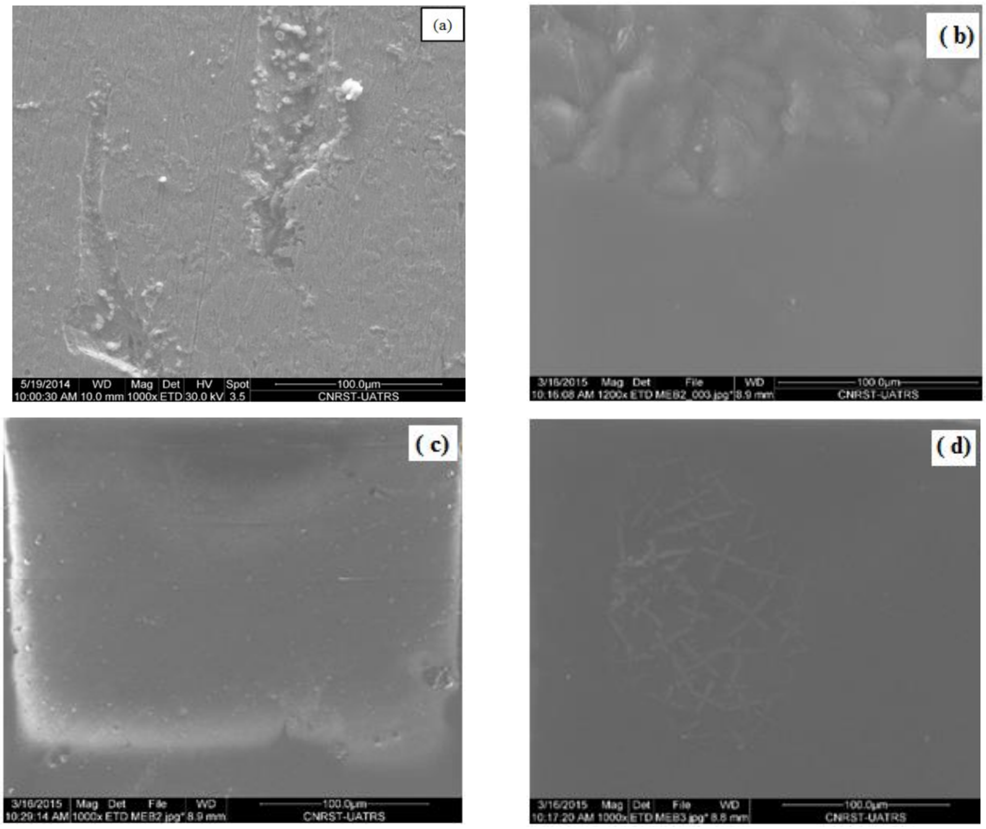


Figure 12: SEM images for the four samples after the immersion for 48 hours in 3% NaCl solution.

a) Coating matrix by the MP_0

The SEM observations clearly show the difference between the four surfaces. In the matrix as a witness 12 (a) constituting without substrate coating (bare carbon steel) shows the damaged area because of the direct attack of the aggressive 3% NaCl solution which greatly impedes the localized corrosion induced by chloride. As we can see from the micrograph of carbon steel surface, it contains deep pits and stains.

b) Coating matrix by the MP_1

The standard protective matrix MP_1 (TGEDA / MDA) submerged during the same interval of time in a 3% NaCl solution. As shown in figure 12 (b), we expect that there is a relatively large spread of electrolytes (chloride ions) through the protective film which may present micropores / defects while inducing a primary corrosion.

c) Coating by the matrix MP_2

In addition, the SEM micrography during the application of the MP_2 matrix (TGEDA / MDA / Zn), we observed in the film surface of the coating some white spots considered as corrosion products according to the literature and this shows that it is concerned with the zinc oxide layer which is necessary for the protection of passivation of metals issued from the couple Zn/Zn^{2+}according to equations 5 and 6 (12 c).

This can be explained by a synergistic effect provided by the coating of passivation issued (Zn/Zn^{2+}).

d) Coating matrix by the MP_3

The coating surface morphology loaded by zinc phosphating (MP_4) was found to be homogeneous, well cristalized and smooth, as it is captured by the image with SEM in figure (12 d). This provides an explanation for the coating which provides an excellent barrier against the penetration of the electrolyte.

Conclusions

In this study we carried out the protection of the carbon steel by the coating method issued from the formulations which are based on a standard oxide polymer (MP_1) and a zinc inorganic filler (MP_2) on the one hand, and an additive Na_3PO_4 added in the matrices (MP_3 and MP_4) on the other hand. This was done in order to decrease the corrosive effect of the medium on the substrate (usually steel).

The main results are :

- The obtained electrochemical results namely the polarization curves resulted by electrochemical parameters (E_{corr} and i_{corr}) and those of the electrochemical impedance spectroscopy (R_{ct}, R_p, R_s, C_f and R_{pf}) are corresponding to each other.
- The corrosion protective effect of the formulated matrix MP_4 gave us the best results.
- The SEM observation shows that the surface of the matrix based on a polymer loaded with oxide zinc phosphate deposited on carbon steel completely protected is due to the formation of a protective layer which limits the penetration of electrolyte through the protective film.

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