

# Synthesis of corrosion inhibitive poly(2,5-dimethylaniline) coatings on low carbon steel

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An attempt has been made towards the synthesis of strongly adherent poly(2,5-dimethylaniline) coatings on low carbon steel substrates, with an objective of examining the possibility of using this polymer for corrosion protection of steel in chloride environment. In this work, the poly(2,5-dimethylaniline) coatings were synthesized by electrochemical polymerization of 2,5-dimethylaniline using sodium salicylate as a supporting electrolyte. The characterization of these coatings was carried out by cyclic voltammetry, UV-visible absorption spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. The results of these characterizations indicate that the aqueous salicylate solution is a suitable medium for the electrochemical polymerization of 2,5-dimethylaniline to generate strongly adherent and smooth poly(2,5-dimethylaniline) coatings on low carbon steel substrates. The performance of poly(2,5-dimethylaniline) as protective coating against corrosion of low carbon steel in aqueous 3% NaCl was assessed by the open circuit potential and the potentiodynamic polarization measurements. The potentiodynamic polarization measurement reveals that the poly(2,5-dimethylaniline) coating increases the corrosion potential and reduces the corrosion rate of low carbon steel almost by a factor of 50. This study clearly ascertains that the poly(2,5-dimethylaniline) has outstanding capability to protect low carbon steel against corrosion in chloride environment. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Conducting polymers have received great attention in many technological areas such as rechargeable batteries, sensors, electromagnetic interference (EMI) shielding, electrochromic display devices, smart windows, molecular devices, energy storage systems, membrane gas separation etc. due to their remarkable physical attributes [1–3]. In most of these applications, the conducting polymer is used as either a film or coating of well-defined structure,

preferably with a large area. The electrochemical polymerization (ECP) has proved a most convenient method for synthesizing novel conducting polymers on metallic surfaces, which has opened an another technologically important area of corrosion protection for conducting polymers [4, 5]. A number of reports on the synthesis and characterization of conducting polymer coatings on oxidizable metals such as iron [6, 8], aluminum [9, 10], zinc [11] etc. have appeared in the literature during the past

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3–4 years. The common feature of these studies is that the synthesis of conducting polymer coatings on oxidizable metals is preceded by the dissolution of the base metal at a potential lower than the oxidation potential of monomer. Thus, the oxidation of the metal appears as a simultaneous and competitive oxidation process at the potentials adequate for the formation of polymer. A successful ECP of conducting polymer on oxidizable metals demands a careful choice of the solvent, supporting electrolyte and the establishment of electrochemical parameters which will strongly passivate the metal without impeding the electropolymerization process.

Among the conducting polymers, polyaniline [12–14] and polypyrrole [15–17] are the most promising conducting polymers for corrosion protection of metals. Nevertheless, the polyaniline is more challengeable due to the low cost of *aniline* monomer as compared to *pyrrole*. The possibility of using polyaniline coating for corrosion protection of metals was first reported by DeBerry *et al.* [14]. It was further proved that the polyaniline has ability to serve as a corrosion protective coating on metals in both acidic and neutral solutions. Unfortunately, due to high polymerization potential only five electrolytes suitable for the ECP of *aniline* on mild steel were reported [4, 5]. Polypyrrole has also been investigated as a possible coating for corrosion protection. However, the main disadvantage of polypyrrole is that the non-aqueous bath is usually required for its deposition.

The incorporation of constituents in the polymer skeleton is a common technique to synthesize polymers having improved properties [18, 19]. This concept has been successfully applied to polyaniline. Considerable work is still needed to understand the basic issues related to the ECP of substituted anilines on oxidizable metals and to explore the possibility of utilizing them as alternative to polyaniline for corrosion protection.

More recently, we have shown that the ECP of *o*-toluidine in the aqueous tartrate solution results into the deposition of uniform and strongly adherent poly(*o*-toluidine) coatings on low carbon steel (LCS) substrates [20]. These coatings exhibit excellent corrosion protection properties and the poly(*o*-toluidine) is found to be most promising coating material for corrosion protection of LCS in aqueous 3% NaCl.

The di-substituted derivatives of conjugated polymers are also potential candidates in many technological applications. Recently, our group has investigated the ECP of 2,5-dimethylaniline in aqueous oxalic acid medium under galvanostatic conditions on LCS substrates [21]. It has been shown that the oxalic acid is a suitable medium for the ECP of 2,5-dimethylaniline on the LCS substrate and it favors the formation of the mixed phase of pernigraniline base (PB) and emeraldine salt (ES) form of poly(2,5-dimethylaniline) at higher current densities, whereas at low current density the major portion of the coating constitutes the PB form. However, these coatings were not able to protect the LCS substrates from corrosion.

The objectives of the present study are:

- (i) to develop an appropriate ECP recipe to synthesize poly(2,5-dimethylaniline) coatings on LCS substrate from aqueous media;
- (ii) to find potentially good, low cost and easily available supporting electrolyte for the ECP of 2,5-dimethylaniline on LCS substrates;
- (iii) to synthesize uniform, compact and strongly adherent poly(2,5-dimethylaniline) coatings on LCS substrates and
- (iv) to examine the possibility of utilizing the poly(2,5-dimethylaniline) coatings for corrosion protection of LCS in chloride environment.

The reasons for selecting the 2,5-dimethylaniline monomer are many and obvious. These reasons are:

- (a) The monomer 2,5-dimethylaniline is commercially available at low cost.
- (b) This study explores the possibility of utilizing the poly(2,5-dimethylaniline) as alternative to polyaniline for corrosion protection of LCS.
- (c) The 2,5-dimethylaniline monomer has quite good solubility in water and therefore it is possible to develop an ECP recipe using aqueous media which will reduce the use of hazardous chemicals as well as the cost of waste disposal.

Recently, Lacaze *et al.* [22] have discovered a general one-step process for ultra-fast electropolymerization of *pyrrole* on oxidizable metals. The process is based on the use of the aqueous sodium salicylate solution and *pyrrole*. They observed that the salicylate salt passivates the substrate without preventing the ECP of *pyrrole* and uniform and strongly adherent polypyrrole films were obtained. The sodium salicylate was chosen as the supporting electrolyte for the ECP of 2,5-dimethylaniline due to its ability to form a non-conducting passive layer on mild steel surface without preventing the monomer oxidation.

The goal of the present paper is to report the new findings about the ECP of 2,5-dimethylaniline on LCS from the aqueous salicylate medium and the ability of poly(2,5-dimethylaniline) to protect LCS against corrosion in chloride environment. In the work reported in this paper, we have made an attempt to synthesize strongly adherent poly(2,5-dimethylaniline) coatings on LCS substrates by ECP from aqueous salicylate medium and examined the ability of these coatings to serve as corrosion protective coatings on LCS. To the best of our knowledge, there are no reports in the literature dealing with the direct deposition of poly(2,5-dimethylaniline) coatings on LCS from aqueous salicylate medium.

The results reported in this paper have shown that the ECP of 2,5-dimethylaniline from the aqueous salicylate solution results into the formation of uniform, compact and strongly adherent poly(2,5-dimethylaniline) coating on LCS substrate. The evaluation of the corrosion

protection performance of these coatings reveals that poly(2,5-dimethylaniline) can be considered as a potential coating material for protection of LCS against corrosion in aqueous 3% NaCl.

## 2. Experimental

Analytical reagents (AR) grade chemicals were used throughout the present study. The 2,5-dimethylaniline monomer was double distilled prior to its use. The aqueous sodium salicylate ( $\text{NaC}_7\text{H}_5\text{O}_3$ ) solution was used as the supporting electrolyte. The concentrations of sodium salicylate and 2,5-dimethylaniline were kept constant at 0.1 M and 0.05 M, respectively.

The chemical composition (by weight%) of the LCS used in this study was: 0.03% C, 0.026% S, 0.01% P, 0.002% Si, 0.04% Ni, 0.002% Mo, 0.16% Mn, 0.093% Cu and 99.64% Fe. The LCS substrates (size  $\sim 10 \times 15$  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.

The poly(2,5-dimethylaniline) coatings were synthesized by ECP of 2,5-dimethylaniline on LCS substrates from aqueous salicylate solution under cyclic voltammetric conditions. The ECP was carried out in a single compartment three electrode cell with LCS as working electrode ( $150 \text{ mm}^2$ ), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetric conditions were maintained using a SI 1280B Solartron Electrochemical Measurement System (U.K.) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, U.K.). The synthesis was carried out by cycling continuously the electrode potential between  $-1.0$  V and  $1.8$  V at a potential scan rate of  $0.02$  V/sec. The number of cycles was varied from 1 to 15. After deposition the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air.

The Fourier transform infrared (FTIR) transmission spectrum of poly(2,5-dimethylaniline) coating was recorded in horizontally attenuated total reflectance (HATR) mode in the spectral range  $4000\text{--}400 \text{ cm}^{-1}$  using a Perkin Elmer spectrometer, 1600 Series II, U.S.A. The optical absorption studies of these coatings were carried out *ex-situ* at room temperature in the wavelength range  $300\text{--}1100$  nm using microprocessor controlled double beam UV-visible spectrophotometer (Hitachi, Model U2000). The structural properties were investigated using X-ray diffraction (XRD) technique. The X-ray diffraction patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having  $\text{Cu K}_\alpha$  ( $\lambda = 0.1542$  nm). Scanning electron microscopy (SEM) was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (U.K.).

The corrosion protection performance of these coatings was investigated in aqueous 3% NaCl solution by using open circuit potential (OCP) and potentiodynamic polarization measurements. For these measurements, a teflon holder was used to encase the polymer coated LCS substrates so as to leave an area of  $\sim 40 \text{ mm}^2$  exposed to the solution. The polarization resistance measurements were performed by sweeping the potential between  $-0.25$  V and  $0.25$  V from OCP at the scan rate of  $0.002$  V/sec. Before polarization the substrates were immersed into the solution and the OCP was monitored until a constant value was reached. The Tafel slopes of the anodic ( $\beta_a$ ) and cathodic ( $\beta_b$ ) parts of the polarization curve were obtained. The corrosion current density ( $I_{\text{corr}}$ ) in  $\text{A/m}^2$  was calculated by using Stern-Geary equation [23] and it is converted into the corrosion rate (CR) in mm per year by using the expression [24]:

$$CR(\text{mm}/\text{yr}) = 3.268 \times 10^3 \frac{I_{\text{corr}}}{\rho} \frac{MW}{z}$$

where MW is molecular weight of LCS (g),  $\rho$  is the density of LCS ( $\text{kg/m}^3$ ) and  $z$  is the number of electrons transferred in the corrosion reaction;  $z = 2$  in the case of LCS reaction. All the measurements were repeated at least four times and good reproducibility of the results was observed.

## 3. Results and discussion

### 3.1. Synthesis of PDMLA coatings on LCS

In order to understand the different processes occurring at the electrode surface, the LCS electrodes were first polarized in 0.1 M aqueous sodium salicylate solution (without monomer) by cycling continuously the electrode potential between  $-1.0$  and  $1.8$  V at a potential scan rate of  $0.02$  V/sec. The first scan of the voltammetric response of the LCS electrode in 0.1 M aqueous sodium salicylate medium is shown in Fig. 1a. The first positive cycle is characterized by

- (i) an anodic peak (A) at  $-0.489$  V;
- (ii) negligibly small oxidation current between  $-0.3$  V and  $0.8$  V and
- (iii) onset of an oxidation wave (B) at  $\sim 1.3$  V and beyond this potential high anodic current flows.

The anodic current decays very sharply and a negligibly small current is observed till the end of the negative cycle.

The anodic peak A is attributed to the dissolution of the LCS electrode surface which produces  $\text{Fe}^{2+}$  ions in its vicinity. These ions interact with the salicylate counter-ions of the electrolyte to form a thin insoluble passive layer at the electrode surface, corresponding to complexation of the  $\text{Fe}^{2+}$  cation by salicylate counter-ions which inhibits the dissolution of the electrode surface. As a result, just after the peak A, the current density decreases and attains a negligibly small value. The

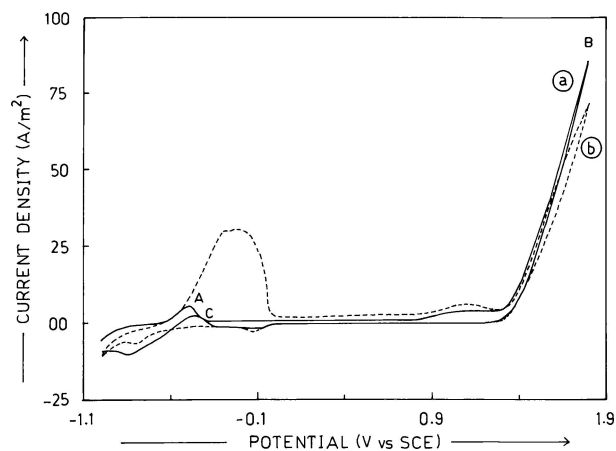


Figure 1 Cyclic voltammogram (a) first and (b) tenth scans recorded during the polarization of LCS electrode in 0.1 M sodium salicylate solution. Scan rate : 0.02 V/sec.

soluble colored products of the reaction diffuse into the electrolyte. In fact, during the polarization process, the color of the electrolyte gradually changes to brownish-pink. It seems that the major portion of the reaction products is soluble which may be due to the presence of carboxylic acid groups on the oligomers produced during the polarization process. The oxidation wave (B) is assigned to the oxidation of the salicylate electrolyte.

On repetitive cycling, the voltammograms identical to that of first scan are obtained. However, the position of the peak A is shifted in the positive direction and the current density corresponding to it increases with the increase number of scans. This may be attributed to the partial stabilization of the LCS electrode surface due to formation of the complexation of the  $\text{Fe}^{2+}$  cation by salicylate counter-ions.

In order to understand the observed CV results, we have performed the XRD measurements of the LCS electrode polarized in 0.1 M aqueous salicylate solution. The XRD patterns of the bare LCS and the LCS electrode polarized in 0.1 M sodium salicylate solution are shown in Fig. 2. The XRD pattern of bare LCS substrate Fig. 2a shows a

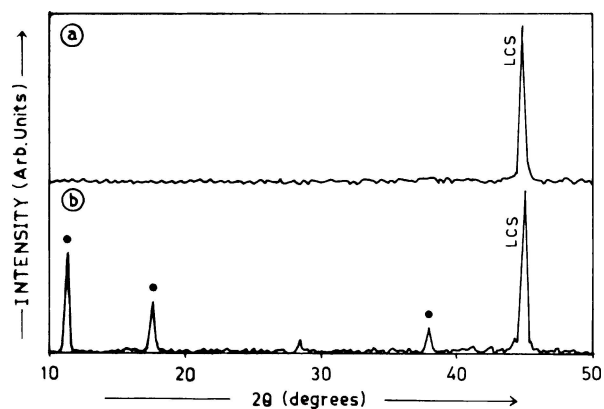


Figure 2 XRD pattern of (a) bare LCS and (b) LCS substrate polarized in 0.1 M sodium salicylate solution. The ● indicates the peaks for iron salicylate.

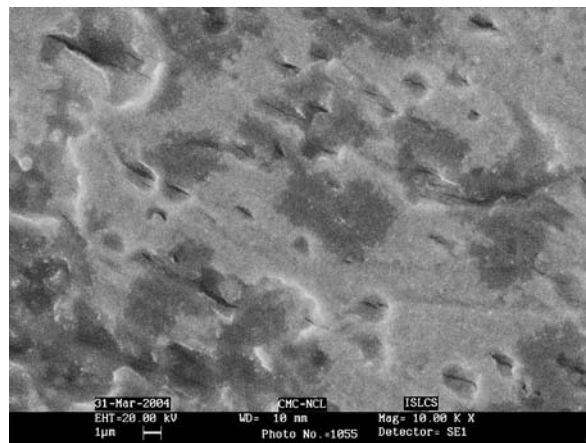


Figure 3 SEM image of the LCS substrates polarized in 0.1 M sodium salicylate solution.

characteristic diffraction peak at an angle of  $45^\circ$ , indicating its polycrystalline nature. Apart from the characteristic peak of LCS, the XRD pattern of the LCS electrode polarized in 0.1 M sodium salicylate solution Fig. 2b indicates the presence of diffraction peaks at angles of  $11.20^\circ$ ,  $18.60^\circ$ ,  $38.00^\circ$  and  $44.20^\circ$  due to the iron salicylate. Thus, the XRD result clearly reveals the formation of the iron salicylate on the LCS electrode surface. Thus, the polarization of the LCS electrode in 0.1 M sodium salicylate solution results into the passivation of the electrode surface via the formation of iron salicylate phase.

The SEM image of the LCS electrode polarized in a 0.1 M aqueous salicylate solution is shown in Fig. 3. It does not indicate the formation of crystalline phases on the LCS electrode surface. Nevertheless, it reveals the deposition of a thin film on the electrode surface, which may be due to the formation of iron salicylate phase.

The first scan of the cyclic voltammogram recorded during the synthesis of poly(2,5-dimethylaniline) coating on the LCS electrode from aqueous solution containing 0.05 M 2,5-dimethylaniline and 0.1 M sodium salicylate at room temperature is shown in Fig. 4a. The behavior of this scan is significantly different from that recorded in aqueous salicylate solution without 2,5-dimethylaniline. Indeed, the anodic peak A is disappeared and the first positive cycle indicates: (i) onset of oxidation wave at  $\sim 0.553$  V followed by oxidation peak ( $A_2$ ) at 1.092 V and (ii) the oxidation wave (B) at  $\sim 1.799$  V and beyond this potential high anodic current flows. During the reverse cycle, the anodic current density decreases rapidly and a negligibly small current is seen till  $-0.169$  V. The negative cycle terminates with a broad reduction peak (C) at  $\sim -0.458$  V.

The non-observance of the anodic peak A corresponding to the dissolution of the LCS substrate when 2,5-dimethylaniline is in the solution, indicates that the 2,5-dimethylaniline is involved in the passivation process and the ECP takes place without dissolution of the electrode surface. The oxidation wave at  $\sim 0.553$  V is attributed to oxidation of 2,5-dimethylaniline since a

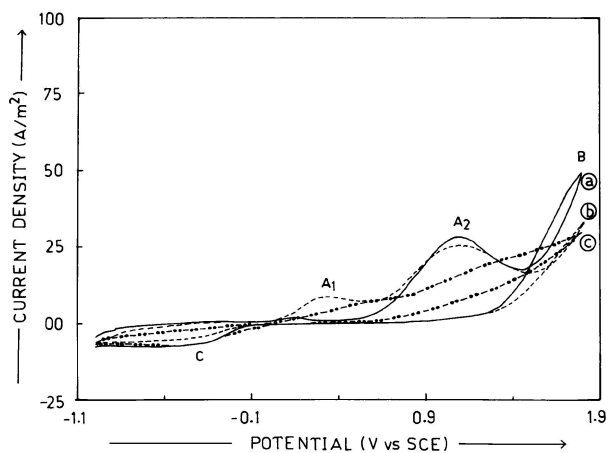


Figure 4 Cyclic voltammogram scans (a) first, (b) second and (c) tenth recorded during the synthesis of poly(2,5-dimethylaniline) coating on LCS substrate under cyclic voltammetric conditions. Scan rate: 0.02 V/sec.

black, uniform film is generated on the LCS substrate. As stated earlier, the oxidation wave (B) is assigned to the oxidation of the salicylate electrolyte. The reduction peak observed at  $\sim -0.458$  V during the negative cycle is attributed to the partial reduction of the deposited poly(2,5-dimethylaniline) film.

During the next scan Fig. 4b, the broad anodic peak  $A_1$  at  $\sim 0.348$  V is observed and rest of the features are similar to that of the first scan. The anodic peak  $A_1$  is assigned to the oxidation of poly(2,5-dimethylaniline) deposited at the LCS surface corresponding to conversion of amine units into radical cations [25]. On repetitive cycling, the voltammograms identical to that of second scan are obtained. However, the current density corresponding to the anodic peaks decrease gradually with the number of scans. Thus, the ECP of 2,5-dimethylaniline on LCS substrate occurs in a single step from aqueous salicylate solution. The visual inspection of the LCS electrode after fifteenth scan reveals the formation of a black colored poly(2,5-

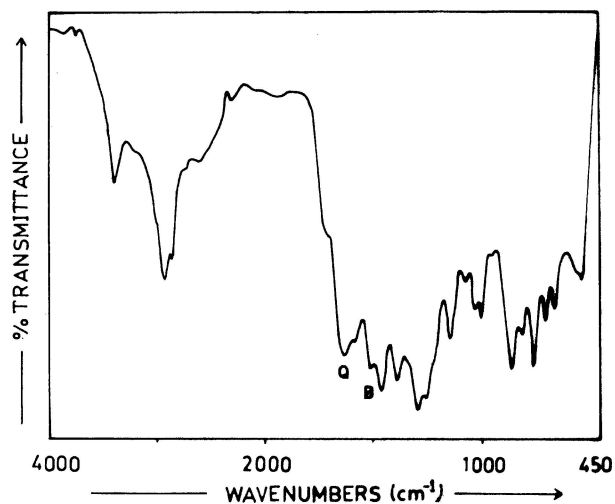
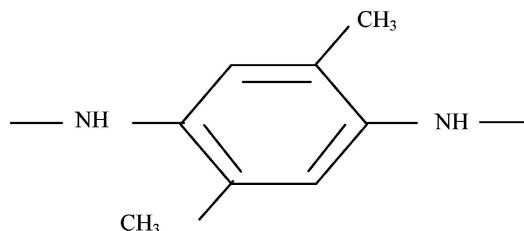


Figure 5 FTIR spectrum of the poly(2,5-dimethylaniline) coating synthesized on LCS substrate under cyclic voltammetric conditions.

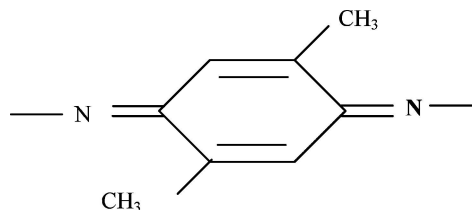
dimethylaniline) coating. The coating is uniform, crack free and strongly adherent to the LCS substrate.

The FTIR spectrum of poly(2,5-dimethylaniline) coating ( $\sim 15$   $\mu\text{m}$  thick) synthesized on LCS under cyclic voltammetric conditions recorded in HATR mode is shown in Fig. 5. This spectrum exhibits the following spectral features:

- (i) A band at  $\sim 3382$   $\text{cm}^{-1}$  due to the characteristic N-H stretching vibration suggests the presence of  $-\text{NH}-$  groups in 2,5-dimethylaniline units [26, 27].
- (ii) The band at  $\sim 2928$   $\text{cm}^{-1}$  is associated with C-H stretching in methylene group.
- (iii) The band at  $\sim 1635$   $\text{cm}^{-1}$  is an indicative of stretching vibrations in quinoid (Q) rings [26–29]:



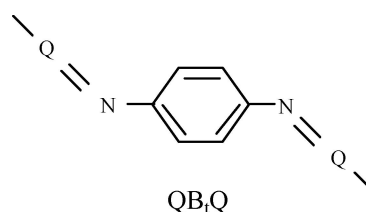
- (iv) The band  $\sim 1511$   $\text{cm}^{-1}$  represents the stretching vibrations of the benzoid (B) rings [26–29]:



- (v) The presence of Q and B bands clearly show that the poly(2,5-dimethylaniline) coating is composed of imine and amine units.

(vi) The band at  $1298$   $\text{cm}^{-1}$  are attributed to the presence of carboxylic groups of sodium salicylate in the poly(2,5-dimethylaniline) coating. The presence of these strong bands reflects the formation of the oxidized form of poly(2,5-dimethylaniline).

(vii) The presence of the C-N stretching band at  $\sim 1384$   $\text{cm}^{-1}$  is consistent with the results reported by Tang *et al* [26], who have also observed the similar bands for poly(2,5-dimethylaniline). The band at  $\sim 1384$   $\text{cm}^{-1}$  is assigned to the C-N stretching in  $\text{QB}_t\text{Q}$  environment, where  $\text{B}_t$  represents a *trans*-benzoid unit:



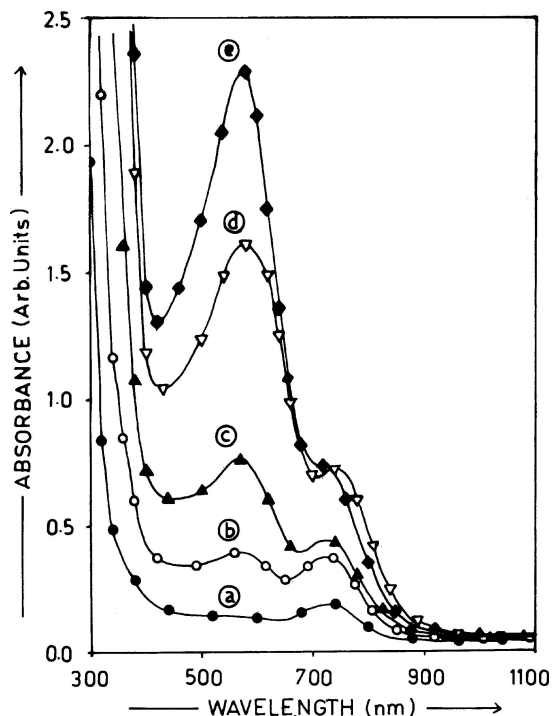


Figure 6 Optical absorption spectra of (a) 3, (b) 5, (c) 12, (d) 15 and (e) 17  $\mu\text{m}$  thick poly(2,5-dimethylaniline) coating synthesized on LCS substrate under cyclic voltammetric conditions.

(viii) The bands at  $1076$  and  $1029\text{ cm}^{-1}$  are attributed to the 1–4 substitution on the benzene ring.

(ix) The observation of the bands between  $800\text{--}700\text{ cm}^{-1}$  reveals the occurrence of the 1–3 substitutions.

Thus, the FTIR spectroscopic study indicates that the ECP of 2,5-dimethylaniline has occurred and results into the formation of oxidized form of poly(2,5-dimethylaniline) on the electrode surface.

In order to identify the formation and deposition of the different oxidation forms of poly(2,5-dimethylaniline) with variation in the coating thickness, we have synthesized the coatings with different thicknesses by varying the number of scans during the synthesis and performed the optical absorption spectroscopy study. The corresponding optical absorption spectra are shown in Fig. 6. It is clearly seen that the overall absorbance increases with the coating thickness. This suggests that the coating thickness increases with the number of scans. These spectra exhibit systematic changes in peak positions and relative intensities with variation in the coating thickness. The optical absorption spectrum of thick ( $\sim 17\ \mu\text{m}$ ) poly(2,5-dimethylaniline) coating deposited with 25 scans is completely different in all respects with the spectrum of the thin ( $\sim 3\ \mu\text{m}$ ) poly(2,5-dimethylaniline) coating deposited with only a single scan.

The optical absorption spectrum of 3  $\mu\text{m}$  thick poly(2,5-dimethylaniline) coating Fig. 6a shows a well defined peak at  $\sim 740\text{ nm}$  and it is attributed to the formation of emeraldine salt (ES) form of poly(2,5-dimethylaniline), which is the only electrically conducting phase of

poly(2,5-dimethylaniline) [30]. The optical absorption spectrum of 5  $\mu\text{m}$  thick poly(2,5-dimethylaniline) coating is shown in Fig. 6b. This spectrum exhibits noticeable difference when compared with Fig. 6a. Firstly, it indicates an increase in the intensity of the peak at  $\sim 750\text{ nm}$ . Secondly, it shows an emergence of another peak at  $\sim 540\text{ nm}$ . The peak at  $\sim 540\text{ nm}$  is signature of the formation of pernigraniline base (PB) form of poly(2,5-dimethylaniline). The PB is the fully oxidized form of poly(2,5-dimethylaniline) and is insulating in nature [30]. The simultaneous appearance of 750 nm peak and shoulder at 540 nm clearly reveals the formation of mixed phase of PB and ES forms of poly(2,5-dimethylaniline). The optical absorption spectra of 12 and 15 and 17  $\mu\text{m}$  thick poly(2,5-dimethylaniline) coatings are shown in Fig. 6c–e. A closer examination of these spectra reveal the following features:

(i) It indicate the formation of mixed phase of PB and ES forms in the coating irrespective of the coating thickness. However, the amount of the PB form is higher than the ES in the coating.

(ii) As the coating thickness increases beyond  $\sim 15\ \mu\text{m}$ , the absorbance of the shoulder peak at  $\sim 750\text{ nm}$  corresponding to the ES remains almost same.

### 3.2. Corrosion protection properties of the poly(2,5-dimethylaniline) coating

In order to assess the corrosion protection performance of the poly(2,5-dimethylaniline) coating, the OCP and the potentiodynamic polarization measurements of bare LCS and poly(2,5-dimethylaniline) coated LCS were performed in aqueous 3% NaCl solution. The OCP of poly(2,5-dimethylaniline) coated LCS substrate immersed in aqueous 3% NaCl was measured as a function of time and the corresponding plot is presented in Fig. 7. In this figure,  $-0.710\text{ V}$  stands for the corrosion potential of bare LCS.

The initial value of the OCP of the poly(2,5-dimethylaniline) coated ( $\sim 17\ \mu\text{m}$  thick) LCS was

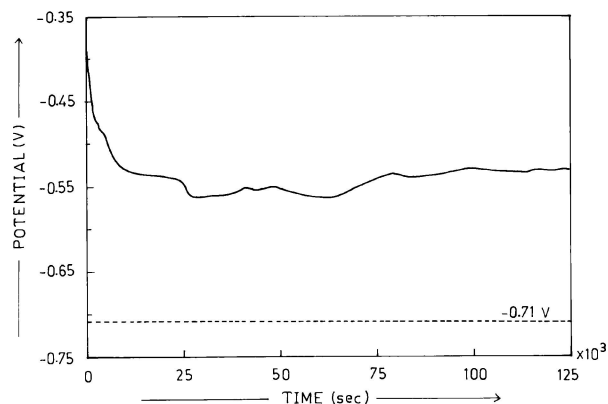


Figure 7 Plot of OCP for poly(2,5-dimethylaniline) coated LCS in aqueous 3% NaCl versus time. The discontinuous line represents the OCP of bare LCS.

measured to be  $\sim -0.395$  V and it is more positive than that of the bare LCS by upto  $\sim 0.315$  V. It is observed that the OCP decreases slowly with the immersion time and attains a nearly steady state value which is more positive than that of the bare LCS by upto  $\sim 0.178$  V. The protection time is often determined by measuring the elapsed time until the OCP of the polymer coated LCS drops to that of the bare electrode. Interestingly, this is not observed for the poly(2,5-dimethylaniline) coated LCS. Instead, the OCP of the poly(2,5-dimethylaniline) coating remains fairly constant  $\sim -0.532$  V over 50 h.

The potentiodynamic polarization curves for bare LCS and poly(2,5-dimethylaniline) coated LCS ( $\sim 17 \mu\text{m}$  thick) recorded in aqueous 3% NaCl solution are shown in Fig. 8. The Tafel extrapolations show that the poly(2,5-dimethylaniline) caused a remarkable potential shift  $\sim 0.320$  V in the corrosion potential ( $E_{\text{corr}}$ ), relative to the value of the bare LCS ( $-0.710$  V). The positive shift in  $E_{\text{corr}}$  confirms the best protection of the LCS when its surface is covered by the poly(2,5-dimethylaniline). Also, the Tafel measurements clearly show that a substantial reduction in the corrosion current density ( $I_{\text{corr}}$ ) occurs for the poly(2,5-dimethylaniline) coated LCS with respect to the bare LCS. The values of the  $E_{\text{corr}}$ ,  $I_{\text{corr}}$  and corrosion rates obtained from these curves are given in Table I. The corrosion rate of LCS is significantly reduced as a result of the reduction in the  $I_{\text{corr}}$ . The corrosion rate of poly(2,5-dimethylaniline) coated LCS is found to be  $\sim 0.007$  mm/year which is  $\sim 50$  times lower than that observed for bare LCS. Further, it is found that the corrosion rate changes significantly (cf. Table I) with the thickness of the poly(2,5-dimethylaniline) coating. It is observed that the corrosion rate decreases with the increase in the coating thickness and it is lowest for the poly(2,5-dimethylaniline) coating having thickness  $\sim 17 \mu\text{m}$ . Thus, these results reveal the capability of poly(2,5-dimethylaniline) to act as a corrosion protective layer on LCS and its thickness significantly affects the corrosion protection properties.

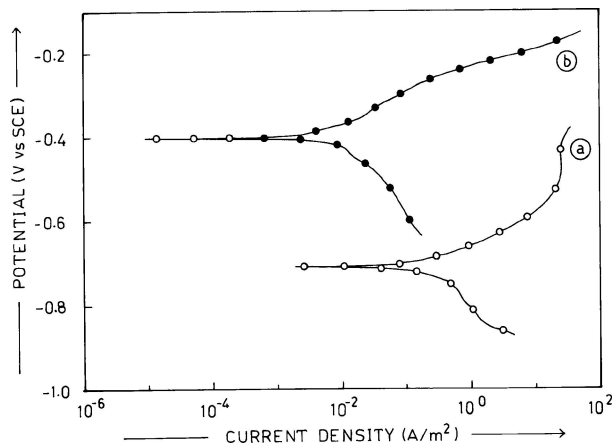


Figure 8 Potentiodynamic polarization curves for (a) bare LCS and (b) poly(2,5-dimethylaniline) coated ( $\sim 17 \mu\text{m}$  thick) on LCS in aqueous 3% NaCl solution.

TABLE I Potentiodynamic polarization measurement results.

Sample	$E_{\text{corr}}$ (V)	$I_{\text{corr}}$ ( $\text{A}/\text{m}^2$ )	CR (mm/yr)
Bare LCS	-0.710	0.3072	0.35
PDMLA coated LCS $3 \mu\text{m}$	-0.480	0.1379	0.16
PDMLA coated LCS $5 \mu\text{m}$	-0.452	0.0719	0.08
PDMLA coated LCS $12 \mu\text{m}$	-0.437	0.0133	0.016
PDMLA coated LCS $15 \mu\text{m}$	-0.401	0.0083	0.009
PDMLA coated LCS $17 \mu\text{m}$	-0.390	0.0058	0.007
PDMLA coated LCS ( $15 \mu\text{m}$ ) kept in air for 30 days at $25^\circ\text{C}$	-0.453	0.0077	0.009

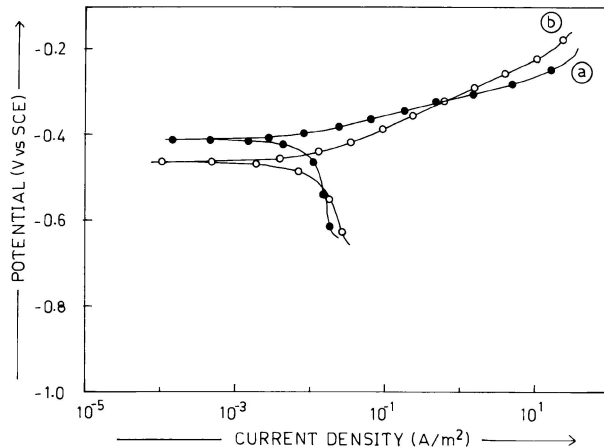


Figure 9 Potentiodynamic polarization curves for poly(2,5-dimethylaniline) coated LCS (a) freshly prepared and (b) after storing in air for 30 days at  $25^\circ\text{C}$  recorded in aqueous 3% NaCl solution.

The outstanding corrosion protection offered by poly(2,5-dimethylaniline) coating to LCS may be attributed to the fact that the deposited polymer is strongly adherent and uniformly covers the entire electrode surface. Furthermore, the delocalized  $\pi$ -electrons in this polymer facilitate its strong adsorption on the LCS surface leading to the outstanding corrosion inhibition.

We have also performed the potentiodynamic polarization measurements by using the poly(2,5-dimethylaniline) coated LCS ( $\sim 15 \mu\text{m}$  thick) substrates after storing them in air at  $25^\circ\text{C}$  for 30 days and the corresponding polarization curve is shown in Fig. 9b. The potentiodynamic polarization curve for freshly prepared poly(2,5-dimethylaniline) coated LCS is also presented in Fig. 9a. These curves clearly reveal that there is no indication of any substantial loss in corrosion protection properties of the poly(2,5-dimethylaniline) coatings. Thus, the poly(2,5-dimethylaniline) coating shows high chemical as well as physical stability because the coating keeps its adherence to LCS substrate even after the storage.

#### 4. Conclusions

In summary, following conclusions have been drawn from the present investigation:

- We have successfully synthesized uniform and strongly adherent poly(2,5-dimethylaniline) coatings

on low carbon steel by electrochemical polymerization of 2,5-dimethylaniline from aqueous salicylate medium. The electrochemical polymerization process occurs without noticeable dissolution of steel substrate.

- The result of the optical absorption spectroscopy reveals the formation of the mixed phase of pernigraniline base and emeraldine salt forms of poly(2,5-dimethylaniline).
- The potentiodynamic polarization study reveals that the poly(2,5-dimethylaniline) acts as a corrosion protective layer on low carbon steel in 3% NaCl solution.
- The corrosion rate of poly(2,5-dimethylaniline) coated low carbon steel ( $\sim 17 \mu\text{m}$  thick) is found to be  $\sim 50$  times lower than that observed for bare steel.
- The corrosion protection properties of these coatings are retained even after storing them in air at  $25^\circ\text{C}$  for 30 days.
- This study clearly reveals that the poly(2,5-dimethylaniline) coating has excellent corrosion protection properties and it can be considered as a potential coating material for corrosion protection of low carbon steel in aqueous 3% NaCl.

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