

A new corrosion protection coating with polyaniline–TiO₂ composite for steel

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Abstract

Organic coating strategies for corrosion protection with inherently conducting polymers have become important because of restriction on the use of heavy metals and chromates in coatings due to their environmental problems. This work presents the synthesis of polyaniline–TiO₂ composites (PTC) and the corrosion protection behaviour of PTC containing coating on steel. PTC was prepared by chemical oxidation of aniline and TiO₂ by ammonium persulfate in phosphoric acid medium. The PTC was characterized by FTIR, XRD and SEM techniques. Suitable coating with PTC was formed on steel using acrylic resin. Using electrochemical impedance spectroscopy, the PTC containing coating's behaviour in 3% NaCl immersion test and salt spray test has been found out. Results indicate that the coating containing PTC is able to maintain the potential of steel in passive region due to its redox property. The resistance of the coating containing PTC was more than $10^7 \Omega \text{ cm}^2$ in 3% NaCl solution after 60 days and $10^9 \Omega \text{ cm}^2$ in the salt spray test of 35 days. But the resistance of the TiO₂ containing coating was found to be less than $10^4 \Omega \text{ cm}^2$ in both the cases. The high performance of PTC containing coating is attributed to the passivation of steel by polyaniline.

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1. Introduction

Conducting polymer coatings such as polyaniline, polypyrrole, etc. have been shown to offer corrosion protection of ferrous and non-ferrous metals. The reviews [1–4] summarize the studies made by various investigators on the corrosion resistant properties of conducting polymers. Incorporation of conducting polymer in organic coating system has been found to offer corrosion protection of metals. Kinlen et al. [5,6] have shown that polyaniline (PANI) containing organic coating on steel is able to passivate the pinholes and defects in the coating and passivation of metal surface through anodisation of metal by PANI and formation of an insoluble iron-dopant salt at the metal surface. de Souza et al. [7] have shown by Raman spectroscopy that polyaniline based acrylic blend is able to protect steel and the dopant forms iron complex as a second protective layer. Dominis et al. [8] have studied the effect of various dopants such as hydrochloric acid, tartaric acid, oxalic acid, dodecyl benzene sulfonic acid,

poly methoxy aniline sulfonic acid and nitrilotri methyl phosphonic acid in polyaniline on the corrosion resistant property of the coating. Samui et al. [9] has shown that lower loading of PANI–HCl is found to be more effective in corrosion protection of steel. Sathiyarayanan et al. [10,11] have found that coatings containing polyaniline are able to protect steel in acid and neutral environment. Plesu et al. [12] have studied the performance of organic phosphorous acid doped polyaniline with acrylic binder on the corrosion protection of steel in 3.5% NaCl solution. TiO₂ is one of the main pigment which is usually used in the organic coatings. Hence a study has been made on the use of PANI–TiO₂ composite (PTC) in coating formulation since polyaniline has been found to enhance the protective property of the coatings. Earlier studies on PANI–TiO₂ composites were mostly concerned with the synthesis and characterization. Su and Kuramoto [13] have studied the conductivity of polyaniline–TiO₂ nano composites. Gurunathan et al. [14] have synthesized and characterized the conducting PANI–TiO₂ composites and studied their use as cathode material in rechargeable battery. Xu et al. [15] have studied the nature of bonding of polyaniline with TiO₂ and showed that the bonding is through hydrogen bonding. The dielectric properties of PANI–TiO₂ hybrid have been studied by

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Lee et al. [16]. Zhang et al. [17] have studied the solid phase photo catalytic degradation of PANI–TiO₂ nano composite. In this paper, the corrosion resistant property of the coating containing synthesized PANI–TiO₂ composites on steel is reported.

2. Experimental

2.1. Preparation of PANI–TiO₂ composite

An amount of 1 M of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid and 25 grams of anatase TiO₂ was added to it. The mixture was stirred well. Pre-cooled 500 ml of 1 M solution of ammonium persulfate was added drop wise to the pre-cooled aniline–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at 5 ± 1 °C. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured PANI–TiO₂ composite thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about 80 °C for 2 h. The dried PANI–TiO₂ composite was fine grinded using mortar and then used as pigment.

2.2. Characterization of PANI–TiO₂ composite

The infrared spectra of the polymer composite were recorded on NICOLET 380 FTIR spectrometer in KBr medium at room temperature in the region of 2500–500 cm^{−1}. X-ray diffraction pattern of PANI–TiO₂ composite was taken with Analytical (Model PW3040/60) X-ray diffractometer using Cu K α radiation in the 2θ range 0–90° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s. The morphology of the composite was analyzed using Hitachi (Model S3000 H) scanning electron microscopy by spreading the pigment over a copper block over which gold was sputtered. The electrical conductivity of the composite was found by four probe resistivity meter.

2.3. Preparation of PANI–TiO₂ composite containing paint

The primer is formulated using commercial acrylic resin (Kondicryl 166, Pidilite, India). The volume solids of the formulation was kept at 30% with 35% pigment volume concentration (P.V.C.). The main pigments used in this formulation were polyaniline, titanium di oxide and PTC along with mica and silica as extender pigments. Di octyl phosphate (D.O.P.) was used as a plasticizer. This primer coat was top coated with aliphatic polyurethane paint. This top coat paint was formulated with acrylic ployol (Kondicryl SVOL-7, Pidilite, India) as base and poly iso cyanate (Grand Polycoats, India) as curing agent. The paint was formulated with 40% volume solids and 18% P.V.C. Rutile titanium di oxide was used as main pigment along with mica and silica as extender pigments.

The pigments were pre mixed and the paint was formulated in an lab attritor. The attritor was run for 45–50 min. The fineness of dispersion of paint was found using Hegmann gauge and it was found to be between 7 and 8. The paint was stored in air tight container. The mix ratio of the polyurethane paint was 2:1 by

weight. The topcoat was applied over the primer applied panels after 24 h of curing at ambient conditions. The specific gravity of the primer was 1.0 and that of top coat was 0.98. The dry film thickness (DFT) of the coating was measured by Minitest thickness meter (Model 600, Electrophysick) and it was found to be 40–45 μ m for primer and 30–35 μ m for the top coat. The adhesion of the coating was tested by Tape test as per ASTM D3359-02 and found to pass the test.

2.4. Evaluation of corrosion resistant properties of the coating

2.4.1. Salt spray tests

Coated mild steel panels were prepared by coating on sand blasted (SA 2.5) specimen of size 15 cm $\times$ 10 cm $\times$ 0.1 cm. The coated panels were exposed to salt spray of 5% NaCl solution as per ASTM B117.

2.4.2. EIS studies

Steel specimens of size 5 cm $\times$ 5 cm $\times$ 0.1 cm were sand-blasted (SA 2.5) and decreased with trichloroethylene and coated with the developed paint. The total thickness of the coating was 100 ± 5 μ m. A glass tube of 1.2 cm dia of length 3 cm was fixed on the coated aluminium with adhesive (m seal) and the exposed area was 1.0 cm² to the solution. The solution of 3% NaCl was taken in the glass tube. A platinum foil and a saturated calomel electrode were placed inside the glass tube. The schematic diagram of the experimental cell assembly is shown in Fig. 1. The assembly was connected to electrochemical impedance analyzer (PARSTAT 2273, EG&G). Impedance measurements were carried out for a frequency range of 100 kHz to 0.01 Hz with an ac amplitude of 20 mV for different immersion time up to 60 days. The impedance values are reproducible ± 2 to 3%. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using the equivalent cir-

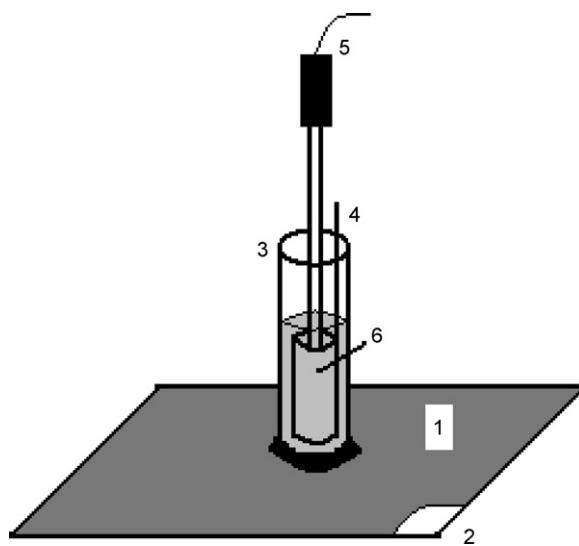


Fig. 1. Experimental cell setup: (1) painted steel panel, (2) paint removed area for making working electrode contact, (3) glass tube, (4) platinum counter electrode, (5) SCE reference electrode, and (6) test electrolyte.

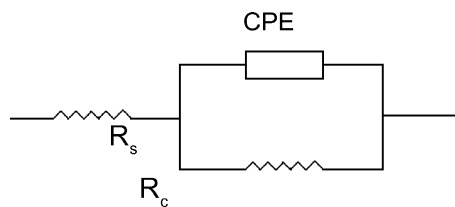


Fig. 2. Equivalent circuit for painted steel panel.

circuit shown in Fig. 2. In the equivalent circuit, R_s is the solution resistance, R_c is the coating resistance and CPE is the constant phase element of the coating capacitance (C_c).

Assumption of a simple $R_c - C_c$ is usually a poor approximation. For the description of a frequency independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used which is defined in impedance representation as

$$Z(\text{CPE}) = Y_0^{-1} (j\omega)^{-n}$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and n is the CPE exponent. Depending on n , CPE can represent resistance ($Z(\text{CPE}) = R$, $n = 0$), capacitance ($Z(\text{CPE}) = C$, $n = 1$), inductance ($Z(\text{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [18]. The following equation is used to convert Y_0 into C_c is [19]

$$C_c = Y_0 (\omega_m'')^{n-1}$$

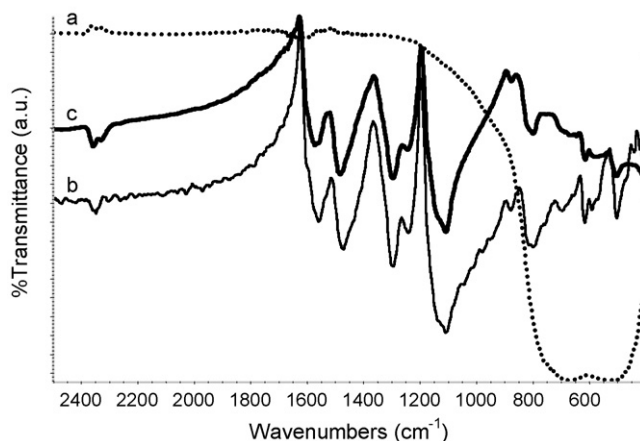
where C_c is the coating capacitance and ω_m'' is the angular frequency at which Z'' is maximum. The experiments were carried out for a period of 60 days in the case of immersion test and 35 days in the case of salt spray exposure test.

3. Results and discussion

The electrical conductivity of PANI–TiO₂ composite is found to be 0.0125 S cm^{-1} . The reported values of the conductivity are $2.4 \times 10^{-3} \text{ S cm}^{-1}$ [16], 0.04 S cm^{-1} [14] and $0.16\text{--}7.0 \text{ S cm}^{-1}$ [15]. The conductivity of the polymer depends upon the nature of dopant and the acid concentration. Hence the difference in the conductivity values observed in this study with that of reported values may be due to the dopant ions present in the polymer.

3.1. Fourier transform infrared spectra

Fig. 3 shows the FTIR spectra of TiO₂, PANI and PANI–TiO₂ composite (PTC). The main characteristics of bands of polyaniline are found (i.e.) the bands at 1574 and 1484 cm^{-1} are the stretching mode of C=N and C=C, the bands at 1297 and 1245 cm^{-1} are to C–N stretching mode of benzenoid ring and the band at 1109 cm^{-1} is assigned to a plane bending vibration of C–H mode which is found during protonation [20]. These peaks when compared to that of pure polyaniline [21] are found to be shifted slightly due to strong interaction of TiO₂ particle with polyaniline. Similar observation has been reported by Lee et al. [16]. In the case of TiO₂, strong absorption around 670 cm^{-1}

Fig. 3. FTIR spectra of (a) TiO₂, (b) PANI, and (c) PANI–TiO₂ composite.

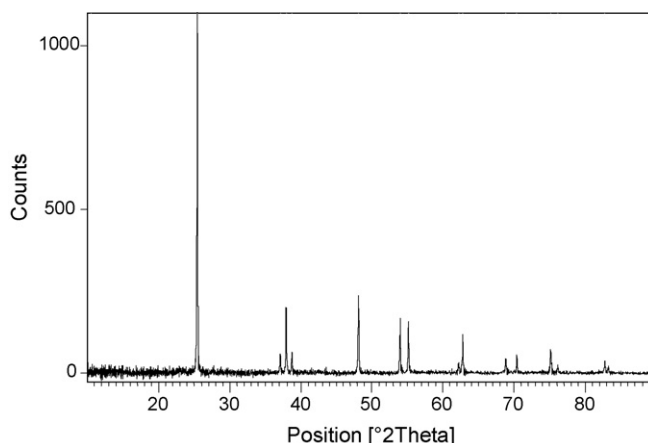
due to Ti–O stretching [14] is observed while this band is found to be weak in PTC due to the presence of PANI.

3.2. X-ray diffraction studies

The XRD pattern of PTC is shown in Fig. 4. It shows that the polyaniline deposited on the surface of TiO₂ particles has no effect on the crystallization behaviour of TiO₂ particles. Xu et al. [15] and Lee et al. [16] have recorded similar observation on the XRD pattern of polyaniline–nano TiO₂ composites.

3.3. Polymerization mechanism

Since the surface of TiO₂ has the point of zero charge (pzc) at pH 5.9 [22], it may be positively charged in the acidic polymerization H₃PO₄ bath. Due to the positive charge on TiO₂, the H₂PO₄[−] ions adsorb on TiO₂. These specifically adsorbed anions would work as a charge compensator for positively charged PANI chain in the formation of PTC. Similar reaction mechanism has been put forward for PANI–MnO₂ composite [23]. The scanning electron micrograph of TiO₂ and PTC are shown in Fig. 5 indicating that TiO₂ particles have a nucleus effect and caused a homogenous PANI core shell type mor-

Fig. 4. XRD pattern of PANI–TiO₂ composite.

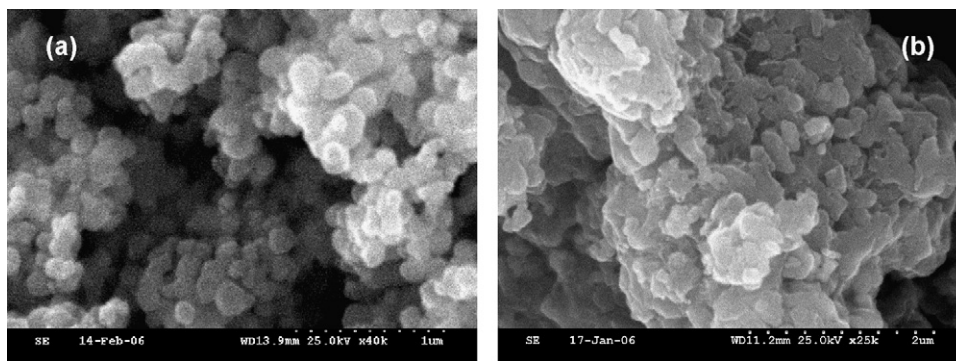


Fig. 5. Scanning electron micrograph of (a) TiO_2 and (b) PTC.

phology leading to uniform coverage of TiO_2 particles by PANI deposit.

3.4. Evaluation of coatings

3.4.1. Open circuit potential studies

The variation of open circuit potentials (OCP) with time for the TiO_2 and PTC containing paint coated steel in 3% NaCl is shown in Fig. 6. The coating containing PTC is able to maintain more noble potential values in comparison to TiO_2 containing coating. This shows that PTC is able to passivate the steel better. Earlier studies have shown that the polyaniline containing coating is able to gain 100–500 mV potential in noble direction in neutral chloride solution due to passivation of iron [24–27].

3.5. EIS studies

The electrochemical impedance spectroscopy is used to find out the protective nature of the coating by measuring the resistance (R_c) and capacitance (C_c) of the coating. R_c can be attributed to the electric resistance of ionic transfer through coating pores. Normally, R_c decreases with time due to the pen-

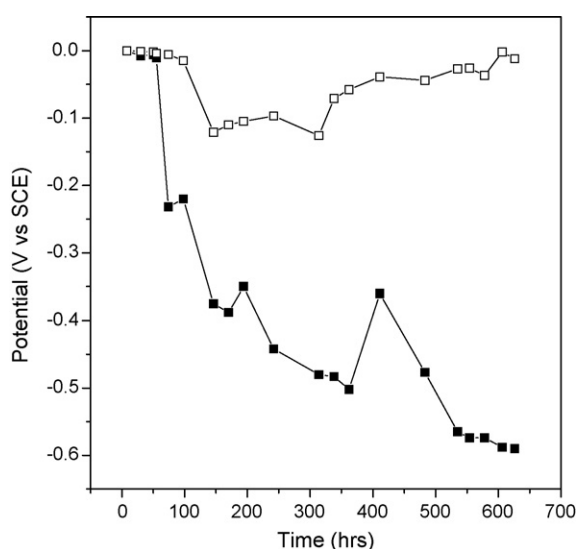


Fig. 6. OCP variation of coated steel in 3% NaCl containing (■) TiO_2 and (□) PTC.

etration of electrolyte through the coating pres. The coating capacitance $C_c = \epsilon \epsilon_0 A/d$, where ϵ denotes the relative dielectric constant of paint film, ϵ_0 is the permittivity of the vacuum ($=8.85 \times 10^{-14} \text{ F cm}^{-1}$), A the active area and d the coating thickness. The effect of increase in dielectric constant with the permeation of water may increase C_c value. Hence variation in capacitance values indicate the water uptake by the film.

3.6. EIS studies of coated steel exposed to 3% NaCl solution

The variations of the impedance of the coated steel by TiO_2 containing coating is shown in Fig. 7. The resistance and capacitance values of the coatings for different immersion period obtained from this figure are given in Table 1. The resistant values of TiO_2 containing coating is $1.0 \times 10^9 \Omega \text{ cm}^2$ initially. On subsequent exposure to sodium chloride solution, the resistance values decrease rapidly. The resistance value of TiO_2 is decreased to $2.8 \times 10^3 \Omega \text{ cm}^2$ after 60 days immersion. The degradation of coating is found to be very faster since the coating resistance is found to be low to that of threshold value of protective coating (i.e. $10^7 \Omega \text{ cm}^2$) [28]. Besides, the impedance spectra shows a diffusion process after 10 days immersion due to diffusion of water and

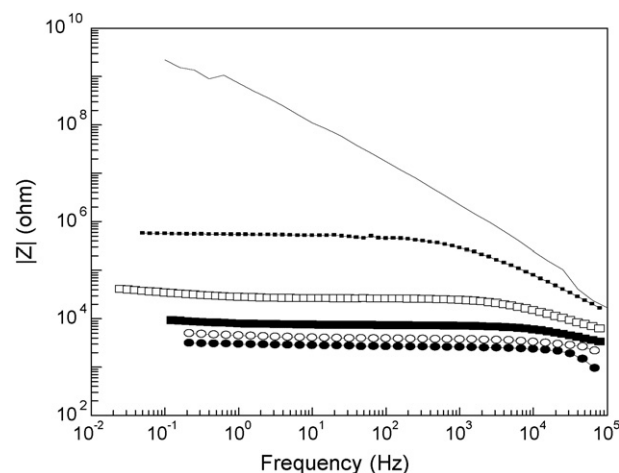


Fig. 7. Impedance plots of TiO_2 containing paint coated steel in 3% NaCl: (—) initial; (▲) 3 days; (□) 10 days; (■) 30 days; (○) 40 days; (●) 60 days.

Table 1

Impedance parameters of TiO₂ and PTC containing paint coated on steel in 3% NaCl

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
TiO ₂ containing coating				
Initial	1.01×10^6	1.79×10^{-9}	0.78	3.09×10^{-10}
3	5.35×10^5	2.67×10^{-9}	0.76	3.43×10^{-10}
10	3.13×10^4	5.70×10^{-8}	0.60	8.14×10^{-10}
30	7.89×10^3	3.54×10^{-8}	0.67	6.35×10^{-10}
40	3.90×10^3	1.07×10^{-9}	0.60	9.77×10^{-9}
60	2.82×10^3	2.24×10^{-9}	0.60	2.02×10^{-9}
PTC containing coating				
Initial	1.08×10^{10}	4.54×10^{-10}	0.87	3.21×10^{-10}
3	3.28×10^8	3.37×10^{-10}	0.87	2.44×10^{-10}
10	2.20×10^8	6.70×10^{-10}	0.82	4.34×10^{-10}
30	1.07×10^8	8.68×10^{-10}	0.79	5.44×10^{-10}
40	7.41×10^7	1.32×10^{-9}	0.77	6.59×10^{-10}
60	2.05×10^7	1.21×10^{-9}	0.81	5.08×10^{-10}

chloride ions through the coating. The Warburg coefficient is found to be increased from $1468 \times 10^{-6} \Omega \text{ cm}^2 \text{ s}^{-1/2}$ to $6867 \times 10^{-6} \Omega \text{ cm}^2 \text{ s}^{-1/2}$. With longer immersion period, the “ n ” value is also found to be nearing to 0.5 with time due to diffusion process. However in a recent study by Shen et al. [29] have shown that a hydrophobic nano TiO₂ coating on 316L stainless steel is able to offer excellent corrosion resistance in chloride containing solution.

The impedance behaviour of PTC containing coating on steel in 3% NaCl for an immersion period of 60 days is shown in Fig. 8. Table 1 also summarizes the resistance and capacitance of the coating obtained from this figure. From table, it can be seen that the resistance value of the coating is initially $1.08 \times 10^{10} \Omega \text{ cm}^2$ and decreased to $2.05 \times 10^7 \Omega \text{ cm}^2$ after 60 days immersion.

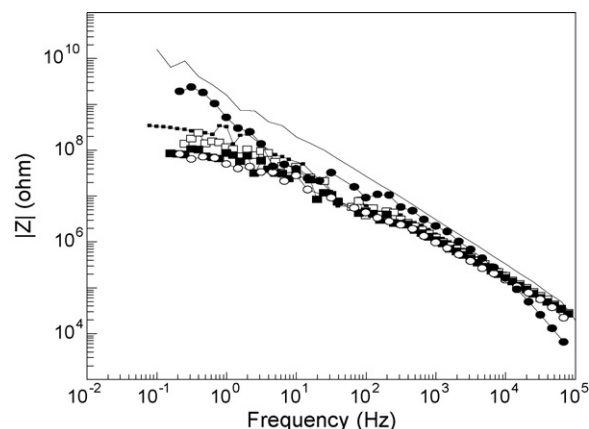


Fig. 8. Impedance plots of PTC containing paint coated steel in 3% NaCl: (—) initial; ($\blacktriangle$) 3 days; ($\square$) 10 days; ($\blacksquare$) 30 days; ($\circ$) 40 days; ($\bullet$) 60 days.

On comparing the resistance values of TiO₂ containing coating, the resistance value of PTC containing coating is nearly 4 orders high. This shows that PTC containing coating is more protective in nature. Besides the n values are more or less constant, i.e. 0.81 ± 0.02 with time which indicate that the surface of steel substrate is not changed. The capacitance value of the coating is found to be in the order of $1.0\text{--}0.3 \times 10^{-9} \text{ F cm}^{-2}$. The very high resistance values, i.e. $>10^7 \Omega \text{ cm}^2$ and low capacitance values ($<1 \text{ nF cm}^{-2}$) indicate the high corrosion protection ability of the PTC present in the coating.

3.7. EIS studies of coated steel exposed to salt spray test

The appearance of the TiO₂ and PTC containing paint coated steel samples after exposure to salt spray fog for 35 days is shown in Fig. 9a and b. It can be seen that the PTC containing coating

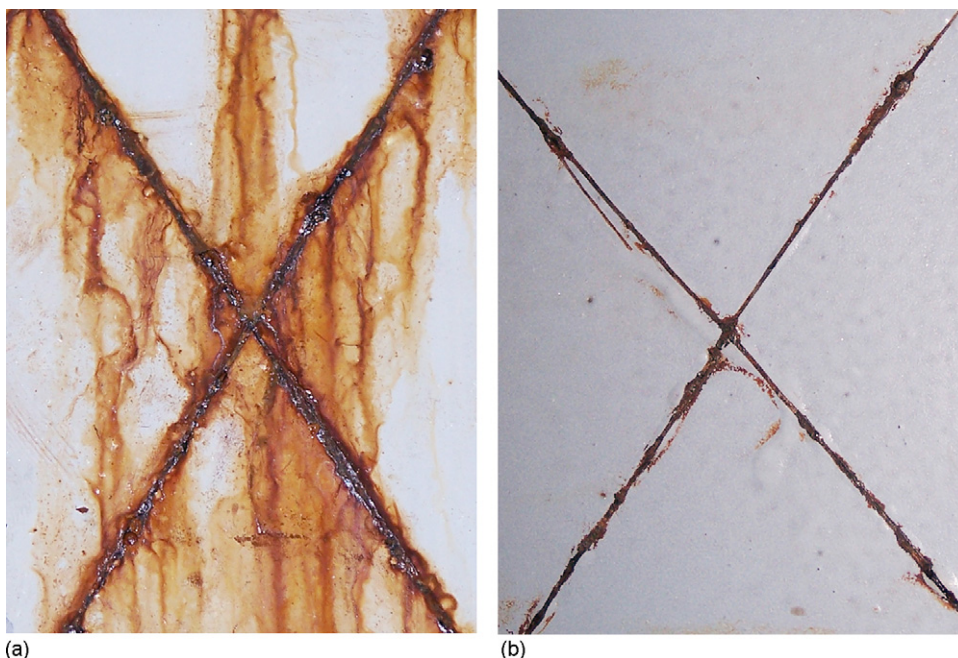


Fig. 9. (a) Photograph of TiO₂ containing paint coated steel after 35 days of exposure to salt spray test. (b) Photograph of PTC containing paint coated steel after 35 days of exposure to salt spray test.

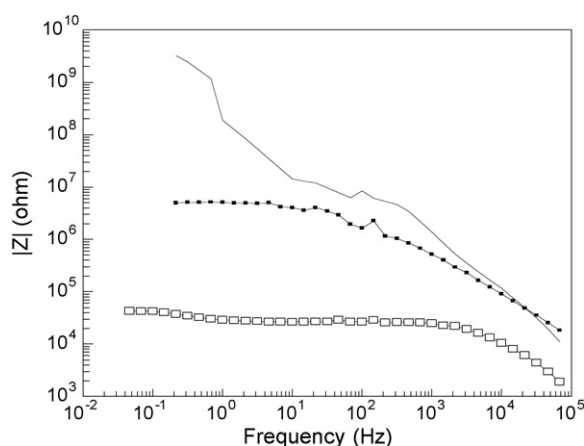


Fig. 10. Impedance plots of TiO₂ containing paint coated steel after salt spray exposure: (—) initial; (■) 2 days; (□) 3 days.

sample is free from rust and blister and also there is no spreading of rust along the scribed areas. However, the TiO₂ containing coating has more corrosion extended area from the scribes.

The EIS studies also conducted on the samples exposed to salt spray periodically in order to access the degree of degradation of the coating. Fig. 10 shows the impedance behaviour of TiO₂ coated sample after salt spray exposure and Table 2 gives the impedance values of the TiO₂ containing coating for different period of salt spray exposure.

The resistance of the coating containing TiO₂ is initially $2.5 \times 10^{10} \Omega \text{ cm}^2$ and decreased drastically to $3.29 \times 10^4 \Omega \text{ cm}^2$ in just 3 days exposure.

Fig. 11 shows the impedance diagram for the PTC containing coated steel exposed to salt spray fog. The resistance and capacitance of the coating obtained from these curves are also presented in Table 2. The resistance value is decreased slightly from the initial value of $4.9 \times 10^9 \Omega \text{ cm}^2$ to 2.58×10^8 after 5 days of salt spray exposure. There after, the resistance value is increased and reaches a steady value of $1 \times 10^9 \Omega \text{ cm}^2$ at the end of 35 days exposure. On comparing the resistance values of TiO₂ containing coating, the PTC containing coating has got nearly 5 orders higher resistance values. The capacitance values remain constant in the range $0.75\text{--}2.0 \times 10^{-10} \text{ F cm}^{-2}$. The n value is not affected much, lying in the range of 0.89–1. This

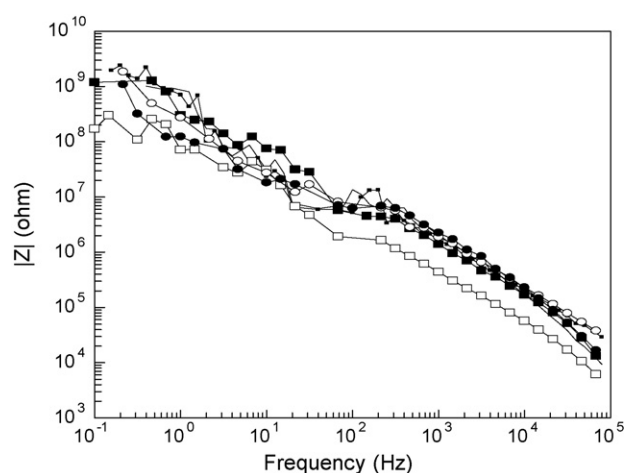


Fig. 11. Impedance plots of PTC containing paint coated steel after salt spray exposure: (—) initial; (■) 1 day; (□) 5 days; (■) 9 days; (○) 14 days; (●) 35 days.

high resistance and low capacitance values of the coating containing PTC after exposure to salt spray fog indicates its high protective nature of the coating.

Both immersion tests and salt spray tests show that the PTC containing coating has got higher corrosion resistance. The better performance may be due to the redox property and uniform distribution of PANI in the coating containing PTC. Earlier studies [25–27,30,31] have shown that the polyaniline containing coating is able to protect the steel by passivating the pin holes and the steel surface beneath the coating due to the redox property of the coating. Corrosion protection of steel occurs via reduction of polyaniline–Emeraldine salt (PANI–ES) to polyaniline–Leucosalt (PANI–LS) with the concomitant release of phosphate dopant. These phosphate ions helps to form passive film on iron at the defect. PANI–LS is assumed to undergo a subsequent re-oxidation by dissolved oxygen to PANI–ES. Due to this cyclic reaction, the coating containing PANI is able to offer higher corrosion protection. But in the case of TiO₂ containing coating, the mechanism of protection is mostly by barrier effect. Due to this, the ingress of water and corrosive ions take place through the defects in the paint coating and thereby the protective property of the coating is decreased.

Due to uniform distribution of PANI, the possibility of forming uniform passive layer on the iron surface is more since PANI has been shown to protect the iron surface by passive film formation [25–27,30,31]. Besides, the better conductivity of PTC may help in forming passive layer in the pin holes and defects in the coating. Xu et al. [15] has shown that the conductivity of the composite is much higher than that of PANI.

4. Conclusion

Polyaniline–TiO₂ composite (PTC) has been prepared by chemical oxidation method in the presence of aniline and TiO₂ by ammonium persulfate oxidant. The XRD pattern shows that the polyaniline has no effect on the crystalline behaviour of TiO₂. The SEM studies of PTC have shown that the TiO₂ particles are fully covered with polyaniline. EIS studies of PTC contain-

Table 2

Impedance parameters of TiO₂ and PTC containing paint coated on steel after to salt spray exposure

Time (days)	$R_c (\Omega \text{ cm}^2)$	$Y_0 (\Omega^{-1} \text{ s}^n)$	n	$C_c (\text{F cm}^{-2})$
TiO ₂ containing coating				
Initial	2.52×10^{10}	1.18×10^{-10}	1	1.18×10^{-10}
2	4.89×10^6	1.76×10^{-9}	0.79	5.10×10^{-10}
3	3.29×10^4	3.28×10^{-9}	0.72	1.49×10^{-9}
PTC containing coating				
Initial	4.96×10^9	8.29×10^{-11}	1	8.29×10^{-11}
1	2.78×10^9	1.75×10^{-10}	0.92	1.64×10^{-10}
5	2.58×10^8	3.14×10^{-10}	1	3.14×10^{-10}
9	1.13×10^9	1.41×10^{-10}	0.97	1.32×10^{-10}
14	1.99×10^9	2.26×10^{-9}	0.89	2.06×10^{-10}
35	1.16×10^9	7.51×10^{-10}	1	7.51×10^{-10}

ing coating in immersion tests in 3% NaCl and salt spray fog indicate that PTC containing coating is able to offer higher protection to steel from corrosion in comparison to conventional TiO₂ pigment containing coating due to passivation ability of polyaniline.

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