Synthesis and anticorrosion properties of polydiphenylamine blended vinyl coatings

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Abstract

Inherently conducting polymers such as polyaniline and polypyrrole containing organic coatings have been found to offer corrosion protection of steel in acid and neutral media. In this study, the use of polydiphenylamine in vinyl coating for corrosion protection of steel in 3% NaCl solution is reported. The polydiphenylamine was prepared by chemical oxidative method of diphenylamine by ammonium persulfate in hydrochloric acid medium. The synthesized polydiphenylamine (PDPA) was blended with vinyl resin at 0–5% concentrations and the corrosion protection performance of the coating on steel was evaluated by EIS for a period of 80 days. It has been found that the coating containing 3% PDPA is able to protect steel more effectively.
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Keywords: Polydiphenylamine; Steel; Corrosion; EIS; Vinyl coating

1. Introduction

Conducting polymers such as polyaniline, polypyrrole containing organic coatings have been found to protect steel from corrosion in acid and neutral media [1]. The principal potential advantage offered by the conducting polymer containing coating is the coating's tolerance to pinhole and minor scratches as shown by Kinlen et al. [2,3] using SRET techniques. The mechanism of corrosion protection of steel by polyaniline has been reported to be based on the formation of a thin oxide layer as a result of electrochemical interaction between the polymer and iron surface [4,5]. The corrosion protection of steel by polyaniline in binders such as acrylic [6], epoxy [7,8], vinyl [9], vinyl acrylic [10], polyvinyl butyral [2,3] has been reported. da Silva et al. [11] have studied the role of counter ions on corrosion protection of steel by polyaniline–acrylic coating. They have shown that the polyaniline blends protect the steel by the redox reaction between Fe and PANI and form a passivating complex film of Fe-doping anion. In most of these earlier studies, polyaniline was used as the pigment. The study made by the authors [12]

on the use of polydiphenylamine (PDPA) as inhibitor for iron in acid has shown that polydiphenylamine is able to protect iron more effectively in very low concentration. Hence, a study has been made on the assessment of corrosion protection property of polydiphenylamine containing vinyl coating on steel in NaCl solutions. This paper deals with the synthesis of PDPA, its characterization and corrosion protection ability of PDPA containing coating on steel in 3% NaCl solution.

2. Experimental

2.1. Preparation of polydiphenylamine pigment

One molar of distilled diphenylamine was dissolved in 500 ml of 4 M solution of hydrochloric acid. Pre-cooled 1 M solution of ammonium persulfate was added drop wise to the pre-cooled diphenylamine-acid mixture for about 1.5 h with constant stirring. The reaction was conducted at $5 \pm 1\,^\circ$C. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured conducting polydiphenylamine thus formed was filtered and repeatedly washed with distilled water to remove excess acid content. The polymer was dried in oven at about $80\,^\circ$C for 2 h. The dried polydiphenylamine was fine grinded using mortar and then used as pigment.

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2.2. Characterization of polydiphenylamine

The infrared spectra of the polymer pelletised with KBr in the region of 2000–500 cm^{-1} were recorded on NICOLET 380 FT-IR spectrometer at room temperature. The X-ray diffraction pattern of polydiphenylamine was taken with Analytical (Model PW3040/60) X-ray diffractometer using Cu α radiation in the 2θ range of 5–75° at the scan range of 0.0170° 2θ with continuous scan type with scan step time of 15.5056 s. The conductivity of the PDPA powder and PDPA blended coating has been found out by four-probe resistance method.

2.3. Preparation of polydiphenylamine containing paint

The polydiphenylamine containing paint was prepared using vinyl resin (M.W. = 30,000) with 0–5% PDPA. The characteristics of paint and coating are: touch dry—1 h; complete dry—2 h; volume solids—30–35%; thickness per coat 50 ± 5 μm; pvc—1–5%.

2.4. Evaluation of corrosion resistant properties of the coating by EIS

Steel specimens of size 5 cm × 5 cm × 0.1 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 ± 5 μm. A glass tube of 1.2 cm diameter of length 3 cm was fixed on the coated ms panel 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–0.1 Hz with an a.c. amplitude of 20 mV for different immersion time up to 80 days. The impedance
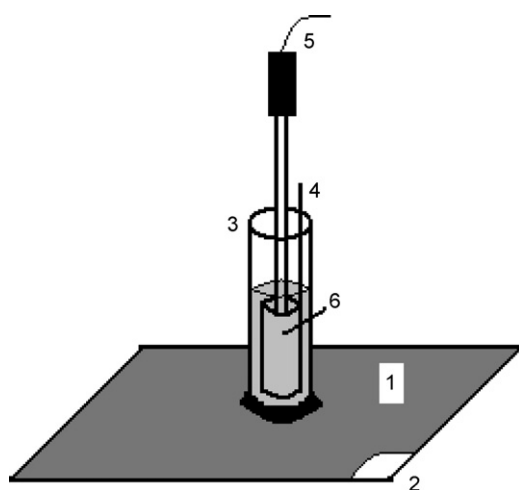

Fig. 1. Experimental cell setup: (1) painted steel panel, (2) paint removed area for making working electrode contact, (3) glass tube, (4) platinum counter electrode, (5) SCE reference electrode and (6) test electrolyte.
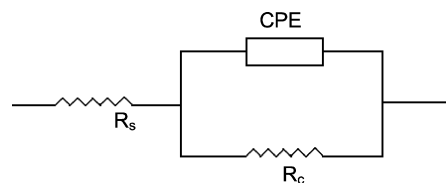

Fig. 2. Equivalent circuit for painted steel panel.

values are reproducible ±2–3%. 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).

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

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

where Y_0 is the CPE constant, ω 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 ($n = 0.5$) [13]. The following equation is used to convert Y_0 into C_{dl} is [14]:

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

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 80 days.

3. Results and discussion

3.1. Fourier transform infrared spectra

The FT-IR spectra of polydiphenylamine is shown in Fig. 3. The spectra is very much similar to that of polyaniline [15]: (i) bands at 1562 cm^{-1} and 1475 cm^{-1} are assigned to nitrogen quinone (Q) and benzenoid ring B [16,17], (ii) band at 1299 cm^{-1} to C–N stretch of a secondary aromatic amine, (iii) band at 876 cm^{-1} to out of plane bending of aromatic C–H, (iv) band at 799 cm^{-1} to 1,4-substituted benzene and (v) a strong band at 1114 cm^{-1} can be explained as an electronic band or a vibration band of nitrogen in quinone. The structure of polydiphenylamine is as follows [18]:

$$-(B-NH-B-B-\overset{+Cl^-}{NH}-B-B-\overset{+Cl^-}{NH}-Q-Q-\overset{+Cl^-}{NH}-B)_n-$$
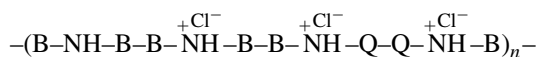
3.2. XRD studies

The XRD pattern of polydiphenylamine is shown in Fig. 4. The pattern is similar to that observed for polyaniline and intense peak at 20–25° has a similar profile as reported in literature [19].
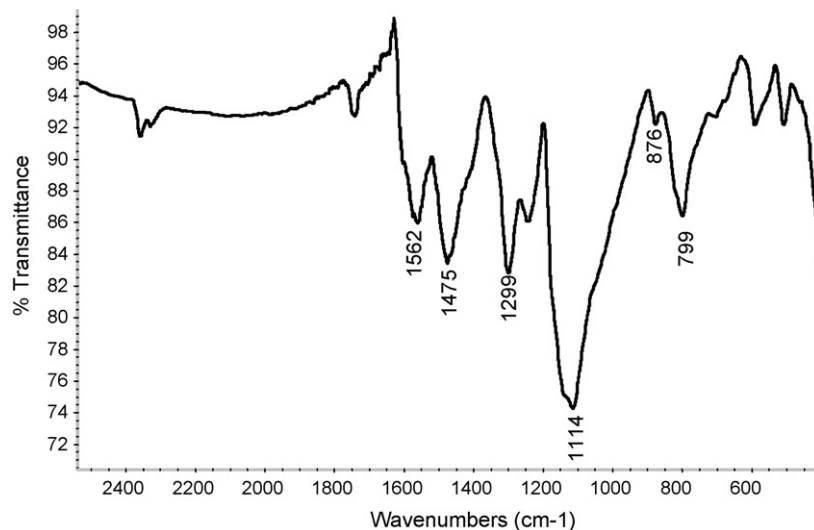
Fig. 3. FT-IR spectra of polydiphenylamine.

3.3. Conductivity studies

The four probe conductivity of PDPA was found to be 2.5 S cm^{-1} and that of coating coating containing PDPA was ≈ 8–10×10^{-6} S cm^{-1}.

3.4. Evaluation of corrosion protection ability of the coating by EIS

The resistance (R_c) and capacitance (C_c) of the coatings obtained from EIS measurements are used to characterize the corrosion protection ability of the coating. Values of R_c above $10^8\ \Omega\ cm^2$ have long been empirically associated with coatings displaying good protection while values below $10^7\ \Omega\ cm^2$ are typically considered to reflect poorly protective coating [20,21]. The decrease in R_c values have been associated with the degradation of coating [22]. The capacitance of the coating C_c is inversely proportional to the thickness of the coating and also depicts on its water content. The change in C_c over time can be used to determine the water uptake of the coating [23].
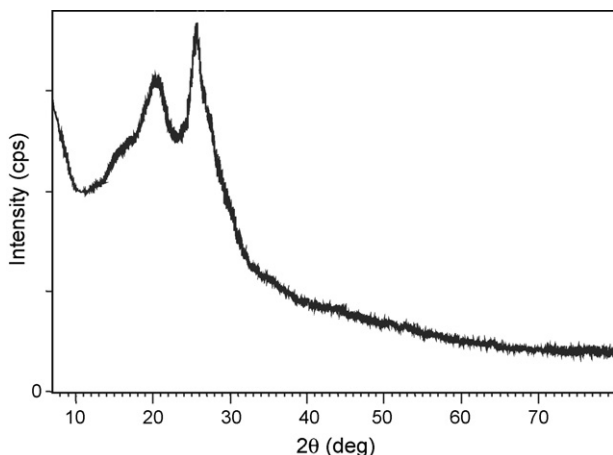

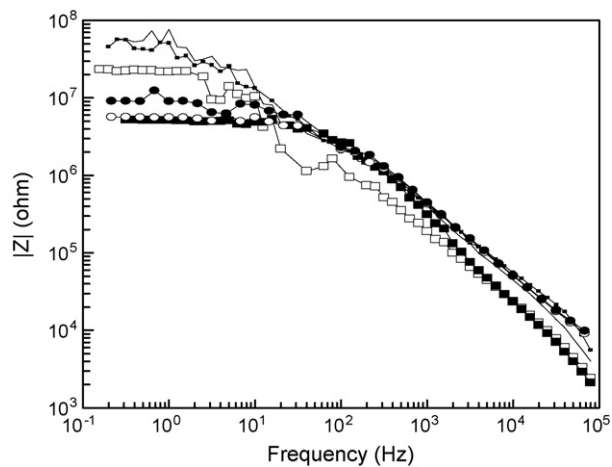Fig. 4. X-ray diffraction pattern of polydiphenylamine pigment.

Fig. 5. Impedance plots of paint coating containing 0% PDPA on steel in 3% NaCl. (—) Initial; (■) 1 day; (□) 3 days; (■) 7 days; (○) 40 days; (●) 80 days.

The impedance behaviour of vinyl coating with out PDPA on steel in 3% NaCl solution is shown in Fig. 5. The variation of resistance and capacitance values of the coating with time is given in Table 1. Initially, the resistance of the coating is $5.9 \times 10^7\ \Omega\ cm^2$ and with time, this value is decreased slowly to $8.9 \times 10^6\ \Omega\ cm^2$ after 80 days of immersion. However, the capacitance values of the coating are not changed significantly during the period of study.

Table 1
Impedance parameters of paint coating containing 0% PDPA on steel in 3% NaCl

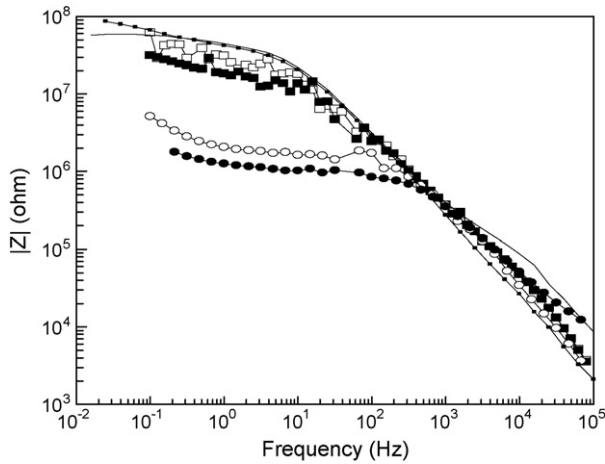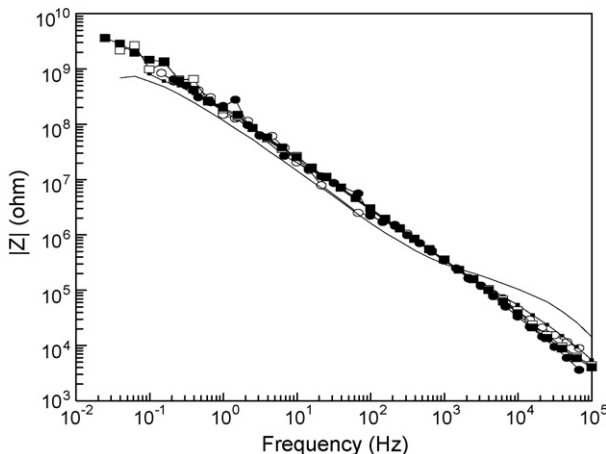| Time (days)	R_c ($\Omega\ cm^2$)	Y_0 ($\Omega^{-1}\ s^n$)	n	C_c (F cm^{-2})
Initial	5.96×10^7	1.02×10^{-9}	0.90	7.55×10^{-10}
1	5.09×10^7	2.02×10^{-9}	0.82	1.22×10^{-9}
3	2.25×10^7	1.94×10^{-9}	0.91	1.40×10^{-9}
7	5.11×10^6	5.59×10^{-10}	1	5.59×10^{-10}
40	5.66×10^6	7.91×10^{-10}	0.91	4.76×10^{-10}
80	8.91×10^6	6.65×10^{-10}	0.93	4.42×10^{-10}

Fig. 6. Impedance plots of paint coating containing 1% PDPA on steel in 3% NaCl. (—) Initial; (■) 1 day; (□) 3 days; (■) 7 days; (○) 40 days; (●) 80 days.

Table 2
Impedance parameters of paint coating containing 1% PDPA on steel in 3% NaCl

Time (days)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	6.08×10^7	6.47×10^{-10}	0.84	9.21×10^{-10}
1	4.75×10^7	7.06×10^{-10}	0.99	7.21×10^{-10}
3	4.18×10^7	9.99×10^{-10}	1	9.99×10^{-10}
7	2.48×10^7	7.85×10^{-10}	0.93	5.88×10^{-10}
40	1.64×10^6	4.60×10^{-10}	1	4.60×10^{-10}
80	1.56×10^6	2.28×10^{-9}	0.81	6.12×10^{-10}

Table 3
Impedance parameters of paint coating containing 3% PDPA on steel in 3% NaCl

Time (days)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	1.07×10^9	2.28×10^{-9}	0.82	2.67×10^{-9}
1	1.39×10^9	7.04×10^{-10}	0.89	8.64×10^{-10}
3	6.62×10^8	2.60×10^{-10}	0.93	8.34×10^{-10}
7	1.24×10^9	2.95×10^{-9}	0.82	2.27×10^{-9}
40	1.28×10^9	8.22×10^{-10}	0.92	8.25×10^{-10}
80	1.22×10^9	8.34×10^{-10}	0.95	8.35×10^{-10}

Table 4
Impedance parameters of paint coating containing 5% PDPA on steel in 3% NaCl

Time (days)	R_c ($\Omega\,cm^2$)	Y_0 ($\Omega^{-1}\,s^n$)	n	C_c ($F\,cm^{-2}$)
Initial	1.36×10^9	5.64×10^{-10}	0.86	7.86×10^{-10}
1	3.99×10^7	1.00×10^{-9}	0.84	5.35×10^{-10}
3	2.10×10^7	2.64×10^{-10}	1	2.64×10^{-10}
7	3.46×10^7	6.19×10^{-10}	0.90	3.99×10^{-10}
40	1.08×10^8	2.10×10^{-10}	0.99	2.09×10^{-10}
80	7.75×10^8	4.94×10^{-10}	0.95	4.09×10^{-10}

The impedance values obtained from Fig. 6 for vinyl coating containing 1% PDPA on steel in 3% NaCl solution are given in Table 2. As in the case of coating without PDPA, the resistance value of the coating is decreased from $6.1 \times 10^7\,\Omega\,cm^2$ to $1.6 \times 10^6\,\Omega\,cm^2$ after 80 days of immersion. But the capacitance values remained in the range of 4.6–$6.5 \times 10^{-10}\,F\,cm^{-2}$.

Fig. 7 shows the impedance spectra of the vinyl coating with 3% PDPA on steel in 3% NaCl. The data obtained from this figure are given in Table 3. It can be seen that the resistance values is decreased to $6.6 \times 10^8\,\Omega\,cm^2$ from $1.1 \times 10^{10}\,\Omega\,cm^2$ after 40 days immersion and increased to $1.2 \times 10^9\,\Omega\,cm^2$ after 80 days immersion. This resistance values are nearly 100 times higher than that of the coating without PDPA. The insignificant variation of capacitance values shows that the coating with 3% PDPA is highly corrosion protective.

The impedance values of the vinyl coating with 5% PDPA on steel in 3% NaCl solution are given in Table 4 and Fig. 8 shows the impedance spectra. The initial resistance value of the coating is found to be $1.4 \times 10^9\,\Omega\,cm^2$. The resistance value of the coating is decreased to $3.5 \times 10^7\,\Omega\,cm^2$ after 7 days immersion and increased to $7.8 \times 10^8\,\Omega\,cm^2$ after 80 days immersion. The capacitance values of the coating remained at $2.0 \times 10^{-10}\,F\,cm^{-2}$ to $7.8 \times 10^{-10}\,F\,cm^{-2}$.

The above studies indicate that the vinyl coating with 3% PDPA is able to protect steel more effectively. The coating containing 1% PDPA is not highly protective due to insufficient
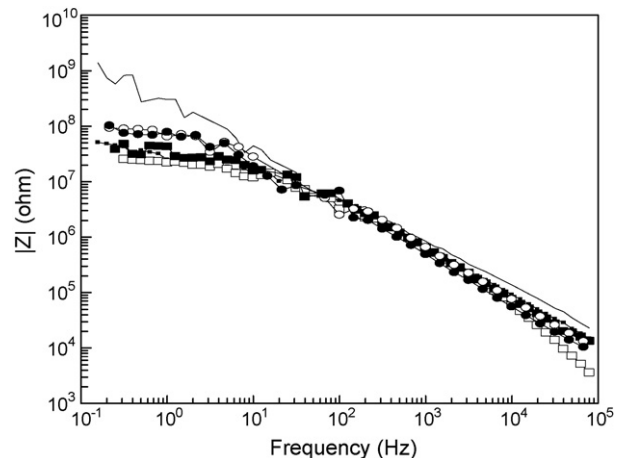

Fig. 7. Impedance plots of paint coating containing 3% PDPA on steel in 3% NaCl. (—) Initial; (■) 1 day; (□) 3 days; (■) 7 days; (○) 40 days; (●) 80 days.

Fig. 8. Impedance plots of paint coating containing 5% PDPA on steel in 3% NaCl. (—) Initial; (■) 1 day; (□) 3 days; (■) 7 days; (○) 40 days; (●) 80 days.
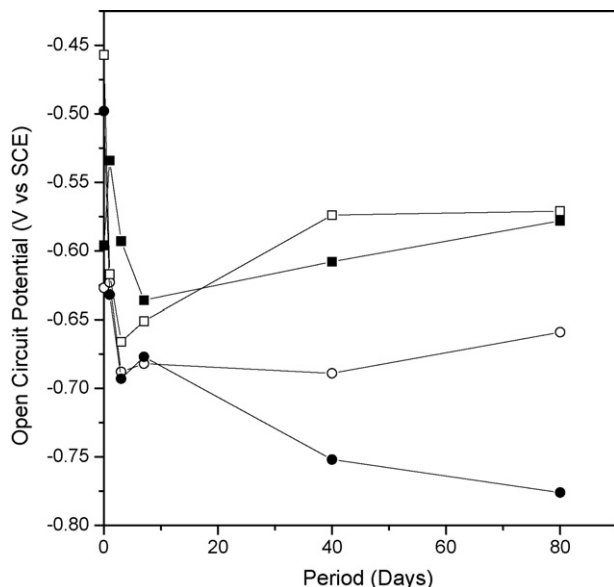
Fig. 9. Variation of open circuit potential value of paint coating containing PDPA on steel in 3% NaCl. (○) 0% PDPA; (●) 1% PDPA; (■) 3% PDPA; (□) 5% PDPA.
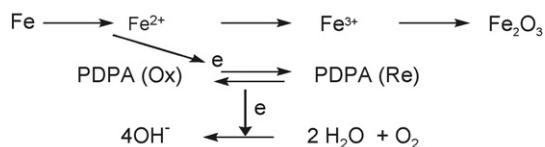

Fig. 10. Mechanism of corrosion protection by PDPA containing coating on steel in 3% NaCl.

re-oxidized to PDPA (Ox) form by dissolved oxygen reduction reaction.

4. Conclusions

Polydiphenylamine can be successfully prepared by chemical oxidation method. FT-IR studies indicate the presence of imine groups in the polymer. Coatings containing with more than 3% PDPA is found to offer higher corrosion protection. The mechanism of protection of PDPA is similar to that of polyaniline.

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amount of PDPA for formation of protective film on iron surface. In the case of coating containing 5% PDPA, the resistance values are one order less than the coating containing 3% PDPA. The lower resistance values in the case of coating with 5% PDPA may be due to release of higher amount of doped chloride ions during the redox reaction of PDPA with iron [11].

The variation of open circuit potential with time for vinyl coating containing 0–5% PDPA is shown in Fig. 9. It can be seen that the coating with 3% and 5% PDPA are able to gain about 70–80 mV in noble direction after 80 days immersion in comparison with the coating containing 0% PDPA. Besides the open circuit potentials of the coatings containing 3% and 5% PDPA are found to be shifted by 60–80 mV in noble direction after 7 days immersion which show the increased polarization of anodic reaction by passivation. Earlier study [9] with polyaniline (10%) containing vinyl coating on steel in 3% NaCl solution has shown that the OCP value is stabilized around +270 mV versus SCE after 28 days immersion and the resistance values of the coating have been found to be in the range of $2.2–6.9 \times 10^5 \, \Omega \, cm^2$ for 28 days immersion. On comparing these values with the resistance values of PDPA containing coating, the resistance values are 3–4 orders high which indicate that the coating containing PDPA offers higher corrosion protection ability.

The mechanism of protection of steel by PDPA is similar to that of PANI since its redox potential is +0.850 V versus SCE [24]. The mechanism of protection of PDPA of iron in neutral solution is shown in Fig. 10. The steel with the coating containing PDPA is passivated due to its redox ability of PDPA similar to polyaniline. The oxide film formed by polyaniline has been reported as either haematite (Fe_2O_3) [25] or a sandwich structure of $\nu \, Fe_2O_3$ overlying magnetite [5,26,27]. During the oxidation process of iron to iron oxide, the PDPA (Ox) is reduced to PDPA (Re) form. The reduced form PDPA (Re) is