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Sulphonate doped polyaniline containing coatings for corrosion protection of iron

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ABSTRACT

Polyaniline containing organic coatings are found to protect steel in acid and in neutral media. Since dopants play an important role in the protection ability of polyaniline, a study has been made on the corrosion protection performance of sulphonate doped polyaniline containing vinyl coating in 0.1 N HCl and 3% NaCl by open circuit potential and impedance measurements. The open circuit potential measurements have shown that the coatings with polyaniline maintain the potential in the noble range whereas the coating without polyaniline exhibit potentials in the active range. EIS studies have shown that the sulphonate doped polyaniline is able to protect steel in acid and in neutral media since the impedance values of the coating remained at $10^{10} \Omega \text{ cm}^2$ even after 100 days exposure whereas the coatings without polyaniline have lost their protection ability after 50 days and 100 days in the acid and neutral media. FTIR studies have shown that PANI is able to protect by forming iron–PANI complexes beneath the coating along with a passive oxide layer.

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1. Introduction

Polyaniline based coatings are found to protect steel from corrosion and corrosion protection by emeraldine salt of polyaniline (PANI–ES) has been ascribed to substrate ennoblement due to the redox property of polyaniline [1–3]. Earlier studies on the corrosion protection of steel in neutral media have shown that coatings containing polyaniline maintain the potential of steel in the noble region [4–21]. Besides, it has been shown [22–24] that the dopants play an important role in the corrosion protection of steel due to the formation of an iron dopant secondary layer. Earlier studies [11,22] report the corrosion protection performance of sulphonate doped polyaniline in poly vinyl butyral and acrylic binder in neutral media. Since the corrosion protection performance of organic coating depends on the nature of the binder, a study has been made on the corrosion protection performance of sulphonate doped polyaniline containing vinyl coating on steel in acid and neutral media and the results are reported.

2. Experimental

2.1. Preparation of sulphonate doped PANI pigment

One molar of distilled aniline was dissolved in 500 ml of 1 M solution of phosphoric acid or 1 M solution of hydrochloric acid. Pre-cooled 1 M solution of ammonium persulphate was added dropwise

to the pre-cooled aniline acid mixture for about 90 min. The reaction was conducted at $5 \pm 1^\circ \text{C}$. After the addition, the stirring was continued for 2 h. A dark-green coloured conducting polyaniline was filtered and washed with distilled water to remove the residual acid

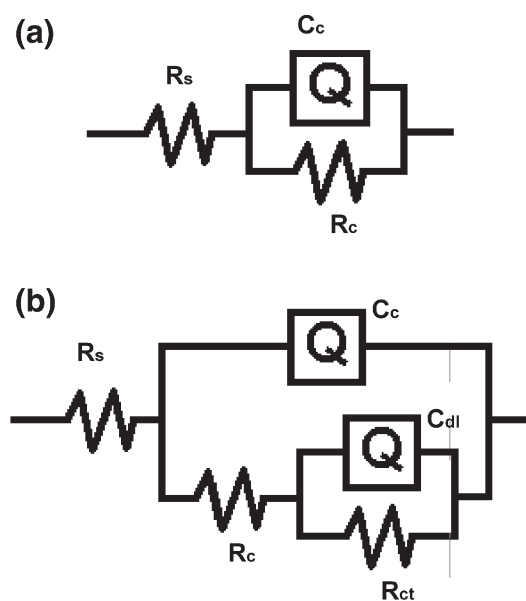


Fig. 1. Equivalent circuit model used to simulate EIS results. (a) With one time constant; (b) with two time constants.

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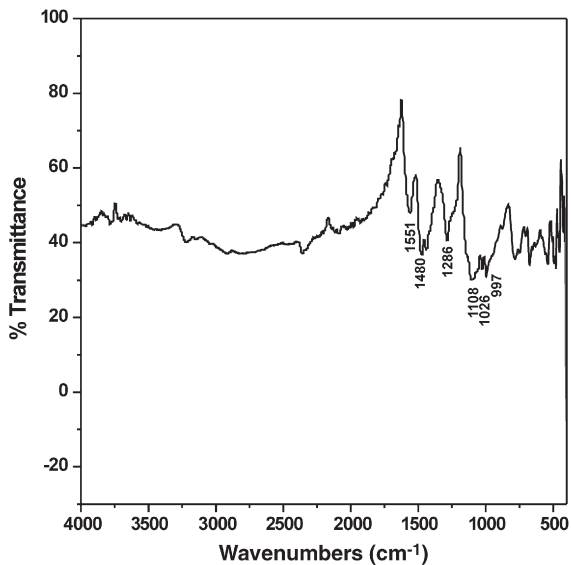


Fig. 2. FTIR spectra of PANI-sulphonate pigment.

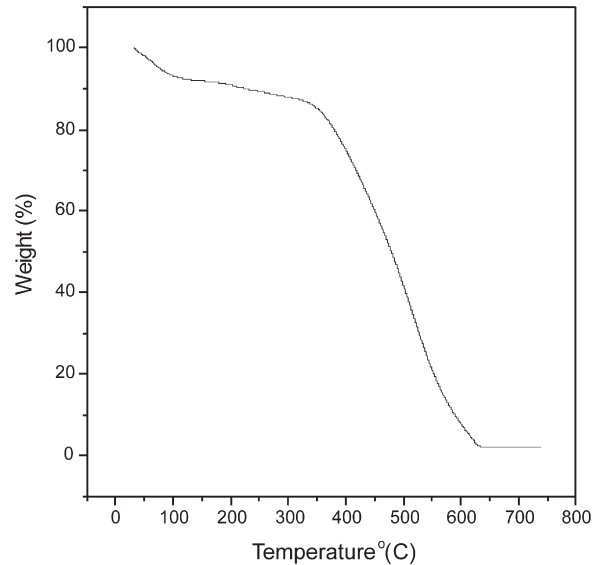


Fig. 4. Thermal stability curve of sulphonate doped PANI.

content. The synthesized polyaniline was dedoped by dispersing and stirring in 1 M NH_4OH for 5 h. The dedoped polyaniline was filtered and dried at 60 °C. Redoping of polyaniline was made by dispersing the polyaniline in 1 M dodecyl benzene sulphonic acid and stirring for 4 h. The sulphonate doped polyaniline was filtered, washed with distilled water and acetone and dried in an oven at 60 °C for 2 h.

2.2. Characterisation of sulphonate doped polyaniline pigment

2.2.1. FTIR analysis

The FTIR spectra of doped polyaniline and coated panels before exposure to corrosive media were recorded on NICOLET 380 FTIR spectrometer using ATR at room temperature. In the case of coated panels exposed to the corrosive media, localized FTIR measurements have been done with NICOLET 380 FTIR along with the NICOLET CENTRAU μ S microscope.

2.2.2. XRD analysis

The x-ray diffraction pattern of the doped polyaniline was taken with an analytical (Model PW 3040 / 60) x-ray diffractometer using $\text{CuK}\alpha$ radiation in the 2θ range 0–90° at a scan rate of 0.017° 2θ .

2.2.3. TGA analysis

The TGA analysis of sulphonate doped PANI has been found out using a thermal analyzer (STA, 1500), Polymer laboratory, Thermo Science Ltd.

2.3. Preparation of paint with doped PANI

The sulphonate doped polyaniline containing paint was prepared using vinyl resin (Mwt. 30,000) with 1% PANI as pigment. The paint was prepared in such a way that it had volume solids of 30 to 33%. The paint was applied on the sand blasted (Sa 2.5) mild steel panel and evaluated after 10 days of curing at room temperature. The coating thickness was $50 \pm 5 \mu\text{m}$.

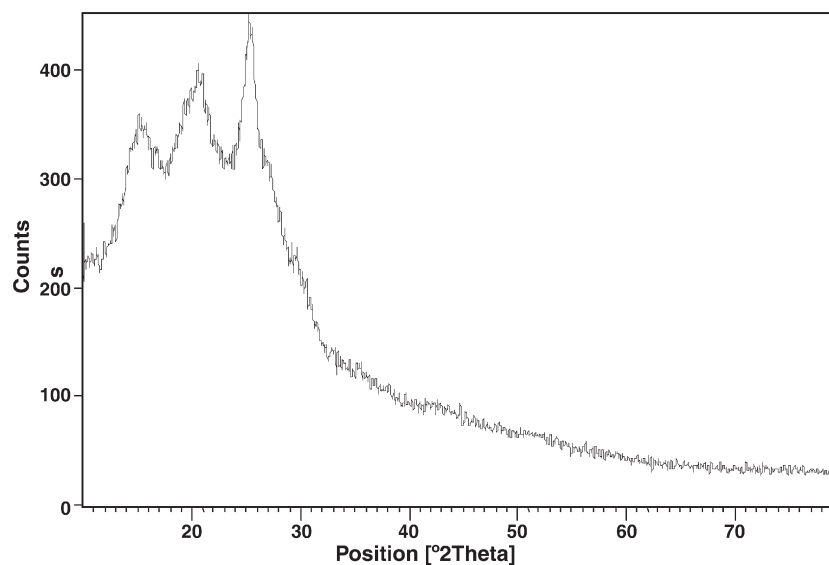


Fig. 3. XRD analysis of sulphonate doped polyaniline.

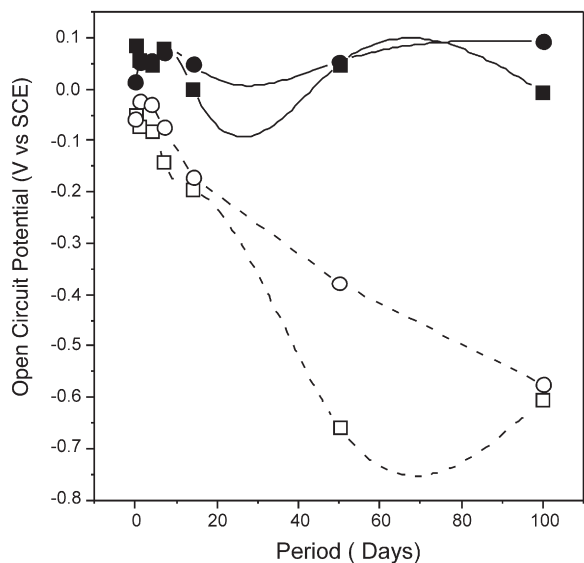


Fig. 5. OCP variation of coated panels. □ Blank in 0.1 N HCl; ○ blank in 3% NaCl; ■ PANI in 0.1 N HCl; ● PANI in 3% NaCl.

2.4. Evaluation of corrosion resistant properties of the coating

2.4.1. Open circuit potential measurements

A glass tube of 1.2 cm diameter was fixed on the coated steel panels with epoxy adhesive (m-seal). Solution of 0.1 N HCl or 3% NaCl was taken in the glass tube and the saturated calomel reference electrode was placed inside the glass tube. The open circuit potential (OCP) of the coated steel was measured with respect to the saturated calomel electrode (SCE) using a high input impedance voltmeter (HP 973 A).

2.4.2. EIS studies

The electrochemical cell as described in Section 2.4.1 with a platinum auxiliary electrode inside the glass tube along with SCE reference electrode was used for EIS measurements. The assembly was connected to an Advanced Electrochemical System (PAR 2273). Impedance measurements were carried out using the Powersine software for a frequency range of 100 kHz to 0.1 Hz with an AC signal of amplitude of 20 mV for different exposure time in 0.1 N HCl and 3% NaCl. A higher AC amplitude was used since the impedance of the

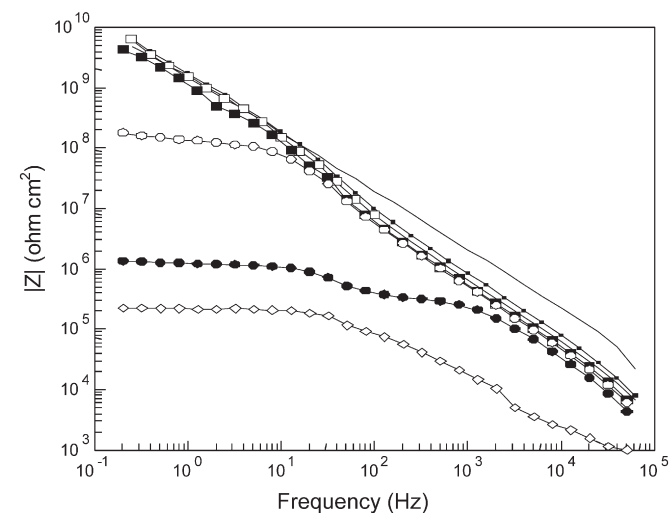


Fig. 6. Impedance plots of vinyl paint coated steel in 0.1 N HCl. — Initial; ■ 1 day; □ 4 days; ● 7 days; ○ 14 days; ● 50 days; ◇ 100 days.

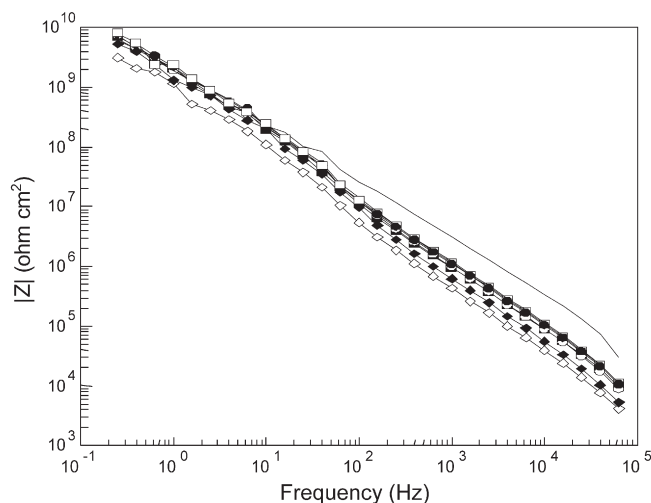


Fig. 7. Impedance plots of sulphonate doped PANI incorporated vinyl coated steel in 0.1 N HCl. — Initial; ■ 1 day; □ 2 days; ● 4 days; ○ 7 days; ● 14 days; ◇ 50 days; ◆ 100 days.

coating was very high. 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 ZsimpWin 3.21 software using the equivalent circuit for impedance data with one time constant as shown in Fig. 1a where R_s is the solution resistance, R_c is the coating resistance and Q is the constant phase element of the coating capacitance. When there exists two time constants, the impedance data were analysed using the equivalent circuit (Fig. 1b) where C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance.

Table 1

Impedance parameters of vinyl coated steel in 0.1 N HCl.

Period Days	Impedance parameters			
	Coating resistance	Coating capacitance	Charge tran resistance	Double layer capacitance
	R_c	C_c	R_{ct}	C_{dl}
	$\Omega \text{ cm}^2$	F cm^{-2}	$\Omega \text{ cm}^2$	F cm^{-2}
Initial	1.45×10^{10}	7.99×10^{-11}	—	—
1	1.33×10^{10}	1.14×10^{-10}	—	—
4	1.89×10^8	6.53×10^{-10}	—	—
7	1.05×10^8	1.91×10^{-10}	—	—
14	2.09×10^8	2.10×10^{-10}	—	—
50	1.76×10^6	7.49×10^{-9}	3.8×10^5	8×10^{-7}
100	3.45×10^6	8.11×10^{-9}	2.5×10^3	7×10^{-7}

Table 2

Impedance parameters of sulphonate doped PANI incorporated vinyl coated steel in 0.1 N HCl.

Period Days	Impedance parameters	
	Coating resistance	Coating capacitance
	R_c	C_c
	$\Omega \text{ cm}^2$	F cm^{-2}
Initial	1.72×10^{10}	5.48×10^{-11}
1	2.50×10^{10}	9.09×10^{-11}
2	1.36×10^{10}	8.81×10^{-11}
4	1.36×10^{10}	9.90×10^{-11}
7	6.48×10^{10}	9.53×10^{-10}
14	4.87×10^{10}	9.13×10^{-11}
50	4.27×10^{10}	1.87×10^{-11}
100	3.94×10^{10}	1.18×10^{-11}

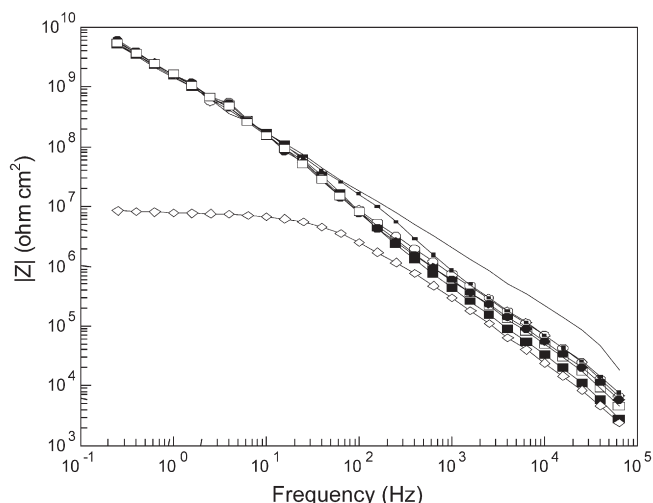


Fig. 8. Impedance plots of vinyl paint coated steel in 3% NaCl. — Initial; ■ 1 day; □ 4 days; ■ 7 days; ○ 14 days; ● 50 days; ◇ 100 days.

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

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

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 ($n > 0$, for ideal capacitance $Z(\text{CPE}) = C$, $n = 1$). The following equation is used to convert Y_0 into C_c or C_{dl} [25],

$$C_c(\text{or})C_{dl} = Y_0(\omega_m^n)^{n-1}$$

where C_c and C_{dl} are the coating and double layer capacitance and ω_m^n is the angular frequency at which Z'' is the maximum.

3. Results and discussion

3.1. Characterisation of sulphonate doped polyaniline pigment

The FTIR spectra of the sulphonate doped polyaniline pigment are shown in Fig. 2. The usual polyaniline characteristic peaks at 1657, 1480,

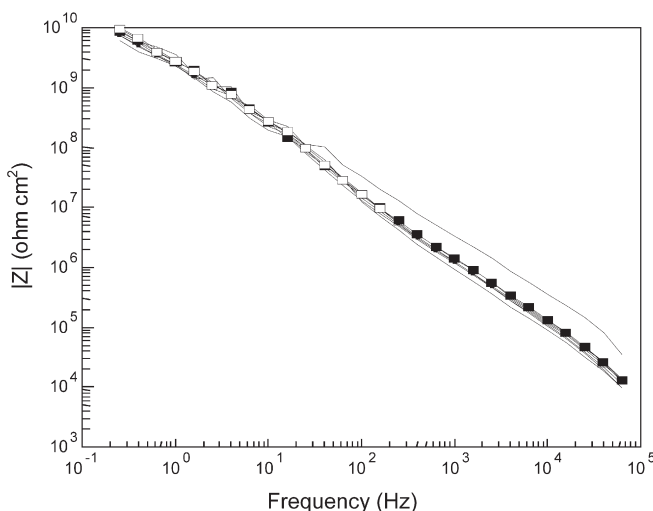


Fig. 9. Impedance plots of sulphonate doped PANI incorporated vinyl coated steel in 3% NaCl. — Initial; ■ 1 day; □ 2 days; ■ 4 days; ○ 7 days; ● 14 days; ◇ 50 days; ◆ 100 days.

Table 3 Impedance parameters of vinyl coated steel in 3% NaCl.

Time Days	Impedance parameters	
	Coating resistance	Coating capacitance
	R_c	C_c
	$\Omega \text{ cm}^2$	F cm^{-2}
Initial	4.81×10^{10}	1.17×10^{-10}
1	3.55×10^{10}	1.07×10^{-10}
4	3.83×10^{10}	1.07×10^{-10}
7	4.39×10^{10}	1.19×10^{-10}
14	6.11×10^{10}	1.21×10^{-10}
50	4.58×10^{10}	1.20×10^{-10}
100	7.83×10^6	5.78×10^{-10}

1286 and 1108 cm^{-1} due to quinoid, benzenoid, secondary amine and doped sulphonate groups are observed. Besides, the peak at 1026 and 997 are due to asymmetric and symmetric O=S=O stretching vibration are observed [26].

The XRD spectra of the polyaniline (Fig. 3) show the peak at $2\theta = 25^\circ$ and reveal that the local crystallinity may be caused by the periodicity perpendicular to the polymer chain [27]. The thermal stability of the polyaniline is shown in Fig. 4 The first weight loss observed up to 105°C is due to loss of moisture, the second stage between 105°C and 350°C is due to the removal of dopants and the weight loss after 350°C corresponds to the decomposition of the polymer [28–31].

3.2. Open circuit potential measurements of coated steel

The variation of open circuit potential values of coated steel in 0.1 N HCl and 3% NaCl is shown in Fig. 5. It can be seen that the coatings containing polyaniline maintain the OCP values in the noble region whereas the coatings without polyaniline show a shift of potential to active region.

3.3. EIS evaluation of coated steel

3.3.1. Corrosion protection performance in 0.1 N HCl

The impedance behaviour of the coated panel (without and with PANI) in 0.1 N HCl solution is shown in Figs. 6 and 7. The variation of coating resistance (R_c), the coating capacitance (C_c), the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values of the coating is given in Tables 1 and 2. In the case of the coating without PANI, the coating is able to offer protection up to 14 days which can be evidenced by the high R_c values greater than $10^{10} \Omega \text{ cm}^2$. After 50 days immersion, the resistance value of the coating decreased and reached $3.45 \times 10^5 \Omega \text{ cm}^2$ after 100 days immersion. Besides, after 50 days immersion, the impedance behaviour shows the occurrence of charge transfer reaction by the existence of two time constants and

Table 4 Impedance parameters of sulphonate doped PANI incorporated vinyl coated steel in 3% NaCl.

Time Days	Impedance parameters	
	Coating resistance	Coating capacitance
	R_c	C_c
	$\Omega \text{ cm}^2$	F cm^{-2}
Initial	2.18×10^{10}	6.84×10^{-11}
1	3.43×10^{10}	7.16×10^{-11}
2	6.64×10^{10}	7.35×10^{-11}
4	7.12×10^{10}	7.33×10^{-11}
7	4.57×10^{10}	7.37×10^{-11}
14	2.35×10^{10}	9.45×10^{-11}
50	5.35×10^{10}	6.08×10^{-11}
100	6.15×10^{10}	2.45×10^{-11}

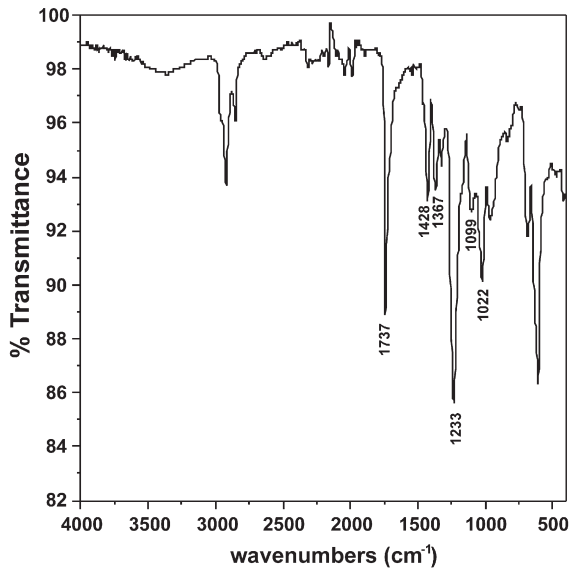


Fig. 10. FTIR spectra of PANI-sulphonate containing vinyl coating on steel before exposure.

the R_{ct} values are found to be 3.1×10^5 and $2.5 \times 10^3 \Omega \text{ cm}^2$ for 50 and 100 days respectively.

On the other hand, the impedance values of the PANI containing coating remained at $10^{10} \Omega \text{ cm}^2$ even after 100 days exposure to 0.1 N HCl. Besides the capacitance values of PANI containing coating remained at very low values in the order of 10^{-11} F/cm^2 .

3.3.2. Corrosion protection performance of PANI containing coating in 3% NaCl

The impedance behaviour of PANI free and PANI containing coated steel in 3% NaCl solution is shown in Figs. 8 and 9 and the impedance values of the coating are given in Tables 3 and 4. In the case of vinyl coated steel, it is found that the R_c values remained high at $> 10^{10} \Omega \text{ cm}^2$ up to 50 days and the R_c value decreased to $7.9 \times 10^6 \Omega \text{ cm}^2$ after 100 days immersion in 3% NaCl. However in the case of coatings with PANI, the resistance values of the coatings have remained at $10^{10} \Omega$

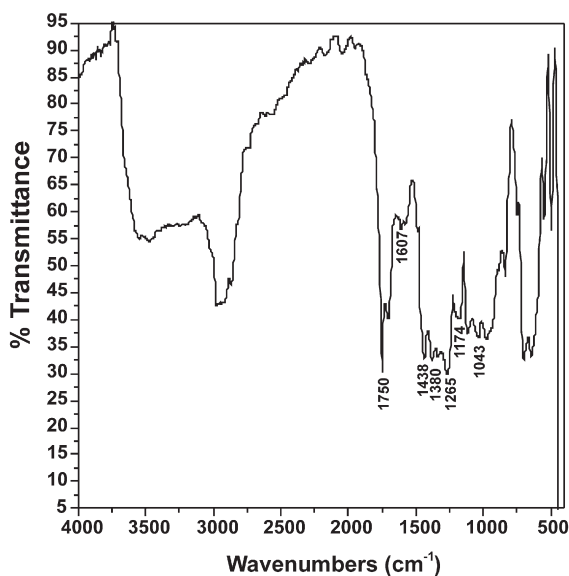


Fig. 11. FTIR spectra of PANI-sulphonate containing vinyl coating on steel after 100 days exposure to 0.1 N HCl.

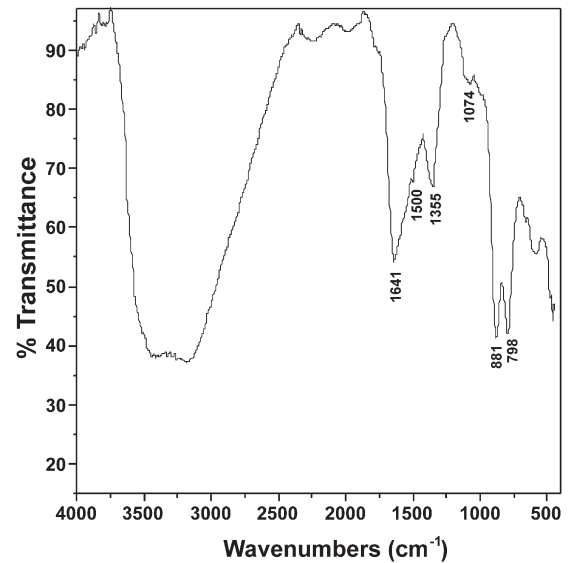


Fig. 12. FTIR spectra of PANI-sulphonate containing vinyl coating on steel after 100 days exposure to 3% NaCl.

cm^2 even after 100 days exposure to 3% NaCl. Even though the R_c values of vinyl coated steel for initial, 1 and 4 days (Table 3) are slightly higher than that of PANI containing coating, the R_c values at the end of 100 days immersion is 4 orders high for PANI containing coating. This shows the higher protection ability of PANI containing coating.

These results show that the sulphonate doped PANI containing coating is able to protect steel more effectively in acid and neutral environments. Immersion tests in 0.1 N HCl and 3% NaCl solution indicate that vinyl coatings protect steel up to 50 days of immersion and thereafter charge transfer reaction has been found to occur due to the existence of two time constants in the impedance spectra. However in the case of PANI containing coatings, it is found to offer protection even after 100 days of immersion due to the passivation effect of PANI which is evidenced by the maintenance of noble OCP values in comparison with that of vinyl coatings [5,6,18]. In the acid media, the passivation of steel by polyaniline takes place by the cathodic conversion reaction of PANI (ES) to PANI (LS) and the converted PANI (LS) is again oxidized to PANI (ES) by the H^+ ions

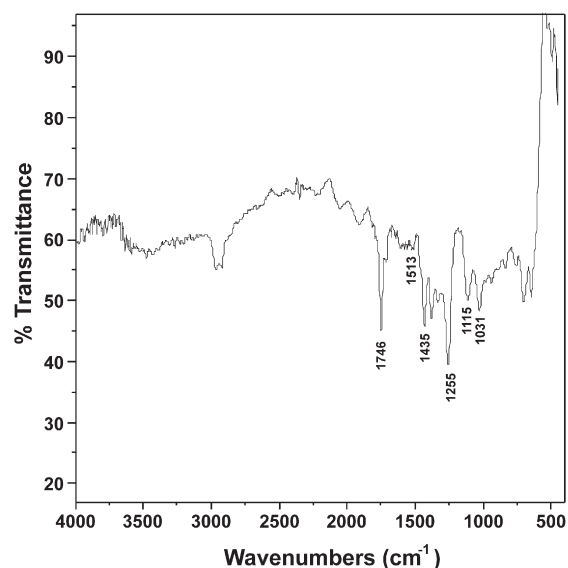


Fig. 13. FTIR reflectance spectra of paint removed area.

reduction to H₂ gas. But in neutral media it is well established that the protection of iron by emeraldine salt (ES) of PANI is due to the reduction of PANI (ES) to PANI (LB) with the release of sulphonate dopants [22–24]. These sulphonate dopants form an iron sulphonate complex along with the passive film. The FTIR spectra of the PANI containing coating before and after exposure to 0.1 N HCl and 3 % NaCl are shown in Figs. 10–12 respectively. It can be seen that the emeraldine state of PANI is maintained for the coating exposed to 0.1 N HCl due to the presence of a peak around 1100 cm⁻¹. But in the case of the coating exposed to 3% NaCl solution, the peak around 1100 cm⁻¹ is found to be absent due to change in the state of polyaniline from conducting to non-conducting. Besides, the peak due to sulphonate at 1026 cm⁻¹ is found to be absent in the coating exposed to 3% NaCl solution which also shows that dedoping has taken place. However reconversion of formed non-conducting PANI to conducting PANI by O₂ reduction is not observed as reported [32–35]. Further the FTIR spectra of the steel beneath the coating exposed to 3% NaCl (Fig. 13) show the predominant peaks of PANI and sulphonate due to the formation of PANI–Fe–sulphonate complexes. Hence the mechanism of protection of PANI in the coating is due to the formation of passive film along with the formation of PANI–Fe–sulphonate complex underneath the coating.

4. Conclusions

The sulphonate doped polyaniline has been synthesized by chemical oxidative polymerisation of aniline and characterized. The corrosion resistance property of the coating with polyaniline has been studied by an open circuit potential method and an impedance method. It is found that the sulphonate doped polyaniline containing vinyl coating offers more corrosion resistance in both acid and neutral media than the vinyl coating. The FTIR studies have shown that the conducting state of polyaniline in the coating is not changed in acid media while it is changed to non-conducting in neutral media. The mechanism of corrosion protection is found to be the formation of PANI–iron–sulphonate complex beneath the coating along with the formation of passive iron oxide film.

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References

- [1] G.M. Spinks, A.J. Dominis, G.G. Wallace, D.E. Tallman, J. Solid State Electrochem. 6 (2002) 85.
- [2] P. Zaras, N. Anderson, C. Webber, D.J. Irrin, A. Guenther, J.D. Stenger Smit, Rad. Phys. Chem. 68 (2003) 387.
- [3] S. Sathiyarayanan, S. Muralidharan, G. Venkatachari, M. Raghavan, Corr. Rev. 22 (2004) 157.
- [4] W.K. Lu, L. Elsenbaumer, B. Wessling, Synth. Met. 71 (1995) 2163.
- [5] B. Wessling, Synth. Met. 85 (1997) 1313.
- [6] T. Schauer, A. Joos, L. Dulog, C.D. Eisenbach, Prog. Org. Coat. 33 (1998) 20.
- [7] M. Fahlman, S. Jasty, A.J. Epstein, Synth. Met. 85 (1323) (1997) 1326.
- [8] D.E. Tallman, Y. Pae, G.P. Bierwagen, Corrosion 55 (1999) 779.
- [9] D.A. Wroblewski, B.C. Benicewicz, K.G. Thompson, C.J. Bryan, Polym. Chem. 35 (1994) 265.
- [10] P.J. Kinlen, V. Menon, Y. Ding, J. Electrochem. Soc. 146 (1999) 3690.
- [11] P.J. Kinlen, J. Ding, D.C. Silverman, Corrosion 58 (2002) 490.
- [12] A.J. Dominis, G.M. Spinks, G.G. Wallace, Prog. Org. Coat. 48 (2003) 43.
- [13] A. Cook, A. Gabriel, D. Siew, N. Laycock, Curr. Appl. Phys. 4 (2004) 133.
- [14] N. Plesu, G. Ilia, A. Pascariu, G. Valse, Synth. Met. 156 (2006) 230.
- [15] A. Cook, A. Gabriel, N. Laycock, J. Electrochem. Soc. 151 (2004) B529.
- [16] J.H. Huh, E.J. Oh, J.H. Chu, Synth. Met. 137 (2003) 965.
- [17] J. Fang, K. Xu, L. Zhu, Z. Zhou, H. Tang, Corros. Sci. 49 (2007) 4232.
- [18] S. Sathiyarayanan, S. Muthukrishnan, G. Venkatachari, D.C. Trivedi, Prog. Org. Coat. 53 (2005) 297.
- [19] T.G. Nguyen, T.N. Nguyen, M.C. Pham, B. Piro, B. Normand, H. Takenouti, J. Electroanal. Chem. 572 (2004) 225.
- [20] S. de Souza, Surf. Coat. Technol. 201 (2007) 7574.
- [21] J.E.P. daSilva, S.I.C. deTorresi, R.M. Torresi, Prog. Org. Coat. 58 (2007) 33.
- [22] S. de Souza, J.E.P. da Silva, S.I.C. de Torresi, M.L.A. Temperini, R.M. Torresi, Electrochem. Solid-State Lett. 4 (2001) B27.
- [23] J.E.P. daSilva, S.I.C. deTorresi, R.M. Torresi, Corros. Sci. 47 (2005) 811.
- [24] R.M. Torresi, S. de Souza, J.E.P. da Silva, S.I.C. de Torresi, Electrochim. Acta 50 (2005) 2213.
- [25] C.H. Hsu, F. Mansfeld, Corrosion 57 (2001) 747.
- [26] M.-Y. Hua, Y.-N. Su, S.-A. Chen, Polymer 41 (2000) 813.
- [27] T. Abdigrim, Z.-Xiqo gang, R. Jamal, Mater. Chem. Phys. 90 (2005) 367.
- [28] J. Stejskal, M. Omastov'a, S. Fedorova, J. Proke's, M. Trchov'a, Polymer 44 (2003) 1353.
- [29] M.V. Kulkarni, A.K. Viswanath, Eur. Polym. J. 40 (2004) 379.
- [30] J.C. Michaelson, A.J. McEvoy, N. Kuramoto, React. Polym. 17 (1992) 197.
- [31] N. Kuramoto, A.M. Genies, Synth. Met. 68 (1995) 191.
- [32] D.K. Moon, M. Ezuka, T. Maruyama, K. Osakada, T. Yamamoto, Macromolecules 26 (1993) 364.
- [33] G. Morea, J.C. Vickerman, J. Walton, Surf. Interface Anal. 22 (1994) 609.
- [34] R. Gašparac, R.C. Martin, J. Electrochem. Soc. 148 (2001) B138.
- [35] R.J. Holness, G. Williams, D.A. Worsley, H.N. McMurray, J. Electrochem. Soc. 152 (2005) B73.