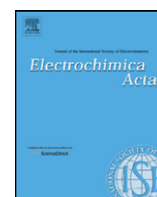




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New polyaniline(PAni)-polyelectrolyte (PDDMAC) composites: Synthesis and applications

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ABSTRACT

Conducting and electroactive polymer blends of polyaniline (PAni) with polyelectrolyte, poly(diallyldimethylammoniumchloride) (PDDMAC) have been synthesized by an in situ polymerization method and the resulting composites have been characterized by FT-IR, UV-Vis, XRD, AFM and electrochemical techniques. The blends are conducting and electroactive with even lower loadings of PAni and can be cast as films. The conductivity of the cast films containing 0.04–1.5 wt% PAni ranged from 4.5×10^{-6} to 42×10^{-6} S/cm. Some of the composites are tested for their corrosion inhibition property for pure iron in 1 M HCl solutions and were found to be active inhibitors.

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1. Introduction

Polyaniline (PAni) has become a well-known conducting polymer material in recent times due to its unique features such as variable electronic conductivity, chemical/electrochemical redox reversibility, corrosion protector/inhibitor, rechargeable battery material, EMI shielder, electrochromism [1–8]. The most important milestone in the chronological history of conducting polyaniline is the success of making the intractable polymer into fibers and films [9]. The main strategies for achieving processability for conducting polyaniline are (i) synthesizing functionalized organic sulphonic acids for doping [10–16], (ii) to introduce substituent groups in the ring (polymers such as alkyl polyanilines) [17], alkoxy polyanilines [18], sulfonic acid ring-substituted polyanilines (SPAN) [19,20] and (iii) blending or compositing with other conventional processable polymers such as PVA, PMMA, PEO [21,22] with more emphasis on PAni-PVA colloidal composites [23–31]. However, most recent studies in literature show that there are two more strategies for attaining processability for polyaniline have become important [32–35], namely, copolymerization and nanotechnology. Li et al. have extensively studied [5,7,32,33] on copolymerization of aniline, chloroaniline, sulfophenylenediamine, *o*-phenylenediamine which generally resulted in processable nano/microparticles with film formability and tunable electronic conductivity. More significantly, they have shown that the nanopar-

ticles of *p*(aniline-co-sulphophenylenediamine) show enhanced solubility, interesting solvatochromism, and widely adjustable electron conductivity moving across nine orders of magnitudes from 10^{-9} to 10^0 S/cm. Further the particles exhibited high adsorbance of toxic metal ions such as Hg^{2+} and Pb^{2+} showing a great promise for recovery/or purification of water.

Conducting polyaniline blends are technologically important materials for which the threshold volume fraction for onset of electrical conductivity can be reduced to as low as 16% compared to conventional percolation values [36,37]. The films or blends formed by conducting polyaniline (PAni) as the guest and an insulating polymer host matrix provide a novel class of conducting materials, which offer attractive mechanical strength and processing abilities imparted by the insulating polymer matrix with tunable levels of electrical conductivity. These blends are normally obtained by in situ polymerization of aniline in the presence of the insulating polymer or blending of polyaniline with insulating host polymer [36,38]. Solution-cast blends employing PAni-DBSA have been investigated with few polymer matrices, such as styrene-butadiene-styrene triblock copolymer (SBS) [39], polystyrene [40,41], sulfonated polycarbonate [42].

Polyelectrolytes are widely used in industrial applications as dispersants in aqueous media, flocculating agents to coagulate slurries and industrial wastes, for sizing in textile and paper processing, and as additives for drilling mud/soil to prevent abrasive damage. More recently, they have been useful in molecular self-assembly techniques for thin film deposition of electrically conducting polymers [43], conjugated polymers for light emitting devices [44], nanoparticles [45] and in second order nonlinear optical (NLO)

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devices [46]. In this article, for the first time to our knowledge, a new series of composites have been synthesized from aniline and poly(diallyldimethylammoniumchloride) (PDDMAC) through an in situ polymerization reaction. Results on these experiments with electrochemical, conductivity and film formation properties of the resulting composites are presented and discussed. The possible application of this material as corrosion inhibitor is also explored.

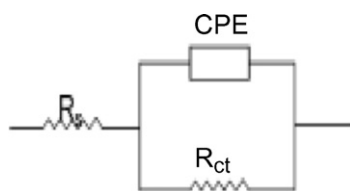
2. Experimental

2.1. Methods and materials

PDDMAC (35 wt% in water, average $M_w < 100,000$) is purchased from Aldrich Chemical Company. All other chemicals (C.D.H Chemicals, India) are analytical grade and used as received. The SEM measurements were performed on a Hitachi-3000H microscope. X-ray diffraction patterns (XRD) were obtained with PANalytical MPD diffractometer using $\text{Cu K}\alpha$ radiation. FT-IR spectra of KBr powder-pressed pellets were recorded on a model no. Paragon-500 from PerkinElmer spectrometer. Conductivity of the samples was measured by four-probe method using KEITHLEY nanovoltmeter after pressing the samples into 1 cm diameter, 1.5 mm thick pellets under 3 ton pressure. TGA experiments were performed with TA instruments Inc., on model SDT Q600 by heating under air at $20^\circ\text{C}/\text{min}$.

2.2. Electrochemical studies

Cyclic voltammetry was performed on AUTOLAB 302 electrochemical system using three electrode assembly consisting of a platinum foil ($2\text{ mm} \times 2.5\text{ mm}$) working electrode, a platinum wire auxiliary electrode and a S.C.E as reference electrode. Solatron Electrochemical Analyzer (Model 1287) was used for Impedance and Tafel polarization measurements. Experiments were made using a conventional three electrode cell assembly. The working electrode was a pure iron (5 mm diameter rod embedded in Teflon rod of 12 mm diameter, Johnson Matthey Ltd., UK) and a rectangular platinum foil of $2\text{ mm} \times 2.5\text{ mm}$ was used as counter electrode and saturated calomel electrode as reference electrode. The polarization was carried out using a Corrware software from a cathodic potential of -0.2 V to an anodic potential of $+0.2\text{ V}$ with respect to the corrosion potential at a sweep rate of 1 mV/s . The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers, washed with distilled water and degreased with trichloroethylene. The solutions were deaerated by nitrogen gas for 10 min before the experiments. Experiments were conducted employing 10–200 ppm of the composites taken from a concentrated aqueous stock solution. The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The impedance data were analysed using the equivalent circuit (shown below) since most of the curves in Nyquist plots show a depressed semicircle.



2.3. Synthesis of PDDMAC-PAni composites

A typical procedure to prepare 10% PDDMAC-PAni composite is as follows. To a 89 ml of 1 M HCl solution were added 10 ml of

PDDMAC solution and 1 ml (0.011 mol) of aniline to make a 100 ml solution. The reaction mixture was oxidized with 3.3 g (0.014 mol) of ammonium peroxydisulphate (APDS) in 10 ml water. The reaction was stirred for 4–6 h and the resulting green precipitate was filtered and washed with 50–70 ml of distilled water to remove impurities. To study the film formation property of the formed composites, nearly half portion of the reaction mixture (after completion of the reaction time 4 h) was taken in a flat dish and heated to 50°C in a vacuum oven until a film is formed.

The percentage of the PAni in the composite was estimated spectrophotometrically, similar to the procedure known in literature [47–49], by monitoring the UV–Vis band at 390–410 nm exhibited by PAni in the composites. For this purpose, first, the optical absorption of the composites was determined after dissolving weighed samples in distilled water. The concentration of PAni in dispersion form was calculated as $c(\text{g}/\text{cm}^3) = Ad/\epsilon l$, where A is the absorbance at the absorption maximum close to 400 nm, d is the dilution before the measurement, ϵ is the absorption coefficient of PAni [48] ($= 31\,500 \pm 1700\text{ cm}^2/\text{g}$ (emeraldine semihydrochloride form in 1 M hydrochloric acid at the wavelength 400 nm), and l ($= 1\text{ cm}$) is the thickness of the cell. The corresponding molar concentration was evaluated as $C = 10^3 c/109$, assuming that emeraldine semihydrochloride contains one molecule of hydrochloric acid per two nitrogen atoms in PAni chain [49]. The cyclic voltammetric behavior of the composites was examined for thin films coated on Pt foil ($2\text{ mm} \times 2.5\text{ mm}$) using paste obtained from dissolving the composite in *m*-cresol.

3. Results and discussion

The polymerization reaction of aniline in presence of PDDMAC is smooth, straightforward similar to aniline polymerization. It is observed that the filtration of the product is little cumbersome due to the viscous nature and it is very difficult to take out the last traces of moisture from the products. The synthesized composites are designated as $x\%$ PDDMAC-PAni, where x is the volume % of PDDMAC in the 100 ml reaction mixture. Table 1 shows the list of composites prepared along with the percentages of PDDMAC and PAni in the composite. It is found that the wt% of PAni in the composite increases with increase of volume fraction of PDDMAC in the feed while the overall yield of the composite gradually decreases (Fig. 1). Thus PAni percentage increases from 0.041% to 1.50% with increase of PDDMAC percentage from 1% to 25%. Though the insulating polymer PDDMAC is present in high weight ratios (ca. 99.5%), all the blends are electroactive and conducting. The higher concentration of PDDMAC in the composite suggests that the PAni formed a highly encapsulated network with PDDMAC. The composition of each constituent is estimated spectrophotometrically by recording absorbance of the band between 390 and 410 nm by using equations described in experimental section [47–49]. The film formation property of the composites was checked by taking a portion of the reaction mixture in a flat dish and drying at 50°C in vacuum oven. Composite with 1% PDDMAC-PAni did not give any film while 10%

Table 1
Yield and the percentages of PAni and PDDMAC in the composites

Composite ^a	Yield of the composite (g)	Percentage of components	
		PDDMAC (%)	Pani (%)
1% PDDMAC-Pani	2.020	99.959	0.041
5% PDDMAC-Pani	1.750	99.915	0.085
10% PDDMAC-Pani	1.255	99.502	0.498
15% PDDMAC-Pani	1.122	98.950	1.050
25% PDDMAC-Pani	0.985	98.478	1.521

^a Feed contains 1 ml aniline, x ml PDDMAC in $((100 - (1 + x))\text{ ml}$ of 1 M HCl solution.

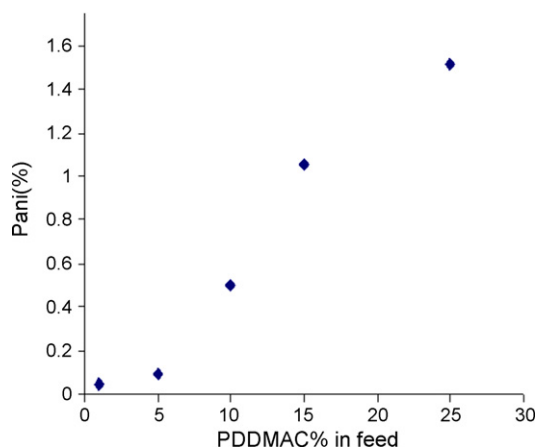


Fig. 1. Graph showing percentage of PANi incorporated into the composites with various amounts of PDDMAC in the reaction mixture.

PDDMAC-PAni composite gave a poor quality film. Only the composites with 15% and above PDDMAC fractions in the feed gave good quality, free standing films.

The composites are characterized by FT-IR spectra (Fig. 2). The data on the main bands observed in the FT-IR spectra of the composites recorded in the region of 4000–400 cm^{-1} are given in Table 2 with their possible assignments. The band at 794–804 cm^{-1} , indicate that there is a head to tail coupling in the polymers and is assigned to C–H_{op}. This band is shifted to 802–804 cm^{-1} for the composites compared to the virgin (794.7 cm^{-1}). Pure PANi showed a band at 1140 cm^{-1} assigned to charge delocalization on the polymer. Band at 1480 cm^{-1} is the characteristic band assigned

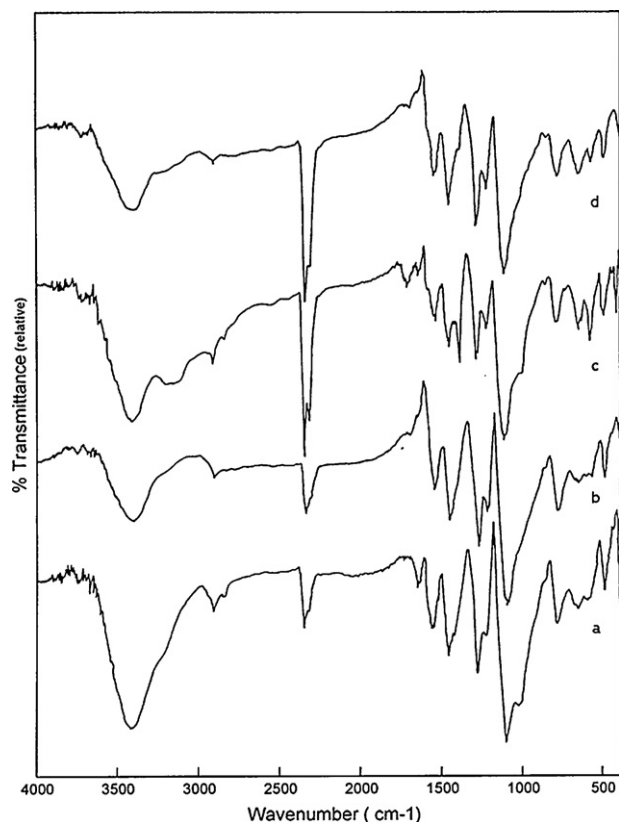


Fig. 2. FT-IR spectra of the composites recorded as KBr pellets: (a) pure PANi–HCl, (b) 1% PDDMAC–PAni, (c) 15% PDDMAC–PAni and (d) 25% PDDMAC–PAni.

Table 2
FT-IR data for PDDMAC-PAni composites

Composite	Frequency (cm^{-1})					
	C–H _{op}	C–N	N–B–N	N–Q–N	CH _(ar)	N–H
PAni–HCl	794.7	1240	1470.7	1116, 1574	2925	3430
10% PDDMAC–PAni	801.5	1242	1472.2	1121, 1560	2925	3431
15% PDDMAC–PAni	802.7	1243	1473.8	1128, 1560	2920	3424
25% PDDMAC–PAni	802.4	1243	1474.2	1135, 1567	2921	3410

Table 3
UV-VIS Absorbance Maxima for PDDMAC-PAni composites in water

Composite	Absorbance maxima (nm)
1% PDDMAC–PAni	435, 870
5% PDDMAC–PAni	430, 917
10% PDDMAC–PAni	421, 858
15% PDDMAC–PAni	398, 875
25% PDDMAC–PAni	405, 865

to N–B–N and the band at 1660 cm^{-1} is due to nitrogen quinoid (N=Q=N) (where B=benzenoid, Q=quinoid) for the pure polymer. The intensity of N=Q=N bands are found to be decreased in the composite materials. The C–N stretching vibrations are observed between 1243 and 1235 cm^{-1} [50–53]. The N–H band is observed as a broad band centered at 3438 cm^{-1} . The aromatic C–H stretching is observed around 2923 cm^{-1} . Overall, the FT-IR studies confirm the formation of polyanilines in presence of PDDMAC.

The composites exhibited more or less the same UV-Visible absorption bands as pure PANi does. The data is collected in Table 3 and the spectra are shown in Fig. 3. In general they exhibit two bands, one around 390–430 nm and another 800–900 nm in the visible region. The band at 390 nm is ascribed to Π to Π^* transition, the other at about 800 nm is assigned to the polaron band [54]. The spectra indicate that the composites have coiled-structure as known for polyaniline composites [54,55].

Conductivity of the composites was measured by four probe method for both pressed pellets and cast films and the data are collected in Table 4. The data shows that the conductivity decreases with decrease in the percentage of PDDMAC in the composite. That is to say that the highest conductivity, 5.33 S/cm is exhibited by pure PANi–HCl system, followed by 0.81 and 0.796 S/cm by 1% PDDMAC-PAni and 5% PDDMAC-PAni, respectively. When the percentage of PDDMAC increased further to 10%, 15% and 25%

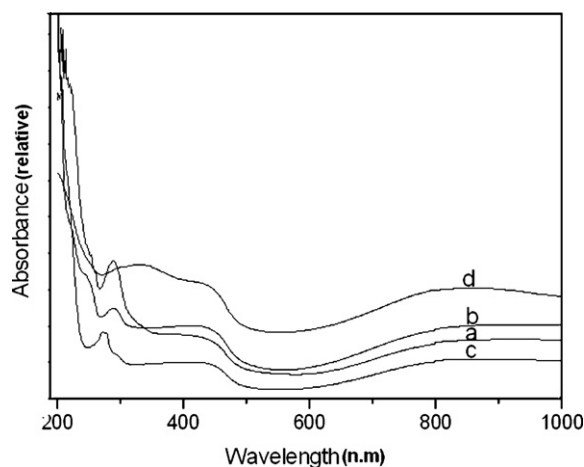


Fig. 3. UV-Vis spectra of the composites recorded in water solvent. (a) 5% PDDMAC–PAni (b) 10% PDDMAC–PAni, (c) 15% PDDMAC–PAni and (d) 25% PDDMAC–PAni.

Table 4
Conductivity Data for PDDMAC-PAni composites

Composite	Conductivity of pellet of purified composite (S/cm)	Conductivity of the film cast from reaction mixture (S/cm)
Pure PAni-HCl	5.329	not formed
1% PDDMAC-PAni	0.812	not formed
5% PDDMAC-PAni	0.7960	4.523×10^{-6}
10% PDDMAC-PAni	1.0615×10^{-3}	5.687×10^{-6}
15% PDDMAC-PAni	0.6923×10^{-3}	27.45×10^{-6}
25% PDDMAC-PAni	0.1809×10^{-3}	41.90×10^{-6}

(i.e., decrease of real PDDMAC% in the composite as determined by spectrophotometry), there is a drastic decrease in conductivity from 1.06×10^{-3} to 1.89×10^{-3} S/cm through 0.692×10^{-3} S/cm. The conductivity of the cast films was also investigated. The films (thickness ~ 0.8 – 1.0 mm) showed still lesser conductivity which fall in the range 4.5×10^{-6} to 42×10^{-6} S/cm. This may be due to the inorganic and lower molecular weight impurities present in the mixture. However, in contrast to the pressed pellets, the conductivity of these films increased with decrease in real PDDMAC concentration (Table 4). The increment is more for 15% PDDMAC-PAni and 25% PDDMAC-PAni composites. This is due to higher loadings of PAni in the composite which may separate as an upper phase upon drying and hence contribute more to the conductivity.

The isolated composites were cast on Pt electrode and were subjected to cyclic voltammetry (CV) in 1 M HCl (Fig. 4). The data is collected in Table 5. It is well known that polyaniline undergoes two separate oxidation and reduction processes [50]. The cast films exhibited similar electrochemical behavior. The well

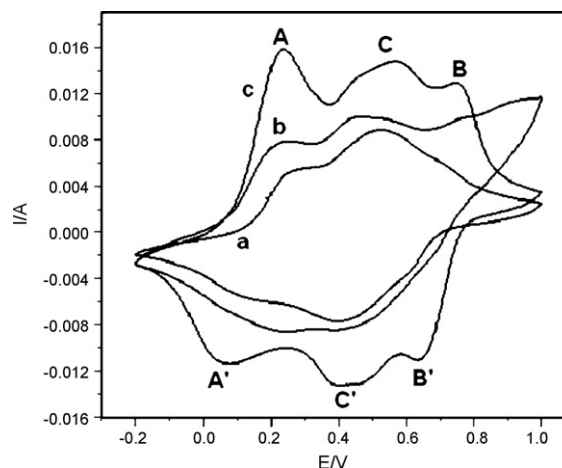


Fig. 4. CVs of cast films of (a) 1% PDDMAC-PAni, (b) 5% PDDMAC-PAni and (c) 15% PDDMAC-PAni on Pt electrode recorded in 1 M HCl solution under 50 mV/s scan rate.

Table 5
Cyclic voltammetry Data of the PDDMAC-PAni composites

Composite	Peak A	Peak B	Peak C
25% PDDMAC-PAni	0.214	0.492	0.786
15% PDDMAC-PAni	0.186	0.552	0.780
10% PDDMAC-PAni	0.150	0.370	0.780
5% PDDMAC-PAni	0.210	0.500	0.730
1% PDDMAC-PAni	0.255	0.536	0.740

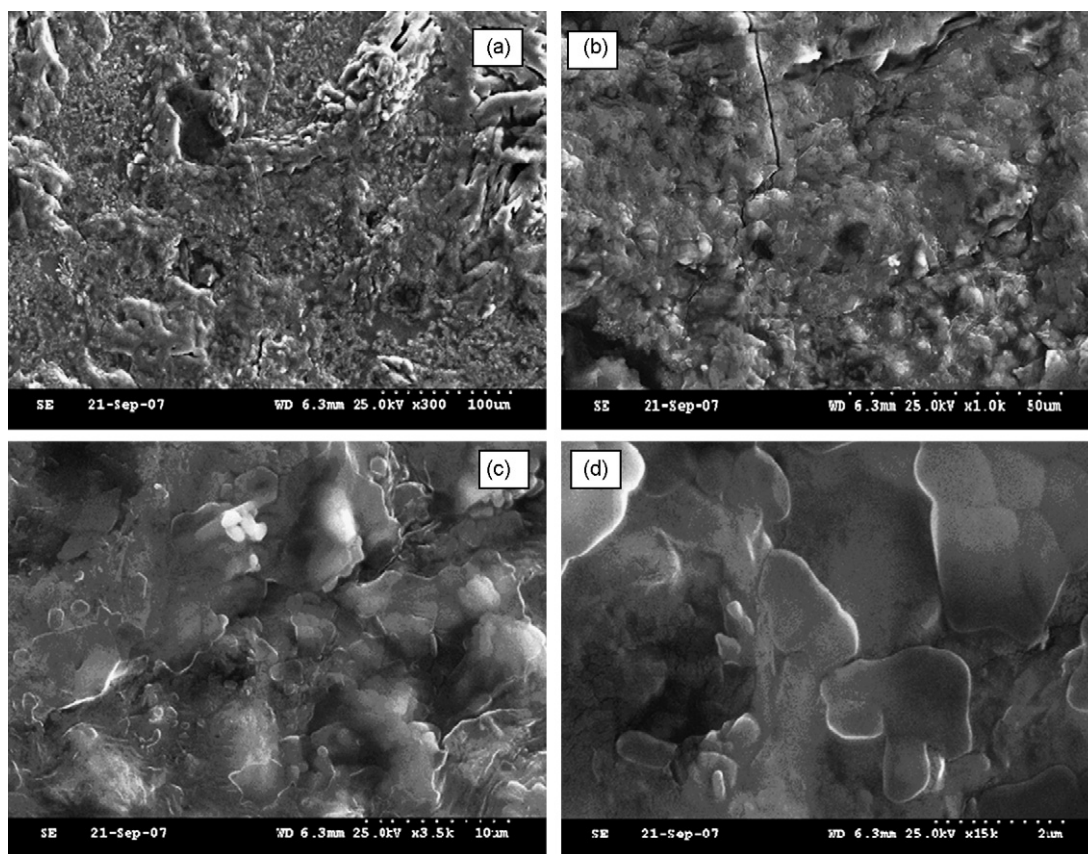


Fig. 5. SEM pictures for 10% PDDMAC-PAni cast films at (a) $\times 300$ (b) $\times 1$ K (c) $\times 3.5$ K and (d) $\times 15$ K.

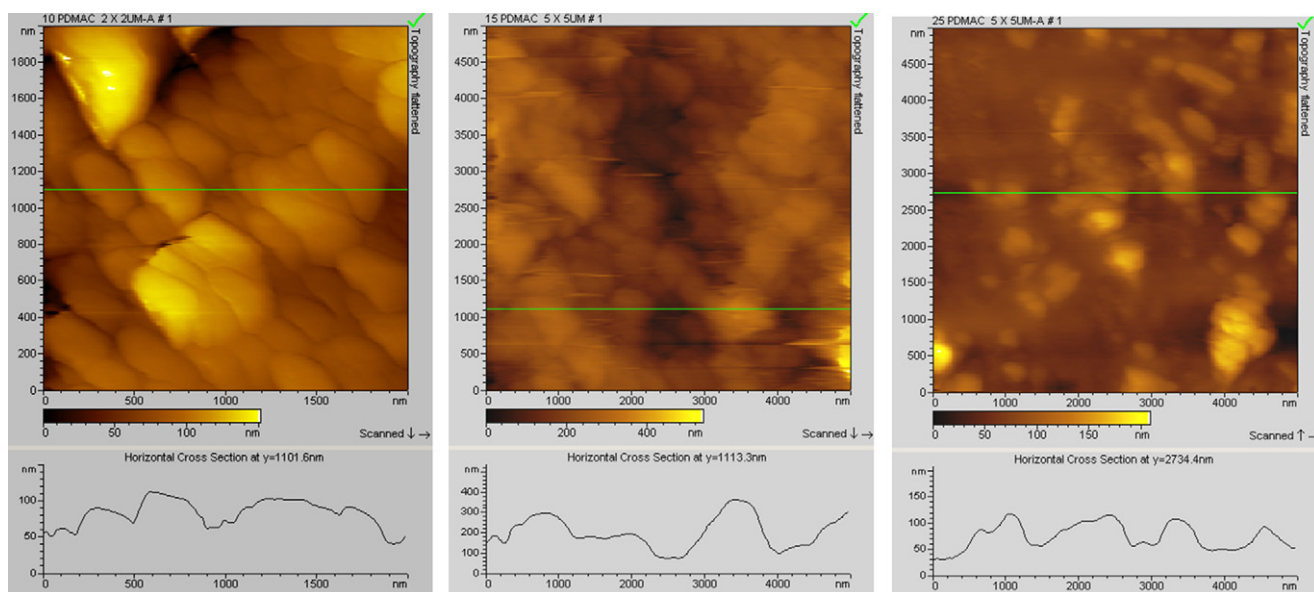


Fig. 6. AFM pictures of (a) 10% PDDMAC-PAni, (b) 15% PDDMAC-PAni and (c) 25% PDDMAC-PAni composites spin-coated on glass plates at 1000 rpm for 5 m.

defined oxidation–reduction responses indicate that the composite is electroactive. The first response (A and A') is due to oxidation–reduction of leucoemeraldine to emeraldine and vice-versa. The second response (B and B') is due to oxidation of emeraldine to pernigraniline (fully oxidized form) and vice-versa. Peaks C and C' are attributed to polyaniline breakdown products obtained when the potential necessary to observe the B and B' couple is exceeded. Oxidation–reduction peak currents increased with increased polyaniline loading in the cast films [54].

Scanning electron micrographs (SEM) for the 10% PDDMAC-PAni cast film are shown in Fig. 5 at various magnifications. They show that the two components are homogeneously composed and there is no phase separation of PAni from PDDMAC. The spin-coated composites (from water) were examined for the surface characteristic by AFM technique (Fig. 6). The micrograph for 10% PDDMAC-PAni shows that the oval shaped polymer beads are homogeneously aligned as bundles which are typically of 500 nm × 200 nm size. Similar morphology is observed for 15% PDDMAC-PAni composite with slight reductions in size of the particles. AFM for 25% PDDMAC-PAni exhibited a small degree of inhomogeneity where polyaniline globules appear to be separated from the host PDDMAC matrix. X-ray diffraction profiles (Fig. 7) of the samples showed a broad peak centered between $2\theta = 15\text{--}30^\circ$ suggesting the amorphous nature of the composites. The sharp peaks at $2\theta = 19, 23, 33, 47, 55$ and 58 are originating from the host polymer matrix PDDMAC. The intensity of these sharp peaks decreases as the concentration of the PDDMAC decreases (while concentration PAni increases) in the composite.

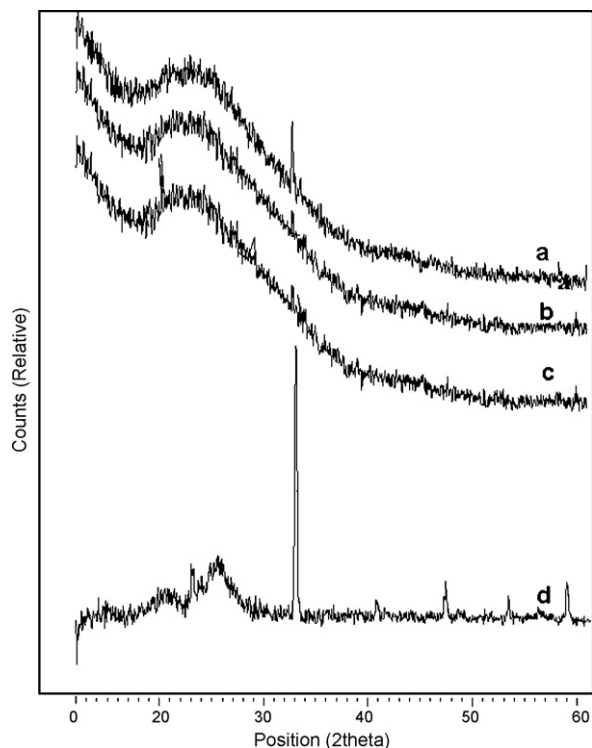


Fig. 7. XRD of the composites (a) 25% PDDMAC-PAni (b) 15% PDDMAC-PAni, (c) 10% PDDMAC-PAni and (d) 5% PDDMAC-PAni.

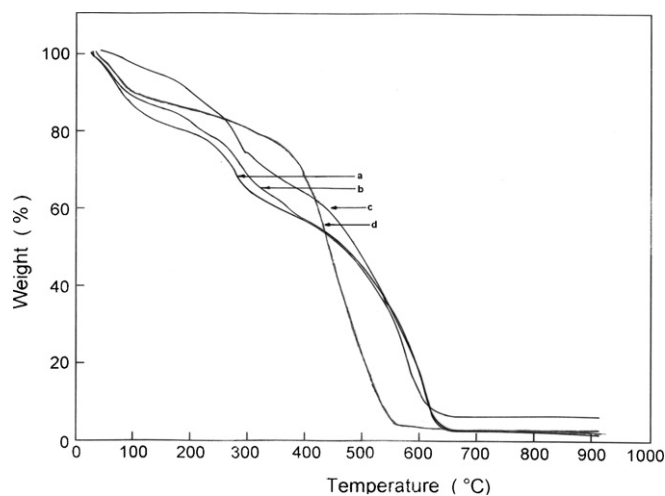


Fig. 8. TGA curves for the composites, (a) 10% PDDMAC-PAni, (b) 15% PDDMAC-PAni, (c) 25% PDDMAC-PAni and (d) pure PAni-HCl.

Table 6
Data on corrosion inhibition by PDDMAC-Pani composite for pure iron in 1 M HCl solution

Concentration of 25% PDDMAC-PAni (ppm)	Impedance method		Tafel polarization method		
	R_{ct} ($\Omega \text{ cm}^{-2}$)	Inhibition efficiency (%)	E_{corr} (mV vs SCE)	I_{corr} ($\mu\text{A cm}^{-2}$)	Inhibition efficiency (%)
Blank	550	–	–510	68	–
10	916	40	–483	38	44
30	948	42	–480	36	47
50	1037	47	–473	34	50
100	1145	52	–486	28	59
150	1170	53	–471	28	59
200	916	40	–472	40	40

Thermal analyses (up to 900 °C) on the samples revealed the stability behavior of the composites compared to the pure polyaniline doped by HCl. TGA profiles of the composites, compared to pure PAni-HCl, are shown in Fig. 8. The composites showed slightly lower thermal stability as pure polyaniline. The thermal stability of the present composites is similar and comparable to many of the other PAni composites [56–58]. Pure PAni-HCl showed (curve d) the loss of moisture (~10%) up to 100 °C. Between 100–150 °C, doped HCl is lost which accounts for the total loss of ~25% and the degradation of polymer occurs after this temperature and continues up to 550 °C (final weight loss of 93%). The first weight loss in the composites takes place around 100–120 °C due to the loss of moisture which account for a mass loss of about 5%, 10% and 15% for 10% PDDMAC-PAni, 15% PDDMAC-PAni and 25% PDDMAC-PAni respectively (curves a, b and c). The second prominent loss of about 25–35% occurs due to doped HCl molecules between 150–280 °C. The degradation of the composites starts from 350–400 °C and continues up to 620–650 °C with a loss of about 96–97% material.

4. Corrosion inhibition (C.I.) studies

A corrosion inhibitor (C.I.) is a chemical compound that, when added in small concentration (ppm), stops or slows down corrosion of metals or alloys. The type of inhibitor and its use depend on the nature of the metal and its environment [59]. Nitrogen, sulphur and oxygen containing compounds are recognized as good inhibitors [60]. Aromatic compound such as aniline, substituted aniline, alkylamine [61,62] are vital materials which work as corrosion inhibitor as they strongly adsorb on metallic surface due to the presence of Π electrons which are believed to interact with empty d-orbital in iron. It is expected that the present soluble composites having quaternary ammonium nitrogens and Π electrons would help in strong adsorption of polymer on the iron surface to give uniform coverage by minimizing Vander Waals repulsive forces.

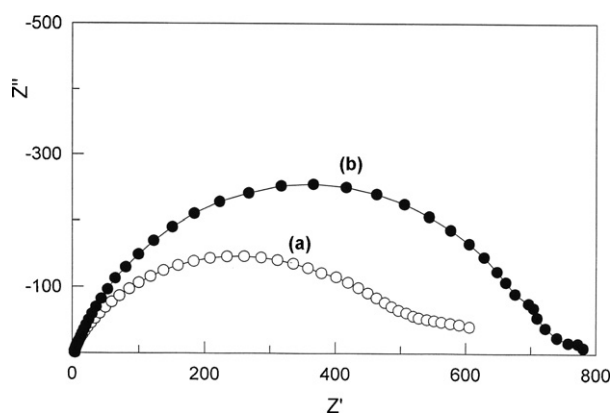


Fig. 9. Nyquist plots for iron in 1 M HCl solution (a) blank and (b) with addition of 200 ppm composite 25% PDDMAC-PAni.

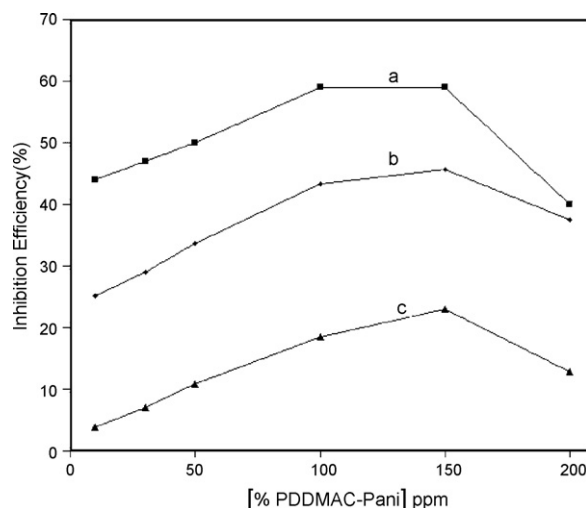


Fig. 10. Corrosion inhibition efficiencies of the composites (a) 25% PDDMAC-PAni, (b) 15% PDDMAC-PAni and (c) 50% PDDMAC-PAni.

Corrosion inhibition property of the composites 15% PDDMAC-PAni and 25% PDDMAC-PAni and 50% PDDMAC-PAni is studied by Tafel polarization (TP) and impedance techniques. The results are given in Table 6 for 25% PDDMAC-PAni composite. The impedance behavior of iron in 1 M HCl with the addition of 150 ppm (compared to blank) concentrations of 25% PDDMAC-PAni is shown in Fig. 9. These curves show a single semicircle indicating the occurrence of a single charge transfer reaction. These curves are depressed in nature which may be due to the origin of micro roughness and other inhomogenities resulted at electrode/solution interface

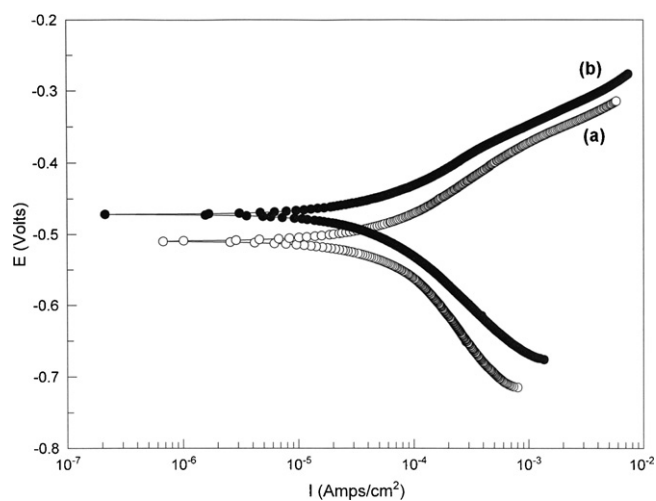


Fig. 11. Tafel polarization plot for iron in 1 M HCl solution (a) blank (b) with addition of 200 ppm composite 25% PDDMAC-PAni.

[63,64]. The charge transfer resistance increased from $550 \Omega \text{ cm}^2$ (blank) to $1170 \Omega \text{ cm}^2$ after addition of 150 ppm of 25% PDDMAC-PAni composite resulting in 53% inhibition efficiency. The studies on 15% PDDMAC-PAni and 50% PDDMAC-PAni, under same experimental conditions, showed an inferior C.I. values as shown in Fig. 10.

The potentiodynamic Tafel polarization curves for blank and with addition of 150 ppm composite are shown in Fig. 11. It is observed that the corrosion potential is shifted to about 40 mV anodic after the addition of the composite. The corrosion current decreased from $68 \mu\text{A cm}^2$ to $28 \mu\text{A cm}^2$ showing about 59% inhibition efficiency. Further addition of the composite resulted in decrease of efficiency (Table 6), suggesting that 150 ppm is the optimum concentration of the additive that can be used. The studies on 15% PDDMAC-PAni and 50% PDDMAC-PAni showed an inferior C.I. values as shown in Fig. 10.

5. Conclusions

A new series of conducting polyaniline–polyelectrolyte composite can be synthesized by using poly(diallyldimethylammoniumchloride) as a soluble host polymer matrix by in situ polymerization method. Water soluble composites are obtained when the PDDMAC contents are increased above 10% from which good quality free standing films can be casted. The new composites are conducting and electroactive with even low loadings of polyaniline. The composite 25% PDDMAC-PAni is useful as corrosion inhibitor for pure iron in 1 M HCl solution.

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