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REVIEW

Enhancement of corrosion protection effect in mechanochemically synthesized Polyaniline/ MMTclay nanocomposites



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KEYWORDS

Polyaniline; Mechanochemical intercalation; Nanocomposites; Corrosion protection **Abstract** Nanocomposite material that consists of DBSA (dodecylbenzensulfonic acid) doped polyaniline (PANI) was prepared by solvent free mechanochemical intercalation method. Organic aniline monomer was first intercalated into the interlayer regions of Na-MMT (sodium montmorillonite) clay hosts and followed by one-step oxidative polymerization. The as synthesized polyaniline clay nanocomposites were treated with DBSA to get PANI-DBSA clay nanocomposites. PANI-DBSA clay nanocomposites in the form of coatings at different concentrations of DBSA on C45 steel were found much superior in corrosion protection over those of conventional polyaniline, based on the series of electrochemical measurement of corrosion potential, polarization resistance and corrosion current in 3.5% aqueous NaCl electrolyte. UV–visible spectroscopy, FT-IR and SEM studies confirm the formation of intercalated polyaniline clay nanocomposites inside the clay nanolayers.

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1. Introduction

Conducting polymers, such as polypyrrole, polythiophane, polyaniline, etc., consisting of conjugated electronic structures have received considerable attention recently because of many promising technological applications. Some specific conducting polymers e.g., polyaniline and its derivatives, have found to display interesting corrosion protection properties. In the past decade, the use of polyaniline as anticorrosion coatings had been explored as the potential substance to replace the chromium containing materials, which have adverse health and environmental concerns (Deberry, 1985; Wessling, 1991; Elsenbaumer et al., 1994; Wrobleski et al., 1994; Wessling, 1994; Wei et al., 1995). Wei et al. demonstrated the corrosion protection effect of polyaniline through a series of electrochemical measurements on the doped or undoped polyaniline coated cold rolled steel (CRS) under various conditions. Wessling et al. claimed a full mechanism that the corrosion protection of polyaniline on steel is attributed to an increase in the corrosion potential and to the redox catalytic property of polyaniline in the formation of passive layer of metal oxide.

Layered materials, such as smetite clays e.g., montmorillonite, attracted intense research interest for the preparation of polymer clay nanocomposites in the past decade, because of their lamellar elements displayed high in plane strength, stiffness as well as high aspect ratio (Pinnavaia, 1983). The olymer clay nanocomposites were found to enhance the gas barrier (Lan et al., 1994), thermal stability (Tyan et al., 1999), mechanical strength Wang et al., 1998) and fire-retardant (Gilman et al., 2000; Chan et al., 2000) properties of polymer clay nanocomposites. Recently, there are a number of reports on the preparation and properties for the lamellar nanocomposites of polyaniline with various layered materials (Biswas and Ray, 2000; Wu et al., 1996; Wang et al., 1998; Chao et al., 1994; Ginnelis and Mehrota, 1991; Choi et al., 2000; Wu et al., 2000). In this paper, we present the first evaluation of corrosion protection effect for the mechanochemically synthesized DBSA doped polyaniline clay nanocomposites on C45 steel. The electrochemical impedance measurements, polarization measurements and corrosion current in 3.5% NaCl electrolyte were

performed. The polyaniline clay nanocomposites were characterized by UV-visible spectroscopy, FT-IR, and SEM studies.

2. Experimental

2.1. Chemicals and materials

The monomer aniline was purchased from Lancaster, UK. Nmethyl -2- pyrrolidone (NMP), N-N-dimethyl formamide (DMF), chloroform (CHCl₃), dodecylbenzenesulfonicacid (DBSA) and ammoniumpersulfate ($(NH_4)_2 S_2O_8$) were purchased from SD fine, India. Montmorillonite clay was obtained from Aldrich, USA.

2.2. Instrumentation

2.2.1. UV-visible Spectrophotometry

All absorption spectra were collected by using Shimadzu, UV - 3100, Japan with a path length of 1 cm². The powdered samples were dispersed in N-methyl -2-pyrrolidone (NMP) for the UV–visible studies.

2.2.2. FT-IR spectra

FT- IR spectra were recorded by Perkin- Elmer spectrometer (FT-IR, 16PC) using KBr pellets. All the spectra were recorded against the background spectrum of KBr.

2.2.3. Scanning electron microscope (SEM)

SEM studies were observed by FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM) with EDAX EDS system. It was used to study the morphology of the various polymer clay nanocomposites.

2.2.4. Corrosion studies

In corrosion studies, a working electrode was made of mild steel (C45). Chemical composition of C45 steel (wt.%): C = 0.46, Si = 0.40, Mn = 0.65, Cr = 0.40, MO = 0.10, Ni = 0.40 and other constituents = 0.63. It was manufactured as cylinder of 10 mm height in way to function as disk electrode with exposed

area of 1.13 cm^3 , surrounded with Teflon tape. Before using, steel electrode was first polished on a sand paper of 1000 grade then on a polishing cloth with alumina slurry (13 µm). For drop coating of HCl doped PANI-MMT and PANI-DBSA on steel electrode the PANI-MMT nanocomposites are dissolved in chloroform, the steel electrode was previously polished with a fine emery paper (p1000) and with alumina slurry (13 µm).

2.2.5. Impedance measurements

Electrochemical impedance measurements were carried out in a one compartment cell containing 3.5 wt.% of sodium chloride solution at open circuit potential (OCP). C45 steel electrode (coated and uncoated) was used as working electrode. A saturated calomel electrode and gold sheet electrode were used as reference and counter electrodes, respectively.

The combination of a Solartron S11287 potentiostat and S11255 frequency response analyzer, both connected to a PC via IEE 488.2 connections was used to record electrode impedance date with modulation amplitude 5 mV in the frequency range between 0.1 Hz and 100 kHz. Evaluation of the impedance data was performed assuming equivalent circuit with Z view software.

2.2.6. Polarization measurements

Anodic polarization measurements were carried out under ambient conditions in a three electrode single compartment cell containing 3.5% NaCl. C45 steel electrode (coated and uncoated) and saturated calomel electrodes were used as working, reference and counter electrodes, respectively using a Solarton S11287 potentiostat connected to a computer via IEE 488.2 connections, measurements were carried out at a scan rate of 5 mV/s.

2.2.7. Preparation of sodium MMT

The montmorillonite of 6 g was dispersed in 400 mL aqueous acetone solution (1:1 by volume) and then treated with 600 mL aqueous sodium chloride (10 mM) at 50 °C for 24 h according to the literature method (Yashimoto et al., 2004) to yield sodium treated montmorillonite (Na-MMT) to extinguish the effect of other cations. After repeated washing by filtration, the clay was dried at 80 °C for 24 h, ground to a fine powder, dried again at 120 °C for further 24 h, and stored in a desiccator.

2.2.8. Preparation of PANI/MMT clay nanocomposites by mechanochemical method

The synthesis of the PANI and substituted PANI-MMT clay nanocomposites was carried out by mechanochemical intercalation method. The synthetic procedure for preparing PANI and various substituted PANI clay nanocomposites is as follows. The mixture of sodium MMT and anilinium chloride was mechanochemically ground with a mortar and pestle at room temperature with few drops of double distilled water for 10 min. The amount of added anilinium chloride was 4.6 mMol/g of MMT. After grinding, a sufficient amount of $((NH_4)_2S_2O_8)$ was added, the molar ratio of $((NH_4)_2S_2O_8)$ to anilinium chloride was 1.5. The mixture was added to the mortar and ground mechanochemically for 30 min (Mac Diarmid and Epstein, 1989). The polymerization lasted for 72 h at room temperature. After standing for 72 h, the obtained dark green powder was washed with double distilled water and repeatedly filtered the solution in Buchner funnel in order to remove the excess ((NH₄)₂S₂O₈), by products and sodium chloride produced by the cation of MMT and the anilinium cations of anilinium chloride. The washing was continued until the filtrate became colorless. The final product was washed with methanol, distilled water and followed by dilute HCl. The HCl doped lamellar polymer clay nanocomposites were obtained. The product was dried under vacuum at room temperature for 12 h and stored in a desiccator. The ratio of DBSA to aniline is increased to 5:1 (TIP-5), 7:1 (TIP-6) and 10:1 (TIP-7) respectively.

3. Results and discussion

3.1. UV-visible studies

Some of the preliminary studies show that the interaction and amount of anilinium ion were measured by UV-visible spectral studies (Wu et al., 2000). The UV-visible spectrum for the intercalated aniline was recorded using dilute suspension of aniline-MMT in NMP solution. Fig. 1(a) shows the UVvisible spectrum of aniline intercalated into the clay galleries. A sharp UV absorption peak was observed at 340 nm and is assigned for the $n \rightarrow \pi^*$ transition of natural aniline. The anilinium ion peak disappeared after mechanochemical intercalation of aniline- MMT in the presence of stoichiometric quantity of oxidizing agent, ((NH₄)₂ S₂O₈). Two new peaks were observed for the polyaniline one at 420 nm and other at 800 nm for HCl doped polyaniline clay nanocomposites (Fig. 1b). The ammonia treated polyaniline clay nanocomposites shows two new sharp peaks assigned for the $\pi \to \pi^*$ and the other at 650 nm was due to polaron $-\pi$ transition (Fig. 1c).

The amount of loading of anilinium ion within clay was measured by UV-visible spectral studies (Mac Diarmid and Epstein, 1989). The quantity of loading of anilinium ion within clay is higher in the case of mechanochemical encapsulated method when compared with solution based exchange reaction at an elevated temperature i.e. at 80 °C.

3.2. FT-IR studies

A FT-IR spectrum of synthesized PANI-MMT nanocomposites together with those of pristine MMT and pure PANI prepared by conventional chemical oxidative polymerization is presented in Fig. 2. The presence of conductive form of PANI in the clay was confirmed by FT-IR studies (Chan et al., 2001). The bands at 1600 and 1560 cm⁻¹ consist of benzenoid and quinoid form of polyaniline backbone and also these bands imply that the charge neutralization with the counter ion is present in the polyaniline chain. The peaks at 1305 and 1245 cm⁻¹ are associated with C–N stretching mode. The strong peak at 1041 cm⁻¹ and the peak at 912 and 840 cm⁻¹ are characteristic vibrations of MMT clay. In the higher frequency side a peak at 3250 cm⁻¹ is assigned for the N–H stretching vibrations (Fig. 2).

3.3. SEM micrographs

SEM micrograph of polyaniline clay nanocomposites by mechanochemical intercalation method with different PANI contents, together with pristine MMT clay was recorded. The observed SEM images show that the surface morphologies of PANI-MMT clay nanocomposites are strongly affected by the PANI content in the clay galleries (Fig. 3). SEM micrograph concludes the formation of polymer clay nanocomposites on clay lattices that are fibril in nature (Yeh et al., 2001).



Figure 1 UV-visible spectra of aniline (a), HCl doped polyaniline clay nanocomposite (b), polyaniline intercalated clay nanocomposites dedoped with dilute ammonia (c).

3.4. The anti-corrosion properties of mechanochemically synthesized PANI-DBSA clay nanocomposites

A soluble PANI which can dissolve completely in common organic solvents was synthesized. Chloroform was employed as a solvent to dissolve soluble PANI for drop-coating on C45 steel electrode surface. Anti-corrosion performance of mechanochemically synthesized PANI-DBSA was studied using EIM and polarization measurements.

3.4.1. Electrochemical impedance measurements

Fig. 4 shows the Nyquist diagrams for the bare C45 steel electrode and PANI coated (with different feed ratios of DBSA to aniline) electrodes recorded at OCP in 3.5% NaCl solution. The charge transfer resistance (R_{CT}), double layer capacitance (C_{DL}) and coating resistance (R_F) values were determined via curve fitting of impedance data using Z-view software and are given in Table 1. Two capacitive depressed curves are also observed in the Nyquist diagrams as in the case of PANI-





Figure 2 FT-IR spectrum of pristine clay (a), polyaniline clay nanocomposite (b) and chemically synthesized polyaniline (c).

MMT coated C45 steel. This behavior, as described in section 4.6.1, can be interpreted using an equivalent circuit containing R_S , C_C , C_{DL} , R_F and R_{CT} as shown in Fig. 5. A good barrier allows very little current flow showing high resistance during impedance measurements. The protective effect of PANI-DBSA is immediately obvious as the R_{CT} value for PANI coated electrodes shows significant increases compared to the bare C45 steel electrode (Table 2).

Both resistance and capacitance values increase with increasing thickness of the PANI film. All values for PANIs reported in Table 2 are beyond this threshold. Repeated experiments show that the $R_{\rm CT}$ and thereby the corrosion efficiency is influenced by the amount of DBSA in the feed. TIP-6, where DBSA to aniline ratio is 7, shows relatively better corrosion protection. In the case of electrochemically coated PANI (syn-



Figure 4 Nyquist plots of the bare C45 steel electrode (\ddagger) and electrode coated with TIP-5 (\Box), (\bigcirc) TIP-6 and (Δ) TIP-7 recorded at OCP in 3.5% NaCl. Solid lines indicate the fitting curve and the magnified portion of TIP-6 at high frequency is shown in the inset.

thesized in the presence of mineral acids), Cl^- ions and water can easily permeate through the film due to the porosity of the film leading to a lower film resistance. When the ratio of DBSA to aniline is increased to 5:1 (TIP-5), 7:1 (TIP-6) and 10:1 (TIP-7) the morphology changes to porous network type and compact film type, respectively.

However, R_{CT} values in the present study could not be correlated to the bulk morphology of the polymer. TIP-5, TIP-6 and TIP-7 exhibit fiber porous network and compact film evidenced by SEM. One can expect better corrosion protection performance by TIP-7 where ingress of corrosive ions such as Cl⁻ is unfavorable. However, R_{CT} values in the present work suggest better anti-corrosion performance for TIP-6 with porous morphology. Therefore, we assume that morphology of post processed material is different from bulk morphology which was later confirmed by TEM studies. Correlation of the values of EIM parameters such as R_{CT} , C_{DL} , etc. with the corrosion protection effect and with already reported results is a difficult task as the results vary widely and are strongly influenced by the composition of the steel, corrosion environment, nature of coating (ES or EB) and top coat (if present).



Figure 3 SEM images of pristine MMT clay (a), PANI clay nanocomposites by 4.6 mMol/gram of MMT (b).

Coating	[DBSA]	$E_{\rm corr, SCE} ({\rm mV})$	$b_{\rm a}~({\rm mV~dec}^{-1})$	$i_{\rm corr}$ (µA cm ⁻²)	$R_{\rm p}\left(\Omega\right)$	C_R (MPY)	
Uncoated	_	-571	40.0	98.80	92	40.12	
TIP-5	5	-506	52.5	15.30	718	6.21	
TIP-6	7	-499	47.4	13.79	805	5.60	
TIP-7	10	-515	49.5	19.04	505	7.74	

Table 1 E_{corr} , b_a , i_{corr} , R_p and C_R values calculated from Tafel plots for bare and PANI-DBSA coated C45 steel electrode in 3.5% NaCl.



Figure 5 Nyquist plots of TIP-6 coated C45 steel electrodes recorded at OCP in 3.5% NaCl (\bigcirc) 0 h, (\Box) 24 h, (Δ) 48 h and (\precsim) 72 h of immersion time.

Figure -91 shows Nyquist diagrams of PANI (TIP-6) coated C45 steel in 3.5% NaCl recorded after different time intervals. The shape of the Nyquist diagrams is not much affected up to 72 h. The R_{CT} values decrease with time but are still higher than with the uncoated electrodes. Bereket and coworkers (Bereket et al., 2005) have also observed such

Table 2 $R_{\rm S}$, $R_{\rm F}$, $C_{\rm C}$, $R_{\rm CT}$ and $C_{\rm DL}$ values from impedance data for bare and PANI-DBSA coated C45 steel electrodes at various exposure times in 3.5% NaCl.

Coating	t/h	$R_{\rm c}/{\rm O}$	<i>C</i> _c /µE	$R_{\rm E}/O$	C _{P4} /mF	$R_{\rm CT}/O$
country	<i>t</i> /11	NS/ 22	00/μ1	TCF/32	CDL/III	ACT/32
Uncoated	0	3.5	-	_	4.2	84.5
TIP-5 ^a	0	4.1	16.4	1.58	2.9	696
	24	4.5	3.9	1.69	3.2	650
	48	4.3	4.9	1.80	2.2	635
	72	4.3	4.9	1.76	2.5	378
TIP-6 ^a	0	4.5	11.9	1.12	4.3	880
	24	4.6	13.5	1.17	4.3	586
	48	4.6	10.6	1.18	4.1	559
	72	4.7	10.5	1.12	3.4	356
TIP-7 ^a	0	4.3	8.3	1.44	3.1	505
	24	3.4	1.9	0.75	1.6	449
	48	3.3	2.2	0.76	1.6	440
	72	4.6	4.7	1.13	2.7	425

^a TIP-5, TIP-6 and TIP-7 denote PANI-DBSA samples where the mole ratios of DBSA/aniline in the feed were 5:1, 7:1 and 10:1, respectively.

Table 3 E_{corr} , b_a , i_{corr} , R_p and C_R values calculated from Tafel plots for bare, passivated and PANI-MMT coated C45 steel electrode in 3.5% NaCl.

Coating	E _{corr, SCE} (mV)	$b_{\rm a}$ (mV dec ⁻¹)	$i_{\rm corr}$ ($\mu A \ {\rm cm}^{-2}$)	$R_{\rm p}$ (Ω)	C_R (MPY)
Uncoated	-571	40.0	98.80	92	40.12
Passivated	-586	39.2	95.50	110	38.80
PANI-MMT	-520	35.5	19.90	519	8.10

a decrease in R_{CT} values for PANI coated 304–stainless steel electrodes. PANI film was generated by electro polymerization of aniline in acetonitrile containing tetrabutylammonium perchlorate and perchloric acid. We believe that soluble PANI DBSA protects C45 steel against corrosion through the formation of a passive layer which could be easily visualized as a gray oxide film underneath the PANI coating (Spinks et al., 2002).

3.4.2. Polarization measurements

The E_{corr} , i_{corr} and Tafel slopes were determined from the Tafel plots of potentiodynamic measurements by extrapolation. The values of $R_{\rm p}$ and $C_{\rm R}$ were calculated using Equation -1 and 2. The E_{corr} , i_{corr} , b_{a} , R_{p} and C_{R} values for uncoated and PANIcoated C45 steel electrodes are summarized in Table 3. The corresponding Tafel plots for bare C45 steel and PANI-DBSA (different feed ratios of DBSA to aniline) coated electrodes are shown in Fig. 6. The corrosion potential of the PANI coated electrode was anodically shifted by 66-72 mV compared to the bare electrode whereas the corrosion current and the corresponding corrosion rate are drastically reduced (Table 1). An anodic shift of 2 mV was reported for PANI-DBSA coated 08U-steel electrodes in 3.5% NaCl by Pud et al., 1999. They cast emeraldine base form of PANI dissolved in NMP on the steel substrate and re-doped it with DBSA in xylene. However, they have found that PANI redoped with CSA and DBSA increases the corrosion current in 3.5% NaCl thereby showing an increase in the corrosion rate.

$$C_{\rm corr} = \frac{C_R \cdot A \cdot d}{0.129.(EW)} \tag{1}$$

$$i_{\rm corr} = \frac{b_a \cdot b_c}{2.303(b_a + b_c)} \cdot \frac{1}{R_p \cdot A}$$
(2)

The better performance in our case may be attributed to the stronger complexation of DBSA with the N-atoms of the polymer backbone. An increase in $E_{\rm corr}$ up to 1650 mV was reported by several investigators. The magnitude of potential



Figure 6 Tafel plots of bare (a) and PANI-DBSA [TIP-5 (b), TIP-6 (c), and TIP-7 (d)] coated C45 steel electrode in 3.5% NaCl.

shift and corrosion current strongly depends on the processing technology, composition of the steel and an insulating polymer top-coat.

The polarization resistances (R_p) calculated from Tafel plots (Table 1) are almost in agreement with the R_{CT} values calculated from impedance data (Table 2). A significant increase in R_p after PANI coating confirms its protective nature against the corrosion of C45 steel. The E_{corr} and i_{corr} values are influenced by the ratio of DBSA to aniline in the feed. TIP-6 having a feed ratio of 10 shows better corrosion performance over the others which was also confirmed by EIM studies. The hydrophobic nature of the long non-polar chain of DBSA, its strong complexation with PANI backbone and poor wettability of polymer in aqueous electrolyte hinder the rate of anion exchange which further reduce the ingress of hydrophilic (and pitting) Cl⁻ ions into the polymer film thereby enhancing corrosion performance (Shreepathi and Holze, 2006).

The poor ingress of Cl⁻ ions into PANI films has been confirmed by in situ UV-visible spectroscopy. UV-visible spectra of PANI-DBSA drop coated onto ITO-coated glass as a function of applied potential progressively shifting in anodic direction have been studied. Spectral responses of PANI, both in acidified (0.5 M H₂SO₄) and acid free (0.1 M KCl), are similar except for the fact that LE-EM-PN transitions occur at lower positive potential in case of 0.1 M KCl. Generally, PANI is electrochemically inactive in acid free aqueous electrolytes. The above results indicate that insertion of Cl⁻ ions into PANI is hindered by hydrophobic nature of the film.

4. Conclusion

The polyaniline clay nanocomposites were successfully synthesized by mechanochemical intercalation method and the corrosion protection aspects of their PANI coating in 3.5% NaCl solution were investigated by polarization technique and electrochemical impedance measurements. The results of present study show that mechanochemically synthesized PANI coatings show better anti corrosion performance than conventional PANI/MMT coatings. The corrosion potential of above prepared PANI/MMT coated C45 steel is positively shifted when compared to the bare C45 steel. The molar feed ratios of DBSA to aniline influence the anticorrosion performance of PANI. The protection of C45 steel against corrosion in 3.5% NaCl can be achieved more effectively when the synthesis was carried out with a feed ratio of DBSA to aniline was 1:7.

The FT-IR and UV-visible spectral studies concluded that the maximum exchange of aniline ion was achieved by this method and the rate of polymerization of aniline could be controlled in a sequential manner. The SEM images show that the surface morphologies of PANI-MMT clay nanocomposites are strongly affected by the PANI content in the nanocomposites. It is concluded that PANI within clay lattice is fibril in nature.

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