Synthesis, Characterization, Anticorrosion Potential And Adsorption Performance Of Polymer Composite On Mild Steel In Acid Media

Karthikaiselvi R[1], Subhashini.S[2]

[1] (Department Of Chemistry, Government Arts College, Coimbatore, Tamil Nadu, India)
[2] (Department Of Chemistry, Avinashilingam University For Women, Coimbatore, Tamil Nadu, India)

Abstract
The synthesized PVPMOA Poly (Vinyl pyrrolidone– o-methoxy aniline) was characterized by FT-IR , Scanning electron microscope(SEM) and Energy-dispersive X-ray spectroscopy (EDX) technique. Gravimetric testing, Impedance studies and potentiodynamic polarization measurements were carried out to evaluate inhibition performance of polymer composite. Impedance results demonstrated that good anticorrosion behavior of composite. Polarization study showed that composite act as mixed type inhibitor. Gravimetric testing data confirmed the adsorption of PVPMOA obeyed Langmuir isotherm model. Metal surface interaction with polymer composite and its surface assimilation further examined by applying SEM and EDX techniques.
Key words: *SEM, EDX, Corrosion Inhibition, composite, Isotherm, Impedance*

I. Introduction

Corrosion control is a vital component in industrial equipment maintenance, tunnels, transmission/collection pipelines, water and wastewater treatment plants, pumping plants, distribution pipelines and storage reservoirs. Corrosion prevention is also an important in national defense asset and control for ships which touch a body of water. Various corrosion mitigation process will be carried out depends on the field of application. In boiler regular descaling treatments are carried out for improving its efficiency,reducing damage and extend its life period. Hydrochloric acid is the most widely used chemical cleaning solvent to remove internal deposits of boiler but may affect underlying metal and damage. Inhibitors are used during these processes to minimize the metal loss due to corrosion. These can adhere to metal surface to form a protective barrier against corrosive agents in contact with metal. The most effective inhibitors are those compounds containing heteroatom like nitrogen, oxygen, sulfur and phosphorus, as well as aromatic rings can affect the corrosion reaction by blocking effect on the metal surface.[1] The earlier studies [2,3] had reported about anticorrosion and adsorption properties of PVP, Poly(o-anisidine) and series of poly (pyrrole-co-o-anisidine). The inhibitive effects of PVP10 and PVP45 on the corrosion of 316L stainless steel at different inhibitor concentration and temperature were also analyzed [4]. The water soluble composite poly(vinylpyrrolidone–methylaniline) inhibitive action on mild steel in hydrochloric acid media and anticorrosion and adsorption properties of polyethylene glycol and polyvinyl alcohol for corrosion of iron in 1.0 M NaCl solution were carried out [5,6]. Experimental and computational chemical studies on the corrosion inhibitive properties of metamizole sodium pharmaceutical drug compound for CS in hydrochloric acid solutions [7].

In this present work, MOA (*o*-methoxy Aniline) had been selected to synthesize water soluble polymer composite. MOA was good corrosion inhibitor but less soluble in water.The soluble nature of MOAwas increased by using good steric stabilizer PVP (Poly vinyl pyrrolidone)and could be used as inhibitor in boiler treatment. In this composite PVPMOA Poly (Vinyl pyrrolidone– o-methoxy aniline) formation of H-bonding between amine / imine unit of *o*-methoxyaniline with PVP matrix was confirmed by IR spectra. Further characterization was done by SEM and EDAX techniques. Anticorrosion performance of PVPMOA on mild steel in acid media was evaluated using Gravimetric, Electrochemical studies, SEM and EDAX techniques.

II. EXPERIMENTAL METHODS

Specimens and Reagents

Merck supplied Ammonium persulphate, oxalic acid, o-methoxy aniline and PVP.*o*-methyl aniline was purified by distillation under reduced pressure. For Gravimetric studies 5 x 1 cm length Mild steel MS specimens were used. For Electrochemical measurements resin coated specimen with 1 cm^2 exposed area were used.

Inhibitor synthesis

PVP with MOAin oxalic acid medium were allowed to polymerise under continuous stirring. Cooling of the system was carried out below -5^{0}C with addition of aqueous acidic solution of ammoniumpersulphate. Bright green composite solution was synthesized after completion of 3 hrs of polymerization [8].

Figure 1 shows the proposed molecular structure of PVPMOA.
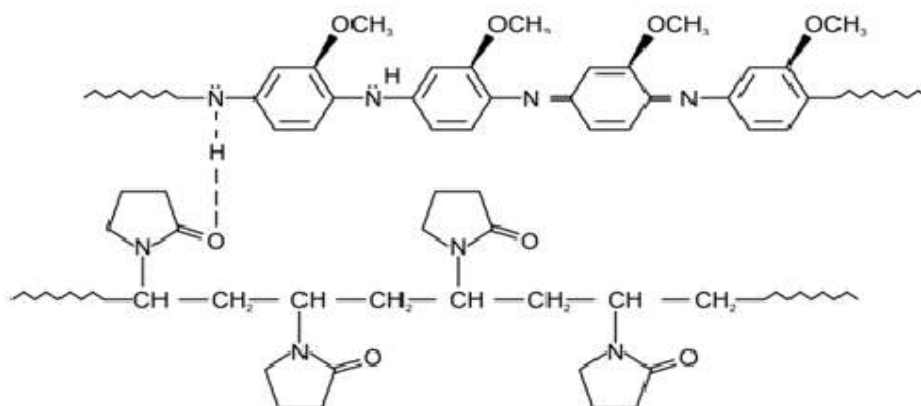
FTIR Spectra

Spectra of polymer composite was recorded using Brooker's double beam spectrophotometer. The structural characteristics of PVPMOA was analysed by FTIR spectroscopy in the range of 2000–400 cm^{-1} spectra of composite is shown in Figure 2 has been obtained in a KBr pressed pellet with PVPMOA. A strong band at 1641 cm^{-1} is due to C=O stretching of PVP being shifted to 1698 cm^{-1} and weakened in composite. The notable shift in the C=O stretching vibrations are due to significant occurrence of H-bonding between POMA and PVP [9].Two peaks at 1583 cm^{-1} and 1421 cm^{-1} are attributed to C=C stretching vibrations of benzenoid and quinonoid rings [10].The amide C-N stretch of PVP is indicated by the appearance of peak at 1295 cm^{-1}. The presence of band at 3192 cm^{-1} is owing to OH group and is also due to the hydrophilic nature of polyvinyl pyrrolidone. Appearance of several peaks in 900-630 cm^{-1} range stands for aromatic H out of plane bending [11].CH and CH$_2$ stretching vibrations in PVPMOA are responsible for the occurrence of peaks at 2972 and 2850 cm^{-1} [12]

Figure 2 FTIR Spectra of PVPMOA
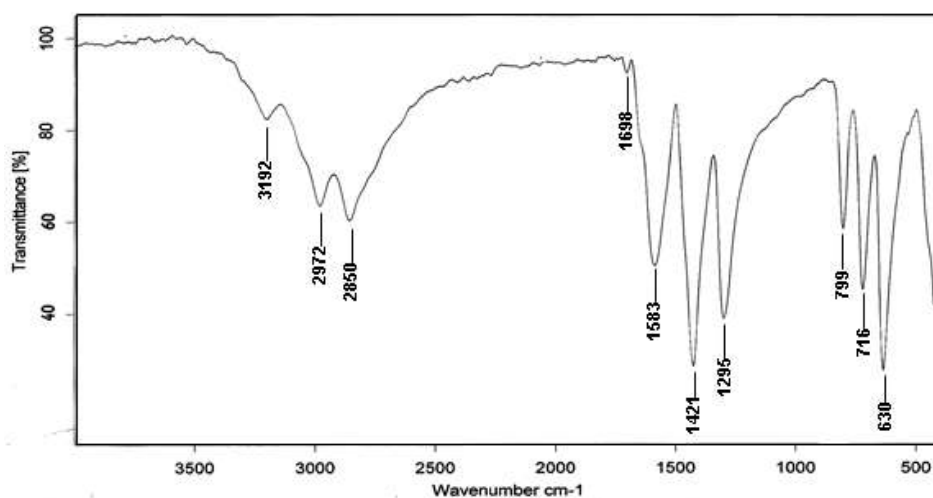
Potentiodynamic polarization technique

In this current-potential curves were recorded by changing the electrode potential automatically from -0.1 V to -1.0 V with respect to SCE at a scan rate of 2 mV sec^{-1}. Applied potential vs. current was plotted and on extrapolation of linear portion to corrosion potential (E$_{corr}$) gives corrosion current (I$_{corr}$). In anodic and cathodic plot, the slope of the linear portion gives Tafel constant.The polarization resistance, R$_p$ was obtained as the slope of the "n versus i" curve at the vicinity of corrosion potential E$_{corr}$.

Impedance studies

Impedance measurements were carried out in a frequency range of 20 kHz to 0.1 Hz with an amplitude of 10 mV peak to-peak using ac signals at respective E_{corr}. Nyquist plots of carbon steel for studied system, containing various concentrations of composite inhibitor were obtained. From the plot impedance parameters like charge transfer resistance (**R_{ct}**) and double layer capacitance (C_{dl}) were determined.

Gravimetric Testing

Weighed samples in triplicate were supported by a glass hook and immersed in 100 ml of acid solution with and without inhibitor for a specific time viz., 1/2 h, 1 h, 3 h, 6 h, 12 h and 24 h. The specimens were taken out and washed with saturated sodium bicarbonate solution and distilled water, dried and reweighed. The inhibitor concentration was also varied from 100 ppm – 2000 ppm.By varying temperature of test solution from 303 K to 343K with half an hourimmersion with different concentrations of inhibitor,temperature studies were conducted. From this data percent inhibition efficiency, free energy (ΔG) change and adsorption isotherm were determined.The change in free energy of adsorption**ΔG_{ads}** for higher temperature in comparison with room temperature at various concentrations of inhibitor was calculated using the following formula [13].

$\Delta G = - 2.303 \times R \times (T_2 - T_1) \times [1.74 + \log (\theta / 1 - \theta) - \log C]$

R – Gas constant, T_1 - Room temperature and T_2-Higher temperature.

III. Results And Discussion

Potentiodynamic polarization

Polarization studies had been conducted in control and in the presence of PVPMOA (Fig 3a). By extrapolating the Tafel slopes for various concentrations of the inhibitor to their corrosion potential E_{corr}, the corrosion current density I_{corr} values were derived. Table 1 results indicated that composite under study brought down I_{corr} value and a maximum decrease in I_{corr} was noted at 2000 ppm with increasing IE. Difference between E_{corr} value in presence and absence of inhibitor in the present studybeing up to 35.29 mV indicating mixed type inhibitor [14]. A noted change in anodic and cathodic slope values was seen such as 17.63 and 39.48 mV / dec in their direction due to the existence of inhibitor. R_p value increased with increase in inhibitor concentration resulting an enhanced covered metal surface area [15].

Table 1.Electrochemical parameters for the corrosion of mild steel in HCl containing PVPMOA

Concentration ppm	E_{corr} mV (SCE)	I_{corr} x 10^{-4} mA/cm^2	b_a mV / dec	b_c mV / dec	IE (%)	R_p (Ohm .cm^2)	IE (%)
Control	-481.11	59.81	153.48	124.9		4.85	
100	-462.03	39.12	144.62	119.09	34.59	7.47	35.07
200	-462.35	31.28	145.5	117.69	47.70	9.3	47.85
400	-453.79	16.39	136.3	99.81	72.60	14.76	67.14
600	-453.75	16.27	138.58	96.17	72.80	15.3	68.30
1000	-445.82	9.12	135.85	85.42	84.75	25.18	80.74
2000	-462.29	7.58	141.39	104.71	87.33	28.2	82.80

Impedance measurements

Parameters derived from nyquist plot revealed that the magnititude of R_{ct} increased with increasing composite concentration and 91.18% IE attained at 2000 ppm concentration. It seems that metal dissolution get actively controlled by adsorption of inhibitor and by the formation of protective layer over metal surface. Double layer formation between charged metal surface and solution act as electrical capacitor and reduced **C_{dl}**value with rise in surface coverage revealed enhanced corrosion inhibition. In the presence of the studied inhibitor, the size of this loop increased withincreasing concentration of composite (Fig 3b). It indicatedthatatvarying concentrations of composite,thesemoleculeswereadsorbedonthesteelsurface, forming a protective layer that inhibits the charge transfer [16]**.**

Figure 3

a) Linear polarization   **b) Nyquist plot**
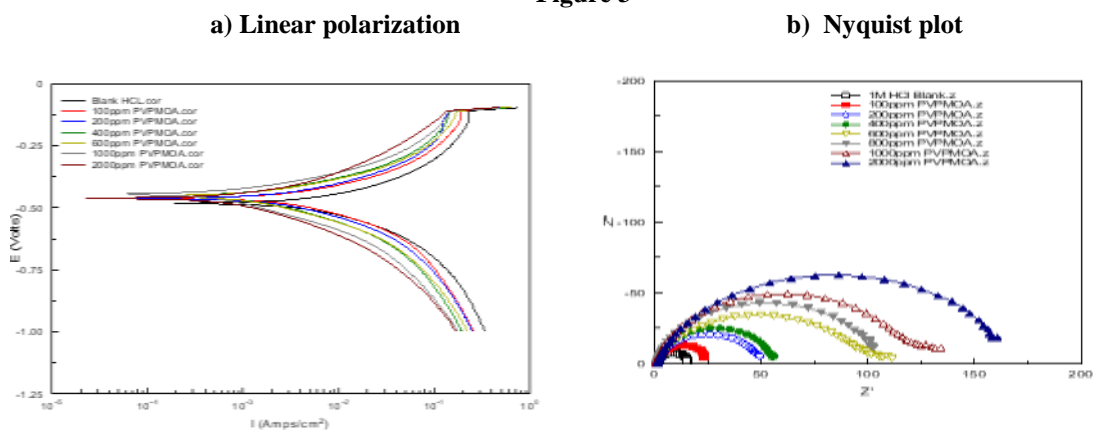
Gravimetric measurements - Effect of Temperature

The increase of corrosion rate CRwas more prominent with rise of temperature for blank solution. For each temperature CR of MSwas decreased in addition of PVPMOA and IE increased.Table 2 reveals that high level of Inhibition 95.56% afforded to mild steel by composite at 323 K temperature. The performance of inhibition efficiency increases up to 323 K and fall in efficiency was noted down from 333 K onwards. Decline in IEwas due to desorption of adsorbed inhibitor from MS surface thusinducing the dissolution of the steel [17]. This decrease in IE also indicated that physical adsorption nature of inhibitor.

Table 2 Effect of temperature on the corrosion inhibition of PVPMOA on mild steel

Conc. (ppm)	303 K		313 K		323K		333K		343K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	1250.72		4246.693		6954.84		10823.88		15675	
100	490.657	60.77	563.536	86.73	854.750	87.71	2715.711	74.91	4415.648	71.83
200	453.136	63.77	405.559	90.45	612.722	91.19	1953.710	81.95	3763.568	75.99
400	375.091	70.01	345.256	91.87	489.621	92.96	1380.045	87.25	3504.930	77.64
600	266.528	78.69	321.899	92.42	425.636	93.88	1161.402	89.27	2512.703	83.97
800	245.266	80.39	307.885	92.75	381.821	94.51	986.055	90.89	1984.455	87.34
1000	225.005	82.01	255.651	93.98	357.479	94.86	904.876	91.64	1779.113	88.65
2000	193.236	84.55	236.541	94.43	308.795	95.56	789.061	92.71	1421.723	90.93

Free energy of adsorption

As temperature increases, $\Delta G_{ads}$was shifted to negative value up to 323 K in composite presence and negative value slightly decreased beyond this temperature. Table 3 indicates that the adsorption was favourable with increasing experimental temperature up to 323 K and slow desorption of the inhibitor from metal surface beyond this temperature. Electrostatic interactions between charged molecules and charged metal ΔG_{ads} values up to -20 kJ mol $^{-1}$ indicates physisorption while those around -40 kJ mol^{-1} or higher are associated with chemisorption as a result of electron transfer from polymer molecules to the metal surface to form a coordinate type of bond [18]. In our study, the values of ΔG_{ads} for the inhibitor lies between -20 kJ/mol and -40 kJ/mol. Therefore, the adsorption of PVPMOA on the metal follows both chemical and physical adsorption [19].

Adsorption Isotherm

The Adsorption of the inhibitor molecule over the metal surface depends on its surface nature, the chemical structure of polymer inhibitor, distribution of charge in the molecule, and type of interaction between polymer molecule and metallic surface [20].Langmuir adsorption isotherm had been found to be the best model for adsorption behavior of studied inhibitor.The results obtained (Table 4) indicated that R^2 values were very close to unity, which signified adherence of PVPMOA to Langmuir adsorption isotherm [21].

Table 3 Free energy of adsorption of PVPMOA on metal

Conc ppm	Free energy change of adsorption ($-\Delta G$ = kJ mol^{-1})				
	303 K	313 K	323 K	333 K	343 K
200	21	26	28	26	26
400	20	25	26	25	24
600	20	24	26	25	24

800	20	24	25	24	24
1000	20	24	25	24	24
2000	18	22	23	23	23

Table 4 Langmuir Adsorption isotherm

| Temperature K	Langmuir isotherm	
	Slope	R^2
303	0.47531	0.9496
313	0.30997	0.9585
323	0.37086	0.9804
333	0.50691	0.9751
343	0.49178	0.9367

Surface examination

The morphology of the synthesized composite was analyzed using SEM.The SEM image of the inhibitor was recorded and this clearly reveals the presence of binary phase in which poly (o-methoxy aniline) chains (Minor phase) are randomly scattered with in the PVP matrix (Figure 4a).The surface morphology of MS after immersion in 1 M HCl without inhibitor was very rough and more cracks seen due to hit of acid (Figure 4b). The SEM image of metal surface (Figure 4c) were smooth and shiny after addition of PVPMOA revealed the well adhesion of inhibitor on the metal surface. No damage was found due to thin layer formation and its protection [22]. This implied that PVP incorporated MOA had more surface adhesion and close packing nature with multiple nucleation of polymer preferentially on the same site of the substrate.

4a)   PVPMOA composite   **4b) Mild steel in HCl**   **4c) Composite deposited on MS**
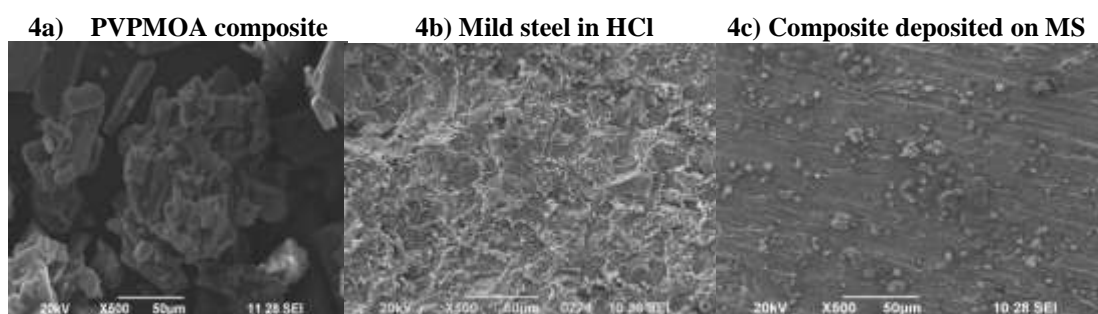
EDX Analysis.

EDX technique used to identify the elemental composition of composite. Spectra obtained (Figure 5a). shows that peaks corresponding to elements Carbon, Nitrogen and Oxygen of composite being analysed. EDX analysis was also carried out after 12 hrs immersion of   MS in corrosive solution with and without inhibitor. The metal surface (Figure 5b) after exposure to blank solution showed the presence of 84.15 % Fe and 15.85 O_2 %. The presence of atomic content of 27.07 % Fe, 55.36 % O_2 , Nitrogen 3.67 % and Carbon 13.90 % (Table 5) confirmed the adsorption of polymer composite on the metal surface (Figure 5c). It revealedthat in the presence of composite, the percentage of ironhas decreased due to decrease in the extent of acid corrosion, thus the increase of carbon, Nitrogen and oxygen peakby the formation of a layer of carbon-based molecules on the surface [23].

5a) Elements inPVPMOAcomposite 5b) EDX spectra of Mild steel
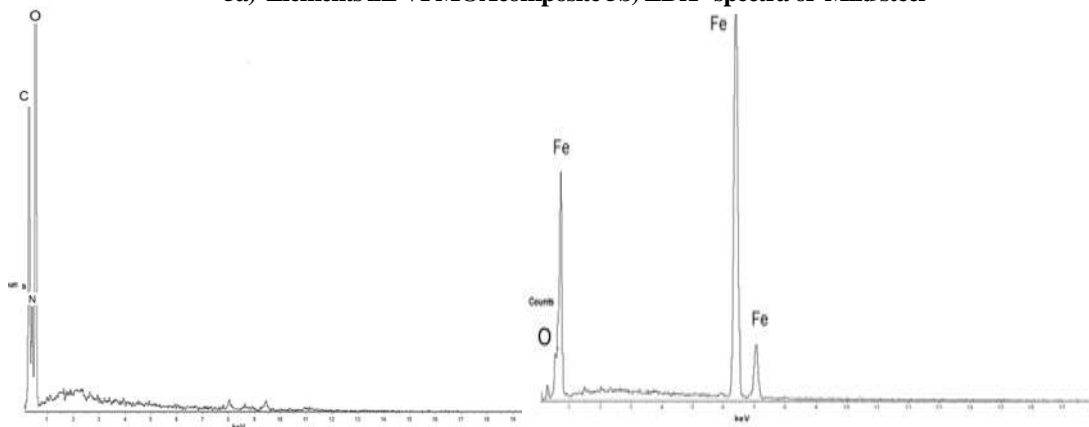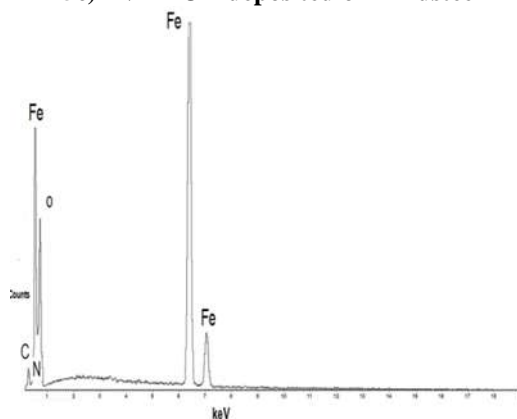
5c) PVPMOA deposited on Mildsteel

Table 5 : Percentage Elemental composition

Inhibitor	Fe (%)	C (%)	O (%)	N (%)
PVPMOA		27.18	51.51	21.31
MILDSTEEL	84.15		15.85	
MS +PVPMOA	27.07	13.90	55.36	3.67

Mechanism of Adsorption

The inhibition of active dissolution of metal was due to the adsorption of the inhibitor molecule on MS forming a protective film. The adsorption mechanism took place by electrostatic attraction between charged molecules and charged metallic ions. The existence of electron density around nitrogen of the amino group formed coordination bonds with Fe atoms. A protective layer on the metal surface shieldedit from the aggressive environment [24].The better inhibition performance of polymethoxy composite could be explained on the basis of steric effects. Methoxy substituted aniline is more planar. The methoxy group attached to polymer at ortho position is perhaps perpendicular to the metal surface. Thus polymethoxy aniline helped in promoting both strong adsorption and uniform surface coverage by polymer composite. The close packed layer was further stabilized by Vander walls forces of cohesion between the alkoxy chains [25]

IV.   Conclusions

The inhibition effect of PVPMOA on mild steel corrosion in 1 M HCl was evaluated by potentiodynamic polarization,EIS measurement, Gravimetric, SEM and EDAX.Weight loss studies with temperature and concentration variable show 95.56 % IE at 323K for 2000 ppm. The corrosion process was inhibited by the adsorption of PVPMOA on the mild steel surface fits Langmuir isotherm.The polarization measurements indicatedthat mixed-type behavior of composite with 82.8% IE derived from R_P values. EIS studies showed 91.18 % protection efficiency. Both physical and chemical adsorption followed by the inhibitor.Combination of polymethoxy aniline with PVP established good surface coverage and it was demonstrated by SEM micrographs. It showed cracks and pits on the mild steel in the absence of inhibitor and a compact granular structure with smooth deposition in the presence of inhibitor proved its strong adsorption. Elemental composition of synthesized composite adsorbed on the mild steel confirmed from EDX.

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