Electrochemical Characterizations of Epoxy Coatings Embedded by Modified Calcium Carbonate Particles

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ARTICLE INFO
Article history:
Received: 5 Aug 2019
Final Revised: 27 Nov 2019
Accepted: 30 Nov 2019
Available online: 09 May 2020
Keywords:
Epoxy Paints
Calcium Carbonate
Electrochemical Behavior
Wear Testing
3.5 wt% NaCl Solution.

ABSTRACT
In this paper, electrochemical behavior of epoxy paints embedded by modified calcium carbonate particles was investigated during exposure to 3.5 wt% NaCl solution. The precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) particles were utilized as inexpensive filler for epoxy paints. Electrochemical impedance spectroscopy (EIS), polarization tests and pin-on-disk method were used to determine the protective properties of epoxy paints on carbon steel substrates. GCC particles with the concentration of 20 wt% were more effective than PCC particles in increasing the corrosion resistance of epoxy paints; however, PCC particles affected obviously the reduction of friction coefficient of epoxy paints under wet condition (3.5 wt% NaCl solution). This behavior may be attributed to the small size and spherical shape of such particles. Values of the friction coefficient for epoxy paints were about 0.5-0.6 under dry condition. The coating resistance increased by about 99% in the presence of GCC particles in 20 wt% after 3 days of the immersion. In addition, equivalent electrical circuits suggested that the ion transport through defects in the paint layer is the controlling factor in the corrosion process after immersion for 7 days. Prog. Color Colorants Coat. 13 (2020), 213-222 © Institute for Color Science and Technology.

1. Introduction
Epoxy coatings are used in various applications due to superior mechanical properties, good adhesion to different substrates, and thermal stability [1-4]. In addition to enhanced mechanical, physical and corrosive properties of such materials, different fillers like rice husk ash [5, 6], SiO$_2$ [7, 8], zinc [9, 10], TiB$_2$ [11], graphite [12] are usually added to epoxy paints. It was found that the effect of such fillers on electrochemical behavior and other properties of produced composite materials depended on the shape, particle size, aggregate size, and the degree of dispersion of the fillers in the matrix [13]. Since CaCO$_3$ particles are inexpensive, available, insoluble in water, and stable at normal temperature, they are widely used in various industries such as paints, plastics and cermets [14, 15]. However, there are limited studies on the addition of CaCO$_3$ particles as reinforcement or filler into epoxy coatings. These investigations were summarized as follows.

Atta et al. [16] prepared various epoxy coatings which contained modified calcium carbonate nanoparticles. Their results demonstrated that the optimum content of CaCO$_3$ particles in epoxy coatings to produce hydrophobicity characteristics was 5 wt%. Boke [2] studied the effects of CaCO$_3$ particles size on the light scattering properties of the coatings. It was found that the replacement of CaCO$_3$ with TiO$_2$ particles could increase the spread rate and the efficiency of TiO$_2$ particles. Azadi et al. [17] investigated the influence of CaCO$_3$ addition to epoxy paints in order to enhance the physical and mechanical properties of such coatings.
Their results showed that such addition provided higher elongation, more hardness and wear resistance of composite coatings with respect to the pure epoxy paint. Yu et al. [18] prepared various epoxy resin/CaCO$_3$ nanocomposites with nanoparticles content varied from 5 to 15 wt%. It was reported that the impact resistance and the cupping property decreased by increasing the coating thickness. Jain et al. [13] investigated the curing characteristics of CaCO$_3$/epoxy nanocomposites. The content of CaCO$_3$ in such specimens varied from 2 to 10 wt%. Their results demonstrated that the incorporation of CaCO$_3$ nanoparticles in the epoxy resins enhanced the rigidity, the thermal stability, and the toughness of resins. Mohan et al. [14] studied the effect of egg-shell nanoparticles on the mechanical, physical, and thermal properties of epoxy coatings. It was shown that the water uptake of epoxy composites embedded by the egg-shell nanoparticles decreased with respect to unfilled epoxy bases.

Thus, due to the limited research about the effect of CaCO$_3$ particles on corrosion properties of epoxy coatings, the aim of the present paper is to investigate the electrochemical behavior of epoxy paints embedded by modified CaCO$_3$ particles in 3.5 wt% NaCl solution. Both ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) particles were used in two concentration (10 and 20 wt%) as low-cost fillers for epoxy paints. In addition, the egg-shell particles as a source of natural calcium carbonate were used as filler to compare the GCC and PCC particles.

2. Materials and Experiments

Commercial epoxy paint was prepared and applied on low carbon steels (St-37) by the brush. Before applying the paint, substrates were polished with SiC abrasive paper to 1000 grit and later degreased with acetone. A white color two-component phenolic epoxy (Interline 984) paint was utilized. The details of the utilized epoxy paints can be found in our previous study [17]. Such paints exhibited an average dry thickness of 1 mm. The curing time was about 24 hrs at 39±2 °C. The details of the prepared samples are reported in Table 1. For a better comparison, the unfilled epoxy paint properties were also investigated as the blank specimen.

The coated PCC, GCC and egg-shell particles were used as fillers. It is reported that egg-shells contain about 95% CaCO$_3$ [14]. It was found that the hydrophobicity of GCC particles increased obviously when coated with the stearic acid [19]. Thus, stearic acid (CH$_3$(CH$_2$)$_{16}$COOH) was used as the surface modifying agent for CaCO$_3$ particles. More details of filler properties are available elsewhere [17]. Fillers with the concentrations of 10 and 20 wt% were used. The morphology of the reinforcement particles was examined under scanning electron microscopy (SEM, Philips-XL30).

Both tests of electrochemical impedance spectroscopy and polarization were done with the test area of 1 cm$^2$. The corrosive environment was the NaCl 3.5 wt% solution. Electrochemical data were obtained through a potentiostat device (Autolab-OGF500 model). A three-electrode cell was applied; saturated calomel electrode, specimen, and the platinum foil as the reference, working, and auxiliary electrodes, respectively. The applied frequency range was from 100 kHz to 10 mHz. Samples were immersed in the corrosive environment for 3 and 7 days for EIS tests (a solution of 3.5 wt% NaCl). In addition, the immersion time for polarization test was about 1 day. The fitting measurement was performed by chi-squared values, which were interpreted by the Z-View software.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Filler type</th>
<th>Filler content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-PCC</td>
<td>PCC</td>
<td>10</td>
</tr>
<tr>
<td>20-PCC</td>
<td>PCC</td>
<td>20</td>
</tr>
<tr>
<td>10-GCC</td>
<td>GCC</td>
<td>10</td>
</tr>
<tr>
<td>20-GCC</td>
<td>GCC</td>
<td>20</td>
</tr>
<tr>
<td>10-E</td>
<td>Egg-shell</td>
<td>10</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Wear tests were done by utilizing a pin-on-disc wear tester according to ASTM G99-05 by a steel pin (3 mm in diameter and the hardness of 60 RC) with the normal load of 2.2 N and the distance of 30 m at 25 °C. The sliding velocity between the pin and the rotating disc was about 0.1 m/s. Dry and wet (3.5 wt% NaCl) conditions were adopted for wear testing. The scheme of the wet condition is presented in Figure 1 [20].

3. Results and Discussion

3.1. Morphology of filler particles

SEM images of GCC and PCC particles are shown in Figure 2. The GCC particles had a mean particle size of 1 µm with disordered morphology; however, the mean particle size of PCC particles was about 0.4 µm with a semi-spherical shape. It was reported that the morphology of filler particles affected the properties of the final composites [13].

3.2. EIS test results

Bode and Nyquist plots for various specimens after immersion for 3 days in 3.5 wt% NaCl solution are shown in Figures 3a and c, respectively. The lowest and the highest absolute impedance values were related to 20-PCC and 20-GCC specimens, respectively. The corrosion rate of epoxy paints decreased when GCC particles were added to the paint as filler. More reduction was observed when the content of GCC particles in the epoxy paint increased from 10 to 20 wt%. The diameter of the arc in the Nyquist diagrams increased for 10-GCC and 20-GCC specimens with respect to that of the blank one. It was found that particles with the optimum size could act as obstacles for the diffusion of corrosive ions from the aqueous environment toward the metallic surface [5, 21]. Due to the similar curves for most specimens in Nyquist plots, it was found that the same corrosion mechanism occurs on the surface of all specimens [22]. However, for the 20-GCC specimen, another electrical element such as the Warburg diffusion element can be added to the electrical circuit. Such resistance is attributed to the diffusion resistance. The value of Ws-R was about 0.1 KΩ.
Bode, Nyquist and the phase angle plots for various specimens after immersion for 7 days are shown in Figures 3b, d and e, respectively. The lowest and the highest absolute impedance values were related to the blank specimen and the 20-GCC specimen, respectively. In addition, the diameter of the arc in the Nyquist diagrams increased in the presence of fillers in the epoxy paint. The lowest phase angles were about -80° and -50° for the 20-GCC and the blank specimens, respectively. It was reported that the higher negative phase angle showed higher resistance against corrosion [23]. Under this condition, all types of fillers were suitable to decrease the corrosion rate of the epoxy paint. More reduction was observed by increasing the amount of GCC particles from 10 to 20 wt%; however, such a phenomenon was not observed for PCC particles. Figure 3e shows that the electrochemical behavior of the epoxy paint without filler particles changed in comparison with other specimens. The lowest phase angle was observed at a low frequency of 1Hz for epoxy paint; however, other specimens showed the lowest phase angle at a higher frequency of 104 Hz. This phenomenon was associated with the barrier protection of filled epoxy paint. A similar trend was also reported by Longhi et al. [3]. It was reported that when the electrolyte penetrated into the paint, the lowest phase angle (about -50°) would be observed in the medium frequency in the phase angle plot. It was noticeable that by increasing the immersion time from 3 to 7 days, the absolute impedance (Log Z) decreased from 4.2-9.2 to 2.4-7.2 kΩ. Such behavior demonstrated that different fundamental processes occur on the surface after increasing the immersion time. Such an event changes the suggested equivalent circuit models. In addition, in the frequency range of 10² to 10⁵, the absolute impedance decreased for both immersion times. Totally, GCC particles were more effective than PCC particles in raising the corrosion resistance of epoxy paints. It was found that the permeability of the resin alters when the CaCO₃ particles are added to the matrix [24]. Moreover, it was reported that by coating the GCC particles with stearic acid, the particle-particle interactions in the polymeric matrix reduced and led to better dispersion of filler in the matrix [19]. The fitting of the experimental data was performed by the suggested equivalent circuit models as shown in Figure 4.

Such equivalent circuits contain solution resistance (Rₛ), constant phase elements of the double layer and the coating (Cₘ and Cᵣ), as well as the resistance of the coating and the double layer (Rᵣ and Rᵣ). The CPE is usually used instead of the ideal capacitance when the behavior of the coating was not ideal due to the surface roughness and other adsorption effects [21]. A similar circuit was reported by other researchers [9, 23, 25]. The coating resistance increased by 99% after immersion for 3 days when 20 wt% GCC particles were added to the epoxy paint. The increase in corrosion resistance was 81.9% for the 20-GCC specimen compared to the pure epoxy paint after 7 days of immersion. In addition, the related parameters are listed in Tables 2 and 3. Table 2 shows that the Rp values for epoxy paints which contained GCC particles were higher than those of the blank ones. Moreover, the CPE had the lowest value for the 20TGCC specimen and the highest for the 20TPCC specimen. It was found that the lower CPE value is attributed to the higher thickness of water adsorption by the surface of the paints to create double layers [26]. Thus, the adsorption of water through GCC particles on the surface of paints was higher than PCC particles. Totally, the differences in the electrochemical behavior of epoxy paints can be explained by the different rates of oxygen reduction on the surface of epoxy paints. In this situation, the electrolyte did not penetrate to the substrate after 3 days. In all, the amount of water adsorption on the surface of paints was responsible for changing the electrochemical behaviors after 3 days for various epoxy paints with different filler types.

### Table 2: The fitted data for the equivalent circuit model in Figure 3a for the immersion time of 3 days.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Rₛ (kΩ)</th>
<th>Cᵣ (nF)</th>
<th>n</th>
<th>Rᵣ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-PCC</td>
<td>2.56</td>
<td>82.0</td>
<td>0.80</td>
<td>0.095</td>
</tr>
<tr>
<td>20-PCC</td>
<td>2.50</td>
<td>99.0</td>
<td>0.78</td>
<td>0.002</td>
</tr>
<tr>
<td>10-GCC</td>
<td>2.78</td>
<td>9.0</td>
<td>0.88</td>
<td>0.400</td>
</tr>
<tr>
<td>20-GCC</td>
<td>3.32</td>
<td>1.0</td>
<td>0.90</td>
<td>11.00</td>
</tr>
<tr>
<td>10-E</td>
<td>3.34</td>
<td>43.0</td>
<td>0.77</td>
<td>0.181</td>
</tr>
<tr>
<td>Blank</td>
<td>3.67</td>
<td>37.0</td>
<td>0.92</td>
<td>0.263</td>
</tr>
</tbody>
</table>
Figure 3: (a) Bode plot after 3 days, (b) Bode plot after 7 days, (c) Nyquist plot after 3 days, (d) Nyquist plot after 7 days and (e) phase angle plot after 7 days for various specimens.

Figure 4: Suggested equivalent circuits for the immersion time of (a) 3 days and (b) 7 days.
The equivalent circuit model changed when the immersion time in the corrosive environment increased. The corrosive ions penetrate through the defects of paint layers and reach the steel substrate, as shown in Figure 5. Since modified CaCO$_3$ particles are not soluble in the water, filled epoxy paints showed better corrosion resistance after 7 days of immersion. Table 3 shows that $R_{coat}$ and $R_{corr}$ values for epoxy paints which contained CaCO$_3$ particles as fillers were higher than those of the blank specimen. The CPE values for filled epoxy paints were lower than the blank specimen due to the lower penetration of corrosive molecules through the coating. When the immersion time increased from 3 to 7 days, the capacitance increased due to higher water absorption. Thus, it was suggested that ion transfer through the paint defects is the controlling factor in the corrosion process after 7 days. Similar behavior was also found in other research [23]. Consequently, corrosion properties of such epoxy paints depended on several parameters such as size, concentration, type, and the morphology of CaCO$_3$ particles as fillers in the epoxy paints. As the size of GCC particles was larger than PCC particles, they could act as better obstacles for the diffusion of corrosive ions through the paint toward the substrate, as shown in Figure 5. However, agglomeration occurred when the amount of PCC particles was increased from 10 to 20 wt%. Thus, the diffusion of corrosive ions was done more easily with respect to the 10-PCC specimen with better dispersion of particles in the paint. It was found that when the filler particles were small, particles had a tendency to agglomerate in the matrix due to the high surface energy [27].

In the high frequency, the resistance of the electrolyte ($R_S$) was a key factor. In the intermediate frequency range, the system was controlled by $C_{coat}$ and $R_{coat}$, while in low frequencies ($10^{-3}$ to $10^{-1}$ Hz), the impedance was related to $C_{dl}$ and $R_{corr}$ [28]. Polarization plots of various specimens are shown in Figure 6. In addition, the related parameters extracted from polarization tests including corrosion current density ($I_{corr}$), corrosion potential ($V_{corr}$), anodic slope ($\beta_a$), and cathodic slope ($\beta_c$) are reported in Table 4.

Table 3: The fitted data for the equivalent circuit model in Figure 3(b) for the immersion time of 7 days.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$R_s$ (Ω)</th>
<th>$C_{coat}$ (µF)</th>
<th>n</th>
<th>$R_{coat}$ (kΩ)</th>
<th>$C_{dl}$ (µF)</th>
<th>n</th>
<th>$R_{corr}$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-PCC</td>
<td>34.6</td>
<td>46</td>
<td>0.77</td>
<td>12</td>
<td>8.90</td>
<td>0.71</td>
<td>1.03</td>
</tr>
<tr>
<td>20-PCC</td>
<td>35.2</td>
<td>140</td>
<td>0.75</td>
<td>8</td>
<td>53.00</td>
<td>0.70</td>
<td>0.61</td>
</tr>
<tr>
<td>10-GCC</td>
<td>32.9</td>
<td>17</td>
<td>0.85</td>
<td>13</td>
<td>2.60</td>
<td>0.74</td>
<td>1.09</td>
</tr>
<tr>
<td>20-GCC</td>
<td>36.6</td>
<td>2</td>
<td>0.82</td>
<td>210</td>
<td>0.40</td>
<td>0.79</td>
<td>2.44</td>
</tr>
<tr>
<td>10-E</td>
<td>32.9</td>
<td>97</td>
<td>0.75</td>
<td>11</td>
<td>11.00</td>
<td>0.75</td>
<td>0.94</td>
</tr>
<tr>
<td>Blank</td>
<td>30.5</td>
<td>440</td>
<td>0.89</td>
<td>0.1</td>
<td>380.00</td>
<td>0.82</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Figure 5: Schematic representation of solution diffusion through the paint after 7 days for (a) blank specimen, (b) 20-GCC and (c) 10-PCC.
Similar to EIS test results, when the immersion time was low, GCC particles acted as effective particles in order to decrease the corrosion current density to about 83% with respect to other CaCO$_3$ fillers. The corrosion potentials for all specimens were in the range of -450-550 mV. When CaCO$_3$ fillers were added to the epoxy paints, both anodic and cathodic Tafel slopes changed; however, the anodic slope reduced significantly with respect to the pure epoxy paint. Such an observation showed that the anodic reaction which was attributed to the dissolution of substrate decreased in the presence of CaCO$_3$ fillers.

### 3.3. Wear test results

Figure 7 shows friction coefficient curves versus the distance for two specimens during wear testing. These specimens showed the lowest and the highest corrosion resistance among filled epoxy paints in the EIS tests. In addition, the mean value of coefficient of friction (COF) for various specimens under wet and dry conditions is reported in Table 5.

As shown in Figure 7, under wet condition, the deviation of COF during wear resistance was lower than that under dry condition. It was reported that under dry condition, the remained wear debris on the surface fluctuates the COF; however, the wet condition during wear testing removes such particles from the wear track [29]. The mean value of COF for specimens under wet condition was higher than dry condition. When the wear test is performed under wet condition and in the presence of the corrosive environment (3.5 wt% NaCl solution), the corrosion products raise the friction coefficient. In addition, the PCC particles were more effective than other types of CaCO$_3$ particles to lower the friction under both wear conditions. Such behavior is attributed to the small size and spherical shape of PCC particles as filler in the epoxy paint. The changes in the potential versus the wear time with respect to the SCE potential are also reported, as shown in Figure 8.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (µA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-PCC</td>
<td>-111.2</td>
<td>83.3</td>
<td>-510</td>
<td>0.455</td>
</tr>
<tr>
<td>20-PCC</td>
<td>-207.9</td>
<td>144.0</td>
<td>-450</td>
<td>5.28</td>
</tr>
<tr>
<td>10-GCC</td>
<td>-366.1</td>
<td>390.6</td>
<td>-525</td>
<td>0.135</td>
</tr>
<tr>
<td>20-GCC</td>
<td>-308.7</td>
<td>142.4</td>
<td>-550</td>
<td>0.024</td>
</tr>
<tr>
<td>10-E</td>
<td>-390.5</td>
<td>155.4</td>
<td>-491</td>
<td>0.153</td>
</tr>
<tr>
<td>Blank</td>
<td>-243.4</td>
<td>917.3</td>
<td>-483</td>
<td>0.147</td>
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</table>
Table 5: The mean value of COF values in wear testing for wet and dry conditions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mean COF value in wet condition</th>
<th>Mean COF value in dry condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-GCC</td>
<td>0.75</td>
<td>0.60</td>
</tr>
<tr>
<td>20-PCC</td>
<td>0.60</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Figure 7: COF versus wear distance for 20-GCC and 20-PCC specimens (a) under wet and (b) dry conditions.

Figure 8: The potential versus the time during wear testing for (a) 20-GCC and (b) 20-PCC specimens.

It was shown that the potential decreased during wear testing. Such reduction was -550 to -585 mV for the 20-GCC specimen and -505 to -540 mV for the 20-PCC specimen. As the condition of specimens was not stable during wear testing, the potential changed continuously. A similar trend was also reported by other studies [29, 30]. During wear testing, the roughness of surface hence the adsorption of water on the surface increased. In addition, formation of more pinholes and weakening of coating or delamination of the paint layer from the metal surface occurred. Thus, such behavior indicated a reduction in the corrosion resistance. It was reported that corrosion properties of coatings strongly affect their wear behavior [31].

4. Conclusion
In this paper, experimental results obtained from electrochemical impedance spectroscopy (EIS) and polarization tests showed that the protective properties of epoxy paints filled with modified calcium carbonate particles on carbon steel substrates in 3.5 wt% NaCl solution improved with respect to unfilled epoxy coatings. When 20 wt% GCC particles were added to
the epoxy paint, the coating resistance increased by about 99% compared to the pure epoxy paint after 3 days; however, the corrosion resistance of epoxy paints raised by about 81.9% after immersion for 7 days. Equivalent electrical circuits suggested that ion transport through the defects in the paint layers may be the controlling factor during the corrosion process after immersion for 7 days. Moreover, polarization test results depicted that about 83% reduction in corrosion current density observed for the 20-GCC specimen comparing to the blank one. In addition, the PCC particles were more effective in decreasing (by about 0.6) the friction coefficient of the epoxy paint under wet condition. The potential decreased from -505 to -540 mV during wear testing for the 20-PCC specimen.

5. References


2. J. W. P. Boke, Calcium carbonate particle size effects on titanium dioxide light scattering in coatings, Master thesis, the Faculty of California Polytechnic State University, United State, 2013.


How to cite this article: