

Corrosion performance of chemically synthesized poly(aniline-*co*-*o*-toluidine) copolymer coating on mild steel

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Abstract A soluble copolymer from aniline and *o*-toluidine [poly(aniline-*co*-*o*-toluidine)] was synthesized by chemical oxidative copolymerization using ammonium persulphate as an oxidant in hydrochloride aqueous medium. The resultant copolymer was 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 copolymer coating was investigated in major corrosive environments, such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere by conducting various corrosion tests which include: immersion test, open circuit potential (OCP) measurements, potentiodynamic polarization measurements and atmospheric exposure test. The corrosion performance of copolymer coating was also compared separately with polyaniline (PANi) and poly(*o*-toluidine) (POT) homopolymer coatings. The surface morphologies of polymer coatings were evaluated using scanning electron microscopy (SEM). The synthesized copolymer exhibited excellent protection against mild steel corrosion; the protection efficiency being in the range of 78–94% after 30 days of immersion. The corrosion performance of copolymer in 5% NaCl and artificial seawater was comparable, which was only marginally better than in 0.1 M HCl. In general, the performance of copolymer coating was found to be better than that of homopolymer coatings.

Keywords Poly(aniline-*co*-*o*-toluidine), Mild steel, Oxidative copolymerization, Immersion test

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Introduction

The need for anti-corrosion coatings coupled with growing environmental concerns has led to new coating formulations employing inherently conductive polymers (ICPs) as a key component. ICPs, in addition to being conductive, are redox active materials, typically with potentials that are positive of iron and aluminium.¹ Among the conducting polymers, polyaniline (PANi), polypyrrole (PPy) and their derivatives have been regarded as the most important conducting polymers owing to their stability and synthesis advantages.^{2–8} The aniline and its derivatives have been predicted to be futuristic materials because of their greater environmental stability, inexpensive raw materials, facile synthesis and their unique conduction mechanism. One of the challenges in developing conducting polymer coatings, in general, has been to overcome the difficulty in processing these materials. The general lack of solubility and fusibility of these materials make the formation of coating on active metals difficult. The direct electrochemical deposition of the coating can be used, but this approach is not straightforward with active metals that oxidize at the deposition potential. The synthesis of copolymers between various monomer molecules has long been utilized to alter the physical-chemical properties of polymer coatings.⁹ The addition of monomers with hydrophobic groups could lower the water uptaking rate, or another group may enhance the stability and adherence.

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 (HClO₄).¹⁰ Electrochemical measurements including E_{OCP} -time curves, potentiodynamic polarization and electrochemical impedance spectroscopy

(EIS) measurements were made in 0.5 M HCl, and every coating gives protection efficiency of greater than 80% after 48 h of immersion. Poly(*o*-toluidine) (POT) was synthesized on copper substrate using cyclic voltammetric technique from an aqueous solution of sodium oxalate.¹¹ The resulting POT coating was uniform and strongly adherent to the Cu substrate. The ability of POT coating to serve as a corrosion protective coating for Cu was examined by potentiodynamic polarization measurements and cyclic voltammetric technique. The results of the study showed that the POT coating has remarkable capability to protect Cu against corrosion in chloride environment. The electrochemical synthesis of poly(*o*-anisidine) homopolymer and its copolymerization with pyrrole have been investigated on mild steel.¹² The protective behavior of coatings against steel corrosion in 3.5% NaCl solution was investigated by carrying out EIS and anodic polarization curves. The synthesized poly(*o*-anisidine) and copolymer exhibited significant corrosion inhibition efficiency against mild steel corrosion. Recently, polytoluidine has attracted greater attention because of its better solubility and processibility than PANi.^{13–16} Co-polymerization of aniline with toluidine might be one of the best methods to modify the solubility of PANi and to combine the advantages of polytoluidine with PANi.

Since the early 1990s, considerable research 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 a lack of knowledge about the chemically deposited polymers and their performance in other corrosive medium such as artificial seawater, distilled water and open atmosphere. Further, it has been observed that copolymers have better solubility than their homopolymers in various organic solvents. This simplifies polymer processibility and is advantageous for producing polymers and copolymers in bulk.¹⁷ In view of the above reasons, a copolymer of aniline and *o*-toluidine [poly(aniline-*co*-*o*-toluidine)] was synthesized by chemical oxidative copolymerization, and the resultant copolymer was deposited on mild steel by solution evaporation. The anticorrosive property of copolymer was investigated in major corrosive environments such as 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere by subjecting it to different corrosion tests which include immersion test, open circuit potential (OCP) and potentiodynamic polarization measurements. The corrosion performance of the copolymer was also compared with the individual homopolymers.

Experimental

Analytical reagents (AR) grade chemicals were used throughout this study. Freshly distilled aniline and

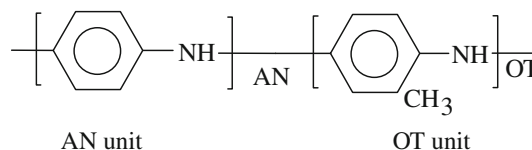
o-toluidine monomers were used for the synthesis of copolymer and individual homopolymers. The polymerization was carried out by chemical oxidative polymerization using ammonium per sulphate as the oxidant in an aqueous acidic medium (1.0 M HCl).

Preparation of specimen

The chemical composition (wt%) of the mild steel used in this study was 0.20% C, 0.043% S, 0.028% P, 0.003% Si, 0.08% Ni, 0.113% Mo, 0.16% Mn, 0.052% Cu, and the balance was iron. The mild steel specimens (size 40 × 15 × 0.3 mm) were polished with a series of emery papers, followed by rinsing in acetone and double distilled water and then dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage.

Synthesis and characterization of poly(aniline-*co*-*o*-toluidine), polyaniline, and poly(*o*-toluidine)

Poly(aniline-*co*-*o*-toluidine) copolymer was synthesized by chemical oxidative copolymerization following the previously described method.^{18–20} A typical procedure of the synthesis of copolymer with a 50:50 monomer ratio is as follows: 29 g of LiCl·H₂O, 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 in a 250-mL two-necked glass flask. The oxidant solution was prepared separately by dissolving 5.5 g (0.024 mol) ammonium persulfate [(NH₄)₂S₂O₈] 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 dropwise for about 2 h at a rate of 1 drop every 3 s at –18°C (total molar ratio of monomer: oxidant = 4:1). The reaction mixture was vigorously stirred for 40 h 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 h 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 available physical and thermal stable parameters of the copolymer are listed in Table 1. The nominal structure of copolymer is as follows:



PANi and POT were also homopolymerized by following the identical synthesis route. The copolymer

Table 1: Physical and thermal stable parameters of the copolymer/monomer ratio of 50:50²⁰

Physical parameters				Thermal stable parameters			Kinetic parameters			
Polymerization yield (%)	Solubility	Intrinsic viscosity (dL g ⁻¹)	Color	T _d (°C)	T _{dm} (°C)	Char yield at 900°C (wt%)	E (kJ mol ⁻¹)	n	ln Z (min ⁻¹)	r
13	NMP (S) DMSO (MS) CHCl ₃ (MS) THF (PS) CCl ₄ (SS)	1.70	Blackish violet	480	600	57	52	1.3	3.4	0.987

NMP = *N*-methyl-2-pyrrolidone; DMSO = dimethyl sulphoxide; THF = tetrahydrofuran; S = soluble; MS = mainly soluble; PS = partially soluble; SS = slightly soluble; T_d = degradation temperature; E = activation energy; n = decomposition reaction order; ln Z = frequency factor; r = linear correlation coefficient

and homopolymers were both characterized using FTIR technique.

Preparation of poly(aniline-co-o-toluidine), polyaniline, and poly(o-toluidine) coatings on mild steel

The coating of poly(aniline-co-o-toluidine) copolymer was obtained on mild steel samples using NMP as the solvent. The solution of copolymer (50% weight) was prepared, and its controlled amount was spread on the mild steel surface; this was followed by evaporation of the solvent at a temperature of 85–90°C.²¹ The pouring of the solution on the steel surface was continued until a thick, uniform and adherent coating was obtained. The weight of the coating per unit area was measured and found to be 5.40 mg cm⁻². Several coated samples were obtained following the identical procedure, and care was taken to ensure that the weight of the coating is maintained to 5.40 mg cm⁻² with a variation of ±5%. A good adherent bluish violet-colored coating of copolymer on mild steel was successfully obtained. The POT coating was obtained based on an identical procedure. However, in the case of PANi, a saturated solution of polymer prepared in NMP was used for deposition of coating. The surface morphology of polymer coatings was evaluated using scanning electron microscopy (SEM) (Model: FEI, Quanta 200), and the micrographs are shown in Fig. 1. The SEM micrographs indicate significant difference between the morphologies of copolymer and single homopolymer coatings. The copolymer film exhibited simple spherical particles of smaller size, and the film was found to be homogeneously covering the steel surface.

Corrosion performance of the poly(aniline-co-o-toluidine), polyaniline, and poly(o-toluidine) coatings

In order to evaluate the corrosion protection performance of the polymer coatings in different corrosive

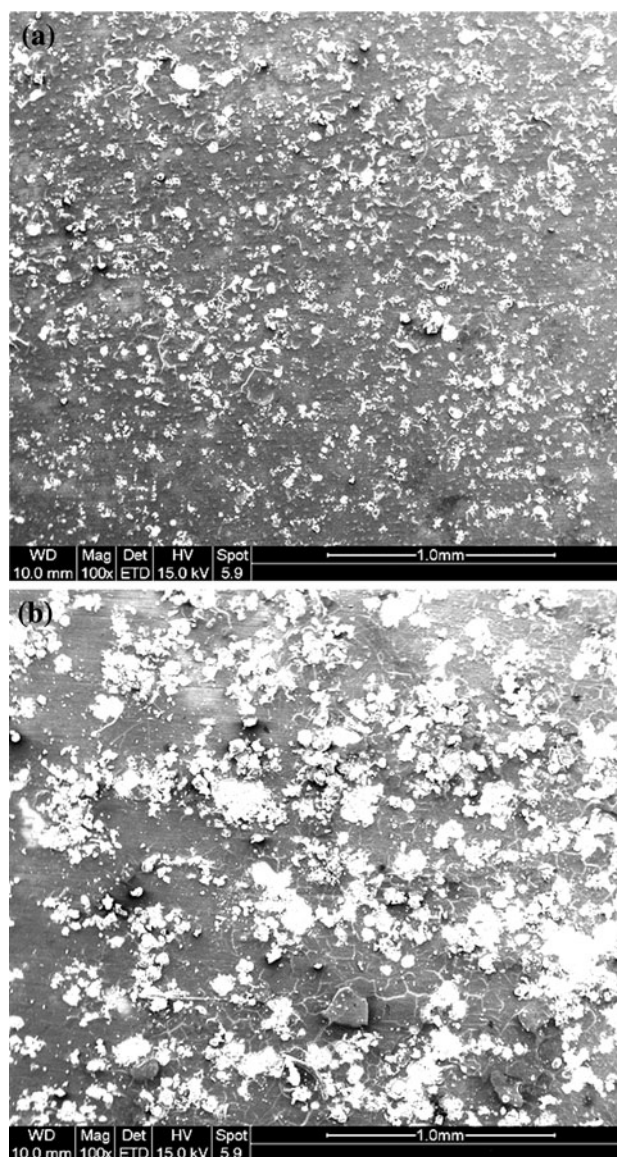


Fig. 1: SEM micrographs of (a) poly(aniline-co-o-toluidine) copolymer and (b) polyaniline-coated steel specimen

environments, uncoated, coated and coated scribed mild steel specimens were subjected to immersion test, OCP and potentiodynamic polarization measurements. The corrosive environments include 0.1 M HCl, 5% NaCl solution, artificial seawater, distilled water and open atmosphere. The tests were done at room temperature under static condition.

Immersion test

After taking the initial weight and dimension, uncoated, coated and coated scribed specimens were suspended in test solution with the help of nylon thread. The tests were carried out under static condition at room temperature for a period extending 30 days. The corrosion rate was calculated from determination of total iron ions (Fe^{2+} , Fe^{3+}) entered into the test solution in the course of corrosion during immersion. The analysis was performed spectrophotometrically^{21,22} using a double beam spectrophotometer [Model: Elico-SL-169 UV-Vis Spectrophotometer]. The corrosion rate was calculated using the following relationship:

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

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^2 ; and t is the exposure time in hours. The protection efficiency (%PE) of the coated specimen was evaluated using the following equation:

$$(\%PE) = \frac{\text{CRu} - \text{CRc}}{\text{CRu}} \times 100 \quad (2)$$

where CRu is the corrosion rate of mild steel in the absence of coating, and CRc is the corrosion rate of mild steel in the presence of coating.

Free corrosion potential measurements

The free corrosion potential measurements of uncoated, coated and coated scribed steel specimens were measured in 0.1 M HCl, 5% NaCl solution, artificial seawater and distilled water. 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 until a steady state was obtained or it decreased to the potential of bare steel.

Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out on an EG&G potentiostat/galvanostat

model 263 A. 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 OCP at a scan rate of 0.001 V s^{-1} . The specimen was allowed to stabilize in the electrolyte for 30 min before the experiment. All the measurements were repeated at least four times to ensure good reproducibility of the results.

Atmospheric test

The poly(aniline-*co-o*-toluidine)-, PANi-, POT-coated steel samples along with uncoated steel samples were weighed and subsequently fixed on a panel which stood on a heavy metallic base and placed on the roof of the department. The exposure time was 30 days. The samples were taken off the panel after the completion of the exposure test and physically examined for coating deterioration. To further examine the effect of atmosphere on the corrosion performance of the polymer coatings, the samples obtained after exposure to open atmosphere were immediately immersed in distilled water and were subjected to potentiodynamic polarization measurements.

Results and discussion

FTIR spectra of poly(aniline-*co-o*-toluidine), polyaniline, and poly(*o*-toluidine)

The FTIR spectra of poly(aniline-*co-o*-toluidine) copolymer, PANi and POT are shown in Fig. 2. The spectrum of the poly(aniline-*co-o*-toluidine) copolymer (Fig. 2a) is consistent with the reported spectrum of the copolymer.²⁰ The broad band centered at 3377 cm^{-1} , a result of the characteristics free N-H stretching vibration, suggests the presence of secondary amino group ($-\text{NH}-$).²³ The small shoulder band at 3293 cm^{-1} corresponds to the hydrogen-bonded N-H vibration. The peak at about 3029 cm^{-1} might be due to C-H stretching on the benzene ring. Peak at 2917 cm^{-1} can be attributed to the C-H stretching vibration in methyl groups, and it gets a little bit stronger with the OT unit. The IR absorption at $1489-1597 \text{ cm}^{-1}$ is associated with the aromatic ring stretching. The peak at exactly 1597 cm^{-1} can be assigned to the quinoid ring, and the one at 1489 cm^{-1} to the benzenoid ring. The weak peak at 1379 cm^{-1} can be attributed to the C-N stretching vibration in the quinoid imine units. A strong peak at 1304 cm^{-1} is because of the C-N stretching vibration in the alternative unit of quinoid-benzenoid-quinoid. A similar sequential structure is observed in the spectra of PANi²⁴ (Fig. 2b). A weak peak at 1236 cm^{-1} can be

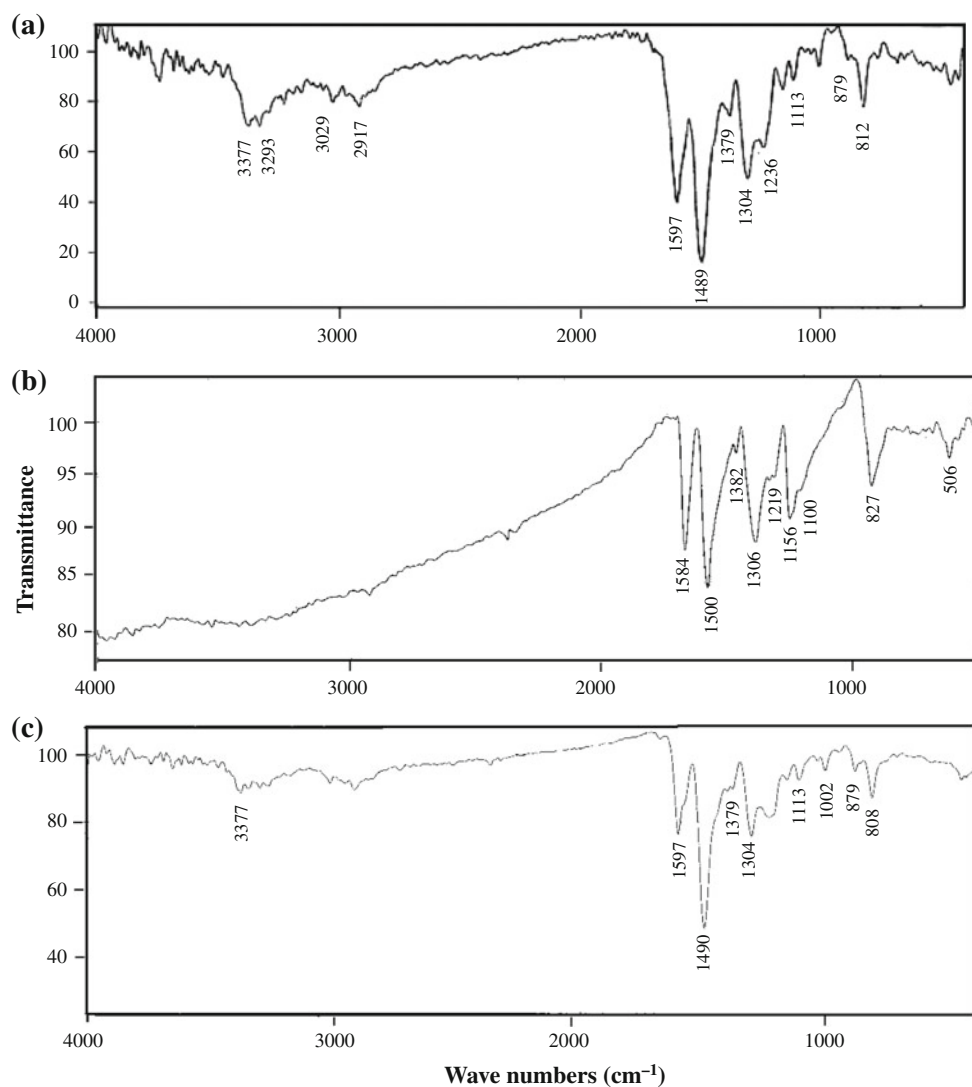


Fig. 2: FTIR absorption spectrum of (a) poly(aniline-co-o-toluidine); (b) polyaniline and (c) poly(o-toluidine) homopolymers

ascribed to the C–N stretching in the benzenoid–benzenoid–benzenoid triad sequence. The peaks at 1113 and 879 cm^{-1} , respectively, should be the result of the C–H in plane and C–H out-of-plane bending vibrations of the 1,2,4-trisubstituted benzene ring on the OT unit (Fig. 2c).

Immersion test

The results of immersion tests for uncoated, coated and coated scribed mild steel specimens in different corrosive solution are shown in Table 2. The results indicate that out of the four selected media for corrosion studies, 0.1 M HCl solution is the most corrosive, whereas the distilled water is the least corrosive. The severity of 5% NaCl solution and that of artificial seawater are almost identical; the corrosion rates of uncoated steel in both media remain almost the same

(6.02 and 7.03 mpy, respectively). In general, the poly(aniline-co-o-toluidine) coatings performed better than the individual homopolymer coatings. The copolymer coating on steel substrate effectively hindered the attack of the corrosive environment. It showed the highest PE of 93.87% in artificial seawater and the lowest PE of 78.41% in 0.1 M HCl solution; the PEs in 5% NaCl solution and distilled water were 93.17% and 91.25%, respectively. 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. The presence of scribed mark on the copolymer coating marginally affected its performance, and only slightly increased the corrosion rate. In fact the %PE of the scribed specimens was higher than the individual homopolymer coatings in artificial seawater and distilled water. This confirms the self-passivating nature of the copolymer coating. The corrosion performance of PANi

Table 2: Results of immersion tests

Corrosive medium	Description of the sample	Immersion period (days)	Corrosion rate (mpy)	%PE
0.1 M HCl	Uncoated steel	30	19.081	–
	Poly(aniline-co-o-toluidine)-coated	30	4.118	78.41
	Poly(aniline-co-o-toluidine)-coated scribed	30	5.002	73.78
	Polyaniline-coated	30	3.411	82.12
	Poly(o-toluidine)-coated	30	13.052	31.69
5% NaCl solution	Uncoated steel	30	6.021	–
	Poly(aniline-co-o-toluidine)-coated	30	0.411	93.17
	Poly(aniline-co-o-toluidine)-coated scribed	30	2.512	58.27
	Polyaniline-coated	30	2.081	65.44
	Poly(o-toluidine)-coated	30	3.522	41.69
Artificial sea water	Uncoated steel	30	7.034	–
	Poly(aniline-co-o-toluidine)-coated	30	0.431	93.87
	Poly(aniline-co-o-toluidine)-coated scribed	30	1.901	72.97
	Polyaniline-coated	30	2.513	64.29
	Poly(o-toluidine)-coated	30	4.112	41.53
Distilled water	Uncoated steel	30	4.031	–
	Poly(aniline-co-o-toluidine)-coated	30	0.351	91.25
	Poly(aniline-co-o-toluidine)-coated scribed	30	1.504	62.52
	Polyaniline-coated	30	1.902	52.61
	Poly(o-toluidine)-coated	30	2.512	37.74

mpy = mills per year; %PE = protection efficiency

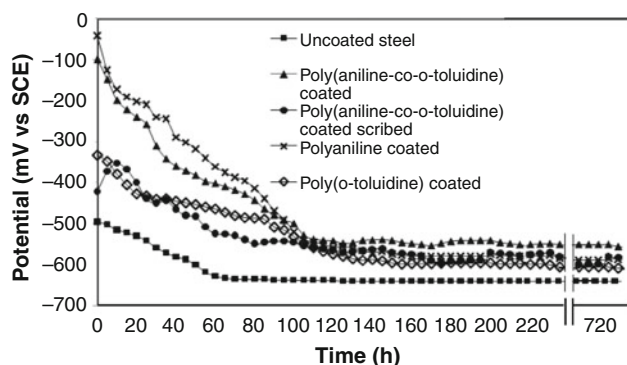


Fig. 3: E_{corr} vs time plot in 0.1 M HCl for (■) uncoated steel; (▲) poly(aniline-co-o-toluidine)-coated; (●) poly(aniline-co-o-toluidine)-coated scribed; (×) polyaniline-coated and (◇) poly(o-toluidine)-coated

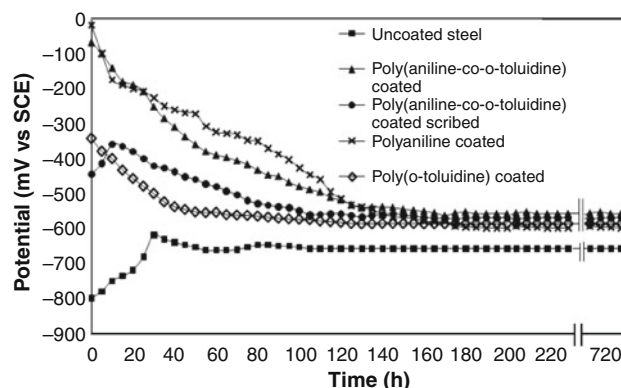


Fig. 4: E_{corr} vs time plot in 5% NaCl for (■) uncoated steel; (▲) poly(aniline-co-o-toluidine)-coated; (●) poly(aniline-co-o-toluidine)-coated scribed; (×) polyaniline-coated and (◇) poly(o-toluidine)-coated

homopolymer coating was found to be better than the homopolymer POT coating in all the media.

Open circuit potential measurements

The OCP values (E_{ocp}) of uncoated, poly(aniline-co-o-toluidine) (both scribed and unscribed), PANi- and POT-coated steels were monitored with time in four different media, and the results are shown in Figs. 3–6. An analysis of the results of OCP measurements in different corrosive solutions shows that when steel is covered with a copolymer or a single homopolymer film, potentials are shifted towards more noble values

compared with the uncoated steel. With an increasing immersion period, there is a continuous increase in the negative potential until a steady potential is obtained. However, the final potential is still nobler than the potential of the uncoated steel. The noble shift in potential is more pronounced for copolymer and PANi coatings than for the POT coating. In the case of coated scribed samples, after an initial decrease in potential, an increase in the potential is observed; this is followed by a constant potential. However, the final potential is again nobler than the potential of uncoated steel.

A noble potential for coated steel in comparison to uncoated steel indicates that polymer-coated systems

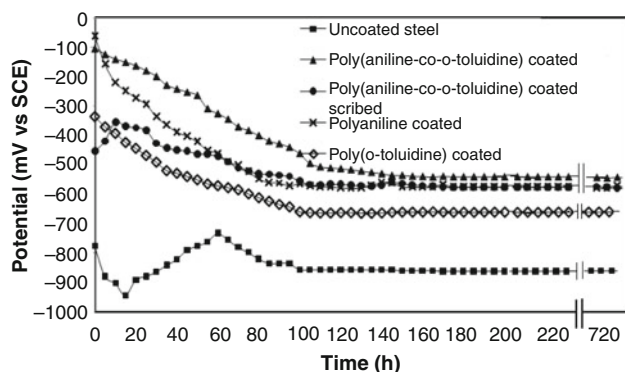


Fig. 5: E_{corr} vs time plot in artificial sea water for (■) uncoated steel; (▲) poly(aniline-co-o-toluidine)-coated; (●) poly(aniline-co-o-toluidine)-coated scribed; (×) polyaniline-coated and (◇) poly(o-toluidine)-coated

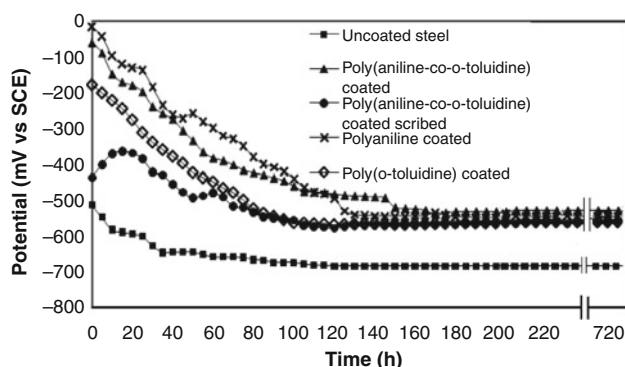


Fig. 6: E_{corr} vs time plot in distilled water for (■) uncoated steel; (▲) poly(aniline-co-o-toluidine)-coated; (●) poly(aniline-co-o-toluidine)-coated scribed; (×) polyaniline-coated and (◇) poly(o-toluidine)-coated

have a greater resistance to corrosion.²¹ The protection offered by the poly(aniline-co-o-toluidine), PANi, and POT is attributed to both barrier effect and formation of passive oxide due to redox reaction at the steel and polymer interface.²⁵ The barrier effect is operative as long as coatings remain intact and isolate the substrate from corrosive environments. The initial OCP started to increase as a result of the initiation of corrosion process under the coating leading to anodic dissolution of steel. As the amount of water held within the pores of the coating increased, the mobility of corrosive species through the film increased. In this context, the porosity of the coating has considerable importance for initiation and progression of corrosion phenomenon under the coating. During this period, the barrier efficiency of the coating had diminished because of the increased amount of electrolyte held by the coating. The behavior of PANi coating in all corrosive solutions is considerable during the initial hours of immersion period; however, the copolymer coating provided best protection during 200 h of immersion. This is attributed to the better barrier behavior of the copolymer

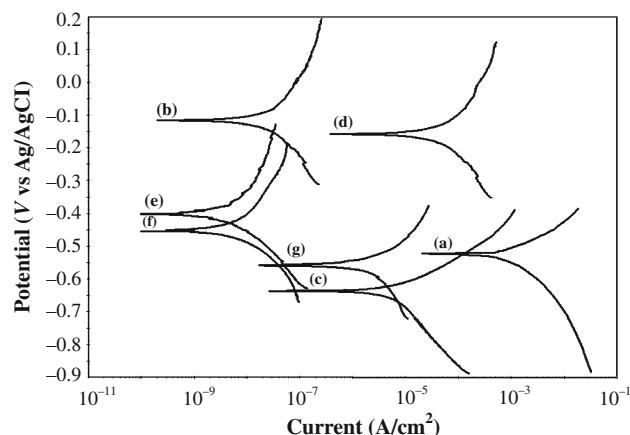


Fig. 7: Potentiodynamic polarization curves in 0.1 M HCl for (a) uncoated steel; (b) poly(aniline-co-o-toluidine)-coated (fresh sample); (c) poly(aniline-co-o-toluidine)-coated (after 1 month immersion); (d) polyaniline-coated (fresh sample); (e) polyaniline-coated (after 1 month immersion); (f) poly(o-toluidine)-coated (fresh sample) and (g) poly(o-toluidine)-coated (after 1 month immersion)

coating than homopolymer coatings owing to the presence of a uniform and dense film of the copolymer on the steel substrate. The better performance of PANi coating than POT coating is probably due to increased participation of the PANi coating in the oxide formation. In the case of the coated scribed sample, though the initial OCP was higher than the coated steel sample owing to the break in the coating, the coating immediately repassivated 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 h. The monitoring of the E_{ocp} was continued for 720 h, and there was no appreciable change in the potential. The findings of E_{ocp} measurements suggest that protection mechanism other than barrier protection is operating and is consistent with the reports of other authors.^{26,27}

Potentiodynamic polarization measurements

The potentiodynamic polarization curves for uncoated, poly(aniline-co-o-toluidine) (both scribed and unscribed)-, PANi-, and POT-coated steel recorded in 0.1 M HCl, 5% NaCl solution, artificial seawater and distilled water, respectively, are shown in Figs. 7–10. The values of corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic beta (b_c), anodic beta (b_a) and corrosion rate obtained from these curves are listed in Table 3. Considering the potentiodynamic polarization curves in 0.1 M HCl (Fig. 7), in the presence of copolymer coating, the corrosion potential of steel was found to shift tending towards a positive direction relative to the potential of uncoated steel (from -522 to -116 mV vs Ag/AgCl electrode), and there was leftward displacement in the anodic and

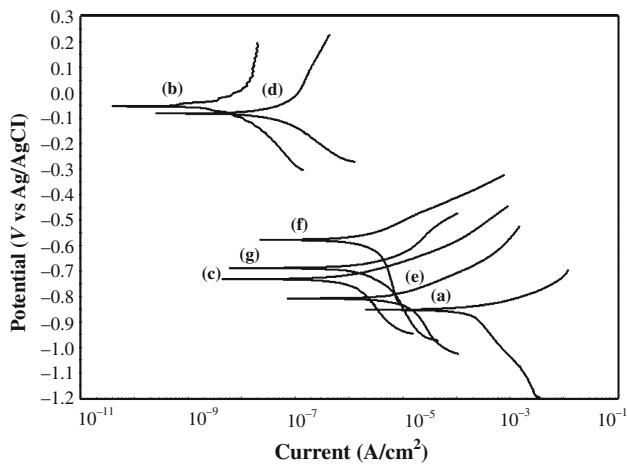


Fig. 8: Potentiodynamic polarization curves in 5% NaCl for (a) uncoated steel; (b) poly(aniline-co-o-toluidine)-coated (fresh sample); (c) poly(aniline-co-o-toluidine)-coated (after 1 month immersion); (d) polyaniline-coated (fresh sample); (e) polyaniline-coated (after 1 month immersion); (f) poly(o-toluidine)-coated (fresh sample) and (g) poly(o-toluidine)-coated (after 1 month immersion)

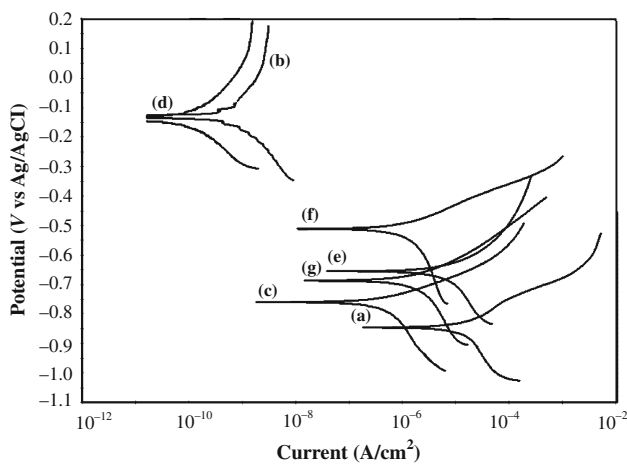


Fig. 9: Potentiodynamic polarization curves in artificial seawater for (a) uncoated steel; (b) poly(aniline-co-o-toluidine)-coated (fresh sample); (c) poly(aniline-co-o-toluidine)-coated (after 1 month immersion); (d) polyaniline-coated (fresh sample); (e) polyaniline-coated (after 1 month immersion); (f) poly(o-toluidine)-coated (fresh sample) and (g) poly(o-toluidine)-coated (after 1 month immersion)

cathodic branch of polarization curves. The positive shift in E_{corr} confirms that the mild steel covered by poly(aniline-co-o-toluidine) copolymer coating depressed the anodic current of the corrosion reaction and offered greater resistance to corrosion.²¹ Also, the corrosion current density (I_{corr}) decreases, which reduces the corrosion rate by an amount of ~ 37000 times lower than the uncoated steel. When the copolymer coating was subjected to one-month immersion, the potential shifted to more negative values compared to bare steel. A negative shift in potential is

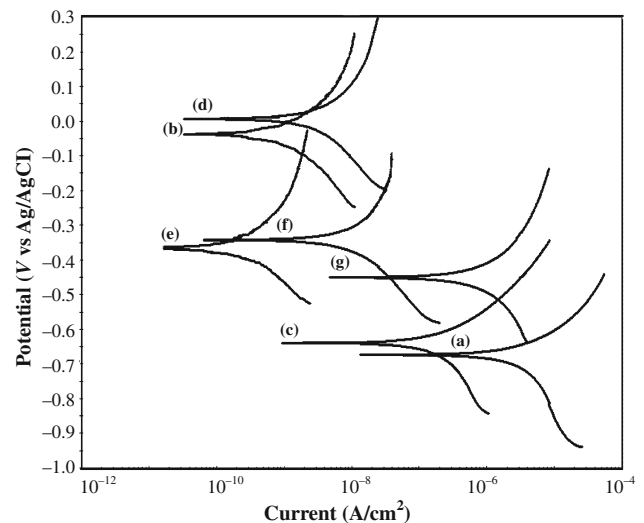


Fig. 10: Potentiodynamic polarization curves in distilled water for (a) uncoated steel; (b) poly(aniline-co-o-toluidine)-coated (fresh sample); (c) poly(aniline-co-o-toluidine)-coated (after 1 month immersion); (d) polyaniline-coated (fresh sample); (e) polyaniline-coated (after 1 month immersion); (f) poly(o-toluidine)-coated (fresh sample) and (g) poly(o-toluidine)-coated (after 1 month immersion)

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_{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 the 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 1-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 by 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. The PANi-coated sample also behaves in a similar manner and shows appreciable reduction in the values of E_{corr} and I_{corr} . The results of potentiodynamic polarization curves in other media, namely, 5% NaCl solution, artificial seawater and distilled water (Figs. 8–10) show a substantial positive shift tendency in the corrosion potential and reduction in I_{corr} for copolymer and homopolymer-coated samples relative to uncoated steel leading to a substantial lowering in the corrosion rate. An inspection of polarization curves gave rise to approximately parallel Tafel lines for the fresh coated samples indicating that the presence of polymer coatings on steel affected the anodic and cathodic reaction mechanisms in an

Table 3: Results of potentiodynamic polarization measurement

Corrosive medium	Description of the sample	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{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
	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
	Polyaniline-coated (fresh sample)	0.068	-145	219.165	545.594	0.008
	Polyaniline-coated (after 1 month immersion)	0.011	-404	366.650	324.352	0.005
	Poly(o-toluidine)-coated (fresh sample)	0.021	-444	306.924	540.484	0.016
	Poly(o-toluidine)-coated (after 1 month immersion)	19.181	-557	5285.189	580.903	1.446
	Uncoated steel	265.112	-851	319.240	82.472	19.951
	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
5% NaCl solution	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
	Polyaniline-coated (fresh sample)	0.090	-82	195.062	474.735	0.007
	Polyaniline-coated (after 1 month immersion)	4.016	-816	1525.198	3680.231	0.362
	Poly(o-toluidine)-coated (fresh sample)	3.001	-577	514.492	108.709	0.223
	Poly(o-toluidine)-coated (after 1 month immersion)	4.678	-688	413.141	161.856	0.352
	Uncoated steel	144.332	-846	423.697	124.747	10.903
	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
	Polyaniline-coated (fresh sample)	0.003	-146	389.171	655.406	0.002
Artificial sea water	Polyaniline-coated (after 1 month immersion)	23.211	-655	6528.480	320.225	3.441
	Poly(o-toluidine)-coated (fresh sample)	7.933	-511	355.779	82.164	0.0592
	Poly(o-toluidine)-coated (after 1 month immersion)	18.90	-686	410.852	124.894	1.424
	Uncoated steel	54.511	-673	1195.031	257.784	4.111
	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
	Polyaniline-coated (fresh sample)	0.081	-23	523.441	858.210	0.006
	Polyaniline-coated (after 1 month immersion)	0.612	-366	370.751	903.402	0.005
	Poly(o-toluidine)-coated (fresh sample)	1.210	-335	153.203	490.078	0.0069
	Poly(o-toluidine)-coated (after 1 month immersion)	89.75	-450	5242.486	2014.212	6.767
Distilled water	Uncoated steel	18.90	-686	410.852	124.894	1.424
	Poly(aniline-co-o-toluidine)-coated (fresh sample)	54.511	-673	1195.031	257.784	4.111
	Poly(aniline-co-o-toluidine)-coated (after 1 month immersion)	0.029	-42	317.469	504.061	0.002
	Poly(aniline-co-o-toluidine)-coated scribed (fresh sample)	3.007	-639	891.824	227.376	0.226
	Poly(aniline-co-o-toluidine)-coated scribed (after 1 month immersion)	1.891	-517	224.946	90.018	0.142
	Polyaniline-coated (fresh sample)	7.826	-600	638.103	107.685	0.590
	Polyaniline-coated (after 1 month immersion)	0.081	-23	523.441	858.210	0.006
	Poly(o-toluidine)-coated (fresh sample)	0.612	-366	370.751	903.402	0.005
	Poly(o-toluidine)-coated (after 1 month immersion)	1.210	-335	153.203	490.078	0.0069
	Poly(o-toluidine)-coated (after 1 month immersion)	89.75	-450	5242.486	2014.212	6.767

Table 3: continued

Corrosive medium	Description of the sample	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{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
	Polyaniline-coated	14.26	-382	571.937	880.731	1.075
	Poly(o-toluidine)-coated	10.71	-581	580.607	104.727	0.980

identical manner. The values of electrochemical parameters favor the existence of a strong passivation coating having barrier effect on the surface of the mild steel coated with both copolymer and homopolymers. In the case of homopolymer coating, the PANi-coated samples provide better protection than POT-coated samples in all media. This is attributed to the better participation of PANi coating in oxide formation and finds support from the results of immersion tests. The potentiodynamic polarization curves for the copolymer-coated steel (both scribed and unscribed) and individual homopolymer-coated steel samples were also recorded after 30 days of immersion in the respective corrosive media. The results indicate that though there is some deterioration in the protective properties of the coating, the corrosion rate is still lower than that of the bare steel. This is indicative of high chemical stability of the polymer coatings.

Atmospheric test

The samples taken after the completion of the atmospheric test were physically examined. Poly(aniline-co-o-toluidine) coating did not show any color change. However, the coating was found to be detached from the substrate in some places. PANi coating showed comparatively poor adhesion and got detached from the surface during the atmospheric exposure but performed better than the POT coating. POT coating showed maximum deterioration during the atmospheric exposure test.

The potentiodynamic polarization curves for uncoated, copolymer and homopolymer-coated steel samples recorded in distilled water after 30 days exposure to open atmosphere are shown in Fig. 11, and the corresponding values of corrosion parameters

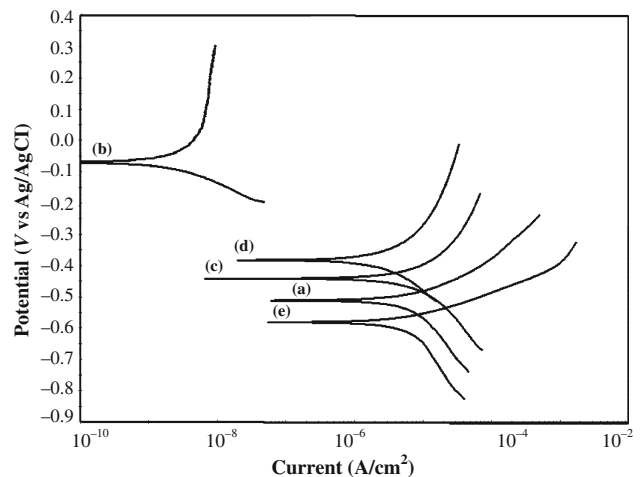


Fig. 11: Potentiodynamic polarization curves in distilled water for (a) uncoated steel; (b) poly(aniline-co-o-toluidine)-coated; (c) poly(aniline-co-o-toluidine)-coated scribed; (d) polyaniline-coated and (e) poly(o-toluidine)-coated steel after 30 days exposure to open atmosphere

obtained from these curves are listed in Table 3. The results of potentiodynamic polarization studies show that the corrosion performance of polymer coatings was only slightly affected during atmospheric exposure test. The corrosion rate of coated samples subjected to open atmospheric exposure is only slightly higher than those polarized before atmospheric exposure. It may be inferred that after one month of atmospheric exposure, though the adherence of the polymer coatings was affected, it still maintained the protective properties giving good protection to the underlying metal. This again suggests that a protection mechanism other than barrier protection is operating.

Conclusions

1. A soluble copolymer from aniline and *o*-toluidine, poly(aniline-*co*-*o*-toluidine) was synthesized by chemical oxidative copolymerization.
2. A good adherent bluish violet-colored coating of copolymer, poly(aniline-*co*-*o*-toluidine), on mild steel was successfully obtained by solution evaporation. The copolymer coating was observed to be more homogeneous and uniform than the individual homopolymer coatings.
3. The results of immersion tests indicate that the corrosion rate for the copolymer-coated steel is significantly lower than the homopolymer coatings in all the corrosive media under investigation. The PEs of the copolymer coatings in different corrosive media are in the following order: Artificial seawater \geq 5% NaCl > Distilled water > 0.1 M HCl.
4. The results of OCP measurements show nobler potentials for copolymer and homopolymer-coated steels compared to the uncoated steel. The electrochemical parameters as derived from potentiodynamic polarization measurements indicate lower corrosion rates for both copolymer and homopolymer-coated steel.
5. The presence of scribed mark on the coating does not significantly affect the integrity of the copolymer coating.
6. Owing to the good performance of the copolymer coating in different corrosive environments, the same may be considered as a suitable candidate material for future industrial assessment.

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