Electrochemical Measurements for the Corrosion Inhibition of Mild steel in 0.5 M HCl Using poly(epichlorohydrin) Derivatives

Noorollahy Bastam, Naser

Department of Chemistry, College of Science, Malek-Ashtar University of Technology, Shahin-Shahr, I.R. IRAN

Hafizi Atabak, Hamid Reza

Chemistry & Chemical Engineering Research Center of Iran, Tehran, I.R. IRAN

Atabaki, Fariborz*⁺; Radvar, Mehran; Jahangiri, SHahrzad

Department of Chemistry, College of Science, Malek-Ashtar University of Technology, Shahin-Shahr, I.R. IRAN

ABSTRACT: *In this article, the inhibition capability of poly(epichlorohydrin) containing phenylhydrazine(PMP), 4-nitrophenylhydrazine(PMN), and 2,4- dinitrophenylhydrazine(PMDN) on mild steel was investigated in 0.5 M hydrochloric acid. The electrochemical studies demonstrate that these polymers act as mixed-type inhibitors but increasing their concentration caused the shift of corrosion potential to cathodic potential. Also, adsorption of these polymers on the mild steel surface obeys a Langmuir adsorption isotherm. The results obtained from the potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) are confirmed by Field Emission Scanning Electron Microscopy (FE-SEM), X-ray Energy Dispersive Spectroscopy (EDS), and Mapping analysis (MAP). The results of this study indicate that samples of PMDN have the lowest corrosion speed.*

INTRODUCTION

Steel and its alloys are widely used in industry [1,2] due to their excellent mechanical properties, as well as low cost[3]. As structural materials, they are used in various industries such as engineering, construction material for chemical reactors, boiler, storage tanks and [4,5]. Therefore, one of the main problems in industry is corrosion of steel and its alloys which plays a very important role in economy [6,7].

The use of corrosion inhibitors is one of the most economical methods to slow or prevent corrosion of metal [8-13]. Corrosion inhibitors have been the subject of numerous studies, and they are usually organic

compounds [14, 15]. The existing data show that addition of corrosion inhibitors in small amounts to environment causes to decrease corrosion rate[4, 16,17]. Corrosion inhibitor adsorption on the metal surface and formation of a protective film [18-21]. In general, the inhibition efficiency depends on: size and shape of molecule, aromatic and double bond, concentration of corrosion inhibitor, the type of metal, the type of corrosive environment, the power of the bond between molecule and the metal, the nature and the state of a protective layer, adsorption centers [11, 22]. Most of efficient compound inhibitors are organic compounds containing hetero-atoms such as oxygen, nitrogen, sulphur or phosphorus in their structure [23-28]. In addition, heterocyclic compound and functional electronegative groups and π electron, play a significant role in inhibition process [29-32]. Polymers, in comparison to a small organic compound, are capable of filming, and because of their high surface area, they can be placed on a metal surface like a film and cover the metal completely[33, 34, 37]. Due to this ability of polymers, they are used as anti-corrosion coatings as well as corrosion inhibitors such as low carbon steel and copper in corrosive environments such as acidic environments.

Polymers have a higher degree of flexibility and stability compared to small organic compounds with higher viscosity, and unlike small organic compounds with active polar centers and large heteroatoms on their surface; These active centers can be easily bonded to the. Polymers are easy to synthesize, more accessible, less toxic and environmentally friendly; Unlike mineral compounds and small organic compounds, they do not cause environmental problems [34-40] .

The aim of the present research is to investigate the inhibitive properties of poly(epichlorohydrin) containing phenylhydrazine(PMP), 4-nitrophenylhydrazine(PMN) and 2,4- dinitrophenylhydrazine(PMDN) in 50, 100, 150 and 200 ppm concentration, also in this work is compared the inhibition abilities of mentioned polymers. The corrosion inhibition of mild steel in 0.5 M hydrochloric acid has been studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves.

EXPERIMENTAL SECTION
Materials
Corrosion tests were performed on a Mild carbon steel, whose compositions are: C = 0.053 wt%; Si = 0.013 wt%;

Mn = 0.192 wt%, P = 0.010wt%, S = 0.006 wt%; Cr = 0.006 wt%; Ni = 0.270wt%; Al = 0/054 wt%, Co = 0/008 wt%; Cu = 0/011 wt%; V = 0/002 wt%; Nb = 0/003 wt%; Ca = 0/001 wt%; As = 0/006 wt%; MO < 0.002 wt%; Zr< 0.002 wt%; W < 0.010wt%; Ti< 0.001 wt%; B < 0.001 wt%; Bi < 0.002 wt%; Sn< 0.001 wt%; Pb< 0.003 wt% and the remained is iron[41]. The working surface area of mild steel samples in 0.5 M HCl solution for electrochemical tests was 1 cm ^{2} . Also, the samples were polished with emery paper of 120 -1200 grit, then they were washed with double distilled water and acetone, and finally dried at room temperature before being used. Phenylhydrazine, 4-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine and dichloromethane were obtained from Merck. Epichlorohydrin and N,N-dimethylacetamide (DMAc) were purchased from sigma-Aldrich, all chemicals were used as received.

Synthesis of corrosion inhibitors
The poly(epichlorohydrin) containing phenyl hydrazine derivatives were synthesized in the laboratory following the procedures reported previously (Scheme 1), Which is as follows:
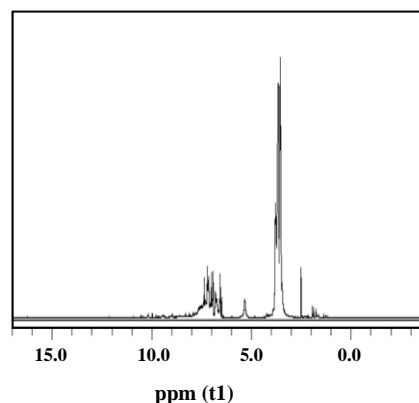
The poly(epichlorohydrin)(PECH), dissolved in DMAc at room temperature. Then phenylhydrazine, 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine dissolved in of DMAc, was added to the PECH solution, individually. The temperature's reactor was raised to 80-90°C for 24 h and after that diluted to twice the volume of DMAc with dichloromethane. Then, the reaction mixture was washed several times with distilled water. Finally, the organic layer was separated, then the dichloromethane was removed by vacuum distillation [42]. The chemical structure of the synthesized corrosion inhibitors were performed by FT-IR, H-NMR and elemental analysis[43]. Analysis calculated for PMP: C, 56.14; H, 6.62; N, 10.19. Found: C: 51.50; H:6.67; N:10.15., PMN: C, 47.76; H, 5.30; N, 13.93. Found: C: 41.48 ;H:4.50 ;N:11.26 .,PMDN: C, 41.55; H, 4.32; N, 13.27. Found: C: 41.55 ;H:4.32 ;N:13.27.(Table 1). FT-IR spectra of the synthesized polymers (PMP, PMN, PMDN) is shown in Fig. 1. The FT-IR spectrum of PMP shows a peak at about 1601 cm^{-1}, which can be assigned to stretching of phenylhydrazine ring skeleton. The characteristic peaks at about 1496 cm^{-1} and 1116 cm^{-1} corresponding to C-N, C-O stretching band, individually.

Table 1: The content of carbon (C wt. %), hydrogen (H wt. %) and nitrogen (N wt. %).

Polymer	Time of reaction (h)	C (wt. %)		H (wt. %)		N (wt. %)	
		Calc.	Found	Calc.	Found	Calc.	Found
PMP	24	56.14	51.50	6.62	6.67	10.91	10.15
PMN	24	47.76	41.48	5.30	4.50	13.93	11.26
PMDN	24	41.55	47.93	4.32	5.20	13.27	9.18

PMP: R , R'= H
PMN: R= H , R'= NO₂
PMDN: R , R'= NO₂
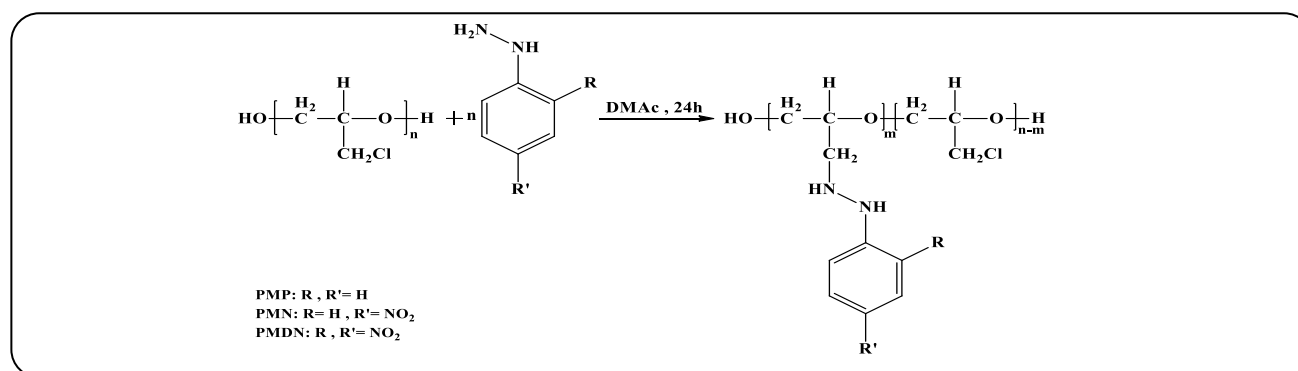
Scheme 1: PECH was modified by phenylhydrazine and its derivatives.
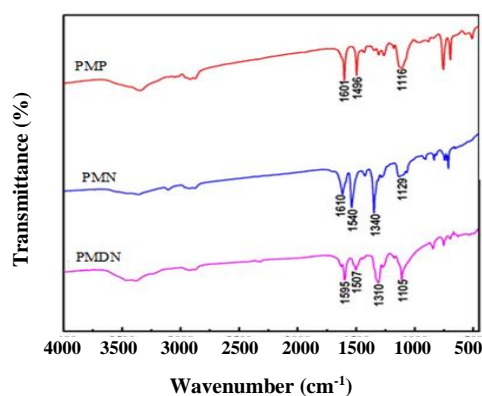
Fig. 1: FT-IR spectra of PMP, PMN and PMDN.

Fig. 2: H-NMR spectrum of PMP.

1129 cm^{-1}, 1540 cm^{-1} and 1340 cm^{-1} represent a stretching of 4-nitrophenylhydrazine ring, C-O stretching band, asymmetric and symmetric stretching vibrations of the –NO₂ group, respectively. The FT-IR results of PMDN show a stretching of 2,4- dinitrophenylhydrazine ring backbone, C-O stretching band, asymmetric and symmetric stretching vibrations of the –NO₂ groups at 1595 cm^{-1}, 1105 cm^{-1}, 1507 cm^{-1} and 1310 cm^{-1}, separately [44,45]. The structure of *PMP* was confirmed by H-NMR spectroscopy. Fig. 2 illustrate the signals at aromatic region. The peaks at around 7.4, 7.2, 7.0 and 6.5 ppm can be related to aromatic protons of *PMP*.

Apparatus and Methods

The FTIR spectrum used for characterization of chemical structure of the synthesized polymers (Jasco-680). ^{1}H-NMR (500 MHz) spectra of the polymers were recorded with CDCl₃ as a solvent by a Bruker Avance 500 spectrometer. Elemental analysis (CHN) was performed by elemental analyzer (Leco, CHNS-932).

Corrosion measurement methods
Electrochemical studies

The electrochemical tests were used a three electrode cells. A saturated calomel electrode was used as

areference, and the counter electrode was platinum. The working electrode was prepared from mild steel.

A PARSTAT 2273 electrochemical system was used to perform electrochemical measurements. Before measurements of the test, in order to achieve a state of equilibrium, the electrode was immersed in the solution at open circuit potential (*OCP*) for 1 h at 25⁰C The potential of potentiodynamic polarization curves was started from a potential of ± 250 mV relative to *OCP* at rapidity 1 mV/s. Electrochemical impedance spectroscopy tests were carried out at a frequency range of 100 kHz to 10 mHz with a range of 10 mV in comparison with open circuit potential and the system temperature was kept at 25 ± 0.1 °C.

Surface analysis: FE- SEM , EDS,(Mapping analysis) MAP

The FE-SEM analysis was performed by immersing the mild steel sample in the test solution in the absence and presence of concentration (200 ppm) of inhibitors (PMP, PMN, PMDN) at 25⁰C for 6 h. After that metal sample was brought out, washed with doubled distilled water, and dried at room temperature. Then the surface morphology of the Mild carbon steel samples was studied by FE-SEM and EDS technique using Model MIRA3-LMU –Czech and SAMX, respectively.

RESULTS AND DISCUSSION

Electrochemical study

Potentiodynamic polarization measurements

Fig. 3 shows the representative *DC* polarization curves of mild steel in 0.5M HCl in the absence or presence of different concentrations of inhibitors.

Electrochemical parameters such as cathodic and anodic Tafel slopes *(βc and βa)*, corrosion current density *(i$_{corr}$)*, corrosion potential *(E$_{corr}$)*, Corrosion Rate (CR), polarization resistance *(R$_p$)* and inhibition efficiency *(%IE)*, were obtained by Tafel extrapolationing which are reported in Table 2.

In Table 2, *E$_{inh}$-E$_B$* is the difference between corrosion potential in the presence and absence of the inhibitors. In order to measure the corrosion current densities and corrosion potential the cathodic and anodic branches of curves were extrapolated in Tafel region. The polarization resistance (*R$_p$*) efficiency of inhibition *(%IE)*, and Corrosion Rate (*CR*) were obtained according to *Eqs*. (1), (2) and (3), respectively [46-48]:
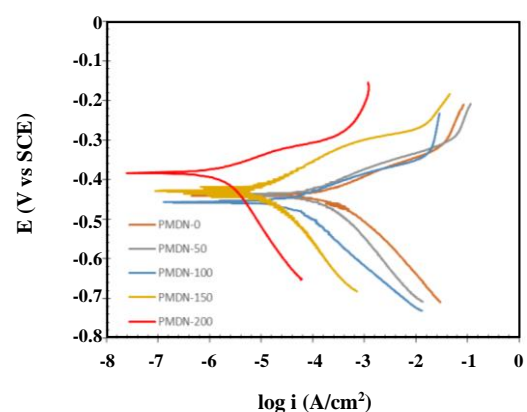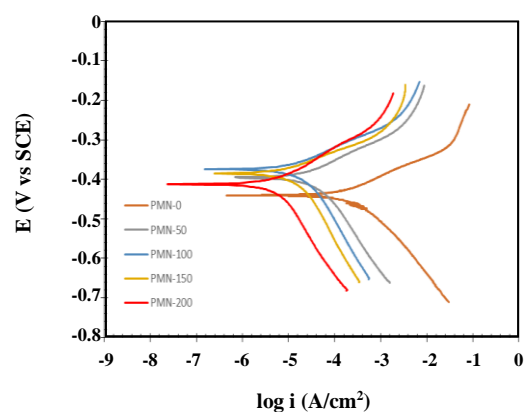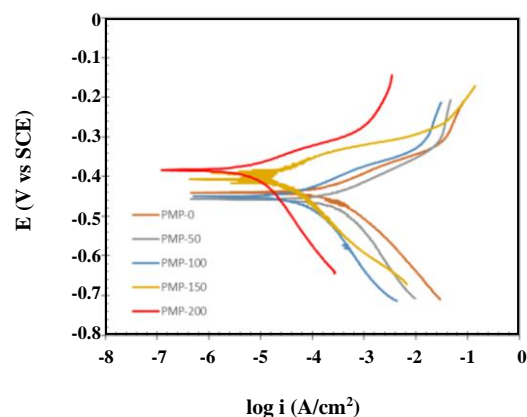

Fig. 3: DC polarization curves in 0.5M HCl with various concentration of inhibitors: (a) PMP, (b) PMN and (c) PMDN.

Table 2: Electrochemical parameters obtained for mild steel from the polarization curves in the absence and presence of different concentration of inhibitors (PMP, PMN and PMDN) in 0.5M HCl.

Samples	β_a(V/dec)	-β_c(V/dec)	E_{corr} SCE(V)	$E_{inh} - E_B$ SCE (V)	$R_p(\Omega.cm^2)$	$i_{corr}(\mu A/cm^2)$	%IE	CR (mmy)
Blank	0.059	0.204	-0.441	-0.017	73.335	222.88	-	2.530
PMP-50	0.061	0.206	-0.458	-0.016	513.70	39.78	82.15	0.451
PMP-100	0.071	0.176	-0.457	0.034	739.36	29.71	86.70	0.337
PMP-150	0.041	0.111	-0.407	0.059	880.75	20.86	90.64	0.237
PMP-200	0.058	0.196	-0.382	0.046	1893.216	10.14	95.45	0.115
PMN-50	0.057	0.21	-0.395	0.067	654.089	29.76	86.64	0.337
PMN-100	0.093	0.200	-0.374	0.056	1322.619	20.84	90.64	0.236
PMN-150	0.046	0.201	-0.385	0.029	1304.445	12.46	94.41	0.141
PMN-200	0.065	0.197	-0.412	0.01	2493.230	8.4	96.23	0.095
PMDN-50	0.051	0.102	-0.431	-0.018	1407.31	10.49	95.29	0.119
PMDN-100	0.046	0.121	-0.459	0.006	1737.27	8.33	96.26	0.094
PMDN-150	0.063	0.129	-0.435	0.059	3311.48	5.55	97.50	0.063
PMDN-200	0.041	0.199	-0.382	-0.017	5721.27	2.58	98.29	0.0290

$$R_p = \frac{(\beta_a \times \beta_c)}{(2.3031 \times icoor(\beta_a \times \beta_c))} \qquad (1)$$

$$\%IE = \frac{j_{corr}^o - j_{corr}}{j_{corr}^o} \times 100 \qquad (2)$$

$$CR = \frac{0.0032 \times i_{corr} \times (M.W)}{n \times d} \qquad (3)$$

Where i^0_{corr} and i_{corr} are the corrosion current densities with and without the inhibitors, respectively. *M.W.* and *d* are molecular weight and density of metal, respectively and n is the number of electrons exchanged in dissolution reaction. According to Fig. 3. and Table 2, it can be seen that the addition of each inhibitor leads to a significant decrease in corrosion current density (*i$_{corr}$*) and Corrosion Rate (*CR*). Furthermore, the increase in the polarization resistance at all inhibitor concentrations is in the order of *PMDN > PMN > PMP*. This may be attributed to the number of heteroatoms in each inhibitor. From the results shown in Table 2, each of the three inhibitors changes the anodic and cothodic slopes compared to the blank sample. So, it can be concluded that these inhibitors behave as mixed-type inhibitors (according to Table 2, |*E$_{inh}$ − E$_B$*| obtained lower than 0.85 V in all concentrations).

Adsorption isotherms

The inhibition efficiency of an organic matter is mostly related to its adsorption on the metal surface in the constant temperature, which organic inhibitor molecules replace the water molecules at the surface of metal as:

$Org_{(sol)} + nH_2O_{(ads)} \rightarrow Org_{(ads)} + nH_2O_{(sol)}$
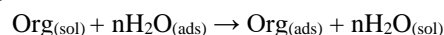
physicochemical properties can effect mainly on the adsorption of these molecules [49].

Surface coverage (θ) can be obtained from polarization readings and is calculated by Eq.(4) [43-45]:

$$\theta = \frac{j_{corr}^0 - j_{corr}}{j_{corr}^0} \qquad (4)$$

Data obtained from polarization measurements were experienced for fitting different adsorption isotherms. By far, for these compounds the best fit was observed with the Langmuir adsorption isotherm by R^2>0.99 (Fig.4) The Langmuir model is an equation based on a monolayer adsorption onto a homogeneous surface as well as without any interactions between the adsorbed molecules where the binding sites have equal affinity and energy[50].

Based on Langmuir isotherm, θ is dependent to inhibitor concentration According to Equations (5) and (6) [46-48]::
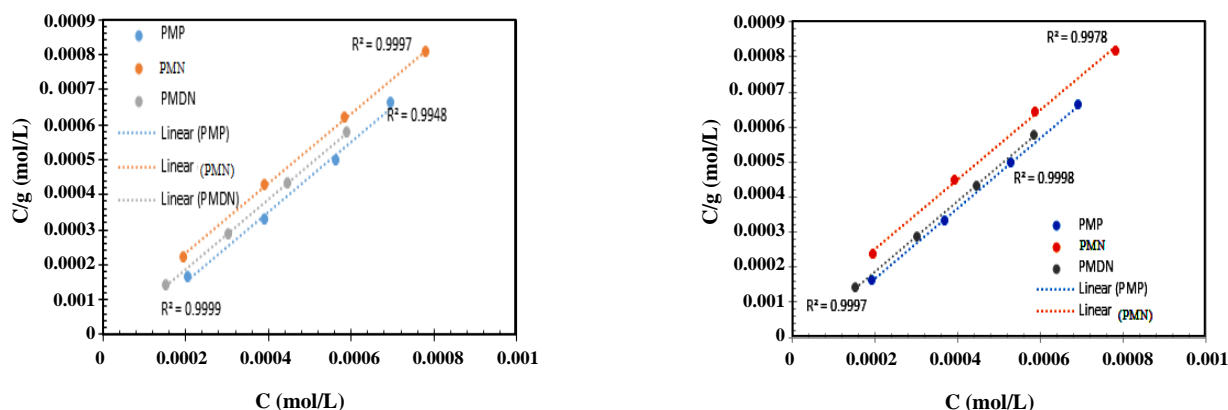
Fig. 4: Langmuir's adsorption plots in 0.5M HCl solutions containing different concentrations of PMP, PMN and PMDN.

$$\frac{C_0}{\theta} = \frac{1}{Kads} + C \qquad (5)$$

$$\Delta G_{ads} = RT \ln(55.5 K_{ads}) \qquad (6)$$

C_0 is the initial inhibitor concentration, θ is the surface coverage, K_{ads} is the equilibrium constant of adsorption process (according to formula (5), if the line relationship is $Y = X + 1 / K$, then the value K of the line relationship is obtained) and ΔG_{ads} is the adsorption free energy. The value of 55.5 being the concentration of water in solution expressed in mole. R is the gas universal constant and T is absolute temperature.

The negative values of ΔG_{ads} suggest the favorability of the inhibitor adsorption. In general the values of ΔG_{ads} around -20 kJ/mol or lower are represented physisorption, while those around -40 KJ mol^{-1} or higher involve chemisorption and values between -20 kJ/mol and -40 kJ/mol indicate both physisorption and chemisorption [51]. The data of isotherm parameters are given in Table 3.

In this case, the values of free energy of adsorption ΔG_{ads} lie in between -29.54 to -33.91 kJ, which represents the spontaneous both physisorption and chemisorption nature of the adsorption.

EIS measurements

To verify the potentiodynamic polarization results and in order to better investigate the mechanism of inhibition, impedance analyses were employed. The corrosion of mild steel in 0.5M HCl solution was evaluated by *EIS*. Nyquist and bode plots of mild steel at 200 ppm

concentration of *PMP, PMN* and *PMDN* are shown in Fig.5.

As is shown in Fig. 5(a), the diameter of the semicircle (polarization resistance) response of steel is remarkably increased after addition of inhibitors. Similar to the polarization test, increasing in the semicircle diameter is in the order of *PMDN > PMN > PMP*. The best fit on the impedance results was achieved by using one time constant equivalent model (Randel circuit), as depicted in Fig. 5. It means that the corrosion reaction of the mild steel dipped in the inhibited solution is under charge transfer control. In this equivalent electrical model, *Rs* and R_{ct} are the solution and charge transfer resistance, respectively. Also, *Q* is a constant phase element (*CPE*) described as *Eq*. (7):

$$Z_{CPE} = 1/Q(j\omega) \qquad (7)$$

Where *Q* and *j* are a non-ideal capacitance and the imaginary function ($\sqrt{-1}$), respectively. ω and n are the angular frequency and the deviation from the ideal behavior of a pure capacitor, respectively. The fitting results extracted from Nyquist and Bode plots are reported in Table 4.

In Table 4, the Impedance obtained at low frequency ($|Z|_{10\ mHz}$) is crucial to explain the corrosion resistance performance of the inhibitor[52]. From Table 5 it can be clearly seen that PMDN has higher R_{ct} and $|Z|_{10\ mHz}$ than two other inhibitors as obtained from polarization results.

Due to better performance of *PMDN* between these three inhibitors and in order to better investigation of inhibition mechanism of *PMDN*, the effect

Table 3: Adsorption constants for Langmuir isotherm model.

sample	K_{ads} (L/mol)	ΔG_{ads} (kJ/mol)
PMP	3333.33	-29.54
PMN	20000	-33.91
PMDN	11111.11	-32.47

Table 4: EIS results obtained from Nyquits and Bode plots for the samples dipped in the 0.5M HCl solutions without and with 200 ppm of corrosion inhibitors.

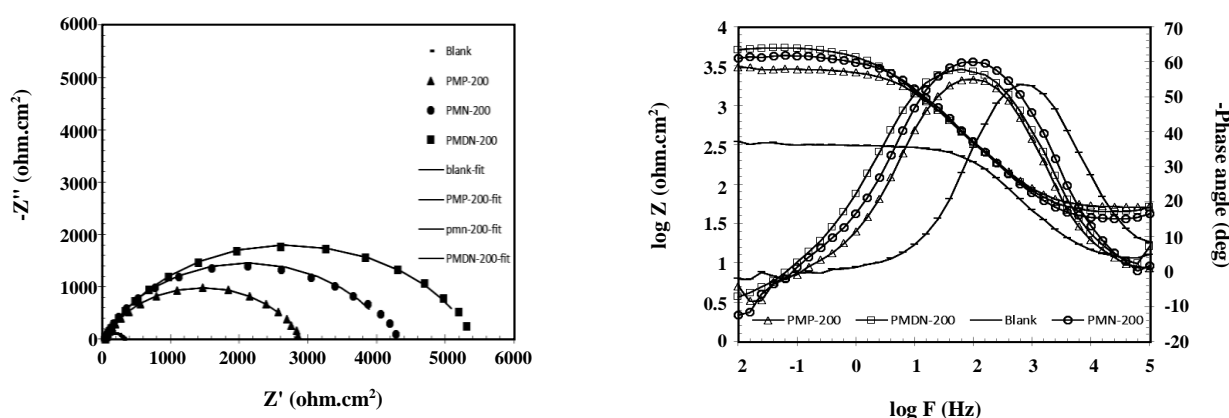| Sample	R_s [Ω cm^2]	Q_{dl} [S.sec^n/cm^2]	n	R_{ct} [Ω cm^2]	$|Z|_{10\ mHz}$
Blank	10.74	1.94×10^{-5}	0.8	300.2	346.035
PMP-200	49.49	2.06×10^{-5}	0.77	2847	3073.477
PMN200	35.32	1.94×10^{-5}	0.77	4159	3976.491
PMDN200	23.36	1.33×10^{-5}	0.69	5481	5011.87

Fig. 5: (a) Nyquist and (b) bode plots of mild steel at 200 ppm concentration of PMP, PMN and PMDN.

of concentration of this inhibitor is studied by *EIS* method. Nyquist and bode plots of mild steel at various concentrations of *PMDN* are depicted in Fig. 6.

Fig. 6. shows that the impedance in low frequency as well as the diameter of semicircle tended to increase when the concentration of the inhibitor increased. The equivalent circuits fitted with the Nyquist plots are depicted in Fig. 6a. According to the bode curves, all concentrations of *PMDN* have one time constant, therefore, the Randel model was used for modeling the impedance data. The fitting results and impedance data obtained from Nyquist and Bode plots are reported in Table 5.

It can be seen from Table 5 that more concentrations of *PMDN* caused higher R_{ct} for the samples immersed in the solutions. From the results reported in Table 5, it can be seen that the values of double layer capacitance

were decreased by increasing the concentration of *PMDN* in the solution. As a result, the mechanism of *PMDN* inhibition in the low pH media is the adsorption of the inhibitor molecules on the surface of the steel. This adsorption may be related to share lone pair electrons of heteroatoms (N and O) with the empty orbitals of Fe on the surface of the steel.

Surface morphology analysis

Fig.7. represents the morphology and composition of the film precipitated on the mild carbon steel surface in 0.05M HCl solution for 6hrs in the absence and presence of 200 ppm concentration of the inhibitors which were, *PMP, PMN* and *PMDN*.

As can be seen from Fig.7a, the metal surface is severely affected by corrosive agents in the absence

Table 5: Electrochemical results obtained from Nyquits and Bode plots for the steel samples dipped in the 0.5 HCl solutions containing various concentrations of PMDN.

Sample	$R_s [\Omega\,cm^2]$	$Q_{dl}[S.sec^n/cm^2]$	n	$R_{ct} [\Omega\,cm^2]$
PMDN-50	15.55	2.45×10^{-4}	0.71	1654
PMDN -100	15.65	1.98×10^{-4}	0.70	2651
PMDN -150	21.60	5.21×10^{-4}	0.70	3194
PMDN -200	23.36	1.33×10^{-5}	0.69	5481
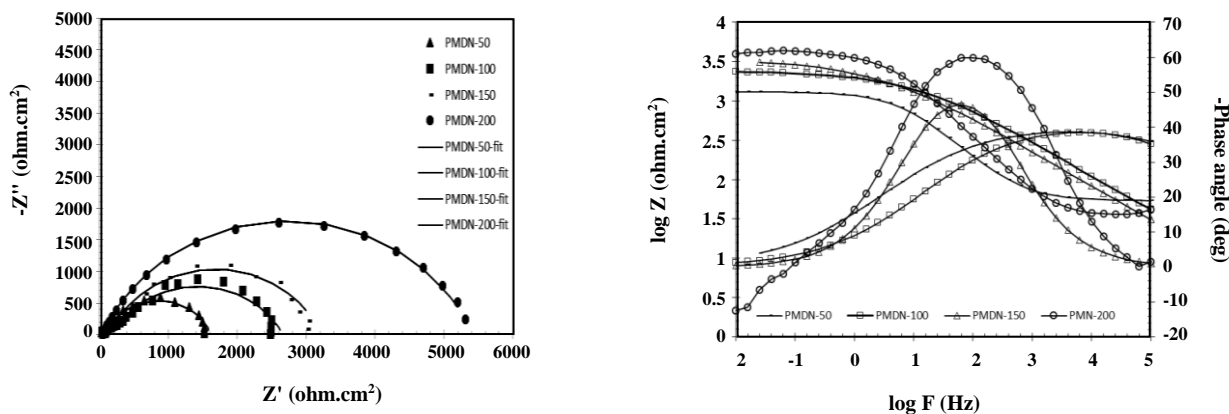
Fig. 6: (a) Nyquist and (b) bode plots of mild steel at various concentrations of PMDN.

of inhibitors. So, corrosive agents cause to produce porous surface with large diameter and deep holes. In contrast, in the presence of the inhibitors (Figs. 7 b–d), the metallic surfaces become relatively more smooth. The improvement of surface morphology in the presence of the inhibitors is attributed to the inhibitive action of the inhibitors by forming a protective film on the mild steel surface. As is shown in Fig. 7, the morphology of the sample immersed in the solution contained PMND is more smooth than two other samples indicating that the adsorbed layer of the inhibitor is more effective than PMP and PMN inhibitors. These results are in good agreement with the polarization and impedance tests.

Fig. 8. and Fig. 9. compares the carbon elemental mapping and *EDS* results of the samples immersed in the acidic solutions in the absence of an inhibitor, and with 200 ppm of the three inhibitors, respectively.

According to Fig. 8 and Fig. 9 an increase in the carbon element concentration on the surface of metal and also, the presence of nitrogen element on the surface of the samples immersed into inhibitor containing solutions suggests forming a complex between organic inhibitors and corrosion products on the surface of steel.

CONCLUSIONS

The effect of inhibition ability of synthesized polymers on corrosion of mild steel in 0.5 M hydrochloric acid was investigated by electrochemical impedance spectroscopy (*EIS*), potentiodynamic polarization. These polymers act as good corrosion inhibitor for mild steel and the inhibition efficiency should increase in the order: *PMP<PMN<PMDN*. The maximum inhibition efficiency of *PMN* and *PMDN* are 97.75% and 98.01% at 200 ppm.

The results of potentiodynamic polarization curves demonstrate that those polymers act as mixed type inhibitors but increasing their concentration caused the shift of corrosion potential to cathodic potential. Therefore, those polymers could be classified as cathodic inhibitors.

As far as the parameters of adsorption are concerned, free energy (ΔG°) indicates that the adsorption of polymers is physical adsorption and chemisorptions. Also, the adsorption of these polymers on the mild steel surface obeys a Langmuir adsorption isotherm. The *EIS* spectra are shown an increase of the charge transfer resistance (*Rct*) values and a decrease of the capacitance
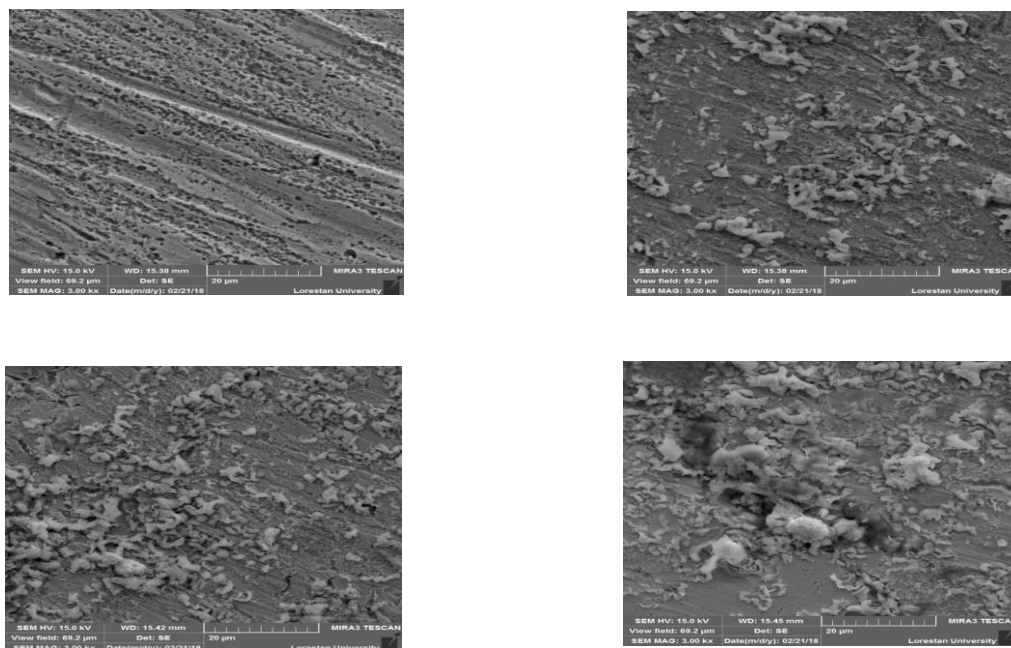
Fig. 7: FE-SSEM images of mild steel electrode surface in (a) 0.5M HCl; (b) 0.5M HCl +200 ppm PMP;
(c) 0. 5M HCl +200 ppm PMN and (d) 0.5M HCl +200 ppm PMDN.
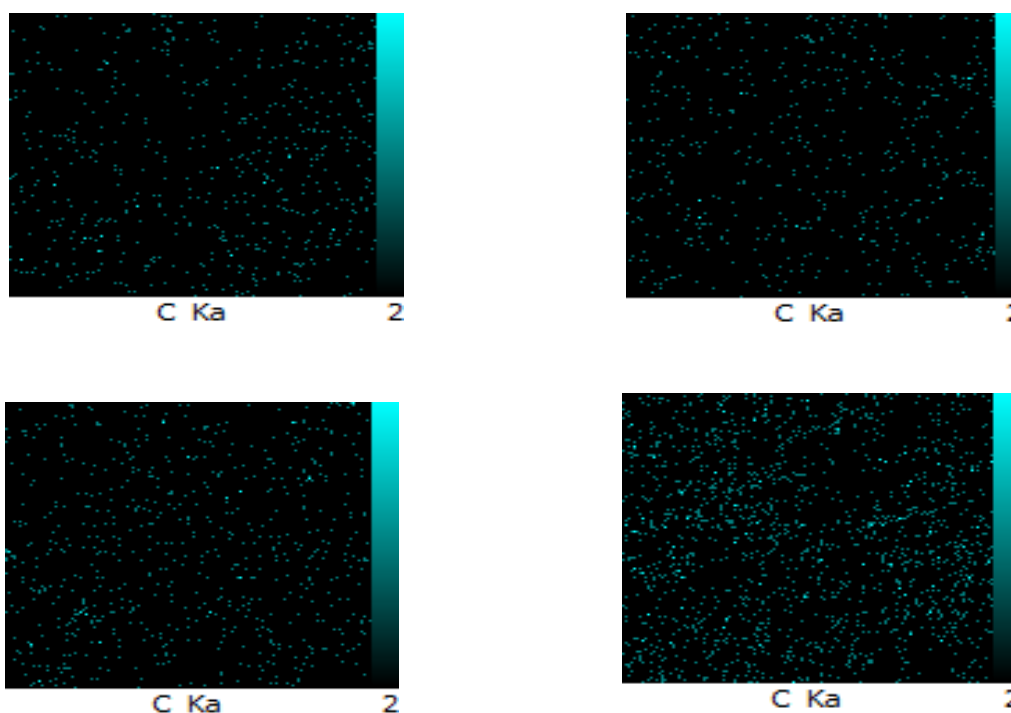
Fig. 8: Carbon elemental mapping of the steel samples immersed in the acidic solutions without an inhibitor (a) and with
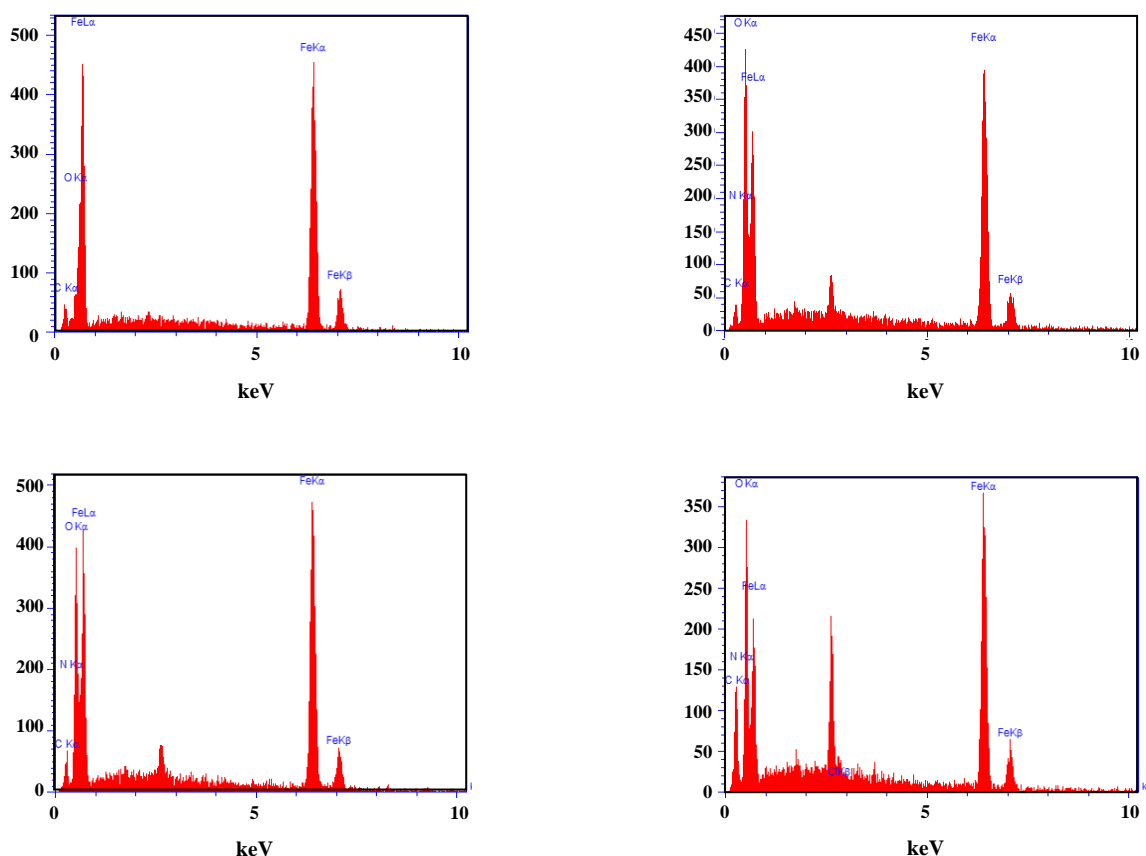*200 ppm of PMP (b), PMN (c) and PMDN (d).*

Fig. 9: EDS results of the steel samples immersed in the acidic solutions without inhibitor (a) and with 200 ppm of PMP (b), PMN (c), and PMDN (d).

(*Cdl*), with increasing of polymers concentrations and replacement of water molecules by adsorption of polymers on the steel surface. The results obtained from the potentiodynamic polarization and *EIS* are confirmed by *FE-SEM, MAP, EDS* study.

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