Poly(Aniline-co-2-Amino-2-Methyl-1,3,Propane Diol): An Electroactive Composite Polymer for Corrosion Inhibition of Mild Steel in Acidic Medium

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ABSTRACT

In the recent time, polyaniline and its composites have been proved as potential corrosion inhibitor for mild steel in acidic medium. The polymer composite of poly(aniline-co-2-Amino 2-methyl 1,3 propane diol) has been deposited potentiodynamically. The corrosion inhibition of effect of composite polymer on mild steel in 1.0 M HCl has been studied by open circuit potential, potentiodynamic polarization, electrochemical impedance spectroscopy and Adsorption isotherm. The results of electrochemical studies have suggested that the composite polymer has shown good corrosion inhibition efficiency on mild steel in 0.1M hydrochloric acid solution. The maximum corrosion inhibition efficiency evaluated up to 74.27% when the concentration of 1.0×10^{-3}M of AMPD added to the monomer.

Keywords: Composite polymer ElS spectroscopy Potentiodynamic polarization Scanning electron microscopy

1. Introduction

The phenomenon of corrosion is as old as the discovery of metals. It has been a menace to the scientific community since it use. So, to prevent metals from the corrosion was a real word a problem for many years. Inhibition of corrosion of mild steel requires theoretical as well as practical attention which attracts researchers to the study the corroding effect and to minimize the loss which occurs due corrosion. The deterioration of metals from corrosion can be prevented by using natural inhibitors as reported by Quraishi *et al.*[1]. Unfortunately, many common corrosion inhibitors are health hazardous for the inhibition of corrosion in aqueous media [2,3]. The most commonly used inhibitors are organic inhibitors in acid solutions, particularly in view of the high corrosion rate [4-11]. The most commonly used organic compounds which contain functional groups such as –COOH,-NH$_2$, -OH etc. are very good corrosion inhibitor for steel and adsorbed on the metal surface through electron sharing[12,13]. The

organic compounds such as acetylenic, amines alcohol and heterocyclic compounds are extensively used as an corrosion inhibitors [14,15]. The conjugated polymers have been widely used for their potential applications and still attracted much attention as the corrosion inhibitor. The polyaniline and its derivatives have good affinity of adsorption on Iron surface in acid media and greatly responsible for corrosion inhibition [16]. The inhibition efficiency observed in the conjugated polymer is not only because of π-electrons but also due to larger molecular size [16]. The effect of some water-soluble polymers have been reported by Khairou and El-Sayed [17,18]. The inhibition efficiency of different molecular weight polyethylene glycol (PEGs) on carbon steel has been reported by Ashassi-Sorkhabi *at al*.[19,20]. The aim of this study is to explore the inhibition effect of a polyaniline in presence of 2, Amino-2-Methyl-1,3-Propane diol AMPD which is an organic compound containing alcoholic and -NH$_2$ groups that acts as corrosion inhibitor in acidic media and render less toxicity with polyaniline causes high inhibition effect by potentiodynamic and electrochemical impedance methods using electrochemical techniques.

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2. Experimental

2.1 Material

Aniline (Reagent grade) from R&M Chemical Essex, U.K used as received. Ammonium persulfate (A.R grade) purchased from (Aldrich, U.K) was used as received. 2, Amino-2-Methyl-1,3-Propane diol (AMPD).Hydrochloric acid (HCl 37.5%) (Aldrich, U.K) was used without further purification. Double-distilled water was used throughout the experiment. Acetone and Ethyl Alcohol were purchased from Systerm^R ChemAR used as received.

2.2 Synthesis of PAni-AMPD Composite

The procedure involved to prepare the composite polymer was as follows. The PAni-AMPD composite was prepared by chemical oxidation method by adding 50mL ml of 10^{-1} M solution of aniline dissolved in 0.1M aqueous hydrochloric acid solution. To the above solution, 25mL of 10^{-1} M solution of 2-Amino-2-methyl-1,3 diol dissolved in distilled water was added. To initiate the oxidative polymerization reaction, 25ml of 0.1M ammonium per sulfate

was added very slowly from the sidewall of the 250 mL Erlenmeyer flask in one portion with minimum disturbance.

The reaction was left for overnight for the completion. The dark green precipitate was obtained and collected by filtration using Whatmann filter paper no. 42 and washed thoroughly with distilled water and subsequently with acetone. The polymer was then dried under vacuum for 24 h at room temperature of 25-27 ^{o}C.

2.3 Characterization

The polymer was synthesized by chemical oxidation of aniline and AMPD by in-situ polymerization method. The as-synthesized polymer was collected in the form of powder, purified by washing with water and subsequently with acetone until the extract became colorless. The composite polymer was characterized by recording its IR spectra using Perkin-Elmer System-2000 Fourier Transform Infrared (FT-IR) spectroscopy using KBr pressed pellets. The scanning resolution of FT-IR was 4 cm-1. The scanning electron microscopy (SEM) equipped with an Oxford INCA 400 energy dispersive X-ray (EDX) using a Leo Supra 50 VP field emission microanalysis system (Bucks, UK) was used to elucidate the morphology of the composite polymer of polyaniline and AMPD. The structure of composite was determined by FTIR spectroscopy System 2000 (Perkin–Elmer, USA).

2.4 Electrochemical Studies

Hydrochloric acid solution of 0.1M diluted from concentrated acid (37%, Aldrich) with double-distilled water. This solution was used as blank. The inhibitors (Aniline+AMPD) x 10^{-3} M were mixed with in different volumetric ratio (mL) in (1:0.5), (1:1), (1:1.5) and (1:2). These inhibitor solutions were exposed to the 0.1M HCl solution. All experiments were carried out in non-deareated solutions under unstirred conditions at 25 ∘C.

2.5 Electrochemical techniques

The electrochemical experiments were carried out using Potentiostat/Galvanostat/ZRA (Gamry, USA).The cylindrical electrochemical cell was used with three conventional electrodes cell assembly: counter electrode-platinum wire; reference electrode saturated calomel electrode; steel plate was used as working electrode (dimension 2.5 cm x 2.5 cm, exposed area 1 cm^{2}, rest being cover with araldite epoxy). The polishing of working electrode was carried out by different grade emery papers and subsequently washed and degreased by distilled-water and acetone, respectively. The working electrode was immersed for 30 mins at 25 ∘C in experimental

solution before each electrochemical measurement to obtain stable open circuit potential (OCP). The fresh

working electrode (mild steel) was used in each measurement.

2.6 Potentiodynamic polarization measurements

The potentiodynamic studies were carried out in 0.1M HCl for different molar concentration of composite polymer

as an inhibitor at the open circuit potential of the system. The polarization was carried out at in the range of -0.3 to

0.3 V from cathodic to an anodic potential with respect to the corrosion potential at a scan rate of 1 mVs^{-1}. The

cathodic-anodic curves of Tafel plot were scanned from (-0.3 to +0.3 vs corrosion potential) to obtain the values of

corrosion potential (E_{corr}) and corrosion current (I_{corr}). To correlate the results of potentiodynamic studies,

electrochemical impedance measurements were also carried out at open circuit potential (V_{ocp}) of the working

electrode in the test solution in the frequency range of 10 KHz to 0.1 Hz. The voltage of 10mV was applied for

sinusoidal wave.

2.7 Electrochemical impedance spectroscopy

The impedance spectra were recorded at V_{ocp} in the frequency range 10 kHz–10 mHz at alternating current

amplitude of ±10mV (rms). The simulation of EIS data were performed by the ZSimWin Demo version 3.2.

The maximum frequencies (f_{max}) of all samples with inhibitor and without inhibitor were obtained from the Bode

plot in the EIS studies.

3. Results and discussion

3.1 FT-IR spectroscopy

FT-IR spectrum of the pure polyaniline and poly(Aniline-co-AMPD) composite in KBr are shown in figure 1 (a b),

respectively. For hydrochloric acid doped polyaniline, the major absorption peaks at 1490 cm^{-1} and 1564 cm^{-1} are

assigned to stretching vibration of -C=C- benzenoid and –C=N quinoid ring, respectively. The strong peak at 1111

cm^{-1}, aromatic CH in-plane-bending modes is observed. The strong band at 1289 cm^{-1} is characteristically seen

which can be attributed to C-N stretching of the polymer. The C-H out of plane bending mode has been as key to

identify the type of substituted benzene. The peak at 790-815 cm^{-1} is assigned to –C–H$_{(aromatic)}$ out-of-plane bending

vibration 1,4 disubstituted aromatic rings [22-24]. The N-H stretching vibrations of $C_6H_4NHC_6H_4-$ groups may be

assigned [22] to the broad band at 3461 cm⁻¹. For poly(Aniline-co-AMPD)2:1 composite all peaks are

characteristically observed almost same or lower frequency.
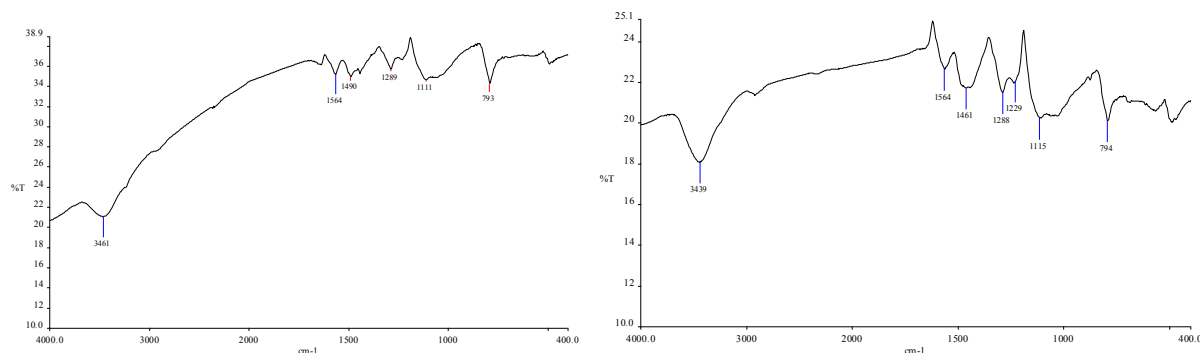

Figure 1-a, b. FT-IR spectrum of polyaniline and poly(Aniline-co-AMPD) 2:1 synthesized in acidic medium using KBr pressed pellet.

3.2 Open circuit potential measurement

The figure 2 (curves a-d) shows the open circuit potential of mild steel electrode with and without composite

polymer of poly(Aniline-co-AMPD), exposed to 0.1 M HCl solution for 30 mins. The corrosion is controlled by

monitoring the oxidation or passivation of the metal surface. The shifting of open circuit potential towards the

more positive potential value indicates the formation of protective passive layer of poly(Aniline-co-AMPD)

composite polymer on the carbon steel and it behaves predominantly as an anodic inhibitor.

3.3 Potentiodynamic polarization

In figure 3, the potentiodynamic polarization curves for mild steel in 0.1 M HCl, the change of concentration of

AMPD solution to aniline has affected the corrosion process on the mild steel. The corrosion kinetics parameters

such as b_a, b_c and E_{corr} that were obtained from the extrapolation of the Tafel curves at different concentration of

composite polymer of poly(aniline-co-AMPD). The small shift of E_{corr} values towards positive and negative potential

in the presence of the inhibitor indicates that there is an interaction between molecules of polymer and the

surface of working electrode. It shows that the composite polymer behaves as a mixed type inhibitor. The

polarization resistance values also increase with increasing the polymer concentration to a certain limit. This

suggests that the inhibition action of these polymers occurs by simple blocking at the surface of the electrode [17].

The i_{corr} values are found dependent on the polymer concentration. These values are given in Table I. The inhibition efficiency ($\eta\%$) is evaluated using following equation:

$$\eta\% = \frac{i°corr - icorr}{i°corr} * 100$$

where i_{corr} and $i°_{corr}$ are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel plots to the corrosion potential. The inhibition efficiency increases up to certain limit by increasing the concentration of polymer. This is attributed to the increase of the –OH, NH$_2$ groups present in 2-amino-2-methyl-1,3-Propane diol. The value of the Tafel constants, b_a decreased from 136 mV dec^{-1} to 73.2 mV dec^{-1} while the value of b_c decreased from 271.8 to 163 mV dec^{-1}. The extent of decrease to b_a being greater than b_c. It is also observed from Table I that there is a significant decrease in corrosion current (I_{corr}) value with the change in concentration of composite polymer. The lowest I_{corr} value was obtained at 1:1 of composite polymer. Thus, the addition of AMPD solution together with aniline acted as a corrosion inhibitor at this optimum concentration, and shifted the E_{corr} values towards more positive potential with respect to the E_{corr} recorded for mild steel electrode without an inhibitor.
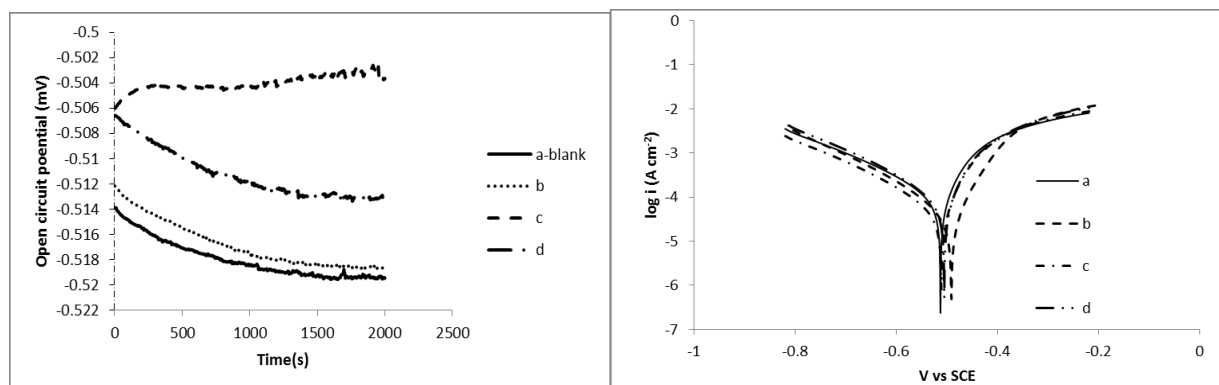

Figure 2.(I) Open circuit potential of carbon steel (a) 0.1 M HCl, poly(Aniline-co-AMPD) (b) 0.5x10^{-3} M (c) 1.0x10^{-3} M (d) 1.5x10^{-3}
(II). Potentiodynamic polarization behavior of mild Steel in 0.1M HCl different concentrations AMPD to aniline (a) blank -0.1 M HCl, b (5.0x10^{-4} M AMPD) c (1.5 x10^{-3} M AMPD), d (2.0x10^{-3} M AMPD)

Table I: Corrosion kinetics parameters derived from the potentiodynamic curves of Mild Steel in 0.1M HCl with the change of conc. of composite.

	I_{corr}	E_{corr}	b_a	b_c	$Rate_{corr}$	I.E%
	$\mu A\,cm^{-2}$	mV	$mV\,dec^{-1}$	$mV\,dec^{-1}$		
Blank	552	-520.7	136.0	271.8	80.21	
AMPD-inhibitor $(x10^{-3}M)$						
0.5	528	-512.0	121.0	235.0	76.79	4.34
1.0	142	-491.0	73.2	163.0	20.65	74.27
1.5	194	-511.5	80.41	192.0	28.28	64.85
2.0	344.0	-505.0	90.19	193.0	50.00	37.68
3.0	388.9	-504.0	97.0	201.0	56.56	29.71

3.5 a.c. Impedance measurements

In figures 4-6, electrochemical impedance spectroscopic studies for mild steel electrode without and with the change in molar ratio of Aniline to AMPD are shown as Nyquist plots. The depressed capacitive loop is seen in the low frequency range. The capacitive loop arises from the electric double layer and charge transfer resistance, the structural inhomogeneity of the surface is reflected by depressed form of semi-circle at the higher frequency curve as seen in as Nyquist plots [25]. Therefore, in the studied frequency range, the equivalent circuit could be described by Randle circuit. In this equivalent circuit, R_{ct} is the charge resistance, R_s is solution resistance and C_{dl} double layer capacitance. The equivalent circuit shown in figure was used to simulate the resistance R_{ct} values, where C_{dl} is the double layer capacitance; it is calculated using the following equation from Bode plot,

$$C_{dl} = 1/2\pi f_{max} \times 1/R_{ct}$$

and the surface coverage (θ) by the inhibitor molecule is given by

$$\theta = (C^o_{dl} - C_{dl})/ C_{dl}$$

where f_{max} is frequency at the maximum of imaginary component of impedance in the semi-circle and these values represented in Table II. The charge-transfer resistance in the Nyquist plot increased from 65.9 to 233.2 $\Omega cm2$ with

the corresponding decrease in C_{dl} value from 2.926×10^{-4} to 1.203×10^{-4} F cm-2 with the increase in the

concentration of AMPD to the aniline in the electrochemical cell. The electronic double layer developed on the

metal solution interface causes the decrease in C_{dl} [26]. The formation of protective layer on the metal/solution

interface is responsible for an increase in R_{ct} values [27-29]. Thus, the these results suggest that better adsorption

of inhibitor occurred as result of a decrease in the double layer capacitance value at the optimum concentration of

1.5×10^{-3} M of AMPD. The diameter of semicircle in the Nyquist plots increased with the change of AMPD

concentration and the similar shape of Nyquist plots remained almost unaltered which predicted the process of

inhibition followed the same mechanism for mild steel in 0.1 M HCl. The inhibition efficiency is also evaluated by

charge transfer resistance values obtained from the Nyquist plots using the following equation:

$$I.E\% = \frac{Rct - Roct}{Rct} * 100$$

where R_{ct} and R_{oct} are the charge transfer resistance value in presence and absence of the inhibitor. Bode plots

shown in figure7-9, the presence of one phase maximum was observed at intermediate frequencies, which

indicated the presence of one time constant attributed to the impedance of the formed protective film[30]. In

Figure 10, Warburg impedance is denoted by a linear line with a slope of 45° in the mid frequency region. In the

Nyquist plot, at low frequency region, the linear line pointed the presence of Warburg impedance (W_w) indicating

the formation of a coating layer. This behavior confirms the Warburg diffusion region corresponding to the semi-

infinite diffusion of ions at the polymer/electrolyte interface. The change in physical characteristics of the polymer

film is denoted by the low frequency Warburg impedance. The corrosion phenomenon is prevented by the

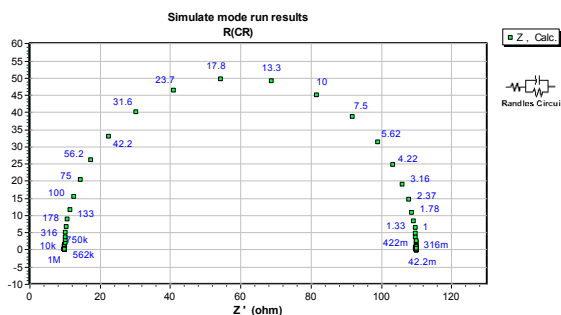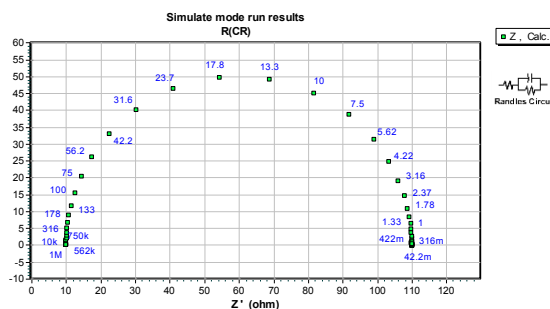copolymer film as the movement of the corrosive solution is under the diffusion control to the electrode [31-34].
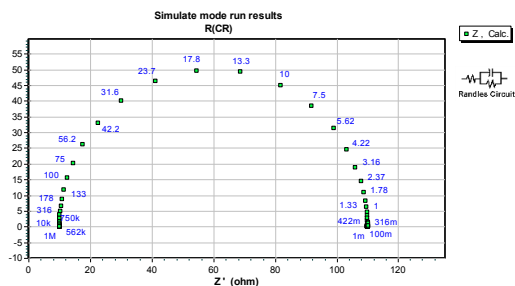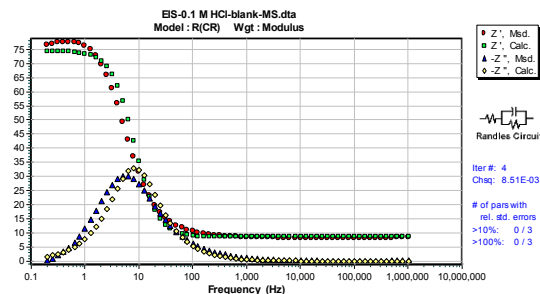

Figure 4
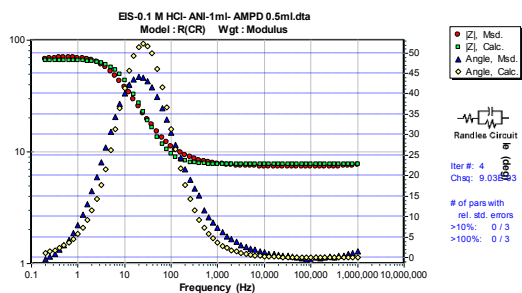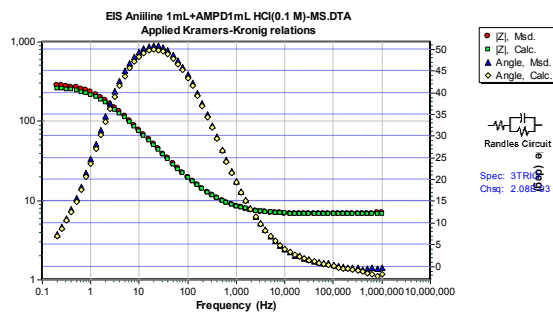

Figure 5

Figure 6

Figure 7
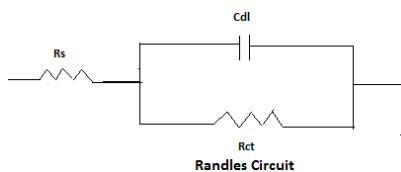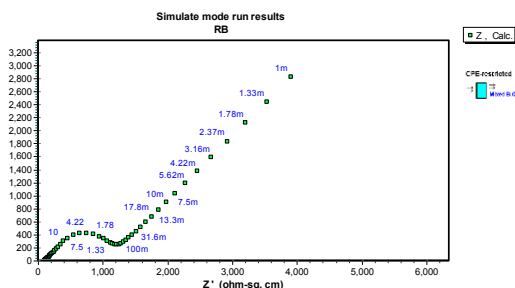

Figure 8

Figure 9

Figure 10. Warburg Impedance behavior of mild steel in 0.1M HCl with the addition of (1.0mM aniline + 1.0mM AMPD)

Table II Electrochemical impedance data deduced from Nyquist
plots by fitting to an equivalent circuit in Figures 5-7

	R_{ct}	C_{dl}	R_s	SC	
	Ωcm^2	Fcm^{-2}	Ωcm^2	θ	%I.E
Blank	65.90	0.0002926	8.53	-	---
AMPD($x10^{-3}$M)					
0.50	117.0	0.0002447	7.80	0.1637	44.44
1.0	182.9	0.0002288	5.7	0.2180	63.96
1.5	233.2	0.0001203	7.8	0.5888	71.74
2.0	72.56	0.0003099	6.06	-0.0591	10.34

sc: surface coverage (θ)

3.6 SEM Study

The electron micrographs of the uncoated carbon steel and carbon steel surface after the deposition of composite polymer are shown in figure 11(a-c). It is observed that the formation of well-passivated layer of composite polymer is shown at low and high magnification which confirms the interaction and adsorption of the composite polymer on the carbon steel electrode.
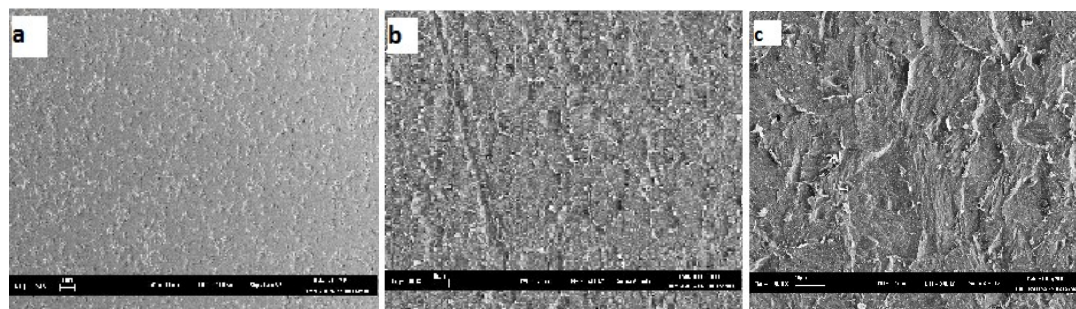

Figure 14. SEM micrographs of uncoated carbon steel and poly(Aniline -co-AMPD)1:1 cast films at (a) 50×100µm-uncoated (b) 500×1 µm (c) 1.00k×10 µm magnification

4. Conclusion

Potentiodynamic study confirms the composite polymer behaved as a mixed type of inhibitor since it controls both anodic as well as cathodic reactions. The ionic species present in the acidic solution are $-NH_2^+$ and $-OH^-$ which are adsorbed on the cathodic and anodic sites of carbon steel, respectively. The anodic sites are also cover by pi-electron of conjugated system and free electron on the nitrogen atoms which reduces the dissolution of carbon steel. Impedance spectroscopy and Langmuir adsorption isotherm predicts that the composite polymer was adsorbed on the metal surface and passivated the corrosion. The inhibition efficiency of poly(ani-co-AMPD)

increases with increase in the inhibitor concentration. The inhibitor showed maximum efficiency of 71.27% efficiency at the optimum concentration.

Acknowledgement

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