Int. J. Chem. Sci.: 9(2), 2011, 493-502
ISSN 0972-768X
www.sadgurupublications.com

ANTICORROSION BEHAVIOR OF POLYANILINE/ POLYPYRROLE COMPOSITE COATINGS ON STAINLESS STEEL

A. SUBATHIRA and R. M. MEYYAPPAN[*]

Department of Technology, Annamalai University, ANNAMALAI NAGAR – 608 002 (T.N.) INDIA

ABSTRACT

The polyaniline/polypyrrole composite coatings were deposited by electrochemical polymerization method onto SS304 electrodes using constant potential technique. This study will provide a better understanding of the corrosion protection mechanism of the composite coatings. The structure of the coating was determined by using Reflection Absorption Infrared Spectroscopy (RAIR). The RAIR peaks ratios of the characteristic peaks were used to monitor the changes in the structure of polymer with respect to the process parameters. The change in corrosion current with process parameter was correlated with the extent of oxidation of the polymer. The mean roughness, rms roughness and the 3-D morphology of the coatings obtained from Atomic Force Microscopy (AFM) were used to correlate the surface energy changes of the coatings.

Key words: Polyaniline, Polypyrrole, Conducting polymer, Corrosion, Reflection absorption infrared spectroscopy (RAIR), Atomic force microscopy (AFM)

INTRODUCTION

The most common strategy for corrosion prevention involves application of one or more layers of coating onto the metal. Traditionally, hexavalent chromium coating is the most effective way to inhibit the corrosion of metals especially steel alloys. The Cr^{6+} that exhibits superior corrosion inhibition is environmentally unsafe. It is believed that Cr^{6+} does not intimately react with human DNA, but instead goes through a reduction to Cr^{5+}, which is responsible for DNA damage[1]. The use of chromate containing compounds has been limited since 1982 due to its carcinogenic effects and the EPA (Environmental Protection Agency) has issued a regulation that by 2007 chromate based coatings should be replaced by an environmentally friendly alternatives. Since the release of this federal mandate on the control of chromate containing compounds, much of the collaborative work has been done in

---

[*] Author for correspondence; E-mail: rmmeyyappan@yahoo.co.in, asubathira2000@yahoo.co.in

the academic, industrial and governmental sectors to provide a suitable method for corrosion control of aluminum alloys[2]. One of the most studied alternatives is the use of conducting polymers for corrosion protection of steel alloys.

There are many proposed mechanisms for corrosion protection, one or more of which could be occurring at any time. The first is a simple galvanic process by which the polymer has a lower oxidation potential than the metal it is protecting; the polymer is preferentially oxidized. Since oxidized polymers are usually insoluble and therefore do not dissolve away as zinc does, corrosion protection with conducting polymers should last longer. Another proposed mechanism is that the polymer reacts with the surface of the metal, requiring that the polymer have an oxidation potential higher than that of the metal. The surface of the metal reacts with the polymer and forms a passivating layer, which inhibits further corrosion by either setting up a barrier or by changing the surface potential or both[3].

Conductive polymers can be synthesized chemically or electrochemically. Chemically synthesized polymer is deposited from dispersion[4] or solution[5]. Electrochemical synthesis of conducting polymers has its advantages; 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.

Polyaniline (PANI) is a macromolecular substance formed by constitutional aniline units. A PANI chain can contain hundreds to thousands of these units, thus being a polymeric material. Polyaniline is synthesized by the polymerization of aniline and creates a structure that connects oxidized and reduced structural units. Polyaniline can exist in several fundamental forms mutually differentiated by the degree of oxidation or protonation. Each form has a characteristic chemical structure, stability, color, and electric properties. The most important is the conducting green protonated emeraldine form of PANI and the corresponding non-conducting blue PANI base. Polypyrrole is a non-carcinogenic compound[6]. It is usually higher in conductivity and lower in reduction potential compared to polyaniline. Of all known intrinsically conducting polymers, polypyrrole is probably the one most frequently used in commercial applications, mainly due to the long-term stability of its conductivity and due to the possibility of forming homopolymers or composites with optimal mechanical properties[7].

Based on the corrosion resistant properties of polyaniline and polypyrrole, in this work, a compact hybrid Polyaniline – polypyrrole composite film is electrochemically synthesized on stainless steel electrode in aqueous oxalic acid solution by constant potential technique and then the corrosion behavior were measured by RAIR and the mean roughness, rms roughness and the 3-D morphology of the coatings obtained from Atomic Force Microscopy (AFM) were used to correlate the surface energy changes of the coatings.

EXPERIMENTAL

The monomers used in electrochemical deposition were 50% aniline (99.5%) and 50% pyrrole (98%). This chemical was bought from Aldrich chemicals. Two stainless steel electrodes (0.9 x 25 x 76 mm) were used as the counter electrodes. The reference electrode used in the experiment is the saturated calomel electrode (SCE), which was purchased from Fischer Scientific Company. Stainless steel coupon (0.9 x 70 x 70 mm) was the working electrode for all the experiments. Oxalic acid was used as the electrolyte. It was purchased Fluka chemical company. All aqueous solutions used in the experiment were prepared by using doubly distilled water.

Electrochemical reaction was performed in a glass beaker. Fig. 1 shows a schematic representation of an electrochemical cell. An EG & G Princeton Applied Research Potentiostat/Galvanostat Model 363 was used for electrochemical polymerization. The stainless steel samples were rinsed thoroughly with double distilled water, hexane and dried by using kim wipes. About 300 mL of electrolyte was used for each experiment.

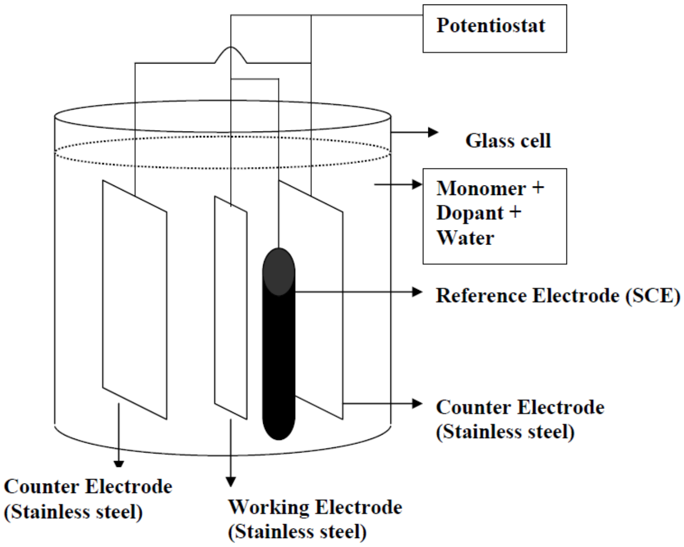

Fig. 1: Sketch of electrodeposition setup

The initial monomer concentration was varied from 0.1 M to 0.3 M. Concentration higher than 0.3 M did not dissolve in the solution. Oxalic acid was used as the electrolyte.

The concentration of oxalic acid was also systematically varied between 0.1-0.3 M. The concentration of oxalic acid used was such that the pH of solution is maintained around 1.5-1.7. The deposition of polypyrrole coating on stainless steel alloy SS-304 takes place at this lower pH (range 1 to 2). The ferrous oxide layer is not stable in the pH range 1 to 2 and allows the deposition of conducting polymer layer onto the substrate. Oxalic acid was also used to in-situ clean the SS-304 substrate. Galvanostatic polymerization (constant current technique) was used to electrodeposits the conducting polymer coating onto SS-304 coupon. The applied current was varied between 2-6 mA/cm^2. The deposition time was varied between 30 sec.-3 minutes. Thus by varying the electrochemical deposition parameters like monomer concentration, electrolyte concentration, applied current density and deposition time the primer properties were optimized. After electro deposition the SS-304 coupons were rinsed with deionised water and heated to 100°C for 1 hr. The thickness of the primer coating was controlled by changing the deposition time and the applied current density. The thickness of the primer coat varied between 0.5-2 microns.

RESULTS AND DISCUSSION

Electrochemical deposition

Constant potential method was employed for electrochemical deposition of polyaniline/polypyrrole. As soon as the experiment started, coating was visible on the stainless steel substrate within few seconds. It was only from 30 seconds deposition that the stainless steel substrate was fully covered by polyaniline/polypyrrole coatings. The polyaniline/polypyrrole coating has a very good adhesion onto stainless steel substrate. If the coating is too thick, coating may act as a physical barrier instead of chemical or electronic diffusion barrier. It was interesting to see change in color of the coating with change in the deposition time and concentration of the monomer. Composite coatings showed blue and black colors with change in concentration and deposition time.

Reflection absorption infrared spectroscopy

The chemical structure and composition of the resulting coatings were determined by using RAIR spectroscopy at a resolution of 8 cm^{-1}. A total of 256 scans were carried out over a scan range of 4000 to 400 cm^{-1}. A background spectrum of bare stainless steel was subtracted from the sample spectrum.

Infrared spectroscopic analysis was performed to study the structure of the electro polymerized polymer coatings on stainless steel substrate. Fig. 2 & 3 shows the IR spectrum of the polyaniline/polypyrrole deposited on stainless steel at different concentration at 1 minute deposition time. Table 1 shows the characteristic peaks of polyaniline coatings and Table 2 shows the characteristic peaks of polypyrrole coating. The IR peaks at 1590 and 1500 cm^{-1} are due to quinoid and benzoid groups respectively. The peaks at 1025 and 930 cm^{-1} are due to pyrrole ring vibrations. The characteristic peak of sulfonic group at 1175 cm^{-1} can attributed to presence of dopant in the coating. Table 3 shows the change in extent of oxidation with change in process parameters for composite. The extent of oxidation increases with deposition time and it decreases with increase in concentration.

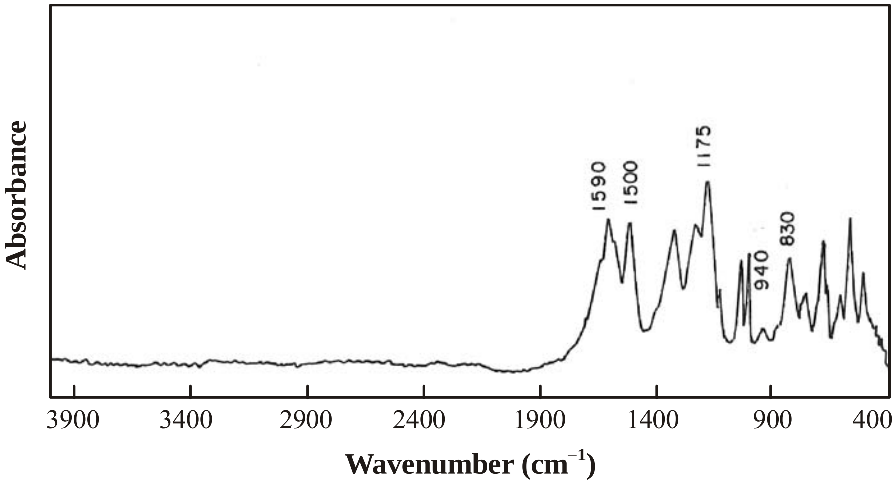

Fig. 2: Infrared spectra of polyaniline/polypyrrole composite coatings formed on stainless steel, 0.1 M composite at 1 minute deposition time

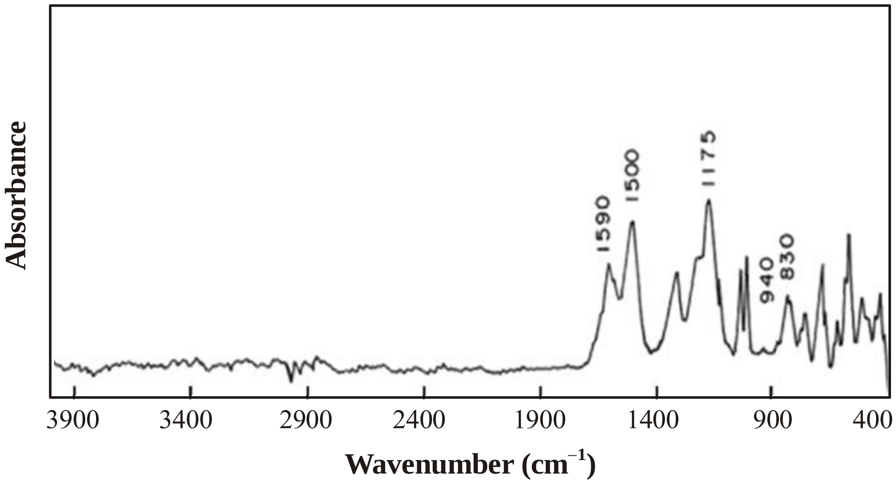

Fig. 3: Infrared spectra of polyaniline/polypyrrole composite coatings formed on stainless steel, 0.2 M composite at 1 minute deposition time

Table 1: Characteristic peaks of polyaniline coatings

Peaks (cm^{-1})	Functional groups
1590	Quinoid
1500	Benzoid
1175	Sulfonic group (dopant)
830	Secondary amine

Table 2: Characteristic peaks of polypyrrole coatings

Peaks (cm^{-1})	Functional groups
1570	C = N stretch
1140	Sulfonic group (dopant)
1025	Pyrrole ring vibration
930	Pyrrole ring vibration

Table 3: Extent of oxidation for polyaniline/polypyrrole composite coatings

Composite coatings	1590/1500	Extent of oxidation
0.1 M, 1 min	1.058	53.40 %
0.1 M, 3 min	1.431	59.85 %
0.1 M, 1min	1.058	53.40 %
0.2 M, 1 min	0.825	46.15 %
0.3 M, 1min	0.586	40.45 %

Atomic force microscopy

The morphology and the roughness of the coatings were determined by using AFM at a scan size of 20 µm. The approximate thickness of the coatings can also be obtained from AFM. The roughness and rms values are noted for each coating that was tested.

Atomic Force Microscopy was used to study the change in morphology of the coatings with process parameters and compare the surface roughness of the coatings. The change in morphology of composite coating with initial monomer concentration of monomer is shown in Fig. 4 & 5. The change in mean roughness and the rms roughness of composite

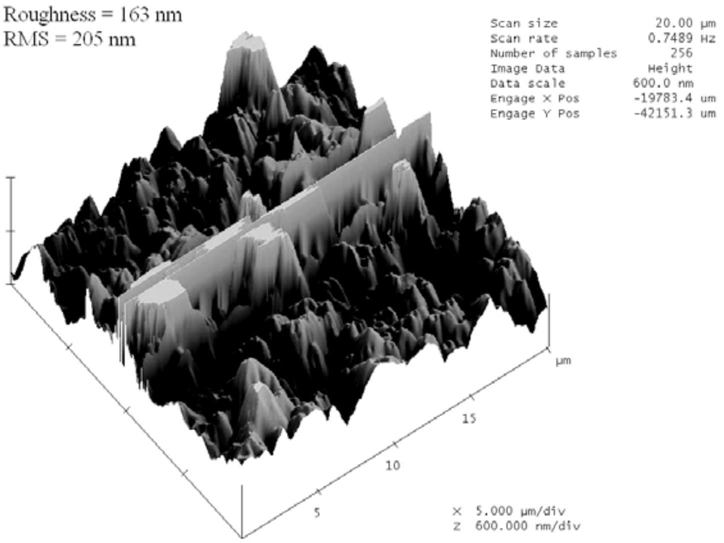

Fig. 4: AFM picture of polyaniline/polypyrrole composite coatings on stainless steel at 0.1 M composite, 1 minute deposition

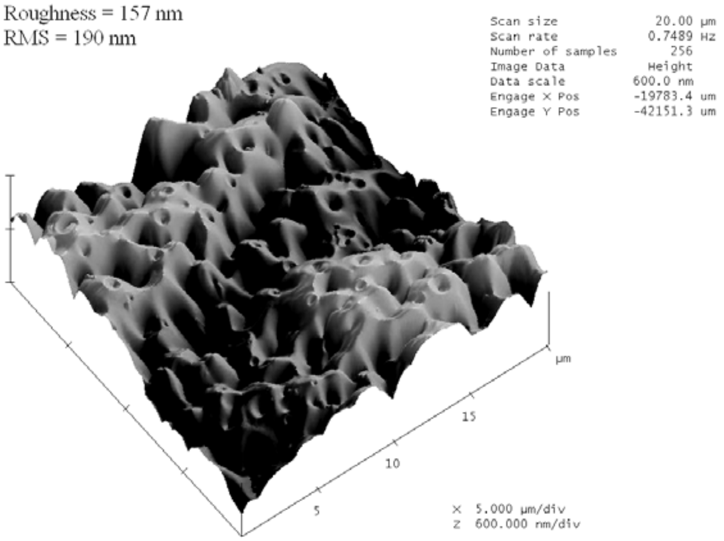

Fig. 5: AFM picture of polyaniline/polypyrrole composite coatings on stainless steel at 0.2 M composite, 1 minute deposition

coatings with monomer concentration of the monomer is shown in Table 4. With increase in the initial monomer concentration the coatings become much smoother. Interestingly, roughness values decrease with the increase in concentration and can be attributed to the smoothening of the surface with increased concentration. The change in morphology with deposition time of composite coating on stainless steel is shown in Fig. 6 & 7. The change in mean roughness and the rms roughness of composite coatings with deposition time is shown in Table 5. Roughness values increased with increase in deposition time.

Table 4: Roughness of polyaniline/polyoyrrole composite coatings on stainless steel with change in concentration of the monomer

Composite coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Ani+Py at 1 min	195	230
0.2 M Ani+Py at 1 min	164	198
0.3 M Ani+Py at 1 min	98	135

Table 5: Roughness of polyaniline/polypyrrole composite coatings on stainless steel with change in deposition time

Composite coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Ani+Py at 1 min	195	230
0.1 M Ani+Py at 3 min	220	255

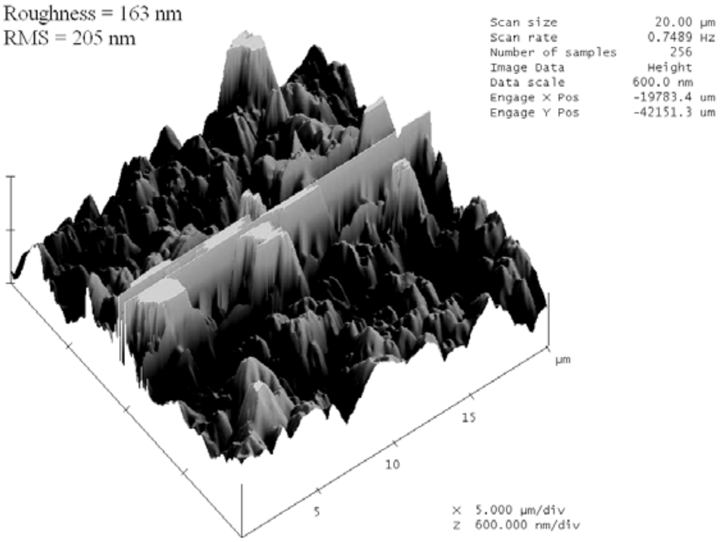

Fig. 6: AFM picture of polyaniline/polypyrrole composite coatings on stainless steel at 1 minute deposition, 0.1 M composite.

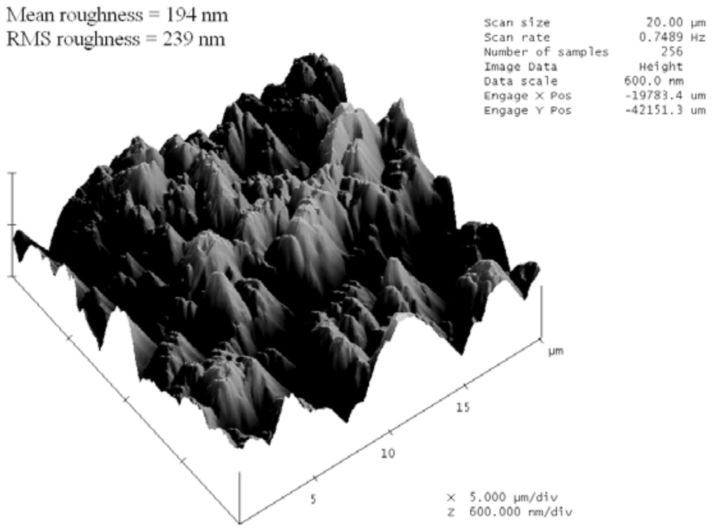

Fig. 7: AFM picture of polyaniline/polypyrrole composite coatings on stainless at 3 minute deposition, 0.1 M composite

CONCLUSION

The formation of polyaniline/polypyrrole composite coatings on stainless steel was successfully achieved by the constant potential method. Electrochemical deposition was carried out at different deposition times and concentrations of monomers. The effect of these parameters were studied by using RAIR and AFM. Infrared spectroscopy was used to understand the structure of the coatings. Atomic force microscopy was used to study the morphology of the coating formed on stainless steel. IR spectra showed the extent of oxidation. The oxidation changes systematically with change in process parameters. As the concentration of the monomer was increased, the extent of oxidation was decreased. As the deposition time was increased, the extent of oxidation was increased. Since the oxidizing form is the conducting form of these polymers, extent of oxidation might affect the corrosion current of the coating. Atomic force microscopy showed the three dimensional morphology of the polyaniline/Polypyrrole composite coatings. The roughness values were also obtained from AFM. In polyaniline/polypyrrole composite coatings showed a decrease in roughness with increase in concentration of monomer.

REFERENCES

1. S. Xianglin and N. S. Dalal, Environ. Health Perspect., **102,** 231 (1994).
2. R. L. Twite and G. P. Bierwagen, Prog. Org. Coat., **33**, 91 (1998).

3. T. P. McAndrew, TRIP, **5**, 7 (1997).
4. B. Wessling, Adv. Mater., **6**, 226 (1994).
5. Y. Wei, J. Wang, X. Jia, J. M. Yeh and P. Spellane, Polymer, **36**, 4535 (1995).
6. L. Wang, X. Li and Y. Yang, Polymers, **47**, 125 (2001).
7. A. Bhattacharya and S. N. Bhattacharya, Synth. Metals, **65**, 35 (1994).

Revised : 29.12.2010 *Accepted : 01.01.2011*