SYSTEMATIC STUDY OF SYNTHESIS OF POLY(O-ANISIDINE-CO-O-TOLUIDINE) COATINGS AND ITS PERFORMANCE AGAINST CORROSION OF COPPER

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ABSTRACT

The synthesis of poly(o-anisidine-co-o-toluidine) coatings on copper was carried out by copolymerization of o-anisidine with o–toluidine. For deposition of these coatings sodium salicylate was used as supporting electrolyte. The systematic study of synthesis of poly(o-anisidine-co-o-toluidine) coatings was done by cyclic voltammetry. The resulting coatings was characterised by UV-visible absorption spectroscopy, nuclear magnetic resonance spectroscopy (NMR).The copolymer formation with the mixture of o-anisidine and o-toluidine monomers was confirmed by by a comparison of the results obtained with the cyclic voltammetry of the individual monomers, o-anisidine and o–toluidine, respectively. In cyclic voltammetry especially the peak A_1 corresponding to the oxidation of deposited monomer shows systematic and sequential variation in intensity with the change of monomer concentration in the copolymer solution. So variation in peak A_1 represents successful synthesis of copolymer. The corrosion protection performance of offered by poly(o-anisidine-co-o-toluidine) coatings to copper was studied in sea water (3% NaCl) solution by potentiodynamic polarization technique. The results of the potentiodynamic polarization measurements that the poly(o-anisidine-co-o-toluidine) coatings provide the better corrosion protection to copper than that of respective homopolymers. The corrosion rate is observed to depend on the feed ratio of o-toluidine used for the synthesis of the copolymer coatings.

1.Introduction

From last two decades considerable attention has been paid to exploit the conducting polymers in various technological application such as rechargeable batteries [1,2], sensors [3,4], electromagnetic interference (EMI) shielding [5,6], electrochromic display devices [7,8], smart windows [9], molecular devices [10], energy storage systems [11], membrane gas separation [12] etc. due to their remarkable physical attributes . The use of conducting polymers as advanced coating materials for corrosion protection of oxidizable metals has become one of the most exciting new research fields in most recent times [13-19]. Mengoli et al. [20] was the first to examine the protective behavior of polyaniline on stainless steel and then in 1985, DeBerry [21] showed that the electrochemically synthesized polyaniline acts as corrosion protective layer on stainless steel in 1 M H_2SO_4. Since then, several research groups [22-26] have systematically investigated the electrochemical synthesis of various conducting polymers on oxidizable metals for corrosion protection purposes. Among the conducting polymers, polyaniline and polypyrrole are the most promising conducting polymers for corrosion protection of metals. The extent of using these of conducting polymers is limited due to the exclusivity of the monomers that are essential for their synthesis [27,28]. To overcome this limitation, different synthesis approaches have been attempted. The first approach involves the synthesis of substituted conducting polymer coatings on oxidizable metals, with a view to explore the possibility of utilizing them as an alternative to parent polymers for corrosion protection. We have developed the appropriate electrochemical polymerization procedures to synthesize strongly adherent poly(o-anisidine) [29,30,32], poly(o-toluidine) [31], poly(2,5-dimethoxyaniline) [33] and the poly (aniline-co-o-anisidine) (PAOA) coatings were carried out on mild steel [34] , The corrosion protective poly(aniline-co-o-toluidine) (PAOT) [35] coatings were synthesized on copper The results of the potentiodynamic polarization measurements showed that the copolymer coatings provided more effective corrosion protection to mild steel and copper than the respective homopolymers.

2.Experimental

a)Materials

The monomers ,o-anisidine and o-toluidine were double distilled prior to being used for the synthesis of homopolymer and copolymer coatings. In the present study the aqueous sodium salicylate solution was used as supporting electrolyte.

The Cu substrates (size ~ 10 x 15 mm and 0.5 mm thick) were polished with a series of emery papers, followed by thorough rinsing in acetone and double distilled water and dried in air. Prior to any experiment, the substrates were treated as described and freshly used with no further storage.

b) Synthesis of poly(o-anisidine), poly(o-toluidine) and poly(o-anisidine-co-o-toluidine) coatings on copper

The poly(o-anisidine) , poly(o-toluidine) and poly(o-anisidine-co-o-toluidine) coatings synthesized on copper substrates by using cyclic voltammetry , the concentration of respective monomer and sodium salicylate were kept constant at 0.1 M each. For the electrochemical copolymerization ,a mixture of o-anisidine and o-toluidine with total concentration of 0.1 M. The copolymer synthesis experiments were carried out by using feed ratio of *o-toluidine* as 10:90, 30:70, 50:50, 70:30 and 90:10, respectively.

The electrochemical polymerization was carried out in a single compartment three electrode cell with Cu as working electrode (1.5 cm^2), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetric conditions were maintained using a PARSTAT 2363-1, EG and G, Princeton Applied Research (U.S.A.) controlled by PowerSuite software (Perkin Elmer Instruments, 2000 supplied by EG and G, Princeton Applied Research, U.S.A.). The synthesis was carried out by cycling continuously the electrode potential between – 1000 mV and 1800 mV at a potential scan rate of 20 mV/sec. After 10 cycles, the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air.

c)Characterization of coatings

The polyo-anisidine ,POT and OAOT coatings were characrerized by cyclic voltammetry , UV-visible absorption spectroscopy , The optical absorption studies of these coatings were carried out *ex situ* in the wavelength range 300-1100 nm using microprocessor controlled double beam UV-visible spectrophotometer (Model U 2000, Hitachi, Japan). SEM was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (U.K.). The ^1H NMR spectra were obtained on a Bruker DSX-300 solid state NMR spectrometer, operating at 300 MHz. The measurements were carried out in DMSO-d_6 solution at ambient temperature.

d)Study of corrosion performance of the coatings

The corrosion protection performance studies were performed at room temperature in aqueous solution of 3% NaCl by using potentiodynamic polarization technique. The polarization resistance measurements were performed by sweeping the potential between – 250 mV and 250 mV from open circuit potential at the scan rate of 2 mV/sec. The corrosion current density (I_{corr}) in A/cm^2 was calculated by using Stern-Geary equation [36] and it is converted into the corrosion rate (CR) in mm per year by using the expression [37]

where I_{corr} is corrosion current density (A/cm^2), EW is equivalent weight of Cu (g) and ρ is the density of Cu (g/cm^3). All the measurements were repeated at least four times and good reproducibility of the results was observed.

3.Result and Discussion

a)Electrochemical synthesis of homopolymers, Polyo-anisidine and Polyo-toluidine and poly(o-anisidine-co-o-toluidine) copolymer coatings on cu

The cyclic voltammogram of the first scans recorded during the electrochemical synthesis of homopolymers i.e. Polyo-anisidine and Polyo-toludine and the copolymer poly(o-anisidine-co-o-toluidine) 50:50 coatings on cu substrate from an aqueous solution of sodium salicylate are shown in fig1. The first positive cycle of cyclic voltammogram is characterize by onset of oxidation wave followed by oxidation peak (B). During the reverse cycle , the anodic current density decreases rapidly and negligibly small current is seen . The negative cycle terminates with a reduction peak (C).

The oxidation wave attributed to oxidation of monomer since a black, uniform film is generated on copper substrate. The reduction peak during negative cycle is attributed to the partial reduction of of deposited polymer film.

The careful examination of these cyclic voltammograms indicates that potential corresponding to the onset of oxidation wave shifts significantly depending on monomer(s) present in electrolyte and it follows the order – o-anisidine < (o-anisidine + o-toluidine) < o-toluidine (386mV < 443mV < 672mV resp.) . The o-anisidine is derivative of aniline (-OCH3) group substituted at ortho-position and o-toluidine is derivative of aniline (-CH3) group substituted at ortho-position The, o-anisidine is more reactive than the o-toluidine in electrophilic substitution reaction as –OCH3 is more electron donating group than –CH3 group. Therefore, the result of cyclic attributed to earlier (lower) oxidation potential of o-anisidine i.e. higher reactivity of o-anisidine than the that of o-toluidine.

$$CR(mm/yr) = 3.268x10^3 \frac{I_{corr}}{\rho} \frac{MW}{z}$$

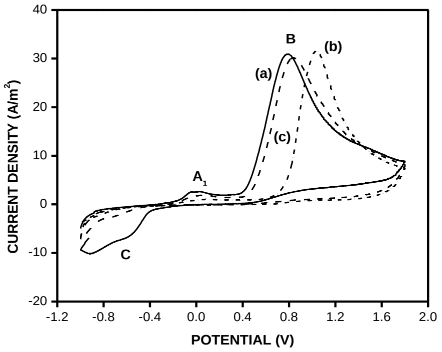


Fig.1 : Cyclic voltammograms of the first scan recorded during the synthesis of (a)Polyo-anisidine, (b) Polyo-toluidine and (c) poly(o-anisidine-co-o-toluidine) 50:50 copolymer coatings on Cu substrates.

During the next scan fig.2 a broad anodic peak A_1 (between -255mV to – 438mV) is observed and the rest of features are similar to that of the first scan .The anodic peak A_1 assigned to oxidation of deposited polymer film at copper substrate corresponding to convertion of amine units in to radical cation. However, again the careful examination of this anodic peak A_1 indicates that the current density corresponding to this peak varies significantly with monomer present in the electrolyte in the following sequence –

Polyo-anisidine > copolymer poly(o-anisidine-co-o-toluidine) 50:50 > Polyo-toludine

Supports the higher reactivity of o-anisindine and the reactivity of copolymer poly(o-anisidine-co-o-toluidine) 50:50 lies in between the Polyo-anisindine and Polyo-toluidine. This is just about the individual polymers i.e. Polyo-anisindine and Polyo-toluidine and the poly(o-anisidine-co-o-toluidine) 50:50 copolymer. Now the question arries, what is the scenario of this peak A_1 for

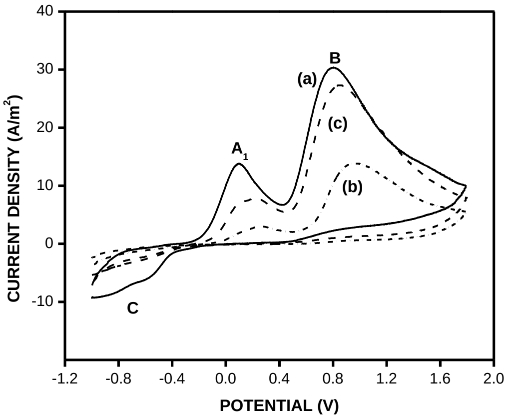


Fig.2 : Cyclic voltammograms of the second scan recorded during the synthesis of (a)Polyo-anisidine, (b) Polyo-toluidine and (c) poly(o-anisidine-co-o-toluidine) 50:50 copolymer coatings on Cu substrates

the other copolymers (i.e. poly(o-anisidine-co-o-toluidine) 10:90, poly(o-anisidine-co-o-toluidine) 30:70, poly(o-anisidine-co-o-toluidine), 70:30, poly(o-anisidine-co-o-toluidine) 10:90) See the fig3 which will give answer to this question i.e. the variation of the peak A_1 for individual polymer along with all copolymers with the different molar feed ratios.

Detailed study of fig 3 indicated that the current density corresponding to A_1 shows systematic variation with the feed concentration of of o-toluidine in the comonomer in the following sequence – Polyo-anisindine > poly(o-anisidine-co-o-toluidine) 90:10 > poly(o-anisidine-co-o-toluidine) 70:30 > poly(o-anisidine-co-o-toluidine) 50:50> poly(o-anisidine-co-o-toluidine) 30:70 > poly(o-anisidine-co-o-toluidine) 10:90) > Polyo-toluidine

It is very interesting to note that peak A1 in it shows the presence of duplex for all the feed ratios of comonomers

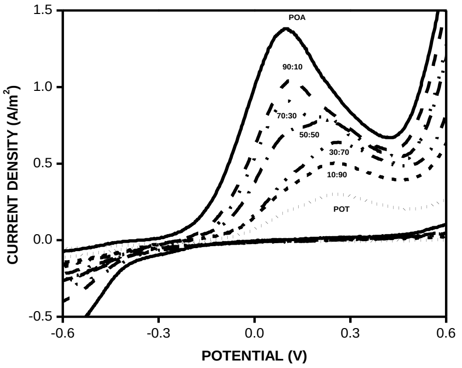


Fig.3 : Variation of the peak A1 as a function of feed ratio of o-toluidine

which supports the formation of copolymer. However the further detailed study of this duplex A1 peak for copolymers indicates that sharpness of duplex peak of poly(o-anisidine-co-o-toluidine) 90:10 is toward lower potential which is quite similar to poly(o-anisidine). While the sharpness of this duplex peak for poly(o-anisidine-co-o-toluidine) 10:90 is toward higher potential which is quite similar to polyo-toluidinne and for poly(o-anisidine-co-o-toluidine) 50:50 the sharpness of duplex was equal and similar for both monomers it shows sequential variation.

On repetitive cycling , the voltammograms identical to that of the second scan. However the current density corresponding to anodic peaks decreases gradually with the number of scans. Thus the electrochemical polymerization of monomer(s) on copper substrate occurs in single step from aqueous salicylate solution. The visual inspection of of copper elecrode after 10 nth scan reveals the formation of black coloured polymer coating .

In order to establish that the poly(o-anisidine-co-o-toluidine) 50:50 is a copolymer rather than a mixture of homopolymers Polyo-anisindine and Polyo-toluidine, these polymers were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of Polyo-anisidine , Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 copolymer recorded in DMSO-d_6 are shown in Fig.4.

The ^{1}H NMR spectrum of Polyo-anisindine [Fig.4(a)] is characterized by the presence of three main signals. The signals in the region of 6.3-7.9 ppm are due to the protons of the aromatic rings. The resonances in the region of 4.1-2.75 ppm are attributed to the methoxy protons . The two strongest peaks at 2.3 and 2.6 ppm are due to protons of DMSO and water in DMSO.

The ^{1}H NMR spectrum of Polyo-toluidine [Fig.4(b)] is characterized by the presence of three main signals. The signals in the region of 6.3-8.0 ppm are due to the protons of the aromatic rings. The resonances in the region of 1.97-2.3 ppm are attributed to the methyl protons . The two strongest peaks at 2.3 and 2.6 ppm are due to protons of DMSO and water in DMSO.

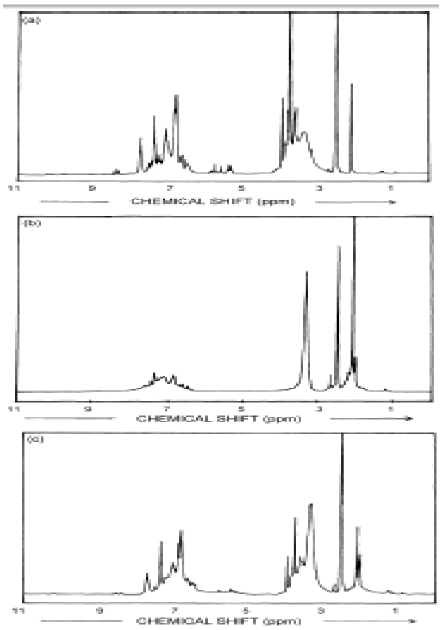


Fig.4 :^{1}H NMR spectra of a)Polyo-anisidine, (b) Polyo-toluidine and (c) poly(o-anisidine-co-o-toluidine) 50:50 copolymer recorded in DMSO-d6 at 300 MHz.

The ^{1}H NMR spectrum of poly(o-anisidine-co-o-toluidine) 50:50 copolymer has essentially the characteristics as that of the Polyo-anisidine and polyo-toluidine. This spectrum is characterized by four main signals which exactly correspond to the four types of protons on the copolymer chains. As can be seen from Fig. 4(c), this spectrum exhibits the signals in a wide range from 6.3 to 7.9 ppm, which are attributed to the aromatic protons on the o-anisidine and *o-toluidine* units. The resonance peaks from 1.87 and 2.3 ppm are assigned to the protons of the methyl groups . The two strongest peaks at

2.3 and 2.6 ppm are due to protons of DMSO and water in DMSO. Again the resonance peaks from 2.8 and 4.07 ppm are assigned to the protons of the methoxy groups . Additionally, two negligibly small signals at 5.1 and 5.95 ppm are assigned to the –NH- linkages. This indicates the formation of high molecular weight poly(o-anisidine-co-o-toluidine) 50:50 copolymer. Thus, ^{1}H NMR spectroscopic study confirms that o-anisidine and *o-toluidine* are indeed able to copolymerize on Cu in aqueous salicylate medium and in the resulting copolymer [38].

The optical absorption spectra of the homopolymers Polyo-anisidine, Polyo-toluidine and copolymer poly(o-anisidine-co-o-toluidine) 50:50 coatings are shown in Fig. 5. As can be seen from Fig. 6, the spectral characteristics of the poly(o-anisidine-co-o-toluidine) 50:50 copolymer are observed to be remarkably different from the individual homopolymers.

The optical absorption spectrum of Polyo-anisidine coating synthesized on Cu [Fig.5(a)] shows a high value of the absorbance between 600-800 nm with a weak shoulder at ~ 744 nm. This shoulder peak at 744 nm is attributed to the formation of emeraldine salt (ES) form of Polyo-anisidine in the coating [39]. The higher value of the absorbance between 600-740 nm may be due to the formation of some species with other oxidation states. Thus, the optical absorption spectroscopy reveals the formation of ES form along with the some other oxidation state species. The optical absorption spectrum of Polyo-toluidine coating [Fig.5(b)] shows a broad well defined peak at about 562 is attributed to the presence of pernigraniline base (PB) form of Polyo-toluidine. The PB is the fully oxidized form of Polyo-toluidine and is insulating in nature [39].

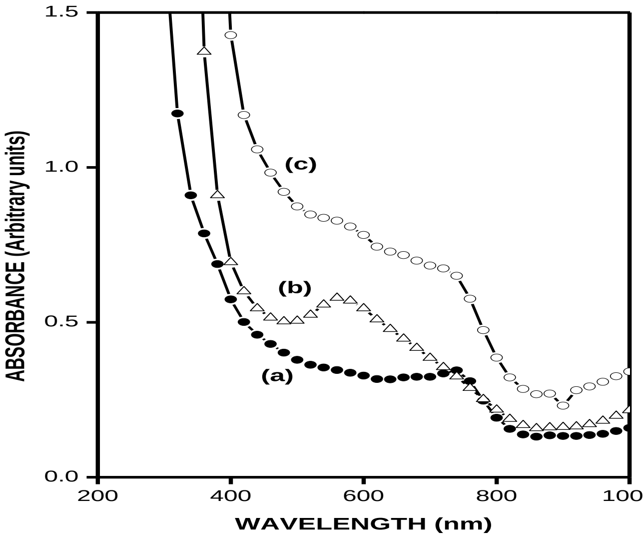


Fig.5 : Optical absorption spectra of of a)Polyo-anisidine, (b) Polyo-toluidine and (c) poly(o-anisidine-co-o-toluidine) 50:50

The optical absorption spectrum of the poly(o-anisidine-co-o-toluidine) 50:50 copolymer coating [Fig.5(c)] shows a broad peaks at about 562 and 720 nm. The simultaneous appearance of 562 and 720 nm reveals the formation of mixed phase of PB and ES .

(b)Corrosion protection performance of the poly (o-anisidine-co-o-toluidine) copolymer and polymer coating

The potentiodynamic polarization curve uncoated Cu recorded and the curves for Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 coated Cu in aqueous 3 % NaCl is shown in Fig.6. The values of the corrosion potential (E_{corr}), corrosion current density (I_{corr}), tafel constants (β_a and β_c), polarization resistance (R_p) and corrosion rate obtained from these curves are given in Table 1. The porosity in coating was calculated using the relation

$$P = (R_{ps}/R_p)\ 10^{(-|\Delta E_{corr}|/\beta a)}$$

where P is the total porosity, R_{ps} is the polarization resistance of the bare Cu, R_p the measured polarization resistance of coated Cu, ΔE_{corr} is the difference between corrosion potentials and β_a the anodic Tafel slope for bare Cu substrate. The porosity in Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 copolymer coating was found to be ~ 2.4×10^{-1}, 2.7×10^{-1} and 1.42×10^{-6} %, respectively.

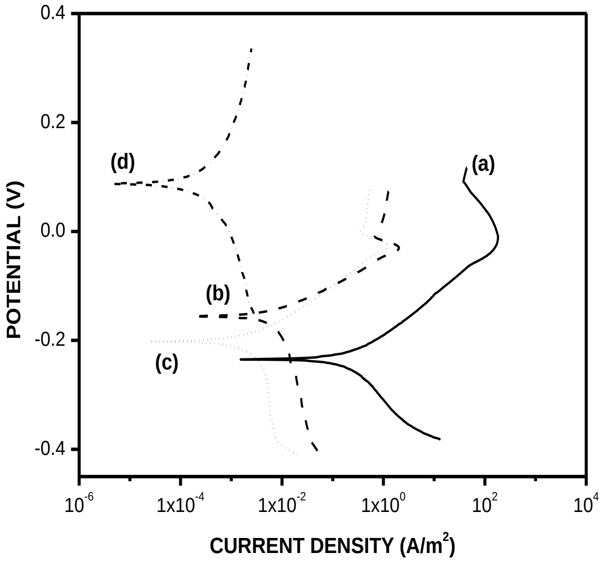
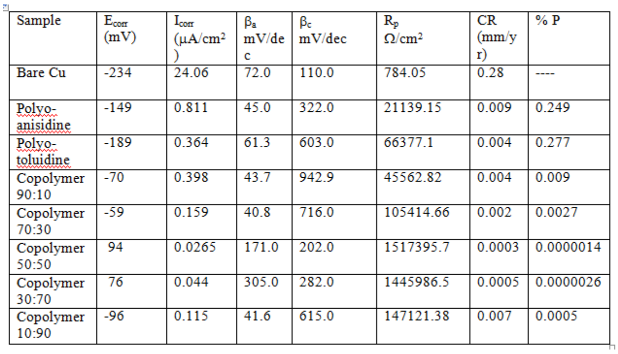


Fig.7 : Potentiodynamic polarization curves for (a) Bare Cu (b) Polyo-anisidine, (c) Polyo-toluidine and (d) poly(o-anisidine-co-o-toluidine) 50:50 coated Cu recorded in aqueous 3% NaCl solution.

The analysis of these potentiodynamic polarization curves shows the positive shift in the E_{corr} and substantial reduction in the I_{corr} of the Cu due to the Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 coatings, which indicates the corrosion resistant characterstics of the Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50. It is found that the shift in the E_{corr} depends on the coating and decreases in the order poly(o-anisidine-co-o-toluidine) 50:50 > Polyo-anisidine > Polyo-toluidine .

Table 1 : Results of the potentiodynamic polarization measurements



Sample	E_{corr} (mV)	I_{corr} (µA/cm^2)	β_a mV/dec	β_c mV/dec	R_p Ω/cm^2	CR (mm/yr)	% P
Bare Cu	-234	24.06	72.0	110.0	784.05	0.28	----
Polyo-anisidine	-149	0.811	45.0	322.0	21139.15	0.009	0.249
Polyo-toluidine	-189	0.364	61.3	603.0	66377.1	0.004	0.277
Copolymer 90:10	-70	0.398	43.7	942.9	45562.82	0.004	0.009
Copolymer 70:30	-59	0.159	40.8	716.0	105414.66	0.002	0.0027
Copolymer 50:50	94	0.0265	171.0	202.0	1517395.7	0.0003	0.0000014
Copolymer 30:70	76	0.044	305.0	282.0	1445986.5	0.0005	0.0000026
Copolymer 10:90	-96	0.115	41.6	615.0	147121.38	0.007	0.0005

This implies that the copolymer poly(o-anisidine-co-o-toluidine) 50:50 coating provides effective protection to Cu against corrosion in aqueous 3% NaCl as compared to that of the corresponding homopolymers.

It is observed that the I_{corr} decreases from 24.3 µA/cm^2 for uncoated Cu to 0.811, 0.364 and 0.0265 µA/cm^2 for Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 coated Cu, respectively. The corrosion rates of Polyo-anisidine, Polyo-toluidine and poly(o-anisidine-co-o-toluidine) 50:50 coated Cu are found to be ~ 0.0095, 0.0042 and 0.0003 mm/year which are ~ 31, 70 and 940 times lower than that observed for uncoated Cu.

4.Conclusion

Strongly adherent poly(o-anisidine-co-*o-toluidine*) coatings were successfully synthesized on Cu substrates from aqueous salicylate solution by using cyclic voltammetry.

The results of present study clearly show that aqueous sodium salicylate solution is a suitable medium for the electrochemical co-polymerization of o-anisidine with *o-toluidine* on the Cu.

The ^{1}H NMR spectroscopic studies reveal that the co-polymerization of o-anisidine and *o-toluidine* takes place on Cu in aqueous salicylate solution.The performance of the poly(o-anisidine-co-*o-toluidine*) coatings as protective coatings against corrosion of Cu in aqueous 3% NaCl solution was investigated by potentiodynamic polarization technique. – reveal that the poly(o-anisidine-co-*o-toluidine*) coatings effectively protect the Cu. The protection of Cu against corrosion in 3% NaCl by the copolymer coatings can be achieved more effectively when the synthesis was carried out with a feed ratio of *o-toluidine* as 50.

5. References

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