



High performance polyaniline containing coating system for wet surfaces

S. Sathiyarayanan*, K. Maruthan, S. Muthukrishnan, G. Venkatachari

Central Electrochemical Research Institute, Karaikudi, Tamil Nadu 630006, India

ARTICLE INFO

Article history:

Received 13 March 2009
Received in revised form 22 April 2009
Accepted 15 June 2009

Keywords:

Moisture paint
PANI
Steel
Corrosion
EIS
FTIR
Salt spray test

ABSTRACT

Application of paint coatings on wet surfaces is rather difficult due to poor adhesion of coatings. For painting of wet surfaces, moisture curable coating systems based on epoxy resin and ketimine are found to be useful. Hence a study has been made on the corrosion protection ability of coating on wet surfaces using epoxy resin, ketimine and polyaniline. Paints with 20–30% PVC were prepared and applied over the wet steel surface and the corrosion protection performance of the coating was found out by salt spray and electrochemical impedance spectroscopic techniques. Coating with 20% PVC is found to offer very high protection since the impedance values are remained at greater than $10^9 \Omega \text{ cm}^2$ after immersion and salt spray tests.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Organic coatings are commonly used to protect metals against corrosion. Protection of steel structures from corrosion in high humidity places especially in coastal areas is rather difficult due to poor adhesion of organic coatings on the metal surface. In such high humidity conditions, organic coatings based on moisture cured urethanes [1] are found to be highly effective. Besides it is reported that epoxy coating with modified curing agents such as epoxy–amine adduct [2] and ketimine [3] is also found to be effective in protection of steel structures under damp conditions. The ketimine hardener in contact with, water hydrolysis releasing free amine, which in turn reacts with epoxy resin and so curing takes place in situ. However, these coating systems are found to contain pinholes through which initiation of corrosion is expected. It has been reported that polyaniline (PANI) containing coatings are found to protect the pinholes and defects in the organic coatings due to passivation ability of the polyaniline pigments [4–7].

In this paper, the corrosion protection performance of the epoxy coating with ketimine curing agent along with polyaniline is reported.

2. Experimental

2.1. Preparation and characterization of PANI pigment

Polyaniline was obtained by oxidative polymerization of distilled aniline dissolved in H_3PO_4 using ammonium persulphate oxidant as reported earlier [8]. The X-ray diffraction pattern of the polyaniline were taken with analytical (Model PW 3040/60) X-ray diffractometer using $\text{CuK}\alpha$ radiation in the 2θ range 0–90° at the scan rate of $0.017^\circ 2\theta$. The FTIR spectra of polyaniline were recorded on NICOLET 380 FTIR spectrometer using ATR at room temperature. The morphology of PANI samples was found out by SEM (Hitachi S3000H) by spreading the powder over a copper block over which gold was sputtered. The electrical conductivity of PANI was found out by four-probe resistance meter. The TGA analysis of PANI was done using thermal analyzer (STA, 1500), Polymer laboratory, Therman Science Ltd.

2.2. Preparation of paint and curing agent

Solid epoxy resin having epoxy equivalent 475–525 was dissolved in xylene in such a way that resin part was 70% by volume in the prepared solution. Micaceous iron oxide (MIO) was used as pigment along with polyaniline and silica and talc as extender pigments. The pigment volume concentration (PVC) of the prepared paints was 20, 25 and 30%.

The curing agent was prepared with polyamide and ketimine. The ketimine was based on amines diphenylamine, triethylamine

* Corresponding author. Tel.: +91 4565 227555; fax: +91 4565 227779.
E-mail address: Sathya.ccri@yahoo.co.in (S. Sathiyarayanan).

and methyl ethyl ketone. The polyamide having the amine value of 210–230 was used for the studies.

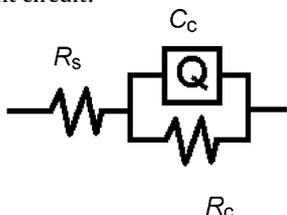
2.3. Preparation of coated panels

The paint was applied on the sand blasted (SA 2.5) mild steel panel and evaluated after 10 days curing at room temperature. Two coats were applied over the moist surface. The dry film thickness (DFT) of the coating was $300 \pm 20 \mu\text{m}$. Since higher coating thickness of $300 \mu\text{m}$ is usually employed for protection of marine structures, the coating thickness of $300 \pm 20 \mu\text{m}$ is used in this study.

2.4. Corrosion testing of coated panels

2.4.1. EIS test

A glass tube of 1.2 cm diameter was fixed on the coated steel panel with epoxy based adhesive. Solution of 3% NaCl was taken in the glass tube and the saturated calomel reference electrode and platinum auxiliary electrode were placed inside the glass tube. The assembly was connected to an Advanced Electrochemical System (PAR 2273). Impedance measurements were carried out using PowerSine software for a frequency range of 100 kHz–0.1 Hz with an ac signal of amplitude of 20 mV for different immersion time in 3% NaCl. The impedance values are reproducible by ± 2 –3%. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) values were calculated using ZsimpWin 3.21 software using the equivalent circuit:



where R_s is the solution resistance, R_c is the coating resistance and Q is the constant phase element of the coating capacitance.

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 [8]:

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

where C_c is the coating capacitance and is the angular frequency at which Z'' is maximum.

2.4.2. Salt spray test

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 for 750 h.

2.4.3. Open circuit potential studies

The open circuit potential of the coated steel was measured with respect to SCE using a high input impedance voltmeter (HP 973 A). The setup for measurements is as described in Section 2.4.1.

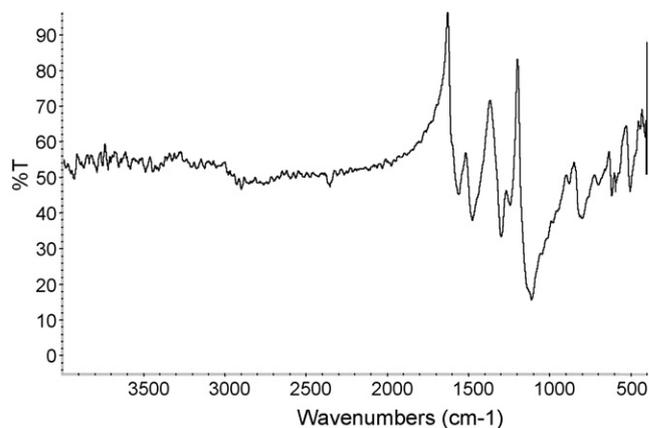


Fig. 1. FTIR spectra of Polyaniline pigment.

3. Results and discussion

3.1. Characterization of PANI pigment

The FTIR spectra of polyaniline pigment is shown in Fig. 1. The main characteristic bands are assigned as follows: bands at 1574 and 1483 cm^{-1} are the stretching mode of C=N and C=C of quinoid and benzenoid rings, the bands at 1300 and 1233 cm^{-1} are due to C–N stretching mode for benzenoid ring while peak at 1113 cm^{-1} is to a plane bending vibration of C–H which is formed during protonation [9].

The thermogravimetric analysis of polyaniline pigment is shown in Fig. 2. It can be seen that the thermal degradation of PANI occurs at 404°C and the initial mass loss at lower temperature is mainly due to release of water (up to 149°C) and dopant anions (246°C) [10,11]. The loss at around 246°C is due to loss of dopant anions which has been confirmed by conductivity measurements [12]. The conductivity of the polyaniline is found to be 0.155 cm^{-1} . The XRD analysis (Fig. 3) has shown that the doped polyaniline has some degree of crystallinity. A maximum peak at 25° can be assigned to the scattering from polyaniline chains at interplanar spaces [13].

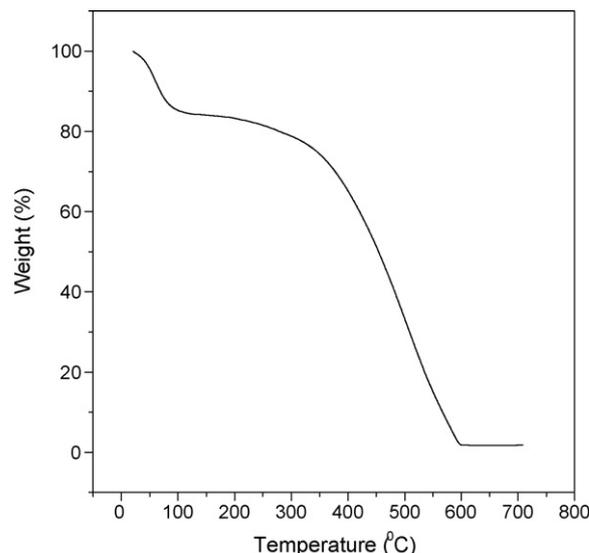


Fig. 2. Thermogravimetric curve of polyaniline powder.

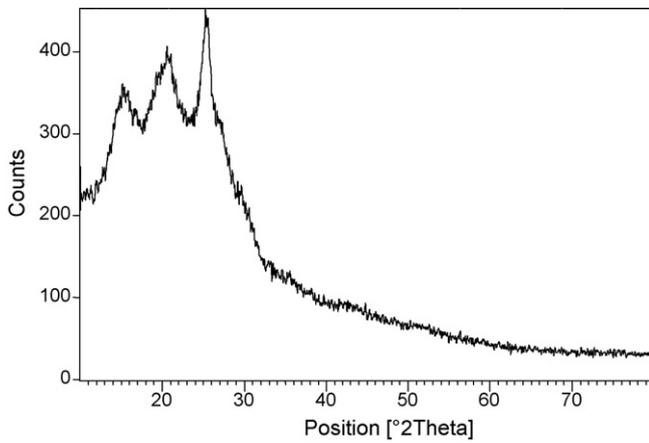


Fig. 3. XRD pattern for polyaniline powder.

3.2. Open circuit potential studies

The changes in the open circuit potential values (OCP) for coatings containing PANI of different PVC values are shown in Fig. 4. It is found that the coatings of 20 and 25% PVC show a shift of potential to active values up to 90 days immersion and after wards show a shift to noble values. After 300 days of immersion, the OCP values reached to the initial OCP values. However, the coating with 30% PVC showed a shift of OCP in the active direction and reached a value of -0.634 V vs SCE after 300 days of immersion. The OCP studies suggest that the coatings with 20 and 25% PVC are able to protect steel by forming a passive layer as evidenced by the attainment of OCP values in noble region. Similar results in shift of OCP values to noble direction for PANI containing coatings are reported earlier [14,6,15,16].

3.3. EIS studies of coated steel

The impedance behavior of coated steel with different PVC is shown in Figs. 5–7. The impedance parameters such as coating

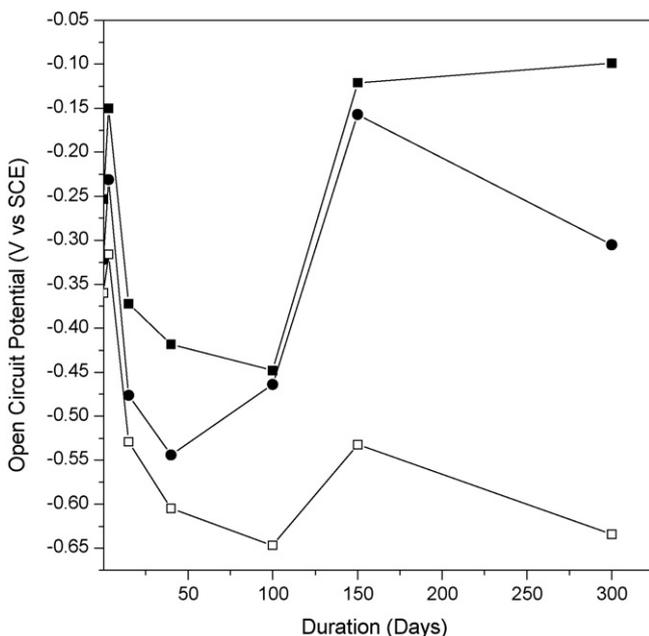


Fig. 4. Variation of open circuit potential with immersion period. ■, 20% PVC; ●, 25% PVC; and □, 30% PVC.

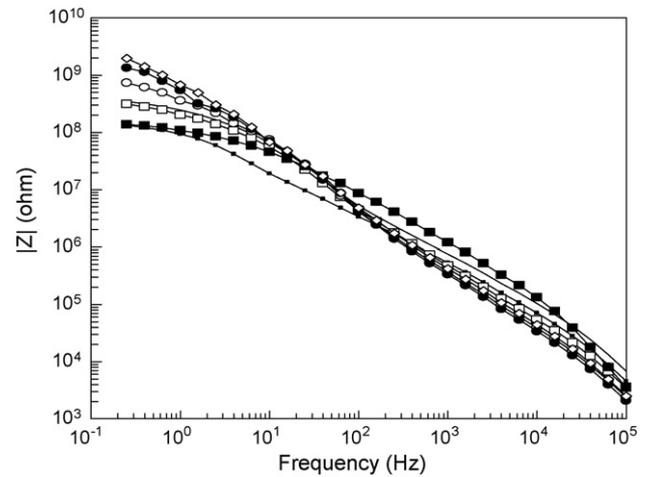


Fig. 5. Impedance behavior of 20% PVC paint coated steel in 3% NaCl. —, initial; ■, 3 days; □, 15 days; ■, 40 days; ○, 100 days; ●, 150 days; and ◇, 300 days.

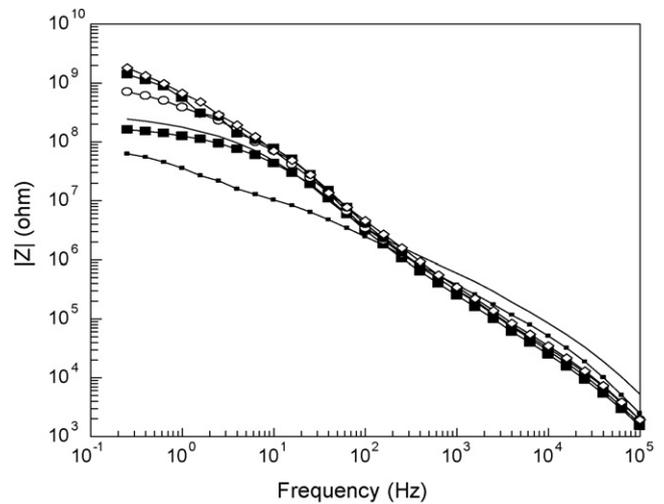


Fig. 6. Impedance behavior of 25% PVC paint coated steel in 3% NaCl. —, initial; ■, 3 days; □, 15 days; ■, 40 days; ○, 100 days; ●, 150 days; and ◇, 300 days.

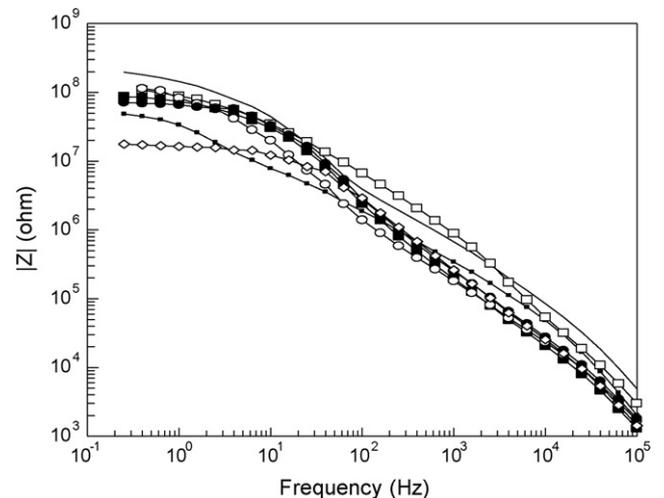


Fig. 7. Impedance behavior of 30% PVC paint coated steel in 3% NaCl. —, initial; ■, 3 days; □, 15 days; ■, 40 days; ○, 100 days; ●, 150 days; and ◇, 300 days.

Table 1
Impedance parameters of PANI containing coating on steel in 3% NaCl.

Duration (days)	PVC 20%		PVC 25%		PVC 30%	
	Coating resistance R_c ($\Omega \text{ cm}^2$)	Coating capacitance C_c (F cm^{-2})	Coating resistance R_c ($\Omega \text{ cm}^2$)	Coating capacitance C_c (F cm^{-2})	Coating resistance R_c ($\Omega \text{ cm}^2$)	Coating capacitance C_c (F cm^{-2})
Initial	3.36×10^8	1.98×10^{-10}	2.38×10^8	2.50×10^{-10}	1.87×10^8	2.45×10^{-10}
3	1.33×10^8	2.94×10^{-10}	5.77×10^7	4.05×10^{-10}	4.58×10^7	4.35×10^{-10}
15	3.11×10^8	3.17×10^{-10}	1.81×10^8	2.40×10^{-10}	1.03×10^8	2.32×10^{-10}
40	1.21×10^8	1.43×10^{-10}	1.54×10^8	4.76×10^{-10}	8.32×10^7	6.28×10^{-10}
100	8.18×10^8	3.15×10^{-10}	7.88×10^8	3.34×10^{-10}	1.09×10^8	8.11×10^{-10}
150	1.99×10^9	3.01×10^{-10}	1.85×10^9	2.99×10^{-10}	6.96×10^7	5.19×10^{-10}
300	3.88×10^9	2.68×10^{-10}	3.39×10^9	2.81×10^{-10}	1.65×10^7	6.08×10^{-10}

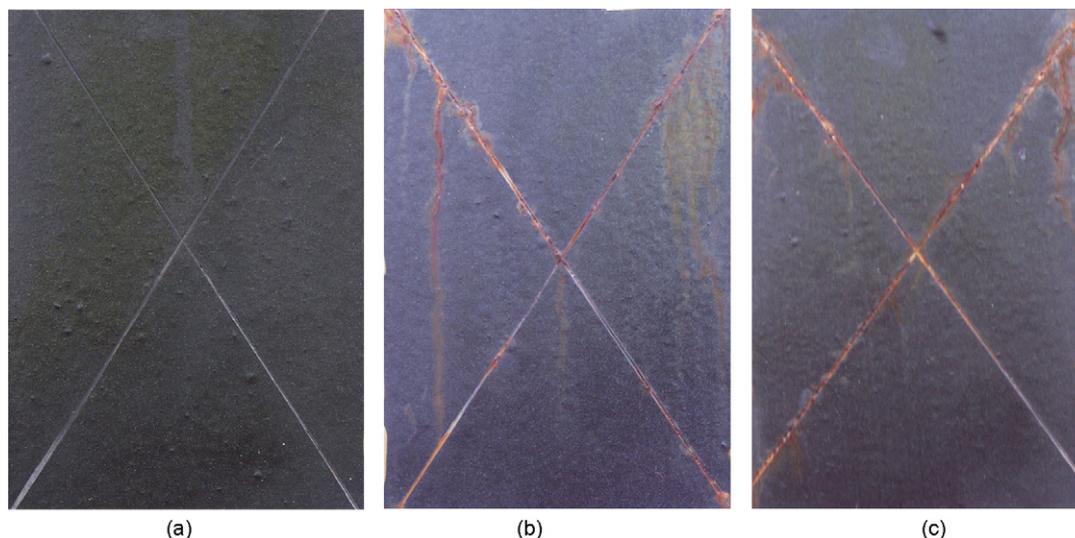


Fig. 8. Photograph of salt spray exposed panels (a) 20% PVC, (b) 25% PVC, and (c) 30% PVC.

resistance (R_c) and the coating capacitance (C_c) derived from these figures are given in Table 1. The coating resistance (R_c) values for the coating with 20% PVC are found to decrease from 3.35×10^8 to $1.21 \times 10^8 \Omega \text{ cm}^2$ after 40 days of immersion and afterwards the coating resistance values are increased to $3.87 \times 10^9 \Omega \text{ cm}^2$ after 300 days of immersion. Similar trend is noticed for the coating with 25% PVC and the coating resistance value is found to be $3.58 \times 10^9 \Omega \text{ cm}^2$ after 300 days of immersion. The higher resistance values exhibited by these coatings indicate the higher corrosion protection ability. In both the cases the capacitance values of the coatings are remained at $2\text{--}5.4 \times 10^{-10} \text{ F cm}^{-2}$. However for the coating with 30% PVC, the coating resistance values are decreased from 1.87×10^8 to $1.65 \times 10^7 \Omega \text{ cm}^2$ after 300 days of immersion. But the capacitance values of the coatings are not markedly affected with immersion time. These result show that the coatings with 20 and 25% PVC are more protective than the coating with 30% PVC.

3.4. Salt spray test

Fig. 8 shows the appearance of the coated panels after salt spray test for 720 h. It can be seen that there is no rusting in the scribed areas of the coated panel with 20% PVC whereas a slight rust formation is found in the scribed areas of 25 and 30% PVC coating. In other areas, some minute blisters are observed. Visual inspection of blistered areas has been made after removal of coating. However, no rusting is noted under the blisters. The impedance behavior of the coated panels after salt spray test is shown in Fig. 9. It is observed that the coating resistance of the coated panel with 20% PVC is found to be at $7 \times 10^9 \Omega \text{ cm}^2$ while the coating resistance values of the coatings with 25 and 30% PVC are $3 \times 10^7 \Omega \text{ cm}^2$ and $8 \times 10^6 \Omega \text{ cm}^2$ respectively. These results show that the coating with 20% PVC is

highly protective in comparison with coatings with 25 and 30% PVC since the coating resistance value is found to be 100–1000 times higher for the coating with 20% PVC. In a similar study made by Kalendova et al. [17], it has reported that the polyaniline coatings with 15–20% PVC are able to offer higher protection in the damaged areas in comparison with that of higher PVC containing coating. It has been explained that the percolation threshold of PANI in coating is 15–16% and hence the coating with 15–20% PVC is able to offer higher protection [18,19]. At higher PVC values, the presence

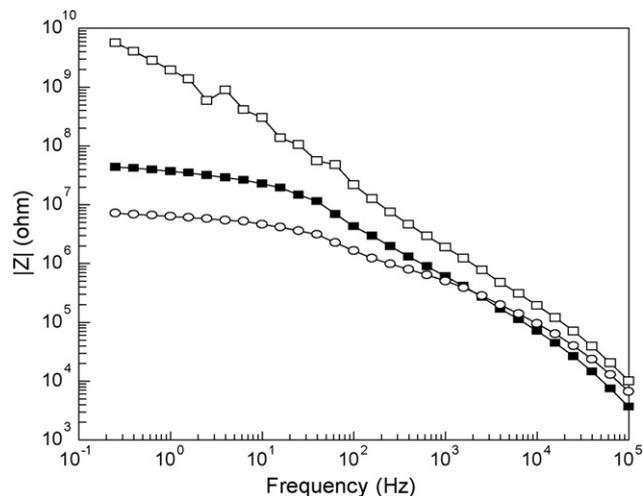


Fig. 9. Impedance behavior of coated steel in 3% NaCl after salt spray test. \square , 20% PVC; \blacksquare , 25% PVC; and \circ , 30% PVC.

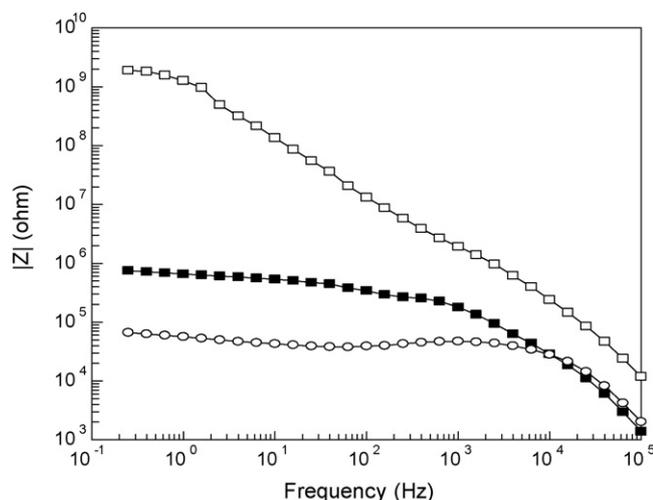


Fig. 10. Impedance behavior of scribed areas in 3% NaCl after salt spray test. □, 20% PVC; ■, 25% PVC; and ○, 30% PVC.

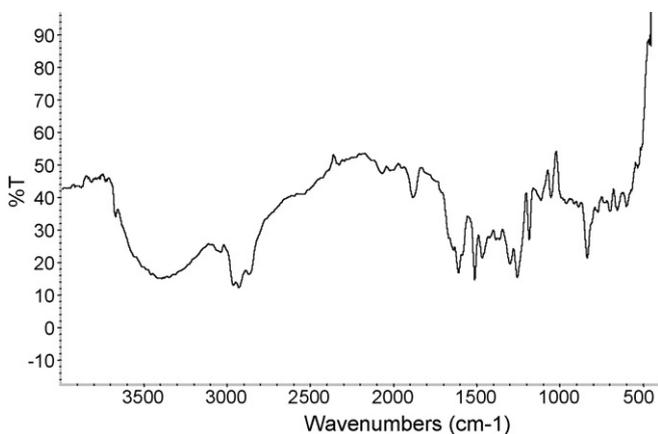


Fig. 11. FTIR reflectance spectra taken on the scribed area of 20% PVC coated panel after salt spray test.

of conducting pathways due to conducting polymer in the coating would promote corrosion rather than to prevent it and hence reduced corrosion protection is observed at higher PVC values.

The extent of corrosion damage in the scribed areas after salt spray test has been assessed by measuring the impedance on the scribed areas. Fig. 10 shows the impedance spectra of scribed areas for 20, 25 and 30% PVC containing coatings after salt spray exposure test. It can be seen that the coating with 20% PVC is able to maintain very high resistance value of $10^9 \Omega \text{ cm}^2$ whereas the other coatings show the resistance values less than $10^6 \Omega \text{ cm}^2$. The presence of polyaniline in the scribed areas has been confirmed from FTIR spectra (Fig. 11) taken on the scribed areas for the coating with 20% PVC after salt spray test. The spectra show the presence of char-

acteristic polyaniline bands at 1608, 1510, 1256, 1112 cm^{-1} due to emeraldine salt form. Besides a new band at 1383 cm^{-1} is observed due to the presence of non-conducting PANI base [20]. These results show that polyaniline present in the scribed areas is converted partially to non-conducting form. Similar results are observed in FTIR spectra for coatings with 25 and 30% PVC.

The mechanism of corrosion protection of iron by polyaniline emeraldine salt containing coating is by the formation of passive Fe_2O_3 [7] and also by the formation of iron-phosphate secondary complex [20] due to redox reaction of polyaniline [4,6]. Hence the protection of iron takes place via the reduction of polyaniline emeraldine salt to polyaniline leucoemeraldine salt with the concomitant release of phosphate ions. The released phosphate ions form iron-phosphate complex along with the passive film formed by the polyaniline. Hence the corrosion protection of polyaniline in the coating is due to its redox property of polyaniline.

4. Conclusions

Both immersion and salt spray tests show that the coating with 20% PVC is able to offer more corrosion protection than that of coatings with 25 and 30% PVC. Polyaniline in the coating is found to offer protection in the scribed areas. The conducting state of polyaniline is changed partially in the scribed areas due to the redox property of polyaniline.

Acknowledgement

The authors thank the Director, CECRI, Karaikudi for his kind encouragement and permission to carry out the work.

References

- [1] J. Schwindt, Mater. Perform. (December) (1996) 25.
- [2] L.O. Cummings, Composition for coating wet surfaces or surfaces immersed in water, US Patent 3993707.
- [3] M. Dhanalakshmi, K. Maruthan, P. Jayakrishnan, N.S. Rengaswamy, Anticorr. Method Mater. 44 (1997) 393.
- [4] P.J. Kinlen, V. Menon, Y. Ding, J. Electrochem. Soc. 146 (1999) 3690.
- [5] B. Wessling, Adv. Mater. 6 (1994) 226.
- [6] A. Talo, P. Passiniemi, O. Forsen, S. Ylassari, Synth. Met. 85 (1997) 1333.
- [7] B. Wessling, Synth. Met. 85 (1997) 1313.
- [8] C.H. Hsu, F. Mansfeld, Corrosion 57 (2001) 747.
- [9] E.T. Karg, K.G. Necho, K.L. Tan, Prog. Polym. Sci. 23 (1998) 277.
- [10] J. Stejskal, M. Omastova, S. Fedorova, J. Prokes, M. Trochova, Polymer 44 (2003) 1353.
- [11] T. Hino, T. Namiki, N. Karamoto, Synth. Met. 156 (2006) 1327.
- [12] X.H. Wang, Y.H. Geng, Z.X. Wang, X.B. Jing, F.S. Wang, Synth. Met. 69 (1995) 265.
- [13] X. Li, G. Wang, X. Li, Surf. Coat. Technol. 197 (2005) 56.
- [14] S. Sathiyarayanan, R. Jeyaraman, S. Muthukrishnan, G. Venkatachari, J. Electrochem. Soc. 156 (2009) C127.
- [15] J.R. Santos Jr., L.H.C. Mattoso, A.J. Motheo, Electrochim. Acta 43 (1998) 309.
- [16] S. Syed Azim, S. Sathiyarayanan, G. Venkatachari, Synth. Met. 157 (2007) 205.
- [17] A. Kalendova, D. Vesely, I. Sapurnia, J. Stejskal, Prog. Org. Coat. 63 (2008) 228.
- [18] H. Scher, R. Zallen, J. Chem. Phys. 53 (1970) 3759.
- [19] I. Krivka, J. Prokes, E. Tobolkova, J. Stejskal, J. Mater. Chem. 9 (1999) 2425.
- [20] I. Sedenkora, J. Prokes, M. Trochova, Polym. Degrad. Stability 93 (2007) 428.