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Application of Pentaglycidyl ether Penta-ethoxy Phosphorus Composites Polymers Formulated by Two Additives, Trisodium Phosphate (TSP) and Natural Phosphate(NP) and their Combination in the Behavior of the Coating on E24 Carbon Steel in NaCl 3.5%

Rachid Hsissou* and Ahmed El Harfi

Laboratory of Agricultural Resources, Polymers and Process Engineering (LARPPE), Team of Polymer and Organic Chemistry (TPOC), Department of Chemistry, Faculty of Sciences, Ibn Tofail University, BP 133, 14000, Kenitra, Morocco

*Corresponding Author, Tel.: +212622678510

E-Mail: r.hsissou@gmail.com

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Abstract- The new synthesized polymer named pentaglycidyl ether penta-ethoxy phosphorus (PGEPEP) was tested in the behavior of the coating on the metal substrate in a marine environment. In the first step, we developed hybrid composites by collecting two charges respectively trisodium phosphate and natural phosphate. In the second step, we applied the different hybrid composites F1 (PGEPEP/TSP), F2 (PGEPEP/NP) and F3 (PGEPEP/TSP+NP) combined from epoxy resin and synthetic filler, natural load and both sets on E24 carbon steel in 3.5% NaCl. Finally, the gravimetric and electrochemical measurements of the composite F3 (PGEPEP/ TSP+NP) are very encouraging and reach a maximum efficiency respectively equal to 93%, 95% and 92%.

Keywords- Polymer, PGEPEP, Coating, Hybrid composite, Epoxy resin

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1. INTRODUCTION

Composite polymers are new hybrid structures reinforced by naturally occurring or synthetic fillers or both [1]. These hybrid composites can have more than one reinforcing phase and one matrix phase [2]. Natural fillers have superior protective properties such as rigidity, flexibility; their main advantages are low cost, easy production and friendly to the environment. On the one hand, the addition of synthetic fillers can improve the anticorrosive properties of the composite such as rigidity and corrosion resistance. On the other hand, the viscosimetric, viscoelastic and rheological properties of the polymer can also be improved [3,4]. Hybrid composite materials can produce high anticorrosive properties such as high specific strength and very good processing [5,6]. High performance composites can be used in a variety of applications such as aircraft processing, wind turbine blades, automobiles, intelligent memory, coating, etc. [7-9].

In our work, we applied the different hybrid composites F1 (PGEPEP/TSP), F2 (PGEPEP/NP) and F3 (PGEPEP/TSP+NP) on E24 carbon steel in a marine environment. After that, we evaluated the performance of F1, F2 and F3 protective formulations in coating behavior using gravimetric and electrochemical methods.

2. MATERIALS AND METHODS

2.1. Used products

During this work, we tested the new macromolecular polymeric polyepoxide pentafunctional phosphorus binder; pentaglycidyl ether penta-ethoxy phosphorus (PGEPEP), which semi-developed structure is shown in figure 1. We also used sodium chloride and the additives trisodium phosphate and natural phosphate.

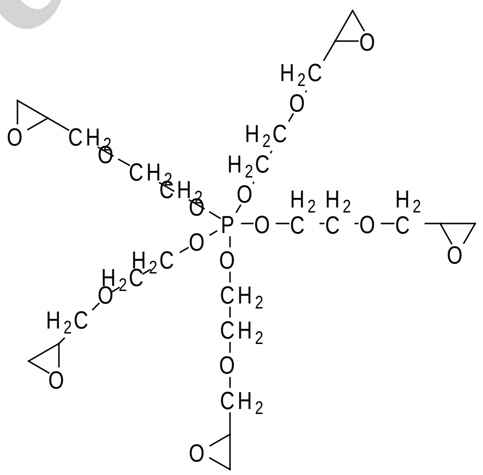

Fig. 1. Semi-developed formula of the pentaglycidyl ether penta-ethoxy phosphorus

2.2. Corrosive test of weight loss

The corrosion rate of the coating behavior is determined from measurements of the weight loss of E24 carbon steel in the absence and in the presence of different composites F1(PGEPEP/TSP), F2 (PGEPEP/NP) and F3 (PGEPEP/ TSP+NP) in 3.5% NaCl at 25 °C after 6 h immersion in the corrosive solution. The corrosion rate w ($mg.cm^{-2}.h^{-1}$) is calculated by the gravimetric method by measuring the weight of the sample before and after exposure in the corrosive solution according to equation 1.

$$w = \frac{(m_1 - m_2)}{S.t} \quad (1)$$

With m_1 is the mass of the sample before the corrosion, m_2 is the mass of the sample after the corrosion, S is the total surface of the sample, t is the corrosion time and w is the corrosion rate.

The protective efficiency of the coating behavior against corrosion of E24 carbon steel was determined using equation 2 [10].

$$PE_W(\%) = \left(1 - \frac{W_{corr}}{W^0_{corr}}\right) \times 100 \quad (2)$$

W^0_{corr} and W_{corr} are the corrosion rates of E24 carbon steel samples without and with each composite, respectively.

The degree of surface coverage (Φ) was calculated using equation 3 [10].

$$\Phi = \left(1 - \frac{W_{corr}}{W^0_{corr}}\right) \quad (3)$$

2.3. Electrochemical cell

The electrochemical measurements were obtained according to a mounting of the three-electrodes cell, namely: the platinum electrode as against the electrode, the saturated calomel reference electrode and the rectangular E24carbon steel working electrode. The contact surface with the corrosive solution is (2×0.5 cm²).

These three electrodes are immersed in a 100 ml container in which are arranged well-spaced orifices of diameters and spacings allowing the introduction of the three electrodes and can also receive stirring systems and temperature control. The stationary measurements were determined in potentiodynamic mode using a potentiostat/galvanostat SP-200 Biologic Science Instruments. The working electrode is previously immersed in the free corrosion potential for 30 min. The scanning speed is 1 mV/s. The determination of the electrochemical parameters (i_{corr}, E_{corr}, β_c and β_a) from the polarization curves is done using a nonlinear regression by the Ec-Lab software. Thus, the protective efficiency η% is evaluated from equation 4.

$$\eta\% = \left(\frac{i^0_{corr} - i_{corr}}{i^0_{corr}}\right) \times 100 \quad (4)$$

With i^0_{corr} and i_{corr} present the current densities of corrosion (A.cm^{-2}), respectively in the absence and in the presence of the protective coating composites.

βc and βa are respectively the Tafel constants of the cathodic and anodic reactions (V^{-1}). These constants are related to the Tafel slope β (V.dec-1) on the logarithmic scale by equation 5.

$$\beta = \frac{\ln(10)}{b} = \frac{2.303}{b} \quad (5)$$

The transient measurements were made in Nyquist mode using the same apparatus with a signal amplitude (10 mV). The frequency domain explored varies from 100 KHz to 10 mHz. Protective efficiency η% was calculated using equation 6.

$$\eta\% = \left(\frac{R_p - R^0_p}{R_p}\right) \times 100 \quad (6)$$

R^0_p et R_p are the polarization resistances, respectively in the absence and in the presence of different composites of the coating behavior,.

2.4. E24 carbon steel coating

In order to obtain interesting results before each test, the plates undergo a polishing of the surface with abrasive paper of finer and finer granulometry: 600, 1200 and 1500; before being soaked in the corrosive solution.

The mixture consists of heating the pentafunctional phosphorus containing epoxy resin PGEPEP with the addition of the charge respectively trisodium phosphate, natural phosphate and the two sets. Then we left the mixture for 30 min to homogenize the composite (PGEPEP/Load). The latter was applied to the surface of E24 carbon steel using a rod producing a very thin film. Finally, the coated substrate is placed in the oven for 24 h at 65 °C [11,12].

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurement

Corrosion rate, surface coverage and protective efficiency values obtained from weight loss measurements of E24 carbon steel coated in the absence and in the presence of different composites F1 (PGEPEP/TSP), F2 (PGEPEP/NP) and F3 (PGEPEP/ TSP+NP) after 6 h immersion in NaCl 3.5% at 298 K are summarized in table 1.

Table 1. Corrosion rate, surface coverage and protective efficiency

Formulations	**Corrosion rate ($mg.cm^{-2}.h^{-1}$)**	**Surface coverage Φ**	**Protective efficiency (%)**
Blank	1.23	-	-
PGEPEP/TSP	0.33	0.73	73
PGEPEP/NP	0.19	0.84	84
PGEPEP/ TSP+NP	0.088	0.93	93

The maximum value of the protective efficiency is obtained in the presence of the hybrid composite (PGEPEP/PTS+PN). Thus, the optimum value of the top coverage of the coating behavior on the surface is obtained in the solution with the polymer formulated by the two fillers.

3.2. Polarization curves

Figure 2 presents the potentiodynamic polarization curves that describe the protective effect of E24 carbon steel in a marine environment by three composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP). The electrochemical parameters taken from the potentiodynamic curves of the metal immersed in the corrosive solution in the absence and in the presence of different composites are summarized in table 2.

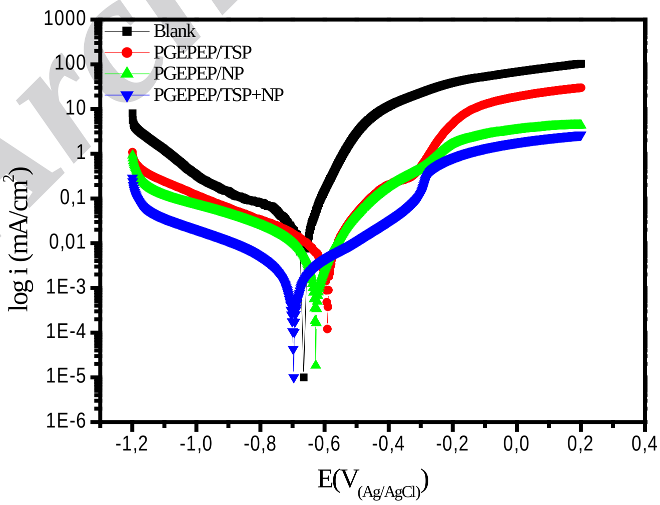

Fig. 2. Polarization curves of E24carbon steel after 30 min of immersion in a marine environment at 298 K

Table 2. Different electrochemical parameters associated with the polarization curves

Formulations	**- E_{corr} (mV/Ag/AgCl)**	**i_{corr} ($\mu A/cm^2$)**	**β_c (mV/dec)**	**β_a (mV/dec)**	**η (%)**
Blank	665	36	405	88	**-**
PGEPEP/TSP	591	8.5	312	117	**76**
PGEPEP/NP	627	4.5	241	139	**87.5**
PGEPEP/ TSP+NP	693	1.8	246	250	**95**

Table 2 shows the values of E_{corr}, i_{corr}, β_c and β_a calculated by a nonlinear regression obtained after the addition of different composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/ TSP+NP).

The stationary polarization curves plotted after 30 min immersion in the presence of different composites are shown in figure 2. We have shown that the addition of the coating results in a displacement of the potential towards higher values and a significant decrease in the current density in both cathodic and anodic domains [13].

However, the decrease in the current density is proportional to the applied composite and a limit value of the corrosion current is obtained to the composite (PGEPEP/TSP+NP) consisting of two charges respectively trisodium phosphate and natural phosphate. The coating behavior of the reinforced composite by mixing two additives is first well adsorbed on the surface of the metal and then simply blocks the diffusion of chloride ions and hydroxyl ions in the corrosive solution. The composite (PGEPEP/TSP+NP) is a highly effective protective formulation of the metal in the marine solution [14,15].

The presence of different composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP) is accompanied by a clear decrease in the current density respectively in the cathode and anode domains. This allowed us to conclude that the addition of the composites acts as a mixed protective coating [16,17].

3.3. Electrochemical impedance spectroscopy

We performed electrochemical impedance spectroscopy of three composites formulated by different charges to confirm the results of the stationary method. Figure 3 illustrates the results of electrochemical impedance spectroscopy of E24 carbon steel coated by different composites (PGEPEP/PTS), (PGEPEP/PN) and (PGEPEP/PTS+PN) immersed for 30 min in a marine environment.

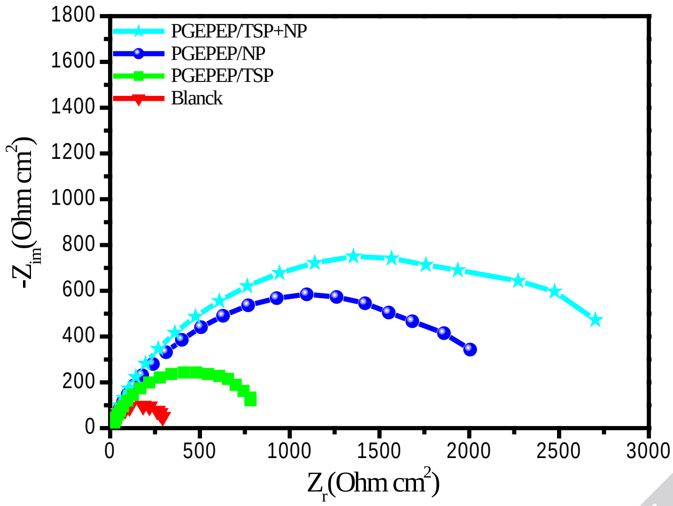

Fig. 3. Electrochemical impedance diagram of three composites studied after 30 min immersion in 3.5% NaCl at 298 K

The values of the charge transfer resistance (R_{tc}) increase with different hybrid composites by different charges, indicating that the adsorption of the composites occurs on the metal surface. The data in table 3 indicate that the increase in charge transfer resistance is associated with a decrease in double layer capacity and an increase in the percentage of protective efficiency. The decrease in double layer capacity (C_{dl}) values could be attributed to the adsorption of composites by different charges on the surface of the metal is well formulated. It has been reported that the protective adsorption of composites on the surface of E24carbon steel is characterized by a decrease in C_{dl} [18,19].

In addition, the reduced C_{d1} values may be due to the replacement of water molecules at the electrode interface with hybrid composites. This phenomenon is generally related to the adsorption of different composites formulated on the metal surface and then leads to a decrease of the local dielectric constant and/or to an increase in the thickness of the electric double layer [20,21]. Indeed, the larger the half circle diameter in the Nyquist diagram of the composites, the better the corrosion resistance will be. The protective effectiveness of the composites depends mainly on the size of the additives incorporated into the polymeric resin (PGEPEP). This can be explained by the presence of two charges in the composite (PGEPEP/TSP+NP) which are responsible for the higher corrosion resistance [22]. Based on these results, we concluded that the values of the polarization resistances of the composite protection films (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/ TSP+NP) are confirmatory with the results of the stasis method.

Figures 4 and 5 present Bode diagrams of E24 carbon steel coating behavior in a marine environment in the presence of three hybrids composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP) respectively by trisodium phosphate, natural phosphate and both sets.

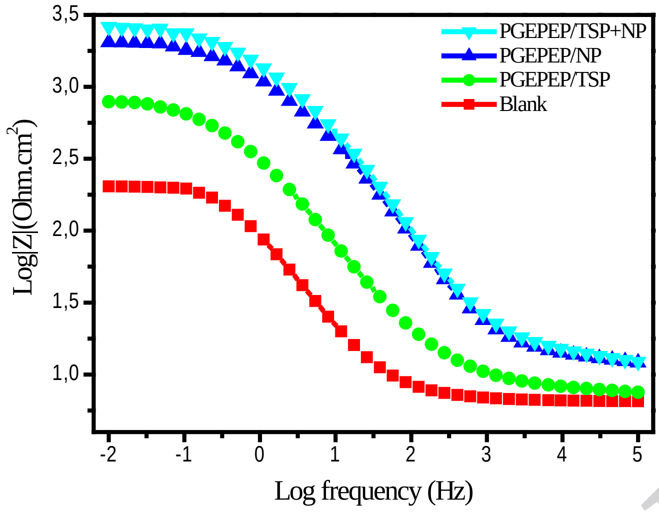

Fig. 4. Bode diagram of three composites studied after 30 min immersion in 3.5% NaCl at 298 K

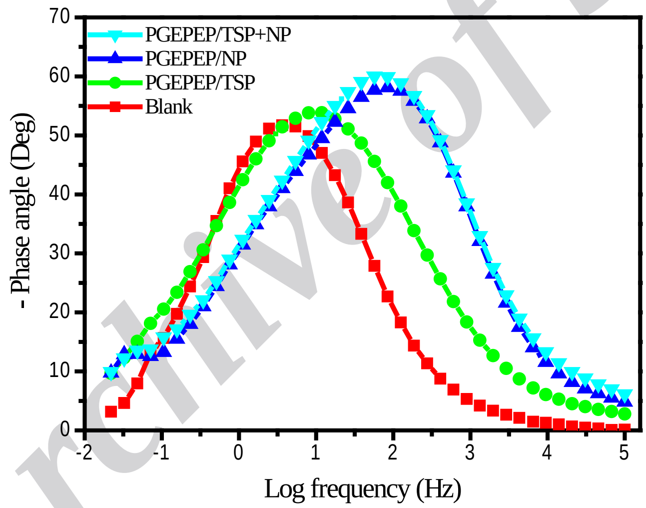

Fig. 5. Phase angle diagram of three composites studied after 30 min immersion in 3.5% NaCl at 298 K

Through figure 4, we observed that the absolute values of the impedance increase with the various composites reinforced respectively by trisodium phosphate, natural phosphate and both sets. Thus, a linear relation between log |Z| as a function of log (f) with a slope close to -1 was observed. This further confirms the greatest protection with different coating composites on E24 carbon steel.

Indeed, figure 5 shows the increase of the phase angles with the different composites respectively (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/ TSP+NP). From figure 5, we found that there are three frequency domains namely low frequencies, intermediate frequencies and high frequencies. At low frequencies, the absolute values of the highest impedance confirm the greatest protection in the presence of different metal coating composites. Then, for intermediate frequencies, the values obtained from the phase angle versus log (frequency) curves of different protection composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP) are respectively equal to: 52 °, 54° 58° and 60 °. This could be explained by the non-ideal structure of the metal/solution interface. Finally, for high frequencies the phase angle values are about zero. This indicates that the behavior of the electrode that corresponds to the resistance of the solution. These results confirm that of the transitional method [23].

The curves of Nyquist and Bode diagrams illustrated in the previous figures 3, 4 and 5 respectively show the existence of an equivalent electrical circuit (figure 6). This is due to the interpretation of the information relating to the properties of the coating behavior. This circuit is composed of: electrolyte resistance (R_s), charge transfer resistance (R_{ct}), double layer capacity (C_{dl}), coating film capacity (C_f) and film resistance coating (R_f).

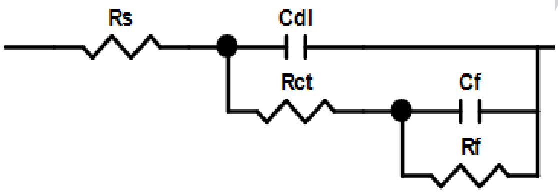

Fig. 6. Equivalent electrical circuit of impedance diagrams obtained in the presence of different composites studied in a marine environment at 298 K

The different values of the electrochemical parameters taken from the Nyquist diagrams and the resulting protective efficacy for the three composites studied (PGEPEP/PTS), (PGEPEP/PN) and (PGEPEP/PTS+PN) are summarized in table 3.

Table 3. Different electrochemical parameters in the presence of the studied composites

Different composites	**Rs (Ω.cm^2)**	**Rct (Ω.cm^2)**	**Cf (μF/cm^2)**	**Cdl (μF/cm^2)**	**R_p (Ω.cm^2)**	**η (%)**
Blank	6.55	0.84	127	2108	223	**-**
(PGEPEP/TSP)	7.56	1.32	7.89	735	873	**74**
(PGEPEP/NP)	12.91	3.5	6.29	167	2146	**89**
(PGEPEP/TSP+NP)	13.24	3.76	4.13	123	2674	**92**

From table 3, we concluded that the values of the polarization resistance of the coating film for the different composites (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP) from the new architecture pentafunctional pentaglycidyl ether penta-ethoxy phosphorus (PGEPEP) and trisodium phosphate, natural phosphate and both sets are confirmatory with the results of the stationary and gravimetric methods.

4. CONCLUSION

After pentafunctional polymer pentaglycidyl ether penta-ethoxy phosphorus synthesis, we developed a hybrid composite of trisodium phosphate, natural phosphate and the two sets respectively (PGEPEP/TSP), (PGEPEP/NP) and (PGEPEP/TSP+NP). Then, we applied the composites formulated in the behavior of the coating in a marine environment. The gravimetric and electrochemical results obtained in this work are quite in reasonable agreement. Finally, the hybrid composite by two charges (PGEPEP/TSP+NP) has a very interesting protective effect.

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