Synthesis, characterization, thermal and electrical properties of composite of polyaniline with cobaltmonoethanolamine complex

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MS received 21 July 2013; revised 8 October 2013

Abstract. The present paper involves the synthesis of polyaniline (PANI) composite with cobaltmonoethanolamine $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex via *in situ* oxidative polymerization by ammonium persulphate. The complex has been synthesized by refluxing method. The composite has been subjected to UV–Visible spectra, FT–IR, X-ray diffraction, SEM and electrical conductivity characterization techniques. Thermal analysis has been done by using TG and DSC techniques. FT–IR absorption peaks confirm the insertion of complex in the backbone of PANI. SEM of the composite also supports its successful synthesis. The XRD of composite also shows crystalline structure hence, proving the successful synthesis of PANI. Thermal analysis shows enhanced thermal stability of polyaniline. In the present composite system, the polymerization of PANI with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex causes strong interfacial interactions between PANI and $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex crystallites, also suggested by the FT–IR and XRD studies, thereby changing the molecular conformation of PANI from compact coil structure to an expanded coil-like structure. As a consequence, there is an enhancement in the conductivity of composite of PANI up to certain dopant concentration. The anticorrosive property of a coating of PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ composite on mild steel coupon in 3 M HNO_3 was evaluated using weight loss measurement and compared with pure polyaniline coating. The said composite has shown anti-corrosive property and can thus, act as a potent dopant for enhancing corrosion resistance of PANI coatings.

Keywords. Polyaniline; oxidative polymerization; cobaltmonoethanolamine complex; thermal analysis; electrical conductivity.

1. Introduction

During past two decades, both fundamental and applied research in conducting polymers and its composites has grown enormously (Skotheim *et al* 1998). Among the conducting polymers, polyaniline (PANI) and its derivatives have attracted much interest because of their higher environmental, thermal and chemical stabilities along with high conductivity (Meixiang 1998). Conducting polymers and its composites have found application as transducers of biosensor (Kros *et al* 2001), electrodes of rechargeable batteries (Kaeami *et al* 2003), artificial nerves and muscles (Yamauchi *et al* 2005), gas sensors (Lin *et al* 1998), solid electrolytic capacitor, diodes, transistors (Noh *et al* 2003), anti-static electromagnetic shielding (Lee *et al* 2001; Koul *et al* 2001) and biomedical applications (Pfaendner 2010). In addition to this, majority of the literature focuses on the use of these materials as anti-corrosive coating on metal surfaces (Sambhu *et al* 2011). Since, corrosion protection of the metal is one of the most serious problems that mankind has to face. In this direction, conducting polymers and their composites have proved as good candidates for use as corrosion

inhibitors that too with environmental friendship. It has been reported that PANI-based coatings can prevent corrosion even in scratched areas, where bare-steel surface is exposed to the aggressive environment (Zarras *et al* 2003). It has also been reported that three layers of coating are required with traditional materials to obtain an adequate protection of metal surfaces against corrosion, whereas a single coat of conducting polymers and their composites can provide the same degree of protection, leading to the substantial savings of material as well as cost of application. It is an established fact now that novel properties of composites can be derived from the successful combination of the characteristics of the parent constituents into a single material. Therefore, the preparation of PANI composites has been the subject of considerable interest since the development of composite materials. The composites of PANI with various metal-oxides, inorganic and organic nanoparticles have been synthesized and properties of PANI have improved significantly. Various composites of PANI with various fillers, binders and dopants have been synthesized, characterized and explored for many applications. For example, composites of PANI with dopants like MoO_3 , ZrO_2 , TiO_2 , WO_3 , Mn_3O_4 and MnO_2 have been synthesized, characterized, and have shown significant applications (Gurunathan *et al* 2003).

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Composites of PANI with MoO_3 have increased thermal stability of the polymer. The conductivity of PANI- MoO_3 is in the order of 10^{-2} S/cm (Koppalkar *et al* 2009). PANI doped with ZrO_2 has shown higher thermal stability because of interaction between PANI and ZrO_2 , which is reported to resist the thermal motion of PANI chains and shields the degradation of PANI in the composites. PANI composites of TiO_2 are proved to act as cathode material in rechargeable batteries. Similarly, PANI composite with Mn_3O_4 have been reported to behave as an NTC material (Majid *et al* 2007). PANI composite with WO_3 has shown sensing properties (Narsimha *et al* 2006). The composites of PANI with other oxides, inorganic and organic substances like iron oxides, MoS_2 , MnO_2 , graphite and platinum have also been reported (Aphesteguy and Jacobo 2004). Therefore, literature shows that the chemical modification of PANI with suitable chemical species, induces varied dimensions in the composite material and desired characteristics can therefore be achieved by suitable chemical synthesis and modifications. Moving on the path of composite materials, insertion of inorganic complexes into the PANI backbone have led to the development of another category of conducting polymers known as hybrid materials, which are the current inquisition among material scientists. These hybrid systems possess varied properties and find applications in various fields like catalysis, sensors, bio-medical field (Greene *et al* 1975) and in corrosion study. Ethanolamines commonly known as aminoalcohols include mono-, di- and tri-ethanolamines. Because of their basic nitrogen atom and hydroxyl group, the chemical properties resemble those of both amines and alcohols. The bifunctional nature of ethanolamines enables them to serve a variety of commercial applications such as inhibitors, surfactants, gas purification and herbicides (Esker *et al* 1999). The complexation of amino alcohols with transition metals have a long and varied history. Amino alcohols form complexes with transition metals like Co, Cu, Cd, Ni, Zn, etc. These complexes show high thermal stability, lubricating properties and corrosion resistant properties. These complexes can prove as successful dopants for increasing the characteristic properties of conducting polymers. Keeping the lubricating, corrosion resistant properties and high thermal stability of complexes of cobalt with monoethanolamine in consideration, we here, report the synthesis and characterization of PANI and its composite with cobaltmonoethanolamine complex. The synthesized material has been subjected to various spectroscopic characterizations. Thermal and electrical properties of the synthesized material is also reported.

2. Experimental

2.1 Materials and physical measurements

Aniline was obtained by Loba Chemicals and was used after distillation. HCl, ammonium peroxodisulphate, cobalt

chloride and monoethanolamine were also provided by Loba Chemicals. *N*-methylpyrrolidone was provided by Merck. All other reagents used were of analytical grade. UV-Visible spectra were taken on Shimadzu UV-190 double-beam spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer RX-1 FT-IR spectrophotometer. The spectra were taken in KBr disks. Surface morphology of the samples was studied on a Hitachi SEM model S-3600N. X-ray diffraction (XRD) was recorded on PW 3050 base diffractometer with $\text{CuK}\alpha$ radiations ($1.54060 \text{ \AA}$). Thermogravimetric analysis coupled with DSC was carried out with universal TA instruments V4.5A in an argon atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The temperature range was from ambient to 800°C . An aluminium pan was used as a reference. The DSC was calibrated by the fusion of indium (99.99% purity). Temperature repeatability of TA is $\pm 0.1^\circ\text{C}$ and ΔH is $\pm 0.02 \text{ mW}$. The experimental procedure involves placing of 15-33 mg of sample in a pan, setting the pressure and heating rate. In this procedure, material was subjected to a linear temperature programme and the rate of heat flow into the material was continuously measured with increase in temperature. The temperature difference as a function of time shows peaks as heat is either absorbed or released by the sample under examination. *I-V* characterization was done by Keithley electrometer/high resistance meter 6517A. The polymer composite was grinded by a mortar and pestle to obtain a fine powder form. The pellets of thickness 1 mm and diameter 12 mm were prepared from this powder material by applying a pressure of 5 ton. *I-V* characteristics of the polymer composites were investigated at room temperature.

2.2 Synthesis of PANI

PANI was prepared by known methods of oxidation with ammonium persulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. To pre-cooled solution of 10 mL distilled aniline dissolved in 150 mL of distilled water with 10 mL of concentrated HCl and 4.5 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 30 mL of water was added drop-wise to the solution with constant stirring. Temperature was maintained at $0-5^\circ\text{C}$. The solutions were kept stirring for about 2 h and were left for more than 1 h. The precipitate resulting from this solution was filtered and washed repeatedly in Buckner funnel under vacuum with distilled water. The precipitate was collected and dried in an oven at about 40°C .

2.3 Synthesis of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex

The cobalt monoethanolamine $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex was prepared by mixing 50 mL of 1 M solution of monoethanolamine to 50 mL of 1 M cobalt chloride solution. A pale violet precipitate resulting from this

reaction upon refluxing is filtered and repeatedly washed with distilled water.

2.4 Synthesis of PANI/[Co(mea)₂(H₂O)₂Cl₂] composite

The polyaniline composite was synthesized by *in situ* polymerization procedure. A typical preparation process for PANI composite is as follows: 10 mL distilled aniline and 10 mL HCl were added to 100 mL distilled water and the mixture was allowed to pre-cool. A calculated amount of [Co(mea)₂(H₂O)₂Cl₂] complex and ammonium persulphate was slowly added to the pre-cooled mixture upon constant stirring for about 3 h at a temperature maintained between 0–5 °C. The mixture was allowed to react for 24 h. A dark green precipitate obtained from the above reaction was washed repeatedly in the filtering funnel with distilled water. The precipitate was then dried in an oven at 40 °C for 24 h.

2.5 Material preparation for corrosion study

The material used for corrosion study is mild steel obtained from the mechanical workshop of the institute. The mild steel sheet of 1 mm thickness was mechanically press-cut into 5 × 5 cm coupons. Mild steel was found to corrode in higher concentrations of HNO₃. It was attributed to the fact that the rate of a chemical reaction increases with increase in concentration (Ita and Offiong 1997; Onuchukwu and Trasatti 1994). The test solution prepared was 3 M nitric acid solution using standard procedure in 10% brine solution maintained at pH 2. An excess amounts of *N*-methyl-pyrrolidone was added to calculate the amount of polyaniline and polyaniline cobaltmonoethanolamine complex separately, so as to make the slurry of these materials for coating on coupons separately. The coatings on the coupons were obtained by dip-coating method, which involves dipping the coupons in the slurry for a period of 1 h followed by air drying. The thickness of films was in the range of 0.8–0.97 mm. All reagents were of AR grade and distilled water was used for the preparation of all solutions.

2.6 Corrosion growth and weight loss measurements

Previously weighed coupons of mild steel were immersed in beakers containing 10 mL of test solution maintained at room temperature. The coupons were retrieved at 24 h intervals progressively for 168 h (7 days). The difference in weight was noted as the weight loss in grams. The corrosion attack in nitric acid is very significant because nitric acid is known to be a strong oxidizing agent. The corrosion of mild steel sample in HNO₃ solution is attributed to the presence of water, air and H⁺, which accelerates the corrosion process. The primary displacement of

H⁺ ions from the solutions is followed by HNO₃ reduction rather than hydrogen evolution, since the acid reduction leads to a marked decrease in free energy. The reaction can be summarized as follows

This reaction leads to the evolution of nitrogen (II) oxide and production of Fe(NO₃)₂, which led to further colouration of the medium. The SEM of the sample on which corrosion was grown was taken before and after coating with PANI and its composite.

3. Results and discussion

3.1 Elemental analysis

The complex formed was analysed for C, H and N and the empirical formula for the complex was found to be [Co(mea)₂(H₂O)₂Cl₂]. The observed percentages of C, H and N are 10.67, 4.90 and 6.20%, respectively, against the calculated percentages of C = 10.57, H = 4.85 and N = 6.16%.

3.2 Optical absorption studies

UV–Vis spectra of (a) pure PANI, PANI doped with (b) 20% [Co(mea)₂(H₂O)₂Cl₂] complex, (c) 40% [Co(mea)₂(H₂O)₂Cl₂] complex, (d) 60% [Co(mea)₂(H₂O)₂Cl₂] complex and (e) pure [Co(mea)₂(H₂O)₂Cl₂] complex are shown in figure 1. The spectra of pure PANI (figure 1a) shows two distinct peaks at 291 and 352 nm, which are attributed to the π – π^* electron transition of the benzenoid

Figure 1. UV–Vis spectra of (a) pure PANI, (b) PANI doped with 20% [Co(mea)₂(H₂O)₂Cl₂] complex, (c) PANI doped with 40% [Co(mea)₂(H₂O)₂Cl₂] complex, (d) PANI doped with 60% [Co(mea)₂(H₂O)₂Cl₂] complex and (e) pure [Co(mea)₂(H₂O)₂Cl₂] complex.

segment and polaron- π^* transitions, respectively. A hump of 641 nm is observed, which is because of the π - π^* electron transition of the quinoid segment. The transitions are matching with the reported results (Koul *et al* 2001). As the concentration of dopant is increased from 20 to 100%, prominent and significant changes are observed. In a sample with 20% dopant concentration, the peaks due to the π - π^* electron transition of the benzenoid segment and polaron- π^* transitions seem to combine with each other. The peak at 291 nm is shifted to 334 nm, which is in continuation with 352 nm peak. The hump observed at 641 nm is increasing its intensity and is reflected as a broad peak with a maximum at 638 nm, which is due to π - π^* transition of the quinoid segment. In sample with 40% dopant concentration peak due to π - π^* transition of benzenoid segment is appearing separately at 292 nm with a slight shift and peak due to polaron- π^* transition is appearing at 322 nm with a significant shift. Interestingly, the peak due to π - π^* transition of quinoid segment is disappearing here. As dopant concentration is increased by another 20%, i.e. sample with 60% dopant concentration, the peak due to π - π^* transition of benzenoid segment is shifted to a higher wavelength side, i.e. 304 nm and peak due to polaron- π^* is appearing at 321 nm, while as peak due to π - π^* transition of quinoid segment is missing here also. With 100% dopant concentration, i.e. in pure $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex, a single peak at 230 nm is observed, which can be attributed to MLCT transition. Therefore, on comparing the UV-Visible spectra of samples with varying concentration of dopant, interaction with the PANI and $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex is confirmed. Beyond 20% dopant concentration, transition due to π - π^* of the quinoid segment is lost. For effective conjugation and transition, 20% concentration of dopant proves to be a limiting concentration.

3.3 FT-IR characterization

FT-IR spectra of (a) PANI, (b) $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and (c) PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ composite are shown in figure 2. PANI shows a hump at 3305 cm^{-1} because of N-H stretching. The strong peak at 2922 cm^{-1} , because of C-H stretching is observed. This absorption is also as a result of overtones or combination of some modes of benzene and quinoid units in PANI. A weak peak at 2852 cm^{-1} is observed because of C-H stretching. The absorption peaks observed in the region of 1600 – 1450 cm^{-1} are because of aromatic ring breathing, N-H deformation and C-N stretching. The peak at 1590 cm^{-1} is because of stretching of $\text{N}=\text{Q}=\text{N}$ in PANI. A weak peak at 1377 cm^{-1} is also present in PANI. The peak at 1164 cm^{-1} in case of PANI can be because of a mode of $\text{N}=\text{Q}=\text{N}$. The peak at 830 cm^{-1} in PANI is because of C-H out of plane bending.

The complex formed is assigned molecular formula, $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$, on the basis of elemental analysis.

Further FT-IR shows the presence of different moieties as well. In case of this complex, we expect the vibrational frequencies due to ethanolamine, alcohol and amine group. Alcohol group involves O-H stretch, which appears at 3349 cm^{-1} in alcohols. Moreover, we observe C-C-O symmetric stretch at about 817 cm^{-1} and O-H in plane and out-of-plane bending vibrations at 1309 and 655 cm^{-1} , respectively, since there is water present as a ligand in the complex which is clearly supported by FT-IR. Though, the appearance of O-H stretch due to H_2O at about 3446 cm^{-1} is similar in alcohols, but the presence of water is very clear from absorption peak at 1627 cm^{-1} due to scissoring of two O-H bonds. This vibration is unique to water only, therefore, the presence of this band along with the O-H stretch vibration at 3446 cm^{-1} is a very strong evidence of presence of water molecule as a ligand in the complex also. The presence of water molecules inside the coordination sphere as a ligand is confirmed from TG studies (figure 5b) also, where removal of two moles of water occur within the temperature of 20 – 275°C . The observed and calculated weight loss corresponds to 15.96 and 15.86% , respectively, therefore, clearly shows that water molecules are embedded inside the coordination sphere, thus, supports the elemental analysis results and empirical formula. The peaks at 1502 , 1116 , 1064 , 731 and 438 cm^{-1} are also observed in the complex, which can be because of $\delta\text{-CH}_2$, $\rho\text{-CH}_2$, $\nu(\text{C-N})$, $\nu\text{-C-O}$, $\tau\text{-CH}_2$, $\nu(\text{C-C})$ and $\nu(\text{M-N})$, respectively.

For successful synthesis of PANI composite with synthesized complex, we compare FT-IR of PANI

Figure 2. FT-IR of (a) PANI, (b) $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and (c) composite of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex with PANI.

(figure 2a), $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex (figure 2b) and PANI composite (figure 2(c)). PANI having a hump at 3305 cm^{-1} because of N–H stretching shows a significant shift of 149 cm^{-1} and appears at 3447 cm^{-1} in the case of composite. The strong peak at 2922 cm^{-1} , because of C–H stretching remains unchanged. The presence of complex as the dopant in the composite is evident from the observation that in case of complex, we observe the absorption peak due to $\nu(\text{O–H})$ of alcoholic group. This $\nu(\text{O–H})$ is also because of presence of coordinated water, which is further confirmed by appearance of a peak at 1627 cm^{-1} . This peak is also present in the case of composite with a less intensity and slight shifting at 1697 cm^{-1} , therefore, proves the presence of complex as a dopant in PANI composite. The presence of dopant in the composite is also evident from the appearance of finger print region absorption peaks like 721 cm^{-1} .

Therefore, from the discussion of FT–IR of pure PANI, $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and the composite of PANI with synthesized complex, the successful synthesis of composite of PANI with this complex is proved.

3.4 X-ray diffraction

Figure 3 shows XRD pattern of PANI $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex composite, respectively. From the XRD pattern of PANI (figure 3(a)), a hump is observed at around 20° . XRD pattern shows amorphous structure of the sample.

Figure 3. XRD spectra of (a) PANI, (b) $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and (c) composite of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex with PANI.

XRD pattern of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex (figure 3(b)) shows various sharp peaks with significant intensities showing compact structure, supporting the results from SEM. The observed data was fitted with Powder X software for structural analysis and the present complex shows monoclinic structure (space group $Pbca$) with lattice parameters, $a = 17.699\text{ Å}$, $b = 8.542\text{ Å}$ and $c = 28.12\text{ Å}$ and corresponding Bragg's angles are $\alpha = \gamma = 90^\circ$ and $\beta = 93.96^\circ$. The various observed parameters (obtained from this analysis) for this system are summarized in table 1. The XRD pattern of PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex composite also shows number of sharp and strong peaks at various 2θ values (figure 3c). Composite has retained peaks of complex at slightly shifted positions. However, these peaks are of low intensity as observed in free complex form. XRD data of composite is verifying the successful synthesis of PANI composite with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex. The composite diffraction data was also analysed by using above software and best fit was obtained with orthorhombic structure (space group $P2/c$) with lattice parameters, $a = 8.149\text{ Å}$, $b = 44.48\text{ Å}$ and $c = 25.82\text{ Å}$ and corresponding Bragg's angles are $\alpha = \beta = \gamma = 90^\circ$. Various parameters like interplanar distance (d), peak intensities, peak area, etc. are also put in tabular form in table 2.

It is quite indicative from the data that crystallinity of the PANI increases with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and make the PANI layers to be very close and consequently, the degree of crystallinity is increased. The increase in the crystalline nature causes an increase in the energy barriers to the segmental motion of the polymeric system. From composite, it is also evident that there are new diffraction peaks at about $2\theta = 15.10, 17.61, 20.45, 21.61, 28.74, 29.90$ and 36.94° , suggesting that the new phases possibility are formed due to the cross-linking of PANI with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex, which may be

Table 1. XRD data of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex.

Pos/ 2θ ($^\circ$)	d -spacing (Å)	Height	Area	FMHW/ 2θ ($^\circ$)
16.483	5.37368	34171.5	629519.5	0.3760
31.258	2.85924	8273.3	199996.1	0.5151
32.367	2.76373	31964.5	688348.2	0.4334
39.566	2.27590	42407.3	962900.6	0.4729

Table 2. XRD data of composite of polyaniline with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex.

Pos/ 2θ ($^\circ$)	d -spacing (Å)	Height	Area	FMHW/ 2θ ($^\circ$)
20.431	4.34326	32380.0	534741.2	0.3432
21.533	4.12348	32055.5	839530.3	0.5708
23.877	3.72369	17241.7	196454.6	0.2474
24.293	3.66097	14453.0	203591.0	0.2887
25.537	3.48526	29814.8	1437125.1	0.9614

Figure 4. SEM micrographs of (a) pure PANI, (b) $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and (c) composite of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex with PANI.

responsible for the formation of orthorhombic phase. Crystallite size (G) of complex and its effect on the grain size of PANI composite was calculated using Scherer's formula

$$G = k\lambda/\beta \cos \theta,$$

where K is Scherer's constant (its value is 0.9), λ the wavelength of X-ray used ($1.5406 \text{ \AA}$), θ the peak position measured in radian and β the full width at half maximum (FWHM) (in radian 2θ) located at 2θ . The calculated average crystallite size for complex and composite are about 51.466 and 52.323 nm , respectively.

3.5 Scanning electron microscope (SEM)

Figure 4 shows SEM images of PANI (figure 4a), $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex (figure 4b) and PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex composite (figure 4c), respectively. Surface morphology of PANI sample shows amorphous structure. SEM of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex is showing a very compact morphology, which has dominated the surface morphology of PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex composite, clearly showing that the composite has been synthesized successfully. Further, SEM image of composite is showing improvement in compactness.

3.6 Thermal analysis

TG/DSC of PANI, $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex, and composite of PANI with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex are shown in figure 5. TG of pure PANI (figure 5(a)) shows two transitions. The first transition starts from 18°C and ends at 85°C with an observed weight loss of 4.33% , which shows that moisture is embedded in the outer layers of the material. The second transition starts from 278°C and ends at 590°C , with a weight loss of 49.82% , which is because of release of organic moieties like C, H and N. In DSC, two endothermic peaks are observed for pure PANI. One having a peak temperature of 70.7°C and the other with a peak temperature of 264.3°C .

TG curve of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex (figure 5b) shows two transitions. The first transition starts from 20°C and ends at 275°C , with an observed weight loss of 15.96% , against calculated weight loss of 15.86% attributed to removal of two moles of H_2O . The second transition starts from 275.38°C and ends at 708.26°C with an observed weight loss of 27.16% , against a calculated weight loss of 26.88% because of removal of 2 moles of CH_2 , one mole of OH and one mole of NH_2 . The residue left behind is CoCl_2 at 708.26°C , which shows stability up to 800°C . The observed weight left is 56% , against calculated percentage of 57.24% .

DSC of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex also shows two transitions, out of which, one is endothermic starting from 20 to 100 °C with a maximum at 70 °C. The second transition is an exothermic transition which combines two transitions of TG curves, starts from 210 °C and ends at 671 °C with a maximum at 434 °C.

TG curve of the composite is shown in figure 5(c). The thermogram can be explained in two transitions. First transition starts from an ambient temperature and ends at 94.76 °C with a weight loss of 15.19%, which is due to

Figure 5. TG/DSC analysis of (a) PANI, (b) $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex and (c) composite of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex with PANI.

loss of moisture embedded in the layers of composite material as final temperature is below 200 °C. Whereas, in the composite, second degradation step has resulted into complete decomposition at 800 °C without any residue left implies that whole complex and PANI have resulted into the composite formation, however, thermal stability of the composite has increased.

On comparing TG of complex and composite, it is evident that in complex, the decomposition process ends at 700 °C with observed 56% residue against calculated weight of 57.24%. The presence of complex in the composite has resulted into enhanced thermal stability as the last transition of composite lasts up to 800 °C with complete decomposition.

3.7 *I-V characteristics*

I-V characteristic as shown in figure 6 exhibits non-linear behaviour for pure PANI and composite of PANI with 20% dopant concentration. From the *I-V* plot, it is evident that as the voltage increases, the change in value of current is significantly lower in pure PANI compared to composite with 20% dopant concentration. Also, it is evident from the graph that the curve corresponding to composite with 20% dopant concentration attains sharp sigmoidal shape showing semiconducting nature and hence, increase in current in the composite compared to pure PANI. In the present composite system, the polymerization of PANI with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex causes strong interfacial interactions between PANI and $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex crystallites, as suggested by FT-IR and XRD studies, thereby changing the molecular conformation of PANI from compact coil structure to an expanded coil-like structure. As a consequence, there is an enhancement in the current with voltage in the composite of PANI with 20% dopant concentration. As the concentration of dopant is increased to 40, 60 and 100%, the resistance increases to a large extent hence, showing insulating behaviour. The increase in current with voltage in composite with 20% dopant concentration only can also be attributed to the prominence

Figure 6. *I-V* plot of (a) pure PANI and (b) composite with 20% dopant concentration.

Figure 7. (I) Variation of weight loss (g) with time (days) for mild steel: (a) uncoated sample, (b) PANI-coated sample and (c) composite-coated sample. (II) Rate of corrosion with time (h) for mild steel: (a) uncoated sample, (b) PANI-coated sample and (c) composite-coated sample.

Figure 8. SEM micrographs obtained before and after corrosion in 3 M nitric acid solution: (a) uncoated steel sample before corrosion, (b) uncoated steel sample after corrosion, (c) steel sample coated with PANI, (d) PANI-coated steel sample after corrosion, (e) composite-coated steel sample before corrosion and (f) composite-coated steel sample after corrosion.

of π - π^* transition of the quinoid segment in this composite as shown in figure 1(b). However, in case of composites with 40 and 60% dopant concentrations, the same peak disappears hence, increase in resistance takes place.

3.8 Corrosion study

A steel sample of composition, copper 0.14%, manganese 0.35, silicon 0.17, sulphur 0.025, phosphorus 0.03% and iron 99.285% was taken as a reference material, SEM image of which is shown in figure 8(a). The significant corrosion growth in HNO_3 takes place at a concentration of 3 M and pH 2 for mild steel samples (Onuchukwu and Trasatti 1994; Ita and Offiong 1997) used as reference material as the conditions were optimized after carrying out experiments with different HNO_3 concentrations. Therefore, the uncoated material, PANI-coated material and composite-coated materials were allowed to corrode in the prepared test solution of HNO_3 and were analysed by the way of changes in weight and morphology. The weight loss measurement recorded as a function of time on different samples is shown in figure 7(I). It is clear from the figure that in uncoated steel sample, weight loss is maximum, whereas in case of PANI composite-coated steel sample, weight loss is minimum. This proves that the synthesised PANI composite acts as a corrosion inhibitor. The figure also reveals that the weight loss of steel samples increase with time. This observation is attributed to the fact that the rate of a chemical reaction increases as the exposure time is increased. In figure 7(II), corrosion rates of mild steel has been given. The corrosion rates of the samples were determined using the standard mathematical relation (Wranglen 1985; Fontana 1987; Vernon 1992).

$$\text{Corrosion rate (mpy)} = 534 W / \rho AT,$$

where W is the weight loss in mg, ρ the density in g/cm^3 , A the total surface area in cm^2 , T the exposure time in hours and mpy the mils per year. The measured density of material used is 78.7 g/cm^3 . Figure 7(II) shows that in uncoated steel sample, preferential corrosion is taking place in the early part. From the plot, it is also clear that the corrosion rates decrease with time, in case of PANI and PANI/composite-coated steel sample. However, the rate of corrosion in case of composite-coated sample is much less compared to that of PANI-coated steel sample. Thus, showing that PANI/composite coating is potent inhibitor for corrosion. This may be attributed to the fact that the composite film acts as a passive layer on the mild steel which prevents the mild steel from significant interaction with environment. As a result of growth of corrosion in steel samples, there would be significant change in surface morphology of the samples for which SEM images of uncoated, PANI-coated and PANI composite-coated samples before and after the growth of corrosion were taken. Figure 8(a-f), which shows that in case of

PANI-coated sample, the effect of corrosion is less than what is observed in uncoated mild steel surface. This prevention effect is looking more enhanced in case of samples coated with PANI composite material which proves that PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ composite improved the corrosion resistance properties of PANI.

4. Conclusions

The preparation of PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ composite was successfully performed by *in situ* polymerization method and incorporation of $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex in the polyaniline matrix was confirmed by optical absorption study, FT-IR, SEM, TG/DSC and XRD studies. Thermal analysis shows enhanced thermal stability of polyaniline. The polymerization of PANI with $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex causes strong interfacial interactions between PANI and $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex crystallites, also suggested by FT-IR and XRD studies, thereby changing the molecular conformation of PANI from compact-coil structure to an expanded-coil like structure. As a consequence, there is an enhancement in the conductivity of composite of PANI up to 20% dopant concentration. Results of the corrosion study showed that in 3 M HNO_3 solution, the effect of corrosion on mild steel coated with PANI/ $[\text{Co}(\text{mea})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ composite is much lower than that on mild steel-coated with pure polyaniline.

Acknowledgements

The authors are grateful to Prof. Rajat Gupta, Director, NIT, Srinagar and Dr S A Shah, Head, Department of Chemistry, NIT, Srinagar, for help and support.

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