

# Polymers as Corrosion Inhibitors for Metals in Different Media - A Review

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**Abstract:** Several works have been done and more are on the pipeline on the influence of organic compounds containing polar functions on the corrosion inhibition of metals in various aqueous media. Corrosion inhibition by such compounds is generally attributed to their adsorption on the metal/solution interface. The specific action of an inhibitor depends on the nature of its interaction with metal surface, which causes a change in either mechanism of the electrochemical corrosion process or in the surface area available for the process. Thus, factors such as physiochemical properties of the inhibitors, the nature and surface charge of the metal, solution composition and pH are important considerations. Polymers function as corrosion inhibitors because of their ability to form complexes through their functional groups with metal ions which occupy large area and by so doing blanket the metal surface from aggressive anions present in solution.

**Keywords:** Polymers, metals, acids, alkaline, corrosion inhibition.

## 1. INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the disastrous effects of corrosion can be summarized below:

- (i). Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircrafts etc.).
- (ii). Reduced value of goods due to deterioration of appearance.
- (iii). Contamination of fluids in vessels and pipes (for instance beer goes cloudy when small quantities of heavy metals are released by corrosion).
- (iv). Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
- (v). Perforation of vessel and pipes allowing escape of their contents and possible harm to the surroundings.
- (vi). Loss of time availability profile – making industrial equipment.
- (vii). Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a cracklike structure, very considerable

weakening may result from quite a small amount of metal loss.

- (viii). Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion and to allow corroded components to be conveniently replaced.
- (ix). Mechanical damage to valves, pumps, etc or blockage of pipes by solid corrosion products.

Virtually all corrosion reactions are electrochemical in nature consisting of anodic and cathodic sites. At the anodic site, dissolution of the metal takes effect leading to the release of electrons whereas at the cathodic site, the electrons react with some reducible component of the electrolyte and they are removed from the metal. Corrosion can be minimized by employing suitable strategies which in turn stifle, retard or completely stop the anodic or cathodic reaction or both.

Among the several methods of corrosion control such as cathodic protection [1, 2], anodic protection [3], coating [4] and alloying, the use of chemical inhibitors is often considered as the most effective and practical method of corrosion prevention. A corrosion inhibitor is a chemical additive which when added to a corrosive aqueous environment reduces the rate of metal wastage. It is widely accepted that inhibitors especially the organic ones work by an adsorption mechanism. The resultant film of chemisorbed inhibitor is then responsible for protection either by physically blocking the surface from the corrosion environment or by retarding the electrochemical processes. The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino ( $-NH_2$ ), carboxyl ( $-COOH$ ) and phosphate ( $-PO_3H_2$ ) although other functional groups or atoms can form coordinate bonds with metal surfaces.

Sanyal [5] and Abd El-Maksoud [6] in their reviews have given a vivid account of organic compounds used as corrosion inhibitors including their classification and

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mechanism of action. Raja and Sethuraman [7] has given a comprehensive review of natural products as corrosion inhibitors for metals in corrosive media. The use of natural products otherwise tagged "green corrosion inhibitors" has been advocated because of the cost, toxic nature and environmentally unfriendliness of inorganic and organic corrosion inhibitors. More so, they are readily available, cheap and a renewable source of materials.

The use of polymers as corrosion inhibitors has attracted considerable attention recently. Polymers are used as corrosion inhibitors because, through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution [8]. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen) that are the major active centres of adsorption.

The present work presents a review of polymers as corrosion inhibitors for various metals in various aqueous corrosive environments.

## 2. POLYMERS AS CORROSION INHIBITORS OF MILD STEEL

The inhibiting effect of 2, 6 ionen, 2, 10 ionen, polyvinylbenzyltrimethyl ammonium chloride (PVBtMA) and latex on low carbon steel in HCl solution has been investigated by potentiodynamic polarization measurements and EIS technique over the temperature range 20-60°C at different inhibitor concentrations. It was found that the inhibition efficiencies increased with the increase in inhibitor concentration. Results obtained also reveal that the inhibitor behaves as anodic inhibitor [9].

Two forms of polymers namely red form with molecular weight of (800,000 g mol<sup>-1</sup>) insoluble in alcohol and green form with low molecular weight (44,000 g mol<sup>-1</sup>) and soluble in alcohol obtained by polymerization of ortho-ethoxyaniline were tested as corrosion inhibitor for mild steel in acidic media [10]. The obtained results showed the adsorption of the polymer alcoholic form obeys Temkin adsorption isotherm with no significant change as function with inhibition efficiencies for a series of molecular weights ranging from 123,000 to 124,000 g mol<sup>-1</sup>.

The inhibition efficiency of polyvinyl pyrrolidone (PVP) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl<sup>-</sup>, in the absence and the presence of Zn<sup>2+</sup> has been reported using weight loss method [11]. Influence of pH, immersion period, N-cetyl-N,N,N-trimethyl ammonium bromide and sodium dodecylsulphate on the inhibition efficiency of the inhibitor system has also been investigated. The nature of the protective film has been analyzed by FTIR and fluorescence spectroscopy. In the presence of PVP, the protective film consists of Fe<sup>2+</sup> - PVP complex; the film is found to be UV-fluorescent. In the presence of PVP and Zn<sup>2+</sup>, the protective film consists of Fe<sup>2+</sup> - PVP complex and Zn(OH)<sub>2</sub>; it is found to be UV-fluorescent

Poly(styrenesulphonic acid)-doped polyaniline has been synthesised and the influence of this polymeric compound on the inhibition of corrosion of mild steel in 1M HCl has been

investigated using weight loss measurements, galvanostatic polarisation studies, electropermeation studies and a.c. impedance measurements [12]. The polymer acts predominantly as an anodic inhibitor. Hydrogen permeation studies and a.c. impedance measurements clearly indicate a very effective performance of the compound as a corrosion inhibitor. The adsorption of the compound on the mild steel surface obeys Temkin's adsorption isotherm.

The polymer-polymer complexes [(PMAAN/PAAmM)c], composed of polymethacrylic acid [PMAAN, N = 1 (Mn = 1.0 × 10<sup>4</sup>), 2 (Mn = 5.0 × 10<sup>3</sup>) and 3 (Mn = 2.5 × 10<sup>3</sup>)] and polyacrylamide [PAAmM, M = 1 (Mn = 5.0 × 10<sup>3</sup>) and 2 (Mn = 2.5 × 10<sup>3</sup>)] were investigated as inhibitors for corrosion of mild steel in cooling water systems [13]. The inhibition abilities of (PMAAN/PAAmM)c against corrosion and scale deposition were evaluated by corrosion tests and physicochemical methods. In a solution with low concentration of ionic species (LC solution), the corrosion inhibition abilities of (PMAAN/PAAmM)c improved at an addition of the polymer higher than 50 ppm. This effect is due to the control of adsorption of the polymers on steel surfaces based on the formation of polymer-polymer complexes. In a solution with high concentration of ionic species (HC solution), the corrosion inhibition abilities of (PMAAN/PAAmM)c were also favourable at an addition of the polymer higher than 20 ppm. This effect is attributed to control of the adsorption of the polymers on steel surfaces and the scale dispersion based on the formation of polymer-polymer complexes.

The corrosion inhibition of low carbon steel in phosphoric acid by polyvinylpyrrolidone (PVP) and polyethyleneimine (PEI) as inhibitors has been reported. Polarization and weight loss studies showed that both polyvinylpyrrolidone and polyethyleneimine are effective for the inhibition of low carbon steel over a wide range of aqueous phosphoric acid solutions [14].

Corrosion inhibition of mild steel in sulphuric acid solution using polyethylene glycol methyl ether (PEGME) has been reported using electrochemical polarization (galvanostatic and potentiostatic) techniques [15]. It was found that PEGME is a very effective corrosion inhibitor for mild steel in acidic medium. Inhibition efficiency increase with increase in the concentration of PEGME but almost remains the same with increasing temperature. Adsorption of PEGME was found to follow the Langmuir's adsorption isotherm. PEGME was also found to function as an inhibitor of mixed type acting by blocking the active sites on the cathodic and anodic regions. Results obtained are summarized in Table 1.

**Table 1. Inhibition Efficiency for Mild Steel in 1 N H<sub>2</sub>SO<sub>4</sub> in the Presence PEGME as Additive at Different Temperatures [15]**

Concentration (M)	Inhibition Efficiency (%)			
	298 K	308 K	318 K	328 K
10 <sup>-7</sup>	48.3	85.6	80.0	62.9
10 <sup>-5</sup>	43.8	88.0	76.0	71.9
10 <sup>-3</sup>	84.2	90.0	86.0	87.5

Umoren *et al.* [16] has reported on the corrosion inhibition of mild steel in  $\text{H}_2\text{SO}_4$  at 30 – 60°C by polyethylene glycol (PEG) and polyvinyl alcohol (PVA) using weight loss and hydrogen techniques. The inhibition efficiency of the inhibitor increased with increase in concentration and temperature. The inhibitors were found to obey Temkin, Freudlich and Langmuir adsorption isotherms from the fit of the experimental data at all concentrations and temperature studied. The phenomenon of chemical adsorption was proposed from the activation parameters obtained. PEG was found to be a better inhibitor than PVA. The values of inhibition efficiency for different concentrations of PVA and PEG at 60°C are given in Table 2.

**Table 2. Inhibition Efficiencies for Mild Steel in 0.1M  $\text{H}_2\text{SO}_4$  Containing Different Concentrations of PVA and PEG at 60°C from Weight Loss and Hydrogen Evolution Measurements [16]**

Inhibitor	Concentration (M)	Inhibition Efficiency (%)	
		Weight Loss Method	Hydrogen Evolution Method
PVA	$1 \times 10^{-4}$	36.31	38.21
	$7 \times 10^{-5}$	36.04	35.46
	$5 \times 10^{-5}$	34.62	33.34
	$3 \times 10^{-5}$	33.33	32.24
	$1 \times 10^{-5}$	32.54	31.14
PEG	$1 \times 10^{-4}$	40.23	55.31
	$7 \times 10^{-5}$	39.49	51.63
	$5 \times 10^{-5}$	37.99	44.72
	$3 \times 10^{-5}$	37.52	35.50
	$1 \times 10^{-5}$	33.03	31.08

The corrosion inhibition of mild steel in 1M  $\text{H}_2\text{SO}_4$  in the presence of polyvinylpyrrolidone (PVP) and polyacrylamide (PA) as inhibitors at 30 – 60°C was studied using gravimetric and gasometric techniques [17]. Results obtained indicate that increase in temperature increases the corrosion rate in the absence and presence of the inhibitors but decreased the inhibition efficiency. The inhibition efficiency increased with increase in concentration of the inhibitors. Both PVP and PA were found to obey Temkin and El-Awady *et al.* Kinetic-thermodynamic adsorption isotherm at all the concentrations and temperatures studied. Physiosorption mechanism was proposed from the activation parameters obtained. PVP was found to be a better inhibitor than PA. Table 3 shows the values of inhibition efficiency obtained at different concentration of PVP and PA at 30°C from weight loss and hydrogen evolution measurements.

Gum Arabic (GA) (a naturally occurring polymer) has also been reported as an inhibitor for inhibition of mild steel corrosion in  $\text{H}_2\text{SO}_4$  at 30 – 60°C using weight loss, evolution and thermometric measurements [18]. Inhibition process was afforded by virtue of chemical adsorption of GA components onto mild steel surface following Temkin adsorption isotherm. Inhibition efficiency increases with increase in GA concentration as well as temperature rise. It was also found from the kinetic/thermodynamics studies that adsorption of

GA onto mild steel surface was spontaneous. Results are summarized in Table 4.

**Table 3. Inhibition Efficiencies for Mild Steel in 1M  $\text{H}_2\text{SO}_4$  Containing Different Concentrations of PA and PVP at 30°C from Gravimetric (Weight Loss) and Gasometric (Hydrogen Evolution) Measurements [17]**

Inhibitor	Concentration (M)	Inhibition Efficiency (%)	
		Weight Loss Method	Hydrogen Evolution Method
PA	$1 \times 10^{-4}$	58.00	50.00
	$8 \times 10^{-5}$	57.50	41.00
	$6 \times 10^{-5}$	53.00	32.95
	$4 \times 10^{-5}$	37.00	26.71
	$2 \times 10^{-5}$	34.00	21.32
PVP	$1 \times 10^{-4}$	67.80	58.00
	$8 \times 10^{-5}$	63.00	54.00
	$6 \times 10^{-5}$	61.00	47.00
	$4 \times 10^{-5}$	59.00	41.00
	$2 \times 10^{-5}$	55.00	36.00

**Table 4. Inhibition Efficiency for Mild Steel in 0.1M  $\text{H}_2\text{SO}_4$  Containing Different Concentrations of Gum Arabic (GA) at Different Temperatures from Weight Loss Measurements [18]**

Concentration (g/l)	Inhibition Efficiency (%)			
	30°C	40°C	50°C	60°C
0.1	4.75	7.58	11.59	12.53
0.2	5.62	12.27	15.08	20.05
0.3	12.04	13.73	21.00	26.46
0.4	17.24	19.49	25.08	29.25
0.5	21.84	25.99	32.92	37.88

Rajendran *et al.* [8] investigated the corrosion behaviour of carbon steel using polyvinyl alcohol (PVA) in neutral aqueous solution containing 60ppm of  $\text{Cl}^-$  in the absence and presence of  $\text{Zn}^{2+}$  ions using weight loss method. It was found that a formulation consisting of 100ppm of PVA and 75ppm  $\text{Zn}^{2+}$  offered 81% inhibition efficiency to carbon steel immersed in a solution containing 60ppm of  $\text{Cl}^-$ . A synergistic effect on inhibition of a combination of PVA and  $\text{Zn}^{2+}$  was observed during the tests. Increased in pH and duration of immersion led to increase in inhibition efficiency of the PVA –  $\text{Zn}^{2+}$  system.

The inhibition effect of some Polyethylene glycols (PEGs) on carbon steel corrosion at 25°C in 0.5N HCl as corrosive medium was evaluated by weight loss, polarization and electrochemical impedance spectroscopy techniques [19]. In order to study the effect of PEGs' structure on the inhibition efficiency, different molecular weights: 400, 1000,

4000 and 10,000  $\text{g mol}^{-1}$  was selected. Results obtained show the effectiveness of polyethylene glycols on corrosion inhibition of C- steel in HCl solution. The inhibition efficiency increases with increase in mean molecular weight of the polymer and its concentration. The adsorption of the studied polymers on C – steel obeys Langmuir isotherm. In a related study, the inhibitive effects of different polyethylene glycols of varying molecular weight (200 – 10,000  $\text{g/mol}$ ) on carbon steel corrosion in 3N  $\text{H}_2\text{SO}_4$  has been reported [20] using weight loss, polarization and electrochemical impedance spectroscopy.. Results obtained showed that the PEGs were effective corrosion inhibitors for carbon steel in the acidic environment. It was found that PEG has an inhibiting effect on the corrosion process and the inhibition efficiency was more than 90 %. The studied polymers were physically adsorbed on the carbon steel surface in the acid medium. The results from the three independent methods employed were in good agreement. The results obtained are summarized in Tables 5 and 6 for C-steel in 0.5N HCl and 3N  $\text{H}_2\text{SO}_4$  in the presence of PEG respectively.

The inhibitive performance of novel synthesized water soluble triblock copolymers-2-(diethylamino)ethyl ethacrylate-block-2-(dimethylamino)ethyl methacrylate – block-2- (N-morpholino)ethyl methacrylate [PDEA-PDMA-PMEMA] and 2-(diisopropylamino) ethyl methacrylate-block-2-(dimethylamino) ethyl methacrylate – block-2- (N-morpholino)ethyl methacrylate [PDPA-PDMA-PMEMA] of two different molecular weight on the corrosion behaviour of mild steel in 0.5M HCl has been reported [21] using potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization methods. Polarization methods indicate that all studied copolymers were acting as mixed type inhibitors. Inhibition efficiencies increase with increase in inhibitor concentration. This reveals that inhibitive actions of inhibitors were mainly due to adsorption on steel surface. Adsorption of the inhibitors was found to follow Langmuir adsorption isotherm. The correlation between the inhibition efficiencies of the studied copolymers and their molecular structures based on quantum chemical calculations indicate that adsorption of the triblock copolymers depend on the charge density of adsorption centres and dipole moments. The experimental results are given in Table 7.

### 3. POLYMERS AS CORROSION INHIBITORS OF ALUMINIUM

The effect of two polyamide compounds on the corrosion behavior of aluminum metal in oxalic acid solution was investigated using potentiostatic and potentiodynamic anodic polarization techniques [22]. The inhibition efficiency increases with increasing polyamide concentration until a critical value and then starts to decrease in high polymer concentrations, indicating low inhibition efficiency. The inhibitive behavior of these compounds was discussed in terms of adsorption of the polyamide compounds on the metal surface and formation of insoluble complexes. The adsorption process was found to obey Temkin adsorption isotherm. The pitting potential varies with concentration of chloride ions according to a linear relationship. The addition of polyamide compounds shifts the pitting potential of aluminum electrode to more positive potentials, indicating an increased resistance to pitting attack.

**Table 5. Inhibition Efficiency for C-Steel in 3N  $\text{H}_2\text{SO}_4$  for Polyethylene Glycols of Varying Molecular Weight from LPR and EIS Methods [20]**

Molecular Weight g/mol	Concentration (M)	Inhibition Efficiency (%)	
		LPR Method	EIS Method
200	$10^{-6}$	23.5	23.5
	$10^{-5}$	38.9	35.1
	$10^{-4}$	73.5	66.2
	$10^{-3}$	86.4	77.4
	$10^{-2}$	93.0	84.2
	$10^{-1}$	96.8	92.0
400	$10^{-6}$	17.7	23.4
	$10^{-5}$	75.1	61.1
	$10^{-4}$	86.4	87.1
	$10^{-3}$	94.4	93.4
	$10^{-2}$	97.1	96.4
	$10^{-1}$	98.4	97.3
600	$10^{-6}$	16.2	14.1
	$10^{-5}$	85.0	79.7
	$10^{-4}$	92.3	93.9
	$10^{-3}$	98.1	96.1
	$10^{-2}$	98.8	97.6
	$10^{-1}$	99.2	98.1
1000	$10^{-6}$	16.1	43.1
	$10^{-5}$	93.0	88.0
	$10^{-4}$	96.8	97.7
	$10^{-3}$	98.9	97.6
	$10^{-2}$	99.1	98.4
	$10^{-1}$	-	98.8
2000	$10^{-6}$	34.3	22.3
	$10^{-5}$	94.4	92.8
	$10^{-4}$	98.0	97.7
	$10^{-3}$	99.1	98.2
	$10^{-2}$	92.2	98.8
	$10^{-1}$	-	-
4000	$10^{-6}$	10.2	51.6
	$10^{-5}$	98.2	97.6
	$10^{-4}$	98.6	98.2
	$10^{-3}$	99.0	98.5
	$10^{-2}$	99.2	98.8
	$10^{-1}$	-	-
	$10^{-6}$	18.3	32.4
	$10^{-5}$	96.7	97.7
6000	$10^{-4}$	98.1	98.2
	$10^{-3}$	99.0	98.5
	$10^{-2}$	99.3	99.0
	$10^{-1}$	-	-
	$10^{-6}$	73.6	57.9
	$10^{-5}$	96.9	97.4
10000	$10^{-4}$	98.1	98.2
	$10^{-3}$	99.2	98.7
	$10^{-2}$	99.2	99.1
	$10^{-1}$	-	-

**Table 6. Inhibition Efficiency for C-Steel in 0.5N HCl for Polyethylene Glycols of Varying Molecular Weight from LPR, EIS and Weight Loss Methods [20]**

Molecular Weight (g/mol)	Concentration (M)	Inhibition Efficiency (%)		
		LPR Method	EIS Method	Weight Loss
400	$5 \times 10^{-5}$	48	53	50
	$1 \times 10^{-4}$	55	74	57
	$5 \times 10^{-4}$	73	78	61
	$1 \times 10^{-3}$	88	80	69
	$5 \times 10^{-3}$	89	81	85
1000	$5 \times 10^{-5}$	65	86	75
	$1 \times 10^{-4}$	79	87	78
	$5 \times 10^{-4}$	82	87	84
	$1 \times 10^{-3}$	88	88	89
	$5 \times 10^{-3}$	91	88	91
4000	$5 \times 10^{-5}$	80	88	79
	$1 \times 10^{-4}$	87	81	84
	$5 \times 10^{-4}$	89	89	89
	$1 \times 10^{-3}$	91	90	90
	$5 \times 10^{-3}$	91	90	93
10000	$5 \times 10^{-5}$	86	89	80
	$1 \times 10^{-4}$	87	91	85
	$5 \times 10^{-4}$	88	91	88
	$1 \times 10^{-3}$	90	92	91
	$5 \times 10^{-3}$	91	92	96

The mechanism of corrosion of aluminium and the effect of polyethylene glycol (PEG) polymer as corrosion inhibitor in acidic media has been studied using the weight loss method, potentiodynamic and galvanostatic polarization measurements [23]. Differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry have been used for the study of corrosion rates for the corrosion of aluminium in acidic medium at short time intervals. Results obtained showed that the corrosion inhibition efficiency of PEG was 94% after 24 h of immersion period.

In aqueous alkaline media (e.g. water-borne metallic paints) aluminium pigments react by the evolution of hydrogen. This corrosion reaction can be inhibited by addition of different water-soluble polymers with carboxyl groups like polyacrylic acids, styrene-maleic acid or styrene-acrylate copolymers. As a rough empirical rule can be stated that the corrosion-inhibiting effect of polymers with carboxyl groups increases with decreasing molecular mass and decreasing acid number. Moreover, the isoelectric point (IEP) of aluminium oxide (pH $\approx$ 9) seems to be an important factor controlling corrosion inhibition (and adsorption) of polymers with carboxyl groups. Thermosetting phenolic resins (resols) inhibit the corrosion reaction of aluminium pigment excellently at pH 8 but less effectively at pH 10.

The corrosion-inhibiting functional group of resols seems to be the chelating ortho-hydroxybenzyl alcohol structural part. In contrast, the nonionic water-soluble polymer polyvinyl alcohol does not inhibit the corrosion reaction. So, one may assume that an ionic interaction between aluminium pigment surface and polymer is necessary (but not sufficient) for corrosion inhibition [24].

**Table 7. Inhibition Efficiencies for Mild Steel in 0.5M HCl Containing Different Concentrations of Studied Triblock Copolymers at 25°C [21]**

Inhibitor	Concentration (M)	Inhibition Efficiency (%)	
		EIS Method	LPR Method
DPI-I	$5 \times 10^{-8}$	40.5	24.0
	$5 \times 10^{-7}$	53.2	58.8
	$1 \times 10^{-6}$	74.3	76.1
	$5 \times 10^{-6}$	83.0	85.2
	$5 \times 10^{-5}$	91.8	88.6
DP-II	$5 \times 10^{-8}$	53.1	23.2
	$5 \times 10^{-7}$	57.3	48.8
	$1 \times 10^{-6}$	69.1	73.1
	$5 \times 10^{-6}$	78.5	75.4
	$5 \times 10^{-5}$	84.5	79.6
DE	$5 \times 10^{-8}$	34.7	27.6
	$5 \times 10^{-7}$	63.7	67.6
	$1 \times 10^{-6}$	66.4	69.5
	$5 \times 10^{-6}$	74.9	74.3
	$5 \times 10^{-5}$	76.1	75.3

Two polymers, polyvinylbenzyltrimethylammonium chloride (PVBA) and polydiallyldimethylammonium chloride (PDDA) were used to inhibit aluminium corrosion in primary cells with Al anodes and alkaline electrolyte. From the results, they inhibited cathodic corrosion reaction predominantly, which was preferable to the aluminium anode. The cathodic inhibiting effect from the result seems to be due to the thicker double layer of the polymer cation [25].

The corrosion inhibition of aluminium in H<sub>2</sub>SO<sub>4</sub> in the presence of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) as inhibitors at 30 – 60°C was studied using gravimetric (weight loss), gasometric (hydrogen evolution) and thermometric techniques [26]. It was found that inhibition efficiency (1%) increased with increase in concentration of both PEG and PVA. Increase in temperature increased the corrosion rate in the absence and presence of the inhibitors but decreased the inhibition efficiency. Both PEG and PVA were found to obey Temkin adsorption isotherm at all concentrations and temperature studied. PEG and PVA inhibited aluminum corrosion by virtue of adsorption which was found to follow physisorption mechanism. The study revealed that PEG was a better corrosion inhibitor for Al than PVA. Experimental results are listed in Table 8.

**Table 8. Inhibition Efficiencies for Mild Steel in 0.1M H<sub>2</sub>SO<sub>4</sub> Containing Different Concentrations of PVA and PEG at 3°C from Weight Loss and Hydrogen Evolution and Thermometric Measurements [26]**

Inhibitor	Concentration (M)	Inhibition Efficiency (%)		
		Gravimetric Method	Gasometric Method	Thermometric Method
PEG	1 x 10 <sup>-4</sup>	50.93	45.07	54.69
	7 x 10 <sup>-5</sup>	40.71	43.66	45.50
	5 x 10 <sup>-5</sup>	34.33	36.62	35.48
	3 x 10 <sup>-5</sup>	28.72	32.39	24.86
	1 x 10 <sup>-5</sup>	22.23	29.58	14.93
PVA	1 x 10 <sup>-4</sup>	43.52	42.25	51.01
	7 x 10 <sup>-5</sup>	42.59	40.85	48.68
	5 x 10 <sup>-5</sup>	40.74	39.43	36.59
	3 x 10 <sup>-5</sup>	39.81	38.03	24.42
	1 x 10 <sup>-5</sup>	37.96	33.80	17.59

Umoren [18] investigated the corrosion behaviour of aluminium exposed to H<sub>2</sub>SO<sub>4</sub> and its inhibition using gum Arabic (GA) (a naturally occurring polymer) at the temperature range of 30 – 60°C using weight loss and thermometric methods. Results obtained indicate that corrosion rate of aluminium decreases in the presence of the inhibitor (GA) compared to its absence. Inhibition efficiency increases with increase in concentration of GA reaching a maximum value of 79.69% at 30°C for GA concentration of 0.5g/L. GA was also found to be physically adsorbed onto aluminium surface following El-Awady *et al.* Kinetic-thermodynamic adsorption isotherm. In a related study, corrosion inhibition of aluminium using the same inhibitor in an alkaline medium (NaOH) at 30 and 40°C has been reported [27] using hydrogen evolution and thermometric techniques. It was found that GA inhibited the alkaline induced corrosion of aluminium. Inhibition efficiency increases with increase in concentration of GA and also with temperature rise. Maximum inhibition efficiency of 76% was obtained at 40°C using 0.5g/L GA concentration. Phenomenon of chemical adsorption was proposed for the inhibition process and GA was found to adsorb onto aluminium surface following Freundlich, Temkin and Langmuir adsorption isotherms. Tables 9 and 10 summarize the values of inhibition efficiency obtained for GA of varying concentration in acidic and alkaline media respectively for the corrosion of aluminium.

The corrosion and inhibition behaviour of aluminium in HCl in the presence of polyvinyl pyrrolidone (PVP), polyacrylamide (PA) and their blends in the temperature range of 30 – 60°C using weight loss, hydrogen evolution and thermometric techniques has been reported [28]. Inhibition efficiency increased with increase in inhibitors concentration and decreases with increase in temperature. PVP was found to have higher inhibition efficiency than PA which was attributed to their differences in molecular structures. Inhibition efficiency was enhanced on blending the two polymers and the optimum inhibition was obtained

at 3:1 blending ratio of PVP: PA. The experimental results are listed in Table 11.

**Table 9. Inhibition Efficiency for Aluminum in 0.1M H<sub>2</sub>SO<sub>4</sub> Containing Different Concentrations of Gum Arabic (GA) at Different Temperatures from Weight Loss Measurements [27]**

Concentration (g/l)	Inhibition Efficiency (%)			
	30°C	40°C	50°C	60°C
0.1	68.75	63.28	62.00	52.42
0.2	72.19	68.29	65.00	55.65
0.3	75.94	72.68	70.00	61.90
0.4	76.88	73.17	71.25	62.90
0.5	79.69	76.01	73.73	67.74

**Table 10. Inhibition Efficiency for Aluminum in 2M NaOH Containing Different Concentrations of Gum Arabic (GA) at Different Temperatures from Hydrogen Evolution and Thermometric Measurements [27]**

Concentration (g/l)	Hydrogen Evolution Method		Thermometric Method
	30°C	40°C	
0.1	19.09	28.41	31.34
0.2	35.23	45.22	49.14
0.3	44.34	55.41	60.99
0.4	47.14	61.41	62.83
0.5	50.24	74.16	75.86

**Table 11. Inhibition Efficiency for Aluminum in 0.1M H<sub>2</sub>SO<sub>4</sub> Containing PA, PVP and their Blends from Weight Loss Measurements at Different Temperatures [28]**

Systems/ Concentration	Inhibition Efficiency (%)			
	30°C	40°C	50°C	60°C
PA (1 x 10 <sup>-4</sup> M)	47	39	31	24
PVP (1 x 10 <sup>-4</sup> M)	49	41	39	35
PVP:PA (1:1)	55	44	34	33
PVP:PA (1:2)	53	43	33	32
PVP:PA (1:3)	52	42	31	29
PVP:PA (2:1)	57	46	35	34
PVP:PA (3:1)	58	48	37	36

#### 4. POLYMERS AS CORROSION INHIBITORS OF IRON

The effect of poly(4-vinylpyridine isopentyl bromide) (P4VPIBr) in three degrees of quaternisation (6, 18 and

79%) on the corrosion of pure iron in molar sulphuric acid was investigated by potentiodynamic, polarisation resistance and weight loss measurements. The inhibition efficiency (E %) of P4VPIBr increases with its concentration to attain 100% around 5 × 10<sup>-6</sup>M. E% values obtained from the

various methods are in good agreement. Polarisation measurements show also that the compound acts as a cathodic inhibitor and adsorbs on the pure iron surface according to the Frumkin adsorption isotherm model [29].

The inhibitive action of ortho-methoxy substituted polyaniline (poly (o-methoxy-aniline)), a new class of conducting polymer on the corrosion of iron in acidic chloride solution has been evaluated by Electrochemical Impedance Spectroscopy (EIS), Linear polarization Resistance (LPR), weight loss (WL) and by Logarithmic Polarization Technique (LPT). Inhibition efficiencies of nearly 80 – 88% have been observed even at 25ppm concentration. Double-layer capacitance studies indicate a strong adsorption of the polymer following Temkin adsorption isotherm is largely responsible for its inhibitive action [30]. Results are summarized in Table 12.

**Table 12. Inhibition Efficiency of Poly (Methoxy Aniline) (PMA) Evaluated by Linear Polarization Resistance and Weight Loss Methods [30]**

Inhibitor	Concentration (ppm)	Inhibition Efficiency (%)	
		Weight Loss	LPR Method
PMA (Cl)	10	63	73
	50	81	83
	100	82	90
	200	85	91
PMA (SMA)	10	71	75
	25	79	84
	50	88	85
	75	92	88
PMA(L)	10	81	82
	25	85	88
	50	88	90
	75	93	92

The inhibitive effect of N-vinyl-2-pyrrolidone (NVP) and polyvinylpyrrolidone (PVP) of different average degrees of polymerization on acid corrosion of iron was investigated [31]. It was found from the result obtained that PVP impacted a more efficient inhibition than NVP at very low concentrations. Protection efficiency of 98% was obtained. The mechanism of inhibition was proposed on the basis of formation of a protective film by PVP molecules on the metal surface.

Also the influence of addition of poly (4-vinylpyridine) P4VP of two average degree of polymerization on the corrosion of Armco iron in 1M H<sub>2</sub>SO<sub>4</sub> has been studied using weight loss, potentiodynamic, polarization resistance and AC impedance (EIS) techniques. Results obtained showed that both polymers reduces corrosion rates and that the compounds act essentially as cathodic inhibitors [32]. The inhibition efficiencies obtained from cathodic Tafel plots, polarisation resistance, EIS and gravimetric methods were in good agreement. The inhibitors were adsorbed on the

iron surface according to the Frumkin adsorption isotherm. Polarisation measurements also show that the compounds act essentially as cathodic inhibitors.

In recent years, polymer amines have been studied as an efficient corrosion inhibitor for iron in acid media. The performance of water soluble polyaniline as corrosion inhibitor for iron in 0.5M H<sub>2</sub>SO<sub>4</sub> has been evaluated by potentiodynamic polarization, linear polarization, and electrochemical impedance spectroscopy and compared with the performance of the aniline monomer [33]. It has been found that polyaniline is an efficient inhibitor, since the maximum efficiency of 84% has been observed at a concentration of 100 ppm, whereas the monomer accelerated the corrosion. FTIR studies have shown that the polyaniline is strongly adsorbed on the iron surface and inhibits the corrosion effectively. However, aniline has been found to improve the passivation tendency of iron at higher concentrations.

The inhibitive effect of poly(p-aminobenzoic acid) on iron in 1M HCl solution was investigated by polarization and electrochemical impedance spectroscopy and compared with that of monomer p-aminobenzoic acid [34]. The effectiveness of poly(p-aminobenzoic acid) is very high in comparison with that of the monomer. The results show that both cathodic and anodic processes were suppressed by p-aminobenzoic acid and poly(p-aminobenzoic acid) of iron dissolution in 1M HCl by their adsorption on the iron surface. The inhibition efficiency of both p-aminobenzoic acid and poly(p-aminobenzoic acid) were found to increase with the inhibitor concentrations. Ultraviolet (UV) reflectance studies of the iron surface after exposure to inhibitor in the acid environment show that poly(p-aminobenzoic acid) is strongly adsorbed on iron surface

The performance of poly(diphenylamine) as corrosion inhibitor for iron in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been evaluated by potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy and compared with the performance of the diphenylamine monomer. It has been found that poly(diphenylamine) is an efficient inhibitor since the maximum efficiency of 96% has been observed at very low concentration of 10 ppm whereas the monomer gave an efficiency of 75% at 1000 ppm. Besides, poly(diphenylamine) has been found to improve the passivation characteristics of iron in 0.5M H<sub>2</sub>SO<sub>4</sub>. FTIR studies have shown that the poly(diphenylamine) is strongly adsorbed on the iron surface and inhibits the corrosion effectively [35]. The inhibition efficiency values are given in Table 13.

The influence of poly(4-vinylpyridine-poly(3-oxide-ethylene) tosylate) P4VPPEO5000Ts, on the corrosion inhibition of iron in molar sulphuric acid solution is studied using weight-loss, polarisation resistance, potentiodynamic and EIS measurements. P4VPPEO5000Ts is an excellent inhibitor and its inhibition efficiency increases with the increase of concentration to attain 100% since  $2.5 \times 10^{-8}$  M. Potentiodynamic polarisation studies clearly reveal that it acts as a mixed-type inhibitor. The polymer studied reduces the corrosion rates. E% values obtained from weight-loss, corrosion current density, polarisation resistance and EIS methods are in good agreement. Adsorption of this compound on iron surface has an S-shaped adsorption isotherm with two consecutive steps indicating Frumkin

adsorption isotherm [36]. Table 14 summarizes the inhibition efficiency values for weight loss and potentiodynamic polarization methods.

**Table 13. Inhibition Efficiencies for Pure Iron in 0.5M H<sub>2</sub>SO<sub>4</sub> with Different Concentrations of Poly(Diphenylamine) [35]**

Concentration (ppm)	Inhibition Efficiency (%)	
	EIS Method	LPR Method
1.0	80	61
2.5	87	63
5.0	80	71
7.5	91	86
10.0	96	89

**Table 14. Inhibition Efficiencies for Pure Iron in 0.5M H<sub>2</sub>SO<sub>4</sub> with Different Concentrations of P4VPPEO5000Ts from Different Methods [36]**

Concentration (M)	Inhibition Efficiency (%)	
	Weight Loss	Potentiodynamic Polarization
$2.5 \times 10^{-8}$	100	98
$10^{-8}$	99	97
$7.5 \times 10^{-9}$	98	94
$5 \times 10^{-9}$	96	88
$2.5 \times 10^{-9}$	83	80
$10^{-9}$	62	63
$7.5 \times 10^{-10}$	61	60
$5 \times 10^{-10}$	58	52
$2.5 \times 10^{-10}$	41	46
$10^{-10}$	39	41

The influence of poly(aminoquinone) (PAQ) on corrosion inhibition of iron in 0.5M H<sub>2</sub>SO<sub>4</sub> has been reported using potentiodynamic polarization and electrochemical impedance spectroscopy measurement [37]. The inhibitive performance of PAQ was compared to that of its monomer o-phenylenediamine (OPD) and was found that the inhibition performance of PAQ was better than OPD which was attributed to the presence of extensive delocalized  $\pi$  electrons. Inhibition efficiency of 90% at 100ppm was obtained for PAQ while inhibition efficiency of 80% at 1000ppm was obtained for OPD. PAQ was found to be a mixed inhibitor. Besides, PAQ was able to improve the passivation tendency of iron in 0.5M H<sub>2</sub>SO<sub>4</sub> markedly. Adsorption of PAQ followed Temkin adsorption isotherm. Experimental results are summarized in Table 15.

Jeyaprabha *et al.* [38] reported on the performance of water soluble polyaniline as corrosion inhibitor for iron in 0.5M H<sub>2</sub>SO<sub>4</sub> evaluated by potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy and compared with the performance of the

aniline monomer. It was found that polyaniline is an efficient inhibitor giving a maximum inhibition efficiency of 84% at 100ppm, while the monomer accelerated corrosion. FTIR studies have shown that the polyaniline is strongly adsorbed on the iron surface and inhibits the corrosion effectively. Adsorption of polyaniline onto iron surface follows Temkin adsorption isotherm.

**Table 15. Inhibition Efficiencies for Pure Iron in 0.5M H<sub>2</sub>SO<sub>4</sub> with Poly(Aminoquinone) at 28°C [37]**

Concentration (ppm)	Inhibition Efficiency (%)	
	EIS Method	LPR Method
10	58	80
25	63	87
50	71	90
75	85	92
100	88	96

## 5. POLYMERS AS CORROSION INHIBITORS FOR COPPER

The effect of layers of poly (o-anisidine) (PVA) [39, 40], poly (o-toluidine) (POT) and poly(o-anisidine-co-o-toluidine) (OAOT) [40, 41] formed on copper surface on copper behaviour in 3% NaCl solution has been reported. Results obtained indicate that they are efficient corrosion inhibitors and at concentration of 0.1M, inhibition efficiency obtained was 85.81%, 98.00% and 99.66% for POA, POT and OAOT respectively.

It has also been reported [42, 43] that films formed in the presence of polyaniline (PANI) and poly (methylmethacrylate) (PMMA) protect copper surface against corrosion. Also studied was the influence of polyaniline (PANI) and poly (orthomethoxyaniline) (POMA) on corrosion inhibition of copper in 0.1M NaCl. Best result was obtained for polyaniline which was attributed to the fact that the polymer film was involved in the formation of oxide film on the polymer – metal surface. This oxide film increases the barrier effect of the polyaniline film hence greater corrosion inhibitor efficiency. The phenomenon of oxide formation was not observed with POMA [43].

The inhibition of copper corrosion by polyvinylimidazole and benzimidazole at room and high temperature as well as in acidic water was assessed by surface-enhanced Raman scattering (SERS) [44]. The performance of polyvinylimidazole and benzimidazole was improved by coating the copper surface with their mixture

Tuken *et al.* studied the effect of films formed from polypyrrole (PPy) polyindole and polypyrrole (Pin/PPy) [45] and polypyrrole and polythiophene (PPy/PTh) [46] on copper corrosion in 3.5% NaCl. It was found that PPy protects copper surface against corrosion. However, PPy/PIn and PPy/PTh film were efficient corrosion inhibitor for copper.

The adsorption and inhibitive effects of polyvinylpyrrolidone (PVP) and polyethyleneimine (PEI) on copper in 2M H<sub>2</sub>SO<sub>4</sub> at 30°C had been investigated by the



means of weight loss, potentiodynamic and in situ surface-enhanced Raman scattering (SERS) techniques [47], according to result obtained, both polymer reduced the rate of anodic (metal dissolution) and cathodic (oxygen reduction) corrosion reaction. Also at all concentrations studied, PVP was found to be a better inhibitor than PEI.

## 6. POLYMERS AS CORROSION INHIBITORS OF OTHER METALS

The effects of poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), sodium polyacrylate (NaPA), polyethylene glycol (PEG), pectin (P), and carboxymethyl cellulose (CMC) on the corrosion of cadmium in a 0.5M hydrochloric acid (HCl) solution were studied with both electrochemical impedance spectroscopy and Tafel plot techniques [48]. Measurements were carried out at cathodic, open-circuit, and anodic potentials. All the investigated polymers had inhibitory effects on both the cathodic (except for NaPA, P, and CMC) and anodic processes, with a predominant anodic inhibiting action. However, NaPA, P, and CMC exhibited a slight cathodic inhibiting action only at higher polymer concentrations. This behavior may be attributed to the very weak adsorbability of the polymers on the cathodic sites. Because PVA and PEG had hydroxy groups, there could be bridging between the polymer and the surface, resulting in an inhibiting effect in the HCl solution. However, PVA had much greater adsorbability on the surface than PEG at the anodic potential. The adsorption of most of the polymers obeyed a Temkin adsorption isotherm, and this indicated that the main process of inhibition was adsorption.

Polyaniline films were grown by electrochemical deposition on 316 and 304 stainless steels and their corrosion performance monitored by following the open circuit potentials in acidic solutions. Poly(o-methoxyaniline) was successfully polymerised on stainless steel electrodes, as shown by cyclic voltammetry and impedance spectroscopy, and provided corrosion inhibition in a similar manner to polyaniline. In 0.5M  $\text{H}_2\text{SO}_4$  the potential climbed to over 0.4V (SHE), to values typical of the partially oxidised form of the polymer and of the metal substrate in a passive state with low rates of corrosion. In 0.5M HCl, the steels were maintained in a passive state for some hours to days (lasting longer with a thicker polymer film), prior to a drop in potential to -0.15V after the onset of pitting corrosion. The fluctuations of potential seen in 0.5M HCl are explained by regions of the oxidised polyaniline, produced by dissolved  $\text{O}_2$ , reaching the metal and causing an increase in the potential and by pits formed at higher potentials rapidly reducing an already oxidised film leading to a drop in the potential [49].

Fluoropolymers with adhesive and anticorrosive properties were investigated by blending statistical phosphonated copolymers with poly (vinylidene fluoride) (PVDF). The copolymers were introduced into PVDF as adhesion promoters and anticorrosion inhibitors. Good dry and wet adhesion properties onto galvanized steel plates were obtained with blends containing mainly phosphonic acid groups. Results of corrosion tests show that the phosphonic acid groups maintain some level of adhesion, thereby preventing the spread of corrosion. However, the number of acid groups and their neighbours influence the

adhesive and anticorrosive properties of the PVDF coatings [50].

Copper and brass pigments corrode in aqueous alkaline media with the absorption of oxygen that can be measured gasvolumetrically. These corrosion reactions can be inhibited by certain polymers; the metallic sparkle and the color of the pigments is preserved. The brass pigment is inhibited more effectively than the copper pigment. Some low-molecular mass styrene-maleic acid (SMA) copolymers are efficient corrosion inhibitors; a low acid number is necessary but not sufficient for corrosion inhibition. At pH 8.5 there is a potential correlation between the acid number of the low-molecular mass SMA and the oxygen volumes absorbed from brass pigment dispersions; oxygen volumes decrease with decreasing acid number. Furthermore, increasing copolymer addition effects an increase of corrosion inhibition. Polyacrylic acids, polyvinyl alcohols and high-molecular mass SMA copolymers are ineffective. The most efficient group of polymers examined in the study is the styrene-acrylate copolymers because by addition of these the overall lowest volumes of oxygen were absorbed by the metal pigments [51].

The effect of various concentrations (0.5 to 30 ppm) of polyacrylamide samples which have different molecular weights (sample A =  $3.4 \times 10^4$ , B =  $1.52 \times 10^4$  and C =  $1 \times 10^4 \text{ g mol}^{-1}$ ) and poly(propenoyl glycine) (sample D) which has the same degree of polymerization (Dp) as sample C on the corrosion behaviour of tin in 1 M NaCl solution were investigated at 20°C using potentiodynamic polarization technique [52]. The various electrochemical parameters ( $I_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $R_p$ ,  $E_{\text{pit}}$  and  $I_p$ ) were calculated from Tafel plots in the absence and presence of these polymers. The data reveal that the inhibition efficiency of polymer C is higher than that of polymer B, while the presence of polymer A (the highest molecular weight) accelerates the corrosion of tin in 1 M NaCl indicating that the inhibition decreases with increasing molecular weight. On the other hand, polymer D shows the strongest inhibition efficiency. For the investigated polymer inhibitors B, C and D, it was found that the experimental data fit Flory-Huggins adsorption isotherm. The effect of temperature on various corrosion parameters and the inhibition efficiency was studied for polymer D(10 ppm) in 1 M NaCl over the temperature range from 20°C to 50°C.

The effects of the addition of poly (4-vinylpyridine) and its additive poly (4-Vinylpyridine poly-3-oxide ethylene) on the corrosion of  $\text{Cu}_{60} - \text{Zn}_{40}$  in 0.51M  $\text{HNO}_3$  were investigated by potentiodynamic and weight loss measurements. Both of the studied polymers decrease the corrosion rate. The inhibition efficiency (E %) increases with the concentration of the polymers respectively. The maximum of inhibition was obtained for poly (4-vinylpyridine poly 3-oxide ethylene (100 percent) at  $10^{-5}\text{M}$ . The inhibition efficiency obtained from cathodic Tafel plots' and weight loss methods were in good agreement. The inhibitors were absorbed on the  $\text{Cu}_{60}\text{-Zn}_{40}$  surface according to the Frumkin adsorption isotherm model [53].

The effect of polyethyleneimine (PEI) as corrosion inhibitor for ASTM 420 stainless steel in 30% aqueous NaCl was studied [54]. The results of linear polarization and cyclic polarization measurements indicate high inhibition effectiveness of the selected organics. Moreover, from cyclic

measurements, it was deduced that PEI acts as an inhibitor against pitting corrosion. Immersion test in the presence of PEI showed remarkable corrosion protection against uniform corrosion. Film persistency immersion testing indicated that once the protective layer is formed, it is very stable in non-inhibited NaCl solution. X-ray photoelectron spectroscopy measurements showed that PEI binding is mediated by electrostatic interactions between PEI and the substrate. A decrease layer of PEI might be effective either in preventing diffusion of ionic species from film or in preventing attack by chlorine from salt water.

Poly(*o*-aminophenol), poly(*o*-aminothiophenol), poly(*m*-anisidine) prepared by chemical oxidation of their monomers using ammonium persulphate at 0°C were evaluated as corrosion inhibitors for steel protection by measuring their corrosion rates in comparison with previously prepared polyaniline and the control sample [55]. The polymers show a high performance as efficient corrosion inhibitors and promising results were achieved when the polymers were incorporated in various paints formulations to replace a major part of the inhibitive pigments and to replace the classical toxic corrosion inhibitors of low molecular weights and low melting points.

The effect of polyvinylpyrrolidone, poly-2-vinylpyridine and poly-4-vinylpyridine as inhibitors of corrosion behaviour of zinc metal in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution has been reported using weight loss technique [56]. It was found that the polymers studied impart significant inhibiting effect on the corrosion rate of zinc metal. The protection efficiency in the presence of polymers reached about 87% at an inhibitor concentration of 0.1M. The results were analyzed in terms of the formation of a protective film on the metal surface.

A corrosion protection coating from polyimide/polyaniline (PI/PAn) blend was prepared by solution blending and the anti-corrosion property of this coating was studied with electrochemical impedance spectroscopy technique. The results show that PAn can react with PI to form chemical bonds between these two polymers and these bonds keep these two polymers as a miscible system. The corrosion protection property of these coating increases with a growth in the PAn component and an excellent anti-corrosion effect emerges when the PAn content reaches 10-15%. The reason why PAn can improve the anti-corrosion property is that PI/PAn blend can form a dense and non-porous polymer film that would prevent some corrupting components from access to the underlying steel surface. And also, PAn may serve as a corrosion inhibiting agent to scavenge any protons and foster a local basic surface environment [57].

The behaviour of corrosion inhibition of mild steel by various cationic and anionic polymers namely polyethyleneimine (PEI), its derivative (PEID), polyarylamine (PAAm) and polydicynodiamide derivative (PDCDA) as cationic polymers and polymaleic acid derivative (PMAD), polyacrylic acid derivative (PAAD) and polyacrylic acid (PAA) as anionic polymers were investigated by corrosion tests and physicochemical measurements [58]. The test was carried out using two pseudo-concentrated solutions with low (LC) and high (HC) concentrations of ionic species like Ca<sup>2+</sup> and Cl<sup>-</sup>. It was found that the cationic polymers lacked inhibition ability while the anionic polymers had more effective inhibition ability. The anionic polymers had a potential to act as corrosion

inhibitors of an adsorption type in LC solution and as both corrosion inhibitors and scale inhibitors of calcium carbonate (CaCO<sub>3</sub>). In LC solution, the inhibition efficiency value of anionic polymers was dependent on number average molecular weight (*M<sub>n</sub>*), content of carboxylic group (-COOH) and concentration of -COOH. In particular, the anionic polymers as inhibitors had an effective range of *M<sub>n</sub>* (103 order). In HC solution, the degree of corrosion of steel was influenced by the concentrations of both anionic polymers and solution components such as Ca ion (CaCO<sub>3</sub>). The anionic polymers were competitively adsorbed with Ca ion on the steel.

The electrochemical copolymerization between pyrrole and *o*-toluidine has been studied as an alternative method for obtaining good quality coating (low permeability and water mobility, high stability), which could also be easily synthesized on steel. The characterization of deposited copolymer coating has been realized by using SEM micrographs, UV-vis and FT-IR spectroscopy techniques and cyclic voltammetry. The protective behaviour of these coatings was also investigated against mild steel corrosion in 3.5% NaCl solution, by means of electrochemical impedance spectroscopy (EIS) and anodic polarization curves [59]. It was found that the monomer feed 8:2 ratio gave the most effective coating against the corrosion of mild steel.

The electrochemical synthesis of poly(*o*-anisidine) homopolymer and its copolymerization with pyrrole have been investigated on mild steel. The copolymer films have been synthesized from aqueous oxalic acid solutions containing different ratios of monomer concentrations: pyrrole:*o*-anisidine, 9:1, 8:2, 6:4, 1:1. The characterization of polymer films were achieved with FT-IR, UV-visible spectroscopy and cyclic voltammetry techniques. The electrochemical synthesis of homogeneous-stable poly(*o*-anisidine) film with desired thickness was very difficult on steel surface. Therefore its copolymer with pyrrole has been studied to obtain a polymer film, which could be synthesized easily and possess the good physical-chemical properties of anisidine. The protective behavior of coatings has been investigated against steel corrosion in 3.5% NaCl solution [60]. For this aim electrochemical impedance spectroscopy (EIS) and anodic polarization curves were utilized. The synthesized poly(*o*-anisidine) coating exhibited significant protection efficiency against mild steel corrosion. It was shown that 6:4 ratio of pyrrole and anisidine solution gave the most stable and corrosion protective copolymer coating.

Electrochemically synthesized polypyrrole coating was modified with very thin graphite layer and top coated with another polypyrrole film. The corrosion behaviour of this coating has been investigated in aqueous sodium chloride solution [61]. The synthesis of polypyrrole coatings was carried out by cyclic voltammetry technique, from aqueous oxalic acid solution. Electrochemical impedance spectroscopy and potentiodynamic measurements were used for corrosion tests. The cyclic voltammograms obtained in oxalic acid solution and the polarisation curves obtained in sodium chloride solution showed that the stability of coating was improved significantly by graphite layer. The impedance spectra also showed that the corrosion process was controlled by the diffusion rate along the coating, even after 96 h immersion period. The Warburg coefficient values were calculated and used to evaluate the barrier property of

coating with time. It was shown that the water up taking process was slowed down by the hydrophobic nature of the graphite layer sandwiched between the two polypyrrole films.

Polypyrrole (PPy) and polyaniline (PANi) coatings were electrosynthesized on copper, by using cyclic voltammetry technique. Then, these coatings were modified with the deposition of zinc particles from aqueous zinc sulphate solution. The electrodeposition of zinc was achieved at a constant potential value of  $-1.20$  V, in the amount of  $\sim 0.75$  mg/cm<sup>2</sup>. The corrosion performance of zinc modified polymer coatings were investigated in 3.5% NaCl solution; by using the electrochemical impedance spectroscopy (EIS), and anodic polarization curves [62]. The zinc particles improved the barrier property of polymer films, due to formation of voluminous zinc corrosion products within the pores of polymer coating. Also, the zinc particles provided cathodic protection to the substrate, where the polymer film played the role of conductance between zinc particles and copper.

Polypyrrole (PPy) film was synthesized on nickel-plated copper electrodes, from monomer containing 0.2 M ammonium oxalate solution. The thickness of galvanostatically deposited nickel layer was 2  $\mu$ m, while  $\sim 0.80$   $\mu$ m thick polymer film was obtained by using cyclic voltammetry technique. The protective behavior of PPy modified nickel coating has been investigated, against copper corrosion in 3.5% NaCl solution using ac impedance spectroscopy, the anodic polarization curves and open circuit potential [63]. It was shown that PPy modified nickel coating could provide important protection to copper for considerable periods, in such aggressive medium. The thin polymer film constituted a physical barrier on top of nickel layer against the attack of corrosive environment for a certain period. Also, it was found that the thin PPy film could increase the protection efficiency and lifetime of nickel coating, by its catalytic behavior on formation of NiO layer.

The corrosion performance of PANi coated samples of polyaniline film synthesized on copper electrodes from monomer containing 0.2 M sodium oxalate solution by using a cyclic voltammetry technique were investigated in 3.5% NaCl solutions by using electrochemical impedance spectroscopy (EIS), anodic polarization curves and open circuit potential-time ( $E_{ocp}-t$ ) curves [64]. It was shown that PANi coating could provide important protection against corrosion of copper in such an aggressive medium. The polymer film behaved like a barrier against the attack of the corrosive environment. It was also found that the polymer film by its catalysing effect led to the formation of very protective copper oxides on the surface.

The synthesis of a polythiophene (PTh) film was achieved on polypyrrole (PPy) coated mild steel (MS) electrode. The synthesis of primary PPy coating was carried out from a monomer containing aqueous oxalic acid solution. The synthesis of top PTh film was achieved in 0.1 M thiophene containing ACN-LiClO<sub>4</sub>. Cyclic voltammetry technique was used for both syntheses. The corrosion behavior of PPy/PTh coated MS was investigated in 3.5% NaCl solution, by using anodic polarization, open circuit potential-time ( $E_{ocp}-t$ ) curves and electrochemical impedance spectroscopy (EIS) [65]. It was shown that the

coating has very low porosity and exhibited excellent barrier property against the attack of corrosive environment, for extensive periods. It was also able to provide anodic protection to MS and an efficiency value of 98.2% was calculated after 220 h of exposure time.

The synthesis of polypyrrole film was achieved on brass and copper electrodes, by using cyclic voltammetry technique, from monomer containing 0.3 M oxalic acid solutions. The corrosion performance of PPy coated samples were investigated in 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions, by using the electrochemical impedance spectroscopy (EIS), anodic polarization curves and open circuit potential ( $E_{ocp}$ )-time curves [66]. It was shown that PPy coating could provide important protection against the corrosion of copper and brass. However, polymer coating gave better results with copper with respect to brass. The protective behaviour was coming from the barrier property of the coating against the attack of corrosive environment.

Electrochemical synthesis of very adherent polypyrrole (PPy) and polyaniline (PANi) films were achieved on 1  $\mu$ m thick nickel (Ni) coated mild steel (MS) samples. Electrodeposition of Ni layer on MS was carried out galvanostatically, in an appropriate bath solution and cyclic voltammetry technique was used for synthesis of the polymer top coats, in monomer containing oxalic acid solutions. The corrosion performances of nickel coated samples with and without polymer top coats were investigated in 3.5% NaCl solution, by using electrochemical impedance spectroscopy (EIS) and anodic polarization curves [67]. It was found that electrodeposited 1  $\mu$ m thick Ni layer had quite porous structure, therefore, it could exhibit restricted barrier property and its protection efficiency diminished with time. It was shown that the presence of a polymer top coat could improve the barrier property significantly and lead to much better protection against the corrosion of underlying MS. PPy film was found to be more effective as top coat on Ni coated MS, with respect to PANi film.

Synthesis of polyindole was achieved on mild steel electrode previously coated with a very thin polypyrrole layer (PPy). Cyclic voltammetry technique was used for both syntheses; oxalic acid solution was used for synthesis of primer PPy coating and polyindole film (PI) was obtained from LiClO<sub>4</sub> containing acetonitrile medium. The corrosion performance of this PPy/PI coating was investigated properly in 3.5% NaCl solution by using anodic polarization and open circuit potential ( $E_{ocp}$ )-time curves and electrochemical impedance spectroscopy (EIS) [68]. This coating exhibited excellent barrier efficiency for a long time (about 190 h) and it was also able to provide a certain anodic protection. After 240 h of immersion time in corrosive test solution, the protection efficiency value was determined to be 98.9%.

A multilayer coating was prepared on mild steel by electrosynthesis of a thin polyphenol film on top of electrosynthesized polypyrrole layer using the cyclic voltammetry technique. The corrosion performance of this multilayer coating (PPy/PPhe) and single polypyrrole coating itself (PPy) were investigated in neutral sulphate solution by using electrochemical impedance spectroscopy (EIS), and anodic polarization curves [69]. It was clearly

shown that the multilayer coating could provide a much effective protection for much longer periods with respect to the single layer for corrosion of mild steel, an efficiency of 98.3% was determined for 240 h. The very thin polyphenol layer has improved the barrier effect of the coating remarkably

**Table 16. Inhibition Efficiency for Pure Iron in 0.5M H<sub>2</sub>SO<sub>4</sub> with Polyaniline [38]**

Concentration (ppm)	Inhibition Efficiency (%)	
	EIS Method	LPR Method
10	40	40
25	42	50
50	55	58
75	70	73
100	70	72

**Table 17. Inhibition Efficiency of P4VPPOE and P4VP Evaluated by Weight Loss Methods [53]**

Inhibitor	Concentration (M)	Inhibition Efficiency (%)
P4VPPOE	$3.33 \times 10^{-5}$	100
	$10^{-5}$	100
	$5 \times 10^{-6}$	98
	$2.5 \times 10^{-6}$	87
	$10^{-6}$	55
	$5 \times 10^{-7}$	25
	$2.5 \times 10^{-7}$	13
	$10^{-7}$	18
	$10^{-8}$	20
P4VP	$3.33 \times 10^{-5}$	92
	$10^{-5}$	93
	$10^{-6}$	66
	$5 \times 10^{-7}$	27
	$2.5 \times 10^{-7}$	16
	$10^{-7}$	10
	$10^{-8}$	19

## CONCLUSIONS

It has been shown that polymers especially the water soluble ones are efficient corrosion inhibitors in different aqueous media. Mechanism of inhibition are mainly attributed to adsorption and depends on the metal, physico-chemical properties of the molecule such as functional groups, steric factors, aromaticity at the donor atom and p-orbital character of donating electrons as well as the electronic structure of the molecules. In other words, the efficiency of polymers as corrosion inhibitor depend not only

on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself, which includes the number of adsorption active centres in the molecule, their charge density, the molecular size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface.

The results of the series of investigations have revealed that the processes involved in corrosion inhibition are not uniform with respect to all classes of compounds so far investigated, and are not even constant or consistent with one inhibitor in a given system. Indeed the overall process in a function of the metal, corrosive, inhibitor structure and concentration as well as temperature.

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