

Anticorrosive properties of PANI–ATMP polymer containing organic coating

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

Central Electrochemical Research Institute, Corrosion-Protective Coatings, Karaikudi 630006, Tamilnadu, India

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Abstract

The conducting polymer polyaniline–amino trimethylene phosphonic acid (PANI–ATMP) was prepared by chemical oxidative method using ammonium persulphate. The polymer was characterized by FTIR, UV and X-ray fluorescence spectroscopy and XRD. The conductivity of the polymer was measured by four probe resistivity meter. The polymer was dispersed in epoxy resin and the corrosion protection property of the coating for steel has been evaluated by salt spray, open circuit potential measurements and EIS. It has been found that the open circuit potentials of coated steel have been shifted to noble direction after the initial shift in the active direction in 3% NaCl. Besides, the charge transfer resistance values have been found to increase with time due to passivation of steel by PANI–ATMP pigment, indicating the protective nature of the coating.

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1. Introduction

The organic coatings containing intrinsically conducting polymers like polyaniline have been found to be useful to replace toxic inhibiting pigments like zinc chromate [1–3]. The mechanism of corrosion protection of steel by polyaniline containing coating has been reported to be based on the formation of thin passive oxide layer due to electrochemical reaction between the polymer and iron surface [2,4–6]. It has been established that the polyaniline primer/top coat combination is superior to primers containing conventional inhibitive components [7]. Further, it is reported that the coated steel with polyaniline containing coating has gained 100–200 mV in corrosion potential in 3% NaCl solution [8,9]. The doped polyaniline containing coatings have found to offer protection even at scribed areas in 3.5% NaCl and 0.1 M HCl solutions [10,11]. But there are reports that the corrosion performance of coatings with conducting polyaniline is not as good as that of non-conducting polyaniline [12–14]. The effects of various dopants in polyaniline on the corrosion protection properties of steel have been studied [15–17]. These studies have shown that there exists a redox process between

the conducting polymer and iron and also a formation of second protective layer at the polymer/metal interface involving the participation of the dopant—anion of the polymer. Studies made by Samui et al. [18] have shown that lower loading of PANI–HCl has been found to be more effective in corrosion protection of steel. In this paper, the corrosion performance of chemically synthesized polyaniline–amino trimethylene phosphonic acid (PANI–ATMP) polymer containing coating on steel is reported.

2. Experimental

2.1. Preparation of PANI–ATMP pigment

One molar distilled aniline was dissolved in 500 ml of 1 M solution of ATMP. Pre-cooled 1 M solution of ammonium persulphate was added dropwise to the pre-cooled aniline–acid mixture for about 1.5 h with constant stirring. The reaction was conducted at 5 ± 1 °C. After the addition, the stirring was continued for 2 h for ensuring complete polymerization. A dark green coloured conducting polyaniline 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 polyaniline was fine grinded using mortar and then used as pigment.

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227133.
E-mail address: azim@cecri.res.in (S. Syed Azim).

Table 1
Paint formulation details

S. no.	Ingredients	Content (wt%)
1	PANI–ATMP	30
2	TiO ₂ (anatase)	35
3	Talc	15
4	Silica	10
5	Aluminium stearate	10

2.2. Preparation of epoxy paint

A 50% weight solution of epoxy (6071 Ciba Geigy India Ltd.) with epoxide equivalent of 500–510 was prepared using 1:1 (v/v) mixture of xylene and methyl isobutyl ketone. The hardener polyamine (Sympol 115, amine value 200–230 mg KOH/g) was dissolved in 50% xylene, methyl isobutyl ketone solvent mixture (1:1). The primer paint with volume solids 30% and P.V.C. 35% was prepared by dispersing pigments such as TiO₂, talk, silica and aluminium stearate along with PANI–ATMP in epoxy 6071 resin using an attritor for 30 min. Table 1 gives the details of the formulation. The formulated paint was characterized for its physical properties such as specific gravity, viscosity, drying time and dry film thickness as per ASTM standards and the values are given in Table 2.

2.3. Characterization of PANI–ATMP pigment

The PANI–ATMP pigment was characterized by the following methods:

- Oil absorption value:** The oil absorption value of PANI–ATMP pigment was found as per ASTM D-281-95. One gram of the pigment was weighed accurately and placed over a clean glass plate. Linseed oil is taken in burette. Linseed oil is added drop by drop on to the pigment and using a spatula the oil is dispersed. The volume of oil required to form a uniform paste is noted down from which the oil absorption value (%) is determined.
- Particle size analysis:** The particle size analysis was carried out with HORBIA LA-910 laser scattering particle size distribution analyzer.
- SEM analysis:** The scanning electron micrograph of PANI–ATMP pigment was analyzed using Hitachi (Model S3000 H) instrument. The pigment was spread over a copper block over which gold was sputtered.

Table 2
Properties of the paint/paint film

S. no.	Property	
1	Specific gravity (weight/gallon cup)	1.01
2	Viscosity (Brook filed viscometer)	300–325 cP
3	Drying time (Sheen drying time recorder)	7 h (tack free dry) 7 days (full cure)
4	Dry film thickness (DFT) (Minitest 600)	40 ± 2 μm

- XRD analysis:** The powder X-ray diffraction of the pigment was analyzed using PAN Analytical (Model PW3040/60) X-ray Diffractometer.
- Florescence spectra:** The florescence spectrum of the pigment was recorded using FLIROMAX-300 Spectrofluorometer in the wavelength range from 400 to 450 nm.
- FTIR analysis:** The FTIR spectra of PANI–ATMP pigment were obtained using Nicolet 380 FTIR Spectrometer in wave number range 2000–500 cm⁻¹.
- UV spectra analysis:** The UV–vis spectra of the PANI–ATMP pigment in the wavelength range 250–900 nm were recorded with Hitachi (Model U 3400) spectrophotometer.
- Conductivity measurements:** The conductivity of the PANI–ATMP pigment was measured for the palletised pigment using a four probe resistance meter.

2.4. Evaluation of coating

The coated mild steel panels were prepared by coating on sand blasted (2.5) specimen of size 15 cm × 10 cm. The dry film thickness was 40 ± 2 μm. The coated steel panels were exposed to salt spray of 5% NaCl solution as per ASTM B117.

The impedance studies of the coated panel were made using the impedance analyzer (6310 EG&G). A glass tube of 0.9 cm diameter was fixed on the coated steel with M-Seal adhesive. A solution of 3% NaCl was taken in the glass tube and the platinum electrode and SCE were placed inside the tube. This assembly was connected to impedance analyzer and impedance spectra were obtained for a frequency range of 100 mHz–100 kHz with an ac amplitude of 20 mV. From the impedance plots, the coating resistance (R_c) and the coating capacitance (C_c) were calculated. The experiments were carried out for a period of 40 days.

3. Results and discussion

3.1. Characterization of pigment

The oil absorption value is found to be 74.4%. The particle size distribution curve obtained for PANI–ATMP pigment is shown in Fig. 1. From the figure it is found that the mean particle size of the PANI–ATMP pigment is 3.975 μm. The scanning electron micrograph of PANI–ATMP pigment given in Fig. 2 shows a globular structure consisting of small globules of pores.

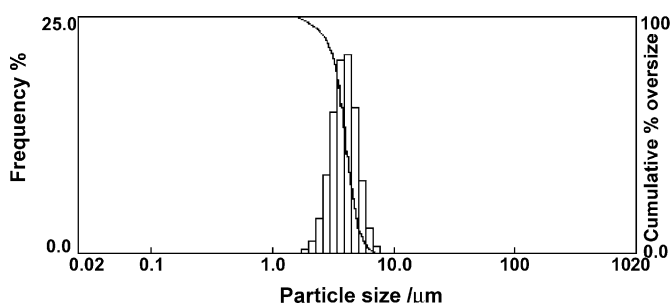


Fig. 1. Particle size curve of PANI–ATMP pigment.

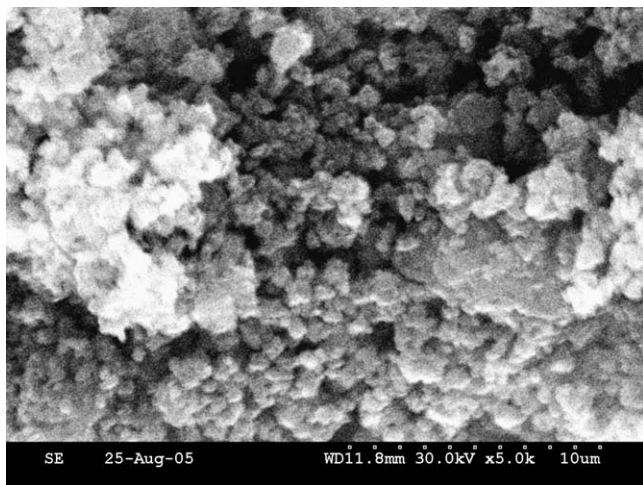


Fig. 2. Scanning electron micrograph of PANI-ATMP pigment.

This porous nature and low particle size of the pigment resulted in higher oil absorption value. Due to highly ordered system, conducting polymer could display a metallic like conductive state. The XRD pattern of the PANI-ATMP pigment is shown in Fig. 3. The intense peak at 2θ around 25° has a similar profile as that of free polyaniline reported in the literature [19,20]. This diffraction pattern also matches well with the PANI standard pattern (00-053-1890). The single characteristic peak around 410 nm of PANI [21] is observed in the fluorescence spectra shown in Fig. 4. The conductivity of the palletised PANI-ATMP pigment was 2.17 S cm^{-1} .

Fig. 5 shows the UV spectra of PANI-ATMP pigment. The absorption peak of polyaniline at 336 nm shows the $\pi-\pi^*$ transition in the benzenoid ring and 578 nm shows the donor-acceptor interaction of quinonoid ring. The well-known cation radicals and localized polaron peaks were observed at 449 and 775 nm. The Fourier transform infrared spectra of PANI-ATMP pigment are shown in Fig. 6. As shown in figure, the characteristic peaks of PANI occur at 1600, 1500, 1350 and 1120 cm^{-1} in agreement with the literature [22]. The peaks at 1500 and 1600 cm^{-1} are due to benzenoid and quinoid groups, respectively. The two strong peaks at 620 and 1120 cm^{-1} are due to out of plane

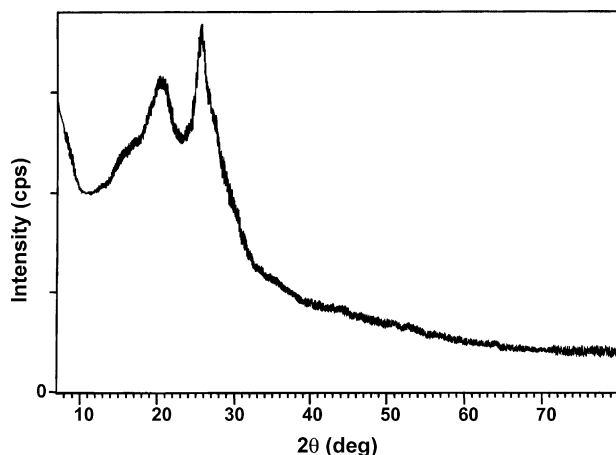


Fig. 3. X-ray diffraction pattern of PANI-ATMP pigment.

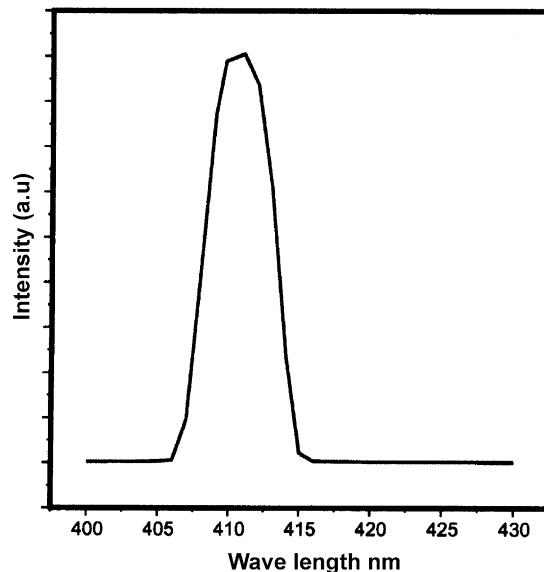


Fig. 4. X-ray fluorescence spectra of PANI-ATMP pigment.

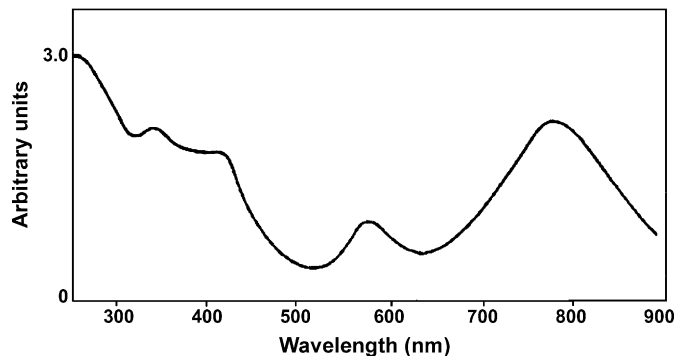


Fig. 5. UV-vis spectra of PANI-ATMP pigment.

and in plane C-H bending motion of quinoid and benzenoid rings, respectively. The peaks at 1250 and around 1350 cm^{-1} are characteristic amines. The peak at 830 cm^{-1} is due to the 1,4-*para*-substituted benzene ring.

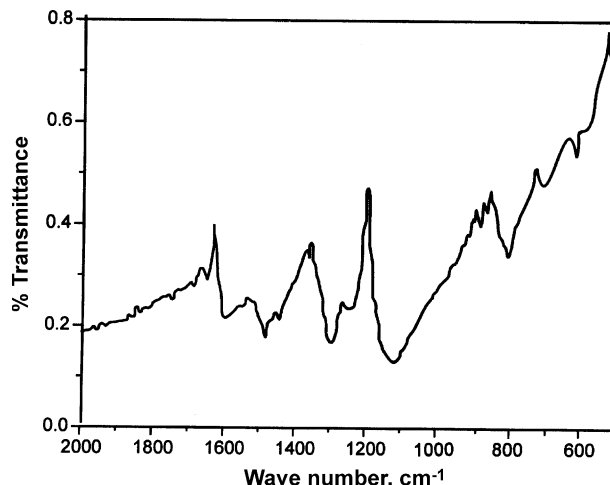


Fig. 6. FTIR spectra of PANI-ATMP pigment.

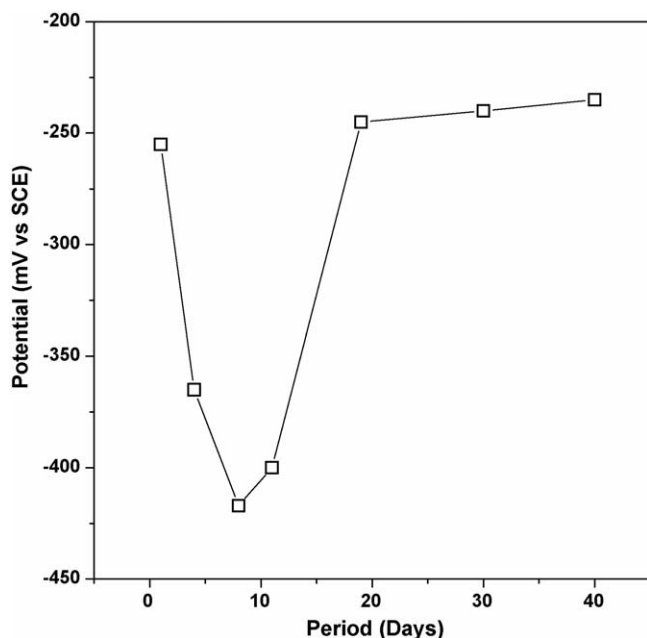


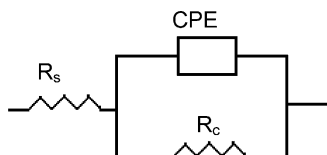
Fig. 7. Variation of open circuit potential for PANI-ATMP coated steel with exposed period in 3% NaCl.

3.2. Potential measurements

The variation of open circuit potential of coated steel in 3% NaCl solution with different periods of immersion is shown in Fig. 7. Initially the potential values shift to active direction from -267 to -418 mV up to 8 days of immersion. Afterwards, the potential values are shifted to noble direction and reached -218 mV after 40 days of immersion. Similar behaviour has been reported in earlier studies [8,9]. This type of behaviour is due to the formation of passive layer on iron surface by PANI-ATMP.

3.3. Electrochemical impedance spectroscopy studies

The impedance behaviour of coated steel in 3% NaCl is shown in Fig. 8. It is found that the diagram consists of one time constant, which is due to the resistance and capacitance of the coating. Using the following equivalent circuit:



where R_s is the solution resistance, R_c the coating resistance and CPE_c is the constant phase element corresponding to the coating capacitance, the resistance and capacitance values of the coating were obtained.

Assumption of a simple $R-C$ is usually a poor approximation. 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

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

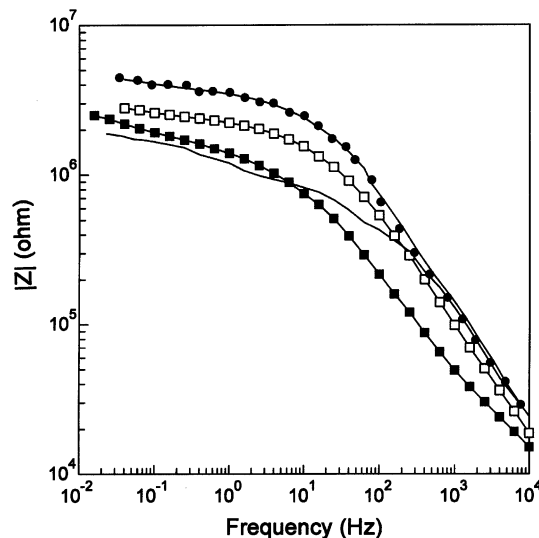


Fig. 8. Impedance plots of PANI-ATMP coated steel in 3% NaCl: (●) 1 day; (■) 8 days; (▲) 20 days; (□) 40 days.

where Y_0 is the CPE constant, ω the angular frequency (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 $n = 0.5$ [23]. The correct equation to convert Y_0 into C_c is [24],

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

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

Table 3 presents the variation of resistance values of the coating with period of immersion. It is found that the resistance value is decreased initially from 3.0 to $0.95 \text{ M}\Omega \text{ cm}^2$ after 4 days of immersion. However, the resistance value is increased to $2.54 \text{ M}\Omega \text{ cm}^2$ after 40 days of immersion. This increase in resistance values with time shows the protective nature of the coating system. The capacitance values were found to be between 10^{-10} and $10^{-9} \text{ F cm}^{-2}$. These capacitance values are typical of an intact coating, which is able to protect the steel [25].

3.4. Salt spray studies

Periodic observation of the exposed coated panel in salt spray chamber was made. It has been found that the coating is intact without any blisters or delamination and no rust formation. Besides the visual observation, the EIS studies were made with the exposed panels. The results are given in Table 1. It can be seen that there is a decrease in resistance values of the coating initially from 2.3 to $0.75 \text{ M}\Omega \text{ cm}^2$ and then increased to $2.11 \text{ M}\Omega \text{ cm}^2$ with time which indicates the protective nature of the coating. It has been established that PANI containing coating is highly corrosion resistant due to its redox characteristics. Besides, the PANI-ATMP pigment can release the phosphonate which can form iron-phosphonate secondary protective layer as has been reported in the case of PANI-camphor sulphonate and PANI-phenyl phosphonate pigment [17]. Due to PANI and

Table 3
Impedance parameters for PANI–ATMP coated steel in sodium chloride solutions

Duration (days)	Immersion studies		Salt spray test		
	R_c ($\Omega \text{ cm}^2$)	C_c (F cm^{-2})	R_c ($\Omega \text{ cm}^2$)	C_c ($\mu\text{F cm}^{-2}$)	Visual observation
1	3.05×10^6	4.50×10^{-10}	2.28×10^6	3.38×10^{-10}	No change
4	9.50×10^5	4.28×10^{-10}	7.35×10^5	2.96×10^{-10}	No change
8	1.09×10^6	3.37×10^{-10}	9.48×10^5	8.90×10^{-9}	No change
12	1.38×10^6	2.05×10^{-10}	1.24×10^6	8.45×10^{-9}	No change
20	1.76×10^6	1.91×10^{-10}	1.50×10^6	7.89×10^{-9}	No change
31	2.09×10^6	8.81×10^{-9}	1.81×10^6	4.32×10^{-9}	No change
40	2.54×10^6	1.59×10^{-9}	2.11×10^6	1.80×10^{-9}	Mild green colour

ATMP, the formation of passive iron oxide layer and iron–ATMP complex layer, the enhanced protection of steel in saline solution has been observed.

4. Conclusion

The PANI–ATMP polymer can be successfully synthesized using ammonium persulphate oxidant. The PANI–ATMP polymer exhibits a crystalline structure similar to PANI. The IR, UV–vis and fluorescence spectra of the PANI–ATMP are similar to those of PANI. The PANI–ATMP pigmented epoxy coating is found to offer corrosion resistance of steel exposed to saline environment. The shift in open circuit potential of the coated steel by 200 mV with time indicates the passive film formation by the PANI–ATMP pigment. The increasing values of coating resistance with period of exposure indicate the high protective nature of the coating.

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