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Corrosion protection of iron by benzoate doped polyaniline containing coatings

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ABSTRACT

Polyaniline containing organic coatings based on vinyl and acrylic resins are found to protect iron in acid and neutral media. Since dopants play an important role in forming salts with iron, a study has been made on the effect of benzoate doped polyaniline on the corrosion protection of iron by polyaniline–vinyl coatings in acid and neutral media. EIS studies have been made on the corrosion protection performance of vinyl coating on steel with 1% polyaniline in 0.1N HCl and 3% NaCl up to 100 days of exposure. It has been found that benzoate doped polyaniline containing coating has found to offer more protection in neutral media than that in acidic media due to passivating ability of benzoate ions in neutral solution, along with iron–polyaniline complex.

1. Introduction

The use of intrinsically conducting polymers (ICP) for corrosion protection of iron is well established [1–3]. Mostly polyaniline (PANI) based coatings have been studied widely. Various studies [4–11] have shown that emeraldine salt of PANI is able to protect steel by stabilizing the potential of iron in passive region by forming protective passive layer. Kinlen et al. [10,11] have provided direct information on the redox process occurring in the PANI coatings. Further studies by de Silva et al. have shown that the formation of iron-dopant complex also passivates steel [12–14]. The corrosion protection performance of polyaniline with dopants like phosphoric [10,11,15,16], hydrochloric [17–19], phosphonic [20,21] and sulfonic acids [10–14,22–26] has been reported. These earlier studies have shown that dopant ions influence the corrosion protection property of polyaniline containing organic coatings. Since benzoate is a good corrosion inhibitor for iron [27] a study has been made on the corrosion protection of iron in acid and neutral media by benzoate doped polyaniline.

2. Experimental

2.1. Preparation of benzoate doped polyaniline

Polyaniline was obtained by oxidative polymerization of distilled aniline in HCl using ammonium persulfate oxidant. The synthesized polyaniline was dedoped by dispersing and stirring in 1 M NH_4OH for 5 h. The dedoped polyaniline was filtered and dried. Redoping of polyaniline was made by dispersing the polyaniline to 1 M benzoic acid and stirring for 4 h. The benzoate doped polyaniline was filtered and washed with distilled water and dried in oven at 60 °C for 2 h.

2.2. Characterisation of benzoate doped polyaniline powder

The FTIR spectra of doped polyaniline were recorded on NICOLET 380 FTIR spectrometer using ATR at room temperature. X-ray diffraction pattern of the doped polyaniline were taken with analytical (Model PW 3040/60) X-ray diffractometer using Cu Kα radiation in the 2θ range 0–90° at the scan rate of 0.017° 2θ. 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 benzoate doped PANI was found out by Four probe resistance meter. The TGA analysis of benzoate doped PANI has been found out using thermal analyzer (STA, 1500), Polymer laboratory, Therman Science Ltd.

2.3. Preparation of paint with doped PANI

The 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 the volume solids of 30–33%.

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 m-seal adhesive. Solution of 3% NaCl was taken in the

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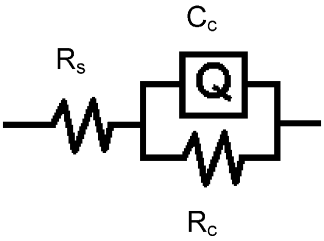
glass tube and the saturated calomel reference electrode was placed inside the glass tube. The open circuit potential of the coated steel was measured with respect to SCE using a high input impedance voltmeter (HP 973 A).

2.4.2. EIS studies

The electrochemical cell as described in this section with a platinum auxillary 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 Powersine software for a frequency range of 100 kHz to 0.1 Hz with an ac signal of amplitude of 20 mV for different immersion time in 3% NaCl. 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 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 [28]

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

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

3. Results and discussion

3.1. Characterisation of benzoate doped polyaniline pigment

The FTIR spectra of benzoate doped 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 [29]. Besides, the band at 1669 cm^{-1} is assigned to carbonyl group of benzoate [30].

The thermogravimetric analysis of benzoate doped polyaniline is shown in Fig. 2. It can be seen that the thermal degradation of PANI occur 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) [31]. The loss at around 240 °C is due to loss of dopant anions which has been confirmed by conductivity measurements [32].

The conductivity of the benzoate doped polyaniline is found to be 0.155 S cm^{-1}.

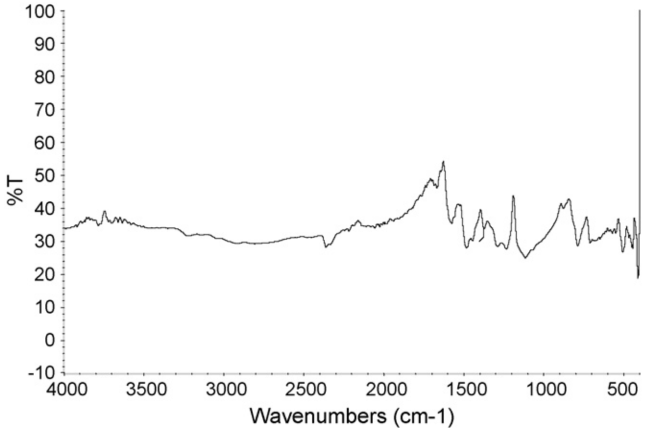


Fig. 1. FTIR spectra of benzoate doped polyaniline pigment.

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 [33].

3.2. Evaluation of coatings

3.2.1. EIS studies of coated steel in 0.1N HCl

The impedance behaviour of vinyl coated steel and PANI containing vinyl coated steel in 0.1N HCl is shown in Figs. 4 and 5. The impedance parameters such as the coating resistance (R_c), coating capacitance (C_c) values are given in Tables 1 and 2.

In the case of vinyl coated steel, the coating is able to offer protection up to 14 days which can be evidenced from the high R_c values greater than 10^8 Ω cm^2. After 21 days immersion, the resistance value of the coating is decreased steadily with exposure period and reached 2.1×10^5 Ω cm^2 after 100 days immersion. Besides, after 21 days immersion, the impedance behaviour shows the occurrence of charge transfer reaction by the existence of two time constants and the R_{ct} values are found to be 3.1×10^5 and 2.5×10^3 Ω cm^2 for 50 and 100 days, respectively.

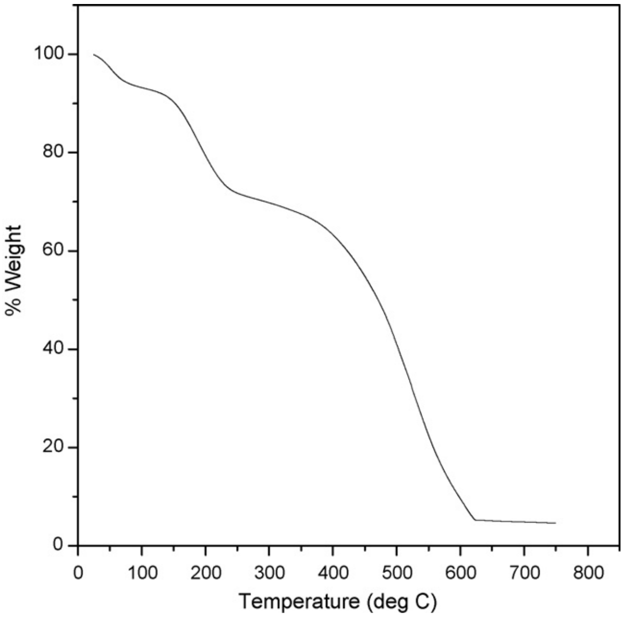


Fig. 2. Thermogravimetric analysis of benzoate doped polyaniline.

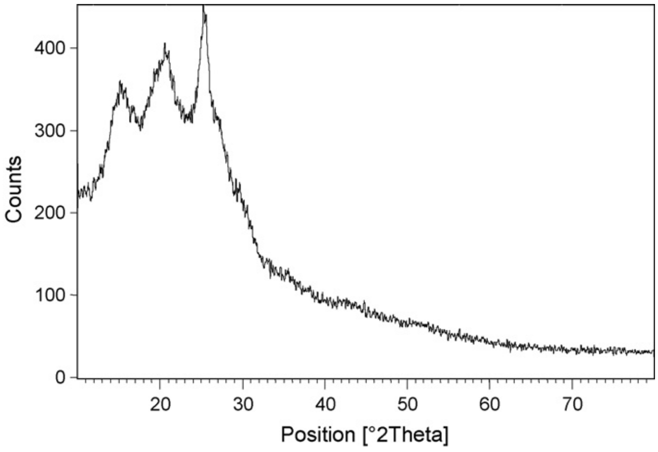


Fig. 3. XRD analysis of benzoate doped polyaniline.

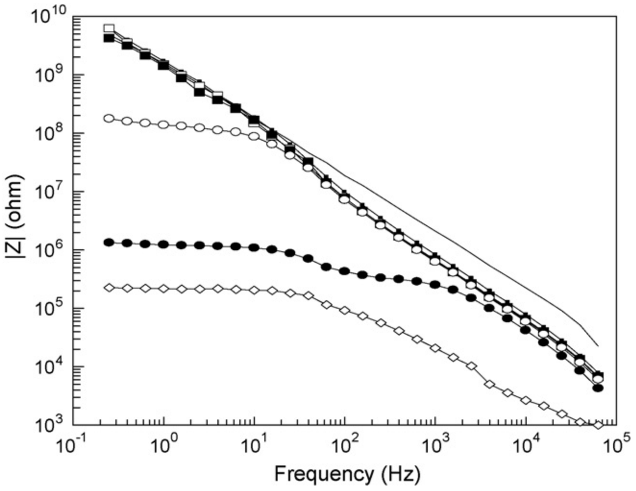


Fig. 4. Impedance plots of vinyl paint coated steel in 0.1N HCl: (—) initial; (▪) 1 day; (□) 4 days; (■) 7 days; (○) 14 days; (●) 50 days; (◊) 100 days.

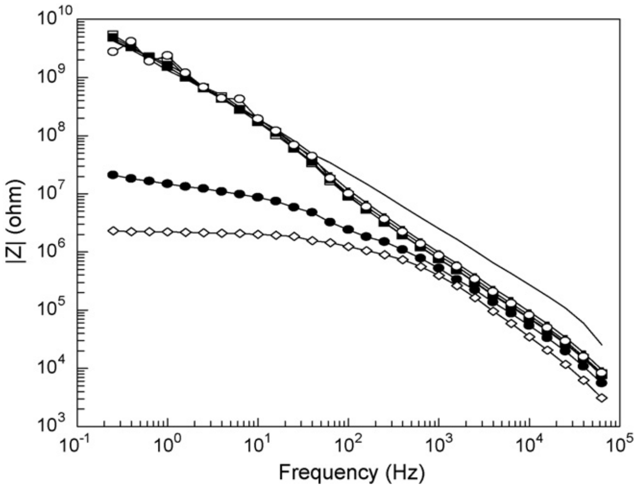


Fig. 5. Impedance plots of benzoate doped PANI containing vinyl paint coated steel in 0.1N HCl: (—) initial; (▪) 1 day; (□) 4 days; (■) 7 days; (○) 14 days; (●) 50 days; (◊) 100 days.

The impedance behaviour of benzoate doped polyaniline containing vinyl coating have shown that the coating is able to offer protection up to 50 days and after that there is a sharp decrease of R_c values after 50 days and reached to $2.1 \times 10^6\,\Omega\,\text{cm}^2$ after 100 days immersion.

The FTIR spectra of coating containing PANI before and after exposure to 0.1N HCl are given in Figs. 6 and 7. It can be seen that the main PANI peaks around $1600\,\text{cm}^{-1}$ (for quinoid structure), $1500\,\text{cm}^{-1}$ (for benzenoid structure), $1300\,\text{cm}^{-1}$ (for C–N stretching mode for benzenoid ring), 1100 and $1200\,\text{cm}^{-1}$ (for protonation-conducting state) are present in both cases. The peak corresponding to the conducting state at around $1100\,\text{cm}^{-1}$ confirms that the polyaniline is remained without any change in its state. However a peak at $3458\,\text{cm}^{-1}$ is obtained in the case of coating exposed to acid which is due to the OH^- group.

The FTIR spectrum of the steel surface beneath the coating is shown in Fig. 8. It shows the presence of polyaniline along with

Table 1
Impedance parameters of vinyl coated steel in 0.1N HCl

Time (days)	Open circuit potential V vs. SCE	Impedance parameters	
		Coating resistance R_c ($\Omega\,\text{cm}^2$)	Coating capacitance C_c ($\text{F}\,\text{cm}^{-2}$)
Initial	−0.049	1.45×10^{10}	7.99×10^{-11}
1	−0.071	1.33×10^{10}	1.14×10^{-10}
4	−0.081	1.89×10^{8}	6.53×10^{-10}
7	−0.141	1.05×10^{8}	1.91×10^{-10}
14	−0.195	2.09×10^{8}	2.10×10^{-10}
21	−0.286	1.97×10^{6}	6.38×10^{-9}
50	−0.657	1.76×10^{6}	7.49×10^{-9}
100	−0.605	2.10×10^{5}	8.11×10^{-9}

Table 2
Impedance parameters of benzoate doped PANI incorporated vinyl coated steel in 0.1N HCl

Time (days)	Open circuit potential V vs. SCE	Impedance parameters	
		Coating resistance R_c ($\Omega\,\text{cm}^2$)	Coating capacitance C_c ($\text{F}\,\text{cm}^{-2}$)
Initial	−0.150	1.82×10^{10}	6.96×10^{-11}
1	−0.009	7.36×10^{9}	1.09×10^{-10}
4	−0.190	1.95×10^{9}	1.18×10^{-10}
7	−0.099	1.40×10^{10}	1.24×10^{-10}
14	−0.139	1.72×10^{10}	9.49×10^{-11}
21	−0.168	4.51×10^{9}	1.12×10^{-10}
50	−0.562	1.81×10^{7}	3.32×10^{-10}
100	−0.605	2.05×10^{6}	4.43×10^{-9}

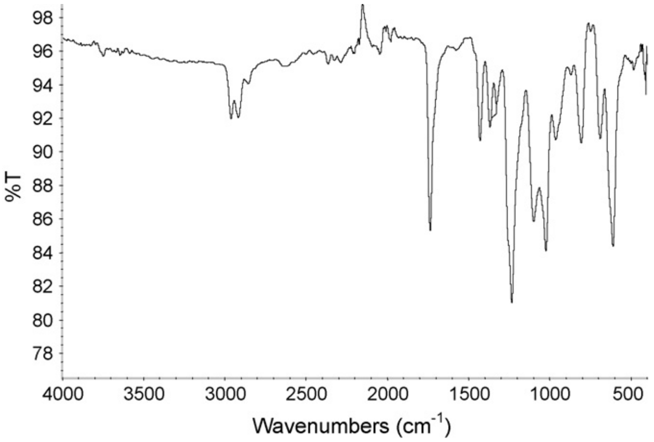


Fig. 6. FTIR spectra of vinyl paint containing benzoate doped PANI.

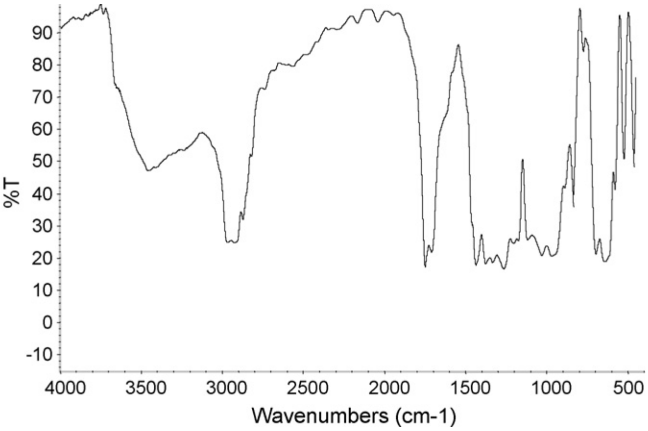


Fig. 7. FTIR spectra of vinyl paint containing benzoate doped PANI exposed to 0.1N HCl for 100 days.

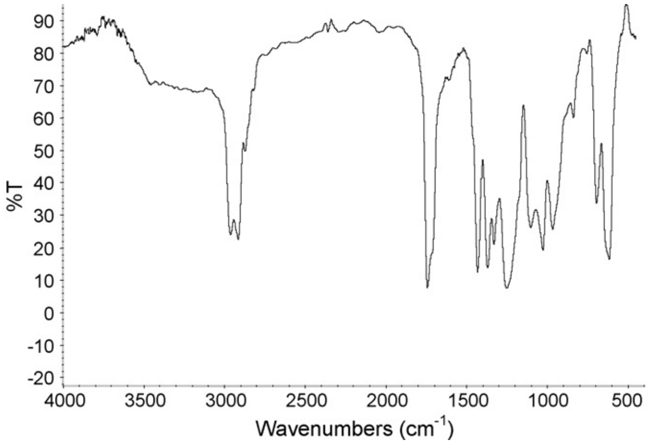


Fig. 8. FTIR spectra of paint removed area exposed to 0.1N HCl for 100 days.

benzoate. This indicates the formation of Fe–PANI complex on the iron surface. Besides, a peak around 480 cm^{-1} shows the presence of Fe_2O_3 on the surface [34].

3.2.2. EIS studies of coated steel in 3% NaCl

The impedance behaviour of vinyl coated steel and PANI containing vinyl coated steel is shown in Figs. 9 and 10. The variation of the coating resistance (R_c) and the capacitance (C_c) values with time is given in Tables 3 and 4. In the case of vinyl coated steel, it was found that the R_c values remained higher than $10^{10}\,\Omega\,cm^2$ up to 50 days and the R_c value decreased to $7.83 \times 10^6\,\Omega\,cm^2$ after 100 days immersion in 3% NaCl. However, in the case of PANI containing vinyl coated steel, the resistance values are remained greater than $1.2 \times 10^9\,\Omega\,cm^2$ even after 100 days immersion and the capacitance values did not change. This shows that the benzoate doped PANI is able to protect steel in neutral media effectively.

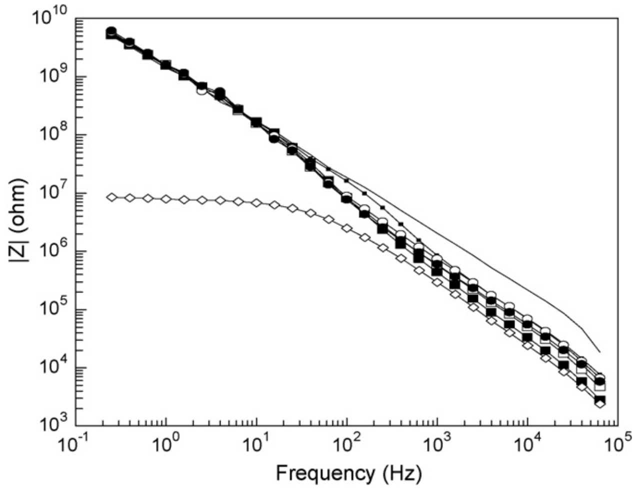


Fig. 9. Impedance plots of vinyl paint coated steel in 3% NaCl: (—) initial; (▪) 1 day; (□) 4 days; (■) 7 days; (○) 14 days; (●) 50 days; (◊) 100 days.

The FTIR spectrum of PANI containing vinyl coated steel after exposure to 3% NaCl for 100 days is shown in Fig. 11. Comparing with that of vinyl coated steel, it is found that the intensity of peaks at 1120 and 1230 cm^{-1} which are due to protonation is found to be decreased considerably in the case of PANI containing vinyl coated steel which indicates that the PANI in the coating is converted into non-conducting form. The FTIR spectrum of the steel surface where the coating has been removed after exposure to 100 days of exposure in 3% NaCl is shown in Fig. 12. It shows the presence of polyaniline along with benzoate on the iron surface due to the formation of Fe–PANI complex. Besides, the presence of Fe_2O_3 on the iron surface is indicated by a peak at 487 cm^{-1} [34].

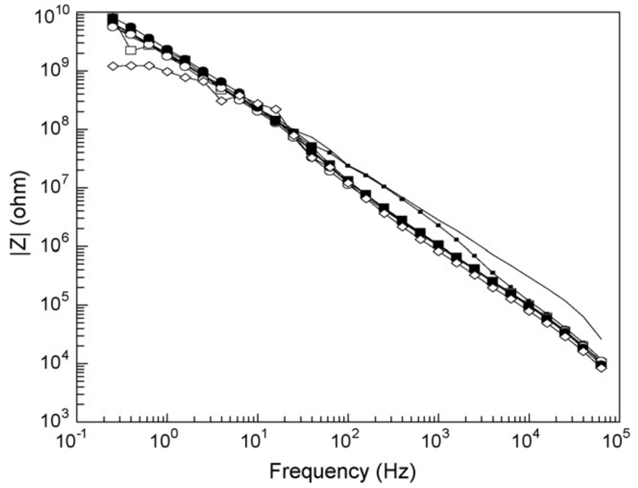


Fig. 10. Impedance plots of benzoate doped PANI containing vinyl paint coated steel in 3% NaCl: (—) initial; (▪) 1 day; (□) 4 days; (■) 7 days; (○) 14 days; (●) 50 days; (◊) 100 days.

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

Time (days)	Open circuit potential *V* vs. SCE	Impedance parameters	
		Coating resistance R_c ($\Omega\,cm^2$)	Coating capacitance C_c ($F\,cm^{-2}$)
Initial	−0.059	4.81×10^{10}	1.17×10^{-10}
1	−0.022	3.55×10^{10}	1.17×10^{-10}
4	−0.028	3.83×10^{10}	1.07×10^{-10}
7	−0.073	4.39×10^{10}	1.19×10^{-10}
14	−0.170	6.11×10^{10}	1.21×10^{-10}
21	−0.206	5.89×10^{10}	1.66×10^{-10}
50	−0.378	4.58×10^{10}	1.20×10^{-10}
100	−0.575	7.83×10^{6}	5.78×10^{-10}

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

Time (days)	Open circuit potential *V* vs. SCE	Impedance parameters	
		Coating resistance R_c ($\Omega\,cm^2$)	Coating capacitance C_c ($F\,cm^{-2}$)
Initial	−0.050	3.74×10^{10}	9.34×10^{-11}
1	−0.059	4.69×10^{10}	7.83×10^{-11}
4	−0.150	4.00×10^{10}	9.42×10^{-11}
7	−0.005	3.32×10^{10}	9.38×10^{-11}
14	−0.030	2.85×10^{10}	1.07×10^{-10}
21	−0.047	3.32×10^{10}	4.58×10^{-10}
50	−0.099	5.04×10^{10}	7.52×10^{-11}
100	−0.091	1.18×10^{9}	9.00×10^{-11}

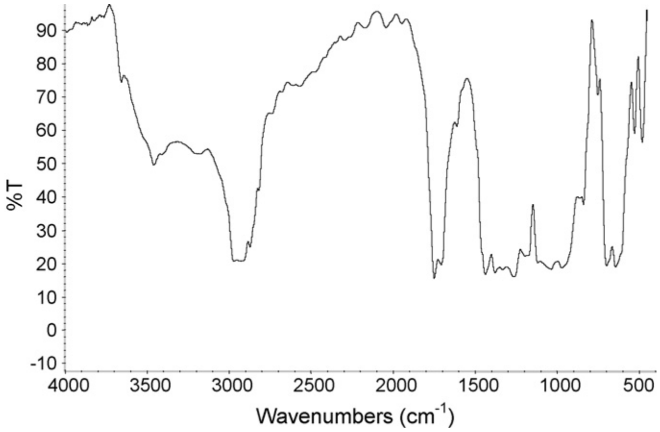


Fig. 11. FTIR spectra of vinyl paint containing benzoate doped PANI exposed to 3% NaCl for 100 days.

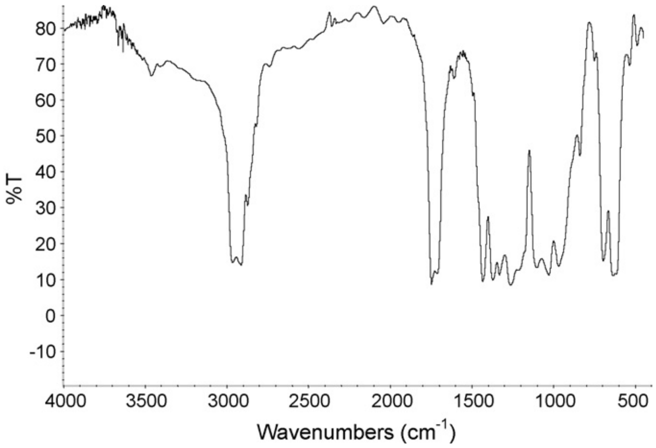


Fig. 12. FTIR spectra of paint removed area exposed to 3% NaCl for 100 days.

3.2.3. *OCP studies of coated steel*

The variation of OCP values with time for coatings with and without PANI are also presented in Tables 1–4 along with coating resistance and capacitance values. It can be seen that the potential values are in the noble region for PANI containing coating in comparison with that of coatings without PANI especially in the neutral media. However, in the acid media, the OCP values are in the noble region up to 21 days for both the coatings and shifted to active region after that.

The mechanism of corrosion protection of iron by emeraldine salt form of polyaniline (PANI-ES) is mainly due to passivation [4–11] of iron along with the formation of iron-dopant salt [12–14]. In this study also it has been found that the open circuit potentials remained in noble values as long as the coating protects the iron surface. Further, it has been found that the conductivity state of polyaniline has remained unaffected in acid media while it is changed in neutral media. But the re-oxidation from PANI-LB to PANI-ES is not observed in neutral media as evidenced from FTIR spectra of coated sample after exposure to NaCl solution. However, the presence of Fe_2O_3 on iron surface is indicated from FTIR spectra as reported by earlier workers [4,6,7]. Besides the presence of Fe_2O_3 on the iron surface, FTIR studies have indicated the presence of polyaniline on the iron surface due to the formation of Fe–PANI complex. Such type of complex formation of iron salts with polyaniline has been reported by Dimitriev and Izumi et al. [35,36].

4. Conclusion

The vinyl coating containing benzoate doped polyaniline is able to protect steel in neutral media better than in acid media. The conducting nature of polyaniline is remained unaffected in acid media whereas it is changed to non-conducting in neutral media. FTIR studies have shown that the polyaniline protects iron by formation of passive iron oxide film along with Fe–PANI complex.

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