



Polypyrrole as a protective pigment in organic coatings

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ABSTRACT

This study deals with the preparation and characterization of polypyrrole (PPy) using ferric chloride and ammonium dichromate as oxidants and also with the addition of a common surfactant in aqueous solution. The combination of oxidant and surfactant in the preparation of PPy has shown that there is an enhancement in conductivity and also in the yield of the PPy. The deprotonated PPy exhibits a better stability with decreasing conductivity. Fourier transform infrared spectroscopy (FTIR) confirmed that the surfactant radical sulphoxide got incorporated into the PPy as a dopant and also the presence of chromate radical was indicated by the appearance of peak at 459 cm^{-1} . Thermo Gravimetric Analysis (TGA) indicates that the weight losses for PPy-Cl and PPy-CrO₄ are 97% and 35–50% at 1000°C, respectively. X-ray diffraction (XRD) studies also give an idea about the size and shape of the polymer. The corrosion resistance property of PPy-incorporated coatings on mild steel substrate in sodium chloride solution indicates that the PPy-CrO₄/epoxy-polyamide coating gives maximum duration of protection compared with other systems.

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1. Introduction

In recent years conducting polymers with conjugated double bonds have attracted considerable interest for the developing of many advanced materials. Polypyrrole, one among the group of conducting polymers, has been the most widely used material for its good electrical conductivity and environmental stability. The pioneering works on corrosion protection properties of conducting polymers such as polyaniline (PANI), polypyrrole and polythiophene (PTh) on metallic surfaces have generated a new dimension in the field of protective organic coatings [1–5]. Polypyrrole was first synthesized by chemical polymerization during early nineteenth century. It was found insoluble in most of the common solvents due to the strong interchain interaction. Usually in chemical polymerization, oxidant agents initiate the chemical reaction. It has also been established that it is very easy to prepare PPy particles of different sizes ranging from micrometers to nanometers with the addition of different dopants. The reported advantages of the PPy-incorporated organic coatings exhibit a good adhesion as well as non-toxic protection to the metal substrate. In addition PPy coatings are capable of providing galvanic protection to the metal and so this coating maintain as a passive domain on the surface. PPy can be prepared by chemical [6] and electrochemical [7] polymerization. The preparation methods and additives influence the properties of

this conducting polymer [8]. Generally oxidizing agents used for the chemical polymerization are the compounds of transition metals like Fe³⁺, Cu²⁺, Cr⁶⁺ and Mn⁷⁺. Addition of surfactants accelerates the polymerization reaction of PPy and also alters its conductivity. The improved properties of thermal stability and moisture resistance can be caused by anionic surfactant as dopant into PPy. Kudoh [9] has prepared PPy by using ferric sulphate as the oxidant and also with the combination of anionic surfactant and concluded that the PPy prepared with surfactant showed high thermal and moisture stability in air.

Chromate conversion coating provides anodic protection against corrosive environment, but the use of these coatings has been the drawback of carcinogenic effect [10] due to the presence of chromium. Therefore it is necessary to develop a new inhibitor to replace the chromate coating for metal surface. Alternatively conducting polymers have attracted as a corrosion inhibitor. The conducting polymers containing chromate particles also enhance the protective action of the PPy on steel surface.

The present study deals with the synthesis of PPy by oxidation polymerization using ferric chloride and potassium dichromate as oxidants separately. The influence of anionic surfactant, dodecyl benzene sulphonic acid sodium salt (DBSNa) during the chemical oxidation of PPy in aqueous solution is also carried out. Also, the PPy prepared are deprotonated and all the materials prepared were characterized by employing atomic adsorption spectroscopy, FTIR, XRD, and their thermal stability were analyzed by TGA. The surface morphological changes in the PPy polymer prepared by chemical as well as in combination with surfactant are evidenced

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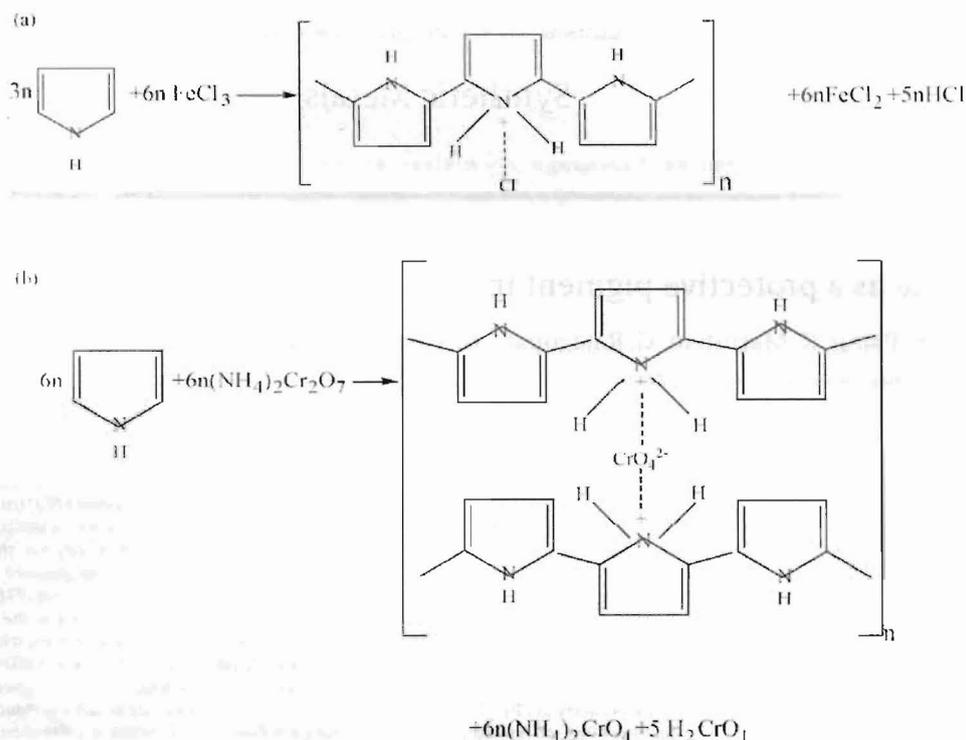


Fig. 1. (a,b) Structure of pyrrole with ferric chloride and ammonium dichromate yield polypyrrole (PPy).

by the SEM analysis. The corrosion resistance properties of PPy are evaluated by incorporating it in epoxy-polyamide polymer and applied onto the steel substrates and tested in sodium chloride electrolyte.

2. Experimental

Pyrrole (Acros) was distilled under vacuum and stored in refrigerator prior to use. The oxidants (ferric chloride and ammonium dichromate, Qualigens) and the surfactant (sodium dodecylbenzene sulphonate, Sigma) were used as received. Epoxy resin of Bisphenol-A type with epoxy equivalent 450–500 supplied by Ciba Speciality Chemicals, Mumbai, and the hardener, polyamide with amine value 210–230, supplied by Synpol Synthetic Polymers Pvt. Ltd., Ahmedabad, were used for this study. Solvent (mixed xylene) was used for adjusting viscosity of the polymer coatings.

2.1. Preparation of polypyrrole

PPy was prepared by chemical polymerization by dissolving 0.1 mol of ferric chloride in 150 ml of distilled water in a reaction vessel and it was continuously stirred at 800 rpm using a mechanical stirrer. To this 0.05 mol of distilled pyrrole dissolved in 50 ml of water was added drop-wise. The stirring was continued for 4 h at room temperature in order to completely polymerize the pyrrole. The PPy was filtered and washed with distilled water repeatedly and dried in vacuum oven at 50 °C for 8 h. Similarly the PPy was prepared by choosing ammonium dichromate as oxidant.

In addition to the oxidant as prepared earlier, 0.01 mol of surfactant (DBSNa) dissolved in 100 ml of distilled water was also added

to the reaction vessel and stirred at a speed of 800 rpm for 15 min. Then 0.15 mol of distilled Pyrrole dissolved in 50 ml of water was added drop-wise and continued the stirring for 4 h at room temperature. The PPy was washed with distilled water and dried in a vacuum oven at 50 °C for 8 h.

Part of PPy powder prepared was treated with an excess solution of ammonium hydroxide separately for 12 h in order to deprotonate them. After the completion of the reaction they were filtered

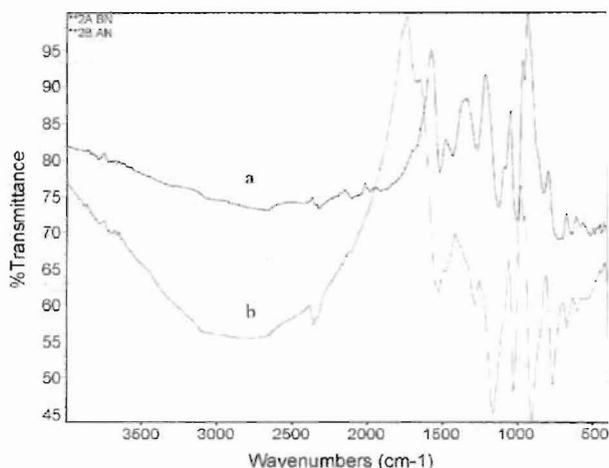


Fig. 2. FTIR spectra of PPy-Cl Prepared by using ferric chloride as oxidant: (a) protonated and (b) deprotonated.

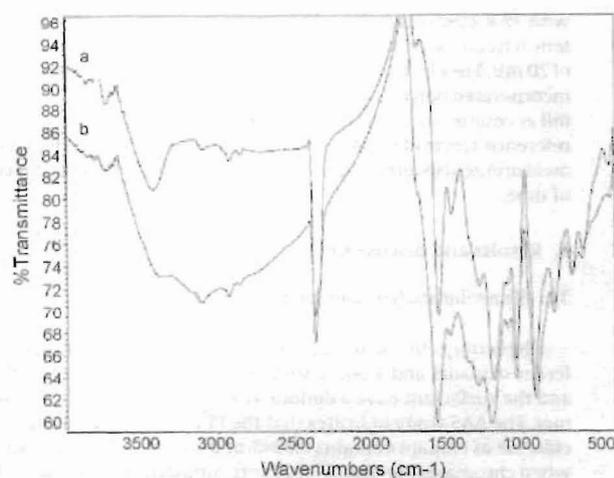


Fig. 3. FTIR spectra of PPY-Cl. Prepared by using oxidant and anionic surfactant: (a) protonated and (b) deprotonated.

and washed with distilled water and dried at 60 °C in vacuum oven.

2.2. Preparation of PPY-incorporated epoxy-polyamide coating

Epoxy resin was diluted with xylene to prepare 49% solution and 1 gm of PPY was added to it. This mixture is ground well to get 1% PPY-incorporated base part for this study. Similarly the hardener, polyamide was also modified to get 49% solution using Xylene as solvent and 1 gm of PPY was added to it and ground well to get 1% PPY hardener solution.

Mild steel panels of 10 cm × 15 cm size were sand-blasted to get a near white surface profile as per Swedish specification SA 2.5 [11]. The base and hardener parts were mixed in the ratio of 70:30 and were applied over sand-blasted steel surfaces by brushing and drying for 15 days. The panels with coating thickness $40 \pm 5 \mu\text{m}$ were selected for corrosion studies. Similarly a set of panels was coated with the epoxy-polyamide coating (without PPY) and used as control for this experiment.

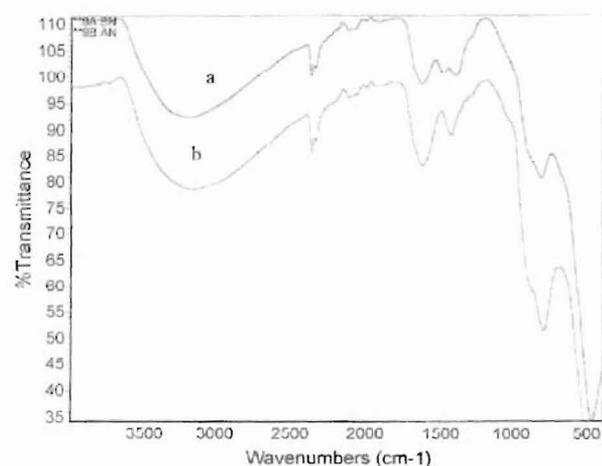


Fig. 4. FTIR spectra of PPY-CrO₄. Prepared by using ammonium dichromate as oxidant: (a) protonated and (b) deprotonated.

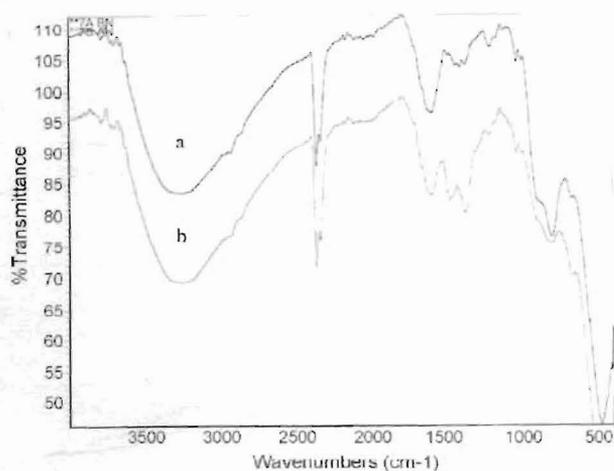


Fig. 5. FTIR spectra of PPY-CrO₄. Prepared by using oxidant and anionic surfactant: (a) protonated and (b) deprotonated.

2.3. Measurements

The PPY composition was measured by elemental analysis using Atomic Absorption Spectroscopy (AAS) (Varian Spectra AA 220, Australia).

PPY powder was used to make 1 mm thick × 12.5 mm dia pellets, and the conductivity was measured by using a four-probe meter connected to Keithley's 2182 nanovoltmeter and 2400 source meter.

The structural properties of the polymer were determined by using Fourier transform Infrared spectrometer (FTIR) model Naxus-670, UK. This spectrum indicates the appearance and disappearance of functional groups present in the polymers.

The optical and grain size of the PPY were studied by X-ray diffraction method using X pert PRO PAN analytical diffractometer with Syn Master 793_s software.

Thermo gravimetric analysis and Differential Scanning Calorimeter (DSC) measurements were carried out in the flow of nitrogen (100 ml m^{-1}) at a heating rate of 10°C m^{-1} using SDT Q600, TA instruments, USA. The TGA and DSC curves were recorded simultaneously.

The surface morphology of the PPY was studied by scanning electron microscope (SEM) model JEOL JSM 35F, Japan.

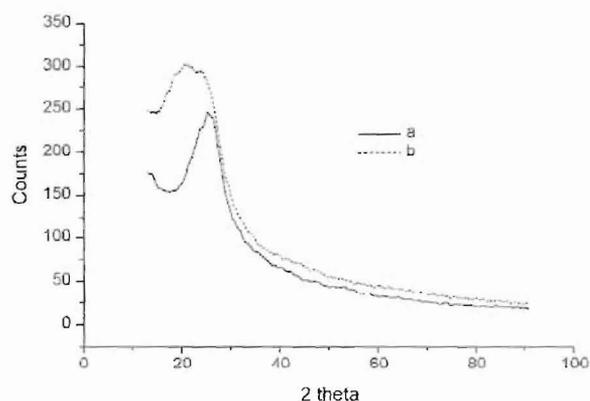


Fig. 6. XRD spectrum of PPY-Cl prepared by using (a) oxidant and (b) oxidant with surfactant.

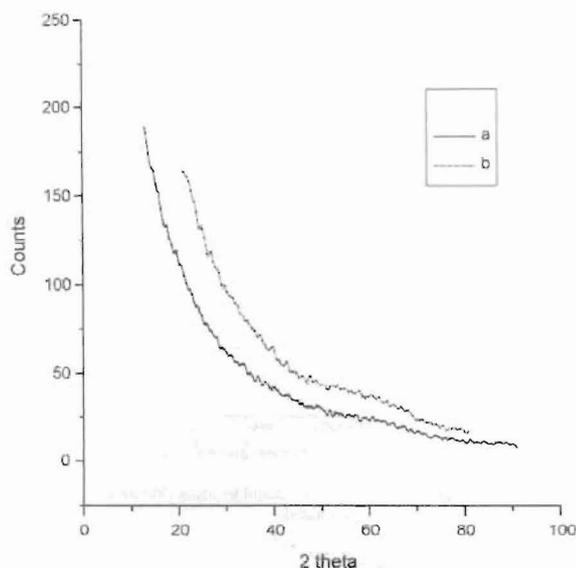


Fig. 7. XRD spectrum of PPY-CrO₄ prepared by using (a) oxidant and (b) oxidant with surfactant.

2.4. Corrosion studies

2.4.1. Accelerated salt spray test

The coated panels in duplicate were scratched at the centre and exposed in the salt spray chamber, where 5% sodium chloride solution was atomized by compressed air to create a fog. This test was conducted in accordance with ASTM standard B117 for 500 h.

2.4.2. Electrochemical impedance measurements

The corrosion resistance properties of epoxy-polyamide coating incorporated with 1% PPY on steel surface was evaluated by ac impedance studies. The impedance measurements were carried out

with PAR electrochemical impedance analyzer (model 6310) system at frequencies 10 kHz to 10 mHz for an applied signal amplitude of 20 mV. The electrochemical cell used for this study consists of PPY incorporated polymer coated steel as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode and 0.5 M NaCl as electrolyte. The impedance measurements were carried out periodically for different durations of time.

3. Results and discussion

3.1. Elemental analysis and conductivity of the PPY

The composition and the properties of PPY prepared by using different oxidants and anionic surfactants indicate that the oxidants and the surfactant have a definite role in conductivity of this polymer. The AAS study indicates that the PPY prepared by using Ferric chloride as oxidant contains 0.624% of iron and 36.2% of chromium when chromates are used as oxidants. Similarly the anionic surfactant incorporated polymerization also contains these elements in the PPY. The presence of excess chromium in the PPY gives higher conductivity than the PPY prepared by the ferric chloride oxidant medium. The highest conductivity of PPY-CrO₄ is 3.07 S cm⁻¹. The conductivity of PPY-Cl is 2.09 S cm⁻¹. The conductivity of the PPY prepared in presence of DBSNa exerts highest order in the range of 7–7.86 S cm⁻¹. The increase in conductivity of anionic-surfactant-incorporated oxidizing agent is mainly due to the modification in the conducting network created from PPY chain. The protonated unit of PPY is stable due to the influence of the surfactant. The anionic surfactant acts as a counter ion in the protonated unit of PPY and so the conductivity of this polymer is more stable than PPY prepared from oxidizing agent. The probable structure of the PPY produced in presence of FeCl₃ and (NH₄)₂Cr₂O₇ as oxidant are given in Fig. 1a and b. It is seen from the figure that each third constitutional pyrrole unit is protonated and ionized with the chloride as well as chromate ions. The presence of the protonated pyrrole unit and the chloride and chromate radicals are induced the conductivity of polypyrrole.

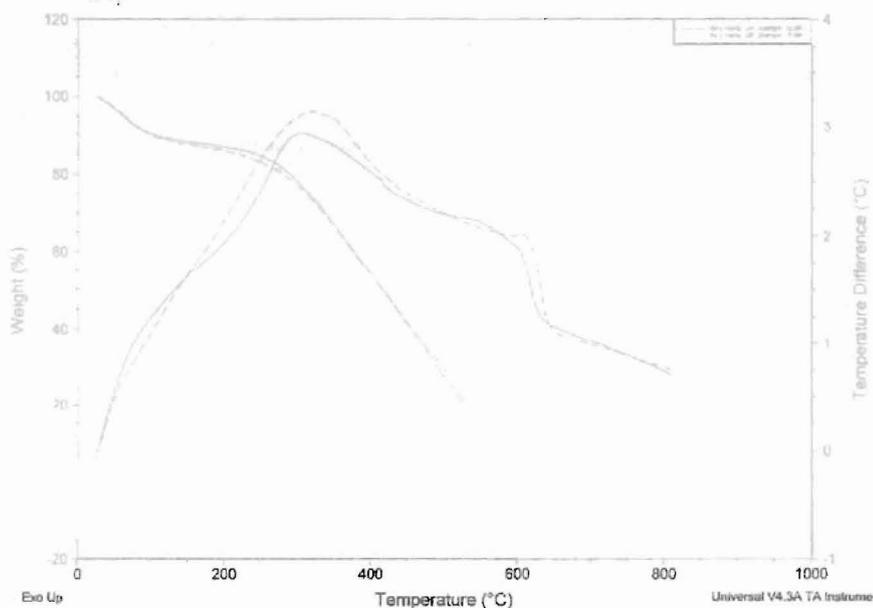
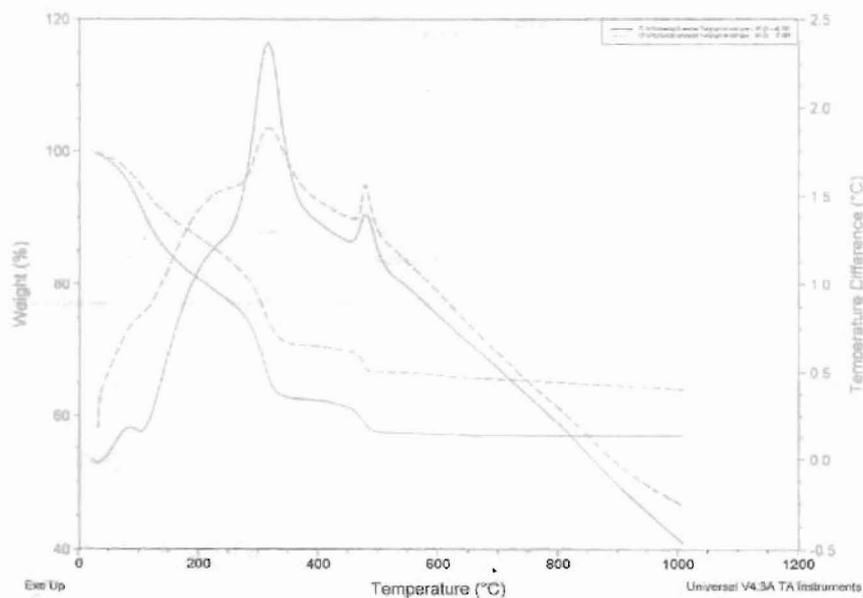
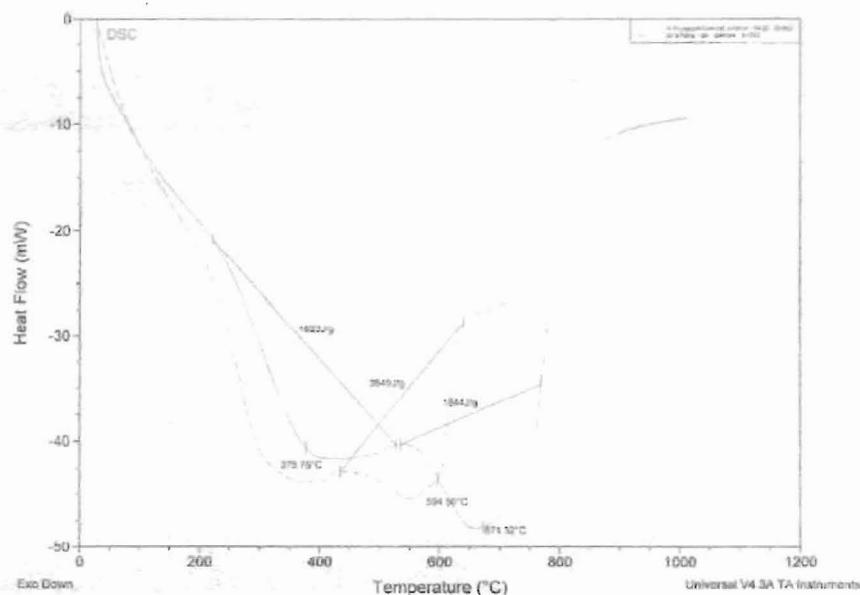


Fig. 8. TGA spectrum of PPY-Cl Prepared by using ferric chloride as oxidant, — Protonated and --- deprotonated.

Table 1

Weight loss data of PPy prepared by different oxidant and surfactant from TGA analysis

Sl.No	Weight loss and Temperature	PPy using FeCl ₃		PPy using FeCl ₃ and surfactant		PPy using (NH ₄) ₂ Cr ₂ O ₇		PPy (NH ₄) ₂ Cr ₂ O ₇ and surfactant	
1.	Temperature Tg °C	50-250	50-250	50-250	50-250	50-250	50-250	50-300	50-310
	Weight loss (%)	11.59	11.79	7.52	11.52	28.56	36.71	46.3	55.17
2.	Temperature Tg °C	250-620	250-620	250-790	250-661	250-510	250-500	300-520	310-540
	Weight loss (%)	85.61	84.38	89.28	85.08	4.52	5.69	2.48	2.2
3.	Temperature Tg °C	620-820	620-820	820-1000	661-1000	510-1000	500-1000	520-1000	530-1000
	Weight loss (%)	0.08%	0.44	1.1	1.3	2.82	0.62	1.3	2.5
4.	Residue	2.72	3.389	2.01	2.10	64.09	56.88	49.93	40.06

**Fig. 9.** TGA spectrum of PPy-CrO₄. Prepared by using ammonium dichromate as oxidant. — Protonated and --- deprotonated.**Fig. 10.** Comparison of DSC spectrum of PPy-Cl. Prepared by using ferric chloride as oxidant. — Protonated and --- deprotonated.

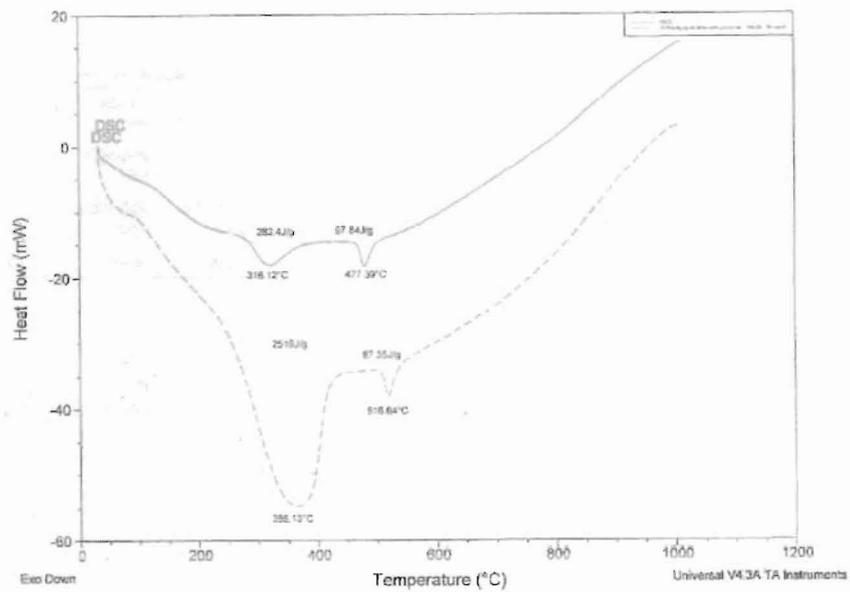


Fig. 11. Comparison of DSC spectrum of PPY-CrO₄. Prepared by using ammonium dichromate as oxidant. — Protonated and — deprotonated.

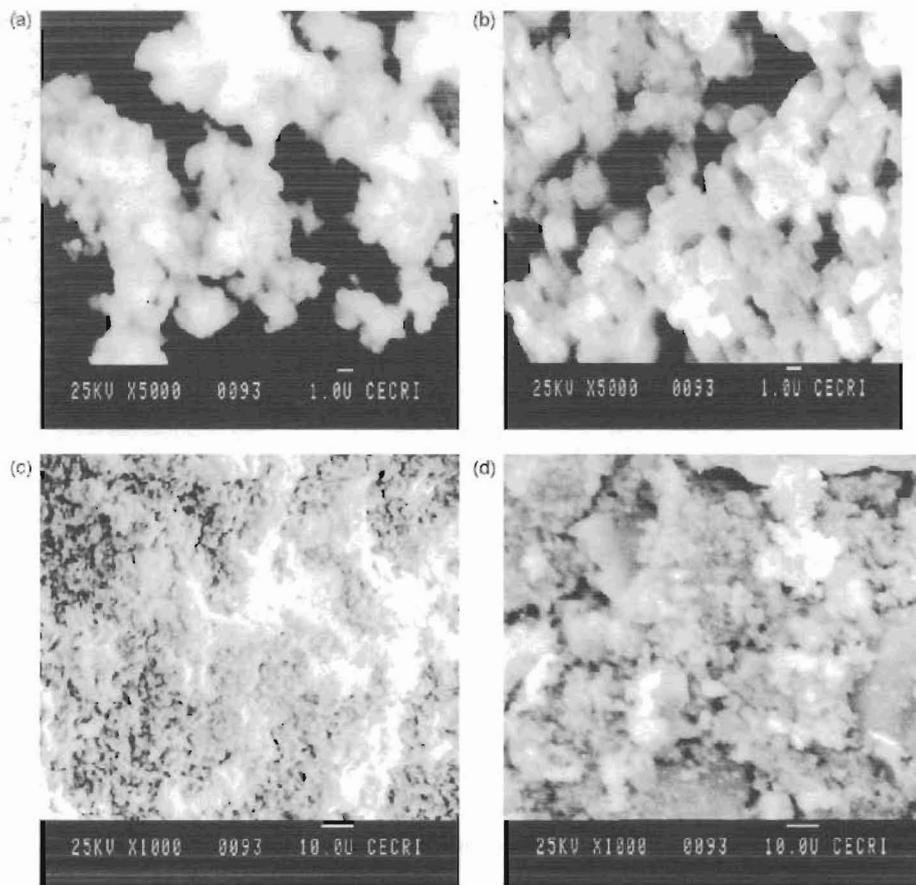


Fig. 12. SEM micrograph of (a) PPY-CI without surfactant, (b) deprotonated and PPY prepared in the presence of surfactant, (c) NaDBS, and (d) deprotonated.

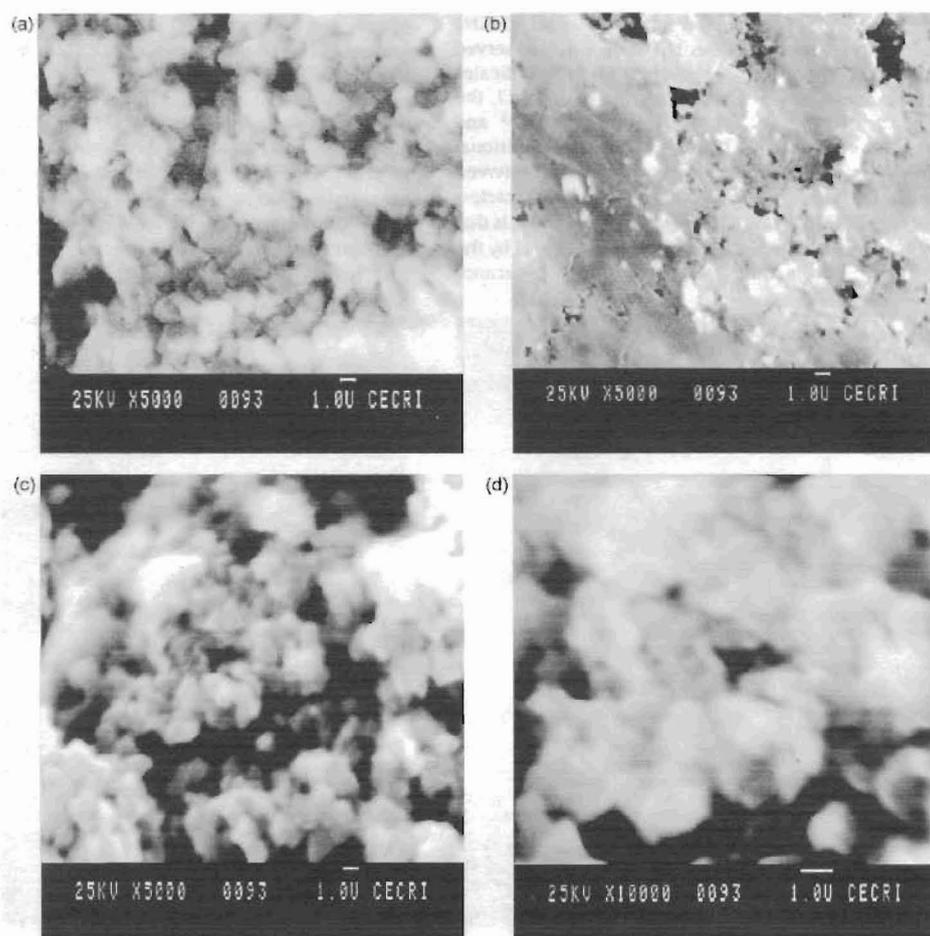


Fig. 13. SEM micrograph of (a) PPy-CrO₄, (b) deprotonated and PPy prepared in the presence of surfactant, (c) NaDBS, and (d) deprotonated.

3.2. Infrared spectroscopic study

The FTIR spectra of prepared PPy-Cl before and after treatment with 1 M ammonium hydroxide are shown in Fig. 2. The most important change after the deprotonation is the disappearance of two peaks, which is observed after treatment with ammonium hydroxide. The peaks at 1443 and 1131 cm⁻¹ are the responsible peaks of protonated nitrogen atom in the polypyrrole. This result is well correlated with the reduced conductivity of neutralized PPy-Cl. The other bands and peaks observed in both the FTIR spectra are similar with slight shifting of frequency region observed. The characteristic band in the region of 1540–1520 cm⁻¹ corresponds

to the C–C stretching vibration in the pyrrole ring. The appearance of broad band around 2000 cm⁻¹ indicates the formation of doped polypyrrole in the process [12,13]. The peaks at 1278 and 1008 cm⁻¹ denote the C–H stretching vibration in the pyrrole ring. The C–C band in the pyrrole is indicated by the peaks at 960 and 906 cm⁻¹ for the protonated and deprotonated PPy-Cl. The band is very broad and sharp for the deprotonated PPy-Cl. This implies that the out of plane-C bond formation is maximum at the peak point 906 cm⁻¹ and so this bond is stronger than the protonated PPy-Cl. Thus the deprotonated PPy-Cl has lower conductivity value than the protonated polymer. The peaks in between 768–831 and 644–672 cm⁻¹ also indicate the N–H vibration in the polymer.

Table 2

Characteristic data obtained from DSC of ppy prepared by using different oxidants and surfactants

SLNo	Characteristic points	PPy using FeCl ₃		PPy using FeCl ₃ and surfactant		PPy using (NH ₄) ₂ Cr ₂ O ₇		PPy (NH ₄) ₂ Cr ₂ O ₇ and surfactant	
1.	Glass transition temperature Tg(°C)	≈50	≈50	≈40	≈65	≈50	≈60	≈40	≈45
2.	a) Reaction-1 Starting Temp(°C)	220	250	207.3	250	262.2	243.1	250	250
	b) Reaction peak temp(°C)	304.7	345.1	375.5	351.3	316	315.4	355.1	371.31
	c) Heat of reaction ΔH (J/G)		1626	1823	1796	282.4	701.3	2519	2767
3.	a) Reaction-2 Starting temp (°C)	420	545	550	540	462.2	448.9	502.1	492.06
	b) Reaction peak temp (°C)	535.8	612.2	671.3	616	477.3	479.5	516.6	509.84
	c) Heat of reaction ΔH (J/G)	3849	1464	1844	4121	505.7	109.0	87.35	93.78

The FTIR spectra of PPy-Cl prepared with surfactant, DBSNa before and after neutralization are presented in Fig. 3. It is observed that the characteristic broad band above 2000 cm^{-1} indicates the formation of polypyrrole. Further, similar to the PPy-Cl, the characteristic peaks of PPy at 1524 , 1442 , and 1274 cm^{-1} and 1020 – 1005 cm^{-1} are also seen in these spectra. The additional broad band formed by the influence of surfactant is seen in between 1200 – 1100 cm^{-1} with the peaks at 1135 cm^{-1} . This is the characteristic peak of sulphoxide (S-O) group in the polymer [14]. This is due to the replacement of the chloride ions present in the PPy-Cl by the sulphoxide ions present in the anionic surfactant. The appearance

of peaks in between 2750 cm^{-1} to 3000 cm^{-1} indicates the presence of $-\text{CH}_2-$ chains from the surfactant gets attached within the polymer.

The comparison of IR spectra of PPy- CrO_4 , before and after treatment with ammonium hydroxide is shown in Fig. 4. The broad absorption band above 2000 cm^{-1} indicates the formation for the polymer. The other characteristic bands and peaks of PPy also observed in this spectrum. The broad band formed in between 1110 and 700 cm^{-1} with the peaks at 797 cm^{-1} indicates that the polymer formation without of plane ring formation (C-C links) in the pyrrole molecule is much higher than the polymer formed by PPy-

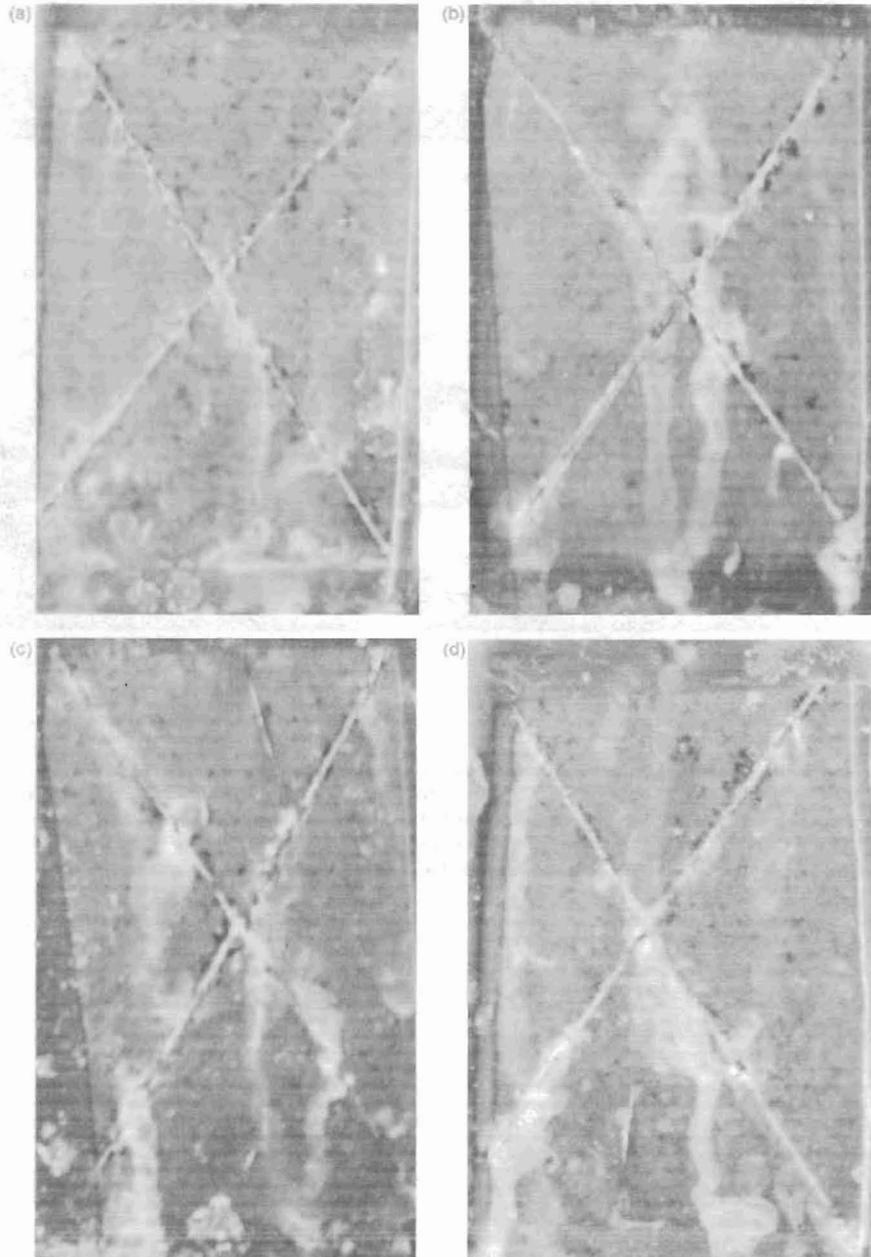


Fig. 14. The photograph of M.S. coated with epoxy-polyamide incorporated with (a) PPy-Cl, (b) deprotonated, (c) PPy-Cl with surfactant, and (d) deprotonated pigments coated specimens after 480 h exposure in salt spray test chamber.

Cl. Thus the molecular weight of the polymer formed by ammonium dichromate is much higher than that of ferric chloride oxidant. The broad band with peak at 459 cm^{-1} indicates the presence of CrO_4^{2-} ions in the polymer. This band is not affected during the deprotonation process and the conductivity of the polymer is not affected by the neutralization.

The FTIR spectra of PPy- CrO_4 prepared in the presence of anionic surfactant before and after treatment with ammonium hydroxide are given in Fig. 5. It is seen from the spectra that both the groups are identical. There is no disappearance of any peaks after neutralization process. The presence of chromate ions is also not affected

by this deprotonation. The presence of this group is indicated by the appearance of peaks at 1135 cm^{-1} and also in between 1100 and 1200 cm^{-1} . This is further implies that the CrO_4^{2-} ions are not in the free state but attached with the pyrrole group with weak Π bonds. The other characteristic polypyrrole band and peaks are also observed in this spectral study.

3.3. X-ray diffraction

Figure 6 shows that the XRD spectrum of PPy-Cl observed a broad peak between 20 and 40 of 2θ value indicates that the PPy-

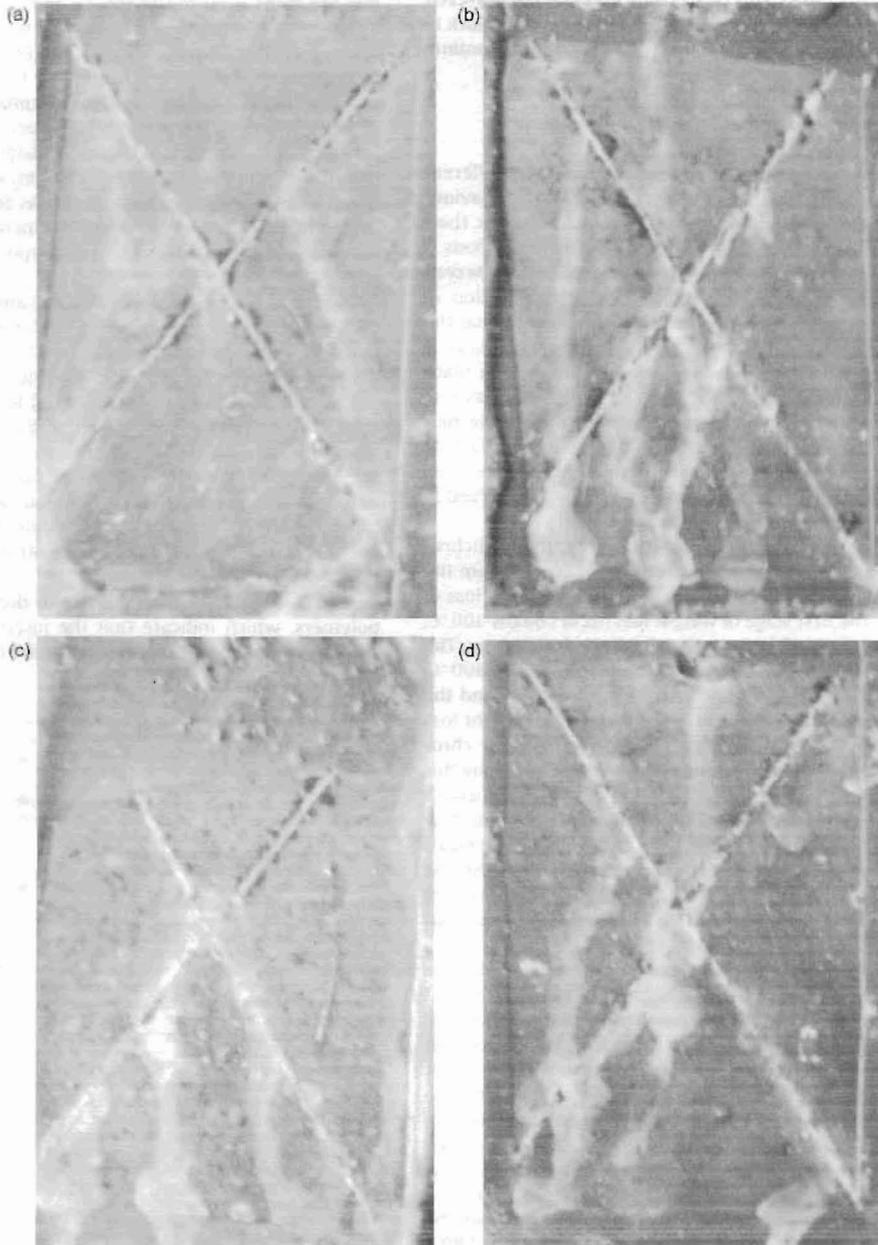


Fig. 15. The photograph of M.S. coated with epoxy-polyamide incorporated with (a) PPy- CrO_4 , (b) deprotonated, (c) PPy- CrO_4 surfactant, and (d) deprotonated pigment coated specimens after 480 h exposure in salt spray test chamber.

Cl is in amorphous form with the particle size below 100 nm. But one sharp intensity peak is observed at 2θ value, which corresponds to the crystalline structure of Fe_2O_3 . This is also indicated by the AAS study, which shows the presence of iron oxide in the PPY-Cl powder. Thus the XRD study indicates the presence of amorphous PPY-Cl and the crystalline iron oxide powder in this polymer. The deprotonated PPY-Cl shows that only the broad peak is observed similar to the protonated PPY-Cl. No sharp peak of iron oxide is observed. This may be due to the iron oxide reacted with the surfactant and washed away from the PPY-Cl.

Figure 7 shows that the XRD spectrum of PPY- CrO_4 show that there are no intensity peaks. This clearly indicates that the PPY- CrO_4 is in amorphous state. Further the PPY- CrO_4 has greenish black in colour, which indicates the incorporation of amorphous chromium oxide, CrO_3 with the polymer [15].

3.4. Thermogravimetric analysis

The thermal stability of the polypyrrole prepared by different methods was studied by TGA. Fig. 8 presents the thermal behaviour of PPY-Cl before and after deprotonation. The characteristic thermal performance of polypyrrole prepared by different methods is given in Table 1. The initial weight loss of below 11% is observed at the temperature below 100°C is due to the evaporation of water molecules present in the polymer. It is well known that the polypyrrole is hygroscopic in nature and so the observed water is eliminated below 100°C . But the main mass loss is taking place above 250°C and steadily decreased up to 620°C . The mass loss of 85% is observed for the PPY prepared by ferric chloride oxidant. No significant change is observed in presence of surfactant and the neutralized polypyrrole as far as thermal behaviour is concerned. Thereafter no appreciable change in weight is observed in the polymer with a residue of 2–3% after 1000°C .

Fig. 9 shows the performance of PPY- CrO_4 prepared by dichromate oxidant and also with anionic surfactant. It is seen from the figure that the weight loss is in three stages with the mass loss of 35% after 500°C . The first stage of weight loss occurs below 100°C , which indicates the loss of water molecules from the polymer. The second phase of weight loss is observed in between 175 and 300°C . This is due to the breaking of bond affinity with the PPY and the Chromate ions in the molecules. In the third stage the weight loss is due to the formation of stable chromium oxide from the chromate molecules and so the appearance of the PPY prepared by this method has slightly greenish colour than the other PPY. So unlike the PPY-Cl, the residue after 1000°C is 64.09% and 56.88% for PPY- CrO_4 prepared by both the methods. This is due to the presence of chromate in the form of amorphous chromium oxide at the end of this thermal analysis, but the actual percentage of chromium present in the residue is 34% and 30.18%. These results are comparable with that of elemental analysis as reported earlier.

The DTA analysis indicates that two exothermic peaks are observed in all the PPY. These two peaks are very broad for PPY-Cl powder and very sharp for PPY- CrO_4 powder. The first exothermic reaction indicates that the chloride ions present in the polymer has been liberated from the molecular structure of polypyrrole. In the second stage the PPY polymer itself broke into fragmentation with the liberation of exothermic reaction energy. Thus we have observed broad peaks in the case of PPY-Cl and PPY-Cl surfactant doped polymers. The sharp peaks in association with PPY- CrO_4 powder is due to the liberation of chromate ion take place with the association of PPY. The liberated chromium is not leaving from the structure and so the weight loss is in minimum in the case of PPY- CrO_4 polymer. The second exothermic reaction indicates that the PPY-Cl is disintegrated and form very low residue of carbon as 2–3%.

But in PPY- CrO_4 the small sharp second exothermic reaction peak indicates that the associated PPY polymers is disintegrated with the residue of chromium particles or chromate pyrroles and remain as 50–65%. There is not much difference in thermal behaviour of deprotonate PPY- CrO_4 .

3.5. DSC analysis

Typical DSC spectra of PPY-Cl and surfactant doped PPY-Cl are given in Fig. 10. The characteristic reaction temperature and enthalpy changes of PPY-Cl, PPY- CrO_4 with surfactants are given in Table 2. It is observed from the figure that two broad exothermic reactions occurred in PPY-Cl and surfactant doped polymer. The second exothermic reaction is in higher order for the surfactant doped PPY-Cl polymer than the PPY-Cl polymer. This is due to the influence of the surfactant. The heat of the second exothermic reaction is 1464 J/g for PPY-Cl deprotonated and 4121 J/g for PPY-Cl surfactant deprotonated polymer. This is explained by the breaking of the surfactant bonded linkage required higher energy than the polymer without these linkages. Thus the polypyrrole prepared in the presence of surfactants has good stability towards the deprotonation with weak bases. This increased stability by deprotonation and thermal stability is also reported by Aldissi and Armes [16].

A typical DSC spectra of PPY- CrO_4 and surfactant doped PPY- CrO_4 polymers are shown in Fig. 11. It is observed from the figure that two exothermic sharp peaks with low level of energy emission are observed for PPY- CrO_4 polymer. But the first exothermic reaction with higher energy (2519 J/g) level emission followed by a small sharp peak with low energy (87.35 J/g) emission has been reported. The data for this figure and the deprotonated polymers are also given in Table 2. From the table it is observed that the deprotonated polymers are in similar behaviour with the protonated polymer. Here also the explanation for requiring higher energy for the break of sulphoxide strong bond with the stable polymer.

The T_g values are more or less in the lower range for all the polymers, which indicate that the intermolecular interaction of individual molecules is controlled by the dipolar connectivity [17].

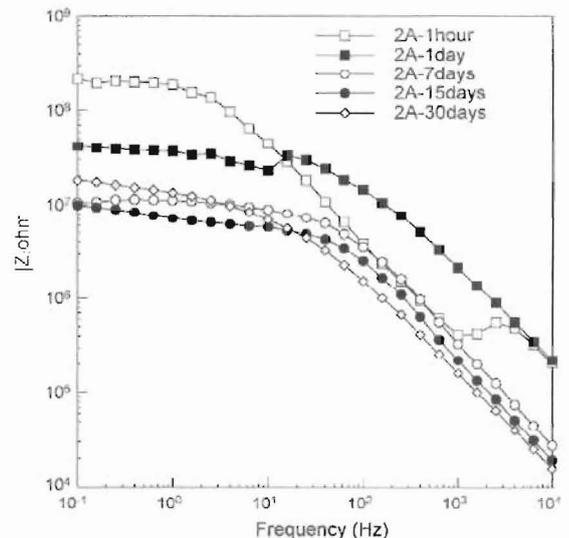


Fig. 16. Bode plots of epoxy-polyamide Ply-Cl-incorporated coating on mild steel in 3% NaCl solution for different durations.

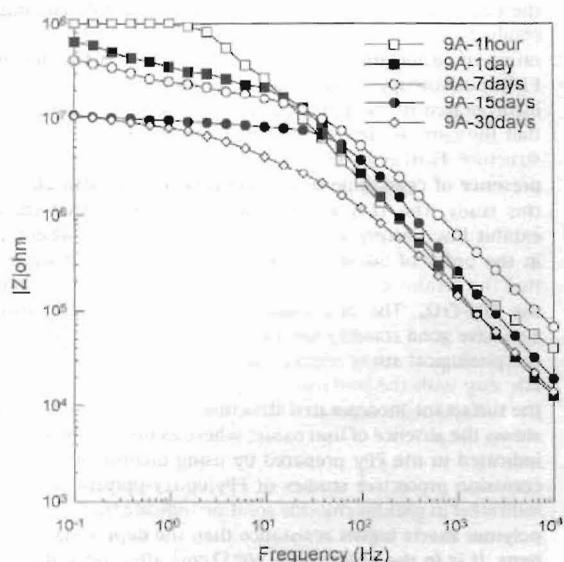


Fig. 17. Bode plots of epoxy-polyamide PPy-CrO₄-incorporated coating on mild steel in 3% NaCl solution for different durations.

3.6. SEM studies

Fig. 12 shows comparison of the morphology of PPy-Cl powder PPy prepared in the presence of the surfactant NaDBS and the deprotonated samples. The SEM study reveals that the globular structured PPy-Cl is highly porous, whereas the PPy-NaDBS particles are more compact than deprotonated PPy-Cl indicate that the globular structure is dissipated and form crystals like tubular morphology with porous structures [18,19].

Table 3

Resistance & capacitance values of PPy incorporated epoxy-polyamide coatings on M.S substrate in 3% NaCl solution

System	Duration (Hours)	Resistance (Ohm.cm ²)		Capacitance (F.cm ²)	
		Protonated	Deprotonated	Protonated	Deprotonated
Epoxy polyamide	1	1.8429 × 10 ⁷		1.2849 × 10 ⁻¹¹	
	24	7.478 × 10 ⁶		8.9697 × 10 ⁻¹¹	
	168	2.355 × 10 ⁶		9.6308 × 10 ⁻¹⁰	
	360	3.0058 × 10 ⁶		1.0445 × 10 ⁻¹⁰	
	720	3.2157 × 10 ⁶		7.8728 × 10 ⁻⁹	
PPy-chloride	1	1.9242 × 10 ⁸	1.2228 × 10 ⁸	6.5398 × 10 ⁻¹⁰	5.4965 × 10 ⁻¹⁰
	24	4.3448 × 10 ⁷	3.6278 × 10 ⁷	1.0822 × 10 ⁻¹⁰	6.1799 × 10 ⁻¹⁰
	168	1.0031 × 10 ⁷	7.6380 × 10 ⁶	3.5242 × 10 ⁻¹⁰	5.3442 × 10 ⁻⁹
	360	5.7925 × 10 ⁶	2.3395 × 10 ⁶	5.4546 × 10 ⁻¹⁰	2.6956 × 10 ⁻⁹
	720	4.8396 × 10 ⁶	1.7318 × 10 ⁶	1.9451 × 10 ⁻¹⁰	3.5704 × 10 ⁻⁸
PPy chloride & surfactant	1	4.7956 × 10 ⁷	5.1231 × 10 ⁶	2.0661 × 10 ⁻¹⁰	2.0445 × 10 ⁻¹⁰
	24	2.4860 × 10 ⁶	4.4208 × 10 ⁶	1.5313 × 10 ⁻¹⁰	4.3168 × 10 ⁻⁹
	168	5.4705 × 10 ⁶	4.3125 × 10 ⁶	3.2076 × 10 ⁻¹⁰	3.2076 × 10 ⁻⁹
	360	4.0956 × 10 ⁶	3.5322 × 10 ⁶	2.2471 × 10 ⁻¹⁰	5.8226 × 10 ⁻⁹
	720	1.5739 × 10 ⁵	3.9833 × 10 ⁵	1.4257 × 10 ⁻¹⁰	4.9383 × 10 ⁻⁹
PPy -chromate	1	7.8234 × 10 ⁷	2.3847 × 10 ⁶	1.4257 × 10 ⁻⁹	1.0716 × 10 ⁻¹⁰
	24	2.5276 × 10 ⁷	2.2901 × 10 ⁶	3.2440 × 10 ⁻¹⁰	1.0880 × 10 ⁻¹⁰
	168	1.9485 × 10 ⁷	1.0770 × 10 ⁶	6.2398 × 10 ⁻¹⁰	1.8802 × 10 ⁻⁹
	360	8.0548 × 10 ⁶	8.2738 × 10 ⁵	3.6859 × 10 ⁻¹⁰	8.0619 × 10 ⁻⁸
	720	7.8010 × 10 ⁶	4.2715 × 10 ⁵	3.0650 × 10 ⁻⁹	2.7915 × 10 ⁻⁸
PPy-chromate & surfactant	1	2.1654 × 10 ⁷	9.5010 × 10 ⁷	6.8040 × 10 ⁻¹⁰	1.2722 × 10 ⁻¹¹
	24	3.2711 × 10 ⁷	3.7984 × 10 ⁷	8.0008 × 10 ⁻¹¹	1.1588 × 10 ⁻¹¹
	168	1.1510 × 10 ⁷	4.8085 × 10 ⁶	1.2651 × 10 ⁻¹⁰	7.8653 × 10 ⁻¹⁰
	360	6.4860 × 10 ⁶	7.5322 × 10 ⁵	1.2395 × 10 ⁻⁸	1.2665 × 10 ⁻¹⁰
	720	1.2112 × 10 ⁶	4.1235 × 10 ⁵	9.0831 × 10 ⁻⁷	1.1402 × 10 ⁻¹⁰

The SEM micrographs of PPy-CrO₄ and PPy-CrO₄-NaDBS are given in Fig. 13. It is seen from this photographs that the globular structured poly pyrrole are significantly smaller than the PPy-Cl. Similar to the PPy-NaDBS, the anionic surfactant play a significant role to influence the morphology of PPy-CrO₄ polymer with the formation of clusters. The deprotonated PPy-CrO₄ shows that the formation of flattened globular granules without any space between them (Fig. 13b) and the particle size of this polymer is in nanometers [20].

3.7. Corrosion resistance studies

3.7.1. Accelerated salt spray chamber experiment

There is no noticeable change in gloss or texture observed up to 400 h of exposure and so the photographs were taken after 480 h of duration. Photographs in Fig. 14a–d give the performance of PPy-Cl, deprotonated with surfactant and deprotonated-polymer-incorporated epoxy-polyamide coatings on steel surface after the exposure period of 480 h. It is observed from the figures that the PPy-Cl gives lesser corrosion products along the scratched area than the other specimens. Further all the four photographs express the view that the corrosion is initiated from the scratches only. The propagation of corrosion from the scratches is observed on the surface of both deprotonated PPy-incorporated coatings. This result indicates that the deprotonated PPy has lower corrosion resistant properties than the protonated PPy-incorporated coatings. This behaviour may be due to the elimination of conductive ions from the PPy-Cl conducting polymer.

Similarly the photographs in Fig. 15a–d show the performance of PPy-CrO₄, PPy-CrO₄ deprotonated, PPy-CrO₄ with surfactant and deprotonated-polymer-incorporated epoxy-polyamide coatings on mild steel substrate after 480 h of exposure in the salt spray chamber. The protective properties of these coatings are also similar to the PPy-Cl-polymer-incorporated coating systems. Corrosion products are seen along the scratched area only. The entire surface of the specimen is not affected by corrosion. The

control panel of epoxy-polyamide coated panels also have the similar performance with the formation of rust is seen on the scratched area. Thus this salt spray experiment indicates that these PPy-polymer-incorporated coatings protect the surface for longer duration provided the polymer is in the protonated form. Considering the best performance of this conducting polymer, the optimum level of this polymer for protective coating up to the level of 10 wt.% has been studied through the salt spray method by Riaz et al. [21] and found that the 6 wt.% is suitable for smart composite coating system.

3.7.2. Electrochemical ac impedance analysis

Figs. 16 and 17 show the Bode's impedance plots of PPy-Cl and PPy-CrO₄-incorporated epoxy-polyamide coated steels in 0.5 M NaCl solution for different durations. The resistance and capacitance values of these coating systems and the deprotonated systems are presented in Table 3. It is seen from these plots that the resistance values offered by these PPy-incorporated polymer coatings have decreased with duration. The impedance plot shows that initially the coatings are in capacitive nature with very high resistance in the order of $10^7 \Omega \text{ cm}^2$. This resistance is high ($1.98 \times 10^8 \Omega \text{ cm}^2$) for the PPy-Cl-incorporated coating, when compared with that of epoxy-polyamide control coating ($1.8 \times 10^7 \text{ cm}^2$). The plots are then inclined and shifted towards the low resistance region. This indicates that the degradation of the coating begins after 15 days with water penetration. The capacitance of the control system has changed from $1.044 \times 10^{-10} \text{ F cm}^{-2}$ (15 days exposure) to $7.87 \times 10^{-9} \text{ F cm}^{-2}$ for 30 days study. But the capacitances of the PPy-Cl-incorporated coatings are in very low range ($1.94 \times 10^{-10} \text{ F cm}^{-2}$) even after 30 days of exposure. This shows that the PPy-Cl-incorporated coatings are not allowing the diffusion of electrolyte into it. The PPy-CrO₄-incorporated coatings also exerted very high resistance of $7.8 \times 10^6 \Omega \text{ cm}^2$ for 30 days of this study and so these coatings also protect the surface for longer duration than the control system. The surfactant-doped PPy-incorporated coatings give high resistance nearly equal to the PPy-Cl- and PPy-CrO₄-incorporated systems. From the table it is seen that the deprotonated PPy-incorporated coatings have low resistance than the protonated PPy-incorporated coatings after 30 days of this study. All the deprotonated PPy-incorporated coatings exerted the resistance of $10^3 \Omega \text{ cm}^2$ after 30 days of duration. This result indicates that the protonated PPy protects the surface for longer duration than the control as well as deprotonated PPy system. This is due to the action of PPy, which is act as conductor even in presence of small quantity in the coating system.

4. Conclusion

Stable conducting polypyrrole was prepared by chemical polymerization using ferric chloride and ammonium dichromate as oxidant. Similarly highly conducting PPy was prepared by using

the same oxidant with anionic surfactant, NaDBS. The improved conductivity of the polymers was due to the effective incorporation of surfactant anions into the polymer as the dopant. The FTIR spectroscopy proved that the sulphoxide radical is effectively incorporated in the PPy structure. The XRD technique indicated that the particle size is in the nanometer range with amorphous structure. Further in addition to the amorphous PPy-Cl, PPy-CrO₄ presence of crystalline iron oxide powders are also observed by this study. The TGA and DSC analysis showed that the PPy-Cl exhibit low percentage of residue after 1000 °C, where as it is in the order of 50–65% for PPy-CrO₄. Thus this analysis shows that the residue contains amorphous chromium oxide along with the PPy-CrO₄. The deprotonated PPy by ammonium hydroxide also have good stability towards thermogravimetric analysis. SEM morphological study shows that the PPy arranged in a systematic way with the presence of sulphoxide dopant is identified in the surfactant-incorporated structure. The deprotonated structure shows the absence of iron oxide; where as the presence of Cr₂O₃ is indicated in the PPy prepared by using dichromate oxidant. The corrosion protective studies of PPy/epoxy-polyamide coating on mild steel in sodium chloride solution indicate that the protonated polymer exerts higher resistance than the deprotonated PPy systems. It is in the order of $5 \times 10^6 \Omega \text{ cm}^2$ after 1-month duration. This study concludes that the PPy obtained by dichromate oxidized method can be used as a corrosion resistance protective pigment for epoxy-polyamide system.

References

- [1] D.W. DeBerry, *J. Electrochem. Soc.* 131 (1984) C302.
- [2] D.W. DeBerry, A. Viehbeck, *Corrosion* 44 (1988) 299.
- [3] C.A. Ferreira, S. Aeyach, A. Couloud, P.C. Lacaze, *J. Appl. Electrochem.* 29 (1999) 259.
- [4] P.A. Kilmartin, L. Trier, G.A. Wright, *Synth. Met.* 131 (2002) 99.
- [5] M. Kraljic, Z. Mandic, L.J. Duic, *Corros. Sci.* 45 (2003) 181.
- [6] S.P. Armes, *Synth. Met.* 20 (1987) 365.
- [7] J. Quyang, Y. Li, *Polymer* 38 (1997) 3997.
- [8] M. Ormstova, M. Trchova, J. Kovarova, J. Stejskal, *Synth. Met.* 138 (2003) 447–455.
- [9] Y. Kudoh, *Synth. Met.* 79 (1996) 17–22.
- [10] R.L. Twite, G.P. Bierwagen, *Prog. Org. Coat.* 33 (1998) 91.
- [11] J.R. Venison, *Structural Steel Painting: The International Decorative Paints*, Allen Devices and Co., Ltd., Bristol, England, 1973, pp. 5–6.
- [12] Z. Ping, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3036.
- [13] P.A. Christensen, A. Hammet, *Electrochim. Acta* 36 (1991) 1263.
- [14] R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 2004, 71–143.
- [15] Kirk, *Other-Encyclopedia of Chemical Technology*, Kirk, Othmer, Vol. 6, John Wiley & Sons, New York, 1993, p. 293.
- [16] M. Aldissi, S.P. Armes, *Prog. Org. Coat.* 19 (1991) 21.
- [17] A.M. Atta, N.O. Shaker, N.E. Maysour, *Prog. Org. Coat.* 56 (2006) 100–110.
- [18] M. Ormstova, J. Pionteck, M. Trchova, *Synth. Met.* 135–136 (2003) 437–438.
- [19] S.S. Pandey, W. Takashima, M. Fuchiwaki, K. Kanato, *Synth. Met.* 135–136 (2003) 59–60.
- [20] F.J. Rodriguez, L.A. Gracia de la Rosa, A. Alatorre, J. Ibenez, L. Godinez, S. Gutierrez, P. Herrasti, *Prog. Org. Coat.* (2007).
- [21] U. Riaz, S.M. Ashraf, S. Ahmed, *Prog. Org. Coat.* 59 (2007) 138–145.