EXECUTIVE SUMMARY OF UGC MRP

Name of the principal Investigator : **Dr. Pritee Prakash Pawar**

File No. : File No. 47- 413/12 (WRO), Dated: 16/03/2013

Period of Report : From (March 2013- March 2015)

Title of Research Project : **“Synthesis of Nano-Structured Conductive Polymers For Effective Gas and Humidity Sensing”**

Dept. and University /College where work has progressed : Dept. of Physics, M.G.S. M ’s A. S. C. College Chopda, Dist:- Jalgaon. M.S. India- 425107.

Effective date of starting the project : March- 2013

Grant approved and expenditure incurred during the period of the report.

a. Total amount approved : Rs. 1,20,000 = 00

b. Total expenditure : Rs. 1,22,863/-

Synthesis of Nano-Structured Conductive Polymers For Effective Gas and Humidity Sensing

SUMMARY OF THE FINDINGS OF THE PROJECT

I. Pure Polyo-anisidine (POA) and Polyaniline (PANI) was synthesized by in-situ chemical oxidative polymerization method.

II. The TiO2/POA and TiO2/PANI composite nanostructure was prepared by an in-situ chemical oxidation polymerization of o-anisidine using APS as an oxidant.

III. Thin films of these prepared conducting homogenous solutions were deposited onto cleaned glass substrates using dip coating for 10 min.

IV. Incorporation of TiO2 during synthesis of POA improved the yield by an amount of 0.2146gm.

V. The conductivity measurement attributed to that the doping of TiO2 nanoparticles within POA matrix form a more efficient network for charge transport between different molecular chains of POA, thus enhancing the conductivity of composite.

VI. In UV-Visible absorption spectrum especially it is observed that for POA/TiO2 composite thin films, the absorption intensity increases with TiO2.

VII. Thus, characterizations UV-Visible, FTIR and SEM of coatings were represent the successful synthesis of POA, PANI, TiO2/POA and TiO2/PANI.

VIII. The EDAX analysis of the POA/TiO2 coating proves that the TiO2–nanoparticles are incorporated in the POA matrix.

IX. As the POA/TiO2 was exposed to LPG, the forward current drastically decreased with an increase in concentration of LPG to 0.1 vol%. so it successfully acts as LPG sensor.

X. These thin films were exposed to NH3 gas, POA/TiO2 nano composite coating shows quicker gas desorption as compared to POA films.

XI. An interaction of H2 with the PANI backbone possibly facilitated by TiO2 nanoparticles.

XII. The experimental results showed that the humidity sensor almost had no humidity hysteresis for PANI/TiO2 as compared to PANI.

NO. OF PUBLICATIONS OUT OF THE PROJECT :03

1. Corrosion protective poly (aniline-co-o-anisidine) coatings on mild steel
   PM Raotole, P Koinkar, B Joshi, SR Patil –

   Journal of Coatings Technology and Research, 12 (4), 757-766, 2015.

2. Performance of Poly (Aniline-co-o-Toluidine) Coatings Against Corrosion of Copper
   PM Raotole, ML Raotole, RS Khadayate, SR Patil - International Journal of Metallurgy and Alloys ,1(2), 29-40, 2016

3. Deposition and Characterization of Poly (O-Anisidine)/TiO2 Nanocomposite for Gas Sensing Application
   PM Raotole, RS Khadayate - International Journal of Polymer Science & Eng., 1(2), 1-7, 2015

Corrosion protective poly(aniline-co-o-anisidine) coatings on mild steel

Article *in* Journal of Coatings Technology and Research · May 2015

DOI: 10.1007/s11998-015-9669-0

4 authors, including:


Pritee Mahesh Raotole
Arts, Science and Commerce College ,Chopda
13 PUBLICATIONS **147** CITATIONS
SEE PROFILE

P. M. Koinkar
The University of Tokushima
6 PUBLICATIONS **5** CITATIONS
SEE PROFILE


Bhavana Joshi
Korea University
54 PUBLICATIONS **299** CITATIONS
SEE PROFILE

Corrosion protective poly(aniline-co-o-anisidine) coatings on mild steel

Pritee M. Raotole, Pankaj Koinkar, Bhavana Joshi & S. R. Patil

Journal of Coatings Technology and Research

ISSN 1547-0091

J Coat Technol Res
DOI 10.1007/s11998-015-9669-0

ONLINE FIRST

Volume 12, Number 3, May 2015

Journal of Coatings Technology and Research

The Official Journal of the American Coatings Association

Indexed in ISI Web of Science®

ACA

Springer

Springer

J. Coat. Technol. Res.
DOI 10.1007/s11998-015-9669-0

Corrosion protective poly(aniline-co-*o*-anisidine) coatings on mild steel

Pritee M. Raotole, Pankaj Koinkar, Bhavana Joshi, S. R. Patil

Abstract Syntheses of corrosion protective poly(aniline-co-*o*-anisidine) (PAOA) coatings were carried out on mild steel by the electrochemical copolymerization of aniline with *o*-anisidine under cyclic voltammetry conditions. An aqueous salicylate solution was used as the supporting electrolyte for the synthesis of PAOA coatings on mild steel. These coatings were characterized with cyclic voltammetry, ultraviolet–visible absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and scanning electron microscopy. The FTIR and ^{1}H-NMR spectroscopy studies reveal that during copolymerization of aniline and *o*-anisidine, there are more *o*-anisidine units than aniline units in PAOA copolymer. The corrosion protection offered by PAOA coatings to mild steel was investigated in aqueous 3% NaCl solutions using the potentiodynamic polarization technique. The results of the potentiodynamic polarization measurements showed that the PAOA coatings provided more effective corrosion protection to mild steel than the respective homopolymers. The corrosion rate was observed to be dependent on the feed ratio of *o*-anisidine used for synthesis of the copolymer coatings.

P. M. Raotole (✉), S. R. Patil
MGSM's Arts, Science and Commerce College,
Dist-Jalgaon, Chopda 425107, Maharashtra, India
e-mail: Pritee_pawar@yahoo.com

P. Koinkar
Center for International Cooperation in Engineering
Education (CICEE), The University of Tokushima, 2-1,
Minamijosanjima-cho, Tokushima 770-8506, Japan

B. Joshi
Department of Materials Science and Engineering, Jimma
University, Jimma 378, Ethiopia

Keywords Corrosion protective coatings, Conducting polymer, Poly(aniline-co-*o*-anisidine), Electrochemical copolymerization, Cyclic voltammetry, Mild steel

Introduction

Conducting polymers are important materials, which may be used in a large number of batteries, capacitors, transistors, photovoltaic cells, light-emitting diodes, Schottky diodes, biochemical analysis, and aircraft fuselage.[1–3] A very important potential application of conducting polymers such as polyaniline (PANI) and polypyrrole (PPY) is the protection of metals against corrosion. As a candidate for protection of metals against corrosion, conducting polymers exhibit several advantages such as light weight, inexpensiveness, ease of synthesis, and effectiveness for corrosion protection, e.g., PANI coating was said to be three to ten times more effective than zinc coating.[4] These conducting polymers are significantly environmentally friendly as compared with those inhibitive metal oxides which pose potential environmental and health concerns[5,6] although they are effective as corrosion inhibitors. The conducting polymers such as polyaniline, polypyrrole, and polythiophene work as a strong oxidant to the steel, inducing the potential shift to the noble direction.[7]

Despite the success of conducting polymer coatings, they are still a long way from replacing the traditional coating systems. Also, the extent to which the conducting polymers can be used is limited due to the exclusivity of monomers that are essential for their synthesis. To overcome this limitation, different synthesis approaches have been attempted. These include the synthesis of (a) substituted conducting polymer coatings, (b) bi-layered composite coatings, and (c) copolymer coatings. The third approach involves the use of copolymerization to prepare new polymers with inbuilt tailor-made properties suitable for the application. Nelofar et al.[8] synthesized soluble copolymers, poly(aniline-co-*o*-toluidine), and poly(pyrrole-co-*o*-toluidine) by chemical oxidative copolymerization, and they observed that the anticorrosive properties of the poly(aniline-co-*o*-toluidine) copolymer were better than poly(pyrrole-co-*o*-toluidine) and homopolymer. Hur et al.[9] reported the electrochemical synthesis of poly(aniline-co-2-toluidine) films on stainless steel in tetrabutylammonium perchlorate/acetonitrile solution containing perchloric acid. They found that the PANI coatings provide much better protection to stainless steel than poly(2-anisidine) and poly(aniline-co-2-anisidine) films. It has been shown that the protection properties of PANI are related to the passivation of steel and the barrier effect, while the protection of steel by poly(2-anisidine) and poly(aniline-co-2-anisidine) films is mainly through the barrier effect. Bereket et al.[10] synthesized poly(aniline-co-2-anisidine) films on stainless steel using the synthesis conditions identical to those used by Hur et al. They found that the PANI, poly(2-anisidine), and poly(aniline-co-2-anisidine) films have a corrosion protection effect for stainless steel in an aggressive medium of 0.5 M HCl solution. However, the durability of the poly(aniline-2-anisidine) films is limited to 3 h.

Recently, we have discovered a simple one-step process for ultra-fast electropolymerization of aniline on mild steel in an aqueous salicylate solution.[11] The poly(*o*-anisidine-co-*o*-toluidine) coatings have also been synthesized on Cu by cyclic voltammetry[12] from an aqueous solution of sodium salicylate for the corrosion protection. It is shown that the aqueous salicylate solution is a suitable medium for the electrochemical polymerization of a monomer and it resulted in deposition of uniform and strongly adherent polymer coatings on Cu substrates. These coatings exhibited excellent corrosion protection properties and can be used as a most promising coating material for corrosion protection of Cu in aqueous 3% NaCl.

Experimental procedure

Materials

All chemicals were of analytical grade. The monomers, aniline, and *o*-anisidine were procured from Fluka and were doubly distilled prior to being used for the synthesis. Sodium salicylate ($NaC_7H_5O_3$) was procured from Merck and used as-received without further purification. Bi-distilled water was used to prepare all the solutions.

Substrate preparation

The mild steel substrate (size ~10 × 15 mm and 0.5-mm thick) was polished with a series of emery papers of different grit size (180, 400, 600, 800, and 1200). After polishing, the substrates were cleaned with 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.

Electrochemical synthesis

The PANI, Poly(*o*-anisidine) (POA), and PAOA copolymer coatings were synthesized on mild steel substrates using cyclic voltammetry. The electrochemical synthesis was carried in a single-compartment, three-electrode cell with mild steel as a working electrode (150 mm^2), platinum as a counter electrode whose size is 3 cm × 5 cm, and saturated calomel electrode (SCE) as a reference electrode. The cyclic voltammetric conditions were maintained using a PARSTAT 2363-1, EG and G, Princeton Applied Research (USA) controlled by PowerSuite software (Perkin Elmer Instruments, 2000 supplied by EG and G, Princeton Applied Research, USA).[13]

PAOA copolymer coatings on mild steel

The aqueous sodium salicylate solution was used as the supporting electrolyte to synthesize PAOA copolymer coatings on mild steel. For the electrochemical copolymerization, a mixture of aniline and *o*-anisidine with total concentration of 0.1 M was used in 0.1 M aqueous salicylate solution. The synthesis of polymer coatings was carried out by cycling continuously the electrode potential between −1.0 V and 1.8 V vs SCE at a potential scan rate of 0.02 V s^{-1}. After 15 cycles, the working electrode was removed from the electrolyte and rinsed with double-distilled water and dried in air. To synthesize homopolymers PANI and POA coatings, the same procedure was used, while concentrations of respective monomer and sodium salicylate were kept constant at 0.1 M each.

The copolymer synthesis experiments were carried out using a feed ratio of *o*-anisidine as 0.1, 0.3, 0.5, 0.7, and 0.9 by taking the following ratios of monomers *o*-anisidine/(aniline + *o*-anisidine) as 10:90, 30:70, 50:50, 70:30, and 90:10, respectively. The synthesized copolymer coatings were abbreviated by taking into consideration the feed ratio *o*-anisidine used for the synthesis. For example, the copolymer coating synthesized with a feed ratio of *o*-anisidine 0.5 was abbreviated as PAOA5.

Characterization of the coatings

The FTIR transmission spectra of films were recorded with a Perkin Elmer spectrometer (1600 Series II, USA) in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm^{-1}. The UV–visible absorption study was carried out by dissolving the film in DMSO solution ex situ at room temperature in the wavelength range 300–1100 nm using a microprocessor-controlled double-beam UV–visible spectrophotometer (Model U 2000, Hitachi). The ^1H NMR spectra were obtained on a Bruker DSX-300 solid-state NMR spectrometer, operating at 300 MHz. The measurements were carried out by dissolving the film in DMSO-d_6 solution at ambient temperature. SEM images were recorded with Leica Cambridge 440 microscope (cambridge, England, U.K.).

Study of corrosion protection performance

The corrosion protection performance of the coatings was evaluated in 3% NaCl solution using the potentiodynamic polarization technique. For these measurements, a Teflon holder was used to encase the polymer-coated substrates so as to leave an area of ~0.4 cm^2 exposed to the solution. All the measurements were repeated at least four times, and good reproducibility of the results was observed.

The potentiodynamic polarization measurements were performed by sweeping the potential between −0.25 V and 0.25 V from Open Circuit Potential (OCP) with the scan rate of 0.002 V s^{-1}. The potentiodynamic polarization curves were analyzed using Corr-view software from Scribner Associates, which performs the Tafel fitting and calculates the value of corrosion potential (E_{corr}), corrosion current density (j_{corr}), and corrosion rate (CR) in mm per year.[14]

Results and discussion

PAOA copolymer coatings on mild steel

The cyclic voltammograms of the first scan recorded during the synthesis of homopolymers, i.e., PANI and POA and the copolymer PAOA5 coatings on mild steel substrate from aqueous salicylate solution, are shown in Fig. 1 to be qualitatively similar to those reported by Pawar et al.[11] and Wankhede et al.[15]

The first positive cycle of these voltammograms is characterized by the onset of the oxidation wave followed by oxidation peak (B), which is attributed to the oxidation of monomer(s) present in the electrolyte. During the reverse cycle, the anodic current density decreases rapidly, and a negligibly small current density is observed until −0.223 V versus SCE. The negative cycle terminates with a reduction peak (C), which corresponds to the reduction of an anodically formed species, but its current density is different. Its current density is negligible for PANI and highest for POA while small for the PAOA5 copolymer. The careful examination of these cyclic voltammograms indicates that potential corresponding to the oxidation peak (B) shifts significantly depending on the monomer(s) present in the electrolyte, and it follows the order aniline (1.351 V) > (aniline + *o*-anisidine(50:50)) (1.240 V) > *o*-anisidine (1.078 V). The *o*-anisidine is more reactive than aniline in electrophilic substitution reactions, as –OCH_3 is an electron donating group, and it adsorbs strongly to a metallic substrate.[16] Consequently, during electrochemical polymerization, *o*-anisidine oxidizes at lower potential than aniline. During the electrochemical copolymerization of aniline with *o*-anisidine, the potential corresponding to the oxidation peak lies between the oxidation peak potentials observed for aniline and *o*-anisidine, which may be due to the higher reactivity of *o*-anisidine than that of aniline.

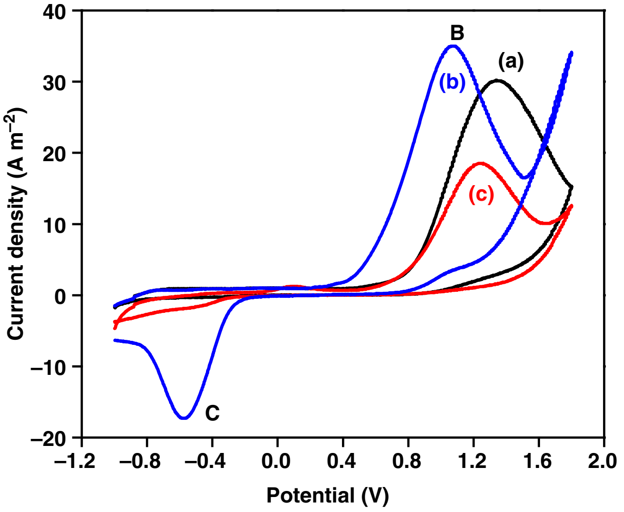


Fig. 1: Cyclic voltammograms of the first scan recorded during the synthesis of (a) PANI, (b) POA, and (c) PAOA5 copolymer coatings on mild steel

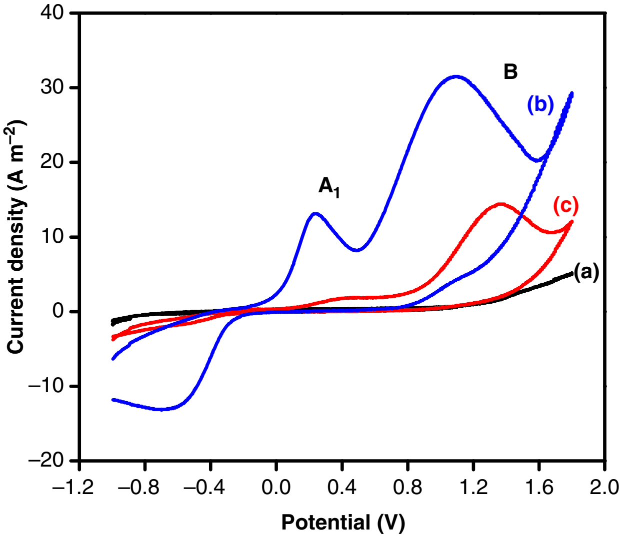


Fig. 2: Cyclic voltammograms of the second scan recorded during the synthesis of (a) PANI, (b) POA, and (c) PAOA5 copolymer coatings on mild steel

The cyclic voltammogram of the second scan recorded during the synthesis of PANI coating on mild steel is shown by curve (a) in Fig. 2. During the second scan, the current densities corresponding to the redox peaks are markedly lower than the one observed during the first scan, indicating the formation of electro inactive coating. The curve (b) in Fig. 2 is a cyclic voltammogram of the second scan recorded during the synthesis of POA coating on mild steel. During the second scan, a broad anodic peak A_1 is observed and rest of the features are similar to that of the first scan. The anodic peak A_1 was assigned to oxidation of deposited film on mild steel corresponding to conversion of amine units into radical cation. However, the current density corresponding to anodic peaks decreases gradually with the number of scans.

The cyclic voltammogram of the second scan recorded during the synthesis of copolymer PAOA5 coating on mild steel is shown by (c) in Fig. 2. The features of this voltammogram are similar to that recorded during the synthesis of POA. However, the current density corresponding to peak A_1 is lower than that observed during the polymerization of *o*-anisidine, which provides the evidence for the formation of copolymer coating on mild steel.

On repetitive cycling, the voltammograms identical to that of second scan are obtained. However, after the third scan, the current density corresponding to the anodic peaks decreases gradually with the number of scans, and the cyclic voltammograms do not show well-defined redox peaks. Cyclic voltammograms of the tenth scan recorded during synthesis of (a) PANI, (b) POA, and (c) PAOA5 copolymer coatings on mild steel are shown in Fig. 3.

The results of cyclic voltammetry suggest that the electrochemical copolymerization of aniline with *o*-anisidine on the mild steel in aqueous salicylate solution generates true copolymer coatings rather than the mixture of the corresponding homopolymers. When the feed concentration of *o*-anisidine in the co-monomer feed is varied, the area of peak A_1 shows the systematic variation. The variation of the area of peak A_1 as a function of the concentration of *o*-anisidine in the co-monomer feed is shown in Fig. 4. It is observed that the area of peak A_1 increases with the increase in concentration of *o*-anisidine in the co-monomer feed.

FTIR spectroscopy results

The FTIR spectra of homopolymers, PANI and POA, and copolymer PAOA5 coatings on mild steel are shown in Fig. 5. The FTIR spectrum of PANI coating synthesized on mild steel under cyclicvoltammetric conditions is presented in Fig. 5a.The broad band at ~3354 cm^{-1} is due to N–H stretching mode, C=N, and C=C stretching mode for the quinoid (*Q*), and benzoid (*B*) rings occur at 1596 and 1511 cm^{-1}, respectively. The band at ~1303 is assigned to the C–N stretching mode for B rings, and the bands between 800 and 700 cm^{-1} reveal the occurrence of the 1–3 substitutions. The band at 1247 cm^{-1} is attributed to the presence of carboxylic groups of sodium salicylate in the polyaniline coating.[17–20]

The FTIR spectrum of the POA coating synthesized on mild steel is shown in Fig. 5b. This spectrum exhibits the following spectral features: a broad band at ~3258 cm^{-1} due to the characteristic N–H stretching vibration suggests the presence of NH groups in *o*-anisidine units; the band at ~1515 cm^{-1} is indicative of stretching vibrations in quinoid (Q) rings; the band ~1484 cm^{-1} represents the stretching vibrations of the benzoid (B) rings; the presence of Q and B bands clearly show that the POA coating is composed of amine and imine units; the bands at 1246 cm^{-1} are attributed to the presence of carbonyl groups of

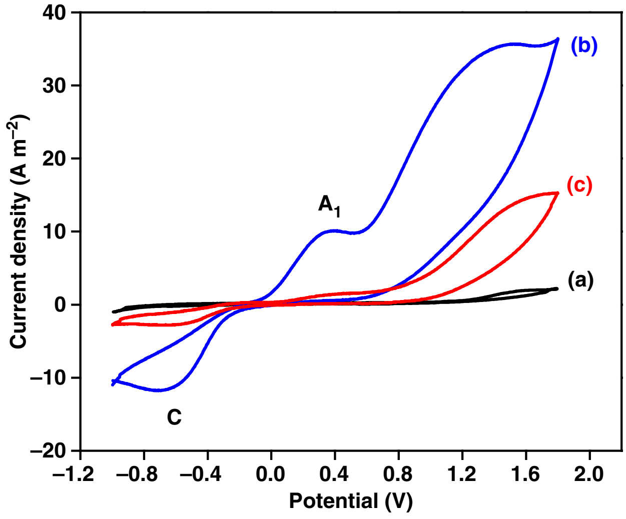


Fig. 3: Cyclic voltammograms of the tenth scan recorded during synthesis of (a) PANI, (b) POA, and (c) PAOA5 copolymer coatings on mild steel

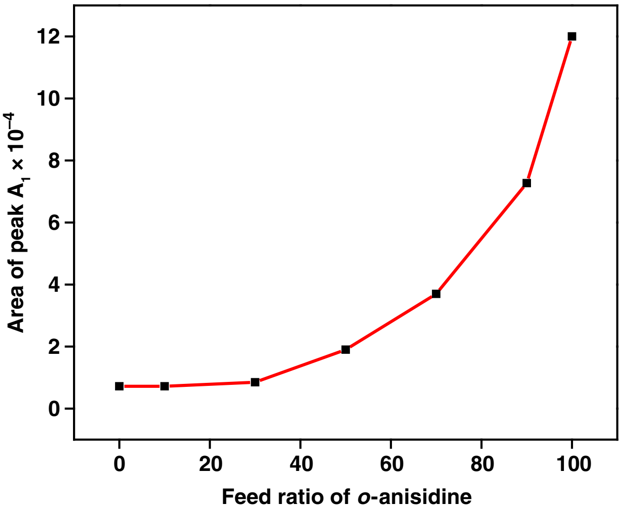


Fig. 4: Variation of the area of the peak A_1 as a function of feed ratio of *o*-anisidine

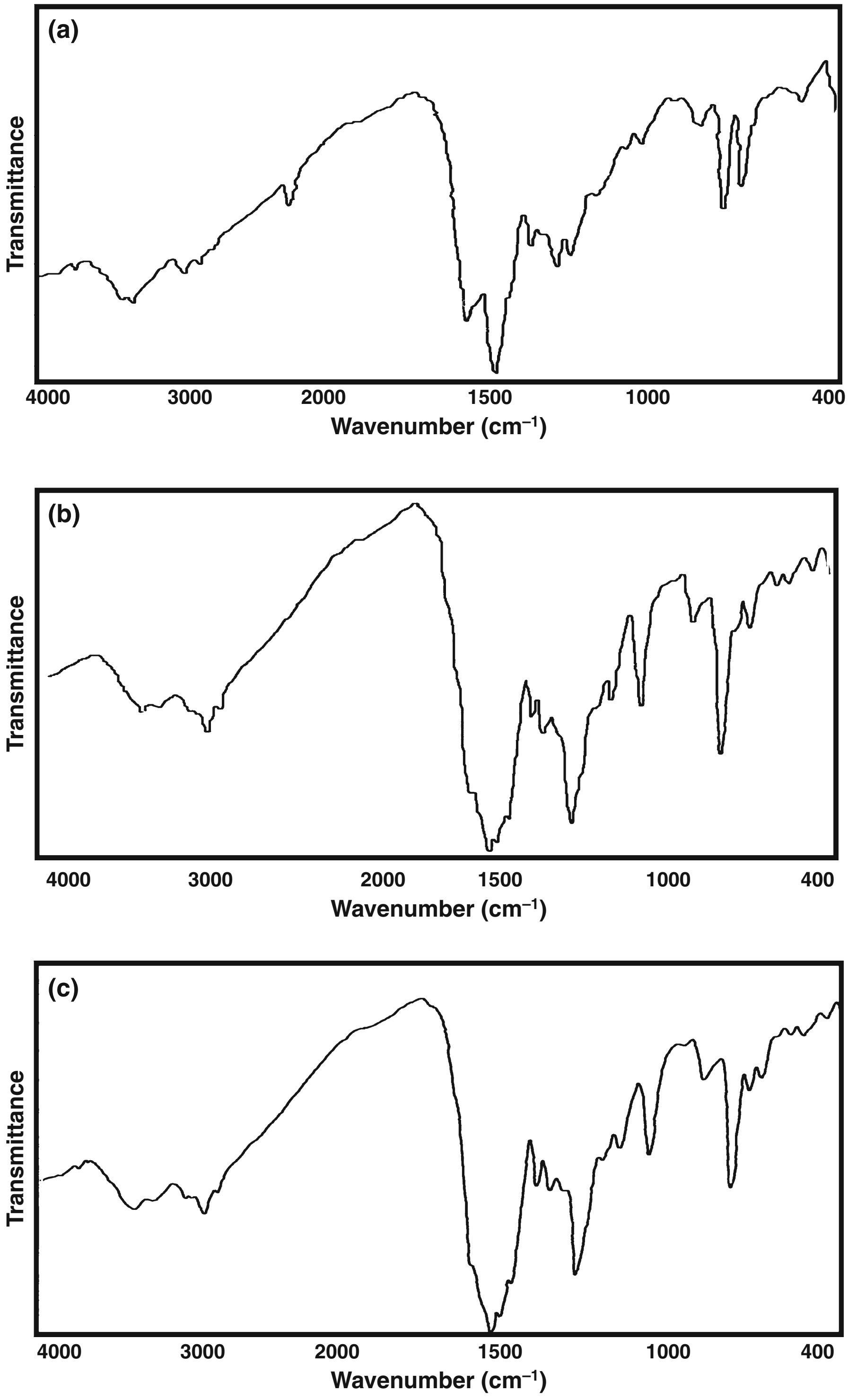


Fig. 5: FTIR spectra of the (a) PANI, (b) POA, and (c) PAOA5. Copolymer coatings synthesized on mild steel substrate using cyclic voltammetry

salicylate in the POA coating; the band at ~1458 cm^{-1} is assigned to the C–N stretching vibrations in quinoid imine units; the bands at 1115, 1021, and 847 cm^{-1} are attributed to the 1–4 substitution on the benzene ring; the band at ~1170 cm^{-1} is considered as a measure of the degree of delocalization of the electrons on POA and is referred to as the electronic like band; and the bands between 800 and 700 cm^{-1} reveal the occurrence of the 1–3 substitutions. Thus, the FTIR spectroscopic study indicates that the electrochemical polymerization of *o*-anisidine has occurred and results into the formation of POA.

The FTIR spectrum of the PAOA5 copolymer coating on mild steel is presented in Fig. 5c. The most striking feature of this spectrum is that it exhibits very similar characteristics to those of POA. Thus, in the resulting PAOA5 copolymer, there are more ***o***-anisidine units.

NMR spectroscopy results

To establish that PAOA5 is a copolymer rather than a mixture of homopolymers PANI and POA, these polymers were further characterized with ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of PANI, POA, and PAOA5, recorded in DMSO-d_6, are shown in Fig. 6. These three ^{1}H-NMR spectra show three common signals:[21–24] (i) Signals in the region of ~6.3–8.2 ppm are due to the protons of aromatic rings. (ii) The two strongest peaks in the region of 2.3–3.5 ppm are due to protons of DMSO and water in DMSO. (iii) Negligibly, small signals in the region 5.2–6.1 ppm are assigned to –NH linkages.

^{1}H-NMR spectrum of POA Fig. 6b is characterized by resonances in the region of 3.5–4 ppm, which are attributed to the methoxy protons along with three common signals.

The ^{1}H-NMR spectrum of the PAOA5 copolymer in Fig. 6c has essentially the same characteristics as

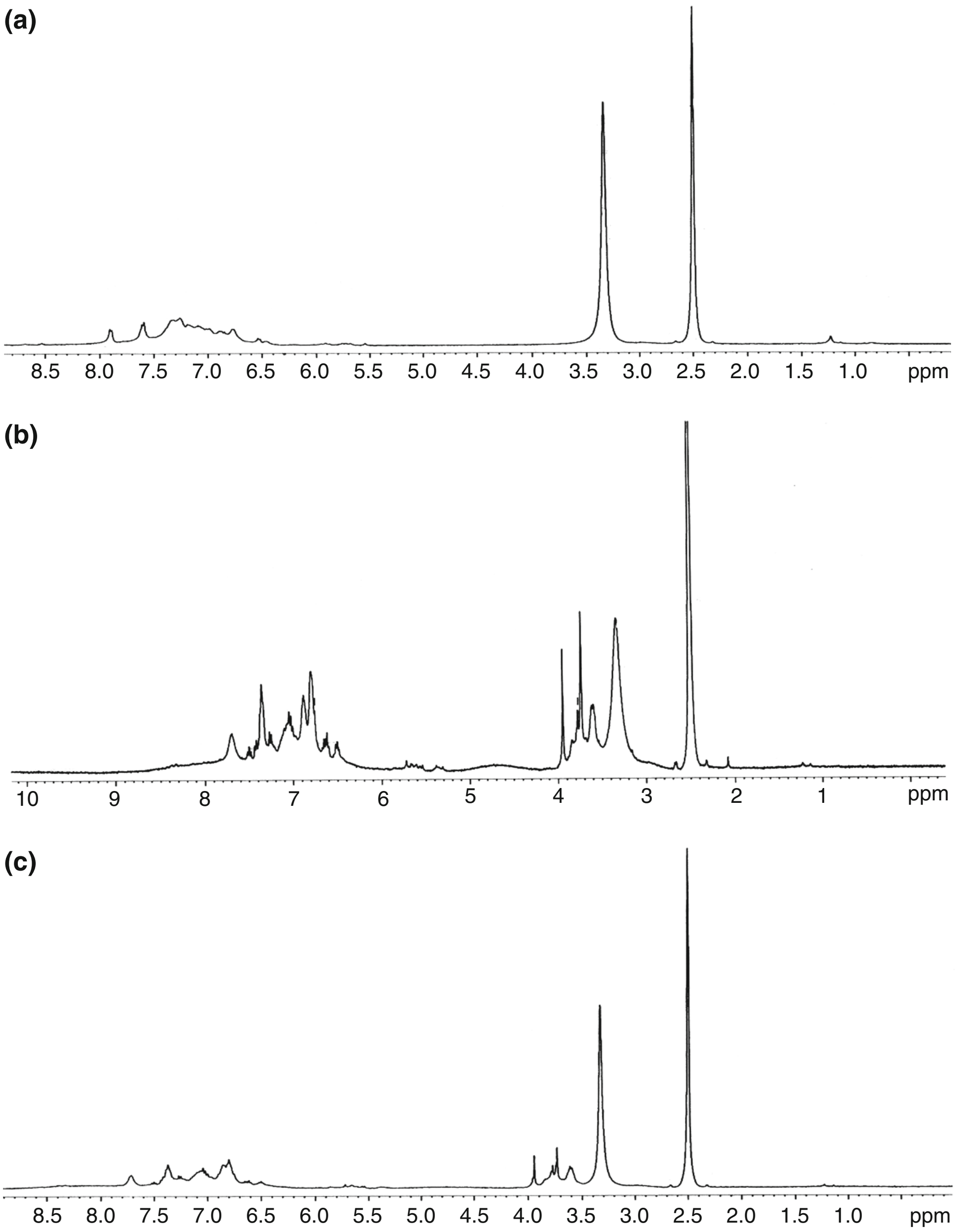


Fig. 6: ^{1}H NMR spectra of (a) PANI, (b) POA, and (c) PAOA5 copolymer on mild steel recorded in DMSO-d_6 at 300 MHz

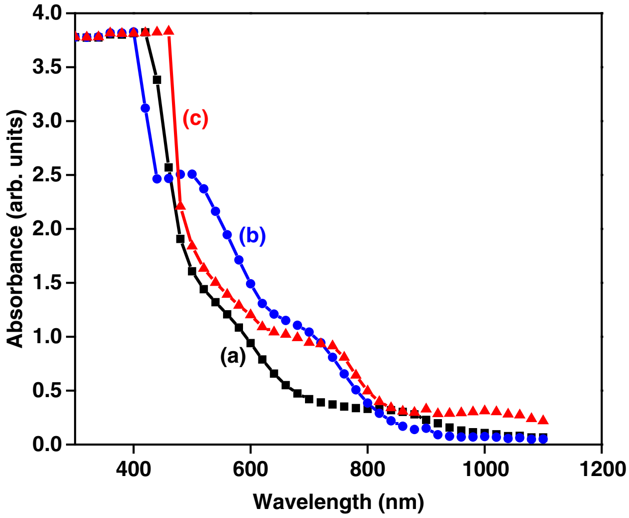


Fig. 7: UV–visible absorption spectra of (a) PANI, (b) POA, and PAOA5 copolymer coatings on mild steel. (The spectrum was recorded ex situ in DMSO solution)

that of POA. This spectrum is characterized by three common signals as explained above that exactly correspond to the three types of protons on the copolymer chains. It also exhibits that the resonance peaks from 3.5 to 4 ppm are assigned to the protons of the methoxy groups on the quinoid ring. Thus, the ^{1}H NMR spectroscopic study confirms that aniline and *o*-anisidine are indeed able to copolymerize on mild steel in an aqueous salicylate medium, and in the resulting PAOA5 copolymer, there are more *o*-anisidine units than that of aniline.

UV–visible absorption spectroscopy results

The UV–visible absorption spectrum of the PANI coating synthesized on mild steel is presented by curve (a) in Fig. 7 which shows a high value of the absorbance between 600 and 800 nm, which may be due to the formation of some species with other oxidation states. Thus, the optical absorption spectroscopy reveals the formation of the emeraldine salt (ES) form along with some other oxidation-state species.[25]

The curve (b) in Fig. 6 is the UV–visible absorption spectrum of the POA coating which shows a well-defined peak at ~500 nm and a shoulder at ~700 nm. The peak at 500 nm is attributed to the formation of pernigraniline base (PB), which is the fully oxidized form of POA. The shoulder at 700 nm is the signature of the formation of the ES form of the POA. The ES is the only electrically conducing form of POA. The simultaneous appearance of the 500 nm peak and the shoulder at 700 nm reveals the formation of the mixed phase of PB and ES forms of POA.

The UV–visible absorption spectrum of the PAOA5 copolymer coating presented by (c) in Fig. 7 shows a well-defined peak at 540 nm, and it is attributed to the formation of the PB form of PAOA5.

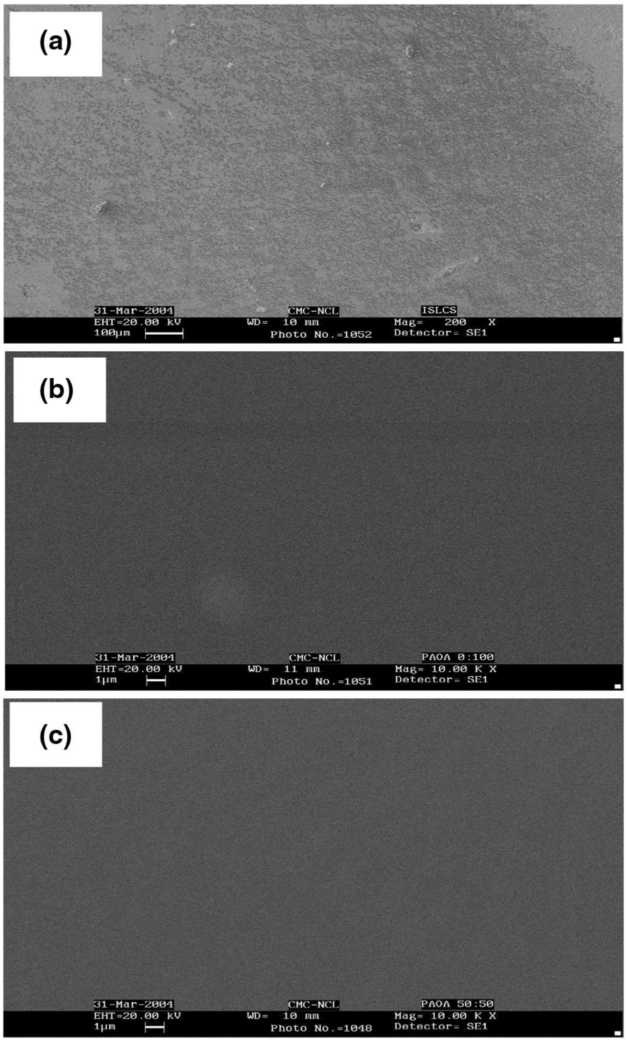


Fig. 8: SEM images of (a) PANI, (b) POA, and (c) PAOA5 copolymer-coated mild steel

SEM results

The surface morphology of the PANI coating in Fig. 8a is rough, and it is characterized by the presence of pores in the coating. The surface morphology of the POA coating in Fig. 8b is relatively uniform and featureless.

The SEM image of the copolymer PAOA5 coating synthesized on mild steel is shown in Fig. 8c. It clearly reveals that the copolymer PAOA5 coating is relatively uniform, featureless, and pore-free.

Evaluation of corrosion protection performance

The porosity in the coating is a very important parameter which decides its suitability to protect the substrate against corrosion. In this work, the porosity in PANI, POA, and PAOA5 copolymer coatings on mild steel substrates was determined from potentiodynamic polarization measurements. The potentiodynamic polarization curves of uncoated mild steel, PANI-coated mild steel, POA-coated mild steel, and PAOA5-coated mild steel (15 cycles) recorded in aqueous 3% NaCl are shown in Fig. 9. The values of the corrosion potential (E_{corr}), corrosion current density (j_{corr}), Tafel constants (β_a and β_c), polarization resistance (R_p), and corrosion rate obtained from these curves are given in Table 1. In order to calculate the porosity of these deposits, we have used the relationship[26]:

$$P = \frac{R_{pol}(\text{uncoated})}{R_{pol}(\text{coated})} 10^{-\left(\frac{|\Delta E_{corr}|}{\beta a}\right)}$$

where P is the total porosity, R_{pol}(uncoated) is the polarization resistance of uncoated mild steel, R_{pol} (coated) is the measured polarization resistance for coated mild steel, ΔE_{corr} is the difference between corrosion potentials, and β_a is the anodic Tafel slope for uncoated mild steel substrate. Table 1 also gives the porosity values in the polymer deposits. The porosity in PANI, POA, and PAOA5 copolymer coating was found to be ~3.2×10^{-2}, 2.25×10^{-3}, and 1.83×10^{-4}, respectively. The significantly lower values of the porosity in PAOA5 copolymer coatings as compared with the respective homopolymer coatings permit substantial improvement of the corrosion resistance by hindering the access of the electrolyte to the stainless steel substrates. The analysis of these potentiodynamic polarization curves shows the positive shift in the E_{corr} and substantial reduction in the j_{corr} of the mild steel due to the PANI, POA, and PAOA5 coatings, which indicates the corrosion resistant character of the PANI, POA, and PAOA5. It is found that the shift in the E_{corr} depends on the coating and decreases in the order PAOA5 > POA > PANI. This implies that the copolymer PAOA5 coating provides effective protection to mild steel against corrosion in aqueous 3% NaCl as compared to that of the corresponding homopolymers.

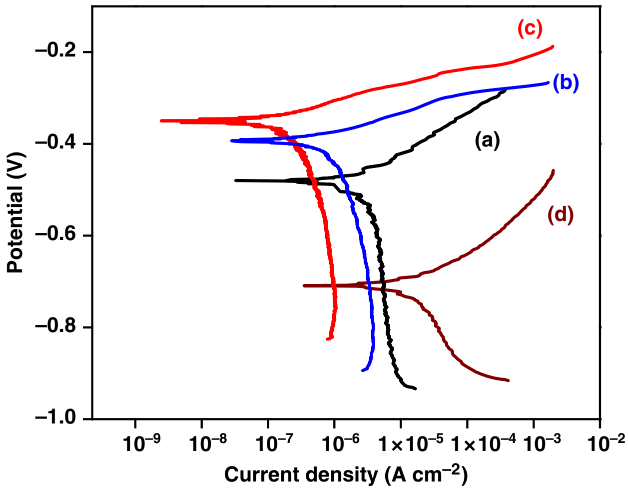


Fig. 9: Potentiodynamic polarization curves for (a) PANI-coated mild steel, (b) POA-coated mild steel, (c) PAOA5-coated mild steel, and (d) uncoated mild steel recorded in aqueous 3% NaCl solution

It is shown that the j_{corr} decreases from 17.79 μA cm^{-2} for uncoated mild steel to 3.67, 1.11, and 0.24 μA cm^{-2} for PANI-, POA-, and PAOA5-coated mild steel, respectively. The corrosion rates of PANI-, POA-, and PAOA5-coated mild steel are found to be ~0.04, 0.01, and 0.0028 mm year,$^{-1}$ which are ~5, 17, and 100 times lower than that observed for uncoated mild steel. The protection efficiency (PE) is calculated using the expression

$$\text{PE} = \left[\frac{R_{pol}(\text{coated}) - R_{pol}(\text{uncoated})}{R_{pol}(\text{coated})}\right] \times 100$$

where R_{pol} (uncoated) and R_{pol} (coated) denote the polarization resistance of uncoated mild steel and polymer-coated mild steel, respectively. The protection efficiencies for PANI, POA, and PAOA5 copolymer calculated from potentiodynamic polarization data are found to be ~84.03, 90.17, and 97.57%. These results

Table 1: Results of potentiodynamic polarization measurements

Sample	E_{corr} (V)	j_{corr} (μA cm^{-2})	β_a (V dec^{-1})	β_c (V dec^{-1})	R_p (Ω cm^{-2})	CR (mm year^{-1})	% P	% PE
Uncoated mild steel	−0.710	17.79	0.0912	0.270	1.66×10^3	0.20	–	–
PANI	−0.464	3.67	0.0947	1.270	1.04×10^4	0.042	32×10^{-3}	84.03
POA	−0.378	1.11	0.046	0.661	1.69×10^4	0.012	2.25×10^{-3}	90.17
PAOA1	−0.359	4.66	0.028	0.274	2.411×10^3	0.025	9.78×10^{-3}	30.95
PAOA3	−0.388	0.43	0.067	0.374	5.78×10^4	0.005	8.74×10^{-4}	97.12
PAOA5	−0.334	0.24	0.0409	−0.518	6.86×10^4	0.0028	1.83×10^{-4}	97.57
PAOA7	−0.344	0.44	0.0242	−0.846	2.32×10^4	0.0051	6.94×10^{-4}	92.84
PAOA9	−0.343	0.63	0.0359	0.416	2.27×10^4	0.0073	6.91×10^{-4}	92.69

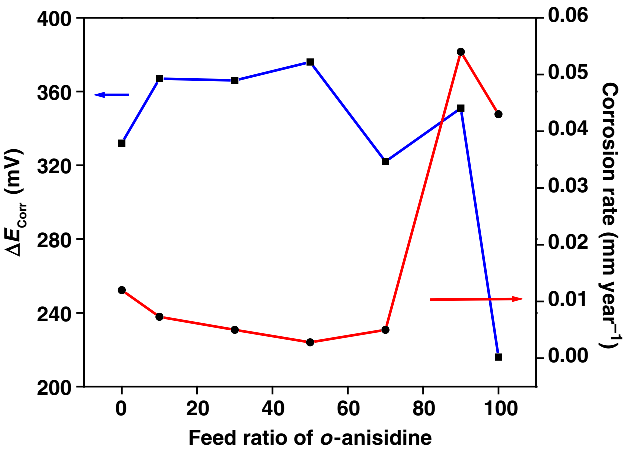


Fig. 10: Dependence of ΔE_{corr} and corrosion rate on the feed ratio of *o*-anisidine

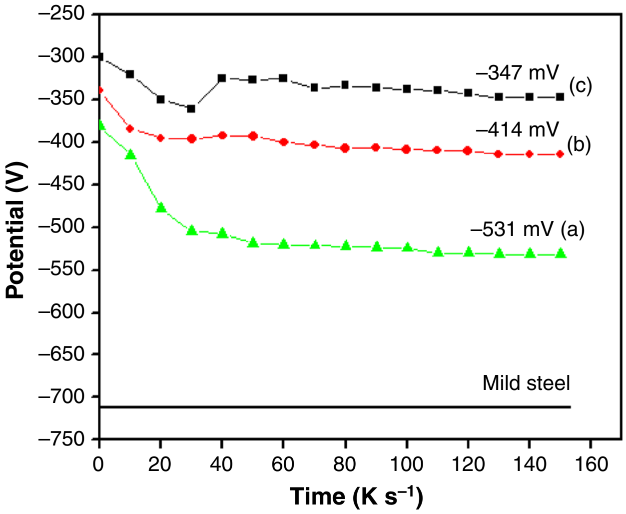


Fig. 11: Open circuit potential/time curve recorded for (a) PANI, (b) POA, and (c) PAOA5 coatings in aqueous 3% NaCl. The continuous line represents the open circuit potential of uncoated mild steel

reveal that the PAOA5 copolymer effectively protects the mild steel and improves the corrosion protection efficiency over what is offered by the corresponding homopolymers.

To investigate the influence of the *o*-anisidine concentration in the co-monomer feed on the corrosion protection properties of the PAOA copolymer coatings, we have synthesized the coatings using a feed ratio of *o*-anisidine as 0.1, 0.3, 0.5, 0.7, and 0.9, and the potentiodynamic polarization measurements were performed in aqueous 3% NaCl solution. The dependence of the positive shift in E_{corr} (ΔE_{corr}) on the feed ratio of *o*-anisidine is shown in Fig. 10. It is found that the ΔE_{corr} increases with the feed ratio of *o*-anisidine, and it attains a maximum value of −0.376 V at 0.5 feed ratio. With further increase in the feed ratio of *o*-anisidine to 0.7, the ΔE_{corr} decreases to −0.366 V, and beyond this it does not show any significant variation in ΔE_{corr}.

The variation of the corrosion rate as a function of the feed ratio of *o*-anisidine is also shown in Fig. 10. It is observed that initially corrosion rate decreases significantly when the feed ratio of *o*-anisidine increases, and it is found to be lowest (~100 times lower than uncoated mild steel) for the feed ratio of 0.5. With further increase in the feed ratio of *o*-anisidine, the corrosion rate increases slowly, and with the feed ratio of 1, the corrosion rate is found to be 0.012 mm year^{-1}. Thus, the more effective protection of the mild steel against the corrosion in 3% NaCl can be achieved by the copolymer coatings synthesized with a feed ratio of *o*-anisidine as 0.5.

Open circuit potential

Conclusive evidence for corrosion resistance of these coatings can be characterized after prolonged exposure to NaCl. So the open circuit potential/time curves recorded in aqueous 3% NaCl for PANI-, POA-, and PAOA5-coated mild steel are presented in Fig. 11. In this figure, −710 mV stands for the corrosion potential (E_{corr}) of uncoated mild steel. The initial open circuit potential values measured for PANI-, POA-, and PAOA5-coated mild steel are −381, −339, and −319 mV versus SCE and are more positive than that of uncoated mild steel. In the early stages of the immersion, the open circuit potential in each case decreases rapidly, and this may be due to the initiation of the water uptake process through the pores in the coating toward the substrate surface. However, these values are more positive than that of uncoated mild steel.

The open circuit potential of PAOA5-coated mild steel remains almost constant for longer periods (41.5 h), and its potential value is more noble with respect to the open circuit value of the uncoated mild steel and homopolymer-coated mild steel. During this immersion period, the PAOA5 coating exhibits barrier behavior by limiting the diffusion of the corrosive species toward the underlying steel substrate. This behavior is attributed to the corrosion protection effect for the mild steel caused by the PAOA5 copolymer coating.

Conclusions

Strongly adherent PAOA coatings were successfully synthesized on mild steel substrates from aqueous salicylate solutions with cyclic voltammetry. The performance of the PAOA coatings as protective coatings against the corrosion of mild steel in aqueous 3% NaCl solutions was investigated by the potentiodynamic polarization technique. The following main findings resulted from this investigation:

- The results clearly show that an aqueous sodium salicylate solution is a suitable medium for the electrochemical copolymerization of aniline with *o*-anisidine on mild steel.
- The FTIR and ^{1}H-NMR spectroscopy studies reveal that the copolymerization of aniline and *o*-anisidine takes place on mild steel in aqueous salicylate solutions, and in the resulting PAOA copolymer, there are more *o*-anisidine units than aniline units.
- The porosity in the coating has been estimated with the potentiodynamic polarization measurements, and the porosity values are significantly lower for the PAOA coatings than for the respective homopolymers, that is, PANI and POA. The copolymer coatings are more compact and strongly adherent to mild steel.
- The potentiodynamic polarization measurements reveal that the PAOA coatings effectively protect mild steel and have higher corrosion PEs than those offered by the corresponding homopolymers.
- The protection of mild steel against corrosion in 3% NaCl by the copolymer coatings can be achieved more effectively when the synthesis is carried out with a feed ratio of *o*-anisidine of 0.5.

Acknowledgments Authors would like to acknowledge UGC for the financial support via minor research project. The first author would also like to acknowledge Prof. P. P. Patil from North Maharashtra University specially for providing the lab for synthesis and testing the corrosion performance of samples as well as for the co-operative environment during this work.

References

1. Skotheim, TA (ed.) *Handbook of Conducting Polymers*, Vol. I–II. Marcel Dekker Inc., New York (1986)
2. Nalwa, HS, *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1–4. Wiley, New York (1997)
3. Aldissi, M, *Intrinsically Conducting Polymers: An Emerging Technology*. Kluwer Academic Publishers, Dordrecht (1993)
4. Mohammad, F (ed.) *Specialty Polymers: Materials and Applications*, Chapter 5, pp. 147–206. I. K. International Publishing House Pvt. Ltd., New Delhi (2007)
5. Cohen, SM, ''Review: Replacements for Chromium Pretreatments on Aluminum.'' *Corrosion*, **51** 71–78 (1995)
6. Twite, RL, Bierwagen, GP, ''Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys.'' *Prog. Org. Coat.*, **33** 91–100 (1998)
7. Ohtsuka, T, ''Review Article Corrosion Protection of Steels by Conducting Polymer Coating.'' *Int. J. Corr.*, (2012). doi:10.1155/2012/915090
8. Tanveer, N, Mobin, M, ''Corrosion Protection of Carbon Steel by Poly (aniline-co-o-toluidine) and Poly (pyrrole-co-o-toluidine) Copolymer Coatings.'' *J. Miner. Mater. Charact. Eng.*, **10** (8) 735–753 (2011)
9. Hur, E, Bereket, G, Sahin, Y, ''Electrochemical Synthesis and Anti-corrosive Properties of Polyaniline, Poly(2-anisidine), and Poly(aniline-co-2-anisidine) Films on Stainless Steel.'' *Prog. Org. Coat.*, **54** 63–72 (2005)
10. Hur, E, Bereket, G, Sahin, Y, ''Anti-corrosive Properties of Polyaniline, Poly(2-toluidine), and Poly(aniline-co-2-toluidine) Coatings on Stainless Steel.'' *Curr. Appl. Phys.*, **7** 597–720 (2007)
11. Pawar, P, Gaikwad, AB, Patil, PP, ''Electrochemical Synthesis of Corrosion Protective Polyaniline Coatingson Mild Steel from Aqueous Salicylate Medium.'' *Sci. Technol. Adv. Mater.*, **7** 732–744 (2006)
12. Pawar, P, Gaikwad, AB, Patil, PP, ''Corrosion Protection Aspects of Electrochemically Synthesized Poly(o-anisidine-co-o-toluidine) Coatings on Copper.'' *Electrochim. Acta*, **52** 5958–5967 (2007)
13. *Electrochemistry and Corrosion—Overview and Techniques.* Application Note CORR-4. EG and G Princeton Applied Research: Princeton, NJ (1989)
14. *Electrochemical Corrosion Software-CorrWare and CorrView*. Scribner Associates Inc., Southern Pines, NC.
15. Wankhede, MG, Gaikawad, AB, Patil, PP, ''Electrochemical Polymerization of o-Anisidine on Low Carbon Steel from Aqueous Salicylate Solution: Corrosion Protection Study.'' *Surf. Coat. Technol.*, **201** 2240–2247 (2006)
16. Huerta-Vilca, D, Siefert, B, Moraes, SR, Pantoja, MF, Motheo, AJ, ''PAni as Prospective Replacement of Chromium Conversion Coating in the Protection of Steels and Aluminum Alloys.'' *Mol. Cryst. Liq. Cryst.*, **415** 229–238 (2004)
17. Tang, J, Jing, X, Wang, B, Wang, F, ''Infrared-Spectra of Soluble Polyaniline.'' *Synth. Met.*, **24** 231–238 (1988)
18. Ohsaka, T, Ohnuki, Y, Oyama, N, Katagiri, G, Kamisako, K, ''IR Absorption Spectroscopic Identification of Electroactive and Electroinactive Polyaniline Films Prepared by the Electrochemical Polymerization of Aniline.'' *J. Electroanal. Chem.*, **161** 399–405 (1984)
19. Zheng, WY, Levon, K, Taka, T, Laakso, J, Osterholm, JE, ''Doping-Induced Layered Structure in *N*-Alkylated Polyanilines.'' *Polym. J.*, **28** 412–418 (1996)
20. Neoh, KG, Kang, ET, Tan, KL, ''Structural Study of Polyaniline Films in Reprotonation/Deprotonation Cycles.'' *J. Phys. Chem.*, **95** 10151–10156 (1991)
21. Mav, I, Zigon, M, ''Synthesis and NMR Characterization of a Novel Polyaniline Derivative.'' *Polym. Bull.*, **45** 61–68 (2000)
22. Wei, Y, Hariharan, R, Patel, SA, ''Corrosion Protection of Carbon Steel by Poly (aniline-co-o-toluidine) and Poly (pyrrole-co-o-toluidine) Copolymer Coatings.'' *Macromolecules*, **23** 758–764 (1990)
23. Li, X-G, Huang, M-R, Hua, Y-M, Zhu, M-F, Qunchen, J, ''Facile Synthesis of Oxidative Copolymers from Aminoquinoline and Anisidine.'' *Polymer*, **45** 4693–4704 (2004)
24. Patil, S, Ph.D. Thesis, North Maharashtra University, Jalgaon, India, 2000
25. Creus, J, Mazille, H, Idrissi, H, ''Porosity Evaluation of Protective Coatings Onto Steel, Through Electrochemical Techniques.'' *Surf. Coat. Technol.*, **130** 224–232 (2000)
26. Chaudhari, S, Mandale, AB, Patil, KR, Sainkar, SR, Patil, PP, ''Formation of Poly(o-anisidine) Coatings on Copper from Aqueous Salicylate Solution.'' *Surf. Coat. Technol.*, **200** 5557–5565 (2006)

Performance of Poly (Aniline-co-o-Toluidine) Coatings Against Corrosion of Copper

Article · September 2016

4 authors, including:

Pritee Mahesh Raotole
Arts, Science and Commerce College ,Chopda

Sandip Patil
MGSM'S Arts Science and Commerce College Chopda, Dist- Jalgaon-425107.

International Journal of Metallurgy and Alloys
Vol. 1: Issue 2
www.journalspub.com

Performance of Poly (Aniline-*co*-*o*-Toluidine) Coatings Against Corrosion of Copper

Pritee M. Raotole[1]*, *Mahesh L. Raotole*[2], *R. S. Khadayate*[3], *S.R. Patil*[1]
[1]MGSM's Arts, Science and Commerce College, Chopda, Dist-Jalgaon, Maharashtra, India
[2]Sharacchandrika Suresh Patil, Institute of Technology, Polytechnic, Chopda, Dist-Jalgaon, Maharashtra, India
[3]G.D.M. Arts, K. R. N. Commerce and M. D. Science College, Jamner, Dist-Jalgaon, Maharashtra, India

Abstract

The corrosion protective poly(aniline-co-o-toluidine) (PAOT) coatings were synthesized on copper (Cu) by the electrochemical copolymerization of aniline with o-toluidine under cyclic voltammetry conditions. Aqueous oxalate solutions were used as the supporting electrolytes for the synthesis of PAOT coatings on Cu. The FTIR and ^{1}*H NMR spectroscopy studies reveal that the copolymerization of aniline and o-toluidine takes place on Cu substrates from an aqueous oxalate solutions and resulting in PAOT copolymer, there are more o-toluidine units than aniline units. The corrosion protection performance of PAOT coatings on Cu was investigated in aqueous 3% NaCl solutions by a potentiodynamic polarization technique. The results of the potentiodynamic polarization measurements showed that the PAOT coatings provided more effective corrosion protection to Cu than the respective homopolymers. The corrosion rate depended on the feed ratio of o-toluidine used for the synthesis of the copolymer coatings.*

Keywords: copper, corrosion protective coatings, conducting polymer, cyclic voltammetry, electrochemical copolymerization, poly (aniline-*co*-*o*-toluidine)

****Corresponding Author***
E-mail: pritee_pawar@yahoo.com

INTRODUCTION

The use of conducting polymers for the protection of oxidizable metals against corrosion is well established, because they can be easily synthesized on metallic surfaces from aqueous media by electrochemical polymerization route.[1–11] Electrochemical synthesis of conducting polymers has its advantages;[12,13] it permits the synthesis without oxidizing agent together with doping with different organic and inorganic ions. Also, electrochemical synthesis takes place directly on the metal surface and is expected to have better adherence than in the case of chemically synthesized conducting polymers. The main problem dealing with electrochemical synthesis of conducting polymers on oxidizable metals is dissolution of the base metal in the beginning of polymerization, so only few electrolytes suitable for polymerization were reported.

At the same time, the extent of using the conducting polymers is limited due to the exclusivity of the monomers that are essential for their synthesis.[12,13] In this context, the use of copolymerization to prepare new polymers with inbuilt tailor-made properties suitable for the application has attracted much interest in recent years. Hur et al.[14] reported the electrochemical synthesis of poly(aniline-*co*-2-toluidine) films on stainless steel in tetra butyl ammonium perchlorate /

acetonitrile solution containing perchloric acid. They found that the PANI coatings provide much better protection to stainless steel than poly(2-anisidine) and poly(aniline-*co*-2-anisidine) films. It has been shown that the protection properties of PANI are related to the passivation of steel and barrier effect, while the protection of steel by poly(2-anisidine) and poly(aniline-*co*-2-anisidine) films is mainly through the barrier effect. Bereket et al.[15] synthesized poly(aniline-*co*-2-anisidine) films on stainless steel by using the synthesis conditions identical to those used by Hur et al.[14] They found that the PANI, poly(2-anisidine) and poly(aniline-*co*-2-anisidine) films have corrosion protection effect for stainless steel in aggressive medium of 0.5 M HCl solution. However, the durability of the poly(aniline-2-anisidine) films is limited to 3 hours.

Shinde et al.[4] synthesized poly(o-toluidine) POT coatings on Cu substrates under cyclic voltammetric conditions from an aqueous solution of sodium oxalate. The POT acts as corrosion protective coating on Cu and reduces the corrosion rate of Cu almost by a factor of 40.

Recently, we have deposited strongly adherent poly(aniline-*co*-*o*-toluidine) coatings on low carbon steel (LCS) substrates by the electrochemical copolymerization of aniline with o-toluidine with sodium tartrate as the supporting electrolyte. The results of the potentiodynamic polarization measurements showed that the poly(aniline-*co*-*o*-toluidine) coatings provided more effective corrosion protection to LCS than the respective homopolymers, Pawar et al.[16–26].

However, considerable research efforts still needed – to synthesize uniform, compact and strongly adherent new copolymer coatings applicable for corrosion protection; to find potentially good, low cost and easily available electrolytes for the electrochemical copolymerization on mild steel and Cu; to explore the possibility of utilizing copolymer coatings for corrosion protection of mild steel and Cu and to provide a better understanding of the merits and limitations to the use of copolymers for corrosion protection.

EXPERIMENTAL PROCEDURE

Materials

All chemicals were of analytical grade. The monomers, aniline and o-toluidine were procured from Fluka and were doubly distilled prior to being used for the synthesis. Sodium oxalate ($Na_2C_2O_4$) were procured from Merck and used as-received without further purification. Bi-distilled water was used to prepare all the solutions.

Substrate Preparation

The Cu substrates (size ~10 × 15 mm and 0.5 mm thick) were carefully ground to grade 1200 emery papers. After polishing, the substrates were cleaned with 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.

Electrochemical Syntheses

The PANI, POT and PAOT copolymer coatings were synthesized on Cu substrates by using cyclic voltammetry. The electrochemical syntheses were carried in a single compartment three electrode cell with Cu as working electrode (150 mm^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 (USA) controlled by Power Suite software (Perkin Elmer Instruments, 2000 supplied by EG and G, Princeton Applied Research, USA).[16]

PAOT Copolymer Coatings on Cu

The aqueous sodium oxalate solution was used as the supporting electrolyte to synthesize the homopolymers PANI and POT and PAOT copolymer coatings on Cu and its concentration was kept constant at 0.2 M. For the electrochemical homopolymerization of aniline and o-toluidine, their concentrations kept constant at 0.3 and 0.1 M, respectively. For the electrochemical copolymerization, a mixture of aniline and o-toluidine a total concentration of 0.1 M was used in 0.2 M aqueous oxalate solution.

The copolymer synthesis experiments were carried out by using feed ratio of o-toluidine as 0.3, 0.5 and 0.7 by taking the following ratios of monomers o-toluidine/(aniline+o-toluidine) as 30:70, 50:50 and 70:30, respectively. The synthesis of polymer coatings was carried out by cycling continuously the electrode potential between – 0.5 V and 1.5 V versus SCE at a potential scan rate of 0.02 V/s (0.2 V/s for PANI). After fifteen cycles, the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air. The synthesized copolymer coatings were abbreviated by taking into consideration the feed ratio of o-toluidine used for the synthesis. For example, the copolymer coating synthesized with a feed ratio o-toluidine 0.5 was abbreviated as PAOT5.

Characterization of the Coatings

The FTIR transmission spectra were recorded with a Perkin Elmer spectrometer (1600 Series II, USA) in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm^{-1}. SEM images were recorded with a Leica Cambridge 440 microscope (Cambridge, England, UK). The UV–visible absorption study was carried out *ex situ* at room temperature in the wavelength range 300–1100 nm using microprocessor controlled double beam UV–visible spectrophotometer (Model U 2000, Hitachi). 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.

Study of Corrosion Protection Performance

The corrosion protection performance of the coatings was evaluated in 3% NaCl solution by using open circuit potential (OCP) measurements and potentiodynamic polarization technique using a electrochemical measurement system (SI 1280B, Solartron, UK). As corrosion of metals occurs most in salty water or sea water. Sea water contains ~3 % by weight of salt (sodium chloride). Hence, for testing the corrosion protection performance of coating we had used 3% NaCl solution as corrosive media.

For these measurements, a Teflon holder was used to encase the polymer coated substrates so as to leave an area of ~0.4 cm^2 exposed to the solution. All the measurements were repeated at least four times and good reproducibility of the results was observed.

The potentiodynamic polarization measurements were performed by sweeping the potential between –0.25 and 0.25 V from Open Circuit Potential (OCP). In fact, in corrosion studies, the appropriate scan rate is very important to determine in the first place, because it would be different dependent on the type of metal used, environment (acidic, basic or neutral) and the types of corrosion inhibitors applied. In literature most of researchers have used scan rate of 0.001–0.002 V/s in case of conducting polymer coatings for potentiodynamic polarization measurement so I had preferred that one.

The used optimized scan rate at 0.002 V/s. The potentiodynamic polarization curves were analyzed by using Corr-view software from Scribner Associates which performs the Tafel fitting and calculates the values of the corrosion potential (E_{corr}), corrosion current density (j_{corr}) and corrosion rate (CR) in mm per year.[17]

RESULTS AND DISCUSSION

PAOT Copolymer Coatings on Cu

Recently, Patil et al.[18] investigated the anticorrosive properties of electrosynthesized POA coatings on Cu from aqueous oxalate medium. It was shown that the polarization of the Cu electrodes in 0.1 M aqueous sodium oxalate solution (without monomer) by cycling continuously the electrode potential between −0.5 and 1.5 V versus SCE at a potential scan rate of 0.02 V/s results into the passivation of the electrode surface via the formation of polycrystalline copper oxalate (CuC_2O_4, H_2O) phase. Therefore, we have made an attempt to synthesize the PAOT copolymer coatings on Cu from aqueous oxalate solution by cycling continuously the electrode potential between −0.5 and 1.5 V versus SCE at a potential scan rate of 0.02 V/s.

The synthesis of PAOT copolymer coatings on the Cu was carried by employing various potential intervals, in order to determine optimum potential window to obtain good quality coatings. It is found that the uniform and strongly adherent PAOT copolymer coatings were obtained when the potential window from –0.5 to 1.5 V versus SCE was used. The effect of the scan rate was also investigated and found that the better quality coatings were obtained with 0.02 V/s scan rate under potentiodynamic conditions.

Cyclic Voltammetry Study

The cyclic voltammograms of the first scan recorded during the syntheses of the PANI (with scan rate of 0.2 V/s), POT and PAOT5 copolymer coatings on Cu from aqueous oxalate solutions are shown in Figure 1. The first positive cycle shows anodic peaks A, B and C. In addition, a shoulder is clearly seen. The peak A is attributed to the dissolution of the Cu electrode.[18]

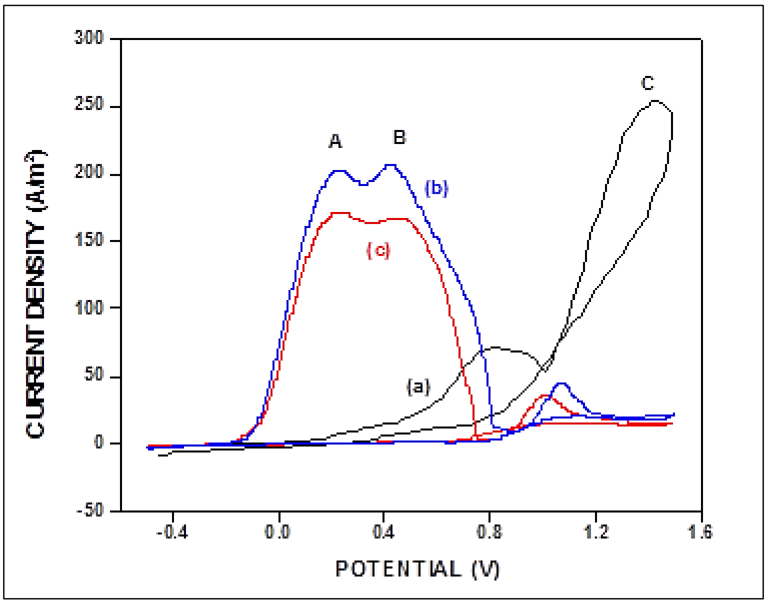


Fig. 1. *Cyclic Voltammograms of the First Scan Recorded During the Synthesis of (a) PANI, (b) POT, and (c) PAOT5 Copolymer Coatings on Cu.*

The visual inspection of the working electrode during the first positive cycle shows that the color of the Cu surface slowly changes to dark black after the shoulder. This observation implies that the deposition of the polymer begins during the first positive cycle. Therefore, the peak B and peak C are attributed to the oxidation of monomer and thus its actual polymerization.[18] The deposition of a thin layer of polymer coating during the first cycle may be responsible for the protection Cu against dissolution and hence negligibly small anodic current densities are observed at high potentials (>1.1 V) during the reverse cycle. The careful examination of first positive cycle shows that – (a) The potential corresponding to anodic peak A differs significantly, depending on the monomer(s) present in the electrolyte, and it follows the order of aniline (0.3 V) > (aniline-*co*-*o*-toluidine) (0.225 V) > o-toluidine (0.196 V). (b)The potential corresponding to peak B also differ considerably and it follows the order of aniline (0.836 V) > (aniline-*co*-*o*-toluidine) (0.460 V) > o-toluidine (0.356 V) and (c) That for peak C – it follows the order of aniline (1.283 V) > o-toluidine (1.048 V) > (aniline-*co*-*o*-toluidine) (0.996 V). These results attributed to the reactivity of o-toluidine being higher than that of aniline during the electrochemical copolymerization of aniline with o-toluidine. During the next scan Figure 2, the broad anodic peak B with a weak shoulder and peak C are observed and rest of the features are similar to that of the first scan. The peak A corresponding to the dissolution of Cu is not observed. As the deposition of the polymer coating begins during the first positive cycle, the peaks B and C are attributed to the polymerization process rather than to the dissolution of Cu.[18] On repetitive cycling, the voltammograms identical to that of second scan are obtained. However, the current densities corresponding to the anodic peaks decrease gradually with the number of scans. The visual inspection of the Cu electrode after tenth scan reveals the formation of dark black colored polymer coatings. The coating is shiny and appears to be like plastic. It is seen that the coating is uniform and strongly adherent to the Cu surface.

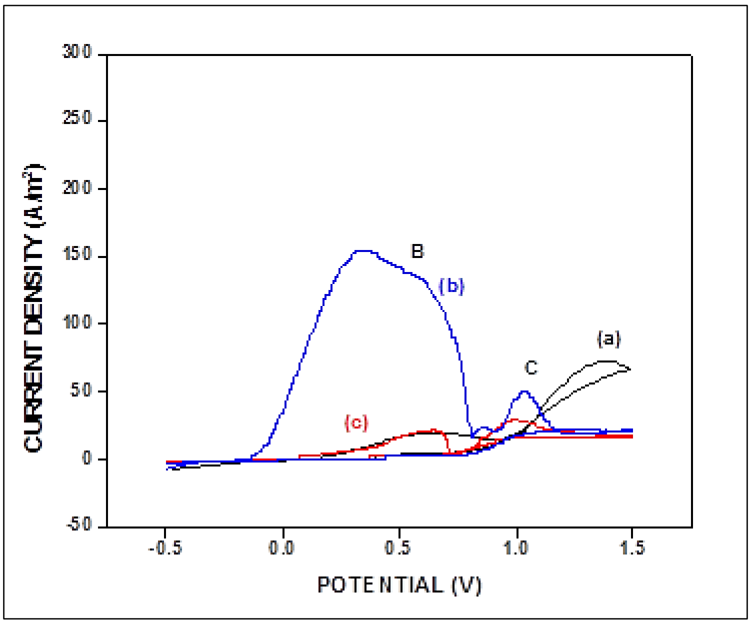


Fig. 2. *Cyclic Voltammograms of the Second Scan Recorded During the Synthesis of (a) PANI, (b) POT, and (c) PAOT5 Copolymer Coatings on Cu.*

FTIR Spectroscopy Results

The FTIR spectra of the PANI and POT homopolymers and PAOT5 copolymer coatings on Cu are shown in Figure 3. The characteristic bands in the FTIR spectrum of PANI (Figure 3a) are assigned as follows[19–22]: the broad band at 3354 cm^{-1} is due to the N–H stretching mode, the C=N and C=C stretching mode for the quinoid and benzoid rings occurs at 3400, 1596 and 1511 cm^{-1}, the band at 1303 cm^{-1} can be assigned to the C–N stretching mode for benzoid rings. The observation of the bands at ~1726 and 1281 cm^{-1} suggests the presence of carboxyl groups of the sodium oxalate in the coating.

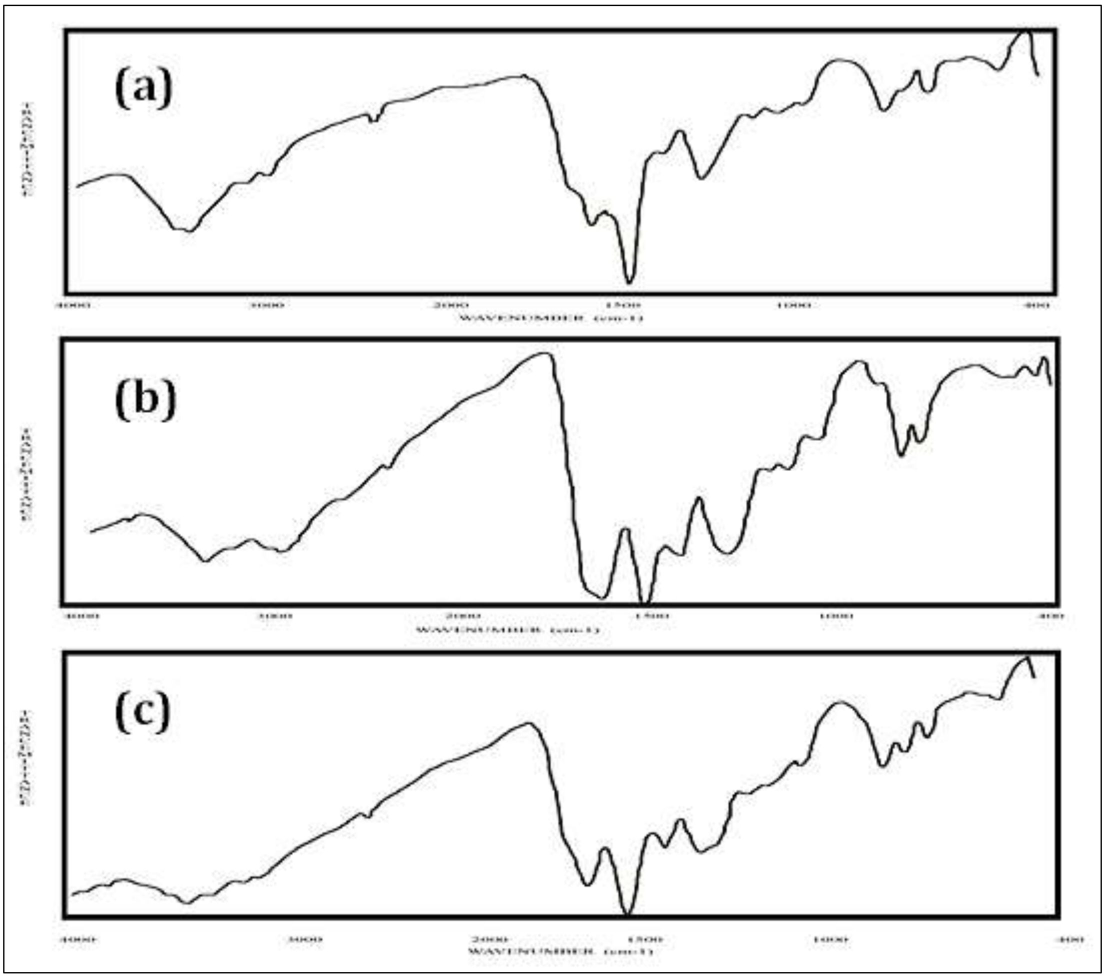


Fig. 3. *FTIR Spectra of the (a) PANI, (b) POT, and (c) PAOT5 Copolymer Coatings Synthesized on Cu.*

The FTIR spectrum of POT (Figure 3b) exhibits the following spectral features.[19–22] – the broad band at ~3437 cm^{-1} due to the characteristic N–H stretching vibration suggests the presence of –NH-groups in o-toluidine units; the band at ~2928 cm^{-1} is associated with the C–H stretching due to methylene group; the observation of the bands at ~1726 and 1281 cm^{-1} suggests the presence of carboxyl groups of the sodium oxalate in the coating; the band at ~1655 cm^{-1} is an indicative of stretching vibrations in quinoid (Q) rings and the band ~1456 cm^{-1} represents the stretching vibrations of the benzoid (B) rings.

The FTIR spectrum of PAOT5 (Figure 3c) exhibits the spectral features of both parent polymers i.e. PANI and POT.

NMR Spectroscopy Results

To establish that PAOT5 is a copolymer rather than a mixture of homopolymers PANI and POT, these polymers were further characterized with^{1}H NMR spectroscopy. The ^{1}H NMR spectra of PANI, POT, and PAOT5 recorded in DMSO-d6, are shown in Figure 4. The ^{1}H NMR spectrum of PANI (Figure 4a) shows the presence of signals in the region of 6.3–7.9 ppm, which are assigned to the protons of the aromatic rings.[23,24] The spectrum of PANI does not show the signal in the region of 1.8–2.1 ppm corresponding to the methyl protons.

The ^{1}H NMR spectrum of POT (Figure 4b) is characterized by the presence of three main signals.[23,24] The signals in the region of 6.2–7.7 ppm are due to the protons of the aromatic rings. The resonances in the region of 2.4–2.2 ppm are attributed to the methyl protons of the quinoidring and those in the region of 1.9–2.2 ppm are due to the methyl protons of the benzoid ring.

The ^{1}H NMR spectrum of the PAOT5 copolymer (Figure 4c) has essentially the same characteristics as that of POT. This spectrum is characterized by three main signals that exactly correspond to the three types of protons on the copolymer chains. As can be seen in (Figure 4c), this spectrum exhibits the signals in a wide range from 6.2 to 7.8 ppm, which are attributed to the aromatic protons on the aniline and o-toluidine units. The resonance peaks from 1.92 to 2.20 ppm are assigned to the protons of the methyl groups on the quinoid ring.

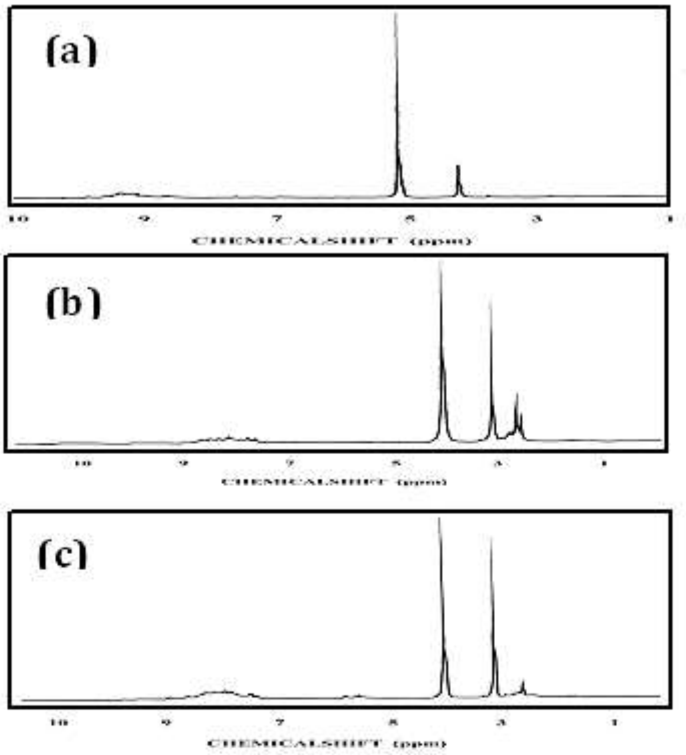


Fig. 4. *^{1}H NMR Spectra of (a) PANI, (b) POT, and (c) PAOT5 Copolymer Recorded in DMSO-d_6 at 300 MHz.*

The two strongest peaks at 2.39 and 3.28 ppm are due to protons of dimethyl sulfoxide (DMSO) and water in DMSO, respectively.[23,24] Additionally, two negligibly small signals at 5.2 and 5.8 ppm are assigned to the –NH linkages. This indicates the formation of a high-molecular-weight PAOT5 copolymer. This supports a higher reactivity of o-toluidine versus aniline in the copolymerization, which is in agreement with the results of cyclic voltammetry and FTIR spectroscopy. Thus, the ^{1}H NMR spectroscopy study confirms that aniline and o-toluidine are indeed able to copolymerize on Cu in an aqueous oxalate medium, and in the resulting PAOT5 copolymer.

SEM Results

The surface morphology of the PANI coating Figure 5(a) is featureless. The surface morphology of the POA coating Figure 5(b) is relatively uniform and featureless. The SEM image of the copolymer PAOA5 coating synthesized on Cu is shown in Figure 5(c). It clearly reveals that the copolymer PAOA5 coating is relatively uniform and fibrous.

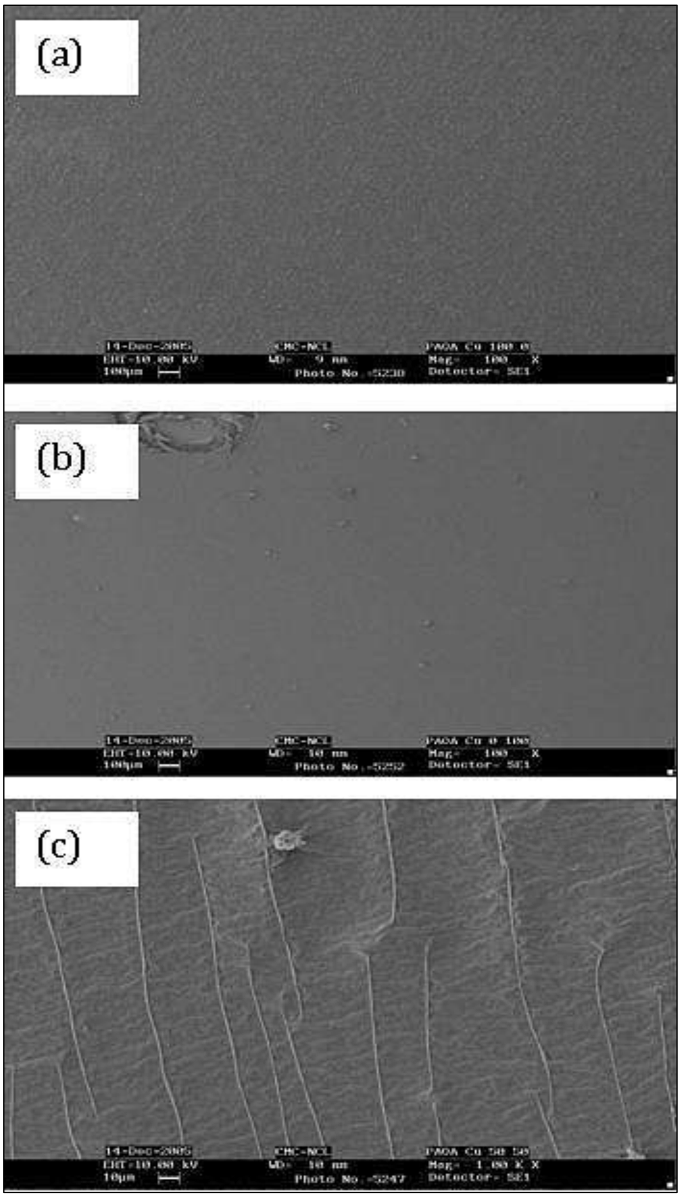


***Fig. 5.** SEM Images of (a) PANI, (b) POT and (c) PAOT5 Copolymer Coated Cu.*

UV–Visible Absorption Spectroscopy Results

The UV–visible absorption spectra of the PANI and POT homopolymer and PAOT5 copolymer coatings are shown in Figure 6. The spectral characteristics of the PAOT5 copolymer are remarkably different from those of the individual homopolymers PANI and POT. The UV–visible absorption spectrum of the PANI coating synthesized on Cu (Figure 6a) shows a high value of the absorbance between 600 and 800 nm, which may be due to the formation of various species with different oxidation states. The UV–visible absorption spectrum of the POT coating (Figure 6e) shows broad peaks at about 560 and weak shoulder at 720 nm. The peak at 560 nm is attributed to the presence of the pernigraniline base (PB) form of POT, which is fully oxidized form of POT and insulating in nature.[25] The shoulder at 720 nm is a signature of the emeraldine salt (ES) form of POT.[25] The simultaneous appearance of 540 and 720 nm reveals the formation of a mixed phase of PB and ES forms of POT. The UV–visible absorption spectrum of the copolymer coatings (Figure 6b–d) shows a well-defined peak at 540 nm, which is attributed to the formation of the PB form of copolymer and the shoulder at 720 nm is a signature of the ES. From figure it is clearly reveal the PAOT5 copolymer shows higher absorbance as compare to PAOT3 and PAOT7copolymers which may improve the film quality.

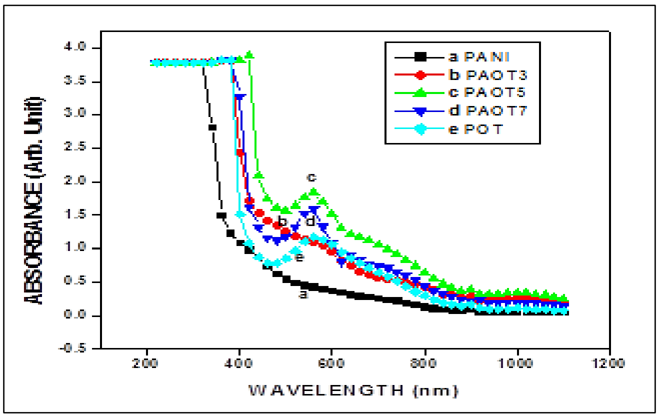


Fig. 6. *UV–Visible Absorption Spectra of (a) PANI, (b)PAOT3, (c) PAOT5, (d) PAOT7, and (e) POT Coatings Synthesized on Cu. (The spectrum was recorded ex situ in DMSO solution.)*

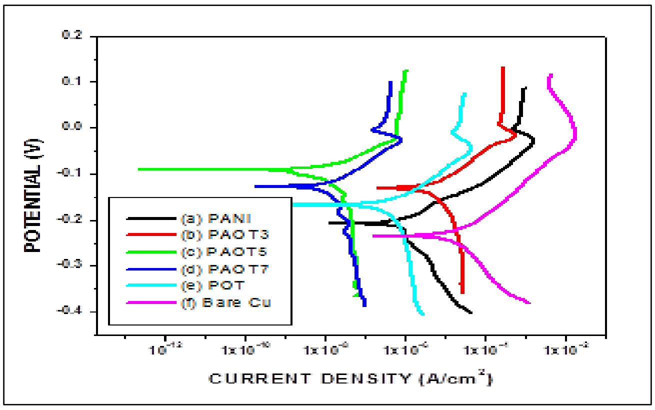


Fig. 7. *Potentiodynamic Polarization Curves for (a) PANI Coated Cu, (b) PAOT3, (c) PAOT5 Coated Cu, (d) PAOT7 Coated Cu, (e) POT Coated Cu, and (f) Uncoated Coated Cu Recorded in Aqueous 3% NaCl Solution.*

Evaluation of Corrosion Protection Performance

The corrosion protection performance of PANI, POT and PAOT copolymer was evaluated in 3% NaCl solution by using potentiodynamic polarization technique. The potentiodynamic polarization curves recorded in aqueous 3% NaCl for uncoated Cu, PANI coated Cu, POT coated Cu, PAOT3, PAOT5 and PAOT7 coated Cu (15 cycles) are shown in Figure 7. The values of the corrosion potential (E_{corr}), corrosion current density (j_{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 corrosion current density [I_{corr} (A/cm^2)] was calculated with the Stern–Geary equation and was converted into the corrosion rate (CR) in millimeters per year as follows:

$$\boldsymbol{CR\left(\frac{mm}{yr}\right) = 3.268\ x\ 10^{3\,\frac{I_{corr}\,EW}{\rho}}} \qquad \text{Eq. (1)}$$

In order to calculate the porosity of these deposits, we have used the relationship

$$\mathbf{P} = \frac{\mathbf{R_{pol}(uncoated)}}{\mathbf{R_{pol}(coated)}}\,\mathbf{10}^{-\left(\frac{|\Delta E_{corr}|}{\beta_a}\right)} \qquad \text{Eq. (2)}$$

Table 1. *Results of Potentiodynamic Polarization Measurements.*

Sample	E_{corr} (V)	j_{corr} (μA/cm^2)	β_a (V/dec)	β_c (V/dec)	R_p (Ω/cm^2)	CR (mm/year)	% P	% PE
Uncoated Cu	-0.234	20	0.072	0.110	$0.784\text{x}10^3$	0.28	----	----
PANI	-0.204	0.966	0.047	-0.141	$0.316\text{x}10^5$	0.011	0.9477	97.52
POT	-0.159	0.684	0.059	-0.481	$0.426\text{x}10^5$	0.007	0.152	98.16
PAOT3	-0.126	4.25	0.047	-0.126	$0.76\ \text{x}10^4$	0.049	0.323	98.99
PAOT5	-0.080	0.017	0.036	-0.287	$1.05\ \text{x}10^6$	0.00019	$4.5\ \text{x}\ 10^{-4}$	99.93
PAOT7	-0.113	0.0287	0.062	-0.585	$1.04\ \text{x}10^6$	0.00033	$1.3\ \text{x}\ 10^{-3}$	99.94

The porosity in PANI, POT, PAOT3, PAOT5 and PAOT7 copolymer coatings was found to be ~ 0.9477, 0.152, 0.323, $4.5\ \text{x}\ 10^{-4}$, $1.3\ \text{x}\ 10^{-3}$ %, respectively. The significantly lower values of the porosity in the PAOT5 copolymer coatings as compared with the respective homopolymer coatings permit substantial improvement of the corrosion resistance by hindering the access of the electrolyte to the Cu substrates.

The analysis of these potentiodynamic polarization curves shows the positive shift in the E_{corr} and substantial reduction in the j_{corr} of the Cu due to the PANI, POT, PAOT3, PAOT5 and PAOT7 copolymer coatings, which indicates the corrosion resistant character of these coatings. It is found that the shift in the E_{corr} depends on the coating and decreases in the order PAOT5 > PAOT7 > PAOT3 > POT > PANI. This implies that the copolymer PAOT5 coating provides effective protection to Cu against corrosion in aqueous 3% NaCl as compared to that of the corresponding homopolymers. The corrosion rates of PANI (0.011), POT (0.007), PAOT3 (0.049), PAOT5 (0.00019) and PAOT7 (0.00033) coated Cu in mm/year which are ~25, 40, 571, 1000 and 848 times lower than that observed for uncoated Cu. It is believed that (-CH3), an electron-withdrawing radical, adsorbs strong to a metallic substrate during the copolymerization of PAOT5 (high coverage). This fact can support the better corrosion inhibition of copolymers than PANI, POT and other copolymers. The protection efficiencies for PANI, POT and PAOT5 copolymer calculated from equation (3) are

$$\text{PE} = \left[\frac{\text{R}_{\text{pol}}(\text{coated}) - \text{R}_{\text{pol}}(\text{uncoated})}{\text{R}_{\text{pol}}(\text{coated})}\right] \text{x}\ 100 \qquad \text{Eq. (3)}$$

found to be ~ 97.52, 98.16, 98.99, 99.93 and 99.94 %. These results reveal that the PAOT5 and PAOT7 copolymer effectively protects the mild steel and improves the corrosion protection efficiency than that offered by the corresponding homopolymers.

CONCLUSIONS

The results reported in this paper demonstrated that the PAOT copolymer effectively protects Cu against corrosion in 3% NaCl and improves the corrosion protection efficiencies with respect to that offered by the corresponding homopolymers, PANI and POT. The following main findings resulted from the present investigation

- Strongly adherent PAOT copolymers were successfully synthesized on Cu from the aqueous oxalate solutions, by using cyclic voltammetry.
- The results clearly show that the aqueous solutions of oxalate were suitable mediums for the electrochemical copolymerization of aniline with o-toluidine on Cu.
- The FTIR and ^{1}H NMR spectroscopy studies reveal that the copolymerization of aniline and o-toluidine takes place Cu and in the resulting PAOT copolymer, there are more o-toluidine units than aniline units.
- The porosity values are significantly lower for the PAOT coatings than for the respective homopolymers, that is, PANI and POT. The copolymer coatings are more compact and strongly adherent to Cu.
- The protection of Cu against corrosion in 3% NaCl by the copolymer coatings can be achieved more effectively when the synthesis is carried out with a feed ratio of o-toluidine of 0.5.
- The CRs of PANI, POT and PAOT5 coated Cu are found to be ~0.01, 0.007, and 0.00019 mm/year, respectively, which are ~25, 40 and 1000 times lower than that observed for uncoated Cu.

Acknowledgement

Authors would like to acknowledge UGC for the financial support via minor research project and North Maharashtra University for financial support via VCRMS scheme. First author would also like to acknowledge Prof. P. P. Patil from North Maharashtra University specially for providing the lab for synthesis and testing the corrosion performance of samples as well as co-operative environment during this work.

REFERENCES

1. Bereket G., Hur E., Sahin Y. *Prog Org Coat*. 2005; 54: 63p.
2. Herrasti P., Ocon P., Ibanez A., *et al*. *J Appl Electrochem*. 2003; 33: 533p.
3. Huerta-Vilca D., Siefert B., Moraes S.R., *et al*. *Mol Cryst Liq Cryst*. 2004; 415: 229p.
4. Shinde V., Sainkar S.R., Patil P.P. *Corros Sci*. 2005; 47: 1352p.
5. Shinde V., Sainkar S.R., Patil P.P. *J Appl Polym Sci*. 2005; 96(3): 685p.
6. Zhang T., Zeng C.L. *Electrochimica Acta*. 2005; 50: 4721p.
7. Sathiyanarayanan S., Devi S., Venkatachari G. *Prog Org Coat*. 2006; 56: 114p.
8. Martins J.I., Bazzaoui M., Reis T.C., *et al*. *Synth Met*. 2002; 129: 221p.
9. Bazzaoui M., Martins L.I., Bazzaoui E.A., *et al*. *Electrochemica Acta*. 2002; 47: 2953p.
10. Moraes S.R., Vilca D.H., Motheo A.J. *Prog Org Coat*. 2003; 48: 28p.
11. Ogurtsov N.A., Pud A.A., Kamarchik P., *et al*. *Synth Met*. 2004; 143(1): 43p.
12. Skotheim T.A. (Ed.), *Handbook of Conducting Polymers*. Vols. I and II, New York: Marcel Dekker Inc.; 1986.
13. Nalwa H.S., *Handbook of Organic Conductive Molecules and Polymers*. Vols. 1–4, John Wiley and Sons Ltd.; 1997.
14. Hur E., Bereket G., Sahin Y. *Prog Org Coat*. 2005; 54: 63p.

15. Bereket G., Hur E., Sahin Y. *Curr Appl Phys*. 2007; 7: 597p.
16. PowerSuite Software, Perkin Elmer Instruments, 2000 supplied by EG and G, Princeton Applied Research, USA.
17. Electrochemical Corrosion software-CorrWare and CorrView, Scribner Associates Inc., 150 East Connecticut Avenue, Southern Pines, NC 28387.
18. Patil S., Sainkar S.R., Patil P.P. *Appl Surf Sci*. 2004; 225: 204p.
19. Tang J., Jing X., Wang B., *et al*. *Synth Met*. 1988; 24: 231p.
20. Ohsaka T., Ohnuki Y., Oyama N., *et al*. *J Electroanal Chem*. 1984; 161: 399p.
21. Zheng W.Y., Levon K., Taka T., *et al*. *Polym J*. 1996; 28: 412p.
22. Neoh K.G., Kang E.T., Tan K.L. *J Phys Chem*. 1991; 95: 10151p.
23. Mav I., Zigon M. *Polym Bull*. 2000; 45: 61p.
24. Wei Y., Hariharan R., Patel S.A. *Macromolecules*. 1990; 23: 764p.
25. Patil S. *Ph.D. Thesis*. North Maharashtra University, Jalgaon, India, 2000.
26. Pawar P. Sainkar S.R., Patil P.P. *J Appl Polym Sci*. 2007; 103: 1868–78p.

Deposition and Characterization of Poly(O-Anisidine)/TiO 2 Nanocomposite for Gas Sensing Application

Article · August 2015

Pritee Mahesh Raotole
Arts, Science and Commerce College ,Chopda

International Journal of Polymer Science and Engineering
Vol. 1: Issue 2
www.journalspub.com

Deposition and Characterization of Poly(*O*-Anisidine)/TiO_2 Nanocomposite for Gas Sensing Application

***P. M. Raotole*[1]**, R. S. Khadayate*[2]**
[1]MGSM's Arts, Science and Commerce College, Chopda, Dist-Jalgaon, Maharashtra, India
[2]G.D.M. Arts, K.R.N. Commerce and M.D. Science College, Jamner, Dist-Jalgaon, Maharashtra, India

Abstract

The poly(O-anisidine) (POA) and Titanium dioxide POA (POA/TiO_2) composite thin film based for gas sensing application are synthesized. Pure POA and POA/TiO_2 composites with 20 wt% of TiO_2 were synthesized by chemical oxidative polymerization of O-anisidine using ammonium persulfate in acidic medium at 0–5°C. Thin films of POA and POA/TiO_2 composites were deposited on glass plate by dip coating method to prepare the chemiresistor sensor. The structural and optical properties of these composite films have been characterized by UV-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM) and FTIR spectroscopy. Finally, the response of these chemiresistor sensors for NH_3 gas was evaluated by monitoring the change in electrical resistance at room temperature. It was observed that the POA/TiO_2 composite thin film based chemiresistor sensors show a higher response as compared to pure POA sensor.

****Corresponding Author***
E-mail: pritee_pawar@yahoo.com

Keywords: conducting polymer, gas sensor, POA/TiO_2 composite, poly(*O*-anisidine), titanium dioxide

Abbreviations: CSA, 10-camphor sulfonic acid; **EB**, emeraldine base; **ES**, emeraldine salt; **FTIR**, Fourier transform infrared spectroscopy; **HATR**, horizontally attenuated total reflectance; **PANI**, polyaniline; **POA**, poly(*O*-anisidine); **SEM**, scanning electron microscopy; **UGC,** University Grants Commission

INTRODUCTION

Polymers are amongst the most widely used materials in the modern world due to their diversified technological applications. The main advantage of these conduting polymers is that they exhibit conductivity ranging from insulator to conductor.[1,2] Polyaniline has attracted a great interest due to its large field of applications like batteries [3], protection of metals against corrosion, [4,5], electrocatalysis, [6,7] biosensors (analysis of ADN, proteins, and antipollution), [8,9] electrochromism (flat-faced screens and diodes) and use in electronic components [10–13].

Titanium dioxide is an important n-type semiconducting material, due to its excellent photocatalytic and electric properties. This material has been widely utilized as photocatalytic material [14,15] and semiconducting electrode material for dye-sensitized solar cells. [16,17] On the other hand, organic conducting polymer materials attracted widespread interest as functional device materials, due to their low cost, ease of processing, and compatibility with flexible substrates.

Polyaniline (PANI), as a well-known conducting polymer, has attracted a considerable interest in recent years because of its good electric, electrochemical, and optical properties and high stability [18,19]. Also this conducting polymer shows the hole conducting properties. By considering the properties of TiO_2 and PANI, therefore, a nano-composite of TiO_2 and PANI will give a new type of organic-inorganic p-n junction material that would be expected to have a potential application in the electronic and optical devises.

EXPERIMENTAL PROCEDURE

Materials

The *O*-anisidine hydrochloric acid (HCl) (35% concentrated), *O*-anisidine was used after double distillation. TiO_2 (99.9%) nanoparticles; with an average particle size of about 10–15 nm. Ammonium peroxide sulfate (APS) (99%), chloroform (99.9%) and ammonia solution (25% concentrated), and 10-camphor sulfonic acid (CSA).

Synthesis of POA and POA/TiO_2 Composite

Pure poly(*O*-anisidine) (POA) was synthesized by *in-situ* chemical oxidative polymerization method at 0–5°C, which has been reported elsewhere [20,21]. The POA/TiO_2 composite was prepared by an *in-situ* chemical oxidation polymerization of *O*-anisidine using APS as an oxidant in presence of colloidal TiO_2 nanoparticles at 0–5°C in air. In a typical procedure, the TiO_2 nanoparticles were suspended in 1 M HCl solution and sonicated for 1 h to reduce aggregation of TiO_2 nanoparticles. The 0.1 M of *O*-anisidine was dissolved in 100 ml of 1 M HCl solution and then mixed with 10 ml of sonicated colloidal TiO_2 nanoparticles by further sonication for 30 min. The 100 ml of 1 M HCl solution containing the APS ($(NH_4)_2S_2O_8$) with an equal molar ratio to *O*-anisidine was then slowly added dropwise to well dispersed suspension mixture for 2 h with a continuous stirring at 0–5°C. After 3 h, a good degree of polymerization is achieved and the dark green precipitate was recovered. The solution was left in undisturbed position for a night for the completion of chemical reaction. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 24 h. The composite powder thus obtained was conductive emeraldine salt (ES) form of POA/TiO_2. The POA/TiO_2 composites were synthesized using 20 wt% of TiO_2 with respect to *O*-anisidine monomer. For emeraldine base (EB), POA/TiO_2 (ES) powder was kept in 0.1 M ammonia solution and stirred for 6 h at room temperature. The precipitate was filtered and washed with deionized water until filtered solution became neutral and then dried in vacuum for 24 h to obtain emeraldine base POA/TiO_2 composite [20].

Thin Film Deposition

Normally POA composite in emeraldine salt (ES) form are not soluble directly in any organic solvent and it is difficult to process it in conducting form. Therefore, firstly POA (ES) and its composites were converted into emeraldine base (EB) form and then protonated with CSA to make it conducting processable solution for film casting. In a typical procedure; the 0.3 g of POA (EB) and the POA/TiO_2 (EB) composite powders were separately mixed with of CSA by grinding in a smooth agate mortar. The, POA/CSA and POA/TiO_2/CSA (with 20 wt% of TiO_2) mixtures were separately added in 30 ml chloroform to prepare the conducting solution. The solution preparation requires 4–5 days of continuous stirring to make the solution homogenous. Thin films of these prepared conducting homogenous solutions were deposited onto cleaned glass substrates using dip coating for 10 min. These sensor films were dried at 60°C in vacuum for 24 h [22].

Characterization

The Ultra-violet-visible (UV–Vis) absorption spectra were recorded using a Hitachi-U-2000. The surface morphology of the prepared thin films was investigated and evaluated by means of scanning electron microscopy (SEM) and E-DAX to characterize the surface morphology with a Leica Cambridge 440 Microscope (UK). Thickness measurement by Tolansky interferometer, conductivity measurement by Four Probe method, The FTIR transmission spectrum of coating was recorded in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm^{-1} using a Perkin Elmer spectrometer (1600 Series II, Perkin Elmer, USA). The NM_3, sensing behavior of POA and POA/TiO_2 nanocomposite films was analyzed by measuring the change of an electrical resistance of the films after NM_3, exposure in air.

RESULTS AND DISCUSSIONS

Measurement of Yield after Synthesis

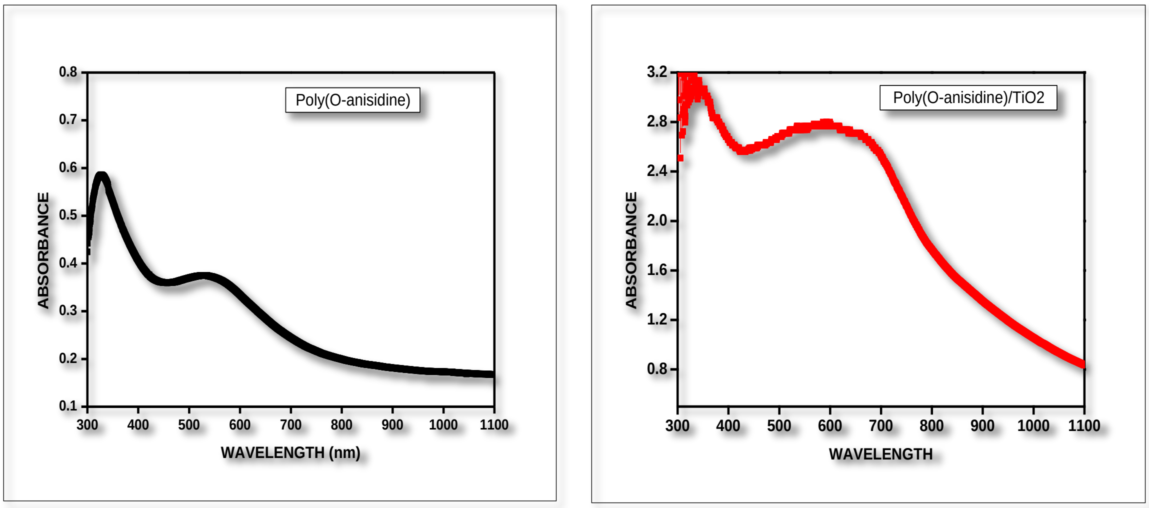
When chemical synthesis of poly (*O*-anisidine) (POA) is carried out as described, the weight of yield is 0.4140 gm. While chemical synthesis of poly (*O*-anisidine) incorporated with TiO_2 nanoparticles (i.e. POA/TiO_2) carried out with as chemical oxidative the weight of yield is 0.6286 gm. So from these results we conclude that incorporation of TiO_2 during synthesis improved the yield by an amount of 0.2146 gm.

Thickness Measurement by Tolansky Interferometer

The films of poly(o-anisidne) and that of POA/TiO_2 deposited on plane clean glass plate. The thickness of these films was measured by Tolansky method and it was observed that the film thickness is also affected by incorporation of TiO_2, means it reduces the film thickness

Conductivity Measurement by Four Probe Method

In comparison to pure POA the conductivity of 20 wt% POA/TiO_2 composite thin film has found to be increased from 0.44×10^{-5} to 3×10^{-5} S/cm. This may be attributed to that the doping of TiO_2 nanoparticles within POA matrix form a more efficient network for charge transport between different molecular chains of POA, thus enhancing the conductivity of composite.



Ultraviolet–Visible (UV–Vis) Spectroscopy

Fig. 1. *(a) UV–Visible Absorption Spectrum of Pure Poly(O-Anisidine) Coating; (b) UV–Visible Absorption Spectrum of POA/TiO_2 Composite Coating.*

Figures 1(a) and 1(b) show the UV-vis absorption spectra of pure POA and POA/TiO_2 composite thin films respectively deposited on the clean glass substrate. The UV-vis absorption spectra for CSA doped POA and POA/TiO_2 composites thin films exhibit two absorption bands at 330 and 560 nm. The bands at 330 and 560 nm are attributed to the p–p* and polaron-p* transition in the conducting POA. Specially; it is observed that for POA/TiO_2 composite thin films, the absorption intensity increases with TiO_2. It may be due to the good absorption property of TiO_2 nanoparticles. In addition, it can be noted that there are some shifts in the peaks for POA/TiO_2 composites thin films as compared to the pure POA thin film. It may be due to that the encapsulation of TiO_2 nanoparticles has the effect on the doping of conducting POA or coordinate complex formation between TiO_2 nanoparticles and POA chains.

FTIR Characterization of POA and POA/TiO_2 Films

The FTIR spectrum of the POA coatings is shown in Figure 2(a). This spectrum exhibits the following spectral features: a broad band at ~3258 cm^{-1} due to the characteristic N-H stretching vibration suggests the presence of –NH- groups in *O*-anisidine units; the band at ~1515 cm^{-1} is an indicative of stretching vibrations in quinoid (Q) rings; the band ~1484 cm^{-1} represents the stretching vibrations of the benzoid (B) rings; the presence of Q and B bands clearly show that the POA coating is composed of amine and imine units; the bands at 1246 cm^{-1} are attributed to the presence of carbonyl groups of salicylate in the POA coating; the band at ~1458 cm^{-1} is assigned to the C–N stretching vibrations in quinoidimine units; the bands at 1115, 1021 and 847 cm^{-1} are attributed to the 1–4 substitution on the benzene ring; the band at ~1170 cm^{-1} is considered as a measure of the degree of delocalization of the electrons on POA and is referred to as the electronic like band and the bands between 800–700 cm^{-1} reveals the occurrence of the 1-3 substitutions. Thus, the FTIR spectroscopic study indicates that the electrochemical polymerization of *O*-anisidine has occurred and results into the formation of POA.

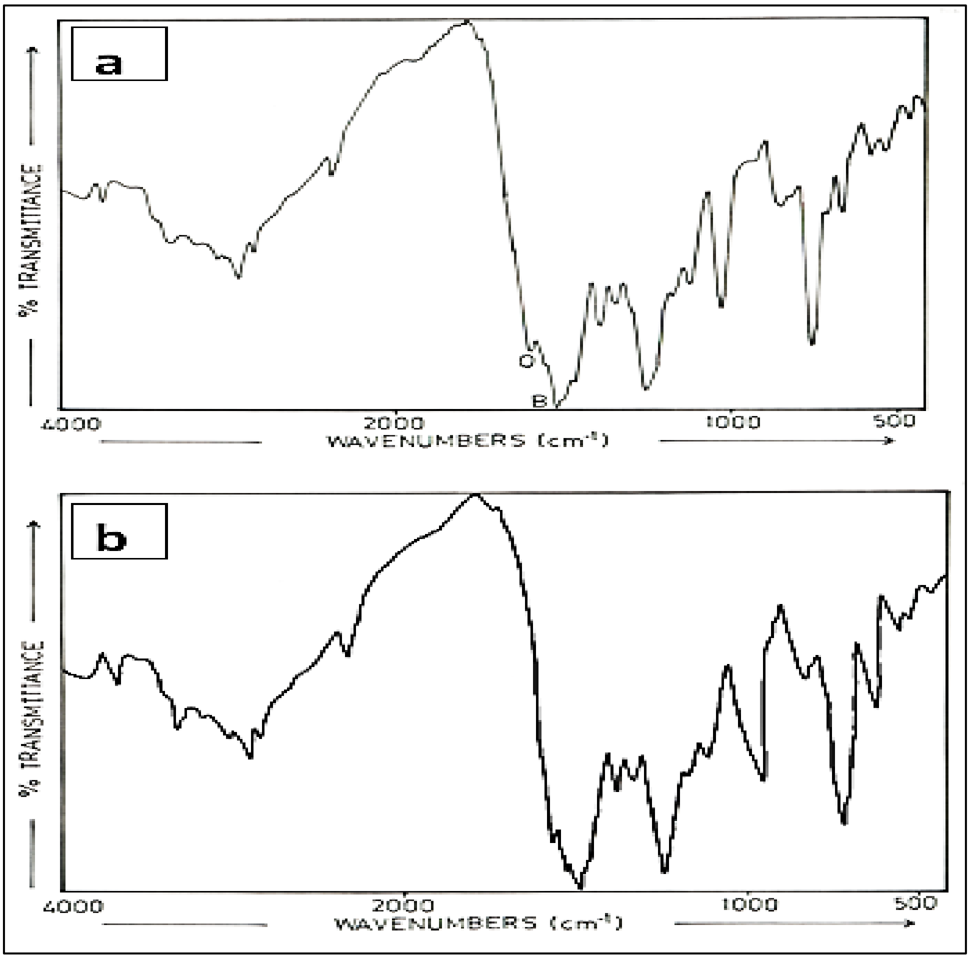


Fig. 2. *FTIR Spectrum of (a) POA and (b) POA)/TiO_2 Composite Coating.*

The FTIR spectrum of the POA coatings is shown in Figure 2(b). For POA/TiO_2 nanocomposite, the IR spectrum is almost identical to that of pure POA, but all bands shift slightly, indicating that some interaction exists between POA and nano-TiO_2. In addition, the absorption band at 1408 cm^{-1} can be assigned to the in-plane bending vibration of O–H on the surface of TiO_2.[23]

SEM Characterization

The surface morphology of the pure POA and POA/TiO_2 nanocomposite coatings synthesized by chemical synthesis were characterized by SEM. The surface morphology of the pure POA coating as shown in Figure 3(a) is relatively rough and it is characterized by the presence of the pores in the coating. Figure 3(b) shows that the surface morphology of the POA/TiO_2 nanocomposite coating is uniform, featureless and pore-free. It seems that the pores present in the pure POA coating are filled up by TiO_2 nanoparticles.

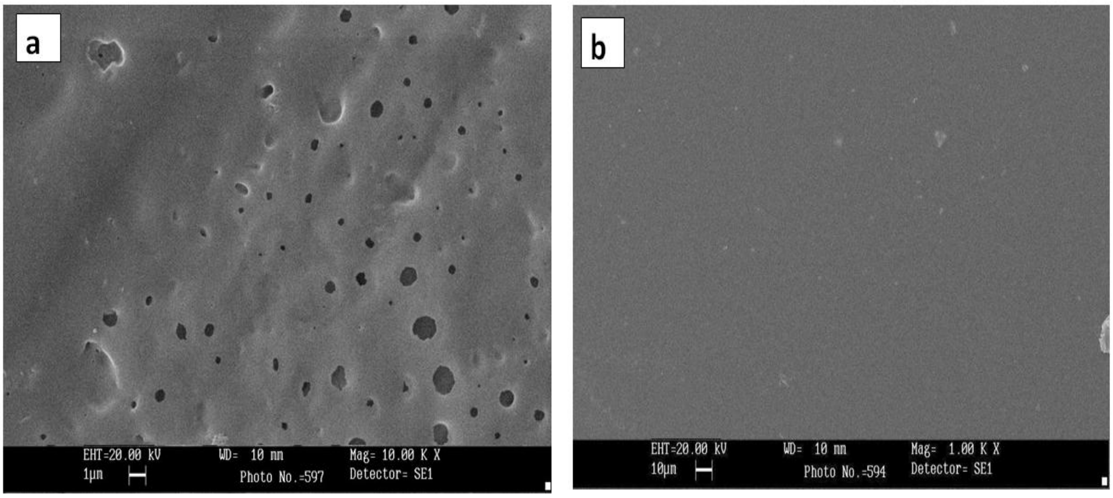


Fig. 3. *Scanning Electron Micrographs of **(a)** POA and **(b)** POA/TiO$_2$ Thin Films.*

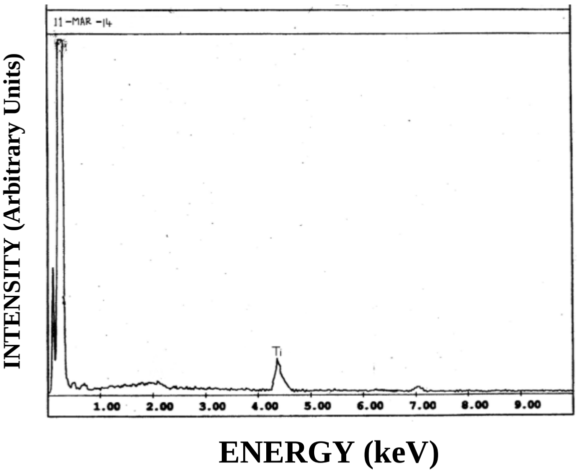


Fig. 4. *E-DAX Analysis of the POA/TiO$_2$ Coating.*

E-DAX Characterization

The E-DAX analysis of the POA/TiO$_2$ coating was also performed to confirm the incorporation of the TiO$_2$-nanoparticles in the POA matrix as shown in Figure 4. Interestingly, the signal due to the Ti is clearly detected in the E-DAX spectrum as shown in Figure 4, which proves that the TiO$_2$-nanoparticles are incorporated in the POA matrix.

NH$_3$ GAS-SENSING PROPERTIES OF POA AND POA/TiO$_2$ FILMS

POA/TiO$_2$ nanocomposite thin film layer when exposed to NH$_3$ gas of different concentrations. The specially fabricated gas sensing apparatus is used for this work, and a certain amount of NH$_3$ gas was injected into the test chamber after the resistance reached a steady value in clean air. Gas exposure time was 150 sec for each pulse of NH$_3$ gas and the chamber was purged with clean air for ca 200 sec after each pulse to allow the surface of the sensitive film to regain atmospheric condition. The measurement was processed at room temperature. Dynamic responses of the sensors based on POA and POA/TiO$_2$ thin films fabricated at room temperature. It can be seen that the resistance of both sensors increases dramatically after exposed to NH$_3$ gas. POA nanocomposite thin films contact with NH$_3$ by gas injection, which may be due to the surface adsorption effect, and the chemisorptions leads to the formation of ammonium. However, the interaction process between the thin film and the adsorbed gas is a dynamical process. Thus, when the thin film is exposed to NH$_3$ gas, the adsorption and desorption processes will simultaneously occur, and the thinner the films, the quicker the gas desorption. Then, the resistance attains a stable value when dynamic equilibrium is attained.

The gas response is defined as (Rgas–Rair)/Rair, where Rair is the resistance of sensor in air and Rgas is the steady resistance of sensor in the presence of a tested gas. The response values of all the samples are plotted as a function of NH$_3$

concentration in Figure 5, indicating a highly linear characteristic and the highest response value for the sensor composed of the POA/TiO_2 as compared to POA.

Table 1. *Response Time (T_1) and Recovery Time (T_2) of Sensors Based on POA and PANI/TiO_2 Thin Films Prepared at RT Exposed to NH_3.*

Concentration of NH_3 (ppm)	**POA**		**POA/TiO2**	
	T_1	**T_2**	**T_1**	**T_2**
30	10	86	4	68
60	8	69	4	49
90	9	57	3	41
120	8	46	5	30
150	9	33	4	18
180	8	16	5	9

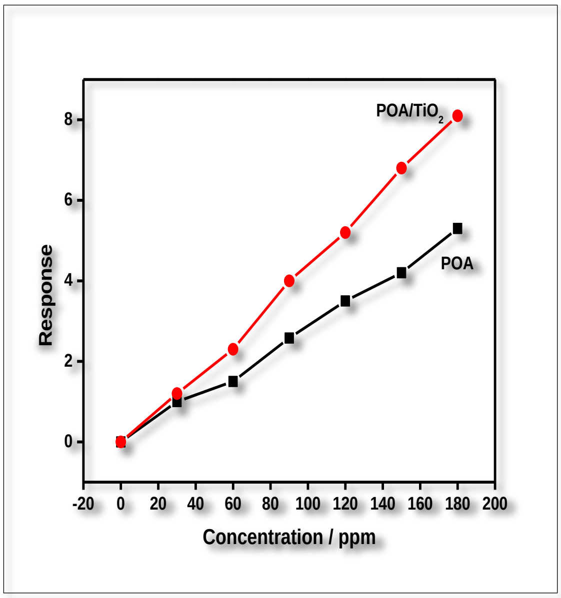


Fig. 5. *Responses of the (a) POA (b) POA/TiO_2 in NH_3 of Different Concentration.*

CONCLUSIONS

- The POA and POA/TiO_2 composite was prepared by an *in-situ* chemical oxidation polymerization of *O*-anisidine using APS as an oxidant in presence of colloidal TiO_2 nanoparticles at 0–5°C in air.
- Thin films of these prepared conducting homogenous solutions were deposited onto cleaned glass substrates using dip coating.
- The resulting coatings were characterized by FTIR, SEM, UV–Visible and E-DAX.
- These thin films were exposed to NH_3 gas, POA/TiO_2nano composite coating shows quicker gas desorption as compared to POA films.

ACKNOWLEDGEMENT

The first author is specially acknowledged for the financial support from University Grants Commission (UGC), New Delhi, and North Maharashtra University, Jalgaon (Maharashtra, India) through the VCRMS Scheme.

REFERENCES

1. Zhang L, Wan M, Wei Y. *Synth Met*. 2005; 151: 1–5p.
2. Pritee Raotole, Patil PP, Gaikwad AB. *Int J Emerg Technol Adv Eng*. 2013; 3(11): 68–73p.
3. Ben-Lin He, Bin Dong, Wei Wang, *et al. Mater Chem Phys*. 2009; 114: 371p.
4. Pritee Raotole, Koinkar P, Joshi B, *et al. J Coat Tech Res*. 2015; 12(4): 757–766p.
5. Pritee Raotole, Patil PP, Mahesh Raotole. *Int J Emerg Technol Adv Eng*. 2013; 3(11): 62–67p.
6. Grzegorz Milczarek. *React Funct Polym*. 2008; 68: 1542p.
7. Andrade Juliano M, Peres Rosa CD, Oestreicher EG, *et al. J Mol Catal B Enzym*. 2008; 55: 185p.

8. Lei Zhang, Chunhua Zhang, JiyingLian. *Biosens Bioelectron.* 2008; 24: 690p.
9. Chetna Dhand, Arya Sunil K, Surinder Pal Singh, *et al. Carbon*. 2008; 46: 1727p.
10. Zhung Li, Wenbin Zhang, Shaojun Dong. *J Electroanal Chem.* 1991; 317: 109p.
11. Lin Niu, Qiuhong Li, Fenghua Wei, *et al. J Electroanal Chem.* 2005; 578: 331p.
12. Ashery A, Farag AAM, Salem MA. *Microelectron. Eng.* 2008; 85: 2309p.
13. Mei-Ying Chang, Chong-Si Wu, Yi-Fan Chen, *et al. Org Electron.* 2008; 9: 1136p.
14. Fujishima A, Honda K. *Nature*. 1972; 23: 37–38p.
15. Housa A, Lachheb H, Ksibi M, *et al. Appl Catal B.* 2001; 31: 145–157p.
16. O'Regan B, Moser J, Anderson M, *et al. J Phys Chem.* 1990; 94: 8720–8726p.
17. Seigo Ito, Zakeeruddin SM, Humphry-Baker R, *et al. Adv Mater*. 2006; 18: 1202–1205p.
18. Kang ET, Neoh KG, Tan KL. *Prog Polym Sci*. 1998; 23: 277–324p.
19. Bhadra S, Khastgir D, Singha NK, *et al. Prog Polym Sci.* 2009; 34: 783–810p.
20. Subodh Srivastava, Sharma SS, Sumit Kumar, *et al. Int J Hydrogen Energy*. 2009; 34: 8444–50p.
21. Subodh Srivastava, Sharma SS, Shweta Agrawal, *et al*. Study of Chemiresistor Type CNT Doped Polyaniline Gas Sensor. *Synth Met*. 2010; 160: 529–34p.
22. Subodh Srivastava, Sumit Kumar, Singh VN, *et al. Int J Hydrogen Energy*. 2011; 36: 6343–6355p.
23. Li J, Zhu L, Wu Y, *et al. Polymer*. 2006; 47: 7361–7367p.