



Electrochemical evaluation of corrosion protection performance of epoxy/polyaniline-imidazole modified ZnO nanocomposite coating on mild steel

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ABSTRACT

In this research, ZnO nanoparticles were modified with imidazole in *o*-xylene solution and characterized using Fourier transform infrared (FT-IR) spectroscopy. Then, nanocomposites of polyaniline-ZnO (unmodified and imidazole modified) were synthesized via in-situ emulsion polymerization method. The synthesized nanocomposites were characterized by FT-IR and scanning electron microscopy (SEM). The anti-corrosion behavior of the epoxy coating in the presence of unmodified ZnO, imidazole modified ZnO and polyaniline-ZnO (unmodified and imidazole modified) nanocomposites were studied in NaCl 3.5 wt% solution at 65 °C for 100 h by electrochemical impedance spectroscopy (EIS). The coating resistance (R_{coat}) of epoxy coating containing unmodified ZnO, imidazole modified ZnO, polyaniline/ unmodified ZnO and polyaniline/ imidazole modified ZnO after 100 h immersion in saline electrolyte was found to be 7.2×10^4 , 1.3×10^5 , 2.3×10^5 and $1.7 \times 10^7 \Omega \text{ cm}^2$, respectively. Accordingly, polyaniline/ imidazole modified ZnO nanocomposite exhibited higher corrosion resistance and provided better barrier properties against ingress of corrosive electrolyte. Prog. Color Colorants Coat. 10 (2017), 181-192 © Institute for Color Science and Technology.

1. Introduction

Mild steel is the most common form of steel which is widely used in industrial applications because of suitable and economic mechanical and machining properties. The poor corrosion resistance of mild steel necessitates the use of corrosion protection methods [1-3]. Among various techniques, organic coatings are one of the most effective and economic ways for the

corrosion control of steel [4-6]. Epoxy resins have been extensively used as coating materials because of their great processability, suitable chemical resistance and effective adhesion to metallic surfaces [7-9]. Nevertheless, epoxy resins can absorb water from surroundings because of their hydrophilic nature. The absorbed water decreases the thermal and

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mechanical properties of the resins, and also initiates corrosion of the substrate metal and delaminates the coating over prolonged exposure [10]. Therefore, over the last decade, considerable attention has been paid to improve the properties of the epoxy coatings. It has been shown that the barrier properties of epoxy can be significantly improved using organic-inorganic hybrid nano-composites such as conducting polymers and nanoparticles. Nanoparticles as nanosized fillers can be dispersed within the epoxy matrix to decrease the porosity of coating. They can also prevent epoxy disaggregation during curing, resulting in a more homogenous coating. There are various reports concerning improving corrosion resistance of coatings using nanoparticles such as; TiO₂ [11], ZnO [12-14], SiO₂ [15], ZrO₂ [16], Fe₂O₃ [17] Al₂O₃ [18], and organoclays [19, 20]. Moreover, it has been demonstrated that surface modification of nanopigments with organic and inorganic compounds can significantly affect the compatibility and dispersion of nanoparticles in epoxy which prevented from agglomerations and improved interaction of nanoparticles with resin matrix and also increased coating corrosion resistance [21-23]. The combination of inorganic nanosized particles with conductive polymers leads to the significant improvement of mechanical and barrier properties of epoxy [24-26]. The presence of conducting polymers such as polypyrrole, polythiophene and polyaniline (PANI) in epoxy enhances the corrosion protection efficiency of epoxy coatings [27]. Among the large number of conducting polymers, PANI is the most promising case for corrosion protection due to its low cost, easy chemical and electrochemical synthesis, good adhesion and environmental stability [28]. It has been reported that coatings containing PANI prevent the local corrosion of metal and are able to protect the scratches and pinholes in the coatings [29]. PANI provides active protection by exchanging electrons with the metallic substrate and stabilizes the potential of the metal in the passive region, maintaining a protective oxide layer on the metal and minimizing the rate of metal dissolution [29]. There are a lot of publications for improving barrier and corrosion protection properties of epoxy coatings by addition of nanoparticles which were modified with a wide variety of materials. To the best of our knowledge, a few published works on the surface modification of nanoparticles with corrosion inhibitors and their composites with conductive polymers are available in the literature. In this research, surface of

ZnO nanoparticles was modified with imidazole and then PANI-imidazole modified ZnO nanocomposite was synthesized via electrooxidative polymerization method. The effect of imidazole modified ZnO nanoparticles and their nanocomposites with PANI on the anticorrosive behavior of epoxy coating on mild steel in NaCl 3.5 wt% at 65 °C was investigated by electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Surface modification of ZnO

Imidazole solution with the concentration of 1 mg/mL was prepared in O-xylene. Then, the appropriate amount of ZnO nanoparticle was added. The obtained dispersion was shaken during 24 h at ambient condition and then centrifuged and washed with acetonitrile and deionized water with a volume ratio of 2:3 for several times. The surface modification of ZnO nanoparticles with imidazole was evaluated by Fourier transform infrared (FT-IR) technique. FT-IR analysis was performed in KBr pellet on a Perkin-Elmer spectrometer in the range of 4000-450 cm⁻¹ at room temperature.

2.2. Synthesis of PANI/ZnO nanocomposites

To prepare the PANI-ZnO nanocomposites in the presence of modified and unmodified ZnO nanoparticles, 0.045 g of ZnO nano powder (unmodified and imidazole modified) was mixed with 0.05 mol (4.5 g) of aniline monomer (Fluka, purity 99.5%) and 0.003 mol (1 g) of dodecylbenzene sulfonic acid (DBSA, Fluka purity 90%) in 200 mL of distilled water and stirred in ice water bath for 2 h. Then, 50 mL of ammonium peroxy disulfate (APS, Merck) solution was added dropwise into the emulsion at 0 °C. After 4 h, the precipitates were rinsed with water and dried for 12 h. The synthesized nanocomposites were characterized by FT-IR as mentioned in section 2.1. The morphology of the nanocomposites was studied by Field emission scanning electron microscope (FE-SEM, Tescan MIRA 3).

2.3. Pretreatments of mild steel surface before coating

The mild steel panels with dimensions of 1×1 cm² were mounted in polyester in such a way that one side of the specimens was in contact with the electrolyte. Samples

were mechanically abraded with abrasive papers (no. 200-3000 grade) to achieve a uniform surface. Then, they were degreased in a solution containing Na_2SiO_3 15 g/L, $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$ 20 g/L, Na_2CO_3 30 g/L and NaOH 30 g/L for 5 min at 40 °C. Finally, they were washed with ethanol in ultrasonic bath (Bandelin Conorex Digital, Iran) for 20 min at 25 °C.

2.4. Preparation of coating

For preparation of coatings, 0.306 g of each prepared powders [unmodified ZnO (ZnO), imidazole modified ZnO (IM-ZnO), PANI- unmodified ZnO (PANI-ZnO), PANI- imidazole modified ZnO (PANI-IM-ZnO)] was dispersed in 3 mL tetraethylene penta amine (TEPA, Fluka purity 85%) and stirred for 12 h. TEPA acts as a hardener and solvent for epoxy resin. Then, 1 g of epoxy resin (MY720, Ciba) was mixed with 0.2 g of suspension and stirred again. Afterwards, obtained coatings were applied on the grinded and degreased surface of mild steel by brushing. The coated samples were dried at 60 °C for 24 h. The thickness of coatings measured by eXacto FN elcometer was about $60 \pm 5 \mu\text{m}$.

2.5. Measurement of anticorrosive performance of coatings

Anticorrosive performance of coatings on mild steel substrate was studied by EIS using Potentiostat/ Galvanostat (EG&G model Parstat 2263) equipped with Frequency Response Analyzer (FRA). The EIS spectra were recorded over a frequency range from 100 kHz to 0.01 Hz with an applied AC perturbation signal of ± 5 mV. EIS measurements were conducted with a three-electrode cell including coated mild steel specimen as working electrode, saturated calomel electrode (SCE) as reference electrode and Pt plate as counter electrode. Data analysis was made with Zview software using appropriate electrical equivalent circuit. The coated samples were immersed in 3.5 wt% NaCl solution at 65 °C for 100 h.

3. Results and Discussion

3.1. Characterization

The FT-IR spectra of ZnO, IM-ZnO and PANI-ZnO, PANI-IM-ZnO nanocomposites are shown in Figures 1 and 2. The obtained results from FT-IR analysis are given in Table 1.

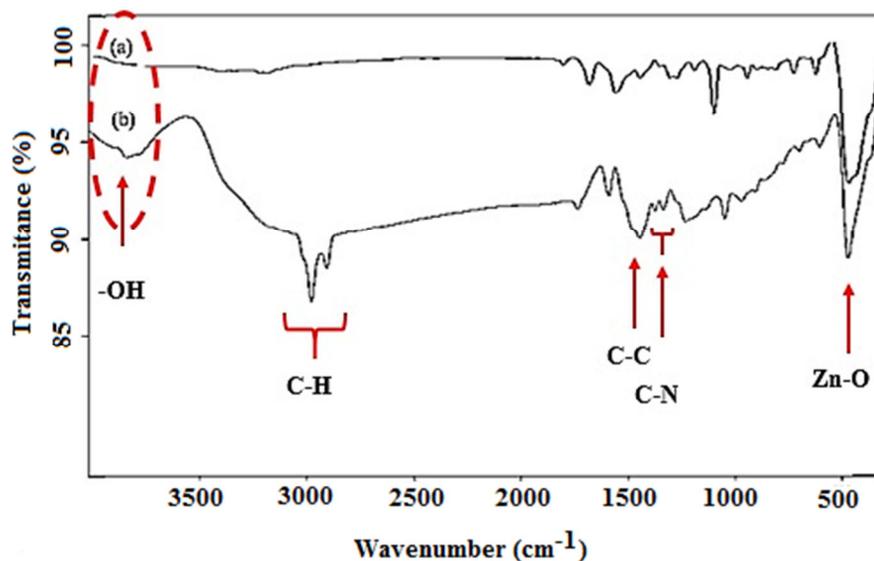


Figure 1: FT-IR spectra of (a) ZnO and (b) IM-ZnO.

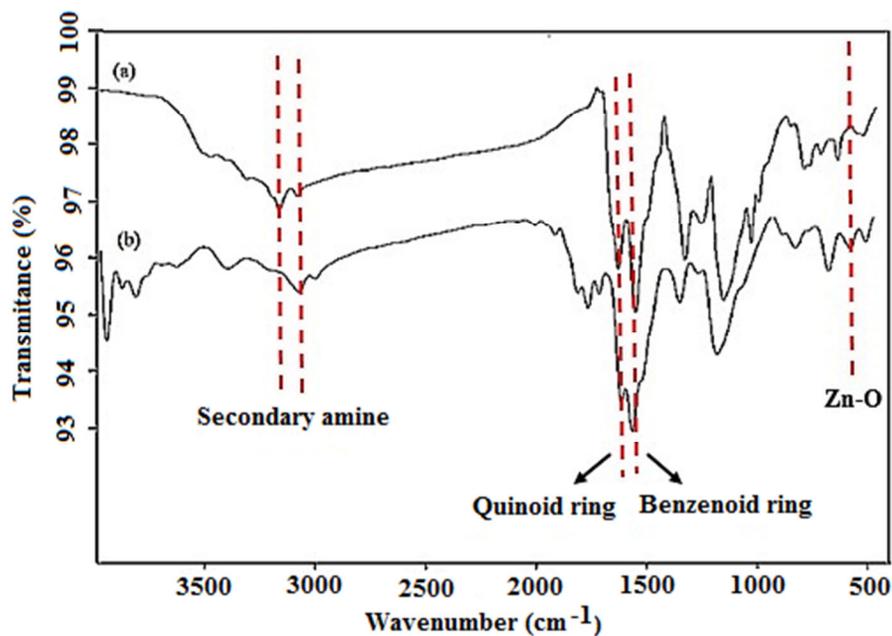


Figure 2: FT-IR spectra of (a) PANI-ZnO and (b) PANI-IM-ZnO.

Table 1: Characteristic absorption peaks obtained from FT-IR spectra of ZnO, IM-ZnO, PANI- ZnO and PANI-IM- ZnO.

| sample | wavenumber (cm ⁻¹) | Absorption peak |
|------------------------------|--------------------------------|-----------------|
| unmodified ZnO | 535 | Zn-O |
| imidazole modified ZnO | 535 | Zn-O |
| | 3750 | -OH |
| | 3126, 3040 | C-H |
| | 1467 | C-C |
| PANI- unmodified ZnO | 1399,1346 | C-N |
| | 3260,3200 | secondary amine |
| | 1592 | Quinoid ring |
| PANI- imidazole modified ZnO | 1512 | benzenoid ring |
| | 3260,3200 | secondary amine |
| | 1592 | Quinoid ring |
| | 1512 | benzenoid ring |
| | 3765 | -OH |
| | 1740 | C-C |
| | 1423,1385 | C-N |

The sharp peak around 535 cm^{-1} in Figure 1 (a, b) can be attributed to Zn-O stretching vibrations. According to Figure 1b, the characteristic absorption peaks of imidazole at ($3126, 3040\text{ cm}^{-1}$), 1467 cm^{-1} and ($1399, 1346\text{ cm}^{-1}$) can be assigned to C-H, C-C and C-N stretching vibrations respectively. The surface modification of ZnO nanoparticles with imidazole can be confirmed by observation of -OH peak at 3741 cm^{-1} . In general, the N-H stretching vibration of imidazole appears at $3500\text{-}3000\text{ cm}^{-1}$ as a sharp peak. The formation of hydrogen bonding between the hydrogen on N-H of imidazole and the oxygen of Zn-O resulted in a wide peak at 3741 cm^{-1} indicating surface modification of ZnO with imidazole. According to Figure 2 (a, b) and table 1, the peaks at 1592 cm^{-1} and 1512 cm^{-1} correspond to the ring-stretching vibrations of the quinoid and benzenoid rings of polyaniline, respectively. The peaks at 3260 and 3200 cm^{-1} are related to the secondary amine [25]. As can be seen, the characteristic peaks of

polyaniline were observed in both PANI-ZnO and PANI-IM-ZnO but the characteristic peaks of imidazole modified ZnO ($3765, 1740, 1423$ and 1385 cm^{-1}) was only observed in PANI-IM-ZnO spectrum. The obtained results are similar to the results observed by others [25, 28]. Figure 3 depicts the SEM images of PANI-ZnO and PANI-IM-ZnO with two magnitudes. According to Figure 3, the majority of the imidazole modified ZnO nanoparticles ($20\text{-}40\text{ nm}$) are dispersed uniformly in the nanocomposite which enhanced its compatibility with epoxy coating through reducing surface hydrophobicity. The unmodified ZnO nanoparticles dispersed with agglomeration which probably resulting poor interaction with epoxy. The SEM images revealed that surface modification of ZnO nanoparticles with imidazole improved dispersability of the nanocomposites in the polymeric matrix because of increasing the steric hindrance between the nanoparticles.

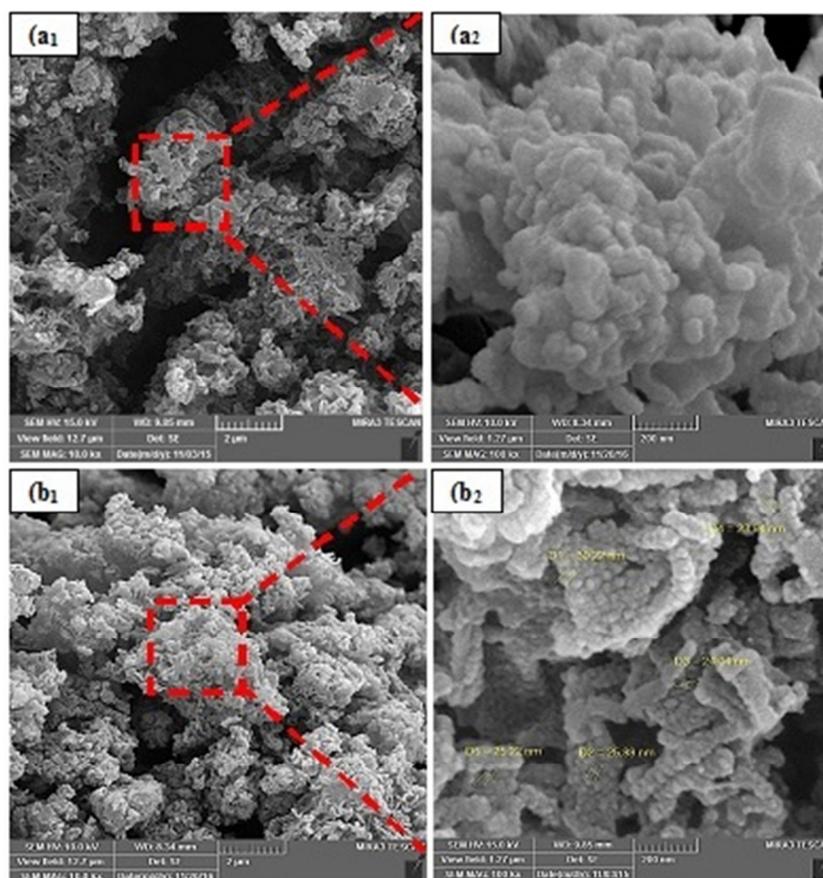


Figure 3: SEM images of PANI-ZnO (a₁, a₂) and PANI-IM-ZnO (b₁, b₂) with two different magnitudes.

3.2. Electrochemical impedance measurements

Figure 4 illustrates the Bode plots of epoxy, epoxy/ZnO, epoxy/IM-ZnO, epoxy/PANI-ZnO and epoxy/PANI-IM-ZnO coated mild steel specimen after various immersion times (2, 48, 72, and 100 h) in 3.5 wt% NaCl solution at 65 °C. Based on the observations made for all coating systems, an equivalent electrical circuit model with two time constant shown in Figure 5. has been proposed to fit the obtained EIS results. In this model, R_s is electrolyte resistance, R_{coat} is coating resistance, CPE_{coat} is constant phase element of coating, CPE_{dl} is constant phase element of double layer and R_{ct} is the charge transfer resistance. Since the coating and the double layer have deviations from the ideal capacitance behavior, constant phase element (CPE) is substituted for the coating capacitance (C_{coat}) and double layer capacitance (C_{dl}) in order to better fitting of the measured EIS data.

The impedance of the CPE is defined by Eq.1.

$$Z_{CPE} = 1 / Y_0(\omega j)^n \quad (1)$$

where Y_0 is the magnitude of admittance of CPE ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$), ω is the angular frequency (rad/s), $j = \sqrt{-1}$ is the imaginary number and n is the CPE exponent which is between 0 and 1. The obtained EIS parameters for all coatings are presented in Table 2. The anticorrosive performance of organic coatings was investigated by a number of various parameters such as R_{coat} , C_{coat} and water uptake of the coating.

R_{coat} is one of the important factors which is related to the electrical resistance of coating pores against the penetration of electrolyte [24]. It has been demonstrated that R_{coat} can be attributed to the number of pores or capillary channels perpendicular to interface according to Eq. 2:

$$R_{coat} = \frac{d}{kNA} \quad (2)$$

where d denotes the length of channel (coating thickness), k is conductance coefficient, N , represents the number of pores and A is the average active area of channel [30].

Table 2: The obtained EIS parameters for epoxy, epoxy/ZnO, epoxy/IM-ZnO, epoxy/PANI- ZnO and epoxy/PANI-IM-ZnO in various immersion times.

| Coating type | time (h) | R_{coat} (Ωcm^2) | C_{coat} (Fcm^{-2}) | R_{ct} (Ωcm^2) | Water uptake (%) |
|-----------------------------------|----------|------------------------------------|----------------------------------|----------------------------------|------------------|
| epoxy | 2 | 1.4×10^3 | 5.7×10^{-12} | 3.2×10^4 | - |
| | 48 | 8.2×10^2 | 3.1×10^{-11} | 1.2×10^4 | 39 |
| | 72 | 8.9×10^2 | 3.9×10^{-11} | 1.8×10^4 | 44 |
| | 100 | 1.2×10^3 | 4.6×10^{-11} | 6×10^4 | 49 |
| epoxy-unmodified ZnO | 2 | 3.6×10^4 | 3.3×10^{-12} | 1.8×10^5 | - |
| | 48 | 4.5×10^3 | 2.6×10^{-11} | 2.2×10^4 | 29 |
| | 72 | 6.3×10^3 | 3.1×10^{-11} | 3.9×10^4 | 38 |
| | 100 | 6.8×10^3 | 4.2×10^{-11} | 7.2×10^4 | 42 |
| epoxy-imidazole modified ZnO | 2 | 1.5×10^4 | 7.1×10^{-12} | 4.5×10^5 | - |
| | 48 | 1.3×10^4 | 2×10^{-11} | 1.2×10^5 | 23 |
| | 72 | 2.1×10^4 | 2.6×10^{-11} | 1.5×10^5 | 30 |
| | 100 | 3.8×10^4 | 3.9×10^{-11} | 1.3×10^5 | 39 |
| epoxy/PANI-unmodified ZnO | 2 | 5.4×10^4 | 2.9×10^{-12} | 4.7×10^5 | - |
| | 48 | 3.9×10^4 | 1.8×10^{-11} | 1.6×10^5 | 21 |
| | 72 | 4.2×10^4 | 2.7×10^{-11} | 2.8×10^5 | 29 |
| | 100 | 4.9×10^4 | 3.5×10^{-11} | 2.3×10^5 | 36 |
| epoxy-PANI-imidazole modified ZnO | 2 | 2.3×10^5 | 6.3×10^{-12} | 3.1×10^8 | - |
| | 48 | 1.6×10^5 | 1.1×10^{-11} | 1.4×10^6 | 10 |
| | 72 | 1.9×10^5 | 1.5×10^{-11} | 7.8×10^5 | 21 |
| | 100 | 2.5×10^5 | 2.6×10^{-11} | 1.7×10^7 | 23 |

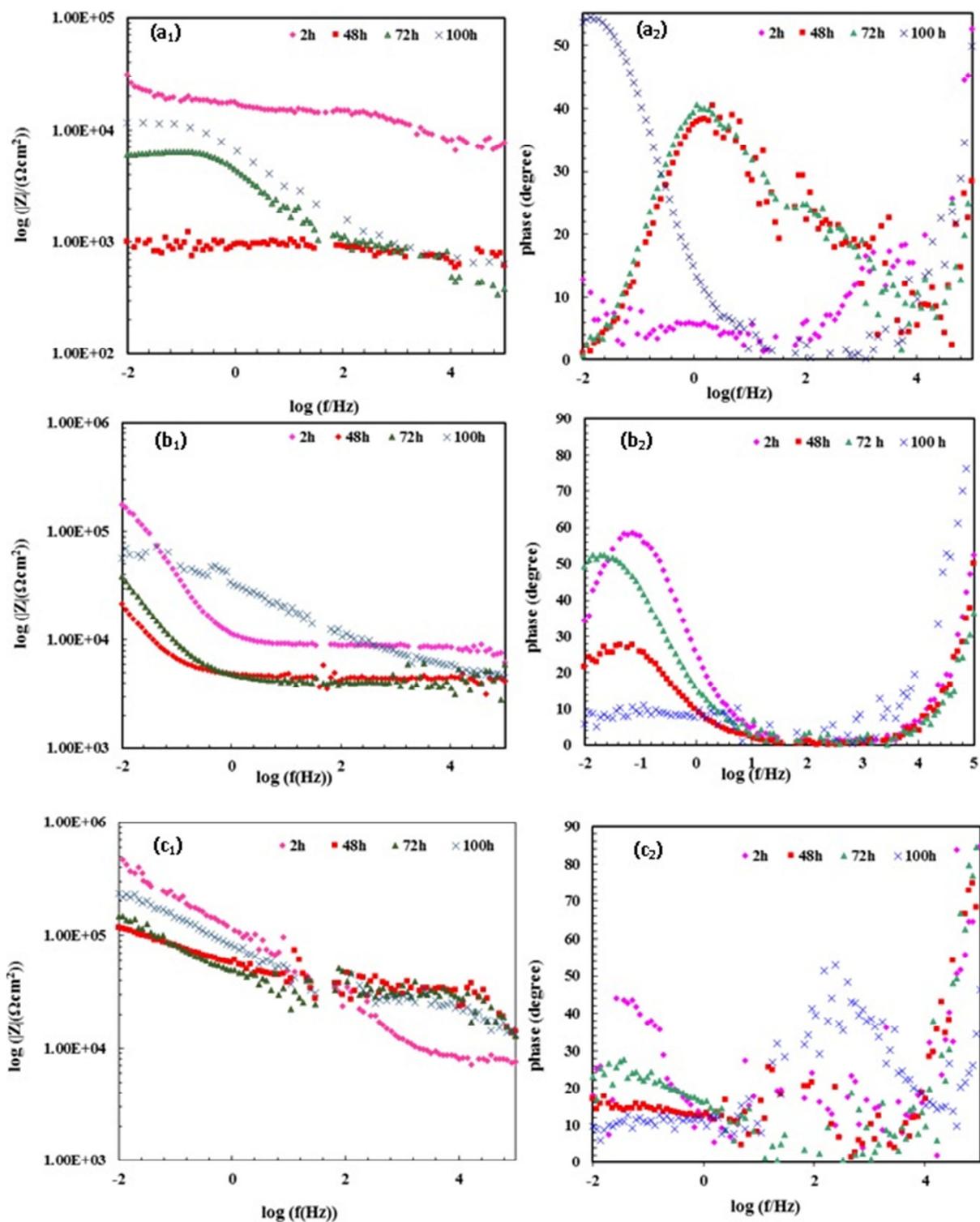


Figure 4: Bode-Phase plots of (a₁, a₂) epoxy (b₁, b₂) epoxy/ ZnO (c₁, c₂) epoxy/IM-ZnO coated mild steel in different immersion times in 3.5 wt% NaCl solution at 65°C.

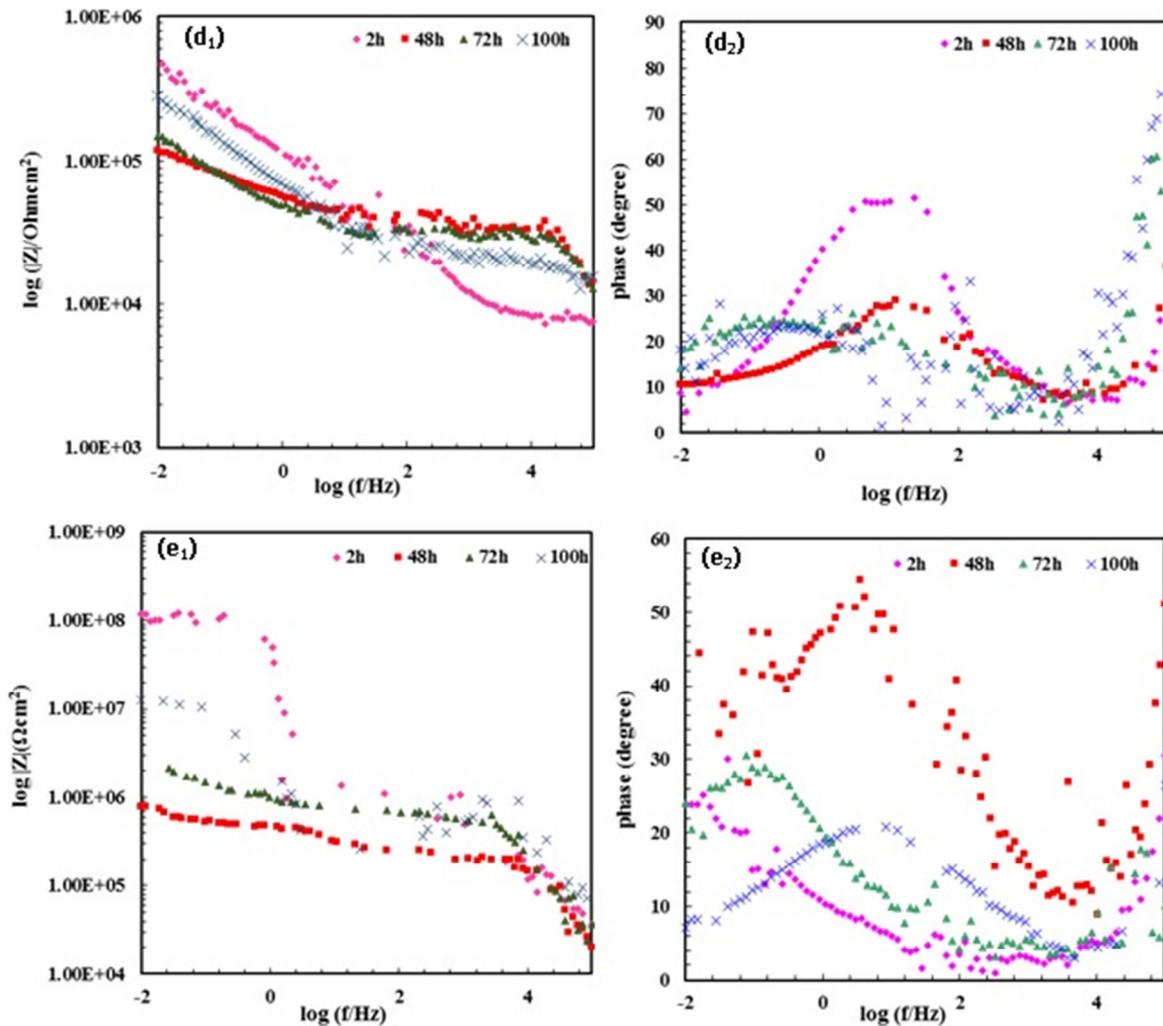


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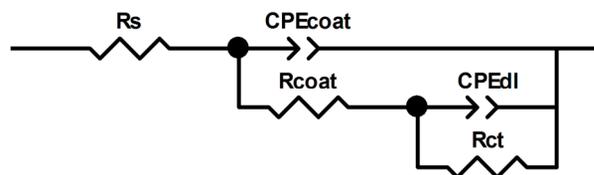


Figure 5. Equivalent electrical circuit model.

According to Table 2, it can be seen that for all coatings R_{coat} values decreased initially due to gradual diffusion of electrolyte into the pores of the coating according to Fick's law. This leads to contact between the electrolyte and the metal surface and to the beginning of the electrochemical processes at the metallic surface. Then, R_{coat} values started to increase

because of filling pores of coatings with corrosion products. The R_{coat} values of all coatings shown in Figure 6.a were compared after 100 h immersion. Neat epoxy has smallest resistance among five coatings, indicating that neat epoxy had a worse anticorrosion performance than other coatings. In the presence of ZnO nanoparticles, corrosion resistance increased. This

may be attributed to two main reasons. First, ZnO nanoparticles produce high barrier properties against electrolyte diffusion into the coating matrix. Second, nanoparticles can increase coating resistance against hydrolytic degradation [26]. Modification of ZnO with

imidazole also improved the corrosion protection performance of epoxy coating. Imidazole modified ZnO nanoparticles have hydrophobic feature which delays the penetration of corrosive electrolyte and increases the corrosion protection properties.

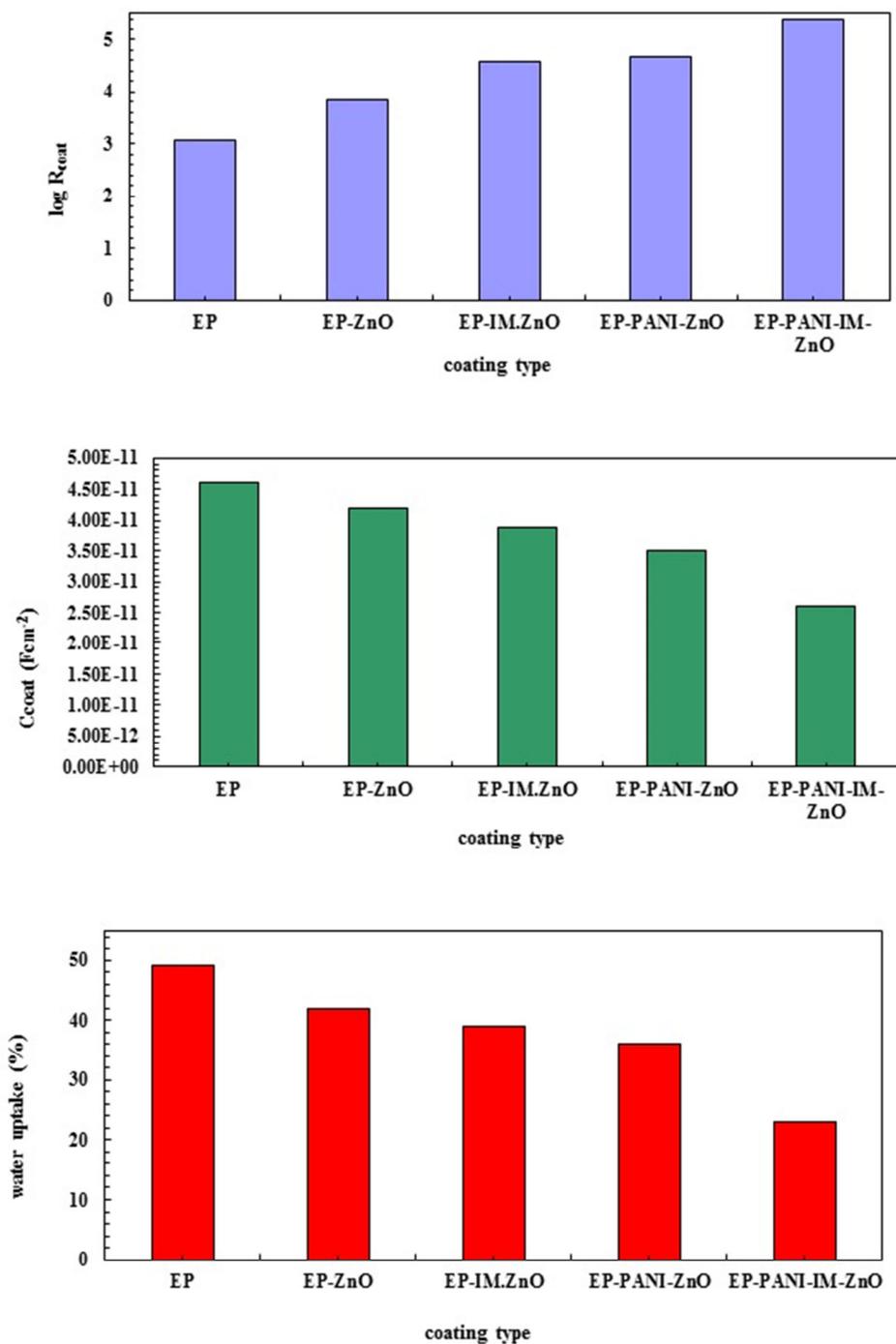
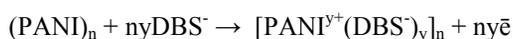
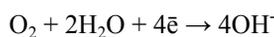
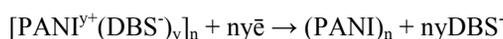


Figure 6: (a) The $\log R_{coat}$ (b) C_{coat} (c) water uptake values of epoxy, epoxy/ZnO, epoxy/IM- ZnO, epoxy/PANI-ZnO and epoxy/PANI-IM-ZnO after 100h immersion in 3.5 wt% NaCl solution at 65°C.

The epoxy/PANI-IM-ZnO has the highest corrosion resistance value. Because of conducting nature of PANI, this polymer intercepts the electrons which were produced during the corrosion reaction of mild steel and transports them to the outside of the coating. PANI can capture Fe^{+2} ions and releases dodecylbenzene sulfonate anions as dopant. Also, the reduction of oxygen and oxidation of PANI take place at the coating/electrolyte interface and compensate the consumption of electron in the PANI coating.

The redox reactions at metal/coating interface can be expressed as follows [31]:



The metal ions can form a protective oxide layer. Therefore, produced passive oxides (Fe_2O_3) occupy the coating pinholes and impeded electrolyte movement in the coating layer so, decrease the number of pores (N) and increase the value of R_{coat} [32].

Coating capacitance (C_{coat}) is a critical factor which is widely used for evaluating the protective performance of organic coatings. As it can be seen from Table 2, coating capacitance increased at first due to water penetration into the coating. This increase of C_{coat} with time can be described based on Eq. 3 [24].

$$C_{\text{coat}} = \epsilon\epsilon_0 \frac{A}{d} \quad (3)$$

where ϵ is the dielectric constant of the coating, ϵ_0 is the permittivity of vacuum ($8.85 \times 10^{-12} \text{ F m}^{-1}$), A is the active area and d is the coating thickness. The dielectric constants of polymeric coatings and water are about 4-8 and 80, respectively. Due to the hydrophilicity of the epoxy coating, it can absorb water. Consequently, water uptake within the coating increases the coating capacitance. According to Table 2 and Figure 6 b, it was observed that epoxy coating in the presence of polyaniline-imidazole modified ZnO has the lowest coating capacitance due to synergistic effect of imidazole modified ZnO nanoparticles and polyaniline on the barrier performance of epoxy coating.

Water uptake percentage of coatings (Φ_{water} %) can be obtained according to Brasher-Kingsburg's equation

(4):

$$\Phi_{\text{water}} = [\log(C_t/C_0)] / \log(\epsilon_w) \times 100 \quad (4)$$

where C_t is the coating capacitance at time t , C_0 is the initial coating capacitance and ϵ_w is the dielectric constant of water (80). Water uptake values of epoxy, epoxy/ZnO, epoxy/IM-ZnO, epoxy/PANI/ZnO and epoxy/PANI-IM-ZnO after 100h immersion in 3.5 wt% NaCl solution at 65°C are shown in Figure 6 c.

Because of hydrophobicity of coating in the presence of imidazole modified ZnO nanoparticles, polyaniline-IM-ZnO had the least wateruptake percentage of 23% after 100 h immersion in saline electrolyte among all the samples and depicted the better anticorrosion properties of epoxy.

4. Conclusion

In this work, the surface of ZnO nanoparticles was modified with imidazole. The polyaniline/unmodified and imidazole modified ZnO nanocomposites were synthesized and characterized by FT-IR and SEM successfully. The corrosion resistance behavior of epoxy coatings in the presence of unmodified ZnO, imidazole modified ZnO, polyaniline-ZnO (unmodified and imidazole modified) was studied by EIS technique in NaCl 3.5 wt% solution at 65 °C for 100 h. EIS results revealed that incorporation of imidazole modified nanopigments in epoxy coating increased the corrosion resistance and reduced the water uptake of the coating by providing hydrophobic feature to the coating which in turn limited the diffusion of water and ion species into the substrate. The water uptake of epoxy containing unmodified ZnO, imidazole modified ZnO, polyaniline/unmodified ZnO and polyaniline/ imidazole modified ZnO after 100 h immersion was 42%, 39%, 36% and 23%, respectively indicating the better performance of epoxy in the presence of imidazole modified ZnO nanoparticles.

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