Original Article

Corrosion resistance of zinc–resin hybrid coatings obtained by electro-codeposition

Alina Crina Ciubotariu\textsuperscript{a,\ast}, Lidia Benea\textsuperscript{a,\ast}, Pierre Ponthiaux\textsuperscript{b}

\textsuperscript{a} Dunarea de Jos University of Galati, Faculty of Engineering, Competences Centre Interfaces – Tribocorrosion and Electrochemical Systems, 47 Domneasca Street, RO-800008 Galati, Romania
\textsuperscript{b} Ecole Centrale Paris, Laboratoire Génie des Procédés et Matériaux, Grande Voie des Vignes, 92290 Chatenay Malabry, France

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Zinc; Resin particles; Hybrid coatings; AFM; Electrochemical techniques; Polarization resistance

Abstract
Pure zinc and zinc hybrid coatings containing phenol–formaldehyde resin particles were prepared by electrodeposition from zinc sulfate electrolytes. The effect of mean diameter size of particles on the morphology and topography of the surfaces was investigated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). It was shown that pure zinc coating has a regular surface, whereas the hybrid coating surfaces have fine surface structure. The corrosion resistance in 0.5 M sodium chloride was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The polarization resistance calculated with both methods indicates that the electrochemical properties of conventional zinc coating were significantly improved by the incorporation of phenol–formaldehyde resin particles.

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1. Introduction

Composite and hybrid materials are material systems consisting of a discrete constituent (the reinforcement) distributed in a continuous phase (the matrix). The new material systems thus formed have characteristics distinct from the properties and behavior, from the geometry and arrangement of their constituents and from the properties of the boundaries (interfaces) between the constituents. Composites are classified either on the basis of the nature of the continuous (matrix) phase (polymer–matrix, metal–matrix, ceramic–matrix and intermetallic–matrix composites) or on the basis of the nature of the reinforcing phase (particle reinforced, fiber reinforced, dispersion strengthened, laminated, etc.). The properties of the composites can be adapted and new combinations of properties can be achieved (Asthana et al., 2006).

Zinc is the most widely used material for protection of steel against corrosion. The successful use of zinc as a coating on steel can be attributed to its sacrificial nature, low cost and ease of application. Zinc is more corrosion resistant than steel in most natural atmospheres. But, in aggressive corrosive environment, zinc coating suffers a severe corrosion. Therefore it is necessary to develop zinc electrodeposited composites and hybrid coatings with better properties such as corrosion resistance, wear resistance and hardness comparative with properties of pure zinc coating.

A number of the relevant works refer to some particles such as B\textsubscript{4}C (Praveen Kumar et al., 2012), CeO\textsubscript{2} (Hamlaoui et al., 2010), graphite (Muralidhara et al., 2012), TiO\textsubscript{2} (Praveen and Venkatesha, 2008), ZrO\textsubscript{2} (Vathsala and Venkatesha, 2011), Al\textsubscript{2}O\textsubscript{3} (Shibli et al., 2010;...
Sancakoglu et al., 2011), V<sub>2</sub>O<sub>5</sub> (Bindiya et al., 2012), SiO<sub>2</sub> (Kondo et al., 2000; Azizi et al., 2005) and (Müller et al., 2002; Gomes et al., 2011) – zinc reinforced system while investigations regarding polymeric particles are relatively limited. Referring to zinc composite coatings containing polymethylmethacrylate (PMMA) (Vasilakopoulos and Bourroulhan, 2010), polystyrene (PS) (Hovestad et al., 1999), stabilized polymeric micelle (SPM; core–shell structures consisting of block co-polymers of polyethers) (Petrov et al., 2005) or PEDOT (poly (3,4-ethylenedioxythiophene)) (Bai et al., 2015) particles on steel there exist a few reports that show adherence and anti-corrosion properties improved (Koleva et al., 2005; Kammona et al., 2009). In 2011 it was reported that ultrahigh molecular weight polyethylene (UHMWPE) could be deposited into cobalt matrix (Benea and Mardare-Pratiea, 2011).

Electrodeposition process offers uniformity of deposits and deposition rate, rigid control of coatings thickness and their quality by controlling the experimental parameters. Moreover it is especially attractive owing to its low equipment cost and starting materials. Zinc electrodeposition is an industrial process and is widely used to coat on steel for enhancing its service life. Electrodeposition of zinc has some advantages such as easy way of deposition and a good corrosion resistance (Beshore et al., 1987; Flinn and Trojan, 1990; Kerr et al., 2000; Mouanga et al., 2009; Wu et al., 2012).

The present work intends to investigate the electro-codeposition of phenol-formaldehyde (PF) resin particles (novolac) with zinc from zinc sulfate plating bath to obtain zinc–resin hybrid coatings. Phenol-formaldehyde resin is a thermostatic polymer, which becomes plastic with increasing temperature, irreversibly solidifies and become insoluble. PF resin type novolac can be obtained from phenol and formaldehyde in acid medium. The properties of PF resin particles type novolac used as dispersed phase for electrodeposition are as follows: molecular weight 3392–3816 g/mol; melting point 70–80°C; typical length, 250 μm; width, 35 μm; thickness, 2 μm; resonance frequency, 41 kHz and nominal force/spring constant, 0.65 N/m. Each AFM image consists of 512 by 512 pixels. AFM images were performed by contact mode in air. Raster scan is the current standard method of AFM data collection. The probe starts by traveling along the “fast scan direction” or in the +x direction. As it reaches the end of the scan region, it takes a small step in the “slow scan direction” or +y direction and scans in the –x direction until it retraces the x displacement. Another small step in the +y direction is taken and the scanner moves in the +x direction to initiate another scan line. Continuing in this manner, an image is formed.

All electrochemical measurements were made using an electrochemical work station Solartron 1286 Electrochemical Interface coupled with a 2895 Solartron Frequency Response Analyzer and the Z-Plot/Z-View Software. An electrochemical cell with platinum as counter electrode, a mercury–mercurous sulfate electrode Hg/HgSO<sub>4</sub>saturated K<sub>2</sub>SO<sub>4</sub> as reference electrode (E = +658 mV/NHE) and pure zinc or hybrid coatings of surface area 2 cm<sup>2</sup> as working electrode were employed. As test solution 0.5 M sodium chloride was used at room temperature (20 ± 1°C).

For potentiodynamic polarization measurements initial potential, I. P. = –1.9 V (Hg/HgSO<sub>4</sub>), final potential, F.P. = –1.2 V (Hg/HgSO<sub>4</sub>) and a scan rate of 1.66 mV/s were used. The polarization curves were recorded after 30 min of immersion. The Tafel parameters for pure zinc and hybrid coatings were calculated by the Tafel extrapolation method.

EIS measurements were performed in the frequency range between 65 kHz and 1 Hz, with an AC sine wave amplitude of 10 mV, frequency per decade: 10 Hz and delay before integration 1 s. The electrochemical impedance spectroscopy diagrams were recorded after 30 min of immersion. All the recorded impedance spectra were analyzed as Nyquist and Bode representations of diagrams.

**2. Characterization of the coatings**

Surface morphology of Zn and Zn–PF resin hybrid coatings was examined with scanning electron microscope type JSM-T220, produced by JEOL Ltd. Atomic force microscope was used for characterization of surface topography and roughness of the deposits. For AFM images, silicon cantilever CSC37 A (Mikromasch, Estonia) with the following features was used: typical length, 250 μm; width, 35 μm; thickness, 2 μm; resonance frequency, 41 kHz and nominal force/spring constant, 0.65 N/m. Each AFM image consists of 512 by 512 pixels. AFM images were performed by contact mode in air. Raster scan is the current standard method of AFM data collection. The probe starts by traveling along the “fast scan direction” or in the +x direction. As it reaches the end of the scan region, it takes a small step in the “slow scan direction” or +y direction and scans in the –x direction until it retraces the x displacement. Another small step in the +y direction is taken and the scanner moves in the +x direction to initiate another scan line. Continuing in this manner, an image is formed.
3. Results and discussion

3.1. SEM coating morphology and EDX analysis

The SEM images of two types of particles used as dispersed phase are presented in Fig. 1(a and b). A closer examination of this SEM images presented shows that the resin particles present a different shape, some of them are spherical and other are discoidal.

Fig. 2(a–c) compares morphological aspects of Zn and Zn–PF resin hybrid coatings under scanning electron microscope. As it can be seen from the micrographs there is an obvious and well distinguishable grain refinement of hybrid coatings surface in the presence of the polymer particles. The polymer particles have an inhibition effect of zinc crystals growth and a catalytic effect in increasing nucleation sites.

These observations are in line with previous studies on zinc hybrid coatings in the presence of different types of polymeric aggregates (Boshkov et al., 2008; Koleva et al., 2008, 2010).

Figure 1 SEM images of phenol-formaldehyde resin particles: (a) mean diameter size of particles 0.1–5.0 μm; (b) mean diameter size of particles 6.0–10.0 μm (250×).

Figure 2 SEM surface morphology of electrodeposited coatings: (a) Zn coating; (b) Zn–PF1 hybrid coating; (c) Zn–PF2 hybrid coating (3500×).

Fig. 3(a and b) shows the cross-sectional SEM images of Zn–PF resin hybrid coatings. The SEM examination on cross sections clearly revealed the presence of resin in the Zn matrix.
In order to evaluate the presence of resin particles in the zinc matrix EDX analysis was carried out too. The phenol-formaldehyde resin contains hydrogen, oxygen and carbon. The presence of hydrogen cannot be determined because it has a very small atomic weight. The average elemental (carbon, oxygen and zinc) composition of the coatings is listed in Table 1.

The results show the presence of carbon and oxygen in the zinc matrix. The average content of unit molecular weight of polymer from hybrid coatings was calculated using the average content of carbon. For hybrid coatings obtained with resin having the mean diameter of particles 0.1–5.0 μm the average value obtained was 3.63 wt% and for hybrid coatings having mean diameter of particles 6.0–10.0 μm it was found 2.1 wt% polymer unit mass into zinc matrix.

3.2. Topography and roughness of the coatings by AFM

The influence of mean diameter size of particles co-deposited with zinc for topography and roughness of the coatings is presented in Figs. 4–6.

<table>
<thead>
<tr>
<th>Type of coatings</th>
<th>Element</th>
<th>Mean values of wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Zn K</td>
<td>100.00</td>
</tr>
<tr>
<td>Zn–PF1</td>
<td>C K</td>
<td>2.79</td>
</tr>
<tr>
<td></td>
<td>O K</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Zn K</td>
<td>96.22</td>
</tr>
<tr>
<td>Zn–PF2</td>
<td>C K</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>O K</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>Zn K</td>
<td>95.03</td>
</tr>
</tbody>
</table>

Figure 3    SEM cross-sectional images of coatings: (a) Zn–PF1 hybrid coating; (b) Zn–PF2 hybrid coating (1000×).
It can be observed that the surface of Zn coating is made up of regular crystals with a uniform grain size. It can be easily seen that, zinc deposit displays the hexagonal zinc plates aligned parallel to the substrate. The arrangement of hexagonal plates can be clearly noticed (Fig. 4).

The hybrid coatings containing PF resin particles with a mean diameter size 0.1–5.0 μm into electrolyte solution change the topography of the coatings. Layers become uniform, with smaller grains, oriented at random (Fig. 5).

By increasing the mean diameter size of PF resin particles in the electrolytic bath to 6.0–10.0 μm the coating remains uniform with smaller grain size compared with pure Zn coating but relatively larger compared with Zn–PF1 coatings (Fig. 6).

In the presence of polymer particles the grain size of zinc crystals decreases because there exists a mechanism competition between nucleation and crystal growth.

Moreover, the incorporated particles are no longer agglomerated and concentrated at a particular region. So the big crystals of the zinc matrix have been reduced resulting in compact and uniform deposit. During composite electrodeposition, the PF resin particles are adsorbed onto the cathode surface, increasing the nucleation rate and retarding the crystal growth.

Roughness is a measure of surface topography. Roughness plays an important role in determining how a real object will interact with its environment. AFM is considered as one of the most powerful methods for surface roughness characterization, because of its accuracy, non-damage to the surface and non-vacuum condition (Feng et al., 2012; Mohamed et al., 2015; Tripathi and Singh, 2015). The values of surface roughness (Ra – average roughness and R_{RMS} – root-mean-squared roughness) determined by AFM method from histograms of the scanned surfaces are presented in Fig. 7.

Surface roughness evaluated by AFM method confirmed the optical aspect of surfaces and indicates that the inclusion of PF resin particles into zinc matrix reduces the dimension size of zinc crystals. The zinc deposit exhibits a higher roughness among all other coatings. This is because of the random distribution of thin hexagonal plates developed in the absence of PF resin particles parallel to the substrate surface. The Zn–PF resin hybrid coatings show a trend of decreasing roughness.
with the increased mean diameter size of particles. The smallest surface roughness for hybrid coatings with lower mean diameter size of particles comparative with surface roughness for zinc coating could be caused by agglomeration of polymer particles during co-deposition. For Zn–PF2 hybrid coating the possibilities for agglomeration are smaller, so that the value of coating roughness decreases.

Further, the zinc–resin hybrid coatings prepared with polymeric particles, showed better surface uniformity. The insertion of PF resin particles into zinc matrix could fill up the spaces between metal crystals and the coatings roughness has been diminished. The PF resin acts as reducing the crystal size of electrodeposited zinc during co-deposition.

### 3.3. Potentiodynamic polarization measurements

The corrosion investigation of each sample began with monitoring the open circuit potential after immersion into the testing solutions till reaching a relatively stable stationary value. Measurements were done by triplicate at least. The potentiodynamic polarization diagrams for coatings in 0.5 M sodium chloride testing solution after 30 min of immersion are presented in Fig. 8.

In corrosion, quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves according to the Stern–Geary equation (Velez et al., 2016).

$$i_{\text{corr}} = \frac{B}{R_p}$$  

(1)

while the Stern–Geary parameter $B$ was calculated using equation:

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

(2)

and $i_{\text{corr}}$ = corrosion current density; $R_p$ = polarization resistance; $b_a$ = anodic slope; $b_c$ = cathodic slope.

Different parameters such as corrosion current density ($i_{\text{corr}}$) and corrosion potential ($E_{\text{corr}}$), anodic ($b_a$) and cathodic ($b_c$) Tafel slopes derived from Fig. 8 using Tafel extrapolation are summarized in Table 2. Corrosion rates (CR) were calculated by Eq. (3):

$$CR \ (\text{mm/year}) = \frac{K \cdot i_{\text{corr}} \cdot (E_{\text{eq}} \text{ wt.})}{d}$$  

(3)

where $K$ – constant equal with 3272; $i_{\text{corr}}$ – corrosion current density calculated from Stern–Geary equation (A cm$^{-2}$); $E_{\text{eq}}$ wt. – the equivalent weight of zinc (g mol$^{-1}$ e$^{-}$) and $d$ is the density of the zinc metal (g cm$^{-3}$).

The corrosion potential is shifted to more negative values for Zn–PF resin hybrid coatings than corrosion potential for Zn coating. From experimental data it was observed that corrosion current density has a big value for Zn coating (72.62 lAc m$^{-2}$), smaller value for hybrid Zn–PF1 (26.62 lAc m$^{-2}$) and the smallest value for hybrid Zn–PF2 (18.40 lAc m$^{-2}$).

Potentiodynamic polarization measurements concluded that the Zn–PF resin hybrid coatings are most resistant in 0.5 M sodium chloride solution than that of Zn coating obtained by electrodeposition using same parameters (current density, time and stirring rate). The results confirm that the dispersed polymeric phase introduced into zinc electrolyte has an obvious corrosion inhibition effect on resulted hybrid coating surfaces.

This improvement of corrosion resistance could be due to the finer surface structure of hybrid coatings compared with pure zinc coating as well as to the incorporation of PF resin particles into hybrid coatings.

### 3.4. Electrochemical impedance spectroscopy measurements

Fig. 9(a and b) shows the Nyquist and Bode plots respectively, of Zn and Zn–PF resin hybrid coatings measured in 0.5 M sodium chloride solution after 30 min from immersion in the corrosive environment.

Two equivalent electrical circuits were used to model impedance data. The models used are presented in Fig. 10 and a good fitting between experimental and theoretical data was
achieved. Impedance parameters of coatings in 0.5 M sodium chloride solution were extracted from the models and the results obtained are listed in Table 3.

The EIS data for Zn and Zn–PF1 hybrid coatings were fitted using circuit from Fig. 10(a) (one time constant) and EIS data for Zn–PF2 hybrid coating were fitted using circuit from Fig. 10(b) (two time constants). On the Figs. 11(a–c) were represented experimental diagrams together with the simulation curves described by the fitting parameters using equivalent circuits from Fig. 10.

In the equivalent circuit used in Fig. 10(a), $R_e$ represents the electrolyte resistance, CPE is constant phase element and $R_p$ is polarization resistance of coatings. For Zn–PF2 coating a second relaxation process includes $R_1$ – coating resistance; $R_2$ – polarization resistance of polymer particles on the coating surfaces, $C_{\text{part}}$ – the pseudo-capacitance of polymer particles insulated on the surfaces. $R_e$ represents the electrolyte resistance. The polarization resistance of coating obtained with polymer (mean diameter size of particles 6.0–10.0 $\mu$m) is $R_p = R_1 + R_2$.

The CPE elements were used to account for the non-ideal frequency response in the equivalent circuit instead of capacitive components ($C_i$) (Imaz et al., 2014). Constant phase elements explain the depression of the capacitance semi-circle, which corresponds to several factors such as distributed surface reactivity, surface inhomogeneity, surface roughness, electrode porosity, impurities, dislocations or grain boundaries (Jorcin et al., 2006).

Table 2: Tafel parameters of Zn and zinc–resin hybrid coatings calculated from polarization potentiodynamic curves obtained after 30 min from immersion in solutions.

| Type of coatings | $E_{\text{corr}}$ (V/SSE) | $i_{\text{corr}}$ $10^{-6}$ (A cm$^{-2}$) | $b_\eta$ (V/decade) | $|b_\zeta|$ (V/decade) | $R_p$ from Tafel ($\Omega$ cm$^2$) | Corrosion rate (mm/year) |
|-----------------|--------------------------|---------------------------------|------------------|------------------|----------------------------|------------------------|
| Zn              | $-1.47 \pm 0.25$         | $72.62 \pm 4.35$                | $0.072 \pm 0.003$| $0.016 \pm 0.001$| $78.82$                   | $1.08$                 |
| Zn–PF1          | $-1.54 \pm 0.17$         | $26.62 \pm 2.27$                | $0.027 \pm 0.009$| $0.045 \pm 0.003$| $281.90$                  | $0.39$                 |
| Zn–PF2          | $-1.60 \pm 0.21$         | $18.40 \pm 1.15$                | $0.036 \pm 0.007$| $0.033 \pm 0.002$| $413.71$                  | $0.27$                 |
Figure 9   Nyquist (a) and Bode (b) plots for Zn and Zn–PF resin hybrid coatings in 0.5 M sodium chloride after 30 min from immersion.

Figure 10   Equivalent circuits used for fitting experimental impedance diagrams.
The impedance of CPE element \( Z_{\text{CPE}} \) is frequency-dependent and can be mathematically expressed as Eq. (4) (Hua et al., 2016):

\[
Z_{\text{CPE}} = \frac{1}{Qj/c_0^n}
\]

where \( Q \) is the frequency independent parameter, \( j \) is the imaginary number \( (j = \sqrt{-1}) \), \( \omega \) is the angular frequency \( (\omega = 2\pi f, f \) is the frequency) and exponent \( n \), defined as a CPE power is an empirical constant ranging from 0 to 1.

The constant phase element is characterized by two parameters, CPE–T and CPE–P. When CPE–P = 1 then CPE can be considered as a pure capacitor and when CPE–P is 0, CPE performs as a pure resistor. If CPE–P = 0.5, a 45° line is produced on the Complex-Plane graph. If a CPE is situated in parallel with a resistor, a Cole-Element (depressed semicircle) is produced. Usually a CPE is used in a model in place of a capacitor to compensate system inhomogeneity. A porous or a rough surface can determine a double-layer capacitance to appear as a constant phase element with CPE–P values between 0.9 and 1 (Lasia, 2002; Orazem et al., 2006; Córdoba-Torres et al., 2015).

The CPE–P parameter for Zn and Zn–PF1 hybrid coatings has the values 0.743 and 0.76, respectively. These values are typical for CPE behavior due to surface heterogeneities as Zn and Zn–PF1 resin hybrid coatings. Zn–PF2 coating has CPE–P = 0.86. For second loop it was found a \( C_{\text{part}} = 0.016 \) \( \text{F cm}^{-2} \) that indicate a decrease in active surface.

The Nyquist plots of Zn and Zn–PF1 hybrid coatings studied exhibit a single semicircle in the frequency range studied. However, the curves differ considerably in their size. This indicates that the same fundamental process is occurring on those two types of studied coatings, but over a different effective area in each case. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of those coatings involves a single time constant.

In general, the corrosion process of zinc and zinc coatings has two loops. For Zn and Zn–PF1 coatings the corrosion rate is higher. In that case the second loop is not possible to be observed.

The two loops in the Nyquist diagrams for Zn–PF2 hybrid coating indicate that the process consists of two relaxations or it is of two time constants. First loop could be associated with faradaic process occurring on metal and the second loop, appeared at low frequency part could be attributed to the corrosion resistance of particles that are incorporated on the surfaces. These particles with higher mean diameter size are the effect of insulating points on the surfaces, reducing the active surface area of coating and therefore increasing the polarization resistance of hybrid coating. The value of polarization resistance for Zn–PF2 resin hybrid coating was evaluated at 411.6 \( \Omega \text{cm}^{-2} \). This value represents the sum between polarization resistance of coating 275 \( \Omega \text{cm}^{-2} \) and 136.6 \( \Omega \text{cm}^{-2} \), the value for polarization resistance of insulating polymer particles on coating surface.

The analysis confirms that the incorporation of polymer particles enhances the corrosion resistance of hybrid coating samples. The polarization resistance obtaining from fitting curve indicates a small value for pure zinc coating (78.27 \( \Omega \text{cm}^{-2} \)) versus polarization resistance of resin hybrid coating samples.

<table>
<thead>
<tr>
<th>Type of coatings</th>
<th>( R_0 ) (( \Omega \text{cm}^2 ))</th>
<th>CPE–T (F cm(^{-2}))</th>
<th>CPE–P</th>
<th>( R_1 ) (( \Omega \text{cm}^2 ))</th>
<th>( C_{\text{part}} ) (F cm(^{-2}))</th>
<th>( R_2 ) (( \Omega \text{cm}^2 ))</th>
<th>( R_p ) (( \Omega \text{cm}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>13.68</td>
<td>0.00064</td>
<td>0.743</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>78.27</td>
</tr>
<tr>
<td>Zn–PF1</td>
<td>12.77</td>
<td>0.0006</td>
<td>0.76</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>282.5</td>
</tr>
<tr>
<td>Zn–PF2</td>
<td>12.60</td>
<td>0.0002</td>
<td>0.86</td>
<td>275</td>
<td>0.016</td>
<td>136.6</td>
<td>411.6</td>
</tr>
</tbody>
</table>

Table 3: Electrochemical parameters of impedance data for Zn and zinc–resin hybrid coatings in 0.5 M sodium chloride solution.
coatings (282.5 \( \Omega \) cm\(^2\) for Zn–PF1 hybrid coating, respectively 411.6 \( \Omega \) cm\(^2\) for Zn–PF2 hybrid coating). As a good polarization resistance it was evaluated for Zn–PF2 coating. The value of polarization resistance for Zn–PF2 hybrid coating was evaluated five times higher than polarization resistance of Zn coating.

As shown previously, the roughness of Zn–PF2 coating is lowest; so that the good protective corrosion for this type of coatings could be explained by blocking surfaces with polymer particles or by forming a better passive layer by interaction of zinc oxide deposit with polymer particles.

This improvement of anticorrosive properties for Zn–PF resin hybrid coating could also be explained by dissolution process that was more pronounced in Zn coating than that in Zn–PF1 and Zn–PF2 hybrid coatings. Results obtained from electrochemical impedance spectroscopy method show that PF resin particles included into zinc matrix decrease the dissolution process of zinc.

EIS results confirmed the higher corrosion resistance of Zn–PF resin hybrid coatings which are in good agreement with the potentiodynamic polarization measurements. The polarization resistance obtained for Zn coating was calculated at 78.82 \( \Omega \) cm\(^2\) with potentiodynamic polarization measurements and 78.27 \( \Omega \) cm\(^2\) with EIS measurements being in a good agreement for both applied methods. For Zn–PF1 hybrid coating the polarization resistance was 281.90 \( \Omega \) cm\(^2\) and 282.5 \( \Omega \) cm\(^2\) respectively. The values of polarization resistance of Zn–PF2 hybrid coating calculated with both electrochemical methods were 413.71 \( \Omega \) cm\(^2\) and 411.6 \( \Omega \) cm\(^2\) respectively. A good agreement was obtained also for polarization resistance values resulting from both applied electrochemical methods for Zn–PF hybrid coatings.

4. Conclusions

Zn–PF resin hybrid coatings were successfully deposited on steel substrates from solution containing 10 g/L PF resin particles with mean diameter size of 0.1-5.0 \( \mu \)m and 6.0–10.0 \( \mu \)m. Phenol–formaldehyde resin particles do not affect the electrodeposition process; they only modify the morphology and topography of the hybrid coatings obtained.

The hybrid coatings containing PF resin particles with a mean diameter size 0.1-5.0 \( \mu \)m into electrolyte solution change the topography of the coatings. The hybrid coating surface becomes uniform, with smaller grains, orientated at random.

By increasing the mean diameter size of PF resin particles in the electrolytic bath to 6.0–10.0 \( \mu \)m the coating remains uniform with smaller grain size compared with pure Zn coating but relatively larger compared with Zn–PF1 coatings.

The Zn–PF resin hybrid coatings show a trend of decreasing roughness with the increased mean diameter size of particles. Electrochemical measurements proved that the Zn–PF resin hybrid coatings are more resistant at corrosive attack in 0.5 M sodium chloride solution than pure zinc coating.

The polarization resistance calculated with both electrochemical methods indicates that the corrosion properties of conventional zinc coatings were significantly improved by the incorporation of PF resin particles into zinc matrix.

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