Research Article

Potential Application of Polymer – Clay Composite as Corrosion Inhibitor for Low Carbon Steel in Acidic Media

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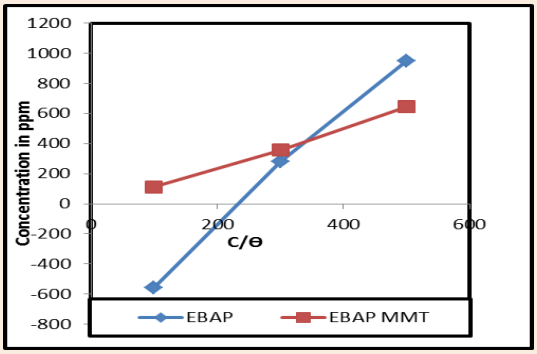
Abstract

A novel polymer – MMT composite has been prepared and evaluated as excellent corrosion inhibitor for mild steel by gravimetric and electrochemical studies. The prepared composite and the polymer were subjected to thermal and spectral studies. The X-ray diffraction result for polymer - MMT composite showed the intercalation of polymer between the clay layers. The FT-IR result shows the successful incorporation of MMT clay in the polymer. The inhibitors obey Langmuir isotherm indicating that inhibition occurs via adsorption of a monolayer on the mild steel surface. Thermodynamic and kinetic parameters have been evaluated.



Keywords: Polymer, Composites, XRD, Corrosion inhibition

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Introduction

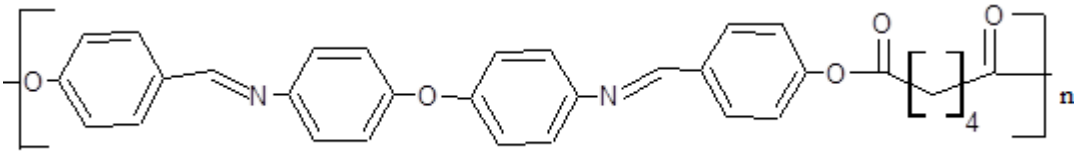
Corrosion of iron and steel in acidic aqueous solutions is one of the major areas of concern in many industries where in acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. The application of nanotechnology in the corrosion protection of metals has recently gained momentum. Nano composites have also proven to be effective alternatives to other hazardous and toxic compounds.

Composites are made from two or more materials with significantly different physical and chemical properties which remain separate and distinct at the microscopic or macroscopic scale within the material. In nano composites, nanoparticles (clay, metal, carbon nanotubes, etc.) act as fillers in a matrix.

Clay composites are the materials in which major component of the material is clay in combination with other materials like metals, polymers etc. Recently, the development and characterization of nanostructured polymer-clay composites has received special attention because of their advantages in comparison to the traditional polymer composites. Minimal additions of nano clay enhance mechanical, thermal, dimensional and barrier performance properties significantly because of the large contact area between polymer and clay on a nano scale [1].

Experimental Details

The polymer was synthesized by condensation of between diacid (Adipic acid) and the diol monomer and the structure of the polymer is represented as,



EBAP

Polymer- MMT composite preparation
Cationic exchange of MMT clay

The alkyl ammonium salt was dissolved in water obtaining 0.1 mol l^{-1} solutions. The suspension of 0.5 g montmorillonite and 10 ml of the water solution of alkyl ammonium cation was used for the sorption procedure performed in two modes. The first set of the suspensions was shaken thoroughly for 2.5 hr at room temperature. All suspensions were centrifuged for 20 min (9000 rpm), the obtained solids were twice washed out in 50 ml of ethanol – water mixture (1: 2, v/v) and then in ethanol (97 %). The washed out solids were separated by centrifugation for 10 min (9000 rpm). The modified Montmorrilonite was dried at room temperature [2].

The organo clay is first suspended in the solvent. Then, the polymer, dissolved in the solvent, was added to the solution whereby it gets intercalated between the swollen clay layers. The last step consists in removing the solvent by evaporation usually under vacuum.

Mild steel specimen preparation

For the weight loss measurements rectangular mild steel specimens (Composition: carbon-0.084%, Mn-0.369%, P-0.025%, Cr-0.022%, Ni-0.013% and Fe-remainder) of size 3 cm X 1cm X 0.1cm were used. For the electrochemical measurements, a cylindrical rod of the same mild steel specimen, embedded in Teflon with an exposed area of 0.785 cm^2 was used.

Methods

Weight loss measurements

Pretreated and pre-weighed mild steel specimens were immersed in 1M Sulphuric acid without and with varying concentrations of the inhibitors at 30-60º C for 3 hr. The specimens were reweighed. From the mass loss the inhibition efficiency (IE) was calculated.

Electrochemical measurements

Polarization and impedance measurements were carried out with Ivium compactstat (potentiostat/ galvanostat) using three electrode cell assembly. Polarization experiments were carried out in the potential range of -200 to +200mV with respect to open circuit potential at a scan rate of 1mV/sec. EIS measurements were carried out by sweeping the frequency from 10 KHz to 0.01Hz with signal amplitude of 10mv/sec using AC signal at the OCP.

XRD and Thermal studies

X-ray diffraction studies were carried out for polymer and the composite using XRD 6000 (Shimadzu, Japan). Thermal analysis of the polymer and the composite was done using Perkin Elmer system in CUSAT, Kochi.

Results and Discussion

Characterization:

The synthesized polymer was characterized by IR spectra**.** The polymer show strong bands around 3410 cm^{-1}, 1690 cm^{-1} and 926 cm^{-1} corresponding to –NH-, -CH=N- and –C-O-C- linkage respectively.

Weight loss studies

The inhibition efficiency of the polymer and the composite for the corrosion of mild steel in 1M sulphuric acid obtained from the three methods are given in Table-1.

It is evident that IE increased with increase in concentration of the inhibitor and the composite shows excellent performance even at low concentration studies. This may be attributed to sufficient adsorption and wider coverage by the composite molecules compared to the polymer.

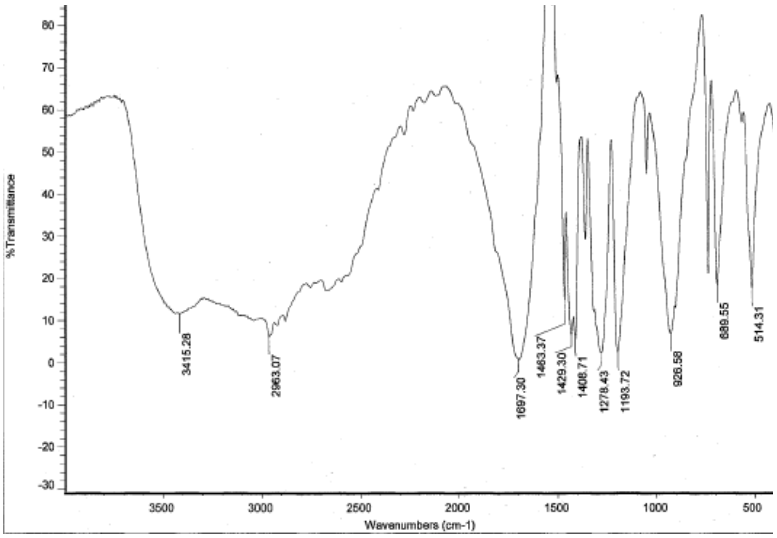


Table 1 Inhibition efficiencies at various concentrations of the inhibitors for corrosion of mild steel in 1M H_2SO_4 obtained by various methods at 30±1° C

Inhibitor	Concentration (ppm)	Inhibition Efficiency (%)		
		Weight loss studies	Polarization measurements	AC impedance spectra
EBAP	100	-18.00	17.60	43.78
	300	30.20	22.30	56.70
	500	79.61	30.46	60.07
EBAP-MMT	100	88.95	43.31	60.90
	300	90.59	54.75	74.43
	500	97.87	57.92	80.35

Effect of temperature

The effect of temperature on the IE of the polymer and composite as obtained by weight loss method is given in Table-2. IE decreased with increase in temperature. The thermodynamic parameters obtained from the results are given in Table-3. E_a values obtained from the slope of Arrhenius plot [Fig. 2] suggest that the inhibitors are adsorbed on the steel surface by physisorption [3]. ΔG values confirm the spontaneity of adsorption process [4]. ΔH and ΔS values show that the adsorption is exothermic and represent a disorder in going from reactant to activated complex in the corrosion process [5].

Adsorption isotherm

To confirm the formation of monolayer of the inhibitor on mild steel surface, the surface coverage values obtained by weight loss method were tested by fitting various isotherms. The best fit was obtained for Langmuir isotherm [Fig-3].

Table 2 Inhibition efficiencies of the inhibitors for corrosion of mild steel in 1M H_2SO_4 obtained by weight loss measurement at higher temperature at 500 ppm

Temperature (K)	Inhibition efficiency (%)	
	EBAP	EBAP-MMT
303	79.61	97.87
313	77.43	93.23
323	67.71	73.18
333	-46.38	70.31

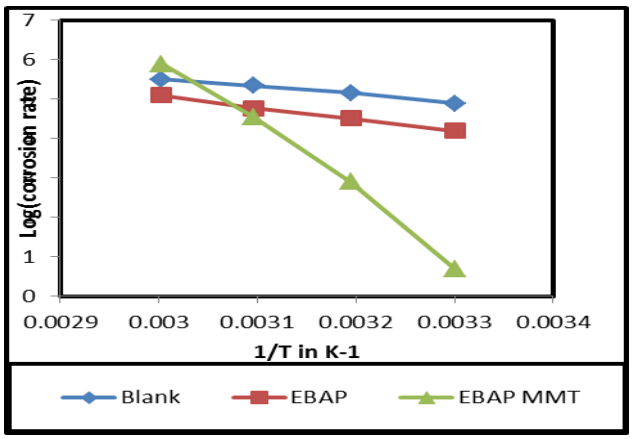


Figure 2 Arrhenius plot

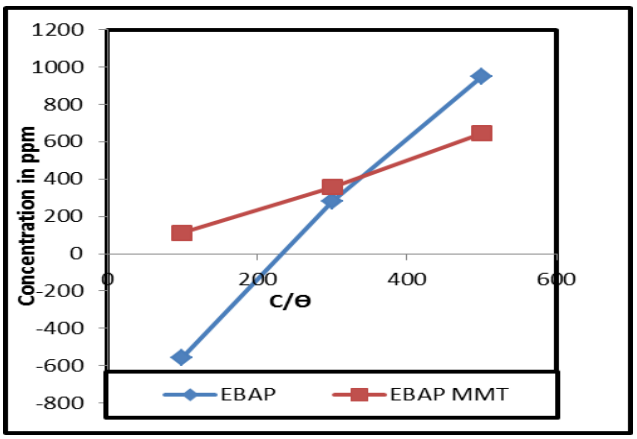


Figure 3 Langmuir plot

Table 3 Kinetic and thermodynamic parameters of the inhibitors

Inhibitor	ΔH^{o}_{ads} kJ/mol	ΔS^{o}_{ads} kJ/mol	$-\Delta G^{o}_{ads}$ kJ/mol				Ea (J)
			303 K	313 K	323 K	333 K	
Blank	-	-	-	-	-	-	58.63
EBAP	1759.97	4.36	13.09	13.72	14.75	18.34	59.19
EBAP-MMT	520.727	3.06	13.717	17.053	20.654	21.454	60.71

AC impedance studies

The effect of the inhibitor concentration on the impedance behavior of mild steel in 1 M H_2SO_4 solution has been studied. Nyquist plot of EBAP is given in Fig.4. It is clear from the figure that the impedance spectra obtained is semicircular in shape. This indicates the corrosion of the mild steel in 1 M H_2SO_4 solution is mainly controlled by a charge transfer process.

The charge transfer resistance (R_t) can be calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [6]. The values for the current inhibitors are given in Table [4]. R_t increases in the presence of inhibitors showing that the polymer and the composite inhibit corrosion. The C_{dl} values obtained by impedance study decreased with increase in concentration.

Table-4 AC impedance data of mild steel in presence of polymers at various concentrations in 1M H_2SO_4

Inhibitor	Inhibitor concentration (ppm)	R_t (ohm cm^2)	C_{dl} (µF/ cm^2)	Inhibition Efficiency (%)
Blank	-	11.3	33.6	-
EBAP	100	20.1	27.6	43.78
	300	26.1	22.2	56.70
	500	28.3	19.9	60.07
EBAP-MMT	100	28.9	22.2	60.89
	300	44.2	21.7	74.43
	500	57.5	18.8	80.34

Polarization studies

Table 5 Potentiodynamic polarization data of mild steel in presence of inhibitors at various concentrations in 1M H_2SO_4

Name of the inhibitor	Inhibitor Concentration (mM)	Tafel slopes (mv / dec) ba	bc	$-E_{corr}$ (mV)	I_{corr} (µAmp/cm^2)	Inhibition Efficiency (%)
	Blank	52	112	467.40	568.0	-
EBAP	100	59	131	468.0	430.7	17.60
	300	63	118	441.3	509.1	22.30
	500	53	168	395.0	474.8	30.45
EBAP-MMT	100	68	135	495.7	322.0	43.30
	300	63	142	487.4	257.0	54.75
	500	63	144	484.7	239.0	57.92

Fig-5 is the Tafel plot for mild steel in 1M sulphuric acid with various concentrations of the inhibitors. The corrosion kinetic parameters derived from the plots are listed in Table-5.The values suggest that the inhibitors are mixed type, inhibiting both cathodic and anodic corrosion processes.

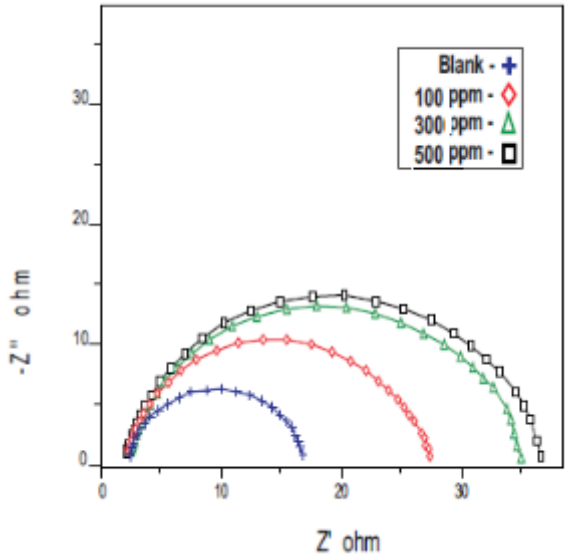


Figure 4: AC impedance spectra of mild steel in presence of EBAP

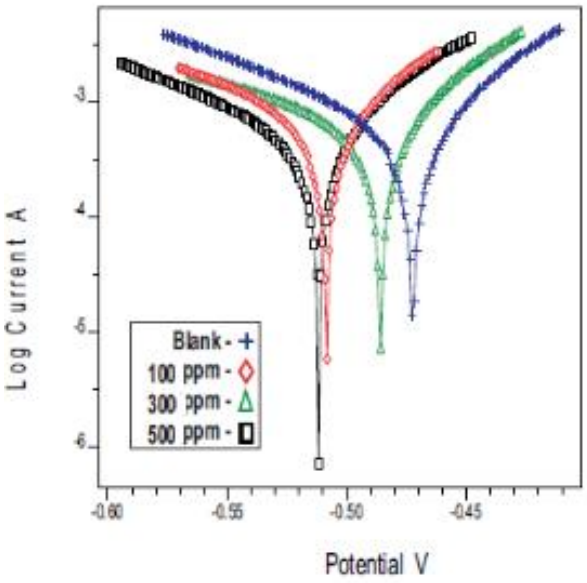


Figure 5: Tafel slope of mild steel in presence of EBAP

XRD Studies

Fig-6 and 7 show the XRD curves of the polymer and composite. It is evident that the composite is crystalline and dense. The polymer shows broad and less intense band in the XRD (Fig:6) showing that it is semi crystalline. The XRD pattern of composite (Fig: 7) shows sharp peaks indicating crystalline structure. The sharp crystalline peak for pure MMT at 2Θ =28º is seen in the composite [7]. It is evident from the XRD studies that there is interaction between the clay and polymer making the matrix stronger. Particle size of the composite (54nm) has been calculated by Scherrer equation using FWHM. According to Kato etal [8], ~~that~~ the polar groups in the polymer will interact with the polar group in the nano clay and the interaction decreases the d-spacing in the composite producing stronger denser composite. Hence it can form a compact protective film on the mild steel surface compared to the porous [9] amorphous polymer.

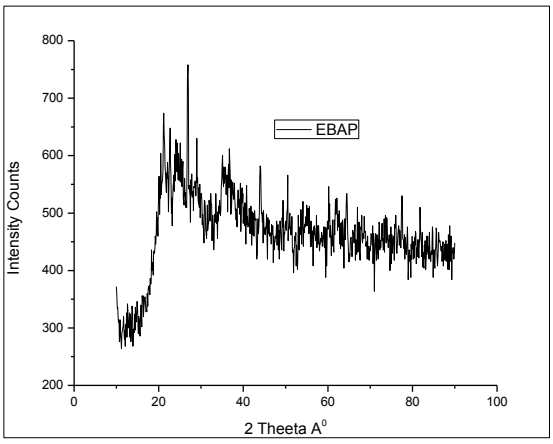


Figure 6: XRD of EBAP polymer

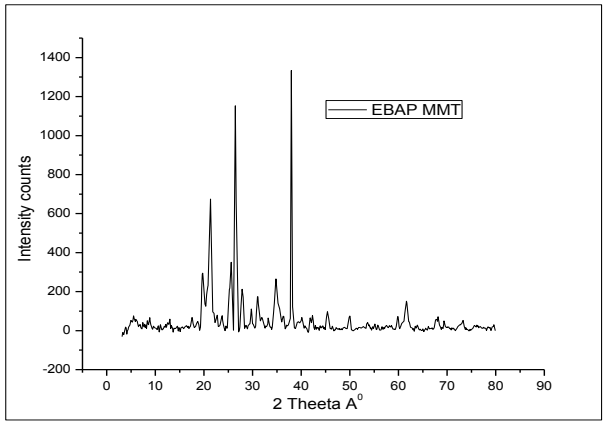


Figure 7: XRD of EBAP-MMT composite

Thermal studies

The thermograms of polymer and the composite are shown in Fig: 8 & 9. From the TGA curve it is evident that the polymer shows complete decomposition at 262ºC but the composite shows quite good stability upto 550ºC. In the

composite, the weight loss around 150ºC is due to the loss of physically adsorbed moisture. The mass loss around 550ºC may be due to the loss of lattice water. From the present result it can be predicted that the thermal stability of polymer-clay composite is enhanced due to the attractive coulomb interaction between the positive group of Polymer layer and negatively charged surface of the clay layer [10].

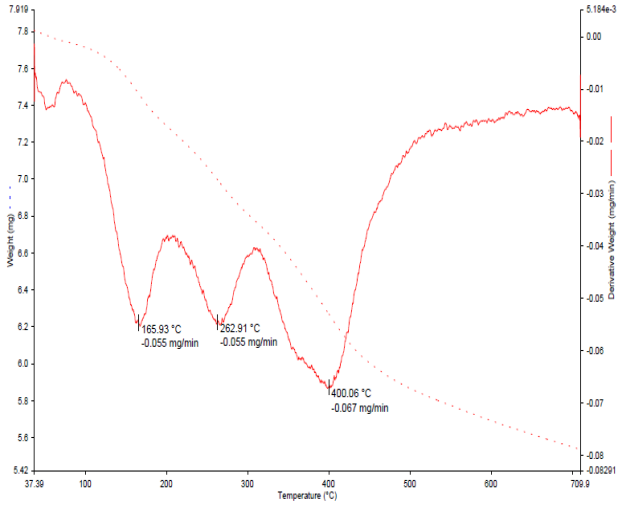


Figure 8 TGA curve of EBAP-MMT Composite

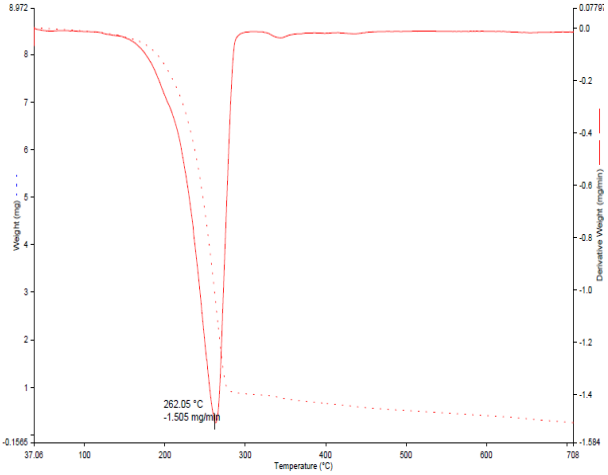


Figure 9 TGA curve of EBAP polymer

Conclusions

MMT clay has been successfully utilized to produce a potential composite useful as an excellent corrosion inhibitor for mild steel.
The composite can be easily prepared and the cost will be low and eco-friendly as the raw material is clay.
The composite inhibit the corrosion of mild steel in 1M H_2SO_4 by the adsorption mechanism and the adsorption obeys Langmuir isotherm.
The composite behave as mixed type inhibitor.

Acknowledgement

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References:

[1] Rajani Srinivasan, Advances in Materials Science and Engineering, Vol 2011 (2011)
[2] Zuzana Navratilova, Petr Wojtowicz, Lenka Vaculíkova and Vera Sugarkova, Acta Geodyn. Geomater., 4(3), 59-65, (2007)
[3] Q.B. Zhang, Y.X.Hua, Electrochimica Acta, 54,1881‑1887, (2009)
[4] A. A. Khadom, A. S. Yaro, A. S. AlTaie, A. A. H. Kadum, Portugaliae Electrochimica Acta, 27(6), 699-712, (2009)
[5] H. Zarrok, A. Zarrouk2, R. Salghi, M. Assouag, B. Hammouti, H. Oudda, S.Boukhris, S. S. Al Deyab and I. Warad, Der Pharmacia Lettre, 5 (2), 43-53, (2013)
[6] D. Ben Hmamou, R. Salghi, A. Zarrouk, M. Messali, H. Zarrok, M. Errami, B.Hammouti, Lh. Bazzi, A. Chakir, Der Pharma Chemica, 4(4), 1496-1505, (2012)

[7] Kassim anvar, Sagadevan Murali, Adzmi Fariz, H.N.M. Mahmud Ekramul, Material science, 10(3),(2004)
[8] Kato.M.A, Usuki, A.Okada, Journal of applied polymer science, 66, 1781-1785, (1997)
[9] Supri A.G.H.Salmah, K.Hazwan, Malaysian polymer journal, 3(2), 39-53, (2008)
[10] Sridhar Pande, Swaruparani H, Mahesh D. Bedre, Ravishankar Bhat, Raghunadan Deshpande, A. Venkataraman, Nanoscience and Nanotechnology, 2(4), 90-98, (2012)

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