

# Electrochemical behaviour of anticorrosive pigmented epoxy coatings on galvanised steel in natural seawater

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## Abstract

Red iron oxide (RIO), zinc chromate (ZC) and zinc phosphate (ZP) pigmented epoxy resins (ER) were coated on galvanised steel and characterised using potentiodynamic polarisation and electrochemical impedance spectroscopic (EIS) studies in natural seawater. Salt spray test was employed to characterise corrosion performance of coated substrates during different exposure time. Adhesive–strength of the anticorrosive pigmented epoxy coated substrates was evaluated using pull-off and tape tests. The surface morphology of anticorrosive pigmented epoxy coatings on galvanised steel is characterised by scanning electron microscope (SEM). The anticorrosive pigmented epoxy resins viz., ZC, ZP showed the good adhesion strength and corrosion resistance compared to RIO. In addition, the good adhesion was maintained throughout the investigated time period.

**Keywords:** EIS, Anti-corrosion pigments, Organic coatings, Galvanised steel, SEM.

## Introduction

Protective coatings have been widely used to protect metallic materials against corrosion. They are used to provide long term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Various kinds of anti-corrosion pigments have been developed and incorporated into the coating matrix to enhance the barrier performance of organic coatings against water, oxygen and aggressive ions [1–3]. Epoxy based coatings comprise the largest generic family of coatings. Endless combinations of epoxy resins with other allow the formulation of a coating system for most applications. Epoxy coatings are often utilized in tank linings. Inhibitive pigments are introduced into organic coatings as the main substance for corrosion inhibition. Pigments present in the coatings may protect the metal by an electrochemical mechanism. It is generally accepted that the coating efficiency is dependent on the intrinsic properties of the organic film (barrier properties), substrate/coating interface in terms of adherence, inhibitive or sacrificial pigments used and the degree of environment aggressiveness. Epoxy based paints are within the best organic coatings employed as a material insulating from a marine medium to protect mild

steel against corrosion. When a metal surface is covered with a polymeric film and then immersed in an electrolytic solution, an interaction is produced between the film and the solution. Water with electrolyte ions is transported through the coating by two simultaneous mechanisms: convection through the pores and coating imperfections (fast step) and by diffusion through the polymeric matrix (slow step). In continuous and defect-free films, only the transport of ionic species through the polymer is favored.

ZP is commonly used because it is known as a green pigment. The addition of ZP to the paints leads to a clear improvement of their barrier function [4]. On the other hand, the RIO pigment, which is insoluble in water, plays a physical role on the barrier behavior of coatings by increasing the length of the diffusional pathways for water and oxygen and thereby decreasing the coating's permeability [5]. ZC has for many years been used as inhibiting pigment for steel. Its toxicity, however, is leading to great restrictions to its use and has caused intensive research on alternative pigments with better human compatibility. ZP, which is probably the most important alternative to chromate, has been used either as soluble inhibitor, in the formulation of conversion coatings and also as anticorrosive pigment in paints [6, 7]. The steel structure continuously exposed to an electrolyte could be successfully protected using the combination of cathodic protection and organic coatings. The coatings need to have some specific properties to ensure long-term protection [8, 9]. Galvanised steel is frequently used in the construction of cooling towers and water containers, owing to its good resistance to corrosion and biofouling. Cooling towers are an integral part of any power plant. Galvanised coatings provide considerable protection to steel immersed in sea water and exposed to salt spray. The factors that influence the corrosion of zinc in fresh water also apply to sea water. However, it is the dissolved salts (primarily sulfides and chlorides) in sea water that are the principal determinants of the corrosion behavior of zinc immersed in sea water. Given the high level of chloride in sea water, a very high rate of zinc corrosion might be expected.

Organic coatings with anticorrosive pigments are extensively studied for the protection of metals from corrosion attack. The strict environmental regulations for coating applications have brought to the development of both solvent free coatings and non-toxic corrosion inhibitor pigments. Electrochemical impedance spectroscopy (EIS) provides a rapid and convenient technique to evaluate the performance of organic coated metals. One of the most successful applications of this technique has been in the evaluation of the properties of polymer coated metals and their performance variation during exposure to corrosive environments [10]. The aim of the present work is to improve the corrosion resistance of galvanised steel in seawater by applying epoxy coating with different formulations of

pigments. The anticorrosive pigments added with epoxy resins were RIO, ZC and ZP, then coated on the galvanised steel, and the corrosion resistances studied using polarisation and electrochemical impedance studies. Adhesive–strength of epoxy coated substrates was evaluated using pull-off and tape tests. Salt spray tests were employed to characterise corrosion performance of coated substrates. Among the anticorrosive pigmented epoxy coating formulations, ZC and ZP showed the best adhesion strength, while the RIO and epoxy resins revealed a good corrosion performance as well.

## 2. Experimental

### 2.1. Samples

Galvanised steel was used as working electrode of composition 0.028% C, 0.147% Mn, 0.01% P, 0.012%Si, 0.059% Al, 0.008%S and 99.736% Zn. The commercial grade epoxy resin was used to prepare the formulation. The coupons were painted with the organic coatings viz., epoxy resin, RIO, ZP and ZC pigmented epoxy resins by brushing to a thickness of  $40 \pm 3 \mu\text{m}$ . An epoxy resin with a pigment concentration of 5 mass % each was formulated. Steel panels coated only with epoxy resin coating without any pigment were used as the reference specimen. After coatings, the samples were cured at 25°C for 10 h and then allowed to store in desiccators at room temperature for 30 days. After a seven-day curing period, edges and back sides of the coated samples were sealed with a mixture of beeswax and colophony resin, leaving a central area of 2 cm x 2 cm unmasked. Three parallel samples were prepared to ensure that the experimental data were reliable. All chemicals used in this study, were of analytical grade having high percentages of purity.

### 2.2. Electrochemical techniques

All the electrochemical measurements were performed in a conventional three-electrode cell, using a large platinum plate as the counter electrode and Ag/AgCl (saturated KCl) electrode as the reference electrode (Advance–Tech Controls Pvt. Ltd, India) in saturated KCl solution with a Luggin capillary bridge. The electrolyte for the electrochemical tests was natural seawater collected from the Eliot beach on the southern coast of Chennai, India. The polarisation experiments were carried out for uncoated and anticorrosive pigmented epoxy coated galvanised steel specimen at a scan rate of 1 mV/s in natural sea water.

The potentiostat/galvanostat (model PGSTAT 12, AUTOLAB, the Netherlands B.V) controlled by a personal computer with dedicated software (GPES version 4.9.005) was used for conducting the polarisation experiments. The EIS measurements were conducted at room

temperature using a potentiostat/galvanostat with frequency response analyser (FRA). The EIS measurements were carried out over a frequency range 100 kHz –10 mHz by using a 20-mV amplitude sinusoidal voltage. The data were acquired in three cycles at each frequency, for providing good precision at all frequencies. The tested area of working electrode was 0.28 cm<sup>2</sup>. All the measurements were performed at the open-circuit potential (OCP). The coated samples were immersed in natural seawater. Data analysis was made using FRA software. All the electrochemical tests were repeated thrice to ensure repeatability.

### *2.3. Analysis of FT-IR spectra*

FT-IR spectra were recorded between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup> with a resolution of 1 cm<sup>-1</sup> using a Perkin-Elmer Model 577 spectrometer. The coatings formed on the galvanised steel surface was washed with water, dried and collected by scrapping from the surface of the specimen for subsequent spectral analysis. The compounds were mixed with KBr powder in a ratio 1:100 for FTIR analysis.

The thicknesses of the cured coating films were measured using an Elcometer 345 instrument to an accuracy of 0.1  $\mu$ m, with measurements carried out on a set of three replicate samples. The coating thicknesses on galvanised steel calculated were ranging from 37.5 to 41.3  $\mu$ m.

### *2.4. Accelerated corrosion tests*

The accelerated test method, namely salt spray test is performed to evaluate the bare corrosion protection of anticorrosive pigmented epoxy coated specimens. According to the specification, natural seawater is atomized in a salt spray chamber at 35°C with the solution pH around 7. The tested panels are placed at an angle of 45° in the chamber, exposed to the salt fog for certain period. These tests were performed with LIEBISCH SL1000 equipment. Two sets of samples were then exposed to a standard salt spray chamber for 300 h and 600 h at 35  $\pm$  1 °C according to ASTM B117.

### *2.5. Adhesion measurements*

The adhesion strength of epoxy coatings and anti-corrosive pigments like red iron oxide, zinc phosphate and zinc chromate pigmented epoxy coatings on galvanised steel was determined by a direct pull-off standardized procedure described in ASTM D4541, using Erichsen Adhesion master 513 MC/525 MC. The adhesion measurements were performed

prior to exposure to natural seawater (“dry” adhesion), and during 300 h and 600 h exposure to natural seawater at room temperature (“wet” adhesion). At certain time intervals the panels were removed from the solution, rinsed with distilled water, dried in air at room temperature for 1 h, and dollies were then glued to panels. After curing of the adhesive for 24 h the epoxy coating and anti-corrosive pigments viz., RIO, ZP and ZC epoxy coatings on galvanised steel was cut around the dolly and the dolly was pulled-off vertically (force increase speed of  $100 \text{ N s}^{-1}$ ) to measure the necessary force i.e. adhesion strength. For each type of protective system three samples were tested and the average value was taken, and only those samples with the interfacial failure were considered.

## 2.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) (Philips XL30) was employed to analyse the morphology of the uncoated and coated galvanised steel surfaces. The samples were examined at various magnifications and the images were recorded photographically.

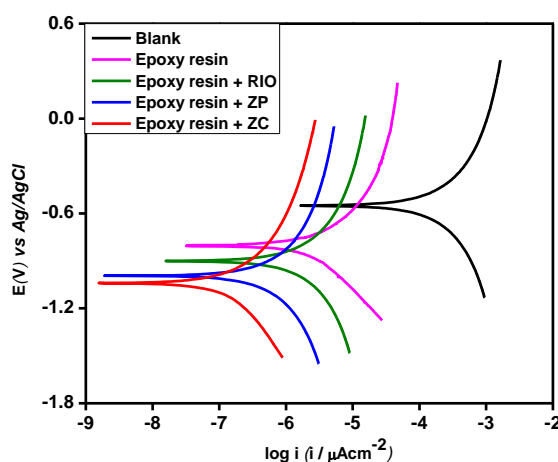
## 3. Results and Discussion

### 3.1. Potentiodynamic polarisation studies

The corrosion behaviour of galvanised steel coated with the epoxy resin and anticorrosive pigmented epoxy resins with RIO, ZP and ZC was investigated using potentiodynamic polarisation studies and the results are shown in Fig. 1. Electrochemical kinetic parameters obtained by extrapolation of Tafel lines are presented in Table 1. It is clear that the anodic and cathodic Tafel slopes are found to increase with the addition of anti corrosive pigments. The increase in  $\beta_a$  and  $\beta_c$  are related to the decrease in both the anodic and cathodic currents respectively. This indicates that the presence of anti corrosive pigments inhibit the corrosion process very effectively. The inhibition efficiency was calculated from the  $I_{\text{corr}}$  values.

$$IE (\%) = \frac{I_{\text{corr(uncoated)}} - I_{\text{corr(coated)}}}{I_{\text{corr(uncoated)}}} \times 100 \quad (1)$$

Where  $I_{\text{corr(uncoated)}}$  and  $I_{\text{corr(coated)}}$  are the corrosion current densities of uncoated and coated galvanised steel respectively.



**Fig. 1** Potentiodynamic polarisation curves for uncoated and coated galvanised steel with anti corrosive pigmented epoxy resins after 1 h immersion in natural seawater.

The shift of  $E_{\text{corr}}$  values towards the negative direction for the steel coated with epoxy resins and anti corrosive pigmented epoxy coatings irrespective of their composition compared to uncoated in seawater can be explained by the domination of cathodic and anodic reaction inhibition. The change of potential in the negative direction can be attributed to the corrosion resistance of the anti corrosive pigmented epoxy coatings on the steel surface. In addition, it is clearly observed from the figures that the steel coated with epoxy resins and anti corrosive pigmented epoxy coatings reduce both the anodic and cathodic current densities, indicating the inhibiting effect of the compounds.

**Table 1** Electrochemical parameters for uncoated and galvanised steel coated with epoxy resin and anticorrosive pigmented epoxy in natural sea water.

Compound	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ mV/dec	$\beta_a$ mV/dec	$CR$ (mm.y <sup>-1</sup> ) $\times 10^{-3}$	$IE$ (%)
Uncoated	-550	2.9	45	70	314	-
ER	-805	0.37	76	112	40	87.24
ER + RIO	-899	0.19	79	114	21	93.45
ER + ZP	-994	0.15	83	116	16	94.83
ER + ZC	-1040	0.11	85	118	12	96.21

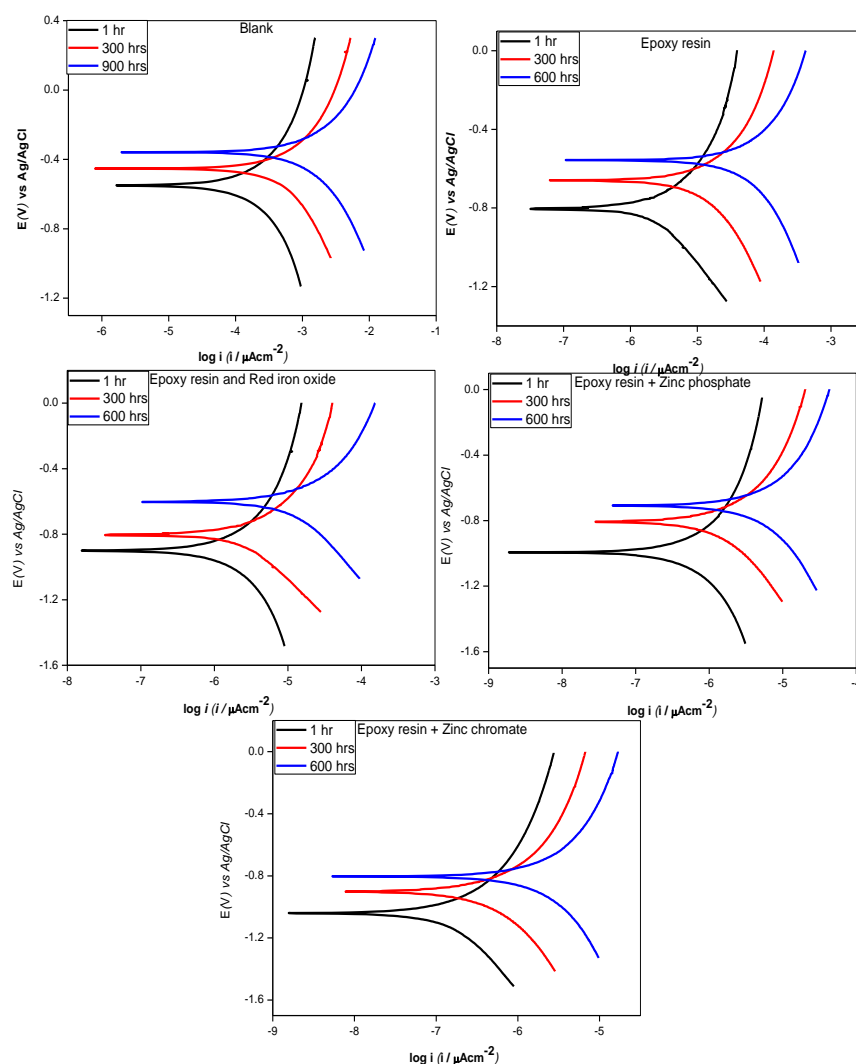


The corrosion rate of uncoated galvanised steel was found to be  $314 \times 10^{-3} \text{ mm.y}^{-1}$  and it was minimized to a lower value of  $40 \times 10^{-3} \text{ mm.y}^{-1}$  in the presence of epoxy coatings. The corrosion rate of epoxy resin, RIO, ZP and ZC pigmented epoxy coated galvanised steel was found to be  $21 \times 10^{-3} \text{ mm.y}^{-1}$ ,  $16 \times 10^{-3} \text{ mm.y}^{-1}$  and  $12 \times 10^{-3} \text{ mm.y}^{-1}$  respectively. The corrosion current density for uncoated galvanised steel is found to be  $2.9 \mu\text{A cm}^{-2}$  and that of epoxy, RIO, ZP and ZC pigmented epoxy resin are 0.37, 0.19, 0.15 and  $0.11 \mu\text{A cm}^{-2}$  respectively. The inhibition efficiency of epoxy resin and RIO, ZP and ZC pigmented epoxy coated on galvanised steel was found to be 87.24, 93.45, 94.83 and 96.21 % respectively. Therefore, the inhibition efficiency of the anti corrosive pigmented epoxy coatings on galvanised steel follows the order, ER < ER–RIO < ER–ZP < ER–ZC.

The inhibiting property of the studied anti corrosive pigmented epoxy coatings is attributed to their ability to chemisorb on the surface of galvanised steel forming few layers of self-assembled films, as anti corrosive pigmented epoxy coatings are reported to form a protective layer. The highest inhibition efficiency was observed for zinc chromate pigmented epoxy coatings because the inhibitive action of chromate seems to be based upon the oxidizing power of Cr (VI), which becomes reduced to Cr (III) in a reaction forming a layer of chromium oxide. It seems that conversion coatings formed on the surface of steel can have a high content of Cr(VI), which acts as a source of oxidizing agent whenever corrosion starts [11]. These electrons interact with the vacant d-orbital of iron present in the steel surface and adsorb strongly thereby blocking more number of the adsorption sites on the steel surface. When compared to epoxy coatings, anticorrosive pigmented epoxy coatings have better efficiency as they contain more electron donating property than the epoxy resins. It has been previously reported in literature, that inhibiting effect depends mainly on concentration of epoxy resins, the molecular structure, size and structure of the side chain in the organic compounds. It is observed that, the inhibition efficiency of the epoxy coatings increases with the addition of anti corrosive pigments as a result of higher surface coverage.

### 3.2. Effect of salt spray time

The uncoated and coated galvanised steel with the epoxy resin and anticorrosive pigmented epoxy resins with RIO, ZP and ZC specimens were sprayed with natural sea water for 300 h and 600 h. The corrosion resistance of sprayed specimens was investigated using potentiodynamic polarisation studies and the curves are shown in Figs. 2(a–e). The corrosion parameters such as  $E_{\text{corr}}$ ,  $I_{\text{corr}}$ , cathodic ( $\beta_c$ ) and anodic Tafel ( $\beta_a$ ) slopes, corrosion rate and the inhibition efficiency (IE %) obtained from the curves are listed in Table 2.



**Fig. 2** Potentiodynamic polarisation curves for (a) uncoated, (b) epoxy resin, (c) red iron oxide, (d) zinc phosphate and (e) zinc chromate coated galvanised steel after exposure to 1, 300 and 600 h in natural seawater.

The cathodic, anodic and corrosion currents were increased after spraying with sea water for 300 h and 600 h. It is observed from the table that the  $E_{corr}$  values are significantly shifted towards more positive region. This effect is more predominant in the case of 600 h. The corrosion rate of the specimens was also increased with increasing spraying time. Consequently the inhibition efficiency has decreased to a greater extent.



**Table 2** Electrochemical parameters for uncoated and galvanised steel coated with epoxy resin and anticorrosive pigmented epoxy resins water during the exposure to 1, 300 and 600 h to natural seawater.

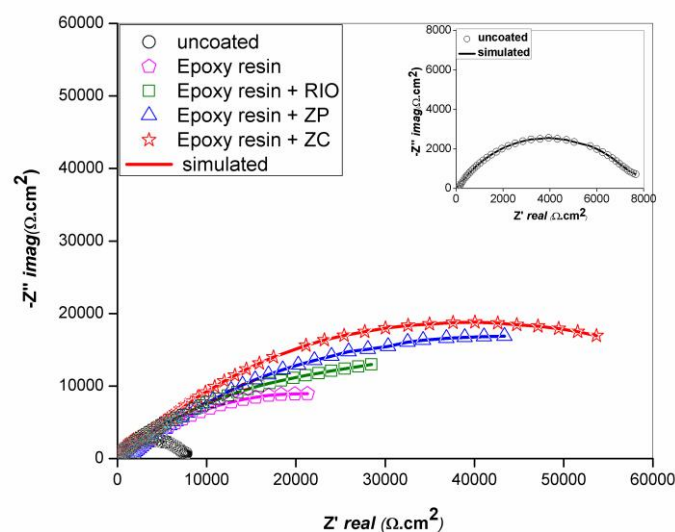
Formulations	Salt spray time (h )	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$\beta_c$ mV/dec	$\beta_a$ mV/dec	$CR$ ( $\text{mm.y}^{-1}$ ) $\times 10^{-3}$	$IE$ (%)
uncoated	1	-550	2.91	45	70	314	-
	300	-453	3.85	41	64	425	-
	600	-358	4.44	37	56	487	-
ER	1	-805	0.37	76	112	40	87.2
	300	-701	1.54	68	97	168	60.0
	600	-603	2.75	60	78	299	38.1
ER+ RIO	1	-899	0.19	79	114	21	93.5
	300	-807	1.27	74	106	139	67.0
	600	-708	2.39	69	92	261	46.2
ER + ZP	1	-994	0.15	83	116	16	94.8
	300	-901	1.15	79	109	125	70.1
	600	-803	2.22	75	95	243	50.0
ER + ZC	1	-1040	0.11	85	118	12	96.2
	300	-969	1.11	82	110	122	71.2
	600	-901	2.15	78	96	235	51.6

### 3.3. Electrochemical impedance spectroscopic measurements (EIS)

Electrochemical Impedance Spectroscopic studies were carried out in order to obtain more information concerning the electrochemical process at the galvanised steel electrode in corrosive sea water in the presence of anti corrosive pigmented epoxy coatings. The impedance diagrams represented in Nyquist plot obtained at open-circuit potential after 1 h immersion in sea water in the presence and absence of anti corrosive pigmented epoxy coatings are presented in Fig. 3.

The quantitative analysis of these spectra was performed using the equivalent circuit shown in Fig. 4(a, b). The equivalent electrical circuit shown in Fig. 4a was used to fit the impedance spectra of uncoated galvanised steel, where  $R_s$  was the solution resistance,  $C_{dl}$  was the double layer capacitance at the galvanised steel/electrolyte interface and  $R_{ct}$  was the charge transfer resistance of the galvanised steel. However, for epoxy and anti corrosive

pigmented epoxy coatings viz., RIO, ZP and ZC, the equivalent electrical circuit, a typical model used for the behavior of the coated galvanised steel in natural sea water, shown in Fig. 4b was used to fit the impedance data, where  $R_s$  was the solution resistance,  $C_c$  was the coating capacitance due to the dielectric nature of surface compound and  $R_c$  expressed the coating resistance and  $n_c$  and  $n_{dl}$  are the coefficients representing the depressed characteristic of the two capacitive loops.



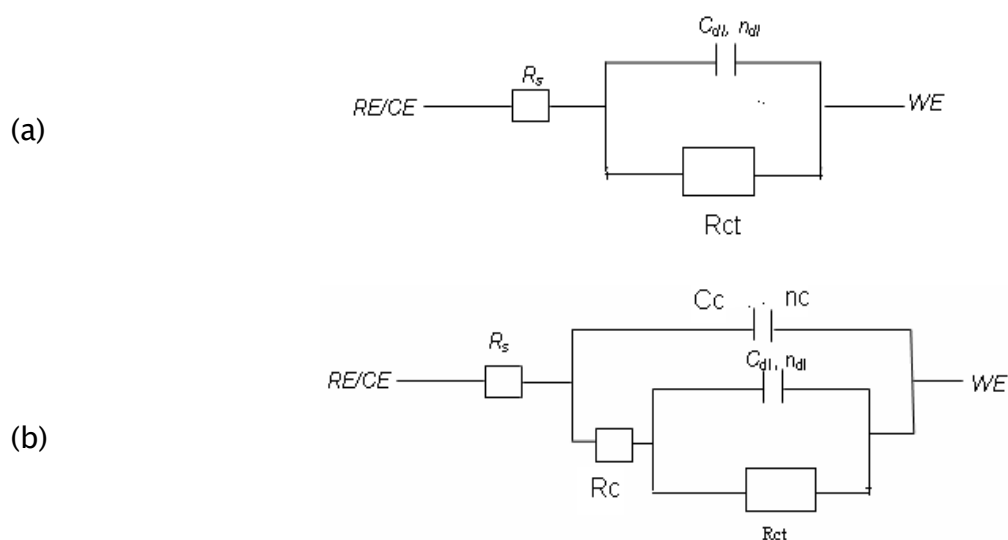
**Fig. 3** Typical Nyquist diagram for uncoated and coated epoxy coatings pigmented with red iron oxide, zinc phosphate and zinc chromate after 1 h immersion in natural seawater.

The experimental results obtained for the uncoated galvanised steel can be represented properly only by using one time constants under capacitive relaxation. For the epoxy and the anti corrosive pigmented epoxy coated galvanised steel, two capacitive loops are necessary to fit the experimental data with an electrical equivalent circuit. Compared with the equivalent electrical circuit proposed for uncoated galvanised steel, this circuit contains an additional  $R_c$  and  $C_c$  couple which appears in the high frequency region of the impedance spectra. The inhibition efficiency of coated galvanised steel with epoxy resins and anti corrosive pigmented epoxy resins was calculated from  $R_p$  values, using the following equation,

$$IE(\%) = \frac{R_{p(\text{coated})} - R_{p(\text{uncoated})}}{R_{p(\text{coated})}} \times 100 \quad (2)$$

where,  $R_{P(\text{uncoated})}$  and  $R_{P(\text{coated})}$  are polarisation resistance of uncoated galvanised steel and coated galvanised respectively. The value of  $R_p$  is calculated as the sum of  $R_c$  and  $R_{ct}$ , i.e.,  $R_{P(\text{coated})} = R_c + R_{ct}$ . Similarly,  $R_{P(\text{uncoated})} = R_{ct}$ . The parameters obtained by fitting the equivalent circuit and the calculated inhibition efficiency are listed in Table 3.

For the coated galvanised steel,  $R_c$  increases and  $C_c$  decreases with different anti corrosive pigmented epoxy resins confirming that the surface film formed by chemisorption of the compound is protective and less permeable. The  $R_c$  value of epoxy, RIO, ZP and ZC pigmented coatings was 4170, 10225, 13470 and 18780  $\Omega \text{ cm}^2$  and the corresponding  $C_c$  value was 27.25, 12.45, 6.78 and 4.22  $\mu\text{F cm}^{-2}$  respectively.



**Fig. 4** Equivalent circuit to interpret performance of the epoxy coatings pigmented with red iron oxide, zinc phosphate and zinc chromate in natural seawater.

Also,  $R_{ct}$  increases and  $C_{dl}$  decreases with the coating of epoxy resin and anti corrosive pigmented epoxy coatings as compared with that of the uncoated galvanised steel, suggesting that only a smaller area of electrode is directly in contact with the electrolyte. The  $R_{ct}$  value of epoxy, RIO, ZP and ZC pigmented epoxy coatings was 11250, 18500, 24490 and 32950  $\Omega \text{ cm}^2$  and the corresponding  $C_{dl}$  value was 38.82, 21.06, 7.22 and 5.45  $\mu\text{F cm}^{-2}$  respectively.

In the presence of RIO, the values of charge transfer resistance were slightly higher due to the iron inhibiting effect. In the presence of ZP, the general shape of the spectrum was the same, although the values for the charge transfer resistance were slightly higher, possibly due to the phosphate inhibiting effect. The chromate, in contrast, produced a growth in the total impedance due to the formation of chromate layer.

**Table 3** Electrochemical impedance parameters and inhibition efficiency for uncoated and galvanised steel coated with epoxy resin and anticorrosive pigmented epoxy resins in natural sea water.

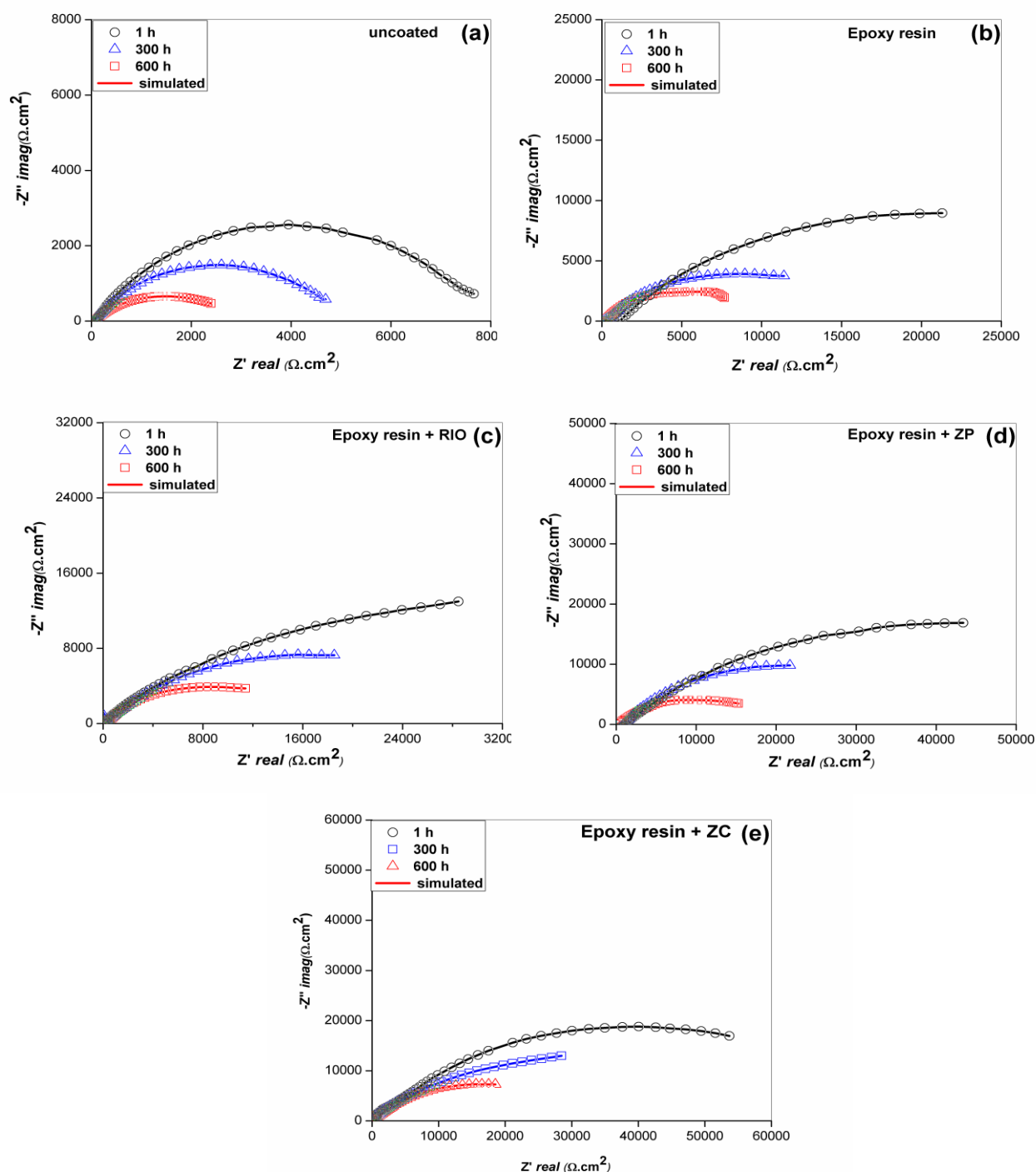
Inhibitor conc. (M )	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_c$ ( $\Omega \text{ cm}^2$ )	$C_c$ ( $\mu\text{F cm}^{-2}$ )	$n_c$	$R_{ct}$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$n_{dl}$	IE (%)
Uncoated	45	-	-	-	1950	195.3	0.69	-
ER	61	4170	27.3	0.84	11250	38.8	0.81	87.4
ER + RIO	75	10225	12.5	0.86	18500	21.1	0.84	93.2
ER+ZP	98	13470	6.9	0.92	24490	7.2	0.88	94.9
ER+ZC	112	18780	4.2	0.95	32950	5.5	0.91	96.2

The inhibition efficiency increases with the addition of anticorrosive pigments into the epoxy resins and the maximum IE for epoxy resin, RIO, ZP, ZC pigmented epoxy resin are 87.35 % , 93.21 % ,94.86 % and 96.23 % respectively. The IE % calculated from EIS show the same trend as those estimated from polarisation measurements i.e., polarisation measurements and EIS study complement each other well. The above result indicated that the ZP and ZC contain epoxy resin prevents the ingress of chloride ions from the electrolyte and proved to be a non-corrosive coating in seawater environments.

### 3.4. Salt spray testing of epoxy systems

Nyquist plots of the galvanised steel coated with the epoxy resin and anticorrosive pigmented epoxy resins with RIO, ZP and ZC are presented in Fig. 5 (a–e) after spraying with natural sea water for 300 h and 600 h. The impedance parameters are given in the Table 4. An equivalent circuit model, proposed by many authors [12, 13], based on the Nyquist plots for epoxy coated samples is also shown in Fig. 4. This model reveals the electrolyte resistance,  $R_s$ , the coating capacitance,  $C_{cp}$ , the coating resistance,  $R_{cp}$ , the charge transfer resistance,  $R_{ct}$ , and the double layer capacitance,  $C_{dl}$

By comparing the impedance spectra obtained at different spraying time for the galvanised steel specimens coated with epoxy resin and anticorrosive pigments viz., RIO, ZP and ZC, the decrease of the inhibition efficiencies at long exposure times may be due to a deterioration of the protective layer formed by the epoxy coatings and anti corrosive pigmented epoxy coatings on galvanised steel surface.



**Fig. 5** Nyquist plots of the uncoated galvanised steel, epoxy coated and the anti corrosive pigmented epoxy coated specimens after spray with natural sea water for 300 h and 600 h.

It was suggested that at the reduced frequencies the electrochemical reactions at the interface between the coating and the metal surface are making progress [14]. At this stage, penetration is completed and the electrolyte phase meets the metal/oxide interface and a corrosion cell is activated. With increased salt spray time (300 and 600 h), the barrier properties of the coating decreased further; however, the radius of the low frequency domain also decreased, suggesting an increase in the corrosion rate, possibly through the presence of further pores in the coating or an increase in the area exposed at the base of the existing pores or flaws [15]. With increased salt spray time, the radius of the high frequency domain is rapidly decreased, suggesting that the barrier properties of the coating is progressively decreased, and the corrosion rate continues to increase to the end of the test. It can be seen from table that anticorrosive pigmented epoxy coatings on galvanised steel has greater resistance than both epoxy coating on galvanised steel and uncoated galvanised steel, indicating the beneficial role of chromium, phosphate and oxide on the overall coating resistance.

**Table 4** Electrochemical impedance parameters and inhibition efficiency for uncoated and galvanised steel coated with epoxy resin, anticorrosive pigmented epoxy resins in natural sea water during 1, 300 and 600 h of exposure time.

Formulations	Salt spray time (h )	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_c$ ( $\Omega \text{ cm}^2$ )	$C_c$ ( $\mu\text{F cm}^{-2}$ )	$n_c$	$R_{ct}$ ( $\Omega \text{ cm}^{-2}$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$n_{dl}$	IE (%)
Uncoated	1	45	-	-	-	1950	195.3	0.69	-
	300	42	-	-	-	1700	220.5	0.65	-
	600	40	-	-	-	1450	245.0	0.60	-
ER	1	61	6170	27.3	0.84	9250	38.8	0.81	87.4
	300	58	1690	38.2	0.80	2580	49.7	0.78	60.2
	600	54	1030	55.4	0.76	1320	69.4	0.74	38.3
ER + RIO	1	75	10225	12.5	0.86	18500	21.1	0.84	93.2
	300	66	2070	33.3	0.81	3150	45.2	0.79	67.4
	600	60	1140	47.2	0.77	1560	58.8	0.75	46.3
ER+ZP	1	98	13470	6.9	0.92	24490	7.2	0.88	94.9
	300	75	2225	31.9	0.82	3500	42.2	0.80	70.3
	600	64	1230	43.6	0.79	1710	54.8	0.77	50.7
ER+ZC	1	112	18780	4.2	0.95	32950	5.5	0.91	96.2
	300	92	2380	29.2	0.83	3670	40.2	0.81	71.9
	600	71	1270	41.5	0.81	1750	52.1	0.79	60.0



In the presence of the pigments, the precipitation, which serves as barrier to prevent water, dissolved oxygen and aggressive ions from reaching the metal surface, is able to minimize incorporation of ions into the coating. In addition to  $R_c$ , charge transfer resistance values were noticeably influenced by inclusion of anti corrosive pigments into the coatings. Since formation of a layer on the specimen surface exposed to pigments could restrict active zones,  $R_{ct}$  as the resistance of the metal surface to electrochemical reactions might meet a significant enhancement. On the other hand, a marked drop in charge transfer resistances of non-pigmented epoxy coatings may be attributed to easier access of aggressive ionic species to the coating/metal interface through the pores and development of active areas on the surface as well.

### 3.5 Analysis of FT-IR Spectra

The FTIR spectra of epoxy resin and investigated anticorrosive pigmented epoxy coatings on galvanised steel, within the spectral range of 400–4000  $\text{cm}^{-1}$  are shown in Fig. 6. A broad peak at 3448  $\text{cm}^{-1}$  is due to N-H stretching and -O-H group of the epoxy resin. Absorption band at 2928  $\text{cm}^{-1}$  confirms the presence of C-H stretch group. The presence of a peak at 1628  $\text{cm}^{-1}$  indicates the formation of carboxylate groups. The peaks in frequency at 1182, 1107 and 1041  $\text{cm}^{-1}$  were attributed to C-O stretching of the ether and ester groups.

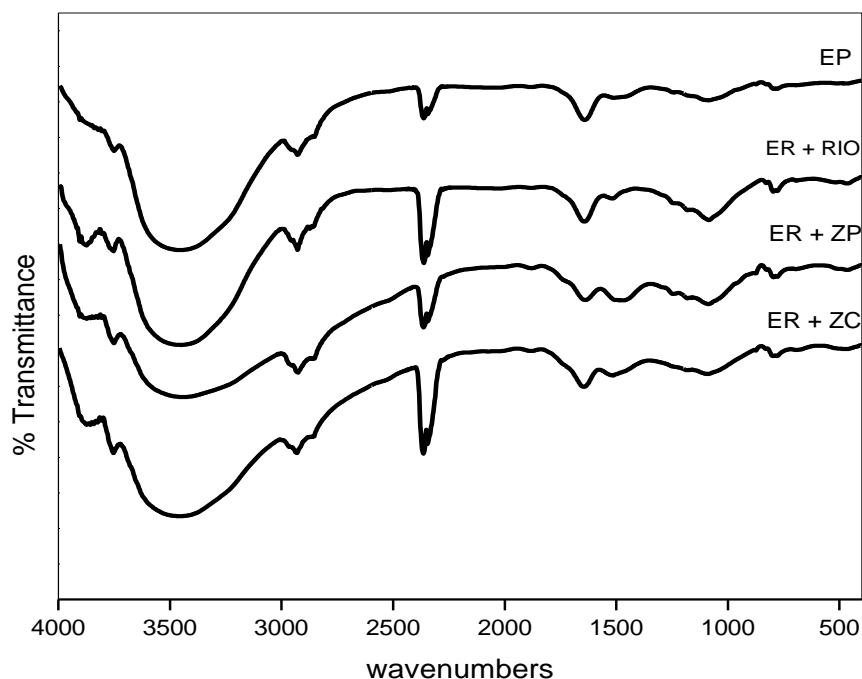


Fig. 6 FT-IR spectra.

### *3.6. Adhesion measurements*

The adhesion strength of epoxy coatings and anti-corrosive pigments viz., RIO, ZP, ZC on galvanised steel was determined by pull-off test prior to exposure to natural seawater as well as during exposure to natural seawater at room temperature. For all examined protective systems it was not possible to measure the pull-off strength prior to exposure to natural seawater since the failure was always cohesive. However, the wet adhesion test showed excellent adhesion strength for the ERION, EZC and EZP compared to epoxy resin coating. The basic function of an organic coating is, first, to act as a barrier so that a complete corrosion cell cannot form, and, second, to prevent the spreading of corrosion from the initial site of electrolyte penetration. Both functions require adequate coating adhesion in the presence of water and/or electrolyte. Thus, one of the most important factors in corrosion prevention by a protective coating is the coating adhesion loss under environmental influence.

In this work, both the dry and wet adhesion of epoxy coatings with anti-corrosive pigments on galvanised steel was measured by the standard pull-off method. The pull-off results of adhesion strength after 1, 300 and 600 h of immersion in natural seawater as well as the adhesion reduction during this time of exposure to natural seawater are shown in Table 5.

There are indications that good adhesion between a high energy surface and the coating layer can occur through intimate contact between the substrate and the molecules of the coating [16]. Anticorrosive pigmented epoxy substrates have higher surface energy than epoxy coated substrate. Furthermore, as a result of chemical interactions between epoxy resins with anticorrosive pigment molecules and galvanised steel surface, dry adhesion strength of epoxy coating increased additionally. In the dry state, all coated specimens indicated no failed regions, proving good adhesive strength.

The adhesion strength of all specimens in the wet stage (immediately, after 300 and 600 h exposure to natural seawater) is decreased in comparison with dry stage. The main reason for failure of most organic coatings is the loss of bonding (if any) between the coating and the substrate after exposure to the humid atmosphere. When a coated galvanised steel surface is exposed to an aqueous environment, water molecules penetrate through the coating layer, after a certain initial period, water molecules are accumulated in the coating/substrate interface, within the oxide layer of galvanised steel. Mechanical interlocking or/and chemical interactions throughout the interface may be affected by this phenomenon and as a result, adhesion strength decreasing will be detected.

The adhesion strength values for epoxy coatings with anticorrosive pigments on galvanised steel deposited vary significantly after 300 h of exposure to a corrosive agent as well as after 600 h of exposure. Thus, the adhesion reduction also varies these protective systems (Table 5). On the other hand, the high adhesion reduction for coating of epoxy resins, anti-corrosive pigments viz., RIO, ZP and ZC on galvanised steel is 62.18, 54.70, 50.54 and 47.98 % after 600 h of exposure to natural seawater. This indicates that this protective system is not very stable in a corrosive environment after longer exposure time. Adhesion of epoxy coatings with anti-corrosive pigments on galvanised steel is significantly reduced after 300 h and 600 h of exposure to natural seawater.

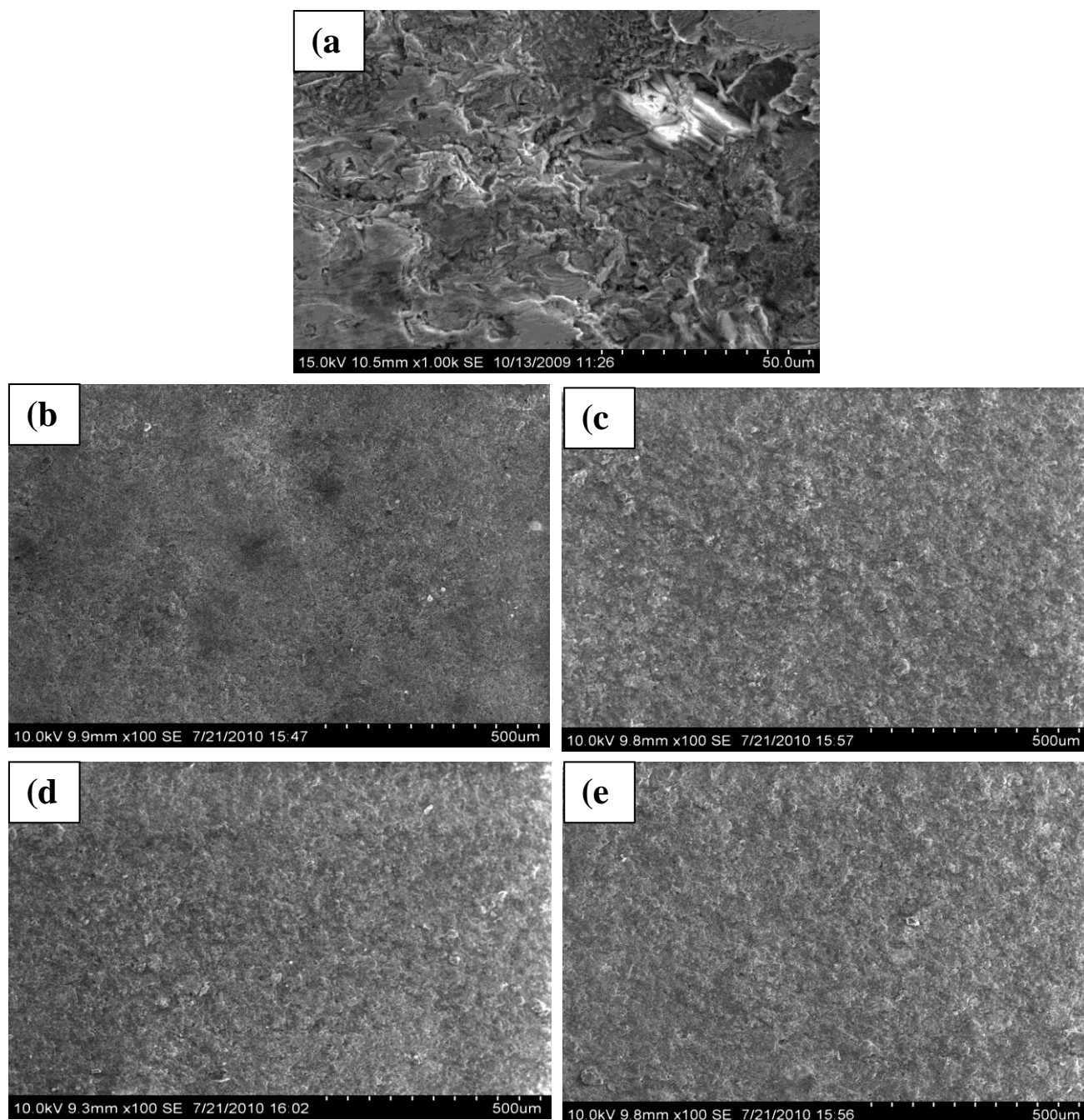
**Table 5** The average values of adhesion strength after 1, 300 and 600 h of exposure to natural seawater and adhesion reduction for epoxy coatings and investigated anticorrosive pigmented epoxy coatings on galvanised steel.

Formulations	Adhesion strength (1 h) ( $\text{N mm}^{-2}$ )	Adhesion strength(300 h) ( $\text{N mm}^{-2}$ )	Adhesion reduction (300 h) (%)	Adhesion strength (600 h) ( $\text{N mm}^{-2}$ )	Adhesion reduction (600 h) (%)
ER	1.56	0.93	40.38	0.59	62.18
ER + RIO	1.81	1.21	33.15	0.82	54.70
ER+ZP	1.86	1.29	30.65	0.92	50.54
ER+ZC	1.98	1.42	28.28	1.03	47.98

### 3.7. Scanning electron microscopy (SEM)

Scanning electron micrographs were taken in order to establish whether inhibition is due to the formation of organic coatings on the metal surface and are shown in Fig. 7. Examination of figures revealed that the anticorrosive pigmented epoxy coatings inhibit corrosion. Epoxy coating has a strong tendency to adhere to the galvanised steel surface. The epoxy molecules adsorb on the metal surface through binder as well as sharing electrons between anticorrosive pigmented epoxy resins and metal atoms. This shows that the inhibition is due to the chemisorptions of anticorrosive pigmented epoxy coatings on the metal surface.





**Fig. 7** SEM graphs of the uncoated galvanised steel (a) and coated galvanised steel with epoxy resins (b) anticorrosive pigmented epoxy coatings: (c); red iron oxide; (d) zinc phosphate; (e) zinc chromate exposed to natural seawater

## 4. Conclusion

It was demonstrated that epoxy coatings with anticorrosive pigments viz., RIO, ZP and ZC can protect the galvanised steel effectively against corrosion. Better electrochemical properties were obtained for epoxy resins with anticorrosive pigments on galvanised steel and can be confirmed by the higher values of coating resistance. The  $R_{ct}$  values of anticorrosive pigmented epoxy coatings, associated with the corrosion processes at the metal substrate, confirmed their good barrier properties.

The corrosion protection efficiency of studied anti corrosive pigmented epoxy coated galvanised steel increased in the order, epoxy resin < RIO < ZP<ZC pigmented epoxy coatings. The smallest adhesion reduction of epoxy resins with anticorrosive pigments on galvanised steel indicates that the anticorrosive pigments enhance the adhesion of epoxy cataphoretic coating.

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