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Evaluation of corrosion protection properties of epoxy coating containing sol-gel surface modified nano-zirconia on mild steel

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Abstract

In this study, the effect of surface modified nano-zirconia (nano-ZrO₂) on the corrosion protection of epoxy coating on mild steel was investigated. An organosilane (trimethoxy methyl silane) was used as a surface modifier to improve the dispersability of the inorganic nanoparticles in the organic coating matrix. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to characterize the sol-gel surface modified nanoparticles. The dispersability of the modified and unmodified nano-zirconia in epoxy coating was examined by field emission-scanning electron microscopy (FE-SEM). Electrochemical impedance spectroscopy (EIS) and salt spray were employed to assess corrosion protection performance of the epoxy coatings. Results showed improved corrosion protection in the presence of the surface modified nanoparticles. Mechanical properties of the coatings were also found to be improved in the presence of modified nanoparticles in tensile and hardness measurements.

Keywords: Nano-ZrO₂, Surface modification; Organosilane; Corrosion; Mild steel.

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1. Introduction

The mild steel is wildly used in construction and many industries such as automotive, military, commercial machines, marine, oil and chemical industries as one of the most significant raw materials due to its good mechanical properties and low cost \(^1,^2\). However, its corrosion resistance needs to be improved in corrosive environments. Organic coatings are generally used to provide higher corrosion resistance for mild steel. Organic resins based on epoxy, urethane, phenolic and vinyl ester are wildly used as a matrix in polymeric coating with high corrosive protection performance \(^3\). However, the corrosive agents such as oxygen, water and ions more or less can penetrate to all of the organic resin binders and cause metal-coating interface disbonding (adhesion loss) and corrosion \(^4,^5\). It is shown that incorporation of corrosion inhibitors \(^6–^8\), anticorrosion pigments \(^9–^11\), adhesion promoters and surface modifiers \(^12–^16\) into the organic resin binders can improve the corrosion protection properties.

Nano composite polymeric coatings are have found great interest in the functional and high performance coatings \(^17\). It has been found that the inclusion of nano-fillers such as clay \([19,36,37]\), titanium oxide (TiO\(_2\)) \([32,38,39]\), silica (SiO\(_2\)) \([40–43]\), silver oxide (Ag\(_2\)O) \([44,45]\) and zirconia (ZrO\(_2\)) \([4,37,46]\) could enhance corrosion protection due to the high surface area. However, application of inorganic nanoparticles in the organic coatings needs great care as the incompatibility could result in defects in the coatings. Organosilanes can be used as surface modifiers for inorganic nanoparticles \(^18,^19\). They have a general chemical structure of \((\text{RO})_3\text{SiX}\) where RO is a hydrolysable alkoxy group and X is an organofunctional group such as methacrylate, amine, epoxy and alkyl groups. It has been shown that silane functionalization of iron oxide and chromium oxide nanoparticles could greatly enhance the corrosion protection and mechanical properties of polyurethane coatings compared to the
unmodified nanoparticles. Zirconia is well known for its excellent mechanical, physical and chemical properties. This paper intends to study the effect of silane modification of nano-ZrO₂ on the corrosion protection properties of epoxy coating by means of electrochemical impedance spectroscopy (EIS) and salt spray.

2. Experimental

2.1- Materials

Epoxy resin (Epikote 828) and polyamine hardener (Epikure F205) were obtained to prepare epoxy coatings. Nano-zirconia was purchased from US-Nano Company with a particle size of 30-40 nm and purity of 99 %. Organosilane (trimethoxy methyl silane) was obtained from Aldrich with purity of 95 %.

The mild steel panels (St12) with the elemental composition shown in Table 1 were used as substrate.

Table 1

2.2- Surface modification of zirconia nanoparticles

In the first step, 90 mL ethanol was mixed with 5 mL water; then, 5 mL organosilane was added into mixture and stirred at 250 rpm for 24 h to perform hydrolysis reactions of silane agent at room temperature. The pH of hydrolysis step was adjusted at 2 with drop-by-drop addition of 1 M acetic acid solution. In the second step, 8 g nano-ZrO₂ was added into mixture. The pH was adjusted at 5.5 with drop-by-drop addition of 1 M ammonia solution and stirred at 350 rpm for 2.5 h to perform surface modification reaction in sol-gel route. In the third step, the mixture was centrifuged at 4000 rpm and residue was washed five times with DI water and dried in vacuum oven at 40 °C for 72 h. The scheme of surface modification of zirconia nanoparticles has been shown in Fig. 1.
2.3- Preparation of coating samples

The nanocomposite coatings were prepared by direct mixing of 2 wt. % unmodified and modified ZrO$_2$ nanoparticles with epoxy resin by high speed mixer (3000 rpm) for 30 min after that, for complete dispersion of nanoparticles 45 cc of the mixture ultrasonicated for 5 min under condition of 90 W power, 25 kHz frequency, 1 min pulse on and 2 min pulse off. Ice-water bath was used for prevention of temperature rising during ultrasonication process. Also a blank epoxy resin containing no nanoparticle was prepared as a reference sample. As ultrasonication may lead to partial polymer chain scission, the blank epoxy resin was also ultrasonicated to ensure that all the conditions for comparison are the same except pigment content. The mild steel plates (10 cm × 15 cm × 0.2 cm) abraded by emery papers no. 600, 800, and 1000 were cleaned by acetone. Then, the epoxy component containing unmodified and modified ZrO$_2$ nanoparticles were mixed with polyamine hardener at stoichiometric ratio (1:0.45 weight ratio of epoxy resin to polyamine). Immediately after mixing of epoxy coatings with hardener, the coating materials were applied on the cleaned mild steel substrates by a film applicator (Elcometer 3520 Baker). The coated steel plates remained at room temperature (25±5 °C and 30±5 RH) for 12 h. To ensure complete curing, the plates were placed in an oven at 80 °C for 2 h. The dry coatings thickness determined by Elcometer 456 was 25±3 µm. A surface area of 75±3 cm$^2$ of the coated mild steel plates was considered to expose salt spray while the rest area was sealed using a hot melt beeswax-colophony mixture. Coating was X-scribed before exposing salt spray. For EIS measurements, the exposed area to 3.5 wt. % NaCl solution was circular with diameter of 1 cm. Triplicates were prepared of each specimen type for EIS and salt spray measurements.

2.4- Techniques and analyses
To evaluate grafting of silane on the surface of ZrO$_2$ nanoparticles Fourier transform infrared spectroscopy (FTIR) was employed. FTIR was measured by Tensor 27 (Bruker, Germany) within wavenumber range of 400-4000 cm$^{-1}$ using KBr pellet. Thermogravimetric (TG) analyzer L-8011 (LINSEIS, Germany) was used under oxygen atmosphere within the temperature range of 25 to 800 ºC and heating rate of 10 ºC/min to evaluate the extent of silane grafting onto the nanoparticles.

A compactstat (Ivium, Netherland) was employed for electrochemical impedance spectroscopy (EIS) measurement on the coated specimens after exposure to 3.5 wt. % NaCl solution for 30 days. The measurements were conducted at open circuit potential (OCP), with 10 mV peak to peak perturbation within frequency range of 100 mHz–10 kHz. A three-electrode cell including Ag/ AgCl (3 M KCl) as a reference electrode, platinum as a working electrode and coated specimen as a working electrode was used to conduct EIS measurements. The Iviumsoft was used to analyze the EIS data. The corrosion protection performance of the coatings was also evaluated by salt spray exposure (ASTM B 117).

The mechanical properties of coatings were measured by the universal tensile machine Roell-Z010 (Zwick, Germany) at room temperature (24±3 ºC and 30±3 RH) with a loading rate of 1 mm/min. Vickers micro-hardness was also measured from the coatings at room temperature.

The dispersion of epoxy coating containing unmodified and modified nano-ZrO$_2$ and the morphology of the cross section of coatings were evaluated by field emission-scanning electron microscope (FE-SEM) Model Mira3 and energy dispersive X-ray (EDS) (Tescan, Czech Republic).

3. Result and Discussion

3.1- FTIR results
FTIR spectroscopy was used to evaluate silane grafting onto the surface of nano-ZrO$_2$. The unmodified and modified nano-ZrO$_2$ particles were placed in vacuum oven at 50 ºC for 24 h. The obtained spectra have been shown in Fig. 2. The assignments of the main FTIR bonds for unmodified and modified nano-ZrO$_2$ particles are tabulated in Table 2.

**Figure 2**

Fig. 2a shows the spectra of the unmodified nanoparticles. The main absorption bands at 514, 578 and 745 cm$^{-1}$ are the characteristic peaks of Zr-O bonds in nano-ZrO$_2$ structures. The peaks at 2855 and 2960 cm$^{-1}$ in spectrum of modified nanoparticles, Fig. 2(b) were assigned to asymmetric stretching of C-H in CH$_3$ section of the organosilane $^5,13,21$. Also the absorption band observed at 1078 cm$^{-1}$ could be assigned to Zr-O-Si bond on the surface modified nanoparticles $^{26}$. In addition, the asymmetric vibration of Si-O-Si bond was appeared at 1181 cm$^{-1}$ indicating successful grafting of silane onto the surface of the nanoparticles. The bending and stretching vibration of –OH groups were observed at 1630 and 3424 cm$^{-1}$, respectively which could be attributed to the adsorbed water on the surface $^{13,21}$. The lower intensity of OH bending and vibration bands indicates lower water adsorption or higher hydrophobicity for the surface modified particles.

**Table 2**

3.2- TGA results

TGA themograms of unmodified and modified nano-ZrO$_2$ particles are shown in Fig. 3.

**Figure 3**

The weight loss was occurred in two stages. The first stage took place in temperature range of 40-200 ºC, the physically adsorbed water was evaporated. The weight loss attributed to this region was about 0.4 and 0.2 wt. % for unmodified and modified nano-ZrO$_2$ particles,
respectively. This result shows that modified nano-ZrO₂ powder has less tendencies to adsorb water molecules because of grafting of silane which made the surface more hydrophobic. This result confirms the lower intensity of absorption bands related to O-H vibrations for the modified particles in the FTIR spectra. The second stage of weight loss was occurred in the temperature range of 200-690 °C. The corresponding weight loss for untreated particle was about 1.3 wt. % which can be attributed to release of water molecules due to condensation reaction of hydroxyl groups on the surface of particles (dehydroxylation). However, the weight loss for modified particles was higher than unmodified particles which was about 2.3 wt. %. Beside dehydroxylation, thermal degradation of organic section of grafted silane onto the surface of the nano-ZrO₂ particles could take place in this region. Therefore, the extent of grafting could be estimated to 1 wt. % (2.3 – 1.3 wt. %) for the degradable section of the organosilane.

3.3- EIS results

The Nyquist plots obtained from EIS measurements for coated mild steel specimens immersed in 3.5 wt. % NaCl solution for 30 days have been displayed in Fig. 4.

**Figure 4**

The radius of semicircles in Nyquist plots, indicating impedance of coated electrodes are increased by addition of unmodified and modified ZrO₂ nanoparticles, respectively. The largest semicircle in Figure 4 is obtained for epoxy coating containing modified ZrO₂ nanoparticles.

The phase angle and impedance vs. frequency for coated specimens has been shown in Fig. 5.

**Figure 5**
According to Figure 5, the impedance at 100 mHz representing the performance of the specimen at near DC current condition is around 30 kOhm.cm$^2$, 400 kOhm.cm$^2$ and 40 MOhm.cm$^2$ for the blank epoxy coating, and the coatings containing unmodified and modified zirconia nanoparticles, respectively. In addition, the phase angle at 10 kHz is near -90 degree for epoxy coating containing modified nano-ZrO$_2$ particles. The most positive phase angle is obtained around -40 degree for the blank epoxy coating. It has been showed that when the current tends to pass through the coating capacitance at high frequency instead of coating resistance (due to high coating resistance), coating shows capacitive behavior where the phase angle of high frequency is near -90 degree. In contrast, when the current passes through the coating resistance (due to low coating resistance), coating shows resistive behavior where the phase angle at high frequencies shifts toward positive degrees $^{20,27,28}$. Consequently, the coating containing modified nanoparticles showed the most capacitive behavior (best performance) among the coated samples.

Figure 6 shows the equivalent circuits used to fit EIS data for different coatings. In this figure, $R_s$, $R_f$, $R_{ct}$, CPE$_{dl}$, CPE$_f$ and $W$ represents solution resistance, film resistance, charge transfer resistance, constant phase element of double layer and that of deposited film and Warburg element, respectively. The used circuits in Fig. 6a and Fig. 6b represent a single-time constant behavior instead of a two-time constant behavior which is often associated with the porous polymeric coatings where corrosion takes place beneath the coating. Interestingly, although some of the coatings were deteriorated and rust spots were visible beneath the coatings, all the spectra save the blank coating's spectra, represented single time constant circuit. In addition, it was not possible to fit the spectra with two-time constant as there was large error for the fitted parameters. It seems that the time constant of coating was too close to that of corrosion; therefore, the coatings screened corrosion process electrochemically. The electrochemical parameters extracted from the EIS data are listed in Table 3.
The $Y_0$ and $n$ parameters presented in Table 3 are the CPE admittance and CPE exponent, respectively. According to the values of $R_f$ listed in Table 3, inclusion of nanoparticles in the epoxy coating led to increase of coating film resistance, which could be related to the barrier effect of the nanoparticles. Considering the normal time-constant distribution, the effective coating capacitance ($C_f$) was calculated from the corresponding CPE parameters according to Eq. 1:

$$C_f = \frac{(Y_0R_f)^\frac{1}{n}}{R_f}$$ \hspace{1cm} (1)

The $C_f$ values derived from the above equation were 37.6, 0.29 and 0.21 nF/cm$^2$ for the epoxy coatings containing no nanoparticle, unmodified nanoparticle and modified nanoparticle, respectively. Considerable decrease of coating capacitance in the presence of modified nanoparticle could be related to the significant decrease in water penetration in the coating. Incompatibility of the particle and polymeric matrix may lead to defect formation at coating/particle interface. It seems that surface modified nanoparticles have better interaction with the epoxy matrix compared to the unmodified nanoparticles.

3.4- Salt spray exposure

The appearance of the epoxy coating samples after 240 h of exposure to salt spray are shown in Fig. 7.

It is clear from Fig. 7 that the corrosion protection of epoxy coatings increased due to addition of nanoparticles to epoxy coating. The surface modification of nanoparticles

Figure 6

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considerably improved the corrosion protection properties of the epoxy coating in comparison with unmodified nanoparticles. Disbonded coating was removed by a sharp blade, and the delaminated area of the coatings was tabulated in Table 4.

Table 4

The delamination area of the coatings from mild steel substrates decreased by addition of nanoparticles in the epoxy coatings. The epoxy coating containing modified nano-ZrO$_2$ particles has the lowest delamination from mild steel probably due to less water penetration in the coating observed in the EIS results. The salt spray exposure results are in good agreement with EIS results where the addition of nanoparticles, especially surface modified one, greatly increased the corrosion protection performance in immersion condition.

3.5- Tensile test results

The surface modification of the nanoparticles can change the surface chemistry and consequently alters their interactions and compatibility with the polymer coating matrix. The change in compatibility of particle and polymer not only affects the corrosion protection performance but also the mechanical properties. The mechanical properties could readily show the change in the interaction of filler and matrix. Therefore, epoxy coating materials prepared according to the mentioned method (see section 2.3) were casted in a wooden mold (ASTM D-628) prepared by laser machine. After casting of epoxy coating material, the filled wooden mold was placed in vacuum oven at 100 ºC for 1 h to cure. Triplicates were prepared for each specimen. Figure 8 shows the tensile specimens after fracture.

Figure 8

The results of tensile test (stress-strain curve) from the blank epoxy and epoxy containing unmodified and modified nanoparticles have been shown in Fig. 9.
As showed in Fig. 9, the surface modification of nanoparticles influenced the mechanical properties of the epoxy coating effectively. The energy at break and maximum load of the epoxy coating are listed in Table 5.

Table 5

According to Table 5, incorporation of unmodified nanoparticles in epoxy coating considerably improved the mechanical properties. Incorporation of unmodified nanoparticles had limited impact on mechanical behavior of the epoxy coating. According to Fig. 9, by addition of modified nanoparticles in epoxy a transition from brittle to tough behavior occurs. Grafting silane structure onto the particles surface increases the physical interaction between particles and matrix dramatically. In addition, ZrO$_2$ nanoparticles have high fracture toughness; consequently, they can increase the epoxy toughness where the particle and matrix are highly compatible.

3.6- Vickers hardness

The hardness measurement test was performed for determining the hardness values of epoxy coatings. The results are shown in Fig. 10.

Figure 10

The results show the hardness values of the epoxy coatings increased due to addition of nanoparticles with high elastic modulus of solid contents compared to polymeric matrix. Higher hardness of the sample composed of modified nanoparticles compared to the one containing unmodified nanoparticles could be related to the better compatibility of the particle with the polymer resulting in less week points and defects in the coating.

3.7- FE-SEM
The cross-sectional images of the coating from the near top, middle and near bottom areas are shown in Fig. 11.

**Figure 11**

The cross-section of the coating containing unmodified nanoparticle reveals considerable differences in the particles distribution across the coating thickness (see Fig. 11a$_1$, b$_1$ and c$_1$). The micrographs clearly show high concentration of zirconia nanoparticle near top of the coatings. Also, the unmodified nanoparticles tend to form agglomerates in the coatings which reflects their incompatibility with the coating matrix. The FE-SEM micrographs from the coatings containing modified nanoparticles show no agglomeration of the nanoparticles across the coating thickness. No considerable difference in the particles distribution across the coating thickness could be observed in the cross-section image of the coating containing modified nanoparticle (see Fig. 11a$_2$, b$_2$ and c$_2$). It seems that surface modification resulted in uniform distribution of particles in the coatings which reflects enhanced nanoparticles compatibility with the coating matrix.

The zirconia weight percentage obtained from EDS analysis for the corresponding FE-SEM images are depicted in Fig. 12.

**Figure 12**

According to Fig. 12, unmodified zirconia nanoparticles tends to migrate to the coating/air interface. It seems that the unmodified nanoparticles tend to migrate to the surface due to incompatibility with the coating matrix. The EDS results from the coating containing modified nanoparticles show uniform distribution of particles across the coating thickness.

The fracture morphology of the coatings is shown in Fig. 13. Evaluation of fracture morphology of coating containing unmodified and modified nano-ZrO$_2$ particles could
indicate brittle or tough behavior of the coatings. The micro ruptures present at the fractured surface of the coating containing unmodified nanoparticles in Fig. 13a; however, for the coating containing modified nanoparticles the size of micro ruptures are reduced (Fig. 13b). The better dispersion (lower aggregates and agglomerates) of modified nanoparticle than the unmodified one in epoxy coating provides more sites for stress concentration which results in better dissipation of energy during stress application. These observations confirm that the use of modified nanoparticles makes the coating tougher as shown in tensile test.

Figure 13

4. Conclusion

The anticorrosion performance of the epoxy coating containing unmodified and modified ZrO₂ nanoparticles with trimethoxy methyl silane on mild steel substrate was investigated. The results are summarized as follow:

- FTIR and TGA results showed that silane was successfully grafted onto the surface of ZrO₂ nanoparticles.
- Results of the salt spray and EIS measurements revealed that the epoxy coating modified with nanoparticle provided better corrosion protection performance compared with the blank epoxy coating. The highest corrosion protection was observed for the coating containing modified nanoparticles.
- Inclusion of unmodified nanoparticles in the epoxy coating increased the mechanical properties compared to the blank epoxy coating. The epoxy coating containing modified nanoparticles showed superior hardness, energy at break and maximum load among the examined specimens. Also incorporation of modified nanoparticles led to a change from brittle to tough behavior.
• SEM micrographs from fracture surface showed a proper dispersion of surface modified particles in the epoxy matrix and the great tendency of unmodified particle for agglomeration.

• Surface modification of nano-zirconia pigments improved mechanical and corrosion protection performance of the epoxy coatings. Therefore, surface modified nano-zirconia could be possible choice for high performance epoxy coatings formulations.

References


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Figure Captions:

**Figure 1:** The scheme of surface modification of a zirconia nanoparticle

**Figure 2:** FTIR results of (a): unmodified- (b): modified nano-ZrO₂ powder

**Figure 3:** TGA thermograms of unmodified and modified nano-ZrO₂ particles

**Figure 4:** The Nyquist plots for (▲) blank epoxy coating; (■) epoxy coating containing unmodified nano-ZrO₂ particles and (♦) epoxy coating containing modified nano-ZrO₂ particles (the measured data points are displayed by symbols and the fitted curve by the equivalent electrical circuits of Fig. 6 are shown by continuous lines)

**Figure 5:** The phase angle (a) and impedance (b) Bode plots for (▲) blank epoxy coating; (■) epoxy coating containing unmodified nano-ZrO₂ particles and (♦) epoxy coating containing modified nano-ZrO₂ particles (the measured data points are displayed by symbols and the fitted curve by the equivalent electrical circuits of Fig. 6 are shown by continuous lines)

**Figure 6:** The equivalent electrical circuits used to fit (a) epoxy coating containing modified nano-ZrO₂ particles, (b) epoxy coating containing unmodified nano-ZrO₂ particles, (c) blank epoxy coating

**Figure 7:** The appearance of (a) the blank coating, (b) epoxy containing unmodified nanoparticles and (c) epoxy containing modified nanoparticles after 240 h of exposure to salt spray

**Figure 8:** The tensile specimens after fracture

**Figure 9:** The tensile plots of (a) blank epoxy, (b) epoxy filled with unmodified ZrO₂ nanoparticles and (c) epoxy filled with modified ZrO₂ nanoparticles

**Figure 10:** The hardness values of (a) blank epoxy coating, (b) epoxy coating containing unmodified ZrO₂ nanoparticles and (c) epoxy coating containing modified ZrO₂ nanoparticles

**Figure 11:** Cross-sectional images of epoxy coating containing unmodified nano-ZrO₂ from near top (a₁), middle (b₁) and near bottom (c₁) areas and epoxy coating containing modified nano-ZrO₂ from near top (a₂), middle (b₂) and near bottom (c₂) areas
**Figure 12:** The weight percentage of Zr at top, middle and bottom of the coating. The rest of elements analyzed were C, O and N

**Figure 13:** The fracture morphology of epoxy coating containing unmodified (a) and modified (b) nano-ZrO$_2$ obtained by FE-SEM
Table 1: Composition of the mild steel substrate

<table>
<thead>
<tr>
<th>element</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Others</th>
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<tr>
<td>Wt.%</td>
<td>99.09</td>
<td>0.12</td>
<td>0.6</td>
<td>0.045</td>
<td>0.045</td>
<td>≤ 0.1</td>
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</table>
Table 2: Characteristic absorption peaks obtained from FTIR spectrum of unmodified and modified nano-ZrO$_2$

<table>
<thead>
<tr>
<th>No.</th>
<th>Functionality</th>
<th>Wavenumber/ cm$^{-1}$ (Unmodified ZrO$_2$)</th>
<th>Wavenumber/ cm$^{-1}$ (Modified ZrO$_2$)</th>
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<tbody>
<tr>
<td>1</td>
<td>Zr-O</td>
<td>514, 578, 745</td>
<td>514, 578, 745</td>
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<tr>
<td>2</td>
<td>Zr-OH</td>
<td>3424</td>
<td>3424</td>
</tr>
<tr>
<td>3</td>
<td>Zr-O-Si</td>
<td>-</td>
<td>1078</td>
</tr>
<tr>
<td>4</td>
<td>-OH bending</td>
<td>1630</td>
<td>1630</td>
</tr>
<tr>
<td>5</td>
<td>-OH stretching</td>
<td>3424</td>
<td>3424</td>
</tr>
<tr>
<td>6</td>
<td>Asymmetric Stretching C-H</td>
<td>-</td>
<td>2855, 2960</td>
</tr>
<tr>
<td>7</td>
<td>Si-O-Si</td>
<td>-</td>
<td>1181</td>
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Table 3: The electrochemical parameters extracted from the EIS data

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>$Y_{0,t}$ ($s^6 \Omega^{-1} \text{cm}^{-2}$)</th>
<th>$n_t$</th>
<th>$R_t$ ($\Omega \text{ cm}^2$)</th>
<th>$Y_{0,dl}$ ($s^6 \Omega^{-1} \text{cm}^{-2}$)</th>
<th>$n_{dl}$</th>
<th>$R_{ct}$ ($\Omega \text{ cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank epoxy</td>
<td>$3.7 \times 10^7 \pm 1 \times 10^8$</td>
<td>0.67±0.01</td>
<td>26144±105</td>
<td>$7.2 \times 10^3 \pm 2 \times 10^3$</td>
<td>0.81±0.02</td>
<td>$2.0 \times 10^4 \pm 1 \times 10^7$</td>
</tr>
<tr>
<td>Epoxy containing unmodified ZrO$_2$</td>
<td>$2.4 \times 10^7 \pm 3 \times 10^10$</td>
<td>0.77±0.02</td>
<td>$3.8 \times 10^3 \pm 1.8 \times 10^4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Epoxy containing modified ZrO$_2$</td>
<td>$3.4 \times 10^{10} \pm 2 \times 10^{11}$</td>
<td>0.90±0.02</td>
<td>$3.9 \times 10^7 \pm 1.1 \times 10^6$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Warburg parameter for the epoxy coating containing unmodified ZrO$_2$ was $1.4 \times 10^9 \pm 2.4 \times 10^8$ ($s^{0.5} \Omega^{-1} \text{cm}^{-2}$)
Table 4: The delamination percentage of the coatings after 240 h exposure to salt spray

<table>
<thead>
<tr>
<th>Coating</th>
<th>Blank epoxy coating</th>
<th>Epoxy coating containing unmodified nanoparticles</th>
<th>Epoxy coating containing modified nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>delamination %</td>
<td>55</td>
<td>41</td>
<td>24</td>
</tr>
</tbody>
</table>
Table 5: The energy at break and maximum load of unpigmented and pigmented epoxy coatings

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Energy at break (MN.m$^2$)</th>
<th>Elongation at break ($\varepsilon_B$)/ %</th>
<th>Maximum load ($\sigma_B$)/ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank epoxy</td>
<td>76</td>
<td>4.2</td>
<td>26</td>
</tr>
<tr>
<td>Epoxy containing unmodified ZrO$_2$</td>
<td>125.2</td>
<td>6</td>
<td>31</td>
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<td>Epoxy containing modified ZrO$_2$</td>
<td>301.7</td>
<td>10.1</td>
<td>30</td>
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Figure 1: The scheme of surface modification of a zirconia nanoparticle
Figure 2: FTIR results of (a): unmodified- (b): modified nano-ZrO$_2$ powder
Figure 3: TGA thermograms of unmodified and modified nano-ZrO$_2$ particles
**Figure 4:** The Nyquist plots for (▲) blank epoxy coating; (■) epoxy coating containing unmodified nano-ZrO2 particles and (♦) epoxy coating containing modified nano-ZrO2 particles (the measured data points are displayed by symbols and the fitted curve by the equivalent electrical circuits of Fig. 6 are shown by continuous lines).
Figure 5: The phase angle (a) and impedance (b) Bode plots for (▲) blank epoxy coating; (■) epoxy coating containing unmodified nano-ZrO$_2$ particles and (♦) epoxy coating containing modified nano-ZrO$_2$ particles (the measured data points are displayed by symbols and the fitted curve by the equivalent electrical circuits of Fig. 6 are shown by continuous lines).
Figure 6: The equivalent electrical circuits used to fit (a) epoxy coating containing modified nano-
ZrO$_2$ particles, (b) epoxy coating containing unmodified nano-ZrO$_2$ particles, (c) blank epoxy coating
Figure 7: The appearance of (a) the blank coating, (b) epoxy containing unmodified nanoparticles and (c) epoxy containing modified nanoparticles after 240 h of exposure to salt spray.
Figure 8: The tensile specimens after fracture
**Figure 9:** The tensile plots of (a) blank epoxy, (b) epoxy filled with unmodified ZrO$_2$ nanoparticles and (c) epoxy filled with modified ZrO$_2$ nanoparticles
Figure 10: The hardness values of (a) blank epoxy coating, (b) epoxy coating containing unmodified ZrO$_2$ nanoparticles and (c) epoxy coating containing modified ZrO$_2$ nanoparticles.
Figure 11: The FE-SEM cross-sectional images of epoxy coating containing unmodified nano-ZrO$_2$ from near top ($a_1$), middle ($b_1$) and near bottom ($c_1$) areas and epoxy coating containing modified nano-ZrO$_2$ from near top ($a_2$), middle ($b_2$) and near bottom ($c_2$) areas.
**Figure 12:** The weight percentage of Zr at top, middle and bottom of the coating. The rest of elements analyzed were C, O and N.
Figure 13: The fracture morphology of epoxy coating containing unmodified (a) and modified (b) nano-ZrO$_2$ obtained by FE-SEM.