

Electrochemical impedance spectroscopy (SIE) evaluation of the effect of immersion time of the protective matrix based on a polymer Tetra Glycidyl of Ethylene Dianiline (TGEDA) on carbon steel in 3% NaCl

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Abstract: In this work, we studied the impact on carbon steel coatings by Tetrafunctional epoxy resin TetraGlycidyl of Ethylene Dianiline (TGEDA) whose thickness of the deposited film on the substrate is estimated by 170 ± 10 microns. To better understand the coating degradation mechanisms, we evaluated the impact of immersion time on the protective matrix by electrochemical impedance spectroscopy (EIS), and we have studied the impact of coated carbon steel with a formulation of Tetra Glycidyl of Ethylene Dianiline (TGEDA) in the presence of 5% of Zinc and 5% of Trisodium Phosphate (Na_3PO_4) in 3% NaCl. The experimental results obtained by the EIS method of carbon steel gave the polarization resistance (R_p) from the formulation TGEDA / MDA / (Methylene Dianiline) / Na_3PO_4 (5%) / Zinc (5%) equal to $68149 \Omega \text{ cm}^2$ and $5385 \Omega \cdot \text{cm}^2$ in a 3% NaCl for an immersion time equal to 1 hour and 12 hours. the effectiveness is equal to 99.7% and 97.86%.

Keywords: Carbon steel, coating, 3% NaCl medium, formulation, epoxy resin, immersion time and electrochemical impedance spectroscopy.

Introduction :

Corrosion is a phenomenon commonly observed in metallic structures, and particularly the carbon steel, which is currently the most widely used metal in the world [1]. Though many methods of protection against corrosion for carbon steel have been studied, the most commonly used method of protection against steel corrosion is the organic protective coating, inorganic or metallic coatings [2].

The organic coating is the most used method of metal bodies protection from atmospheric corrosion. The paint film acts as a physical barrier between corrosive electrolyte and carbon steel substrate. However, it is well known that the coating is permeable to water, oxygen and corrosive ions which are presented in the corrosive electrolyte. Moreover, using organic coatings, the spread of corrosive products will be prevented at the initial sites of electrolyte permeation into the metal surface. Therefore, the adhesion forces which attach the coating to the metal surface can also affect the coating corrosion performance [3–7].

Epoxy is one of the most common barrier coating material used in severe corrosion environments including marine environment [8, 9]. Due to the hydrophilic chemical groups of cured epoxy structure (such as hydroxyl group (–OH), carboxyl group (C=O), phosphine oxide group (P=O) and amino group (N–H)), epoxy has exhibited hydrophilic properties [10–13].

This allowed us to test our epoxy resin which is standard synthesized optimized or formulated to develop appropriate coatings in industrial or natural corrosive such as our case. The choice of the charges has been carefully chosen by substituting toxic zinc chromate [14] by a green additive compliance zinc phosphate environment. The toxicity of this compound is 50 times lower than that of chromates [15-17]. Therefore, the prediction of the coatings' life span is very important in controlling corrosion.

Experimental material and procedures

The chemical structure of the studied compound is presented in Figure 1. Tetra Glycidyl of Ethylene Dianiline (TGEDA) was synthesized in the laboratory through two steps [18-20]. The resin epoxy TetraGlycidyl of Ethylene Dianiline (TGEDA) is obtained by condensing the Epichlorhydrin (2, 3-Epoxy Chloro Propane1) and Ethylene Dianiline in the presence of Triethylamine.

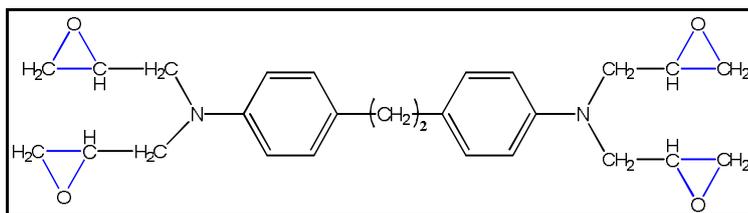


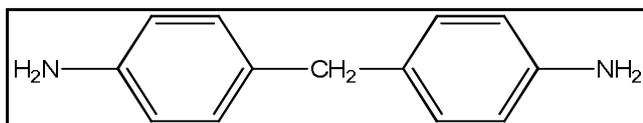
Figure 1. Structure of Tetra Glycidyl of Ethylene Dianiline (TGEDA)

Thermal behavior

The crosslinking is an important factor that determines the thermal behavior of the resin. For the stoichiometric ratio 1:1 there is a crosslink at every amine–epoxy junction, i.e. all amine groups react with all epoxide groups. In non-stoichiometric epoxy resin, the presence of an excess amine groups increased the number of un-reacted amine groups, thus influencing the thermal stability of the non-stoichiometric composite [21, 22].

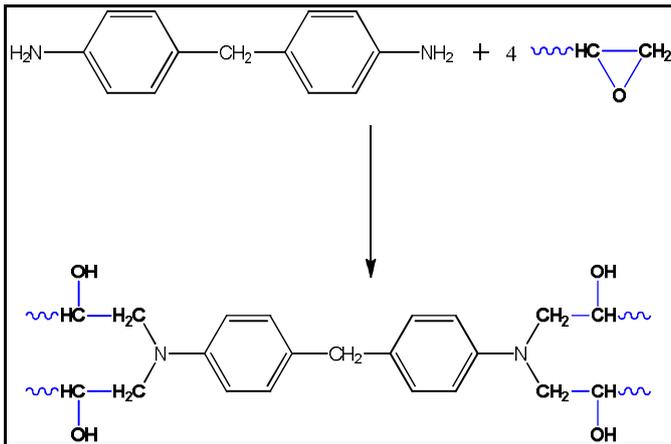
During crosslinking, thermosetting resins become insoluble and infusible by exothermic chemical reactions (polyaddition reaction irreversible) between the epoxy prepolymer and the hardener. The resulting material is an infinite three-dimensional network. Most formulations require a supply of heat to crosslink [18, 23].

Thus, our crosslinking was performed by primary diamine curing whose chemical formula was as follows: (Scheme 1).



Scheme 1. Chemical structures of 4, 4'-Methylene Dianiline (MDA) using as curing epoxy resins.

MDA is a reactive agent (the free NH₂ groups make it capable to react with epoxy groups); it was expected to act as crosslinking agent. (Scheme 2).



Scheme 2. Reaction with MDA

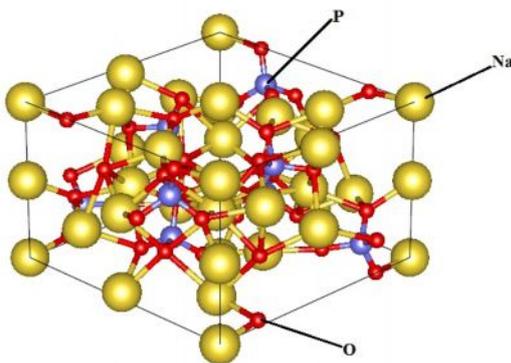
Carbon steel coated by TGEDA

Carbon steel (CS) specimen having composition 0.11% C, 0.47 % Mn, 0.24 % Si, 0.0210% P, 0.14 % Cu, 0.1 % Ni, 0.12 % Cr, 0.02 % Mo, 0.03 % Al, <0.12 % Co, <0.003 %V, 0.06 %W, the rest of which was Fe were used. Coupons were cut to 5 cm ×1 cm ×0.2 cm dimensions. Before each experiment, the electrode surface was cleaned with a sequence of emery papers of different grades (60, 180, 220, 360, 400, 800 and 1200), degreased with ethanol and washed with bi-distilled water.

The used experimental procedure includes the following steps:

- Adding an amount of TGEDA and the curing agent (MDA) and two charges the first of which is zinc-based powder and the second is trisodium phosphate (Na_3PO_4) (Scheme 3) in the presence of épichlorhydrine as a solvent.
- Maintaining the stirring for about one hour to evaporate the solvent existing in our sample.

Na_3PO_4 room temperature refinement (TOF neutron diffraction data). Space group $P\bar{4}2_1/c$. $a = b = 10.81111(34) \text{ \AA}$, $c = 6.81831(34) \text{ \AA}$.



Scheme 3. Crystallographic data of the Na_3PO_4 at room temperature [24].

Characterization

Scanning electron microscopy (SEM)

The morphology of the coating was observed by a scanning electron microscope of JEOL-JSM 5500 type. The analysis is performed with an acceleration voltage of 0.5-30 kV.

Electrochemical measurements

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 2).

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.

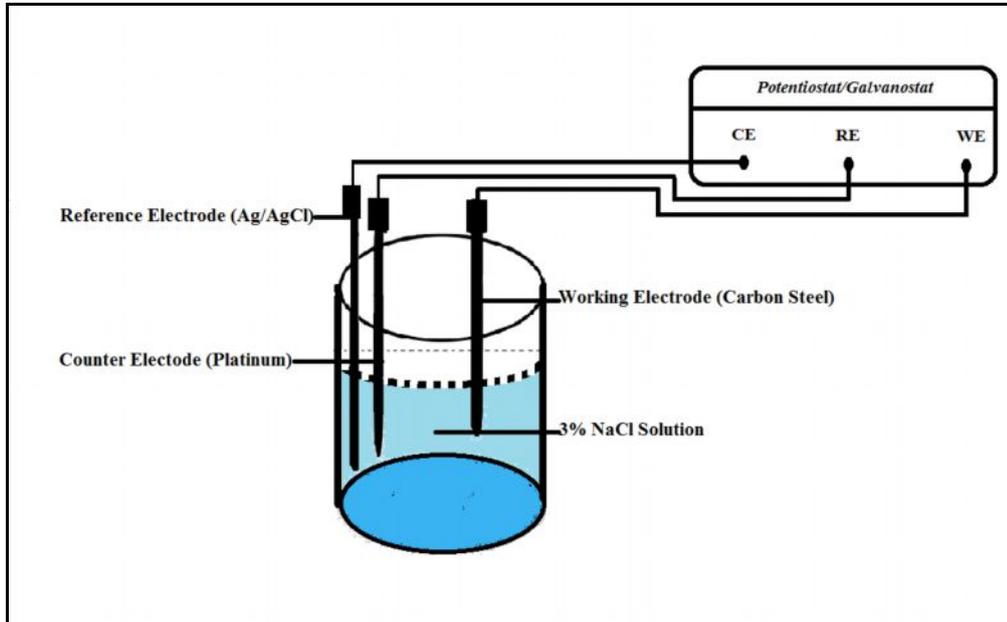


Figure 2. Schematic illustration of the electrochemical cell for EIS measurement.

For all EIS measurements an excitation amplitude of 10mV peak-to-peak in the frequency range from 0.1 Hz to 100 kHz.

Results and discussion

Morphological observations of the epoxy coating

The morphological photographs of selected Na_3PO_4 /Zn /epoxy composites were examined by SEM micrographs 50 μm and 100 μm as shown in Figure 3.

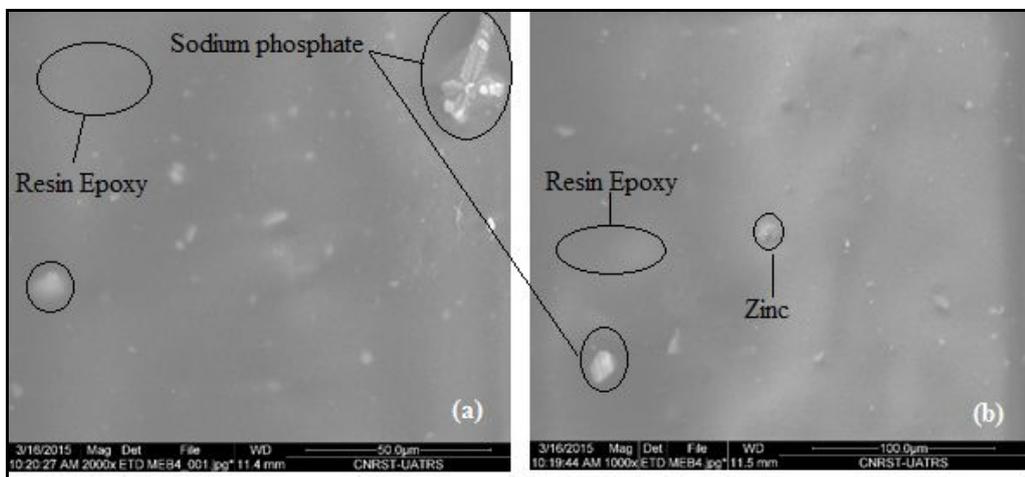


Figure 3. SEM images (a) and (b) of carbon steel surface treated by epoxy / zinc phosphate.

They consist of agglomerations of crystallites having similar shape. It is obvious that the particles are tightly embedded in the epoxy matrix with evidence of composite formation. This indicates good cohesion between the particles and matrix, which is very important to reach a strong interfacial adhesion. In addition, the micrograph shows a good distribution of particles within the polymer matrix. High compatibility between the particles and polymer matrix is observed.

Effect of immersion time

The EIS is a useful technique for long time tests, because they do not significantly disturb the system and it is possible to follow it over time [25]. Experiments are performed at open circuit potential. To observe the evolution of phenomena occurring on the interface at short immersion times, impedance spectra, in the with coating solution, are traced for seven typical immersion times, without removing the cooking electrode to obtain each spectrum.

Figure 4 shows the evolution of the spectra, in Nyquist representation, depending on the duration of immersion in the 3% NaCl solution at 298 K.

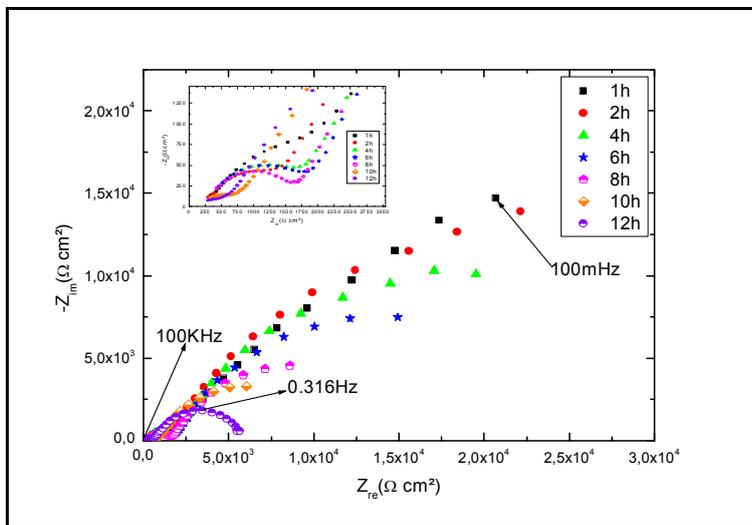


Figure 4. Electrochemical impedance Diagrammes obtained at E_{corr} for different immersion times for epoxy / zinc phosphate

The equivalent circuit shown in Figure 5 was chosen to be reasonably adapted to the experimental results. This circuit is composed of:

- R_s is the resistance of the electrolyte ($\Omega.cm^2$)
- R_{pf} is the resistance of the pores of the coating ($\Omega.cm^2$) that have a certain ionic strength. R_{pf} corresponds to the diameter of the first semi-circle with high frequencies of the Nyquist diagram.
- R_{ct} is the resistance of charge transfer ($\Omega.cm^2$),
- C_f is the dielectric capacity of the coating film (F / m),
- C_{dl} is the double layer capacity (polarization capability) of the substrate (F / m).

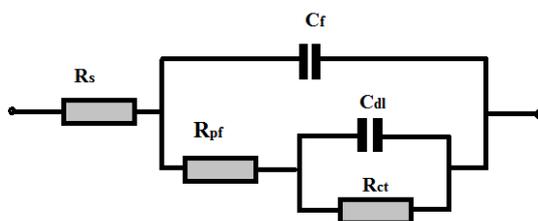


Figure 5. The proposed equivalent circuit for features for adjusting the impedance spectra obtained in the presence of different formulations for ordinary steel in 3% NaCl.

Table 1 Parameters obtained by fitting the Nyquist plots with the equivalent circuit for the carbon steel electrode.

Immersion time (h) for formulation (epoxy / zinc phosphate)	R_s ($\Omega.cm^2$)	C_f ($\mu F/cm^2$)	R_{pf} ($\Omega.cm^2$)	Q_{ct} ($\mu F/cm^2$)	R_{ct} ($\Omega.cm^2$)	R_p ($\Omega.cm^2$)
1h	200	16	5.688	3	62661	68149
2h	260	21	2641	25	52645	55026
4h	263	25	3928	27.5	50644	54309
6h	264	2	1703	50	23717	25156
8h	228	2.5	1528	101	14176	15476
10h	221	26	795	109	11008	11582
12h	293	28	500	149	5178	5385

The developments of the barrier properties of coating in its course of immersion can be evaluated through the pore resistance values R_{pf} obtained from modeling electrochemical impedance diagrams. The resistance of pores indicates the ease with which the electrolyte penetrates inside the coating [26-29]. The electrolyte circulation may occur through pre-existing pores or formed by local hydrolysis of the polymer matrix [30]. Mansfield attributes the evolution of R_{pf} during the immersion coating, to the penetration of the electrolyte in their pores [31]. So we followed its evolutions during the immersion to evaluate coatings barrier properties (Figure 6).

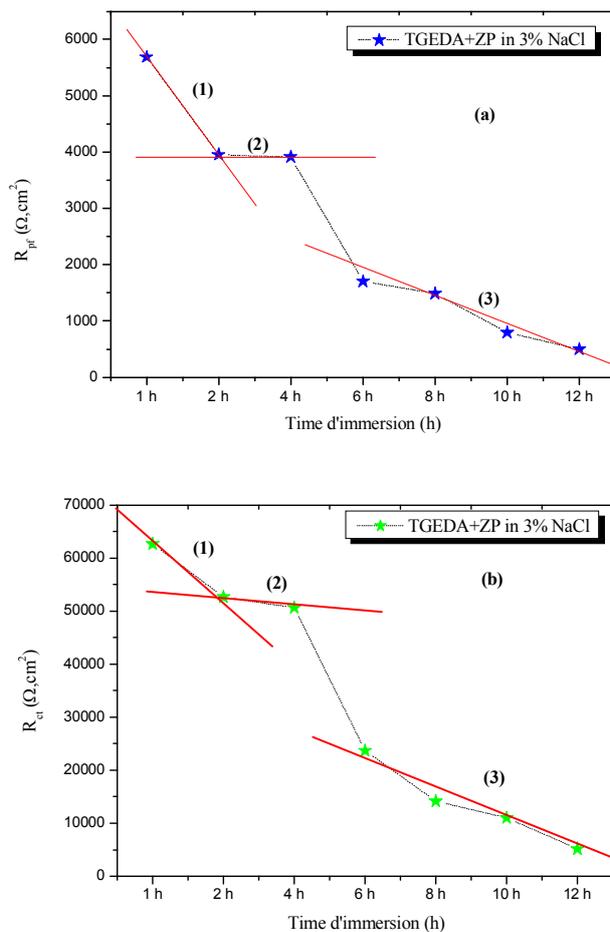


Figure 6. Evolution of the resistance of the coating pores R_{pf} (a) and R_{ct} is the charge transfer resistance (b) by epoxy / zinc phosphat matrix during various immersion times at 298 K in 3% NaCl.

The decrease of R_p values during the immersion time is usually simply related to the penetration of the electrolyte (water and ions). Miskovic-Stankovic et al distinguish it from that of pure water. According to them, the first portion of the curve corresponds to the penetration and saturation of the water coating and the second corresponds to the penetration of the electrolyte into the macropores [32]. Hu et al confirm this statement [33]. During the first two stages, It would be the results of increasing the amount of electrolyte in the coating [34]. The third step would be due to the presence of electrolyte to the metal surface associated with the release and degradation of the coating, resulting in the development of the electrochemical process and the corrosion of the substrate [35].

The evolution of R_{ct} values with the immersion time is similar to that of the resistance of R_{pf} porosities described previously (Figure 6a). The decrease of R_{ct} values corresponds to an increase in the corrosion rate and a development of the corroded surface under the coating (Figure 6b) [36].

Adsorption mechanism

Zinc metal powder in contact with an iron-containing metallic substrate initiates electrochemical reactions; it is often added to coating materials designed for metal protection to serve as a “sacrificial anode”. The mechanism of action of the zinc is explained by electrochemical theory in terms of cathodic protection of the ferrous substrates [37]. Zinc metal reacts with oxygen; water and carbon dioxide present in air to give rise to corrosion products such as zinc oxide, zinc hydroxide and zinc carbonate. According to the literature, zinc oxide and zinc hydroxide possess some anticorrosion properties [38].

During corrosion of a zinc/steel couple in neutral NaCl solution, Zn dissolves to form Zn^{2+} ions, whereas dissolved oxygen is reduced on the steel surface, to form hydroxyl ions(Figure 7):

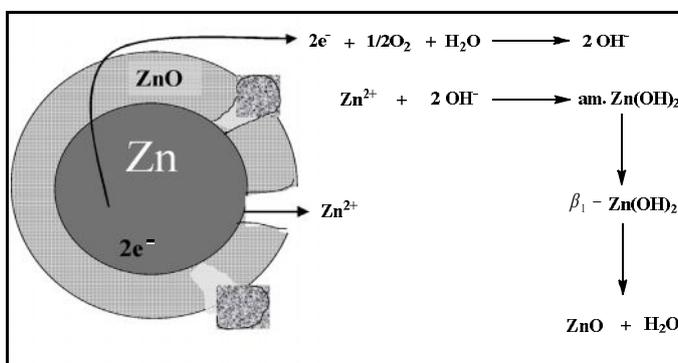
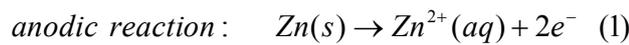


Figure 7. Behaviour and properties of Zn-pigmented coatings under corrosion conditions: electrochemical phase of Zn action in a coating.

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 electrons (Eq.2) helping to reduce the degradation of the coating (Figure 8)[39].

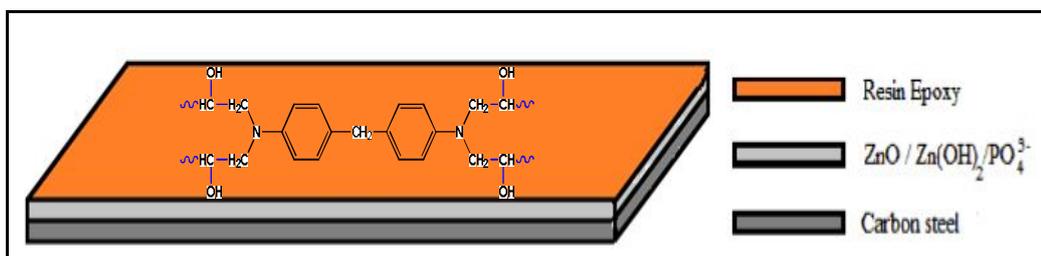


Figure 8. Diagram of the passivation coating induced by the presence of Zinc-phosphate pigments [40].

Conclusions

In this study, we carried out the protection of the carbon steel by the coating method issued from the formulation who is based on a standard oxide polymer, a zinc inorganic filler and an additive Na_3PO_4 in the matrice. This was done in order to decrease the corrosive effect of the medium on the substrate (usually steel).

Conclusions drawn from the work are as follows:

- The surface morphology examined by SEM showed in the case of zinc phosphating, the coating was crystallized with small needles covering the steel surface completely.
- The electrolyte was transported into the coating the free volume but also through the defects of the coating, and the defects are the main transport paths for the electrolyte.
- Zinc phosphate treatment is more effective method for preventing the corrosion on epoxy coated carbon steel than other treatment such as blasting.

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