

## Pitting corrosion protection of low nickel stainless steel by electropolymerized conducting polymer coating in 0.5 M NaCl solution

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**Abstract.** Conducting polymers of polyaniline (PANi) and poly(*o*-phenylenediamine) (PoPD) were electropolymerized by cyclic voltammetric technique on low nickel stainless steel (LN SS) in H<sub>2</sub>SO<sub>4</sub> solution containing aniline and *o*-phenylenediamine monomers. The coatings were characterized by Fourier transform infrared spectroscopy, UV-visible and scanning electron microscopic techniques and the results are discussed. The corrosion protective properties of PANi and PoPD coatings on LN SS in 0.5 M NaCl were evaluated using potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) techniques. The potentiodynamic polarization and electrochemical impedance spectroscopic results indicate that the PoPD coating inhibits the corrosion of LN SS in 0.5 M NaCl solution more effectively than PANi.

**Keywords.** Stainless steel; IR spectroscopy; cyclic voltammetry; pitting corrosion; EIS; SEM.

### 1. Introduction

Corrosion of steel has been a perennial problem, causing loss of about 100 billion dollars annually world wide. Efforts to prevent corrosion by efficient and environmentally compliant methods are going on throughout the world (Sitaram *et al* 1997) though it can never be conquered. Stainless steel is widely used in many fields due to their exceptional corrosion resistance. Most stainless steel equipment failures are caused by chloride ions, especially in cooling water systems. In an environment containing chloride ions, localized corrosion such as pitting and crevice corrosion are still serious problems for stainless steel (Osaka *et al* 1989). Pitting corrosion of stainless steel is a destructive form of corrosion in engineering structures as it causes perforation of equipments and their failure. Recently, conducting polymers have received considerable interest as corrosion protective coatings for oxidizable metals. It is now well established that electrochemical polymerization is a simple and most convenient method for synthesizing novel conducting polymers on metallic surfaces to protect corrosion (Sathiyarayanan *et al* 1992; Beck *et al* 1994; Su and Iroh 1999; Cascalheira *et al* 2003; Tuken *et al* 2007). Among the different families of conducting polymers, the polyaniline (PANi) has been the most widely studied due to its environmental stability and the ease of synthesis (Jasty and Epstein 1992; Ahmad and MacDiarmid 1996; Liu and Levon 1999; Wessling and

Posdofer 1999; Bereket *et al* 2005). PoPD was first electrodeposited on 304 SS from aqueous solutions of phosphoric acid and sulphuric acid by D'Elia *et al* (2001) and Hermas *et al* (2006), respectively. There are only a few reports available on the growth of PoPD (Dai *et al* 1998) and Yano (1995) proposed a mechanism for the electropolymerization of *o*-phenylenediamine which takes place through electrochemical process.

The present work deals with the electropolymerization of PANi and PoPD on LN SS by cyclic voltammetry in H<sub>2</sub>SO<sub>4</sub> solution and characterization of these coatings by Fourier transform infrared spectroscopy, UV-visible and scanning electron microscopic techniques. The study includes investigation of corrosion protecting nature of PANi and PoPD coatings on LN SS in 0.5 M NaCl solution and a comparison with that of uncoated LN SS using potentiodynamic polarization and electrochemical impedance spectroscopic techniques.

### 2. Experimental

#### 2.1 Specimen preparation

The composition of LN SS is C = 0.063%, Si = 0.44%, Mn = 7.15%, P = 0.054%, S = 0.013%, Cr = 16.48%, Ni = 4.10%, N = 0.105%, Cu = 1.23% and the rest Fe. The entire test specimens were cut into an overall apparent size of 1 × 1 × 0.3 cm<sup>3</sup> and one side of the specimens were embedded in epoxy resin to study the corrosion inhibition in 1 cm<sup>2</sup> only. The specimens were polished using silicon carbide emery

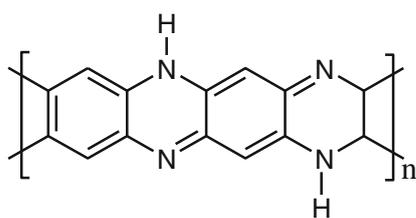
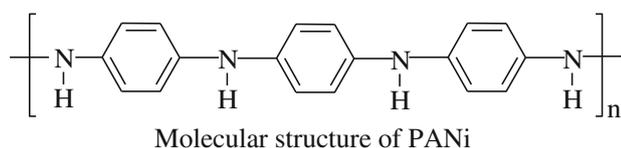
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papers of grit 120–1200 followed by washing with doubly distilled water. They were then degreased with acetone and dried at room temperature.

## 2.2 Electrochemical studies

All the electrochemical measurements were performed using electrochemical workstation (Model No. CHI760, CH Instruments, USA) and the experiments were carried out at a constant temperature of  $28 \pm 2^\circ\text{C}$  with 0.5 M NaCl solution as the electrolyte. A platinum and a saturated calomel electrode were used as auxiliary and reference electrodes, respectively. The working electrode was a stainless steel specimen of  $1\text{ cm}^2$  area. The tip of the reference electrode was positioned very close to the surface of the working electrode with the aid of a fine Luggin capillary in order to minimize the ohmic potential drop. The remaining uncompensated resistance was reduced by the electrochemical workstation.

**2.2a Electropolymerization of polyaniline and poly(*o*-phenylenediamine):** The electropolymerization process was carried out in a one compartment cell with three electrodes. Analytical grades of *o*-phenylenediamine, aniline and  $\text{H}_2\text{SO}_4$  were used. Both *o*-phenylenediamine and aniline were distilled before use and stored in dark. PANi was electrodeposited between  $-0.2$  and  $1.0\text{ V}$  at a scan rate of  $0.05\text{ V s}^{-1}$  from 0.5 M  $\text{H}_2\text{SO}_4$  solution containing 0.1, 0.2 and 0.3 M concentrations of aniline monomer. The polymer, PoPD was deposited on LN SS by cyclic voltammetry between  $-0.5$  and  $1.2\text{ V}$  at a scan rate of  $0.05\text{ V s}^{-1}$  from 0.1 M  $\text{H}_2\text{SO}_4$  solution containing 0.03, 0.05 and 0.07 M concentrations of *o*-phenylenediamine monomer. Among them, the best coating of 0.2 M aniline and 0.05 M *o*-phenylenediamine monomers were taken for this study due to the homogeneous and adherent polymer layer formed on the electrode surface. The polymer coated specimens were rinsed with distilled water for subsequent testing.



**2.2b Potentiodynamic polarization studies:** The potentiodynamic polarization curves of LN SS specimen of uncoated and PANi and PoPD coated specimens were recorded from  $-1.0$  to  $0.3\text{ V}$  at a scan rate of  $0.01\text{ V s}^{-1}$ . In all the cases, the open circuit potential (OCP) was established first and then the polarization measurements were carried out.

**2.2c Electrochemical impedance studies:** Electrochemical impedance studies were carried out using the same experimental setup as that of potentiodynamic polarization studies and the applied ac perturbation signal was about  $0.01\text{ V}$  with a frequency range 100 kHz and 1 Hz. All impedance measurements were carried out at the open circuit potential.

## 2.3 Surface characterization studies

The FT-IR spectra of the polymer film were recorded using NICOLET 380 FT-IR instrument by peeling off the surface of the coated sample. Pellets of the polymer coatings were prepared using bulk KBr. The UV-visible absorption spectral studies were performed in the wavelength range 190–800 nm using microprocessor controlled double beam spectrophotometer (Model: Perkin Elmer Lambda 25). The surface of the substrate and nature of the polymer film formed on the surface of the specimens were analysed by scanning electron microscope (JSM 840A Scanning microscope, JEOL, Japan).

## 3. Results and discussion

### 3.1 Electrochemical studies

**3.1a Synthesis of conductive PANi and PoPD polymers:** PANi was electrodeposited on LN SS in 0.5 M  $\text{H}_2\text{SO}_4$  solution by cyclic voltammetry in the potential range between  $-0.2$  and  $1.0\text{ V}$  at a scan rate of  $0.05\text{ V s}^{-1}$ . The cyclic voltammogram of coated PANi is shown in figure 1(a). The peak intensity of polyaniline is increased with the increase in the number of cycles indicating the formation of a PANi film on the electrode surface. It is seen that the PANi layer on the surface of the electrode is covered with a pale green colour substance. There are two broad oxidation and two reduction peaks observed during the growth of the polymer film. The first oxidation peak (a) at the potential of  $0.3138\text{ V}$  belongs to the formation of the leucoemeraldine cation radical i.e. oxidation of the leucoemeraldine (LE) to emeraldine salt (ES) and the reverse reduction process occurs with a peak potential at  $0.4597\text{ V}$  (c). The second anodic peak (b) occurring at  $0.2734\text{ V}$  is due to further oxidation of the ES into the fully oxidized form of PANi, the pernigraniline (PE) with a corresponding cathodic peak (d) at  $0.5552\text{ V}$  belonging to the reverse process.

The magnitude of the current density of the final voltammogram increases implying an increase in the thickness

of PANi on electrode surface. The cyclic voltammogram of coated PoPD is shown in figure 1(b). The current response increases with increase in the number of cycles indicating growth of the electroactive PoPD film on the stainless steel surface. It is seen that an adherent PoPD (red colour) layer is formed on the surface of the electrode after 50 cycles. The cathodic peak at  $-0.2143$  and the anodic peak at  $1.1366$  V are varied with increasing number of cycles. The rate of polymerization of aniline was found to be higher than that of *o*-phenylenediamine.

It is evident from cyclic voltammetry that PoPD is less conducting than PANi. The molecular mass of PoPD is higher than that of PANi. Consequently, PoPD has better

inhibition properties than PANi. This in turn leads to lower corrosion of stainless steel and hence low conductance.

**3.1b Potentiodynamic polarization studies:** Potentiodynamic polarization curves of the uncoated LN SS and PANi and PoPD coated LN SS specimens immersed in 0.5 M NaCl solution are shown in figure 2. The cathodic and anodic Tafel line of uncoated LN SS and PANi and PoPD coated LN SS specimens were recorded with a potential sweep from  $-1.0$  to  $-0.3$  V. The values of corrosion potential ( $E_{\text{corr}}$ ), current density ( $I_{\text{corr}}$ ), breakdown potential ( $E_b$ ), repassivation potential ( $E_p$ ) and corrosion rate obtained from these curves are presented in table 1.

As evident in figure 2 the anodic current density values of PoPD decrease when compared to the PANi and uncoated specimens. This indicates that the PoPD coating restricts anodic reaction of stainless steel specimens in the aggressive medium. The  $E_{\text{corr}}$  values of PANi coated stainless steel shifts from  $-0.9524$  to  $-0.9231$  V. The PANi and PoPD coated LN SS shows lower current density compared to the uncoated specimen indicating the protecting behaviour of PANi and PoPD coatings. The repassivation potential of PoPD coated LN SS shifts towards nobler direction from  $-0.0984$  to  $-0.0486$  V when compared to uncoated specimen. In addition, the  $I_{\text{corr}}$  value of PoPD coated specimen decreases from  $12.49 \mu\text{A}$  to  $-5.78 \mu\text{A}$  and the current density of uncoated specimen increases due to the anodic dissolution of the alloy.

Further, the pitting potential of PoPD coated stainless steel is shifted from  $0.0366$  to  $0.1629$  V in the positive direction. The inhibitive property of PoPD is greater than PANi due to the presence of  $\pi$ -electron density clouds coexisting with nitrogen atom in PoPD than in PANi. The larger molecular size of PoPD also ensures the greater adsorption and large coverage on the LN SS surface and thereby decreases the effective area for corrosion reaction by blocking the reaction sites. The improvement of corrosion protection is due to the barrier effect against corrosive ions and electroactive interaction of adhesive polymer on the surface (Refaey 2005).

**3.1c Electrochemical impedance spectroscopy:** The impedance measurements provide information on both the resistance and capacitive behaviour of the interface and make it possible to investigate the performance of a polymer

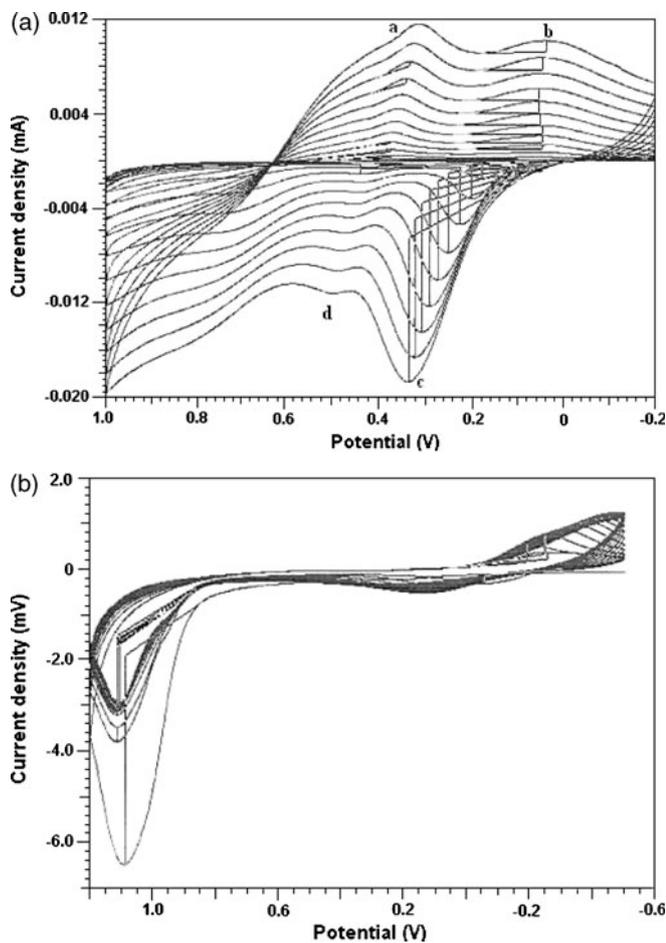


Figure 1. Cyclic voltammograms of (a) PANi and (b) PoPD.

Table 1. Potentiodynamic polarization parameters for uncoated and coated SS in 0.5 M NaCl solution.

Sl. No.	System	$E_{\text{corr}}$ (V)	$I_{\text{corr}}$ ( $\mu\text{A}$ )	$E_b$ (V)	$E_p$ (V)	Corrosion rate (mpy)
1.	Uncoated	$-0.9524$	12.49	0.0366	$-0.0984$	11.43
2.	PANi	$-0.9231$	7.45	0.1344	$-0.0631$	6.823
3.	PoPD	$-0.9083$	5.78	0.1629	$-0.0486$	5.293

coating as a protective layer against metal corrosion (Song 2005).

The Nyquist plots for uncoated LN SS and PANi and PoPD coated LN SS in 0.5 M NaCl solution are shown in

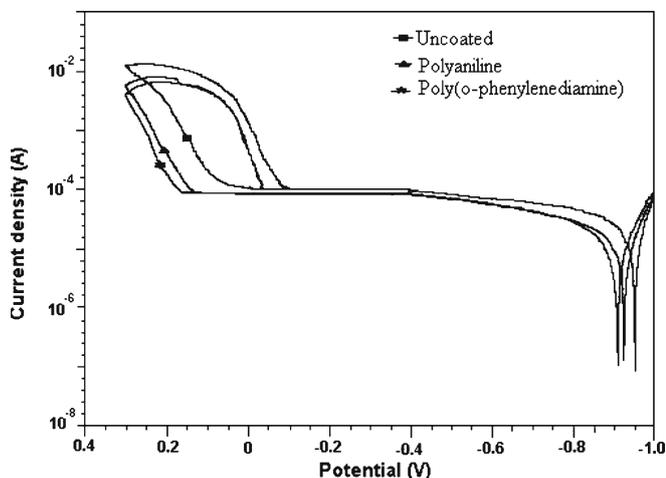


Figure 2. Potentiodynamic polarization curves of uncoated and coated SS.

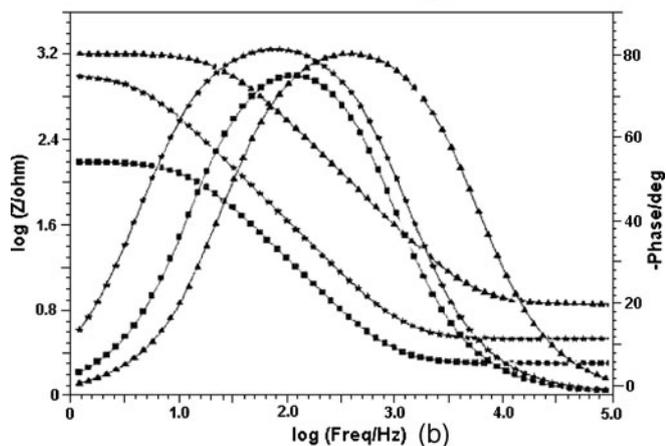
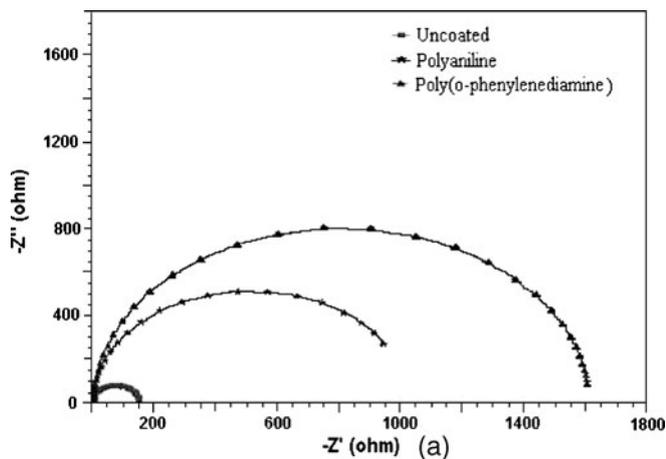


Figure 3. (a) Nyquist plots of uncoated and coated SS and (b) Bode plots of uncoated and uncoated and coated SS.

figure 3(a) and the corresponding Bode plots are presented in figure 3(b). The charge transfer resistance ( $R_{ct}$ ) increased for both PANi and PoPD coated LN SS compared to the uncoated specimen. The  $R_{ct}$  values increase in the order: uncoated specimen and PANi and PoPD coated specimens. This indicates better protective behaviour of PoPD coating in corrosive medium. The low value of  $R_{ct}$  for uncoated specimen is due to the easy penetration of the corrosive chloride ions through stainless steel surface.

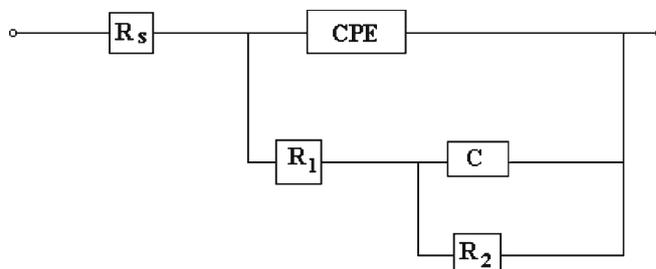
The double layer capacitance ( $C_{dl}$ ) of PoPD decreases to a lower value than that of PANi and uncoated specimen, indicating the thickening of the PoPD polymer film. The values of the different components present in the equivalent circuit evaluated using fitting procedure and the impedance parameters obtained are given in table 2. The equivalent circuit used for fitting the curve is shown in figure 4.

### 3.2 Surface characterization

3.2a FT-IR analysis: The FT-IR spectrum of PANi is shown in figure 5(a). The broad peak around  $3400\text{ cm}^{-1}$  is due to the stretching vibrations of N-H. The peaks at  $1567\text{ cm}^{-1}$  and  $1488\text{ cm}^{-1}$  are due to the C=C and C-C stretching vibrations of the aromatic ring carbons, respectively. The peak at  $1395\text{ cm}^{-1}$  is assigned to the aromatic C-H bending vibration. The peaks at  $1302$ ,  $1137$  and  $814\text{ cm}^{-1}$  indicate the presence of C-N stretching vibrations of the aromatic ring. The out-of-plane C-H bending vibrations are observed at  $744\text{ cm}^{-1}$  and the N-H plane bending

Table 2. Impedance parameters for uncoated and coated SS in 0.5 M NaCl solution.

Sl. No.	System	$R_{ct}$ (k $\Omega$ )	$C_{dl}$ ( $\mu\text{F}$ )
1	Uncoated	150	0.83
2	PANi	1000	0.41
3	PoPD	1600	0.30



$R_s$  - Ohmic resistance of the solution  
 $C$  - Capacitance  
 $R_1$  - Charge transfer  
 $R_2$  - Resistance of the polymer film  
 CPE - Constant phase element

Figure 4. Equivalent circuit.

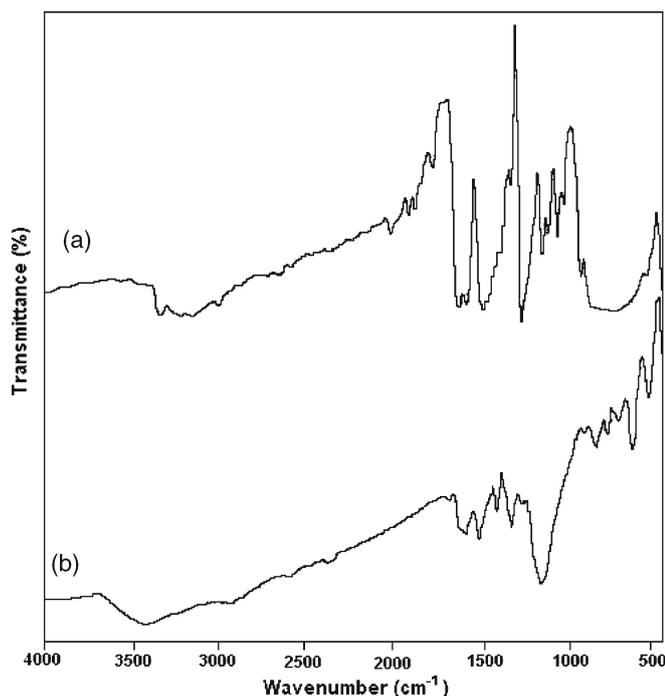


Figure 5. FT-IR spectrum of (a) PANi and (b) PoPD.

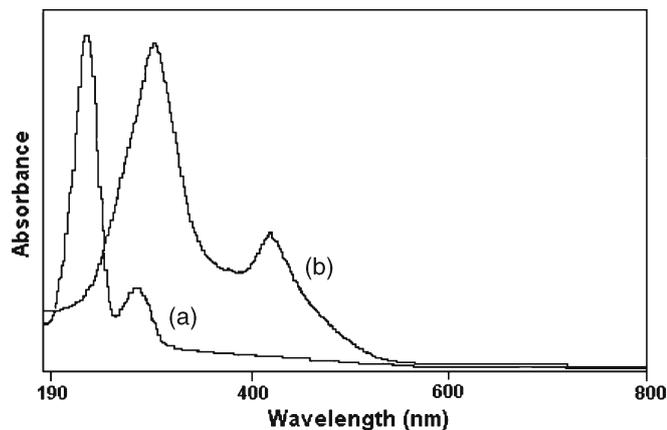


Figure 6. UV-vis spectra of (a) PANi and (b) PoPD.

vibrations occur at  $600\text{ cm}^{-1}$ . The N–H torsional vibrations are found at  $507\text{ cm}^{-1}$ .

Figure 5(b) shows the FT-IR spectrum of PoPD. The stretching vibrations of N–H peak are observed around  $3377\text{ cm}^{-1}$  and the peak at  $2024\text{ cm}^{-1}$  indicates the presence of combination of N–H bands. The N–H bending vibration modes can be assigned in the region  $1918\text{ cm}^{-1}$ . The peaks observed at  $1633$  and  $1587\text{ cm}^{-1}$  are due to the C=C ring stretching vibrations of the aromatic ring. The C–C stretching vibrations of the aromatic ring are observed at  $1495\text{ cm}^{-1}$ . The C–N ring stretching vibrations are observed at  $1330$ ,  $1269$ ,  $1143$  and  $1116\text{ cm}^{-1}$ . The peaks at  $1060$  and  $1023\text{ cm}^{-1}$  correspond to the in-plane C–H bending

vibrations. The out-of-plane C–H bending vibrations are observed at  $747\text{ cm}^{-1}$  and the peak at  $447\text{ cm}^{-1}$  indicates the presence of torsional vibration of N–H (Silverstein and Webster 1996).

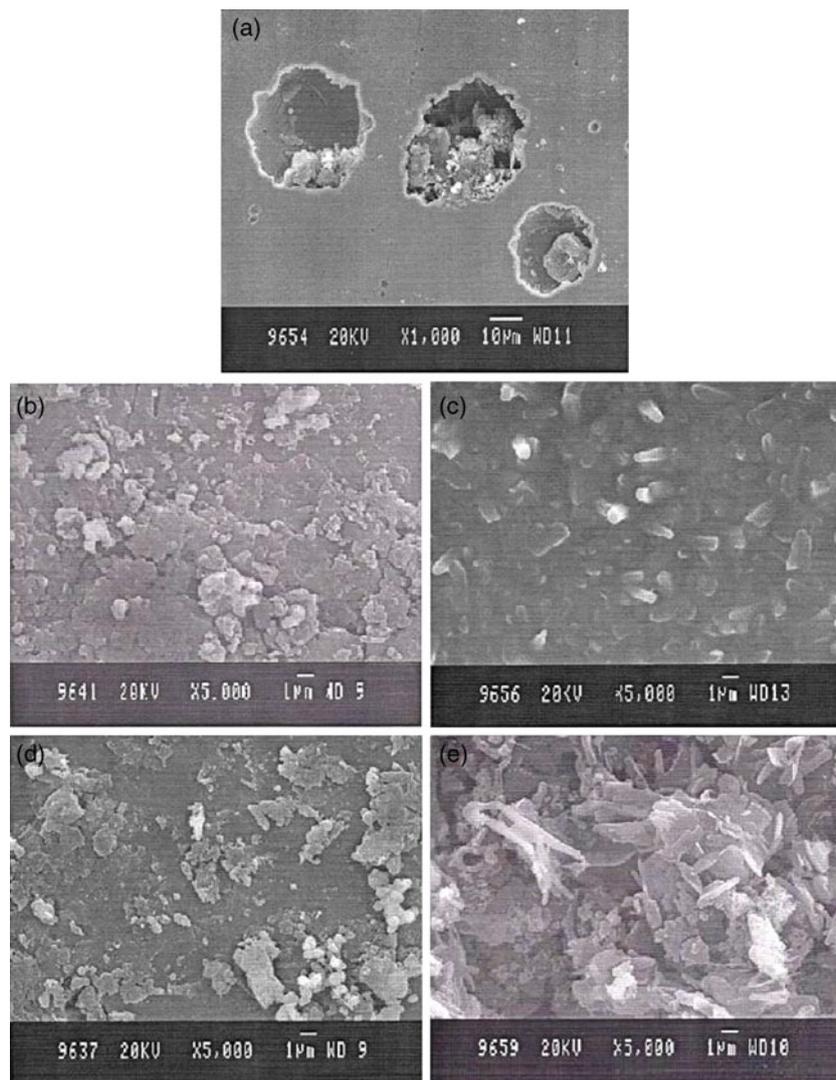
**3.2b UV-visible spectral studies:** The UV-visible spectrum of PANi is shown in figure 6(a). The absorbance at  $285\text{ nm}$  is attributed to the  $\pi \rightarrow \pi^*$  transition of the benzenoid moieties in the PANi structure and the absorbance at  $208\text{ nm}$  is due to the benzenoid-quinoid transition in the emeraldine form of PANi. In the case of PoPD as shown in figure 6(b), the absorbance at  $300$  and  $410\text{ nm}$  are assigned to the electronic transitions corresponding to both aniline and phenazine radicals.

**3.2c SEM analysis:** The morphology of the uncoated LN SS is shown in figure 7(a). The SEM analysis was carried out on LN SS at an impressed potential of  $0.04\text{ V}$  (just above the pitting potential of uncoated specimen) after immersing the sample for  $30\text{ min}$  in  $0.5\text{ M NaCl}$ . The SEM image shows that the uncoated LN SS surface is covered with a high density of pits. The SEM micrographs of the as-deposited PANi and PoPD coatings on LN SS are shown in figures 7(b) and (c), respectively. These pictures show homogeneous films formed over the surface. However, the PANi layer seems to be discontinuously covered on the stainless steel surface. From the SEM micrographs (figure 7c) of PoPD film on the LN SS it is evident that, there is an adherent, compact and uniform coating of the film on the metal surface.

The SEM analysis of coated PANi and PoPD was carried out on LN SS at an impressed potential of  $0.04\text{ V}$  after immersing the sample for  $30\text{ min}$  in  $0.5\text{ M NaCl}$  as shown in figures 7(d) and (e). In the case of PANi coated sample (figure 7d) its surface shows some areas where the coating has been destroyed by the environment. The coating, however, seems to be rougher than the as-deposited film. The PoPD coating on LN SS shows a rough surface as that of the initially deposited one implying that the coating is not considerably influenced by the medium. This is further evident from the fact that the film is homogeneous and completely covered on the substrate. This result proves the effectiveness of PoPD coating as a protective layer to inhibit the corrosive action of  $\text{Cl}^-$  ion on the substrate.

#### 4. Conclusions

Electropolymerized coatings of PANi and PoPD on LN SS were successfully carried out by cyclic voltammetric technique. The PANi and PoPD coated on LN SS were characterized by potentiodynamic polarization, electrochemical impedance spectroscopy, FT-IR and scanning electron microscopic techniques. Adherent, homogeneous (pale green) PANi and PoPD (red colour) polymer films were



**Figure 7.** SEM images of (a) uncoated LN SS, (b) PANi coated SS, (c) PoPD coated SS, (d) PANi coated SS in NaCl and (e) PoPD coated SS in NaCl.

formed on LN SS after electropolymerization. FT-IR and UV-visible spectral results of PANi and PoPD coatings clearly reveal the participation of both monomers in the electropolymerization process resulting in the formation of polymer coating on the metal surface. The potentiodynamic polarization, electrochemical impedance and SEM results reveal that the PoPD acts as a better protective layer than PANi on LN SS against pitting corrosion in 0.5 M NaCl solution.

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