Evaluation of Corrosion Resistance in 3.5% NaCl Solution of Hybrid Coatings Obtained from Plastics Materials

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Abstract: In this work, the corrosion resistance of hybrid coatings obtained from plastic materials was evaluated and compared with the corrosion resistance of Zn coatings. Zinc and hybrid coatings were obtained by electrodeposition from zinc sulphate electrolyte. For obtained hybrid coatings it was used as disperse phase two type of plastic materials: phenol-formaldehyde resin and epoxy resin. Polarization was used to measure the corrosion rate and behaviour of zinc and hybrid coatings in 3.5% NaCl solution. Tafel curves show that the including particles of plastic materials in zinc matrix disturbs the cathodic reactions and reduces anodic reaction leading to decrease of corrosion current and increase the corrosion resistance of hybrid coatings obtained at the same electrodeposition parameters as zinc coatings. Smallest values of corrosion rate were evaluated for hybrid coatings obtained with phenol-formaldehyde resin as disperse phase that indicates a good corrosion resistance in 3.5% NaCl solution.

Keywords: plastic materials, zinc, electrodeposition, corrosion resistance

1. Introduction

Hybrid materials are mixtures of two or more components whose properties complement each other, resulting in a material with properties superior to that specific to each component [1]. The advantages of these new materials can be stated as follows: corrosion resistance, breaking strength, wear resistance, high-temperature resistance, surface hardness, dimensional stability, vibration damping capacity, environmental resistance, thermal conductivity or thermal insulation, conductivity electricity, wetting capacity, relatively low price etc. [2-21].

Corrosion is a material degradation caused by the chemical reaction with other materials and/or the environment [22]. There are a limited number of papers concerning hybrid coatings with plastic materials as disperse phase. Such coatings present good anticorrosion properties. Zinc coatings have good corrosion resistance in most neutral media. When exposed to the atmosphere, zinc provides good corrosion protection for steel, but in rural and marine environments in conditions of moisture and chloride pollution decreases the corrosion efficiency of zinc coatings. For alkaline and marine environments can be used cadmium coatings for o good corrosion protection of steel. Zinc is preferred as coatings for steels used in water or the marine environment because it is non-toxic such as cadmium and can be used in applications requiring welding. The lifespan of zinc coatings is dependent on the thickness of the layer and less on the method of application, and the electrolyte sulfate electrodeposits are much better than those of cyanide electrolytes [23]. The excellent performance of zinc coatings lies in the fact that they form dense, adherent films of corrosion products and thus the corrosion rate is 10 or 100 times lower than that of ferrous materials, the corrosion rate depending on the environment. For these reasons is necessary to improve the corrosion behaviour of pure zinc coatings using different disperse phase included in the zinc matrix. Phenol formaldehyde resin and epoxy resin are used usually as polymeric coatings because act as a barrier to protect steel from different corrosion environments and are widely used for industrial applications [24-26].

For obtaining zinc hybrid coatings are used different methods: hot-dip galvanizing, thermal diffusion or cementation, metallization or spraying, contact process (without external power source) and electrodeposition [27]. Among the processes to produce hybrid coatings, the electrodeposition has

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further demonstrated that a smoother surface, better bonding between disperse phase and metal, a higher microhardness and good corrosion behavior can be achieved. More than that electrodeposition gives uniform deposits and deposition rate, the thickness of the layers can be controlled by electrodeposition parameters and is an attractive method owing to low-cost equipment and raw materials [28].

The aim of this work was to evaluate the behaviour and corrosion resistance in 3.5% NaCl solution of zinc and hybrid coatings with disperse phase plastic materials obtained by electrodeposition in a zinc sulphate electrolyte. As disperse phase for electrodeposition it was used two types of plastic materials: phenol-formaldehyde resin and epoxy resin. The corrosion resistance of hybrid coatings and pure zinc coatings in 3.5% NaCl solution was estimated using electrochemical methods (open circuit potential and potentiodynamic polarization method). Corrosion resistance was evaluated using the values of corrosion current, polarization resistance and rate of corrosion for hybrid coatings versus the values of same parameters for pure zinc coatings. The values of parameters mention before indicate o good corrosion resistance for hybrid coatings versus corrosion resistance of zinc coatings in tested medium.

2. Materials and methods
2.1. Preparation of pure zinc coatings and hybrid coatings
As substrate for electrodeposition, it was used DC04 carbon steel with the following chemical composition and mechanical properties: C 0.04%; Mn 0.20%; Si 0.02%; P 0.018%; S 0.012 %; Al 0.060%, yield strength 140-210 MPa at 20℃; tensile strength 270-350 MPa at 20℃ and elongation A80 38% at 20℃. Typical applications for this type of carbon steel are to be found in the automotive industry, the domestic appliance sector, metal furniture, drums, radiators, fans, small welded tubes and small profiles.

The sulphate electrolytes used for electrodeposition of pure zinc coatings and hybrid coatings are: 1.078 mol/L $ZnSO_4 \cdot 7H_2O$; 0.232 mol/L $Na_2SO_4 \cdot 10H_2O$; 0.045 mol/L $Al_2(SO_4)_3 \cdot 18H_2O$. To improve the characteristics of the electrolyte solution the conductivity was increased by using sodium sulphate. The acidity of electrolyte was maintained and stabilized at a value of pH=3.8 with aluminium sulphate. The parameters for electrodeposition used for pure zinc and hybrid coatings was: current density of 30 mA/cm^2, 40 mA/cm^2 and 50 mA/cm^2; electrodeposition time of 30 min for 40 mA/cm^2 and 60 min for 30 mA/cm^2 and 50 mA/cm^2. The disperse phase added in the electrolyte solution for obtaining hybrid coatings was in the quantity of 25g/L plastic materials particles in zinc sulphate electrolyte solution with a mean diameter size of particles 6-10 μm. The properties of phenol-formaldehyde resin used as disperse phase are molecular weight 3392–3816 g/mol; melting point 70–80℃; viscosity at 120℃ 35–45 Pa·s, free phenol <1%, water content < 0.5%. The phenol-formaldehyde resin is not esterified. The properties of epoxy resin used as disperse phase are weight 900–1200 g/mol; density 1.18-1.25 g/cm^3; melting point 64–76℃; epoxy index 0.185-0.220 equivalents in 100g resin 100%; free volatile compounds <1%. Homogeneity of the system was maintained by stirring with a rate of 800 rpm. All electrodeposition was carried out at room temperature. Surfactants or additives were not used in the zinc sulphate electrolyte because they could react with plastic material particles.

The symbols for tested samples are presented in Table 1.

Table 1. Symbols of samples used for corrosion tests

Samples	Electrodeposition parameters
Zn1	current density: 30 mA/cm^2, time 60 min
Zn2	current density: 40 mA/cm^2, time 30 min
Zn3	current density: 50 mA/cm^2, time 60 min
PF/Zn1	current density: 30 mA/cm^2, time 60 min, 25 g/L phenol-formaldehyde resin, mean diameter size of particles 6-10 μm
PF/Zn2	current density: 40 mA/cm^2, time 30 min, 25 g/L phenol-formaldehyde resin, mean diameter size of particles 6-10 μm
PF/Zn3	current density: 50 mA/cm^2, time 60 min, 25 g/L phenol-formaldehyde resin, mean diameter size

	of particles 6-10 μm
Ep/Zn1	current density: 30 mA/cm^2, time 60 min, 25 g/L epoxy resin, mean diameter size of particles 6-10 μm
Ep/Zn2	current density: 40 mA/cm^2, time 30 min, 25 g/L epoxy resin, mean diameter size of particles 6-10 μm
Ep/Zn3	current density: 50 mA/cm^2, time 60 min, 25 g/L epoxy resin, mean diameter size of particles 6-10 μm

The parameters that varied were current density and time for electrodeposition. The other parameters (*p*H, stirring rate, temperature, quantity and dimension of plastic materials particles added in the electrolyte) were maintained at same for all samples.

2.2. Characterization of the coatings
2.2.1. Thickness of the coatings
The thickness of coatings was evaluated using an optical microscope via sample cross-section.

### 2.2.2. Corrosion tests by electrochemical methods
To evaluate the open circuit potential and potentiodynamic polarization parameters (corrosion potential, anodic and cathodic Tafel slopes, corrosion current density, polarization resistance and corrosion rate) it was used a Voltalab PGP 201 and the values were recording and evaluate using VoltaMaster 4 software. For a good reproducibility of obtained data, each type of sample was tested three times.

Electrochemical measurements were performed in a three-electrode open cell with tested samples (pure zinc coatings, phenol-formaldehyde/zinc hybrid coatings and epoxy resin/zinc hybrid coatings) as working electrode (W.E.), a platinum plate as a counter electrode (C.E.) and a saturated calomel electrode (SCE) as a reference electrode (SCE = +241 mV/NHE). Monitoring of open circuit potential was for 60 min till the values of corrosion potential were stable vs. saturated calomel electrode potential used. For polarization curves, it was used initial potential (I.P.) –1.5 V (Hg/Hg$_2$Cl$_2$), final potential (F.P.) –0.8 V (Hg/Hg$_2$Cl$_2$) and a scan rate of 0.5 mV/s. The Tafel parameters were recorded after 30 min of immersion of the tested samples in 3.5% NaCl solution.

3. Results and discussions
3.1. Thickness of the coatings
The thickness of the coatings obtained in cross-section using optical microscopy are presented in Figure 1 (a, b and c).
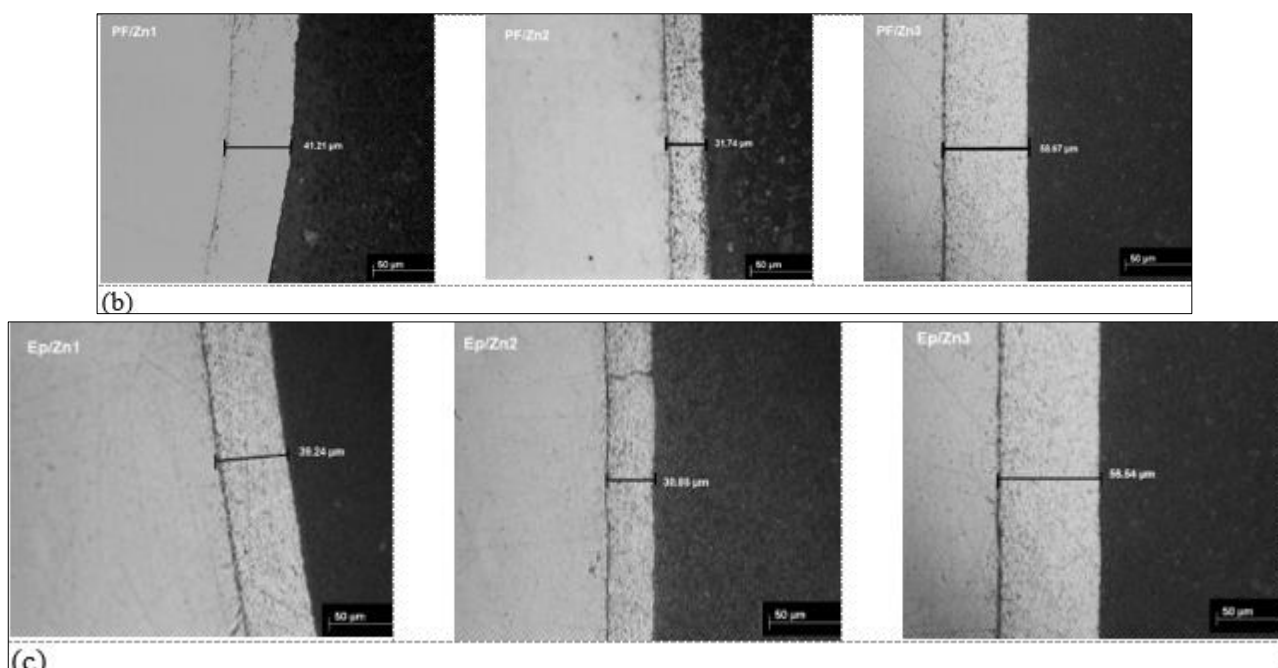

(a)
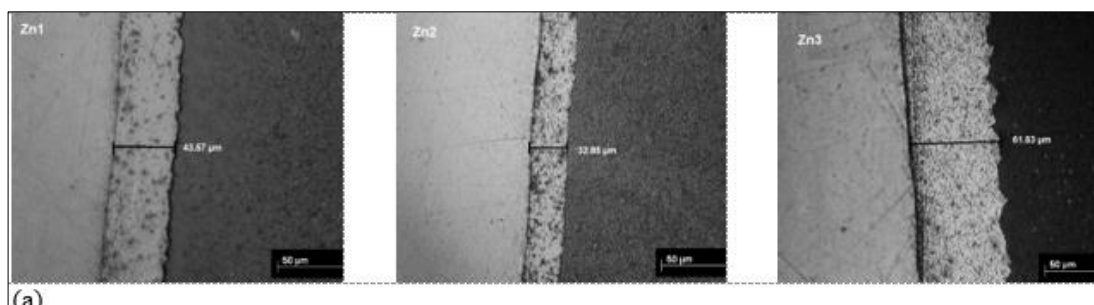
Figure 1. Cross - section images obtaining with optical microscopy showing the thickness of (a) zinc coatings, (b) phenol formaldehyde resin/zinc hybrid coatings and (c) epoxy resin/zinc hybrid coatings (X 500)

The values of layers thickness presented in Table 2 indicate an increase of layers thickness with an increase of current density and time for electrodeposition. The highest values were obtained for coatings obtained of 50 mA/cm^2 with electrodeposition time of 60 min and the smallest values were obtained for samples obtained of 40 mA/cm^2 with electrodeposition time of 30 min. Also, it could be observed that the smallest values of thickness layers it was obtained for coatings with plastic materials, probably the plastic materials used as disperse phase have an inhibition effect of zinc crystals growth and a catalytic effect in increasing nucleation sites, considering that the trends and influence of the polymers will be the same that in previous studies [29, 30].

The thickness of the coatings is an important parameter because the life cycle of the materials depends on their thickness. The function of corrosion rate it possible to obtained optimal layers thickness of a coating using optimum electrodeposition parameters.

Table 2. The thickness of pure zinc coatings and hybrid coatings

Type of samples	Thickness of the coatings layers, μm
Zn1	43.57
Zn2	32.85
Zn3	61.83
PF/Zn1	41.21
PF/Zn2	31.74
PF/Zn3	58.67
Ep/Zn1	39.24
Ep/Zn2	30.85
Ep/Zn3	56.54

3.2. Electrochemical corrosion measurements

Open circuit potential (OCP) tests give information about the stability of the tested samples. By using OCP is measured only the resting potential measured between reference and a working electrode. The evolution of the potential during time is due to the reactions at the hybrid material-solution interface. OCP is a thermodynamic parameter which tells about the thermodynamic tendency of metallic materials to participate in the electrochemical corrosion reactions with the corrosion environments.

The results obtained from the monitoring of OCP during 60 min for all tested samples are presented in Figures 2 (a, b and c).
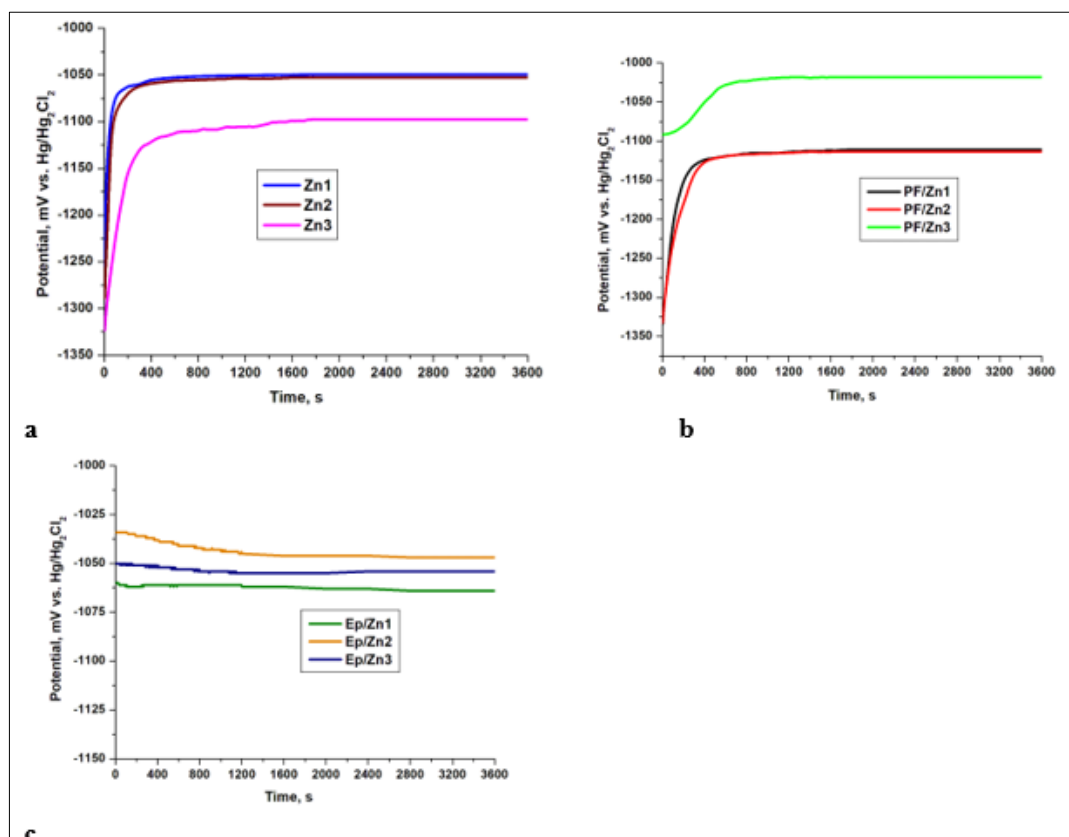

Figure 2. Evolution of open circuit potential measurements for (a) zinc coatings,
(b) phenol-formaldehyde/zinc hybrid coatings and (c) epoxy resin/zinc hybrid
Coatings in 3.5% NaCl solution

From the values of the OCP for all tested samples it could be observed that the variation of potential in time is very slow. Samples are stabilized in approximatively 10 min after immersion in 3.5% NaCl solution. Epoxy resin/zinc hybrid coatings samples are more stable in tested solution because the OCP has the smallest variation in time. For samples tested the values of the OCP are in the range of -1018 mV and – 1113 mV.

The results of open circuit potential recording for Zn3 and PF/Zn3 showed that pure zinc coatings sample presented a more active potential than the PF/Zn3. That fact indicate that the surface of pure zinc coatings is more susceptible to corrosion comparing with surfaces of hybrid coatings.

The Tafel curves obtained after 30 min of immersion in 3.5% NaCl solution in the potential range from -1.5 V to -0.8 V are presented in Figures 3 (a, b and c). Quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation [31]:

$$j_{corr} = \frac{B}{R_p} \qquad (1)$$

While the B parameter (Stern-Geary parameter) was evaluated using the equation:

$$B = \frac{b_a \cdot |b_c|}{2.303 \cdot (b_a + |b_c|)} \qquad (2)$$

j_{corr} means the corrosion current density; R_p means polarization resistance and b_a, b_c means anodic and cathodic Tafel slopes.

By using Tafel extrapolation can be calculated different parameters (corrosion potential, Tafel slopes, corrosion current density, polarization resistance, corrosion rate) that indicate corrosion behaviour of samples tested. These parameters are presented in Table 3.
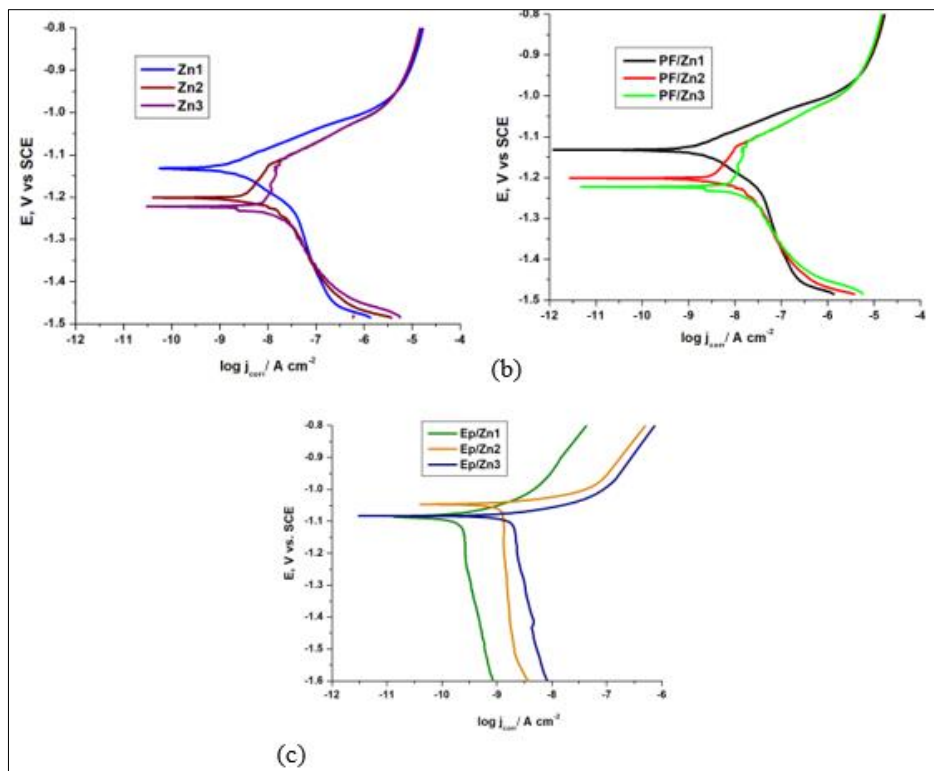

Figure 3. Tafel curves of (a) zinc coatings, (b) phenol-formaldehyde resin/zinc hybrid coatings and (c) epoxy resin/zinc hybrid coatings in 3.5% NaCl solution after 30 min from immersion time (logarithmical)

Table 3. Tafel parameters of zinc coatings and hybrid coatings with plastic materials evaluated from polarization curves obtained in 3.5% NaCl solution after 30 min of immersion

Type of samples	E_{corr} (vs SCE), V	β_a, V/decade	$|\beta_c|$, V/decade	$j_{corr} \cdot 10^{-6}$, A/cm²	R_p, Ω·cm²
Zn1	-1.133	26.54	22.17	160.16	32.75
Zn2	-1.204	43.18	27.14	91.80	78.82
Zn3	-1.222	33.45	28.40	53.51	124.63
PF/Zn1	-1.132	25.75	24.59	10.07	542.37
PF/Zn2	-1.201	31.60	37.10	20.08	369.02
PF/Zn3	-1.222	47.64	26.97	20.51	364.58
Ep/Zn1	-1.085	26.30	48.00	46.25	159.51
Ep/Zn2	-1.046	21.10	161.80	76.36	106.14
Ep/Zn3	-1.082	24.30	71.20	52.60	149.55

From the data presented in Table 3, it could be concluded that by adding phenol-formaldehyde resin and epoxy resin in electrolyte solution was obtained hybrid coatings with a better corrosion resistance than zinc coating in 3.5% NaCl solution. A higher value of polarization resistance and a smaller value of corrosion current density indicate a good corrosion resistance of materials. For polarization resistance it was calculated values between 32.75-124.63 Ω·cm² for zinc coatings, 364.58-542.37 Ω·cm² for phenol-formaldehyde resin/zinc hybrid coatings and 106.14-159.51 Ω·cm² for epoxy resin/zinc hybrid coatings. These values indicate an improvement of corrosion resistance of zinc coatings in 3.5% NaCl solution by adding in electrolyte solution plastic materials particles.

Using the values of corrosion current density and equation (3) it was evaluating the corrosion rate of tested samples (Figure 4).

$$CR \ (mm/year) = \frac{K \cdot j_{corr} \cdot EW}{d} \tag{3}$$

where k is a conversion factor equal with 3272, j_{corr} is corrosion current density calculated from Stern–Geary equation (A/cm^2); EW represents the equivalent weight of corroding species (g), while d is density of the corroding species (g/cm^3). For hybrid coatings the equivalent weight values are not influence too much by the polymers because these materials (phenol formaldehyde resin and epoxy resin) were used as disperse phase and zinc used as matrix is majority in hybrid coatings. In order to evaluate the corrosion rate of hybrid coatings it was used the equivalent weight of zinc. Because the density of plastic materials is very tiny comparing with the density of zinc for evaluate corrosion rate it was used the density of zinc metal (zinc density = 7.133 g/cm^3, density of phenol formaldehyde resin = 1.16 - 1.21 g/cm^3 and density of epoxy resin = 1.18 - 1.25 g/cm^3).
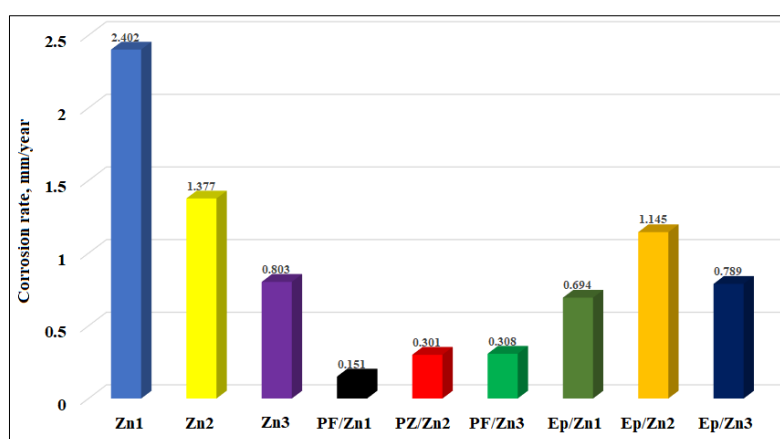

Figure 4. The corrosion rate of tested samples

Comparing the values of corrosion rate obtained for tested samples could be concluded that phenol-formaldehyde/zinc hybrid coatings have very good corrosion resistance in 3.5% NaCl with smaller values of corrosion rate between 0.151-0.308 mm/year. Good corrosion resistance was obtained for epoxy resin/zinc hybrid coatings with corrosion rate values between 0.694-1.145 mm/year. The corrosion rate for zinc coatings has the highest values between 0.803-2.402 mm/year that indicate the smallest corrosion resistance of zinc in 3.5% NaCl comparing with corrosion resistance of hybrid coatings.

It was remark only one exception for zinc coatings obtained at 50 mA/cm^2, electrodeposition time 60 min where the value of corrosion rate (0.803 mm/year) was smaller than epoxy resin/zinc coatings obtained at 40 mA/cm^2, electrodeposition time 30 min (1.145 mm/year).

From corrosion rate data obtained for hybrid coatings can be concluded that these types of coatings could be used for industrial purposes to minimise the losses of zinc generated from corrosion in an aggressive environment.

4. Conclusions

Corrosion of materials is an important concern for the materials scientist. This natural phenomenon causes substantial financial losses in different industries and requires extensive efforts to limit its impact.

The research presented shows that it could be possible to obtain hybrid coatings, by adding plastic materials particles in electrolyte solution, with very good corrosion resistance in an aggressive environment using electrodeposition, a method with low cost and easy to used.

From the values of layers, thickness obtained it was observed an increase of layers thickness with increases current density and time for electrodeposition.

The values of the open circuit potential for all tested samples shows that the variation of potential in time is very slow, that indicates good stability of the tested materials in 3.5% NaCl.

By adding plastic materials particles in sulphate electrolyte solution, it was obtained hybrid coatings with a better corrosion resistance than zinc coatings in 3.5% NaCl solution.

Hybrid coatings obtained with plastic materials could be used for industrial purposes, method of obtaining is easy with low cost and the hybrid coatings obtained present an improvement of corrosion rate comparing with zinc coatings.

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