

Synthesis and Characterization of Poly Anthranilic Acid Metal Nanocomposites

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ABSTRACT

Intrinsically conducting polymer metal nanocomposites were synthesized by polymerising anthranilic acid (PANA) with metal salts like ferric chloride, Zinc oxide and Magnesium oxide by chemical oxidation method. Polyanthranilic acid-iron nano composite (PANA-Fe), Polyanthranilic acid-Zinc nano composite (PANA-Zn) and Polyanthranilic acid-magnesium nano composite (PANA-Mg) synthesized were characterised by UV-Visible and FTIR studies. FTIR spectra of polymer-metal nano composites showed peaks in the region between 1690 cm^{-1} and 1490 cm^{-1} which corresponds to the deformation in different types of N-H bond. The participation of the -NH group in polymerization was confirmed by the appearance of a peak around 3431 cm^{-1} . Cyclic voltammetric studies revealed the presence of an adherent polymer film on the glassy carbon electrode and showed redox behavior of the polymer metal nanocomposites. The XRD (XRay Diffraction) studies showed a rather more crystalline behaviour of the nano composites and the grain size was calculated using Scherrer's formula and it was found to be in nano range. SEM (Scanning Electron Microscope) analysis showed a rather mixed crystalline and amorphous behavior. EDAX (Energy Dispersive X Ray Spectroscopy) confirms the incorporation of the metals iron, Zinc and Magnesium in the polymer-metal nano composites. The inhibition efficiency of the polymer-metal nano composites were calculated for stainless steel in acidic environment using electrochemical impedance spectroscopy (EIS) and polarization (Tafel) studies and the prepared PANA-Fe and PANA-Zn nano composites showed effective anti-corrosive behavior on stainless steel in acid medium.

Keywords: Poly Anthranilic Acid; Polymer Metal Nanocomposites; Cyclic Voltammetry; EIS; SEM; TEM

1. Introduction

For the past few decades polyanilines and substituted polyanilines have emerged as efficient class of corrosion inhibitors for mild steel (MS) and stainless steel (SS) in acidic media. The passivation of the metal surface is responsible for the protective activity of polyaniline and substituted polyanilines [1]. This was elucidated with potential and polarisation measurements on stainless steel. The general observation is that there is a significant potential shift towards more noble values and an increase of the polarisation resistance takes place [2,3]. Intrinsically conducting polymers definitely possess promising potential for application in intelligent corrosion protection coatings. Incorporation of metals and metal oxides in intrinsically conducting polymers (ICP) can enhance electron transfer through a direct or mediated mechanism with improved conductivity and enhanced stability. It has been reported earlier that the formation of pitting corrosion [4,5] is inhibited by the application of conducting

polymers on SS surface. The protective behaviour of conducting and insulating forms of polymers on SS has also been reported earlier [1,6]. Insulating coatings act as a barrier against diffusion to polymer/metal interface of corrosive ions but conducting polymer coatings stabilize the metal within the potential range of the passive region.

Synthesis and characterization of sulfonated polyanilines has been dealt with extensively in literature, but only few papers pay attention to their parent carboxylated derivatives [7-16]. Moreover, most of these reports are limited to the study of the copolymers formed by either chemical or electrochemical polymerization of aniline and substituted aniline with o-amino benzoic acid (anthranilic acid) [7,8,10,12,16]. A comparison between the homopolymers synthesized electrochemically from ortho, meta and p-aminobenzoic acids was reported for the first time by Thiemann and Brett [13,14]. The preparation of a poly (anthranilic acid)-palladium nanoparticle composite material by polymerization of anthranilic acid (AA) monomer using palladium acetate (PA) as the oxidant had been already carried out earlier [17]. Poly (anthranilic

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acid) was first reported as a self doped conducting polymer and an efficient corrosion inhibitor for mild steel in acidic solution [18] by Sudhish Kumar Shukla *et al.*

The aim of this work is to prepare poly (o-aminobenzoic acid) metal nano composites (metals introduced were Zinc, Magnesium and iron) and study their electrochemical and corrosion behavior on SS.

2. Experimental

2.1. Materials

o-aminobenzoic acid (Aldrich), hydrochloric acid, potassium per sulphate, ferric chloride, zinc oxide and magnesium oxide were used as such.

2.2. Synthesis of Poly (Anthranilic Acid)—Iron Nano Composite

Anthranilic acid and ferric chloride was taken in the ratio of 1:2. Ferric chloride itself acted as an oxidant. The monomer was dissolved in 0.1 M hydrochloric acid and a suitable amount of aqueous solution of ferric chloride was added slowly into the monomer. The solution was kept stirring for about 3.0 h at room temperature, it was then left overnight in the refrigerator, after which the brownish black powder obtained was filtered, dried and was found to be soluble in dimethyl sulphoxide, N-methyl pyrrolidine, diethylene glycol and sodium hydroxide to give reddish brown solutions.

2.3. Synthesis of Poly (Anthranilic Acid)—Zinc Nano Composite

Anthranilic acid (monomer), potassium per sulphate (oxidant) and zinc oxide were taken in the ratio of 1:2:1. The monomer was dissolved in 0.1 M hydrochloric acid and the aqueous solution of the oxidising agent was slowly added into monomer and metal salt solution. The solution was kept stirring for about 3.0 h at room temperature, it was then left overnight in the refrigerator, after which the brownish black powder obtained was filtered, dried and was found to be soluble in dimethyl sulphoxide, N-methyl pyrrolidine, diethylene glycol and sodium hydroxide to give reddish brown solutions.

2.4. Synthesis of Poly (Anthranilic Acid)—Magnesium Nano Composite

The same procedure was followed as done for Poly (Anthranilic Acid)—magnesium Nano Composite using magnesium oxide.

2.5. Characterizations

The solution of the polymer metal nano composites in dimethyl sulphoxide was used for recording the UV-VIS

spectra. For recording the UV-Vis absorption spectra, a computer controlled JascoV-500 spectrophotometer was used. The FT-IR spectra were recorded using a SHIMADZU instrument. The X-ray diffraction (XRD) patterns were recorded for the powdered materials using a BRUKER (D8 ADVANCE) X-ray diffractometer. The polarization and impedance studies were carried out using electrochemical workstation (mode 650C), CH-Instrument Inc., TX, USA. The polarization measurements were carried out from cathodic potential of -0.7 V vs. Ag/Ag^+ to an anodic potential of $+0.7$ V vs. Ag/Ag^+ with respect to the open circuit potential at a sweep rate $50 \text{ mV}\cdot\text{s}^{-1}$ to study the effect of inhibitor on stainless steel corrosion. The electrochemical studies were carried out in a three electrode cell [19,20]. Pt was used as counter electrode and silver-silver chloride electrode as reference electrode. In the case of cyclic voltammetric studies the polymer and the metal polymer nano composites were coated on a glassy carbon electrode by dissolving a pinch of the polymer sample in DMSO. For impedance studies the stainless steel strip was used as the working electrode and it was embedded in araldite, so as to expose a surface area of 1.0 cm^2 . The electrode was polished successively on the emery paper and then degreased with trichloroethylene.

The charge transfer resistance was obtained from the diameter of the semi circles of the Nyquist plots. The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation [18]

$$\text{IE}\% = (R_{ct} - R_{ct}^0)100/R_{ct} \quad (1)$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor.

The surface coverage values (θ) were calculated from the C_{dl} values according to the equation [18].

$$\text{Surface coverage } (\theta) = (C_{dl} - C_{dl(i)})/C_{dl} \quad (2)$$

The corrosion inhibition efficiency from the polarization studies (IE%) was evaluated from the measured I_{corr} values using the relationship[18]:

$$\text{IE}\% = (I_{corr}^0 - I_{corr})100/I_{corr}^0 \quad (3)$$

where I_{corr}^0 and I_{corr} are the corrosion current densities in absence and in presence of the inhibitor.

3. Results and Discussion

3.1. UV-VIS Studies

UV-VIS spectra of Poly(o-amino benzoic acid) exhibits three bands around 272 nm, 375 nm and 562 nm as shown in **Figure 1**. The first (shoulder) about at 272 nm is attributed to the JI-JI^* transition for the benzenoid ring, the band at 375 nm for quinoid rings and 562 nm for

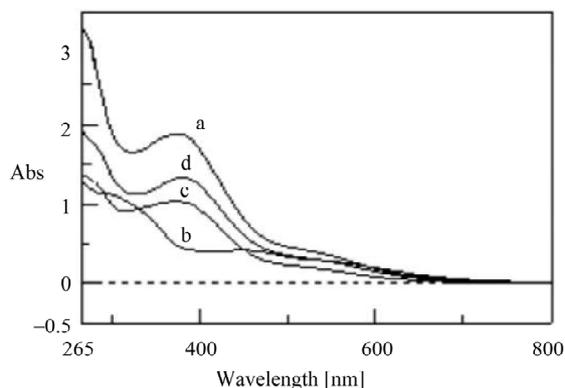


Figure 1. UV-VIS spectra of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg nanocomposites.

polaronic transition due to the emeraldine state of the polymer. This is in agreement with the results reported earlier [18]. Introduction of the metals (iron, Zinc and Magnesium) showed a slight hypsochromic shift in the bands.

When Zinc is introduced, hypsochromic shift is observed with peaks at 261 nm, 373 nm and at 570 nm. In the case of iron added composites also hypsochromic shift is observed with peaks at 262 nm, 368 nm and 565 nm, the shift is expected due to less conjugation along the polymeric chain and the steric effect of the bulky COOH group and the incorporated metal into the polymeric matrix. In the case of magnesium included composites the peaks appeared at 266 nm, 372 nm and 565 nm.

3.2. FTIR Studies

The FTIR spectra as shown in **Figure 2** shows the following bands for poly (anthranilic acid) namely a band at 3431 cm^{-1} (N-H stretching), 2615 cm^{-1} (O-H stretching), 1691 cm^{-1} (C=O), 1558 cm^{-1} (quinoid C=C stretching), 1506 cm^{-1} (benzenoid C=C stretching), 1450 cm^{-1} (stretching of aromatic ring), 1373 cm^{-1} (C-N stretching for secondary aromatic amine), 1247 cm^{-1} (C-H stretching), 1166 cm^{-1} (N=Q=N stretching Q = quinoid ring), 1081 cm^{-1} and 1045 cm^{-1} (aromatic C-H in plane bending), 821 cm^{-1} and 756 cm^{-1} C-H out of plane bending and confirms 1,4 disubstituted benzene ring). This result is similar to the one published by Rao and Sathyanarayana. Yan *et al.* who had similar observations from X-ray photon spectroscopy for poly (2-aminobenzoic acid) [12].

Introduction of iron into the polymeric chain causes an increase in the O-H stretching from 2615 to 2854 cm^{-1} . Appearance of additional bands around 675 cm^{-1} confirms the metal stretching (Further confirmed by EDAX). In the case of PANA-Zn and PANA-Mg the bands were almost similar to PANA indicating the absence of any kind of chemical interaction between the polymer and the

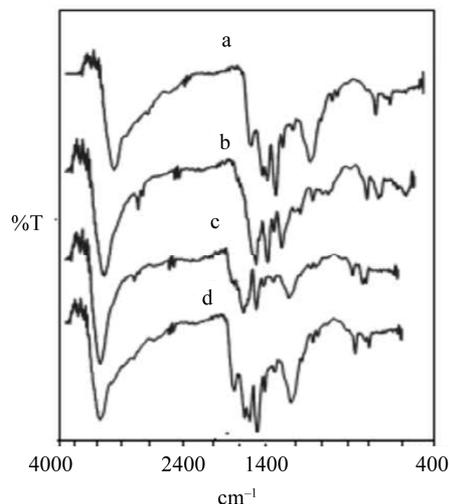


Figure 2. FTIR behaviour of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg nanocomposites.

metal.

3.3. Cyclic Voltammogram Behaviour of Polymer Metal Nano Composites

Cyclic voltammogram of PANA and its metal nano composites were recorded by cycling the potential between -0.2 V and 1.2 V in 0.1N HCl as shown in **Figure 3**. Here appeared one anodic and a broad cathodic peak for polymer. Similarly metal introduced composites also exhibited anodic and cathodic peaks but potential of peaks is different from polymer this might be due to incorporation of metal ions. As the scan rate increases the peak current of polymer and polymer metal composites also increased linearly, it is indicating an adherent film on the glassy carbon electrode, this was further confirmed by a straight line graph obtained by plotting peak current Vs scan rate as presented in **Figure 4**.

3.4. EIS and Polarisation Studies

Electrochemical impedance measurements were carried over a frequency range from 1000 Hz to 0.01 Hz at open circuit potential. The simple equivalent Randle circuit for studies is given in **Figure 5**. The presence of a single semi circle (**Figure 6**) shows the coating acts as a barrier. It is seen that introduction of metal atom increases the values of R_{ct} and reduces the C_{dl} . The charge transfer resistance (R_{ct}) value for bare SS is low ($40\ \Omega\text{cm}^2$), whereas for the metal polymer nano composites it is high. Also the decrease in C_{dl} is attributed to increase in thickness of electronic double layer [19]. The increase in R_{ct} value is attributed to the formation of protective film on the metal/solution interface. These observations suggest that metal PANA composites function by adsorption at metal surface thereby causing the decrease in C_{dl} values

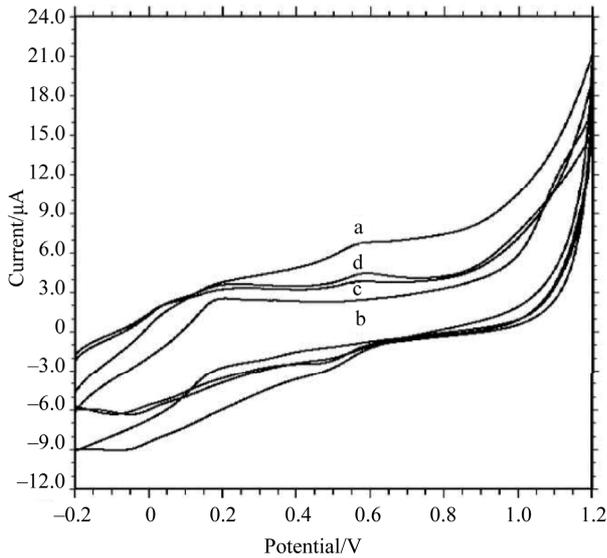


Figure 3. Cyclic voltammogram of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.

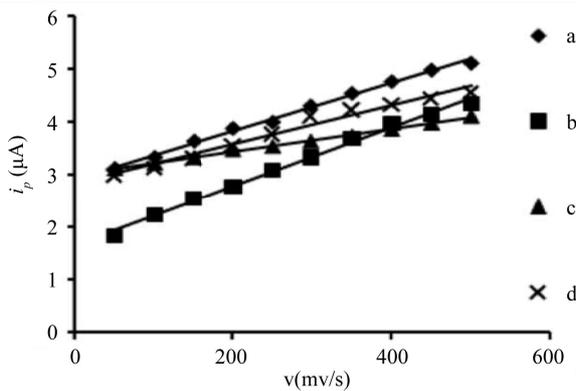


Figure 4. Plot of peak current Vs scan rate.

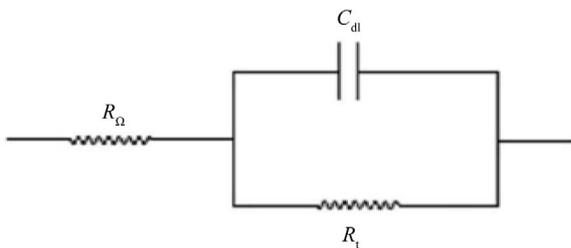


Figure 5. Electrical equivalent circuit.

and increase in R_{ct} values. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) derived from these curves are given in **Table 1**. From the table it is clear that the R_{ct} value increases gradually and is maximum for PANA-Zn indicating that the PANA-Zn film imposes a certain inhibition to the corrosion process of the steel and then comes PANA-Fe. The inhibitor efficiency for PANA-Mg and the polymer without the metal is the same indicating that this metal composite is not a

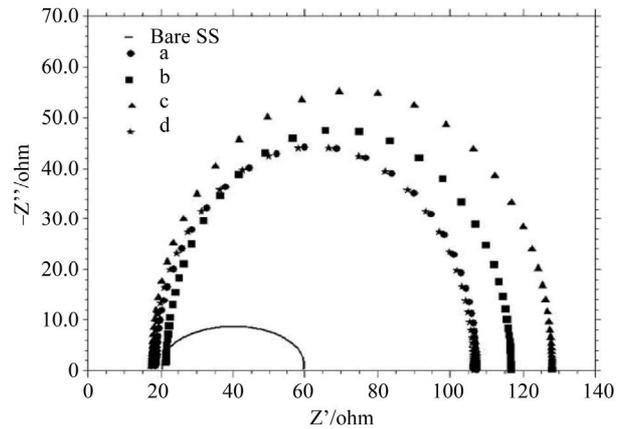


Figure 6. Electrochemical Impedance spectra of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.

Table 1. R_{ct} , C_{dl} , I.E% and Surface Coverage (θ) for PANA, PANA-Zn, PANA-Fe and PANA-Mg.

polymer	$R_{ct}(\Omega\text{cm}^2)$	$C_{dl}(\mu\text{Fcm}^{-2})$	I.E%	θ
Blank	40.00	211.1	-	-
PANA	88.56	161.7	54.83	0.23
PANA-Fe	95.22	103.0	57.99	0.51
PANA-Zn	110.50	100.2	63.80	0.53
PANA-Mg	88.50	201.5	54.80	0.05

good inhibitor. The surface coverage value (θ) also is higher in the case of Zinc when compared to Fe.

3.5. Polarisation Studies

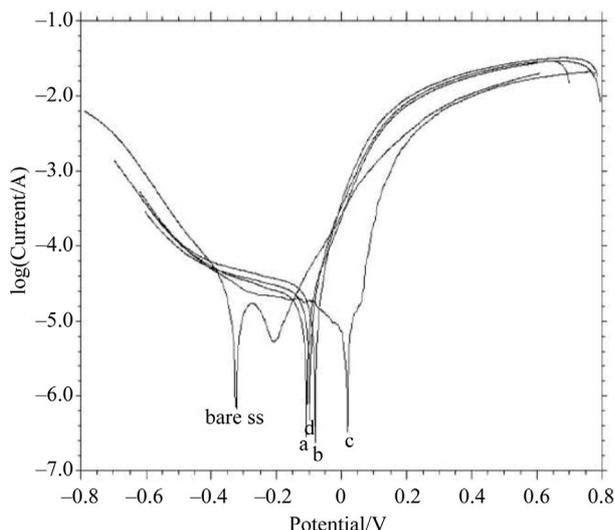
The polarisation behavior of SS in 1.0 M HCl without metal and with metal is shown in **Table 2**. Tafel curves show that the protective action of the polymer metal composite promotes a change of the corrosion potential to more positive values for stainless steel coated with PANA-Zn and PANA-Fe. The observations of the present results pointed out the remarkable capability of PANI-Zn and PANA-Fe to protect steel against corrosion in 1.0 M HCl solutions. By comparison, it can be found that the EIS data are consistent with the Tafel curves of each PANA film-covered stainless steel electrode in **Figure 7**.

3.6. XRD Behaviors of Polymer and Polymer Metal Nano Composites

The X-ray powder diffraction patterns for the polymers of o-amino benzoic acid as in **Figure 6** are typical of semi crystalline polymers. Polymers with high crystallinity usually show higher conductivity. The particle size was calculated using Scherrer equation [20]. In the case of the polymer metal nano composites the particle size was 2.0 nm. On introducing the metals the particle size

Table 2. Polarization data for polymer and metal polymer nano composites.

polymer	E_{corr}	I_{corr}	IE%
Blank	-0.3247	19.27	-
PANA	-0.1077	15.95	17.23
PANA-Fe	-0.0817	12.15	36.95
PANA-Zn	-0.0220	10.05	47.85
PANA-Mg	-0.0980	15.18	21.22

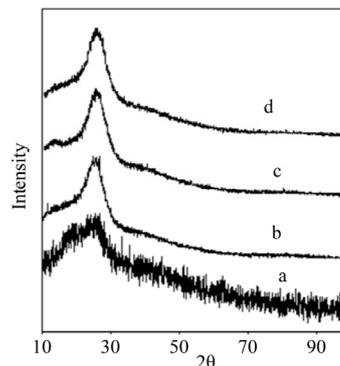
**Figure 7. Tafel plot for (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.**

of the nano composites gradually increased. XRD pattern as shown in **Figure 8** shows a broad peak for PANA, in the case of polymer metal composites the peaks are rather sharp indicating more crystallinity and hence more conductivity.

3.7. SEM and EDAX Behaviours of Polymer and Polymer Metal Nano Composites

The SEM micrographs were used to investigate the morphology of the polymer and metal polymer nano composites. Polyanthranilic acid displays spherical shaped structures (**Figure 9**). PANA-Fe shows an agglomerated structure. The polymer metal nanocomposites especially the PANA-Zn and PANA-Mg exhibits mixed granular and agglomerates morphology which may result from intramolecularly hydrogen bonded amino benzoic acid units [21].

EDAX confirms the incorporation of Fe, Zn and Mg into the polymer matrix as shown in **Figure 9**. Sharp intense peaks were obtained in the case of PANA-Fe composite. In the case of PANA-Zn composite, though the peak for Zn was less intense, the incorporated Zn provided better inhibition on SS. As far as PANA Mg

**Figure 8. XRD of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.**

composite is concerned, the peak due to Mg is very weak and its inhibition property is also almost similar to the PANA as revealed from EIS and polarization studies.

3.8. TGA/DTA

The weight loss patterns in **Figure 10** are in good agreement with previous reports on polyaniline. The TGA curve for PANA showed a rapid decomposition from about 100 until about 800°C. DTA curves showed endothermic peaks around 95°C, while exothermic peaks were observed.

The first weight loss observed around is 125°C and 250°C due to loss of moisture, the second weight loss is due to the removal of dopants and the weight loss after 295.64°C corresponds to the decomposition of the polymer [22-25]. In the case of PANA-Fe, the polymer metal nanocomposite is stable up to 664.46°C and after this temperature it starts decomposing. In PANA-Zn the first weight loss observed up to 200.24°C is due to loss of moisture and the removal of dopants and the weight loss after 295.04°C corresponds to the decomposition of the polymer. In PANA-Mg the first weight loss observed up to 204.18°C is due to loss of moisture and the removal of dopants and the weight loss after 296.26°C corresponds to the decomposition of the polymer.

3.9. TEM

TEM as in **Figure 11** shows a light coloured crystalline like structure as in PANA, when iron is introduced it shows both dark (metal) and light coloured region (polymer) tightly bounded crystalline with sponge like structure, when zinc is incorporated there is more darker granular structure indicating that more of zinc is incorporated when compared to iron. Magnesium used nanocomposites shows sponge covered granular like structure.

4. Conclusion

Chemical Synthesis of PANA, PANA-Fe, PANA-Zn and

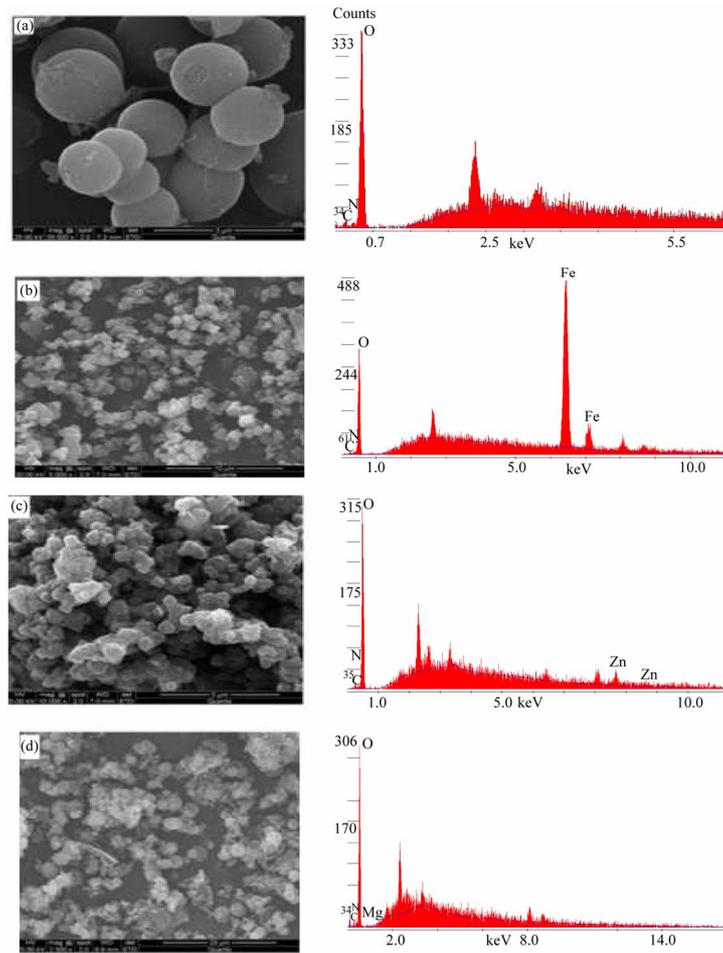


Figure 9. SEM photograph and EDAX behaviour of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.

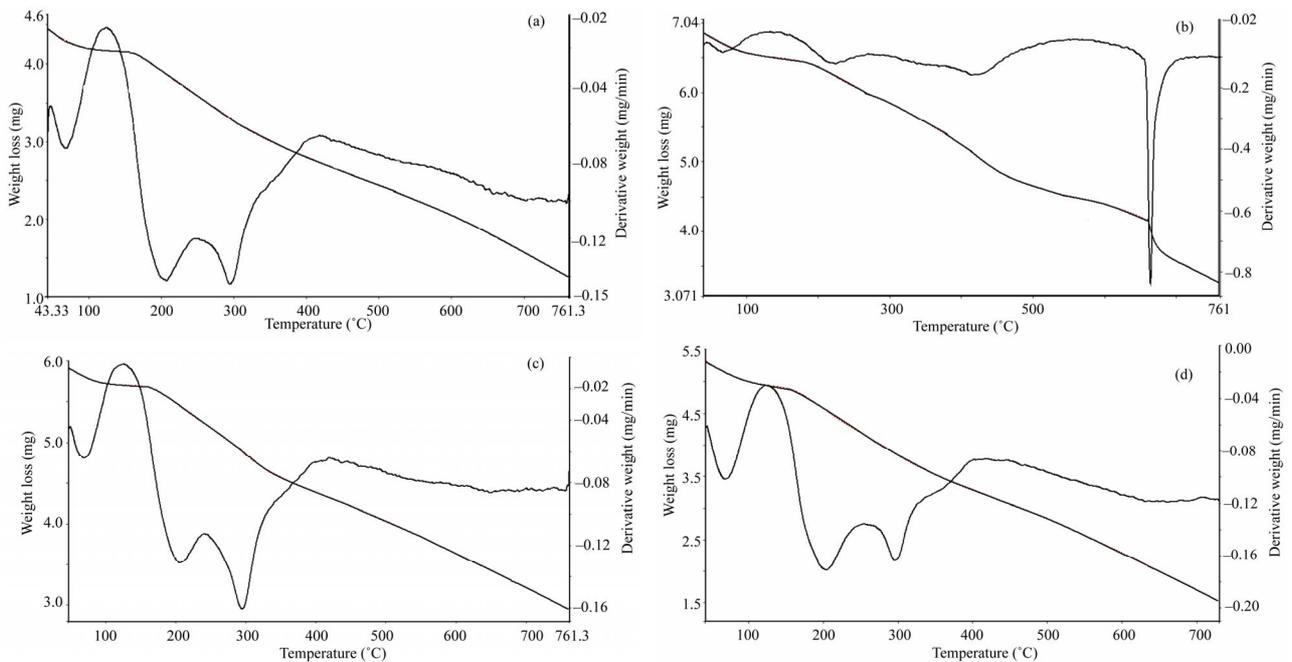


Figure 10. TGA/DTA curves of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.

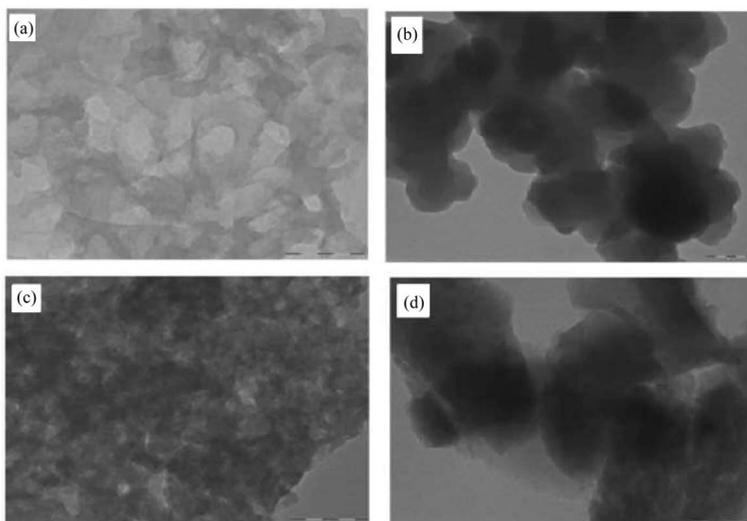


Figure 11. TEM images of (a) PANA; (b) PANA-Fe; (c) PANA-Zn; (d) PANA-Mg.

PANA-Mg were successfully carried out. The characterization of the chemically synthesized nano composites was done by using UV-Vis and FTIR studies. EIS and polarization studies agreed very well indicating PANA-Zn and PANA-Fe act as very good anti corrosive agents for SS. CV studies revealed an adherent film on GC electrode. SEM studies show a mixed granular morphology in the case of Zn and Mg introduced polymer nano composites. Thus the chemically prepared polymer metal nano composites especially the PANA-Zn and PANA-Fe can be used as an anti corrosive pigment for paints.

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