

Preparation of polyaniline–TiO₂ composite and its comparative corrosion protection performance with polyaniline

S. Sathiyarayanan, S. Syed Azim, G. Venkatachari *

Central Electrochemical Research Institute, Karaikudi 630006, India

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Abstract

Due to strict environmental regulations on the usage of chromate in the coating industries, search for effective inhibitive pigment in replacing those chromate pigments has become necessary. In recent years it has been shown that electrically conducting polymers such as polyaniline (PANI) incorporated coatings are able to protect steel due to their passivating ability similar to that of chromates. This work presents the comparative corrosion protection performance of the coatings containing polyaniline and polyaniline–TiO₂ composite (PTC) on steel in acrylic binder. The PANI and PTC were prepared by chemical oxidative method of aniline by ammonium persulfate. The polymers were characterized by FTIR, XRD and SEM. The corrosion protection performance of the coatings containing PANI and PTC on steel was evaluated by immersion test in 3% NaCl for 60 days and salt fog test for 35 days. The performance of the coatings in both the tests was investigated by open circuit potential measurements and EIS technique. It has been found that the open circuit potential values of PTC containing coating are more nobler by 50–200 mV in comparison to that of coatings with PANI. Besides, the resistance values of the coating containing PTC were more than 10⁷ Ω cm² in the 3% NaCl immersion test after 60 days and 10⁹ Ω cm² in the salt fog test of 35 days which were two orders high in comparison to that of PANI containing coatings. The better performance of PTC containing coatings may be due to uniform distribution of polyaniline which can form uniform passive film on the iron surface.

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1. Introduction

In recent years, polyaniline containing organic coatings have been shown to replace the chromate containing primer coatings [1–4]. It has been shown by Wessling et al. [2–4] that samples of mild steel with undoped polyaniline (PANI) and with an epoxy topcoat have exhibited corrosion rates slightly slower in 3.5% NaCl solution and 100 times slower in 0.1N HCl solutions than those of samples coated with epoxy alone. Further it has been shown that an oxide layer has been formed between the PANI coating and the steel surface which is composed mainly of Fe₂O₃ above a very thin Fe₃O₄ layer [2–6], Kinlen et al. [7,8] have shown the occurrence of the redox process in the polymeric layer by scanning reference electrode technique and proposed a model. Santos et al. [9] have shown that the sprayed

polyaniline coating on steel is able to protect in 3% NaCl solution due to passive film formation. Wang et al. [10] have shown that conducting polyaniline containing epoxy coating has got antifouling property. Using electrochemical methods, the corrosion resistant properties of polyaniline epoxy blended coating on steel have been reported [11]. It has been shown that emeraldine base is most effective in saline solution while protonated polyaniline is effective in acid media. de Souza et al. [12] have shown that sulfonate doped polyaniline with acrylic coating protects the carbon steel in chloride solutions by forming a passivating complex with dopant anion and also by barrier effect. Samui et al. [13] have studied the protection performance of the paint containing PANI–HCl and shown that lower loading of PANI–HCl has been found to be more effective. da Silva et al. [14] have studied the role of counter-ions on the protection of steel by polyaniline acrylic coating. They have shown that the polyaniline containing coating protects steel by two step protection mechanism. First a redox reaction between Fe and PANI forms a passive layer and a second layer by forming a complex

* Corresponding author.

E-mail address: gvchhari@gmail.com (G. Venkatachari).

salt layer with iron and dopant. Recent studies by the authors [15–17] have shown that polyaniline containing organic coatings are able to protect steel in acid, neutral and alkaline environments. Plesu et al. [18] have shown that the acrylic dispersion based on PANI doped with anions containing phosphonates provides improved corrosion protection of carbon steel. In all the earlier studies, the corrosion protection of polyaniline containing coating have been studied using polyaniline sprayed coating or polyaniline blended resin coating. The most of the paint formulations contain TiO_2 as one of the filler material and it is worthwhile to study the corrosion protection performance of PANI– TiO_2 composite containing coatings. Earlier studies [19–22] on polyaniline– TiO_2 composite (PTC) deal mainly with the properties such as electrical conductivity, thermal stability and spectroscopic characteristics. Hence a comparative study has been made on the corrosion protection performance of PANI and PTC containing coatings on steel in sodium chloride solutions.

2. Experimental

2.1. Preparation of PANI– TiO_2 composite

One molar of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid and 25 g of anatase TiO_2 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 $5 \pm 1^\circ\text{C}$. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured PANI– TiO_2 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– TiO_2 composite was fine grinded using mortar and then used as pigment. The polymerization mechanism of PANI on TiO_2 particles can be explained as follows.

Since the surface of TiO_2 has the point of zero charge (pzc) at pH 5.9 [23], it may be positively charged in the acidic polymerization H_3PO_4 bath. Due to the positive charge on TiO_2 , the H_2PO_4^- ions adsorb on TiO_2 . 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– MnO_2 composite preparation [24].

2.2. Characterization of PANI– TiO_2 composite

The PANI– TiO_2 composite was characterized by the following methods:

- (i) *Conductivity measurements.* The conductivities of the PANI and PANI– TiO_2 composite were measured for the palletized pigment using a four probe resistance meter.
- (ii) *XRD analysis.* The powder X-ray diffraction of the TiO_2 , PANI and the PTC composite were analysed using PHILIPS (Model PW3040/60) X-ray Diffractometer using $\text{Cu K}\alpha$

radiation in the 2θ range $5\text{--}75^\circ$ at the scan rate of $0.0170^\circ/2\theta$ with continuous scan type with scan step time of 15.5056 s.

- (iii) *FTIR analysis.* The FTIR spectra of TiO_2 , PANI and the PTC composite were obtained using Nicolet 380 FTIR Spectrometer in wavenumber range $2000\text{--}500\text{ cm}^{-1}$.
- (iv) *SEM analysis.* The scanning electron micrographs of TiO_2 , PANI and PANI– TiO_2 composite was analysed using Hitachi (Model S3000 H) instrument. The pigment was spread over a copper block over which gold was sputtered.

2.3. Preparation of PANI– TiO_2 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 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 prepared 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 paint applied panels after 24 h of curing at ambient conditions. The specific gravity of the primer was 1.0 and the dry film thickness (DFT) was 40–45 μm . The specific gravity of the top coat was 0.98 and the dry film thickness was 30–35 μm .

2.4. Water uptake studies of coating

The total paint system was applied over $5\text{ cm} \times 7.5\text{ cm}$ glass plates by means of brush and allowed to cure for 7 days at ambient temperature. These coated glass panels were weighed and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed after regular time intervals after removing the surface water by means of a filter paper. The weight gain was measured up to 10 days. The accuracy of the weight measurement is $\pm 0.1\text{ mg}$.

2.5. Evaluation of corrosion resistant properties of the coating

2.5.1. Salt spray tests

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

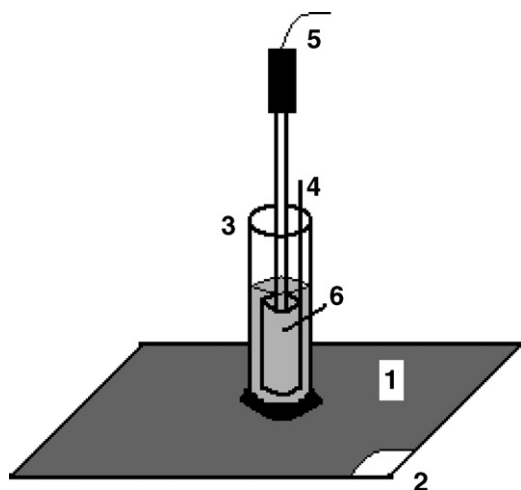


Fig. 1. Experimental cell setup. 1, Painted steel panel; 2, paint removed area for making working electrode contact; 3, glass tube; 4, platinum counter electrode; 5, SCE reference electrode; 6, test electrolyte.

2.5.2. EIS studies

Steel specimens of size $5\text{ cm} \times 5\text{ cm} \times 0.1\text{ cm}$ were sand-blasted (Sa 2.5) and degreased with trichloroethylene and coated with the developed paint. The total thickness of the coating was $100 \pm 5\text{ }\mu\text{m}$. A glass tube of 1.2 cm diameter of length 3 cm was fixed on the coated steel panels with adhesive (m seal) and the exposed area was 1.0 cm^2 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 0.1 Hz with an ac amplitude of 20 mV for different immersion time up to 60 days. Since the impedance values have not changed much below 0.1 Hz, the experiments have been conducted up to 0.1 Hz. The impedance values are reproducible $\pm 2\text{--}3\%$. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using the equivalent 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). The constant phase element (CPE) is defined in impedance representation as

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

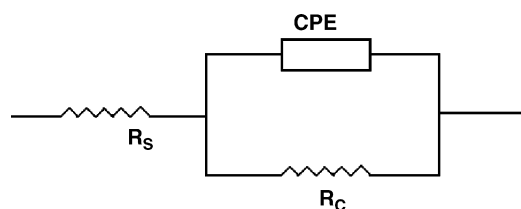


Fig. 2. Equivalent circuit for painted steel panel.

where Y_0 is the CPE constant, ω the angular frequency (in rad s^{-1}), $j^2 = -1$ 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 ($n = 0.5$) [25]. The following equation is used to convert Y_0 into C_c is [26],

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

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

3.1. Electrical conductivity studies

The electrical conductivity of PANI–TiO₂ composite is found to be 0.0125 S cm^{-1} . This shows that the prepared composite is of conducting nature. However, the conductivity of the composite is found to be less than that of pure PANI ca. 2.2 S cm^{-1} . The reported values of the conductivities of PANI–TiO₂ composites are $2.4 \times 10^{-3}\text{ S cm}^{-1}$ [27], 0.04 S cm^{-1} [28] and $0.16\text{--}7.0\text{ S cm}^{-1}$ [29]. The difference in conductivity values may be due to the presence of different dopant ions.

3.2. X-ray diffraction studies

Fig. 3 shows the XRD pattern of TiO₂, PANI and PTC. It can be seen that the XRD pattern of PTC is more or less similar to that of TiO₂. Further the broad diffraction peak of PANI at $2\theta = 25^\circ$ is absent in the PTC which indicates that the presence of TiO₂ in the polymerization system strongly affects the crystalline behaviour of formed PANI and the interaction of PANI and TiO₂ restrict the crystallization of PANI. When polyaniline adsorbed on the surface of TiO₂ particles, the molecular chain of adsorbed PANI is confined and the degree of crystallinity decreases. But in the case of PANI–MnO₂ composites, it is reported that the crystallographic phase of MnO₂ is distorted due to polymerization reaction [24]. It also confirms that the polyaniline deposited on the surface of TiO₂ particles has no effect on the crystallization behaviour of TiO₂ particles. Lee et al. [27] and Xu et al. [29] have recorded similar observation on the XRD pattern of polyaniline–nano-TiO₂ composites.

3.3. Fourier transform infrared spectra studies

The FTIR spectra of TiO₂, PANI and PANI–TiO₂ composite (PTC) is shown in Fig. 4. Close examination of the figure reveals that the PTC contains all the main characteristics of bands of polyaniline, 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 [30]. These peaks when compared to that of pure polyaniline [31] are found to

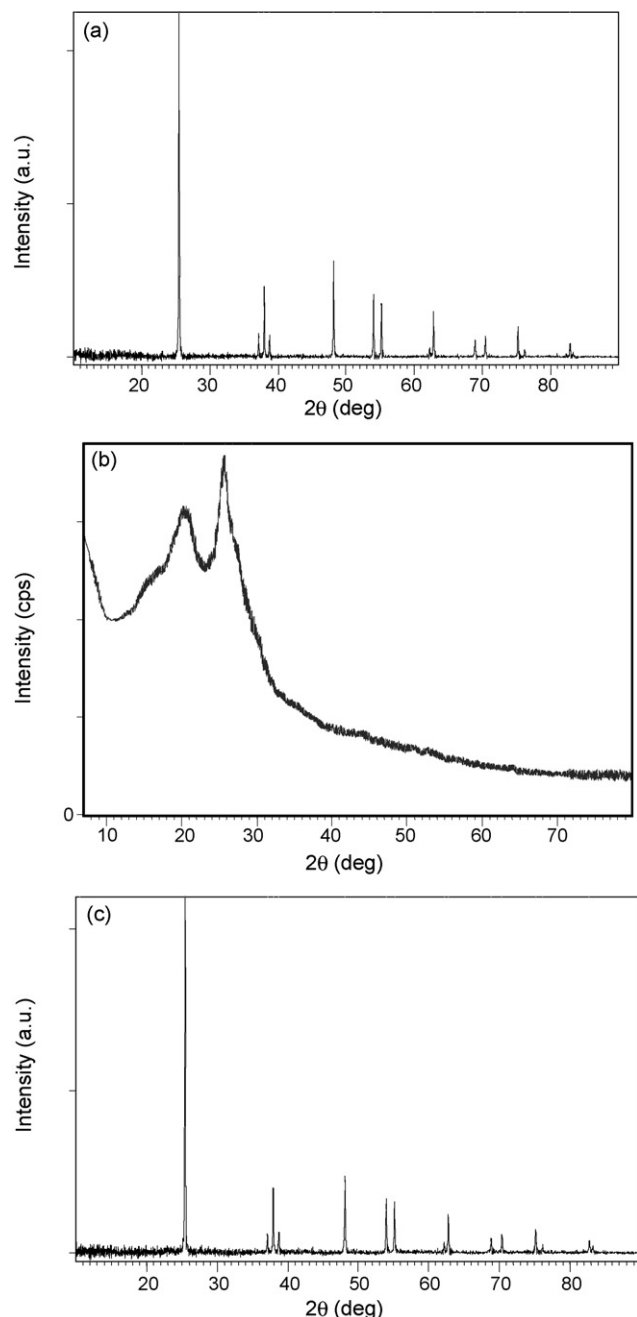


Fig. 3. XRD pattern of (a) TiO₂ (b) PANI and (c) PANI–TiO₂ composite.

be shifted slightly due to strong attraction of TiO₂ particle with polyaniline. Similar observation has been reported by Lee et al. [27]. In the case of TiO₂, strong absorption around 670 cm⁻¹ due to Ti–O stretching [29] is observed while this band is found to be weak in PTC due to the presence of PANI.

3.4. Morphology of polymer

The scanning electron micrographs of TiO₂, PANI and PTC are shown in Fig. 5a–c, respectively. It can be seen that large sized crystals of TiO₂ is fully covered by PANI in the case of PTC.

3.4.1. Evaluation of coatings

3.4.1.1. Water uptake studies. The results of water uptake of the paint films are shown in Fig. 6. In general it is seen that PTC containing coating has got lower water absorption than that of PANI containing coating.

3.4.1.2. Open circuit potential studies. Fig. 7 shows the variation of open circuit potentials (OCP) with time for the PANI and PTC containing paint coated steel in 3% NaCl and after salt spray test. The OCP values are found to be shifted to active direction initially and revert back to noble direction with subsequent exposure to the electrolyte. The initial active direction shift is attributed to oxidation of Fe to Fe²⁺ at the pin hole areas and the corresponding localized conversion of emeraldine to leucoemeraldine in the polymeric coating at the Fe/Blend interface. As PANI was reduced, the phosphate anions which are available as dopants got released and they are available at the interface and they would react with Fe cations to form a passivating complex which results in shift of OCP in the noble direction. Similar observation has been made by de Souza et al. [12] while studying the PANI–Fe interface using Raman spectroscopy and reported that the physical meaning of the attainment of OCP around –0.400 V can be related to the equilibrium potential of the reduced polymer. Further, the coating containing PTC is able to maintain slightly more noble potential values in comparison to that of PANI containing coating. This shows that PTC in the coating 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 [9,2,11,32].

3.4.1.3. 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 penetration of electrolyte through the coating pores. The coating capacitance $C_c = \epsilon \epsilon_0 A / d$, where ϵ denotes the relative dielectric constant of paint film, ϵ_0 the permittivity of the vacuum ($=8.85 \times 10^{-14}$ F cm⁻¹), A the active area and d is the coating

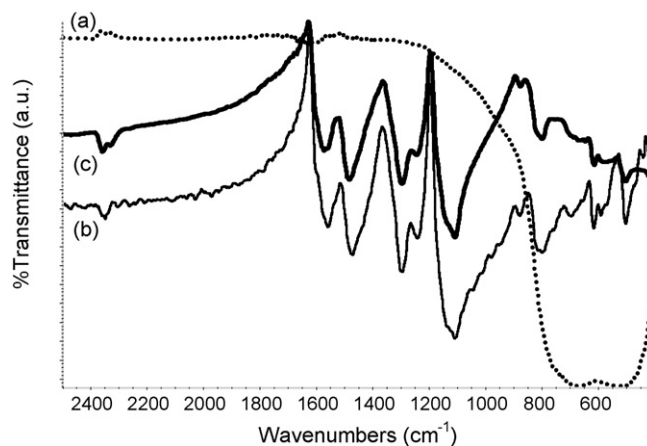


Fig. 4. FTIR spectra of (a) TiO₂, (b) PANI and (c) PANI–TiO₂ composite.

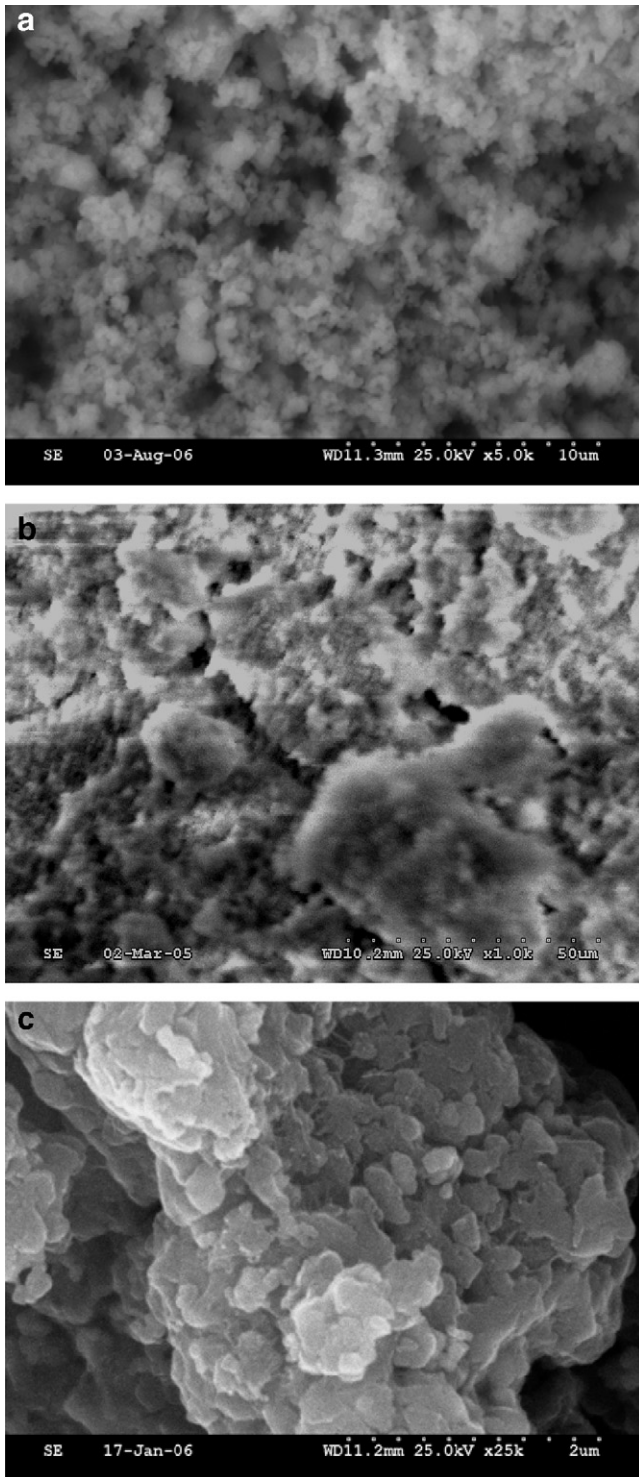


Fig. 5. Scanning electron micrograph of (a) TiO_2 , (b) PANI and (c) PTC.

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.

3.4.1.4. EIS studies of PANI containing paint coated steel exposed to 3% NaCl solution. Fig. 8 shows the variation of the impedance values of the coated steel by PANI containing coating in 3% NaCl. The variation of the resistance and capacitance

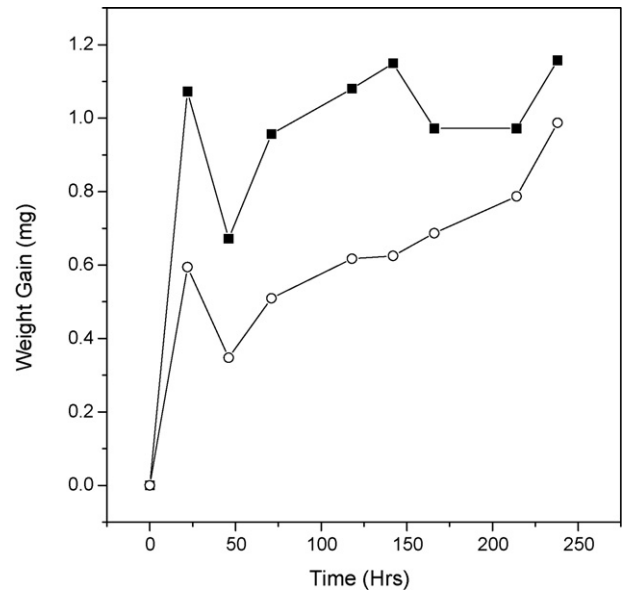


Fig. 6. Water uptake of paint films. (■) PANI and (○) PTC.

Table 1

Impedance parameters of PANI containing paint coated 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})
Initial	2.08×10^9	4.33×10^{-10}	0.85	2.86×10^{-10}
3	1.32×10^8	5.29×10^{-10}	0.84	3.09×10^{-10}
10	1.78×10^6	1.04×10^{-9}	0.78	3.49×10^{-10}
30	7.71×10^6	2.01×10^{-9}	0.75	5.06×10^{-10}
40	4.82×10^6	1.78×10^{-9}	0.77	4.48×10^{-10}
60	4.65×10^5	8.23×10^{-10}	0.93	4.67×10^{-10}

values of the coating with immersion time is given in Table 1. Eventhough the polyaniline is conducting in nature, the dc conductance of the paint coating containing polyaniline has been found to be in the order of $10^{-6} \text{ S cm}^{-1}$. Besides, the impedance spectra show the presence of one time constant. Hence, the variation of impedance of the coated steel is mainly due to variation of resistance and capacitance of the coating. The resistance of the coating is $2.08 \times 10^9 \Omega \text{ cm}^2$ initially. On subsequent exposure to sodium chloride solution, the resistance values decrease slowly. At the end of 60 days exposure, the resistance value is $4.6 \times 10^5 \Omega \text{ cm}^2$. The capacitance values of the coating remain more or less constant.

The results of the impedance studies of PTC containing coating in 3% NaCl solution are shown in Fig. 9. Table 2 gives the impedance values of the coatings. Initially, the resistance

Table 2

Impedance parameters of PTC containing paint coated 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})
Initial	4.02×10^8	8.07×10^{-10}	0.87	5.24×10^{-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}

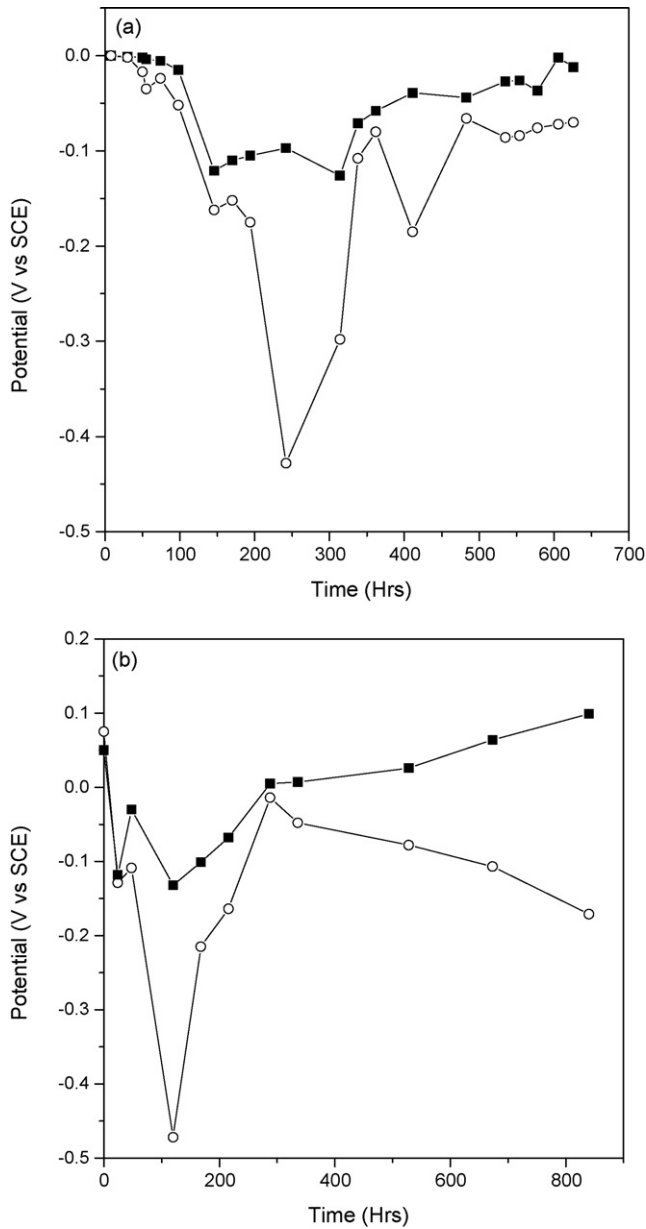


Fig. 7. OCP variation of coated steel (a) after immersion in 3% NaCl and (b) after salt spray exposure. (○) PANI; (■) PTC.

value of the coating is $4.02 \times 10^8 \Omega \text{ cm}^2$. At the end of 60 days immersion period, the resistance value of the coating is $2.1 \times 10^7 \Omega \text{ cm}^2$. On comparing the resistance values of the PANI containing coating, the resistance value of PTC containing coating is nearly 2 orders high. This shows that the PTC containing coating is more protective. The high performance of PTC containing coating may be due to uniform distribution of PANI in the coating which can help in forming a uniform passive film on the iron surface. Zhang [33] has shown that polyaniline–alumina composite containing coating is able to protect steel efficiently due to effective hindrance of corrosive ions and better passivation by the composite particles. The capacitance values of the coating are in the range of 2.4×10^{-10} to $6.8 \times 10^{-10} \text{ F cm}^{-2}$. This shows that no delamination has occurred during the period of study.

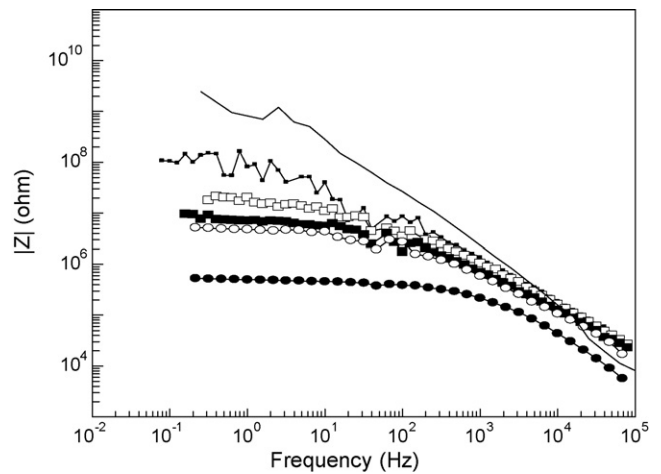


Fig. 8. Impedance plots of PANI containing paint coated steel in 3% NaCl. (—) Initial; (■) 3 days; (□) 10 days; (●) 30 days; (○) 40 days; (●) 60 days.

3.4.1.5. *EIS studies on PANI containing paint coated steel after salt spray tests.* Fig. 10a and b shows the appearance of the PANI and PTC containing coatings after exposure to salt spray fog for 35 days. It can be seen that the PTC containing coating sample is free from rust and blister and also there is no spreading of rust along the scribed areas. However, the PANI containing coating has got more corrosion extended areas from the scribes.

Besides visual observation, the protective nature of PANI and PTC containing coatings on steel after salt spray exposure has been found out by EIS. The results of the impedance studies of coated steel after exposure to salt spray for different duration are shown in Figs. 11 and 12. The resistance and capacitance values of the coating after salt spray exposure are given in Tables 3 and 4.

The PANI containing coating shows a resistance value of $2.9 \times 10^9 \Omega \text{ cm}^2$ initially. However, the resistance value is decreased to $1.5 \times 10^6 \Omega \text{ cm}^2$ after 5 days exposure. Afterwards, the resistance values increase steadily and reach a value of $2.0 \times 10^7 \Omega \text{ cm}^2$ after 35 days exposure.

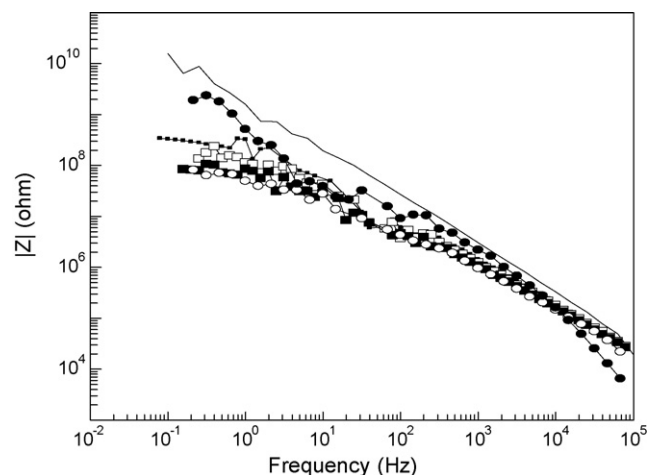


Fig. 9. Impedance plots of PTC containing paint coated steel in 3% NaCl. (—) Initial; (■) 3 days; (□) 10 days; (●) 30 days; (○) 40 days; (●) 60 days.

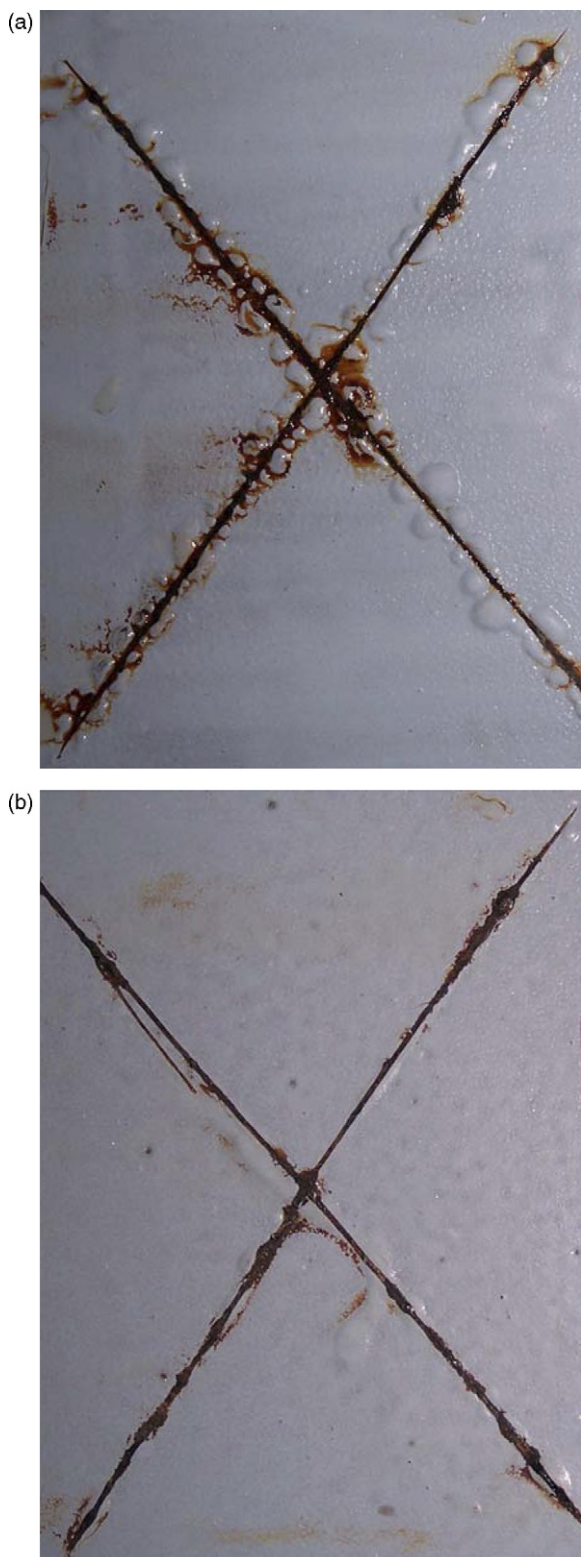


Fig. 10. (a) Photograph of PANI containing paint coated steel after 35 days of exposure to salt spray test. (b) Photograph of PTC containing paint coated steel after 35 days of exposure to salt spray test.

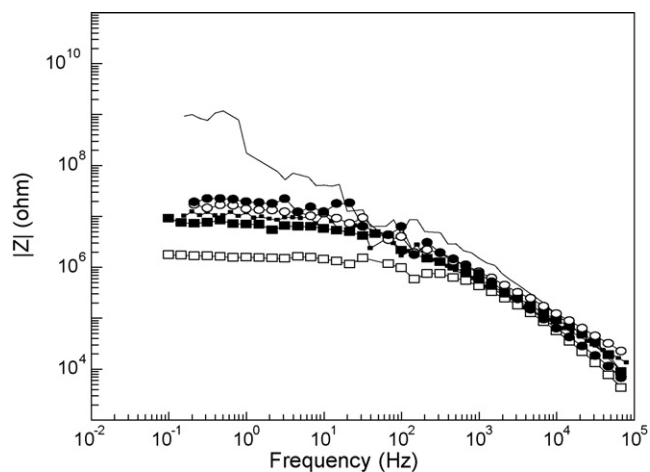


Fig. 11. Impedance plots of PANI containing paint coated steel after salt spray exposure. (—) Initial; (■) 1 day; (□) 5 days; (■) 9 days; (○) 14 days; (●) 35 days.

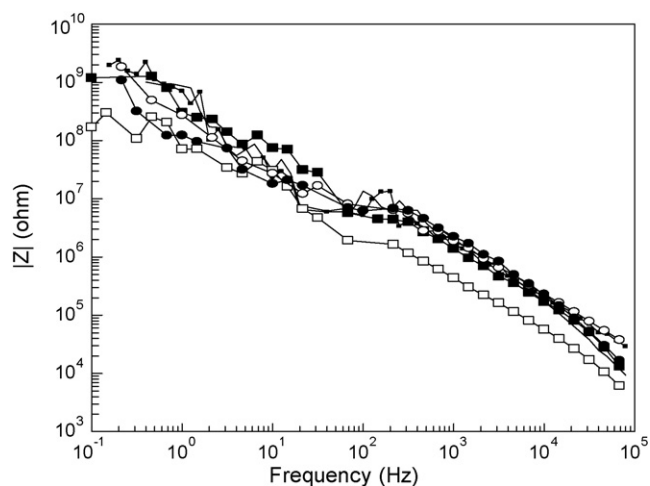


Fig. 12. Impedance plots of PTC containing paint coated steel after salt spray exposure. (—) Initial; (■) 1 day; (□) 5 days; (■) 9 days; (○) 14 days; (●) 35 days.

In the case of PTC containing coatings, the resistance values of the coating is decreased slightly to $2.5 \times 10^8 \Omega \text{ cm}^2$ from $4.96 \times 10^9 \Omega \text{ cm}^2$ after 5 days of salt spray exposure. Afterwards, the resistance values increase steadily and reach $1.2 \times 10^9 \Omega \text{ cm}^2$ after 35 days of salt fog exposure. On comparing the resistance values of PANI containing coating, the PTC containing coating has got nearly 100 times higher resistance

Table 3

Impedance parameters of PANI containing paint coated steel exposed to salt spray test

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
Initial	2.96×10^9	1.24×10^{-10}	1	1.24×10^{-10}
1	1.07×10^7	1.41×10^{-9}	0.83	5.84×10^{-10}
5	1.51×10^6	3.14×10^{-10}	1	3.14×10^{-10}
9	7.59×10^6	1.07×10^{-9}	0.83	4.09×10^{-10}
14	1.49×10^7	1.02×10^{-9}	0.82	4.00×10^{-10}
35	2.07×10^7	2.47×10^{-10}	1	2.47×10^{-10}

values due to better passivating ability by PTC. Besides, the capacitance values of the composite containing coating are very low in comparison with that of PANI containing coating, which shows the lower water absorption ability of the PTC containing coating.

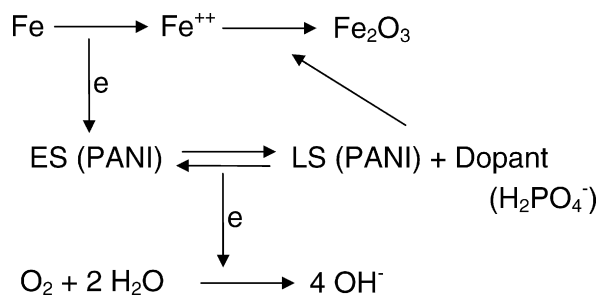
It has been stated [34] that polyaniline containing coating can protect metals by four possible mechanisms viz.

- (i) Anodic protection or ennoblement [4].
- (ii) Protection via the formation of an insoluble iron counter-anion salt [7].
- (iii) Protection due to the inhibitory properties of the counter-anion [35].
- (iv) Suppression of the kinetics of the oxygen reduction reaction through increase in substrate potential due to the production of PANI induced/maintained oxide films [36].

Mostly it is well established that iron over coated with organic film containing PANI-ES becomes passivated with either Fe_2O_3 [6] or a sandwich structure of $\nu \text{Fe}_2\text{O}_3$ overlying Fe_3O_4 [4,37,38].

In this study, it has been found that steel coated with polyaniline containing coatings exhibit noble open circuit potential values and increase in resistance values of coating with longer exposure period in sodium chloride immersion test and salt spray test. Hence the mechanism of protection of iron by PANI containing coating is by the formation of passive film due to redox reaction of iron and PANI and also by the secondary reaction of formation of dopant–iron complex [7,8,12,39]. Hence the protection of iron takes place via the reduction of polyaniline emeraldine salt (PANI-ES) to polyaniline leucoemeraldine salt (PANI-LS) with the concomitant release of phosphate anions. These released phosphate ions form iron–phosphate complex along with the passive film formed by PANI. The reduced PANI-LS can undergo re-oxidation to PANI-ES by the dissolved oxygen present in the medium. The evidence for re-oxidation of PANI-LS to PANI-ES by oxygen has been proved by Gasparac and Martin [40].

The protection of iron by PANI can be schematically represented as



Both immersion tests and salt spray tests show that the PANI– TiO_2 composite (PTC) containing coating has got higher corrosion resistance. The better performance of PTC containing coating may be due to the uniform distribution of PANI in the coating which can facilitate to maintain the passive layer uniformly on the iron surface [32,41,42].

Table 4

Impedance parameters of PTC containing paint coated steel exposed to salt spray test

Time (days)	R_c ($\Omega \text{ cm}^2$)	Y_0 ($\Omega^{-1} \text{ s}^n$)	n	C_c (F cm^{-2})
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}

4. Conclusions

PANI– TiO_2 conducting composite can be successfully prepared by chemical polymerization of aniline and TiO_2 in the presence of phosphoric acid using ammonium persulfate as oxidant. The FTIR spectra of PTC is similar to that of PANI. XRD pattern of PTC indicates that the crystallinity of TiO_2 is not altered by PANI coating. The impedance studies of coated samples in 3% NaCl immersion test and salt spray test have shown that the PTC containing coating has got higher corrosion resistant property than that of PANI containing coating. The higher corrosion protection ability of PTC containing coating may be due to the formation of uniform passive film on iron surface.

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