

## Research Article

## Corrosion Performance Evaluation of Chemically Synthesized Polyaniline and its Co- and Ter-polymer Coatings on Mild Steel in Different Media

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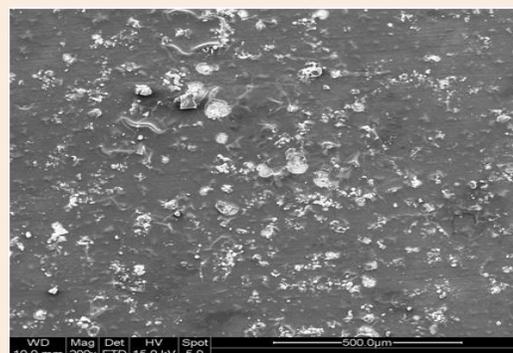
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**Abstract**

The present paper deals with the corrosion performance evaluation of a number of conducting polymers which include homopolymers, PANi and poly (o-toluidine), copolymers, poly (aniline-co-o-toluidine), poly (aniline-co-2,3-xylidine) and poly (2-pyridylamine-co-aniline) and terpolymer, poly (2-pyridylamine-co-aniline-co-2,3-xylidine) in different corrosive media which include 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere. The polymers were synthesized by chemical oxidative polymerization. The resultant polymers were characterized by Fourier transform infrared (FTIR) spectroscopy and chemically deposited on mild steel specimens using N-methyl-2-Pyrrolidone (NMP) as solvent via solution evaporation method. The anticorrosive properties of homopolymers, copolymers and terpolymer coatings were investigated by conducting immersion test, open circuit potential measurements, potentiodynamic polarization measurements, and atmospheric exposure test. The surface morphologies of polymer coatings were evaluated using scanning electron microscopy (SEM).

**Keywords:** Conducting polymers, Chemical synthesis, Copolymers, Terpolymer, Potentiodynamic polarization measurements, Atmospheric exposure test, SEM

Among the selected polymers terpolymer, poly (2-pyridylamine-co-aniline-co-2,3-xylidine) exhibited highest protection efficiency against mild steel corrosion in all the corrosive media under investigation after 30 days of immersion. In general, the performance of copolymer, poly (aniline-co-o-toluidine) was found to be better than that of other copolymers and homopolymer coatings.

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**Introduction**

Conducting polymers are one of their own kinds among the class of polymers owing to their electrical conductivity, low cost, fusibility, stability, good optical properties, non-toxic nature, low density, ease in synthesis and doping primacy [1-6]. Along with copious applications [1, 2, 7, 8] intrinsically conductive polymers have achieved demanding interest in the field of corrosion control coatings owing to their conductive ability and also due to the strict environmental regulations over conventional heavy metals coatings. ICP's belongs to those classes of polymers which have  $\pi$ -conjugation along the polymer backbone. The partial oxidation or reduction possibility to ICP's through doping has made them the most distinctive materials. Among the conducting polymers, polyaniline (PANi), polypyrrole (PPy) and their derivatives are considered as the most important conducting polymers owing to their stability and synthesis advantages [9-11]. In corrosion protection of metals they have been used both as film-forming corrosion inhibitors and as protective coatings. As corrosion inhibitors they have performed better at low concentrations, as compared to simple organic molecules due to extensive delocalization of  $\pi$  electrons [12-15]. Conducting polymers have been used as corrosion inhibitor coatings that are either chemically or electrochemically

deposited on the metallic substrate [16-23]. Chemical deposition is the best way in view of application practicality, whereas electrochemical deposition is burdensome and virtually impossible on large equipment such as ships, bridges and pipelines [24]. A number of studies have been reported in the literature on the use of homopolymer PANi for the corrosion prevention of mild and stainless steels [25-30]. Despite the success claimed for homopolymers as corrosion protection coatings a number of problems associated with these materials prohibit them as replacement for traditional coating systems. The major drawbacks associated with the homopolymers have been the difficulty in processing these materials and limited number of available coatings monomer.

The general lack of solubility and fusibility of these materials make the deposition of coating on active metals difficult. The direct electrochemical deposition of the coating can be used, but this approach is not straight forward with active metals that oxidize at the deposition potential. Further, the number of conjugated  $\pi$ -bond coatings monomer that are essential for electrical conductivity are also limited and constitute a major drawback. The synthesis of copolymers between various monomer molecules has long been utilized to alter the physical-chemical properties of polymer coatings [31]. The addition of monomers with hydrophobic groups could lower the water uptaking rate or another group may enhance the stability and adherence. These facts motivated the studies subjecting to the development of multilayered coatings consisting of combination of conducting polymers [32, 33] and new design polymeric materials (co- and terpolymers) with designed properties [30, 31, 34-36]. The coatings of these materials have shown better corrosion performance than individual homopolymers coatings.

Since early 1990,s considerable work has been reported dealing with the corrosion performance behavior of electrochemically deposited conducting polymers, mainly in HCl and NaCl solution. A review of literature on conducting polymers reveals that our knowledge about the chemically deposited polymers and their performance in other corrosive medium such as artificial seawater, distilled water and open atmosphere is lacking. Further, it has been observed that terpolymer and copolymers have better solubility than their homopolymers in various organic solvents. This simplifies polymer processibility and is advantageous for producing polymers and copolymer in bulk [37]. In view of the above a homopolymer PANI, a series of soluble copolymers, poly (aniline-co-o-toluidine), poly (aniline-co-2,3-xylydine) and poly (2-pyridylamine-co-aniline) and terpolymer, poly (2-pyridylamine-co-aniline-co-2,3-xylydine) were synthesized by chemical oxidative polymerization. The resultant polymers were deposited on mild steel by solution evaporation. The anticorrosive property of polymers was investigated in major corrosive environments such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere by subjecting them to different corrosion tests which include: immersion test, open circuit potential (OCP) and potentiodynamic polarization measurements. The corrosion performance of the terpolymer was also compared with the individual copolymers and homopolymers.

## Materials and Methods

The chemical composition of mild steel (in weight %), analyzed by optical emission spectrophotometer, used in this study was: C: 0.20; Cr: 0.078; Ni: 0.08; Cu: 0.052; Si: 0.003; Mo: 0.113; Mn: 0.16; P: 0.028 and Fe balance. Mild steel coupons of dimension 4.0×1.5×0.13 cm were polished with a series of emery papers washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. The prepared specimens were used as substrate for the synthesis of conducting polymer coatings. Before synthesis of any conducting polymer coating, the specimens were subjected to above treatment and freshly used with no further storage. The test solutions were prepared as per standard procedure. All solutions were made using double distilled water.

### *Chemical Synthesis and Characterization of Conducting Polymers*

Conducting polymers were synthesized by chemical oxidative polymerization using ammonium persulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  as an oxidant in hydrochloride aqueous medium.

#### *Synthesis of Polyaniline (PANi) Homopolymer*

10 ml (0.1097 mol) of aniline was dissolved in 150 ml of 1.5 M aqueous HCl solution in a 500 ml glass bulb and cooled to 0 °C. The oxidizing agent was prepared by dissolving 12.5 g (0.0548 mol) of ammonium persulfate in 150

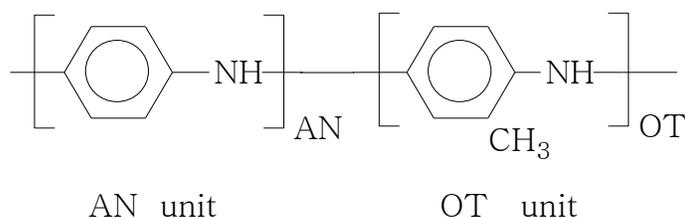
ml of 1.5 M HCl aqueous solution. Aniline solution was vigorously stirred and the oxidant solution was added drop wise. The addition was performed at 0 °C during a period of 1 hour. After the oxidant was dropped in, the reaction mixture was left with constant stirring at 0 °C for additional three hours. Subsequently, the mixture was left to warm up to room temperature. Polyaniline was collected on a Schott funnel, washed with 1 M HCl and distilled water, until the washing liquid became colorless. The obtained polyaniline hydrochloride was converted to the base form by stirring with 0.1 M aqueous ammonium hydroxide solution for 48 hours; this was followed by washing with water and methanol. Finally, the polymer was dried at room temperature in air and then dried under dynamic vacuum for 48 hours.

### **Synthesis of Poly (*o*-toluidine) (POT) Homopolymer**

5.4 mL (0.05 mol) of *o*-toluidine was dissolved in 100 mL of 1 M HCl taken in a 250-mL two-necked glass flask. The oxidant solution was prepared separately by dissolving 5.5 g (0.024 mol) ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] in 50 mL of 1 M HCl. Both solutions were cooled in an ice-sodium chloride (2:1 wt %) bath to -18°C. The monomer solution was then treated with the oxidant solution, which was added drop wise for about 2 hrs at a rate of 1 drop every 3 sec at -18°C (total molar ratio of monomer: oxidant = 4:1). The reaction mixture was vigorously stirred for 40 hrs at -18°C. The homopolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The hydrochloride salt was subsequently neutralized twice in 150 mL of 0.1 M ammonium hydroxide for 24 hrs to obtain the homopolymer base. The homopolymer base was washed with excess water.

### **Synthesis of Poly (aniline-co-*o*-toluidine) Copolymer**

Poly (aniline-co-*o*-toluidine) copolymer was synthesized by chemical oxidative copolymerization following previously described method [38-40]. A typical procedure of the synthesis of copolymer with a 50:50 monomer ratio is as follows: 29 g of LiCl·H<sub>2</sub>O, 4.7 mL (0.05 mol) of aniline, and 5.4 mL (0.05 mol) of *o*-toluidine were dissolved in 100 mL of 1 M HCl taken in a 250-mL two-necked glass flask. The oxidant solution was prepared separately by dissolving 5.5 g (0.024 mol) ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] in 50 mL of 1 M HCl. Both solutions were cooled in an ice-sodium chloride (2:1 wt %) bath to -18°C. The monomer solution was then treated with the oxidant solution, which was added drop wise for about 2 hrs at a rate of 1 drop every 3 sec at -18°C (total molar ratio of monomer: oxidant = 4:1). The reaction mixture was vigorously stirred for 40 hrs at -18°C. The copolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The hydrochloride salt was subsequently neutralized twice in 150 mL of 0.1 M ammonium hydroxide for 24 hrs to obtain the copolymer base. The copolymer base was washed with excess water. A blackish violet solid powder was obtained which was left to dry in ambient air for 1 week. The copolymer exhibits the following nominal structure:

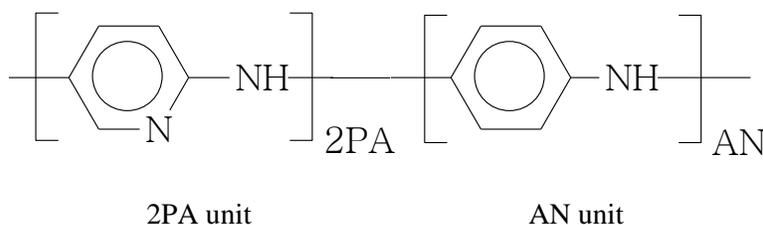


**Scheme 1**

### **Synthesis of [Poly (2-pyridylamine-co-aniline)] (2PA-co-AN) Copolymer**

A copolymer from 2-pyridylamine (2PA) and aniline (AN), poly (2PA-co-AN) was also synthesized via the chemical oxidative copolymerization following previously described method [38, 41]. A typical procedure of the synthesis of

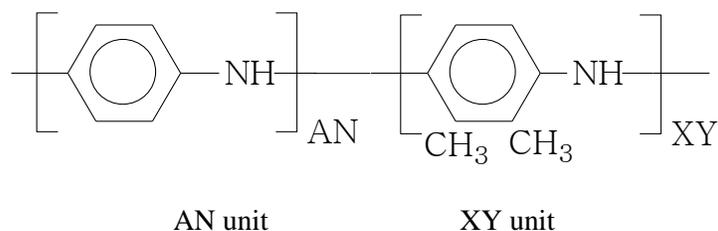
copolymer with a 30:70 monomer ratio is as follows: 1.412 g of 2-pyridylamine and 3.28 mL of aniline were dissolved in 40 mL of 1 M HCl taken in a 200 mL two-necked glass flask. The oxidant solution was prepared separately by dissolving 11.4 g (50 mmol) of ammonium persulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  in 35 mL of 1 M HCl. The monomer solution was then treated with the oxidant solution which was added drop wise at 19 °C for about 2 hrs (total molar ratio of monomer: oxidant = 1:1). After the first few drops, the reaction solution turned blue-violet. The reaction mixture was stirred for 10 hrs at ambient temperature. The copolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidants and oligomers. The hydrochloride salt was subsequently neutralized in 0.1 M ammonium hydroxide for 24 hrs to obtain the base form of the poly (2PA-co-AN) copolymer. The copolymer base was washed with excess water. A bluish black solid powder was left to dry in ambient air for 1 week. The poly (2PA-co-AN) copolymer has the following nominal structure:



Scheme 2

### Synthesis of [Poly (aniline-co-xylylidine)] (AN-co-XY) Copolymer

A copolymer from aniline (AN) and 2, 3-xylylidine (XY), poly (AN-co-XY) was synthesized via the chemical oxidative copolymerization following previously described method [39, 42]. A typical procedure for the preparation of the 50:50 copolymer was as follow: 3.5 mL of aniline and 7.5 mL of 2, 3-xylylidine were dissolved in 40 mL of 1 M HCl taken in a 200 mL two-necked glass flask. The oxidant solution was prepared separately by dissolving 11.4 g (50 mmol) of ammonium persulphate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  in 35 mL of 1 M HCl. Both solutions were cooled in an ice-sodium chloride (2:1 wt %) bath to -8°C. The monomer solution was then treated with the oxidant solution which was added drop wise at -8°C for about 2 hrs (total molar ratio of monomer: oxidant = 1:4). After the first few drops, the reaction solution turned blue-violet. The reaction mixture was vigorously stirred for 48 hrs at -8°C. The copolymer hydrochloride salt was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidants and oligomers. The hydrochloride salt was subsequently neutralized in 0.2 M ammonium hydroxide for 24 hrs to obtain the base form of the poly (AN-co-XY) copolymer. The copolymer base was washed with excess water. A blackish violet solid powder was left to dry in ambient air for 1 week. The nominal structure of poly (AN-co-XY) copolymer is as follows:



Scheme 3

### Synthesis of [Poly (2-Pyridylamine-co-aniline-co-2, 3-xylylidine)] (2PA-co-AN-co-XY) Terpolymer

Poly (2PA-co-AN-co-XY) was synthesized by chemical oxidative polymerization of 2-pyridylamine (2PA), aniline (AN) and 2, 3-xylylidine (XY) following previously described method [43]. A typical procedure of the synthesis of



[44, 45] using a double beam spectrophotometer [Model: Elico-SL-169 UV- Visible Spectrophotometer]. The corrosion rate was calculated using the following relationship:

$$\text{Corrosion rate} = \frac{m}{s \times t} \text{ [gm}^{-2}\text{h}^{-1}\text{]} \quad (1)$$

Where, 'm' is the mass of corroded metal (calculated from the total iron content determined in the test solution); 's' is the area of the test metal in m<sup>2</sup>; and 't' is the exposure time in hrs. The protection efficiency (%PE) of the coated specimen was evaluated using the following equation:

$$(\%PE) = \frac{CR_u - CR_c}{CR_u} \times 100 \quad (2)$$

Where,  $CR_u$  is the corrosion rate of mild steel in absence of coating and  $CR_c$  is corrosion rate of mild steel in presence of coating.

### ***Free Corrosion Potential Measurements***

The free corrosion potential measurements of uncoated, coated and coated scribed mild steel specimens were measured in different media. The change in voltage against saturated calomel electrode (SCE) used as reference electrode was plotted vs time. The potential measurement in a particular medium was continued till a steady state was obtained or it went down to the potential of bare steel.

### ***Potentiodynamic Polarization Measurements***

The potentiodynamic polarization measurements were carried out on an EG&G potentiostat/galvanostat model 263A. The experiments were carried out using a corrosion cell from EG&G model K0047 with Ag/AgCl electrodes (saturated KCl) as reference and Pt wire as counter electrode. The potentiodynamic polarization measurements were performed by sweeping the potential between -0.25 and 0.25 V from open circuit potential at a scan rate of 0.001 V/s. The specimen was allowed to stabilize in the electrolyte for 30 minutes prior to the experiment.

### ***Scanning Electron Microscopy***

The surface morphology of homopolymers, copolymers and terpolymer coatings obtained on mild steel specimens was evaluated using scanning electron microscopy (SEM). (Model: FEI, Quanta 200 and JEOL JSM 6510 LV).

### ***Corrosion Behavior of Homopolymer Coatings on Mild Steel***

Polyaniline (PANi) has been extensively used as an anticorrosive conducting coating material [46, 47]. Mengoli et al [48] were the first to exploit conducting polymer in the inhibition of corrosion of iron. They deposited the sulfur bridged PANi on iron surface by dipping an iron strip in an alkaline water methanol solution of aniline mixed with an inhibitor allyl amine or potassium chromate and ammonium sulphide. The film thickness was estimated to be more than 1.15 μm. It exhibited some porosity but fair adhesion and a salt fog resistance close to 80 hrs. In a subsequent paper De Berry [49] confirmed that stainless steel, in the presence of PANi, is passivated considerably under highly acidic conditions. Passivation occurred in the damaged areas of the coating. The polymer PANi was used in the inhibition of corrosion of stainless steel (SS) 410 and 430. The electroactive PANi coatings were obtained on the metals of interest by electrochemical treatment in 1.0 M aniline and pH 1.0 perchloric acid solution. The dried film coated SS 410 was tested in 0.2 M H<sub>2</sub>SO<sub>4</sub> and extent of corrosion was measured and a metal loss of 25 μm/year was found. The base stainless steel showed a loss of 3.1 × 10<sup>4</sup> μm/year. While studying conducting polymers, Ahmad and MacDiarmid [50] reported the inhibition of corrosion of iron and steel. The metals investigated include: pure iron, CS

1018, SS 304, SS 410 and SS 430. Among the conducting polymers the best polymer was found to be polyaniline due to its greater environmental stability, easy solution processibility and proper open circuit potential (OCP) in acidic media. The passivation region for SS 430 in 2 N H<sub>2</sub>SO<sub>4</sub> was -0.2 to 1.0 V vs saturated calomel electrode (SCE). The minimum potential (0.2 V vs SCE) needed for passivation of SS 430 was also exhibited by voltamograms of SS 430 in 2 N H<sub>2</sub>SO<sub>4</sub>, where passivation peak minimum occurred at -0.27 V (SCE). It was concluded that for the selection of a conducting polymer for corrosion protection of iron the determination of minimum potential required for passivation in a given corrosive medium is crucial. The V<sub>OCP</sub> of the conducting polymer chosen for corrosion prevention should be a little higher than the minimum passivation potential of the iron. Wessling [51] also reported that mild steel, stainless steel and Cu could be passivated by PANi. It was found that coats of chemically synthesized PANi induced an oxide formation on the metal surface, making corrosion potential of stainless steel to shift to the direction of noble metals and thereby decreasing the corrosion current. Later, Santos et al. [25] showed that similar chemical films were also able to protect carbon steel in 3% NaCl solution. Emeraldine, a form of PANi, was able to protect steel from corrosion in 0.1 M H<sub>2</sub>SO<sub>4</sub>+0.1 M Na<sub>2</sub>SO<sub>4</sub> and also in 0.2 M H<sub>2</sub>SO<sub>4</sub>+0.2 M NaCl, if the problem of adhesion is controlled since the film of polymer separated from metal [52].

It was found however that if the steel is dipped in a solution of phosphoric acid or chelating agent like chromotropic acid or alizarin a good adhesion of polymer is obtained and corrosion was inhibited for longer period (>30 days) of time. The chelating agents or phosphoric acid worked as cement between stainless steel and polymer. In comparison between the conducting emeraldine salt [ES] and non-conducting emeraldine base [EB] form of PANi the majority of studies show that in sodium chloride solution it is non-conducting form that provides the best protection [5, 53], whereas in HCl it appears that it is conducting form which provide the better protection [54], with the undoped non-conducting form having poor adhesion [55]. McAndrew [56] reported that EB had a very high coating resistance (10<sup>8</sup> Ω cm<sup>2</sup>) on steel in 3% NaCl solution and EB blend coating also showed improved corrosion resistance. The high barrier property of EB to corrosive species was attributed to the formation of a dense and strong adherent polymer film [56, 57]. There has been considerable debate as to which form of PANi offers higher corrosion protection: ES or EB. Direct comparison was made between the two forms of PANi and it was found that EB was superior to ES [53, 58]. The reason for the difference in performance is not clear at this stage, although the different forms of the polymer differ substantially in properties (conductivity, permeability, reduction potential) and composition (counter ion).

Spink et al [59] carried out a comparative study on the performance of PANi coatings (both ES and EB forms) with epoxy [EP] coating for corrosion protection of plain carbon steel in a saline solution. While the EB and ES coatings produced higher dissolution rates compared with EP coating, the behavior of coatings was clearly different and short periods of reduced corrosion rates were evident from both ES and EB coatings. The difference in corrosion rates caused by the different forms of polyamide may be associated to different inherent pH. EB produces a highly alkaline environment that is conducive to passive oxide formation while ES produces a mildly acidic environment in which the formation of passive oxide layers is less likely.

The corrosion protection performance of the homopolymers, polyaniline (emeraldine base) and poly (o-toluidine) coatings in different corrosive environments, such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere was carried out on uncoated, coated and coated scribed mild steel specimens by conducting various corrosion tests which include: immersion tests, open circuit potential (OCP) measurements, potentiodynamic polarization measurements and atmospheric exposure test. The results of immersion tests in different corrosive solutions are shown in Table 1. The test was carried out under static condition at room temperature for the duration of 30 days. Out of the four different corrosive solutions selected for corrosion studies, 0.1 M HCl is the most corrosive (corrosion rate; 19.081 mpy) whereas distilled water is the least corrosive (corrosion rate; 4.031 mpy). The severity of 5% NaCl solution and artificial seawater is almost identical; the corrosion rates of uncoated steel in both media remain almost same (6.021 and 7.034 mpy, respectively). The results of immersion test showed that the polyaniline coating exhibited better performance than the poly (o-toluidine) coating in all the corrosive media. The %PE of polyaniline coating in different media ranged between 82.12-52.81 whereas for poly (o-toluidine) coating the %PE ranged from 41.69 to 31.69. The performance of homopolymer polyaniline was found better in 0.1 M HCl solution where it showed a PE of 82.12%. The protection offered by polyaniline is attributed to both barrier effect and formation of passive oxide due to redox reaction at the steel and polymer interface [8]. The polymer coating on the

steel substrate behave as an effective barrier for the protection of steel against corrosion in different corrosive media subjected to investigation and showed the lower metal concentration released from the coated metal relative to the corresponding uncoated metal. The corrosion performance of polyaniline coating was found to be better than the homopolymer poly (o-toluidine) coating in all the corrosive media.

**Table 1** Corrosion data obtained by immersion test and potentiodynamic polarization measurements

Corrosive medium	Description of the sample	Protection efficiency (%) obtained by Immersion tests	Corrosion data obtained by potentiodynamic polarization measurements				
			$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	Cathodic beta (mV)	Anodic beta (mV)	Corrosion rate (mpy)
0.1 M HCl	Uncoated steel	–	1994.110	-522	279.435	138.311	150.412
	Polyaniline coated	82.12	0.068	-145	219.165	545.594	0.008
	Poly(o-toluidine) coated	31.69	0.021	-444	306.924	540.484	0.016
5% NaCl solution	Uncoated steel	–	265.112	-851	319.240	82.472	19.951
	Polyaniline coated	65.44	0.090	-82	195.062	474.735	0.007
	Poly(o-toluidine) coated	41.69	3.001	-577	514.492	108.709	0.223
Artificial sea water	Uncoated steel	–	144.332	-846	423.697	124.747	10.903
	Polyaniline coated	64.29	0.003	-146	389.171	655.406	0.002
	Poly(o-toluidine) coated	41.53	7.933	-511	355.779	82.164	0.059
Distilled water	Uncoated steel	–	54.511	-673	1195.031	257.784	4.111
	Polyaniline coated	52.61	0.081	-23	523.441	858.210	0.006
	Poly(o-toluidine) coated	37.74	1.210	-335	153.203	490.078	0.0069

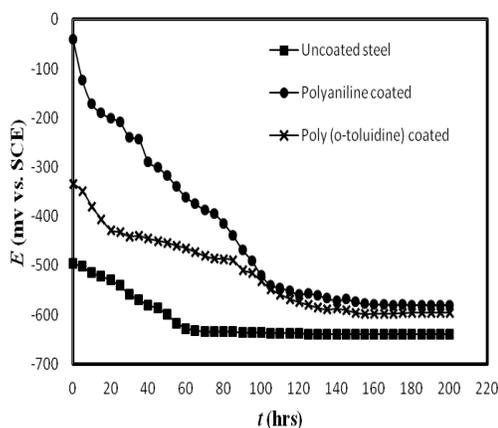
An analysis of the data obtained from potentiodynamic polarization measurements (Table 1) for both coating systems with uncoated steel specimens recorded in different corrosive media showed that the homopolymer polyaniline coated sample shows a substantial positive shift in  $E_{\text{corr}}$  and reduction in  $I_{\text{corr}}$  relative to the uncoated steel. The values of electrochemical parameters favor the existence of a strong passivating coating having barrier effect on the surface of the mild steel coated with polyaniline and poly (o-toluidine) homopolymers. The polyaniline coated samples provide better protection than poly (o-toluidine) coated samples in all media. The better performance of polyaniline coating than poly (o-toluidine) coating is probably due to more participation of polyaniline coating in the oxide formation and finds support from the results of immersion tests.

The OCP values ( $E_{\text{ocp}}$ ) of uncoated, polyaniline coated and poly (o-toluidine) coated steels were monitored with time in four different media. The typical OCP results are shown in Figure 1 and 2. Considering the results of OCP measurements, when steel is covered with a single homopolymer film, potential is shifted towards more noble values compared with the uncoated steel. With increasing immersion period, there is a continuous increase in the negative potential till a steady potential is obtained. However, the final potential is still nobler than the potential of uncoated steel. The noble shift in potential is more pronounced for polyaniline coating than for poly (o-toluidine) coating.

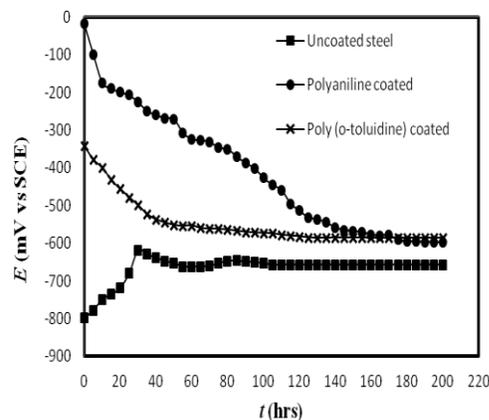
### **Corrosion Behavior of Copolymer and Terpolymer Coatings on Mild steel**

Co-polymerization of aniline with aniline derivatives might be one of the best methods to modify the solubility of PANi and to combine the advantages of PANi. The PANi, poly (2-toluidine) (PT) and poly (aniline-co-2-toluidine)

(co-PT) were synthesized on stainless steel (SS) under cyclic voltammetry conditions from acetonitrile solution using tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte and perchloric acid [ $\text{HClO}_4$ ] as acid [60]. The coatings were characterized by cyclic voltammetry, FTIR and UV- visible spectroscopy. The ability of PANi, PT and co-PT to serve as corrosion protective coatings for stainless steel was examined by electrochemical measurements which include  $E_{\text{OCP}}$ -time curves, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements made in 0.5 M HCl solution. The results of the study revealed that all the coatings acts as corrosion protective coatings on stainless steel and every coating gives protection efficiency greater than 80% after 48 hrs of immersion. Adhering conducting films of PANi, poly (2-iodoaniline) (PIANi) and poly (aniline-co-2-iodoaniline) (co-PIANi) were synthesized by using cyclic voltammetry in acetonitrile solution containing tetrabutyl ammonium perchlorate (TBAP) and perchloric acid [ $\text{HClO}_4$ ] on 304 SS electrodes [61].

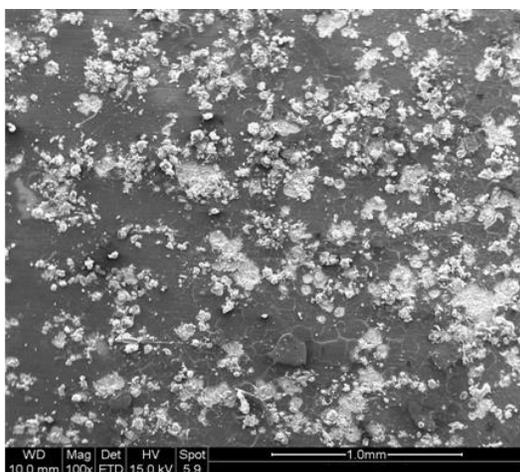


**Figure 1**  $E_{\text{corr}}$  vs time plot in 0.1 M HCl for (■) uncoated; (●) polyaniline and (×) poly (o-toluidine) coated steel

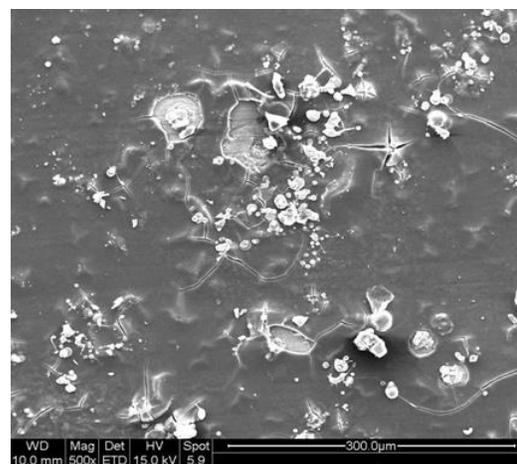


**Figure 2**  $E_{\text{corr}}$  vs time plot in 5% NaCl solution for (■) uncoated; (●) polyaniline and (×) poly (o-toluidine) coated steel

The typical SEM photomicrographs of polyaniline and poly (o-toluidine) coated steel specimen is shown in Figure 3.



(a)



(b)

**Figure 3** SEM micrographs of (a) polyaniline; (b) poly (o-toluidine) coated steel specimens

The structure of these polymer films were characterized using electrochemical method, FTIR and UV-visible spectroscopy. The corrosion performance of coated electrodes was investigated in 0.5 M HCl solutions by potentiodynamic polarization technique, open circuit potential-time curves and electrochemical impedance spectroscopy. FTIR and UV-visible results showed that polymer and copolymer were different from that of PANi. PIANi and co-PIANi behaved in a similar manner with regard to corrosion protection of 304 SS in 0.5 M HCl. EIS measurement shows that every coating gives protection efficiency greater than 75% after 48 h of immersion time in corrosive test solution. The copolymer films PANi-co-POA and poly (aniline-co-o-anisidine) were carried out on copper (Cu) electrode by using cyclic voltammetric conditions from 0.075 M aniline and 0.075 M anisidine containing sodium oxalate solutions [62].

AC impedance spectroscopy, anodic polarization plots and open circuit potential-time curves were used to evaluate the corrosion performance of copolymer coated and uncoated electrodes in 3.5% NaCl solution. The synthesized copolymer films were strongly adherent and homogeneous. It was found that thin copolymer film produced at high scan rate by its catalyzing effect led to the formation of highly protective copper oxides on the surface whereby providing a better protection for long exposure times. The corrosion protection efficiency of a thin film of electrochemically synthesized conducting polymers such as polyaniline, poly N-methylaniline and its copolymer poly (aniline-co-N-methylaniline) on carbon steel in 0.1 M HCl was investigated by potentiodynamic polarization measurements [63]. Of the compounds studied, the copolymer poly (aniline-co-N-methylaniline) coating showed high protection efficiency than other coatings. The PANi, poly (2-chloroaniline) (PCIANi), and poly (aniline-co-2-chloroaniline) (co-PCIANi) films were synthesized by electrochemical deposition on 304 L SS from an acetonitrile solution [64]. The structural properties of these polymer films were characterized by spectroscopic (FTIR and UV-visible) and electrochemical (cyclic voltammetry) methods.  $E_{OCP}$ -time curves, potentiodynamic polarization and EIS measurements showed that these films have significant protective performance against corrosion of SS in 0.5 M HCl solution. The PANi and co-PCIANi films are able to provide an effective anodic protection in addition to barrier properties for cathodic reaction while PCIANi films can provide only barrier properties.

EIS results showed that every coating gives protection efficiency of about 80% after 48 h of immersion in HCl solution. In a recent paper Yalcinkaya et al [34] successfully synthesized poly (o-anisidine) and poly (pyrrole-co-o-anisidine) from oxalic acid solution by using cyclic voltammetry technique. The EIS measurements was carried out in 3.5% NaCl solution and results revealed that the corrosion process occurring within the pores of the copolymer film was under diffusion control, even after 48 h exposure time. The cyclic voltamograms recorded for copolymer coated SS showed that the obtained film had good stability under polarized conditions, the feature of these curves were indicative for regularly oxidation-reduction behavior of polymer film, without any significant degradation. The electrochemical synthesis of polypyrrole (PPy) and poly (pyrrole-co-o-anisidine) were achieved on 3012 aluminium alloy (Al) from 0.1 monomer (pyrrole: o-anisidine, 8:2) containing 0.4 oxalic acid solution using the cyclic voltammetry technique [65]. The synthesized films were characterized by FTIR spectroscopy. The thermal stability of films was determined by thermo gravimetric analysis (TGA) technique. Surface morphologies were characterized by scanning electron microscopy (SEM) images. It was found that copolymer coated Al provides better barrier property against of corrosion in 3.5 % NaCl solution. In a recent study, a terpolymer film of pyrrole, o-anisidine, and o-toluidine was electrochemically synthesized on low carbon steel [35]. The synthesized terpolymer was found to be completely different in aspect of morphology, stability and other structural properties when compared to single polypyrrole film. The electrochemical measurements realized for corrosion behavior of this coating on steel indicated to low permeability and better stability in severe corrosive conditions.

The corrosion performance of copolymers, poly (aniline-co-o-toluidine), poly (AN-co-XY), and poly (2PA-co-AN) and a terpolymer, poly (2PA-co-AN-co-XY) in different corrosive solutions such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere was carried out on uncoated, coated and coated scribed mild steel specimens by conducting various corrosion tests which include: immersion tests, open circuit potential (OCP) measurements, potentiodynamic polarization measurements and atmospheric exposure test. The results of immersion tests are shown in Table 2.

Considering the results of immersion test, the poly (aniline-co-o-toluidine) copolymer coatings performed better than the other copolymers coating in all the corrosive media except 0.1M HCl. A slightly better performance of

the copolymer coating in neutral and basic solutions appears to be because of the better barrier effect of the copolymer film. Considering the performance of individual copolymer coatings in different corrosive solutions, the

**Table 2** Results of immersion test- immersion period 30 days

Corrosive medium	Description of the sample	Corrosion rate (mpy)	% PE
0.1 M HCl	Uncoated steel	19.081	–
	Poly (aniline-co-o-toluidine) coated	4.118	78.41
	Poly (aniline-co-o-toluidine) coated scribed	5.002	73.78
	Poly (AN-co-XY) coated	3.02	84.17
	Poly (AN-co-XY) coated scribed	10.90	42.87
	Poly (2PA-co-AN) coated	5.02	73.66
	Poly (2PA-co-AN) coated scribed	11.45	39.93
	Poly (2PA-co-AN-co-XY) coated	1.145	93.99
	Poly (2PA-co-AN-co-XY) coated scribed	7.031	63.15
5% NaCl solution	Uncoated steel	6.021	–
	Poly (aniline-co-o-toluidine) coated	0.411	93.17
	Poly (aniline-co-o-toluidine) coated scribed	2.512	58.27
	Poly (AN-co-XY) coated	0.806	86.16
	Poly (AN-co-XY) coated scribed	2.912	51.63
	Poly (2PA-co-AN) coated	1.501	75.08
	Poly (2PA-co-AN) coated scribed	3.511	41.68
	Poly (2PA-co-AN-co-XY) coated	0.291	95.16
	Poly (2PA-co-AN-co-XY) coated scribed	2.081	65.44
Artificial sea water	Uncoated steel	7.034	–
	Poly (aniline-co-o-toluidine) coated	0.431	93.87
	Poly (aniline-co-o-toluidine) coated scribed	1.901	72.97
	Poly (AN-co-XY) coated	1.011	85.64
	Poly (AN-co-XY) coated scribed	3.411	51.50
	Poly (2PA-co-AN) coated	1.808	74.28
	Poly (2PA-co-AN) coated scribed	4.00	43.13
	Poly (2PA-co-AN-co-XY) coated	0.240	96.58
	Poly (2PA-co-AN-co-XY) coated scribed	2.260	67.85
Distilled water	Uncoated steel	4.031	–
	Poly (aniline-co-o-toluidine) coated	0.351	91.25
	Poly (aniline-co-o-toluidine) coated scribed	1.504	62.52
	Poly (AN-co-XY) coated	0.602	85.11
	Poly (AN-co-XY) coated scribed	2,081	48.37
	Poly (2PA-co-AN) coated	1.145	71.59
	Poly (2PA-co-AN) coated scribed	2.511	37.70
	Poly (2PA-co-AN-co-XY) coated	0.226	94.37
	Poly (2PA-co-AN-co-XY) coated scribed	1.450	64.02

poly (AN-co-XY) coating exhibited better performance than the poly (2PA-co-AN) copolymer coating in all corrosive media. It showed the highest PE of 86.16% in 5% NaCl solution; this is followed by artificial seawater (85.64%), distilled water (85.11%) and 0.1 M HCl (84.17%). The copolymer poly (2PA-co-AN) offered relatively lower corrosion protection; it showed the highest PE of 75.07% in 5% NaCl solution and lowest PE of 71.59% in distilled water. The better anticorrosive properties of poly (AN-co-XY) copolymer coating than poly (2PA-co-AN) coating to the mild steel may be attributed to the fact that the delocalized  $\pi$  electrons in xylylene diisocyanate facilitate its strong adsorption on mild steel leading to outstanding corrosion inhibition. The presence of scribed marks also diminished the protection of both copolymers.

Considering the corrosion performance of poly (2PA-co-AN-co-XY) terpolymer, the performance of coating was found better than individual copolymers in all the corrosive solutions subjected to investigation. The outstanding corrosion protection offered by terpolymer coating to the mild steel substrate may be attributed to its better barrier property in addition to its ability to form passive oxide at the steel/polymer interface and the presence of homogeneous, uniform and strongly adherent coating covering the entire specimen surface. The terpolymer, due to its better barrier property, effectively hindered the attack of corrosive environment and lengthens the diffusion path of electrolytes and other corrosive species, thereby decreasing the corrosion rate. The presence of scribed mark on the terpolymer coating marginally affected its performance and only slightly increases the corrosion rate of the underlying steel.

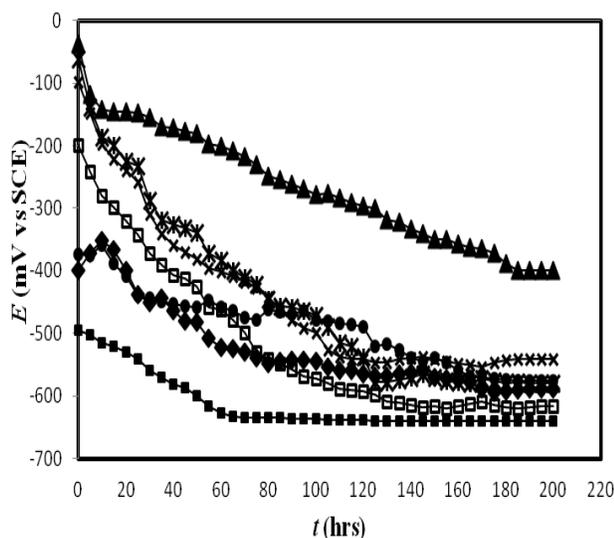
This confirms the self passivating nature of the terpolymer coating. The self passivating nature of the terpolymer is attributed to the incorporated homopolymer polyaniline which has the ability to repair artificial defects and restore the passive state of the underlying metal substrate. Corrosion of metals involves the transfer of electrical charges in aqueous solution at the metal electrolyte interface. Corrosion protection is often afforded by isolating the metal from the corrosive environment by using polymer coatings [66]. Electrochemical measurements such as open circuit potential and potentiodynamic polarization have been used to assess the protective properties of coatings in different corrosive solutions. Protection is afforded by the oxidation or passivation of the metal, shifting the corrosion potential towards more positive values and modifying the oxygen reduction reaction. Due to this reaction, the OCP was found to shift to more noble values indicating the formation of protective passive film on iron [67].

The OCP values ( $E_{ocp}$ ) of uncoated, poly (2PA-co-AN-co-XY) terpolymer, poly (aniline-co-o-toluidine) copolymer (both scribed and unscribed), poly (AN-co-XY) and poly (2PA-co-AN) coated steels were monitored with time in four different media, and the results of 0.1 M HCl and 5 % NaCl solution are shown in Figures 4 and 5. An analysis of the results of OCP measurements of poly (2PA-co-AN-co-XY) terpolymer, poly (aniline-co-o-toluidine), poly (2PA-co-AN) and poly (AN-co-XY) copolymer coated steel in different corrosive media revealed that the presence of both terpolymer and copolymers coatings on mild steel substrate shift the  $E_{ocp}$  values towards more noble direction with respect to  $E_{ocp}$  value of uncoated steel for the same condition.

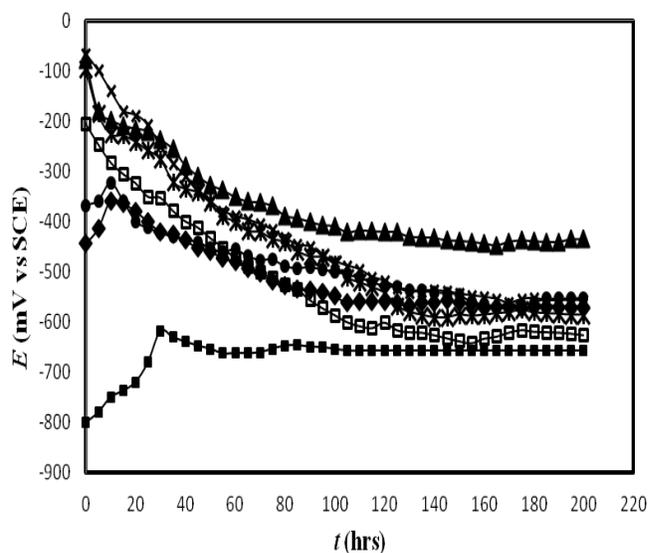
The positive shift in the potential is more pronounced for terpolymer coating in all corrosive solutions. With increasing immersion period there is an increase in negative potential till a steady potential is reached. However, the final potential is still nobler than the potential of uncoated steel. The noble shift in potential is more pronounced for terpolymer than copolymers, but poly (aniline-co-o-toluidine) performs better than the poly (2PA-co-AN) and poly (AN-co-XY). In case of terpolymer coated scribed samples, after an initial decrease in potential, an increase in potential is observed, this is followed by a constant potential. However, the final potential of scribed samples is again nobler than the potential of uncoated steel. The remarkable noble shift in OCP values for terpolymer and copolymers coated steel specimens indicate that inhibition mechanism of conducting polymers is related with both passivation and barrier effect. The barrier effect is operative till the polymer coating remains adherent and undamaged and prevents the contact of the steel substrate with the corrosive environments.

As the immersion is continued, the initial OCP started to increase as a result of the initiation of corrosion process under the polymer coating leading to the anodic dissolution of steel. During immersion the electrolyte penetrates via the pores in the coating and develops the electrolyte pathways with time through coating. The corrosive species along with the water diffuse through these paths towards the steel surface. When the sufficient amount of electrolyte reaches to the steel surface the corrosion processes are initiated at coating/steel interface and as a consequence the  $E_{corr}$  value shifts to less noble value. The behavior of copolymers, poly (aniline-co-o-toluidine), poly (AN-co-XY) and poly (2PA-co-AN) in all corrosive solutions is appreciable during the initial hrs of immersion

period, whereas the terpolymer coating provides the best protection during the entire period of immersion. The better barrier effect of the terpolymer coating is due to the formation of a dense and uniform film on steel substrate. For terpolymer coated scribed specimens, though the initial OCP was higher than the uncoated sample due to the break in the coating, however, the coating immediately re-passivated as a result of redox reaction and attained a potential close to the potential of coated steel and matched up to the end of immersion period of 200 hrs. The finding of OCP measurements suggests that protection mechanism other than barrier effect is operating.



**Figure 4**  $E_{\text{corr}}$  vs time plot in 0.1 M HCl for (■) uncoated; (▲) poly (2PA-co-AN-co-XY) coated; (●) poly (2PA-co-AN-co-XY) coated scribed; (×) poly (aniline-co-o-toluidine) coated; (◆) poly(aniline-co-o-toluidine) coated scribed (\* ) poly (AN-co-XY) coated and (□) poly (2PA-co-AN) coated



**Figure 5**  $E_{\text{corr}}$  vs time plot in 5% NaCl solution for (■) uncoated; (▲) poly (2PA-co-AN-co-XY) coated; (●) poly (2PA-co-AN-co-XY) coated scribed; (×) poly (aniline-co-o-toluidine) coated; (◆) poly(aniline-co-o-toluidine) coated scribed; (\* ) poly (AN-co-XY) coated and (□) poly (2PA-co-AN) coated

In order to compare the stability and barrier properties of polymer coatings under polarized conditions the potentiodynamic polarization curves were recorded in different corrosive mediums. The values of corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), cathodic beta ( $b_c$ ), anodic beta ( $b_a$ ) and corrosion rate obtained from these curves are listed in Table 3.

The results of potentiodynamic polarization measurements for polymers coating in different corrosive solutions suggest about the barrier property and the stability of copolymer and terpolymer coatings under simulated conditions. It was apparent that the polymer film shifted the corrosion potential value due to its physical barrier behavior between corrosive environment and metal substrate. For the same reason the current values corresponding to anodic metal dissolution at higher potential values were lower than the uncoated sample.

The results of potentiodynamic polarization measurements of poly (aniline-co-o-toluidine) copolymer and poly (2PA-co-AN-co-XY) terpolymer coated steel specimens (both scribed and unscribed) in different corrosive medium, suggest that the presence of both coatings on the steel substrate reduces anodic dissolution and provide the perfect coverage and best protection. The copolymer and terpolymer coatings caused a remarkable positive shift in the values of both corrosion potential and corrosion current density. The shift in  $E_{\text{corr}}$  confirms that the mild steel covered by polymer coating depressed the anodic current of the corrosion reaction and offered the greater resistance to corrosion.

**Table 3** Results of potentiodynamic polarization measurements

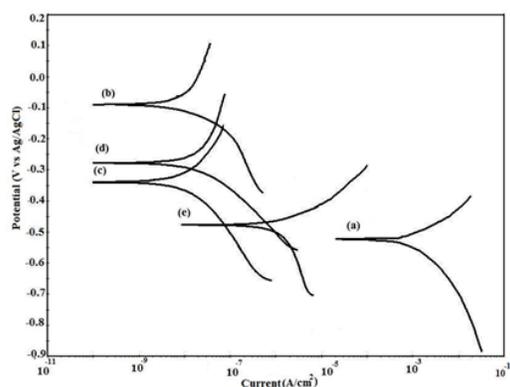
Corrosive Medium	Description of the sample	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	Cathodic beta (mV)	Anodic beta (mV)	Corrosion rate (mpy)
0.1 M HCl	Poly (aniline-co-o-toluidine) coated (Fresh sample)	0.063	-116	366.650	324.352	0.004
	Poly (aniline-co-o-toluidine) coated (After 1 month immersion)	9.073	-636	243.782	107.756	0.068
	Poly (aniline-co-o-toluidine) coated scribed (Fresh sample)	8.838	-465	4793.001	718.272	6.665
	Poly (aniline-co-o-toluidine) coated scribed (After 1 month immersion)	27.251	-606	1034.761	119.681	8.055
	Poly (2PA-co-AN-co-XY) coated (fresh sample)	0.003	-72	248.706	2035.945	0.002
	Poly (2PA-co-AN-co-XY) coated (After 1 month immersion)	0.017	-337	219.235	274.371	0.013
	Poly (2PA-co-AN-co-XY) coated scribed (fresh sample)	0.035	-276	155.251	693.189	0.008
	Poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)	1.107	-476	305.617	63.796	0.834
5% NaCl solution	Poly (aniline-co-o-toluidine) coated (Fresh sample)	0.024	-52	330.191	286.733	0.002
	Poly (aniline-co-o-toluidine) coated (After 1 month immersion)	2.136	-731	466.338	102.234	0.161
	Poly (aniline-co-o-toluidine) coated scribed (Fresh sample)	0.514	-484	99.819	95.046	0.038
	Poly (aniline-co-o-toluidine) coated scribed (After 1 month immersion)	2.349	-637	134.235	81.934	0.177
	Poly (2PA-co-AN-co-XY) coated (fresh sample)	0.001	-152	227.405	557.768	0.001
	Poly (2PA-co-AN-co-XY) coated (After 1 month immersion)	0.029	-448	315.469	242.031	0.019
	Poly (2PA-co-AN-co-XY) coated scribed (fresh sample)	0.188	-317	128.687	475.719	0.014

Artificial seawater	Poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)	5.055	-566	379.648	84.808	0.881
	Poly (aniline-co-o-toluidine) coated (Fresh sample)	0.018	-132	406.084	3435.895	0.001
	Poly (aniline-co-o-toluidine) coated (After 1 month immersion)	5.480	-760	424.644	104.105	0.413
	Poly (aniline-co-o-toluidine) coated scribed (Fresh sample)	1.321	-519	301.139	140.367	0.099
	Poly (aniline-co-o-toluidine) coated scribed (After 1 month immersion)	5.616	-616	2417.776	131.213	0.042
	Poly (2PA-co-AN-co-XY) coated (fresh sample)	0.010	-128	937.240	2506.961	0.005
	Poly (2PA-co-AN-co-XY) coated (After 1 month immersion)	0.174	-495	178.127	1121.180	0.013
	Poly (2PA-co-AN-co-XY) coated scribed (fresh sample)	0.071	-324	196.144	455.403	0.009
Distilled water	Poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)	14.390	-595	452.239	241.427	1.081
	Poly (aniline-co-o-toluidine) coated (Fresh sample)	0.029	-42	317.469	504.061	0.002
	Poly (aniline-co-o-toluidine) coated (After 1 month immersion)	3.007	-639	891.824	227.376	0.226
	Poly (aniline-co-o-toluidine) coated scribed (Fresh sample)	1.891	-517	224.946	90.018	0.142
	Poly (aniline-co-o-toluidine) coated scribed (After 1 month immersion)	7.826	-600	638.103	107.685	0.590
	Poly (2PA-co-AN-co-XY) coated (fresh sample)	0.048	-82	186.565	1447.230	0.003
	Poly (2PA-co-AN-co-XY) coated (After 1 month immersion)	0.901	-347	98.128	499.017	0.068
	Poly (2PA-co-AN-co-XY) coated scribed (fresh sample)	0.106	-316	134.807	1201.611	0.008

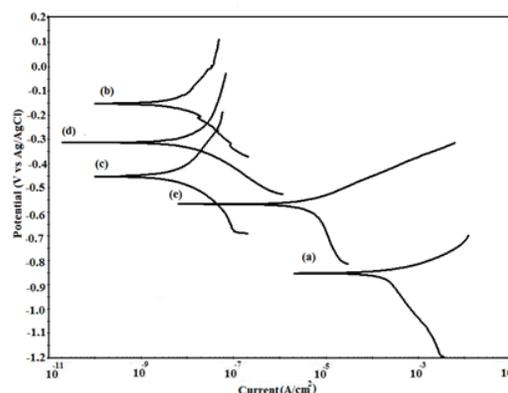
Poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)	1.481	-563	225.324	86.672	0.217
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In case of terpolymer the shift in all electrochemical parameters is more pronounced than the copolymer and homopolymer PANi. In case of poly (aniline-co-o-toluidine) copolymer, when the coating was subjected to one month immersion the potential shifted to more negative values compared to bare steel. A negative shift in potential is attributed to the activation of corrosion process at the coating/metal interface as a result of deterioration in the coating due to longer exposure to the corrosive solution. However, the values of  $I_{\text{corr}}$  and corrosion rates are still lower than the bare steel indicating that protection other than barrier is operating. There is a change in the values of both Tafel slopes indicating that corrosion of mild steel in presence of copolymer coatings is under both anodic and cathodic control. A large deviation in the Tafel slopes values for the coated scribed and coating exposed to one month duration (where integrity of the polymer coatings is affected) has been observed.

A very high value of Tafel slope is indicative of non-linearities in Tafel plot. The non-linearities in the Tafel plot is caused due to one or more of the complications like concentration polarization, oxide formation which may or may not lead to passivation, a mixed control process where more than one cathodic, or anodic, reaction occurs simultaneously, and potential drop. In case of coated scribed sample the value of  $E_{\text{corr}}$  is higher than the unscribed sample but during the progress of immersion the coating repassivated and offered protection against corrosion. The electrochemical parameters revealed that terpolymer coating has high chemical as well as physical stability and the coating keeps its adherence to the steel substrate. The typical potentiodynamic polarization curves are shown in Figure 6 and 7.



**Figure 6** Potentiodynamic polarization curves in 0.1 M HCl for (a) uncoated steel; poly (2PA-co-AN-co-XY) coated (Fresh sample); (c) poly (2PA-co-AN-co-XY) coated (After 1 month immersion); (d) poly (2PA-co-AN-co-XY) coated scribed (Fresh sample) and (e) poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)



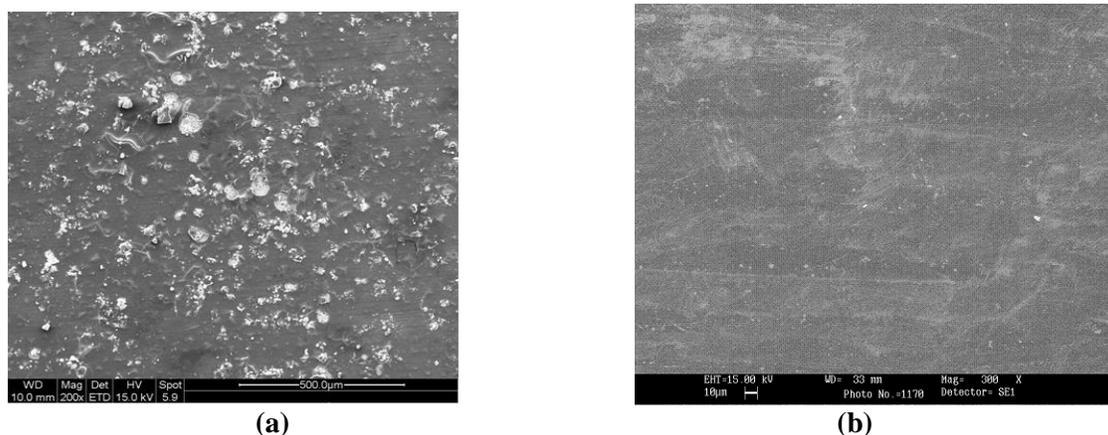
**Figure 7** Potentiodynamic polarization curves in 5% NaCl solution for (a) uncoated steel; (b) poly (2PA-co-AN-co-XY) coated (Fresh sample); (c) poly (2PA-co-AN-co-XY) coated (After 1 month immersion); (d) poly (2PA-co-AN-co-XY) coated scribed (Fresh sample) and (e) poly (2PA-co-AN-co-XY) coated scribed (After 1 month immersion)

Considering the results of atmospheric exposure test [Table 4] for terpolymer and copolymer coating the corrosion rate of coated sample is only slightly higher than those polarized prior to atmospheric exposure. It may be inferred that after one month of atmospheric exposure though the adherence of the terpolymer coating was affected but it still maintained the protective properties giving good protection to the underneath metal. This again suggests that protection mechanism other than barrier protection is operating.

**Table 4** Results of atmospheric exposure test

Corrosive Medium	Description of the sample	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ (mV)	Cathodic beta (mV)	Anodic beta (mV)	Corrosion rate (mpy)
Distilled water (measurements done after 1-month exposure to open atmosphere)	Uncoated steel	15.271	-511	642.265	169.347	1.152
	Poly (aniline-co-o-toluidine) coated	5.337	-74	135.603	1551.400	0.004
	Poly (aniline-co-o-toluidine) coated scribed	15.88	-441	504.540	556.322	1.051
	Poly (2PA-co-AN-co-XY) coated	0.218	-97	201.298	1175.603	0.093
	Poly (2PA-co-AN-co-XY) coated scribed	0.204	-215	130.909	556.084	0.750
	Polyaniline coated	14.26	-382	571.937	880.731	1.075
	Poly(o-toluidine) coated	10.71	-581	580.607	104.727	0.980

The typical SEM micrographs of copolymer and terpolymer coated samples are shown in Figure 8. SEM micrographs of the terpolymer coating show a uniform, compact and featureless structure. The film was homogeneously covering the steel surface, without any crack or significant defect. The SEM micrographs of copolymers coating indicates significant difference in their morphologies compared to the morphology of terpolymer coating.



**Figure 8** SEM micrographs of (a) poly (aniline-co-o-toluidine) copolymer and (b) poly (2PA-co-AN-co-XY) terpolymer coated steel specimens.

## Conclusions

The coatings of terpolymer, copolymers and homopolymers on mild steel were successfully obtained by solution evaporation. The terpolymer coating was observed to be more homogenous than the individual copolymers and homopolymer coatings. The results of immersion tests indicate that the corrosion rate of terpolymer coated steel was significantly lower than the individual homopolymers and copolymers coated steel in all corrosive medium under investigation; the protection efficiency being in the range of 93.99% - 96.58%. Among the series of copolymers, in general, the performance of poly (aniline-co-o-toluidine) copolymer was better than other copolymers. The results of open circuit potential measurements show nobler potential for terpolymer, copolymers and homopolymers coated steels compared to the uncoated steel. The electrochemical parameters as derived from potentiodynamic polarization

measurements indicate lower corrosion rate for terpolymer and copolymer coated steel in comparison to uncoated steel.

Open circuit potential measurements and potentiodynamic polarization measurements results are in good agreement with each other. Owing to the good performance of the terpolymer and poly (aniline-co-o-toluidine) coating in different corrosive environments the coating may be considered as a candidate material for future industrial assessment.

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