

ELECTROCHEMICAL BEHAVIOUR OF NEW POLYMER COMPOSITE COATINGS ON CARBON STEEL IN ACID MEDIUM

Zoia PAHOM¹, Florina BRANZOI^{2*}, Gheorghe NECHIFOR³

In this research, potentiostatic and cyclic voltammetry electrodeposition methods were utilized for the obtained of new composite polymer: polypyrrole - sodium dioctyl sulfosuccinate/poly N-ethylaniline (PPY-AOT/PNEA) coatings over carbon steel of type OL 37 electrode for corrosion protection. The sodium dioctyl sulfosuccinate as a dopant ion employed in electropolymerization process can have a important effect at the corrosion protection of the composite polymeric film by stopping the penetration of aggressive ions. The polymeric composite coatings were characterized by cyclic voltammetry, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. The corrosion performance of PPY-AOT/PNEA coated carbon steel was studied by potentiostatic and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in 0.5M H₂SO₄ solutions. The effects of the corrosion measurements indicated that PPY-AOT/PNEA coatings ensure good corrosion protection of carbon steel in aggressive environments.

Keywords: polypyrrole – sodium dioctylsulfosuccinate/poly N-ethylaniline film, electropolymerization, corrosion protection, OL 37 steel, coating characterization

1. Introduction

In last years, progress of protective coatings of conducting polymers over active metals is one of the on a large scale studied domain the field of corrosion protection [1–5]. Organic coatings are frequently used to protect these metals and its alloys against corrosion. The efficiency of these protective coatings which ensure a barrier to the substrate depends on numerous factors: type of conducting polymer, electrodeposition method that has been used on the electrode's surface and the aggressive medium [3-9]. Metals (iron, zinc, aluminum, magnesium) and its alloys are widely employed in numerous practices the research in corrosion

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protection of these in various aggressive media. Conducting polymers as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH) and their derivatives are the most elaborated organic polymers have attracted important consideration in the scientific and technological domains in recent years due to their properties like: electrical, optical, thermal, biological and environmental properties [7-18]. Conducting polymers are able to doped and de-doped quickly too great charge density and as an effect are potential active materials for application in numerous electrochemical practices [19-23]. Conducting polymers are likewise intriguing molecular frame since their capacity to strong change properties when developed by an electric signal [22-24]. The composites based of conducting polymers have a series of particular properties like as improved chemical stability, thermostability and right barrier attributed. The synthesis of new polymeric composites from different monomer molecules has been realized to enhance the physico-chemical properties of polymer coatings, to increase for long period protection, for improved adherence and to better the electrochemical properties. However, by achieved suitable of electrodeposition of polymeric composite, it is possible to increase the mechanical and protective properties of the polymer in scope to be utilized as a very good anticorrosive film in different aggressive media. Many studies have been accomplished related on the protective comportment of conducting polymers onto numerous metallic surfaces [9-26]. This can be realized by obtaining organic coatings which have great applications in many domains of materials that they are easy to obtain and pliable to project at large scale [16-28]. Furthermore, they can be readily produced to establish coatings and thin films and were successfully accomplished to enhance the corrosion resistance of some electrode surfaces. The electrochemical and morphological behavior of the obtaining film is different from method to another method, character of the substrate, doping anion and type of the electrolyte. A lot of studies have explained that composite coating can be used as corrosion inhibitors for the corrosion protection of various metals in different media [18-30]. The conducting polymers have efficacious corrosion protection when they are in the conducting form like oxidized and doped state and they lose the protection in its reduced form of the film [22-34]. A successful electropolymerization needs the achieved of a passive film, which could be efficient to hinder the dissolution of the oxidizable metal without stopping the deposition of the monomer and its further oxidation and in final it to obtain a composite film uniform, coherence and adhesion to the substrate electrode. A successful electropolymerization is achieved on a passivated film in order to hinder the dissolution of the oxidizable metal without stopping the deposition of the monomer and its further oxidation. The final result is to give a uniform composite film, coherence and adhesion to the electrode's substrate.

This study involves the synthesis, electrochemical and spectroscopic characterization of composite (PPY-AOT/PNEA) and the corrosion performance of this polymeric composite. The new composite (PPY-AOT/PNEA) which was deposited onto OL 37 surface by potentiostatic and cyclic voltammetry methods in synthesis solutions of 0.1 M polypyrrole, 0.1M N-ethylaniline, 0.05 M sodium dioctyl sulfosuccinate and 0.3 M oxalic acid. Characterization of the new composite polymer coatings has been realized by cyclic voltammetry, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM) techniques. Corrosion tests of PPY-AOT/PNEA coated on OL 37 were analyzed by potentiostatic, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in 0.5 M H_2SO_4 solutions.

2. Experimental

2.1 Materials and Instruments

In this paper, a carbon steel type of OL 37 specimen has been utilized as a material for the corrosion investigation. The chemical composition of working electrode OL 37 is: C% 0.15, Si 0.09%, Mn 0.4 %, Fe% 99.293, P% 0.023, S% 0.02, Al% 0.022, Ni % 0.001 and Cr% 0.001. All chemicals have been reagent grade, sodium dioctyl sulfosuccinate (AOT), N-ethylaniline (NEA), pyrrole (PPY); have been given from Fluka, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was received from Merck. In all measurements, the synthesis solutions have been accomplished with bidistilled water: NEA 0.1M, AOT 0.05M, PPY 0.1M and 0.3M $\text{H}_2\text{C}_2\text{O}_4$. The electrochemical polymerization and characterization were accomplished by using a single -compartment cell with the conventional three electrodes set up at room temperature. The cell was connected to a VoltaLab potentiostat coupled to a PC running VoltaMaster software. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate as an auxiliary electrode. The working electrode was a carbon steel OL 37 disk with a surface area 0.5 cm^2 . A potentiostat VoltaLab PGZ 402 was used in all electrochemical experiments. The composite polymeric coating structure has been carried out by Bruker optics FT-IR spectrometer with ATR in the spectral range $4000\text{-}650\text{cm}^{-1}$. SEM was realized to characterize the surface morphology with JEOL JSM-5500LV microscope.

2.2 Methods

Before each measurement the OL 37 electrode was pre-treat by mechanical polishing with emery papers of different grades 250 to 4000 grit, degreased with acetone. After polishing, the OL 37 electrode was washed with acetone and doubly distilled water and dried at room temperature. PPY-AOT/NEA coatings have been synthesized by the electrochemical polymerization of N-ethylaniline and Pyrrole-AOT on OL 37 electrode surface from synthesis solution using cyclic voltammetry (CV) and potentiostatic technique. The

synthesis solution comprises 0.3 M oxalic acid, 0.1M N -ethylaniline, 0.05M sodium dioctyl sulfosuccinate (AOT) and 0.1M pyrrole. Electrosynthesis was accomplished by scanning the potential between -0.9 and 1.2V at a scan rate of 20mV/s by cyclic voltammetry technique and potentiostatic methods at 1.6V and 1.8 V applied constant potential. After deposition the OL 37 electrode has been remote from the electrolyte and rinsed with double distilled water and dried in air. To investigate the corrosion performance protection of the composite-polymer coated OL 37 electrode were used open-circuit potential, potentiostatic, potentiodynamic polarization and electrochemical impedance spectroscopy measurements in corrosive solutions. The adherence of the coating has been realized by the “standard sellotape test”, which represents of cutting the film into small squares, sticking the tape and then stripping it. The percentage adherence has been achieved by calculating the ratio of the number of the remaining adherent coating squares to the total number of the squares.

The electroactivity of coatings has been examined in a solution of 0.3 M oxalic acid by cyclic voltammetry technique. The corrosion protection of the coated electrode has been examined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements in 0.5M H_2SO_4 solutions. Tafel tests were effectuated by scanning the potential from cathodic to anodic potentials versus to open circuit potential at a sweep rate of 2mV/s. Electrochemical impedance measurements were accomplished in the frequency domain of 100 kHz to 10 mHz with amplitude 10mV at the open circuit potential of PPY-AOT/PNA coated and uncoated electrodes.

3. Results and Discussion

3.1 Electrodeposition PPY-AOT/PNEA coating

Before electrodeposition of PPY-AOT/PNEA, the working electrodes OL 37 was first polarized in 0.3M aqueous oxalic acid solution by cycling the potential electrode, this procedure has been presented in previous papers [14, 16]. The insoluble species obtained from passivation mechanism consist of iron oxides and iron oxalates such as Fe (Ox) (FeO , Fe_2O_3) and FeC_2O_4 which inhibits metal dissolution without impeding the electrodeposition process. The passivated electrode OL 37 under electropolymerization process has been also presented in the literature [16-20]. The electropolymerization of NEA and Py monomers has been achieved on the surfaces of the passivated OL 37 as working electrode. After passivation, the electropolymerization of monomers has been started without changing the polymerization conditions. The polymeric composite was achieved by cyclic voltammetry technique at potential range -900 to 1400 mV and at sweep rate 50mV/s.

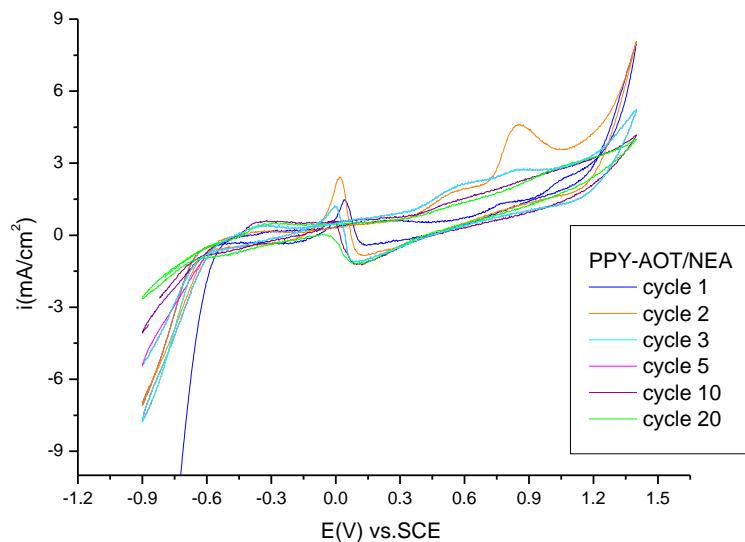
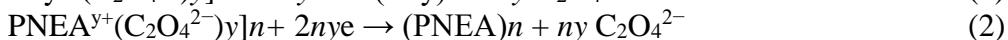
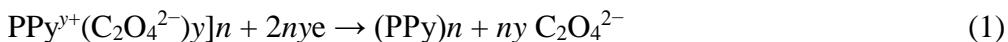


Fig.1 Cyclic voltammograms obtained during deposition PPY-AOT/PNA on OL 37 electrode in 0.3 M oxalic acid solution containing 0.1M PY + 0.05M AOT+0.1M NEA - at the potential interval between -0.9 and 1.4V vs.SCE at a sweep rate of 50 mV/s

Fig. 1 indicates some cycles of cyclic voltammetry (CV) of PPY-AOT/PNEA deposition onto OL 37 electrode from synthesis solution. The small oxidation peak located on the first cycle of potential scan starts at around -420 mV, this value is related to electro-dissolution of Fe (the formation of the passive layer which consists in FeO and FeC_2O_4). The second oxidation peak at about 620 mV and the third oxidation peak at 850 mV could be both assigned to the oxidation of the monomer (NEA, PY) and to the constitution of radical cations. The oxidation seems to be the first step in the polymerization of the conducting polymers. In the reverse scan, a reduction peak was observed at a potential of 132 mV due to the reduction of polymers deposit. A broader peak observed at 25 mV was attributed to the hydrogen reduction reaction. The second cycle indicates that the anodic current rose at about 650 mV and 980 mV vs (SCE) establishing the peak value for anodic oxidation of the monomer and this fact proves that the polymer has been obtained. Over the second cycle, the values of current intensity for oxidation and reduction peaks have been increased with the number of cycles, showing that the electrochemical growth of the conducting polymer has been achieved. It can be observed a methodical increase of the electrode surface as a consequence of the real deposition of PPY/PNEA polymers. Due to the presence of consecutive positive cycles, the oxidation potential of the PPY/PNA polymers has been proven. It could be also seen the deposition of the polymers layers. The oxidation-reduction process of the PPY-AOT/PNA is observed at -400/+980 mV in concordance to the reaction:



This redox method (1-2) is attributed to oxidation and reduction of composite polymer [23].

A black smooth and adherent film on the OL 37 surface can be observed at the end of the experiment. The visual examination of the OL 37 electrode surface after electrodeposition reveals the formation of a black colored PPY-AOT/PNEA. The coating is uniform, compact and adherent to the OL 37 surface. The coating adherence evaluated by "the standard sellotape" was established to be ~80%.

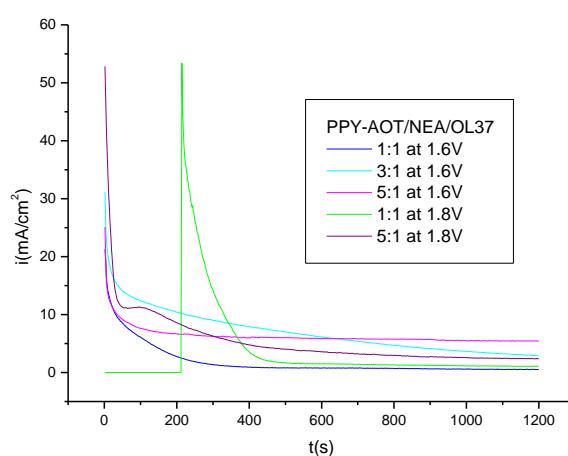


Fig. 2 Potentiostatic deposition of PPY-AOT/PNEA/OL 37 at potential 1.6V and 1.8V vs SCE for 1200 s in different molar ratio for PNEA and PPY-AOT;

PPY-AOT /PNEA polymeric composite films have been electrodeposition over OL 37 carbon steel surface undertaken under potentiostatic conditions from 0.3 M oxalic acid, 0.1M N -ethylaniline, 0.05M sodium dioctyl sulfosuccinate and 0.1M pyrrole. From Fig. 2, it can be observed the „current density –time” curves obtained during the formation of PPY-AOT/PNEA coatings on OL 37 at 1.6 and 1.8 V applied potential in different molar ratio. After the oxidation time of 1200 s, the initial form of the „current density –time” curves during the polymer deposition measurement shows that the polymer deposition has been done by nucleation and growth onto electrode surface [14]. At the beginning, the current fell sharply down due to electro-adsorption of the electrolyte and PY-NEA monomers. After approximately 50 s the current rose and this is due to the dissolution of the passive layer and formation of the polymer on the iron substrate. In the final stage, the current remained constant as the composite polymeric films have been obtained onto OL 37. The transient change of the upper side is linear with the nucleation time variation, the electrochemical verify and the difference in

the molar ratio of PPY: NEA. When the applied potential has been 1.6V at 5:1 and 3:1 molar ratio, the current is nearly constant at 8 mA/cm² and 6 mA/cm², the current was bigger than others potentiostatic polymerization conditions and the obtained films were compact and adherent. (The visual inspection of the OL 37 electrode after electrodeposition shows the formation of a black PPY-AOT/PNEA layer. The coating is uniform, compact and adherent to the OL 37 surface. The coating adherence estimated by "the standard sellotape" was established to be ~80%).

The electrochemical characteristics such as the applied potential were established to have a great consequence on the induction time. It should be mentioned that the 1.6 V applied constant potential in 5:1 for PPY: PNEA molar ratio has a short induction time for formation of electropolymerised coating and it was favorable for the formation of high-quality PPY-AOT/PNEA coatings. As well, it can be said from Fig. 2 that the electrodeposition at 1.8 V applied constant potential in 1:1 for PPY: PNEA molar ratio has a longer induction time for obtained of PPY-AOT/PNEA coating and it was less favorable to the formation of great quality coatings.

3.2 Electrocharacterization of PPY-AOT/PNEA coating

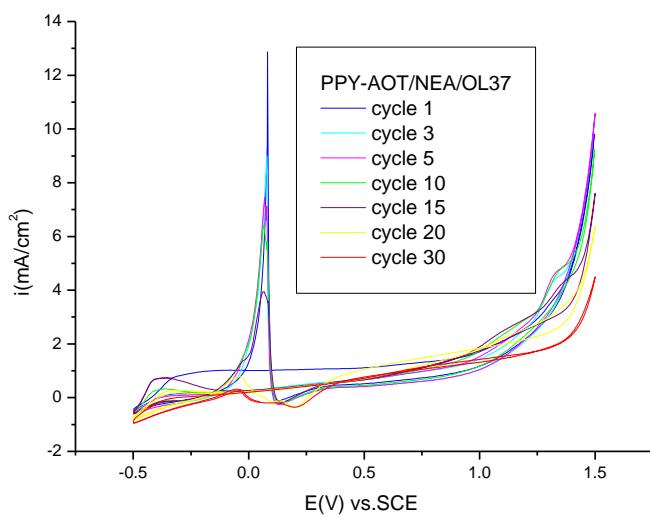


Fig. 3 Cyclic voltammograms of OL 37 electrode coated with PPY-AOT/PNEA/OL 37 in 0.3M H₂C₂O₄ solution monomer free at potential interval -0.5 and 1.5V vs. SCE and scan rate of 20mV/s

The polarization behavior of modified electrode PPY-AOT/PNEA/OL 37 in 0.3 M oxalic acid without monomer is presented in Fig. 3 in the potential interval of -0.5 and +1.5 V vs. SCE and the sweep rate of 20mV/s. Examining the Fig. 3, it could be said that the electrochemical behavior of coating film is depending on the number of cycles and the electrodeposition parameters.

The resistance of any conducting polymer in reduced and oxidized forms is an important characteristic for different applications. The main reason that establishes the lifetime of a conducting polymer is the permanent chemical presence of the matrix itself. The stability of PPY-AOT/PNEA polymeric composite coating was conducted by cyclic voltammetry (more than 15 cycles) in electrolytes without monomers (see Fig. 3). The presence of oxidation and reduction wave after more than 15 cycles points out the steadfastness of these electroactive layers [18, 25, 29-35]. Cyclic voltammetry has been performed in the wide potential domain in order to investigate all the physical and electrochemical properties of the composite films. These films could be cycled repeatedly between the oxidized and reduced form without significant decomposition of the polymeric composite coatings. The current density decreases with each cycle and finally reaches a steady a value that is consistent with the reported results in the literature [18, 25, 26, 30, 35].

3.3 FT-IR studies

The composite polymer structure has been analyzed by Fourier transform infrared (FT-IR) spectroscopy at a resolution 4cm^{-1} (over four scans) in the spectral range $4000\text{-}650\text{ cm}^{-1}$. The FT-IR data display the existence of the important absorption bands noticed for PPY and PNEA deposited over OL 37 electrode.

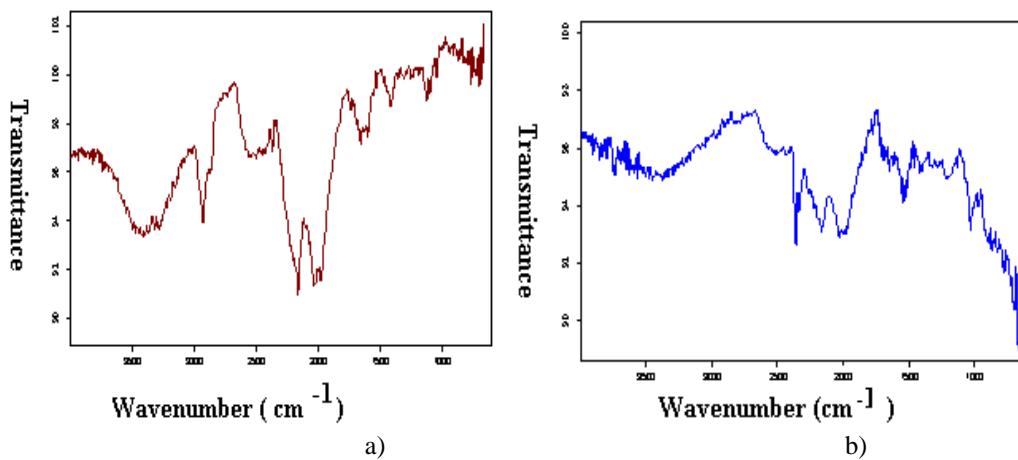


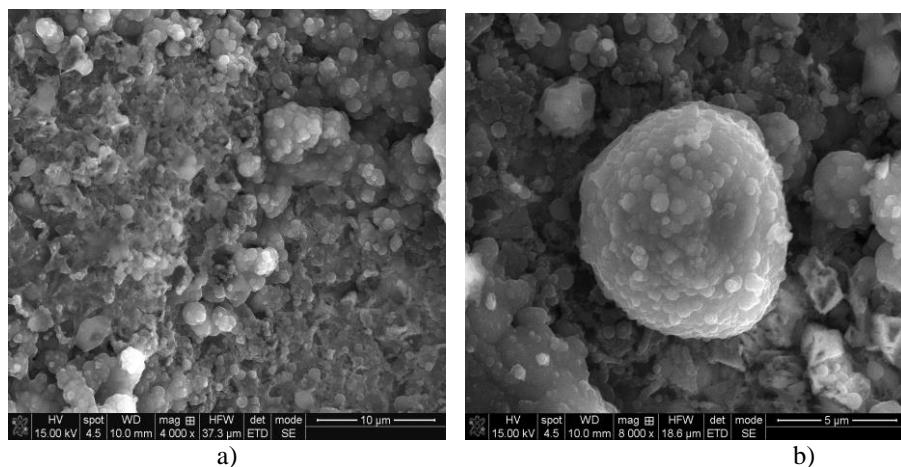
Fig. 4 FT-IR spectra of PPY-AOT/PNEA/OL 37 electrodeposition onto OL 37 electrode at a) potentiostatic at 1.6V potential applies and b) cyclic voltammetry technique in 1:1 molar ratio for PPY-AOT: PNEA

The FT-IR spectrum of PPY-AOT/PNEA/OL 37 electrodeposition by potentiostatic at 1.6V potential applies and by cyclic voltammetry technique in 1:1 molar ratio coating on OL 37 from aqueous oxalic acid medium is shown in Fig. 4a-b. The main characteristic bands of the FT-IR spectrum of PPY-AOT/PNEA

(Fig. 4) coating on OL 37 are ascribed as follows: a broad band located at 3345cm^{-1} is due to the characteristic N-H stretching vibration suggests the presence of NH groups in N-ethylaniline units. The peaks appearing at 1342 and 1308 cm^{-1} are due C-N stretching vibration in aromatic amine. The main characteristic bands for the aromatic ring in PPy is obvious at 1542 and 1476cm^{-1} represents C=C stretching vibration. The bands at approximately 1643 cm^{-1} , 1516 and 1474 cm^{-1} correspond of stretching vibration in quinoid rings and benzenoid rings. The peak at 1209 cm^{-1} is assigned for the C-N stretching vibration of the pyrrole ring. The bands at about 1381 and 1309cm^{-1} are assumed toward N-H stretching vibration of the pyrrole ring. The peak near at $1200\text{-}1250\text{ cm}^{-1}$ is characteristic of the existence of the carboxyl group of the anionic surfactant AOT as dopant in the polymeric composite film. The observation of the peaks at 2988, 2856 cm^{-1} is attributed to the aliphatic C-H stretching vibration of the CH_2 and CH_3 groups in the anionic surfactant-AOT. The presence of the bonds C=O, C-O, C-H, CH_2 is verified by their stretching modes at 1788 cm^{-1} , 1378 cm^{-1} , 1106 cm^{-1} and $1100\text{-}700\text{ cm}^{-1}$, have been most presumably related with the screening of anionic surfactant in the polymer matrix. The peaks which can be established at 1106 , 831 and 970 cm^{-1} are assigned to the in-plane and out-plane C-H of the aromatic rings and to out of plane vibrations of C-H bands of doped PPy in $\text{H}_2\text{C}_2\text{O}_4$ medium. The peaks located at 1060, 1100, and 670 cm^{-1} correspond to in plane and out of plane of the N-H chains which are remarked in the PPy-AOT/PNEA/OL 37 polymer composite layer.

3.4 SEM analysis

Using scanning electron microscopy (SEM), the morphology and structure of the composite polymer coatings PPy-AOT/PNEA obtained onto the carbon steel OL 37 substrate have been analyzed. The SEM micrographs of PPy-AOT/PNEA coatings deposited on OL 37 are illustrated in Fig. 5.



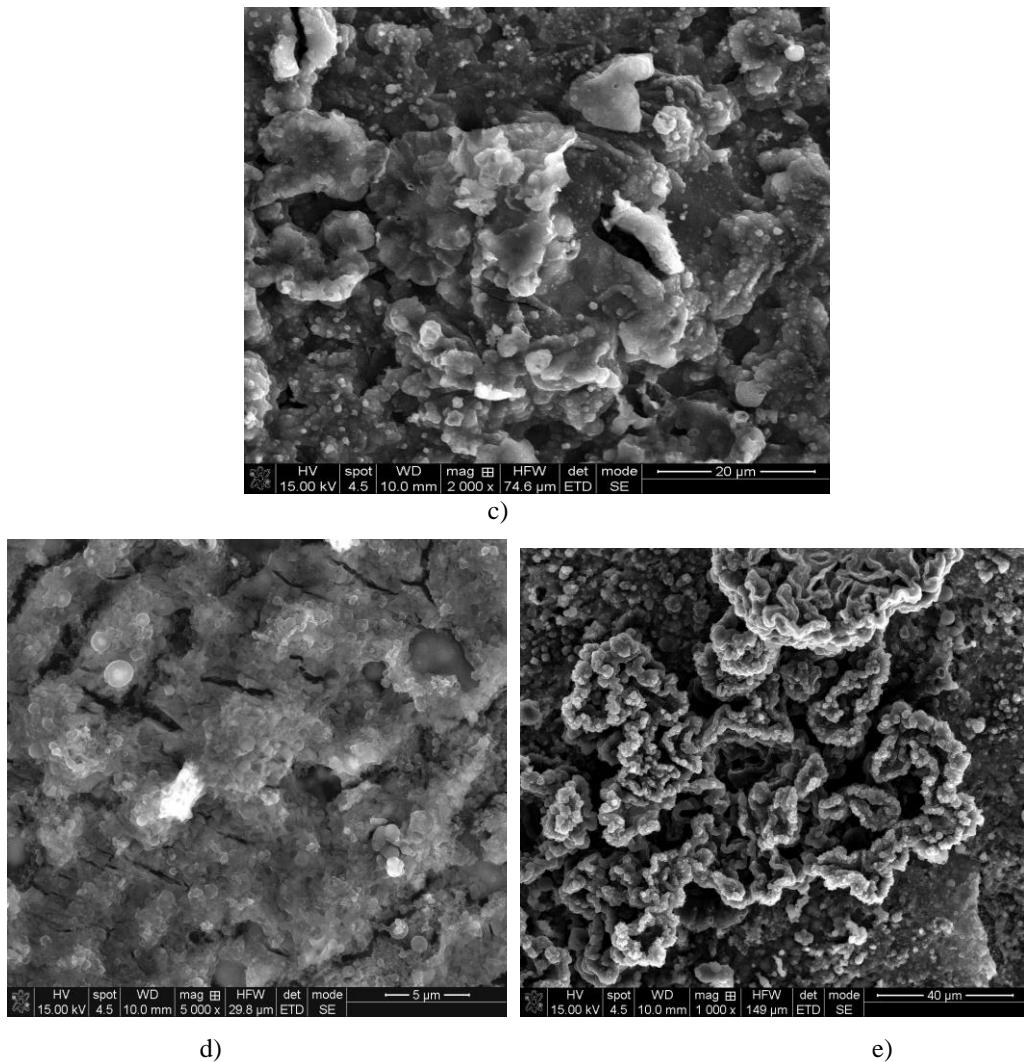


Fig. 5 SEM micrographs of carbon steel type OL 37 electrode coated with PPY-AOT/PNEA/OL 37 a) by CV, b-c) at 1.6V and 1.8V in 1:1 molar ratio and d-e) after 24 h and 96h immersion time in 0.5M H₂SO₄

Fig. 5 shows a thick black layer of the deposited PPY-AOT/PNEA obtained using cyclic voltammetry and potentiostatic technique indicating that the coated polymer composite has been obtained. Looking at Fig. 5 a-c it can be seen that the PPY-AOT/PNEA composite polymer has a uniform size, cauliflower composition with a small globulous microstructure. The grains have a dimension of 5 μ m with an average thickness of 40 μ m. The film is very well defined, compact and adherent onto the carbon steel surface which is comparable with the literature [16, 20, 25, 26, 32-36]. The listed micrographs prove that the film is uniformly deposited on the carbon steel surface; the coating is almost perfect as

there is no crack remarked. The anionic surfactant sodium dioctyl sulfosuccinate sodium (AOT) as dopant incorporated into conducting polymers influences the characteristics of the composite polymer coating. By immersion period (24 h and 96h) in 0.5M H₂SO₄ solution, visible change in the surface morphology of the composite coating has held after the electrochemical measurements. It can be observed at the SEM micrographs: 5d-e which shows the diffusion of aggressive ions SO₄²⁻ in the coated substrate. [16, 20, 31-36].

3.5 Electrochemical studies

The anticorrosion properties of the achieved of PPY-AOT/NEA/OL 37 composite polymer have been examined in 0.5M H₂SO₄ by potentiodynamic polarization technique and electrochemical impedance spectroscopy. Polarization curves of uncoated and PPY-AOT/PNEA coated OL 37 in 0.5 M H₂SO₄ medium are shown in Figs. 6-8. Composite polymer coated surfaces displayed important reduction in anodic and cathodic currents which showed decrease of the cathodic and anodic process. Corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes determined by extrapolation of linear portions of the anodic and cathodic Tafel curves of OL 37 electrode coated with composite polymer are presented in table 1. Also, electrochemical studies were accomplished in 0.5M H₂SO₄ solution for to assess the protection effect of the composite coatings against corrosion. Hence, polarization comportment of OL 37 electrode has been analyzed with those obtained for PPY-AOT/PNEA composite coated carbon steel achieved by cyclic voltammetry and potentiostatic methods in different proportions (molar ratio).

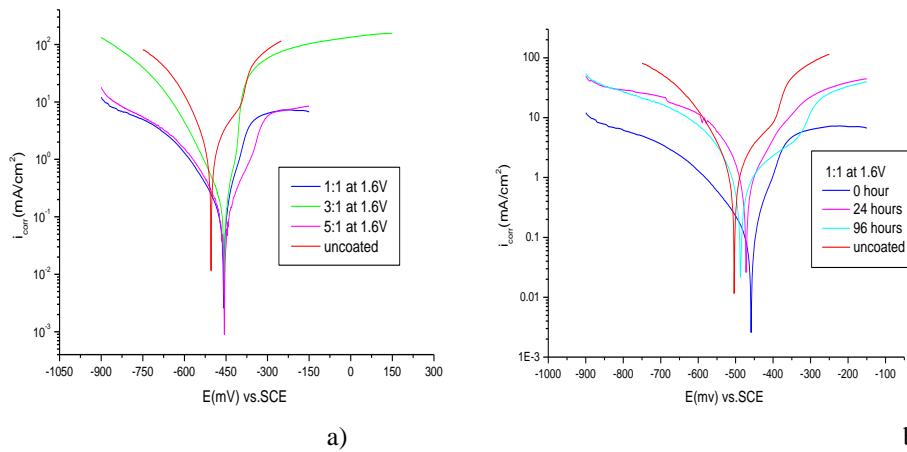


Fig. 6 Polarization curves for PPY-AOT/PNEA a) coated and uncoated of OL 37 electrode in 0.5M H₂SO₄ using potentiostatic technique for electrodeposition in different molar ratio and b) at different immersion times

Tafel slopes getting from the polarization measurements are indicated in Fig. 6-8 and the suitable kinetic parameters (corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants, polarization resistance (R_p) and corrosion rates) are indicated in table 1. Figs. 6-8 compare the corrosion behaviour of the OL 37 uncoated and OL 37 coated with PPY-AOT/PNEA composite polymer. Analyzing of this polarization curves it can be observed that corrosion potential of coated surface of OL37 are shifted to more positive potential as compared to those of the uncoated electrode. This fact it can may be as a result of the attack of corrosive species that come into the pores of composite polymer resulting to the formation of passive films which hinder corrosive of carbon steel. Examination of the polarization curves in Fig. 6 and table1 appeared that the kinetic corrosion parameters of uncoated of OL 37 and their comparison with the characteristics from coated surface electrode at different immersion times in 0.5M H_2SO_4 solutions show that these coatings inhibit the anodic dissolution of metal (Fe) in the aggressive solution. The variation of protective PPY/AOT/PNEA coating in function an immersion time is showed in Fig. 6b and table 1, it can be observed that after the immersion period from 96 h is indicating a slight increase in corrosion rate. This fact is as a result for the deterioration of surface morphology by increasing immersion time because of to modify active surface and to the constitution of some deficiency on the polymeric composite film allowing to the admission of the corrosive ions at the metal/composite interface.

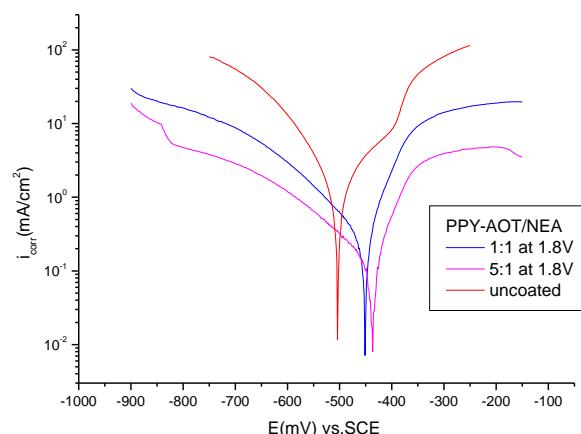


Fig. 7 Polarization curves for PPY-AOT/PNEA coated and uncoated of OL 37 electrode in 0.5M H_2SO_4 using potentiostatic technique at 1.8V potential applied for electrodeposition

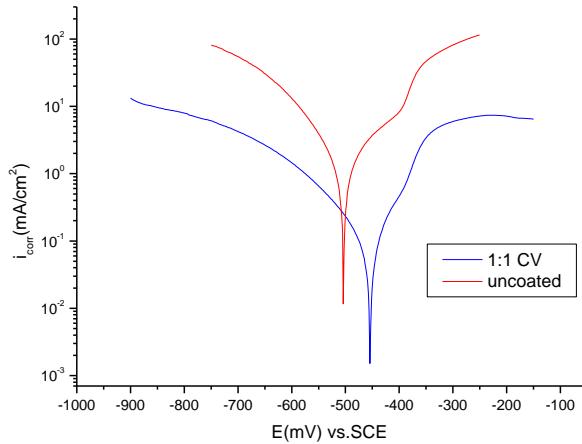


Fig. 8 Polarization curves for PPY-AOT/PNEA coated and uncoated OL 37 electrode in 0.5M H_2SO_4 using cyclic voltammetry technique for electrodeposition

It can be said from Figs. 6-8 and table 1 that current density (i_{corr}) and corrosion rate values decrease significantly when the PPY-AOT/PNEA composite polymer is electrodeposited by potentiostatic technique at 1.6V potential applied in molar ratio 5:1; 1:1 and by voltammetry cyclic method (1:1).

Table 1

Electrochemical polarization parameters of coated and uncoated of carbon steel OL 37 electrode in 0.5M H_2SO_4 solutions at 25°C

The system PPY-AOT/PNEA/OL 37	E_{corr} (mV)	i_{corr} (mA/cm²)	R_p (Ωcm)	R_{mpy} (mil/yr)	$P_{\text{mm/year}}$ (mm/yr)	b_a (mV/decade-de)	$-b_c$ (mV/decade-de)	E (%)	% P
OL 37 + 0.5 M H_2SO_4	-508	0.897	13.82	419	10.63	101	83	-	
PPY-AOT /PNEA 1.6V 1:1 molar ratio	-459	0.11	140	51.33	1.30	60	113	88	0.0 19
PPY-AOT /PNEA 1.6V 3:1 molar ratio	-457	0.15	87	70	1.77	50	90	83	0.0 38
PPY-AOT /PNEA 1.6V 5:1 molar ratio	-453	0.080	217	37.33	0.94	78	96	91	0.0 13
PPY-AOT /PNEA 1.8V 1:1 molar ratio	-453	0.26	60	121	3.07	58	133	71	0.0 55
PPY-AOT /PNEA 1.8V 5:1 molar ratio	-437	0.12	131	56	1.42	62	144	87	0.0 16
PPY-AOT /PNEA CV 1:1 molar ratio	-454	0.086	188	40	1.01	70	96	90	0.0 18
PPY-AOT /PNEA 1.6V 1:1 molar ratio after 24h	-473	0.52	28	243	6.15	85	70	42	0.2 07
PPY-AOT /PNEA 1.6V 1:1 molar ratio after 96h	-487	0.54	26	252	6.40	127	80	40	0.3 31

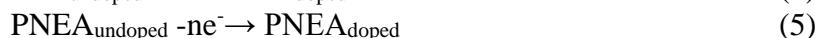
R_{mpy} – the corrosion rate in mil/year (milinches/year); $P_{\text{mm/year}}$ – the corrosion rate in mm/year; E% – the efficiency of the used coated, $E\% = (i_{\text{uncoated}} - i_{\text{coated}}) / i_{\text{uncoated}} \times 100$

The corrosion performance of the composite polymer has a higher value when the molar ratio is 5:1 and 1:1 PPY -AOT: PNEA obtained by potentiostatic (at 1.6V) and CV methods. The coating has a greater anticorrosive efficiency since the polymer PPY film was doped with anionic surfactant of type dioctyl sulfosuccinate sodium (AOT). The use of great anions improves the anticorrosion protection of the composite film by stopping the penetration of corrosive ions. The protection result can be determined by the fact that the anionic surfactant (AOT) competitively is adsorbed on the OL 37 surface blocking the active sites and hence the SO_4^{2-} anion is hindered from touching the OL 37 surface and protection is accomplished. The corrosion rate of PPY-AOT/PNEA coated OL 37 has been indicated to be ~10 times lower than which was remarked for uncoated OL 37. Anticorrosion properties of PPY-AOT/PNEA coated OL 37 electrode appeared that the composite polymer coated electrode had noticeably higher corrosion resistance and smaller corrosion rate compared to uncoated OL 37 electrode. The corrosion protection effectiveness of the composite coating is more than 90% (91% for PPY-AOT /PNEA at 1.6V in 5:1 molar ratio).

The corrosion mechanism of OL 37 coated with composite polymer and uncoated in H_2SO_4 solution can be realized thus [27]:

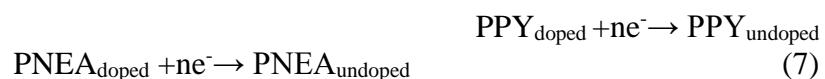
-anodic reaction (3-5): is dissolution of Fe

Anodic reactions:



Cathodic reactions:

-cathodic reaction (6-8) is reduction of the oxygen by reaction:



-Chemical reactions:



The porosity of these composite coatings (PPY-AOT/PNEA) is an important parameter for see when a coating is suitable or not for protection. The porosity of the coatings has been assessed with the following relationship [30-32]:

$$P = \frac{R_p(\text{uncoated})}{R_p(\text{coated})} 10^{-(I \Delta E_{corr} I / \beta_a)} \quad (9)$$

P is total porosity,

R_p - the polarization resistance for uncoated and coated electrodes

ΔE_{corr} -the difference between corrosion potential of coated and uncoated electrodes and β_a is the anodic Tafel slope for uncoated OL 37 electrode.

It can be seen from table 1 that the porosities of PPY-AOT/PNEA coated OL 37 electrode by electrodeposition technique are 0.013, 0.015, 0.016 and 0.018 at potential applied: 1.6V and 1.8V (in 5:1 and 1:1 molar ratio) and by cyclic voltammetry (in 1:1 molar ratio). The meaningfully smaller measure of the porosity in the PPY-AOT/PNEA coatings indicates important improvement of the protective effect by preventing the admission of the aggressive environment on the OL 37 electrode surface. The best effectiveness is accomplished of PPY-AOT/PNEA obtained by electrodeposition at 1.6V applied potential in molar ratio 5:1 and very good efficiency by cyclic voltammetry in molar ratio 1:1. The results getting in this research can be presented by the anticorrosion performance of composite polymer on the electrochemical properties of working electrode. The corrosion protection properties of PPY-AOT/PNEA composite coated on OL37 electrode in H_2SO_4 solution have been also examined by electrochemical impedance spectroscopy (EIS). Impedance measurements were accomplished at open circuit potential on the frequency range from 100 kHz to 40 mHz with an AC wave of ± 10 mV (peak-to-peak) and the impedance effects were achieved at a rate of 10 points per decade change in frequency. EIS experiments yield knowledge regarding to investigation the anticorrosive protection of a composite coating as a protective layer at corrosion of OL 37 electrode in aggressive environments. Fig. 9 shows the Nyquist impedance plots recorded for PPY-AOT/PNEA coatings of OL 37 electrode and for uncoated electrode in sulfuric acid medium.

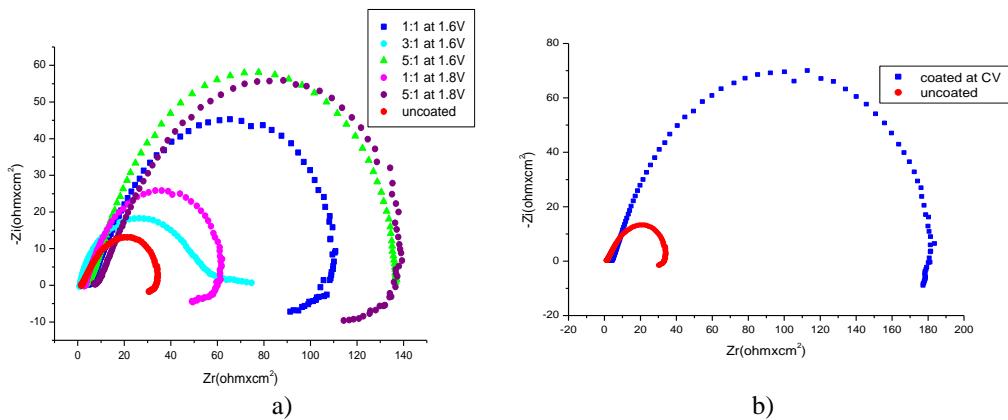
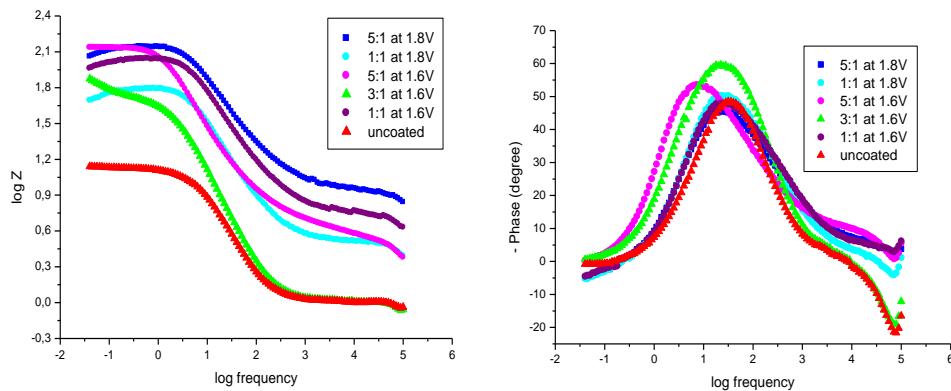


Fig. 9 Nyquist plots for uncoated and PPY-AOT/PNEA coated of OL 37 electrode using (a) potentiostatic method and (b) cyclic voltammetry technique for electrodeposition

It can be observed from Fig. 9 the Nyquist plots for PPY-AOT/PNEA coated on working electrode showing only one semicircle that is typical for a

charge transfer reaction. Fig. 9 also displays that the diameters of the capacitance loops in the existence of the composite coatings are higher than those in the non-existence of coatings, proposing that these coatings has very good anticorrosion properties over OL37 electrode in 0.5 M H₂SO₄. It could be said that the diameters of the capacitance loops of PPY-SDS/OL37 coatings (see Fig. 9) achieved by potentiostatic method at 1.6 V (in molar ratio at 5:1) and by CV (in molar ratio at 1:1) are higher than those achieved at 1.8V potential applied and as a consequence the protection effectiveness of this coatings is bigger. In the present research, for all the coatings examined, the electrochemical impedance spectra are appeared by one semicircle, with a high frequency capacity loop and low frequency inductive loop [14-16, 31-33]. As well, these capacitive loops are not exact semicircles and this occurrence is attributed to frequency diffusion, greatly assigned to roughness and inhomogeneities of the electrode surface [30-36].

The Bode diagrams are presented in Figs. 10-11 are in agreement with Nyquist diagrams. It can be said that in absence of PPY-AOT/PNEA coatings the OL 37 electrode presents one time constant suitable to a phase angle of about -45° at average and low frequencies, this case denotes an inductive comportment with low diffusive trend. Also, in the presence of the PPY-AOT/PNEA coatings, on the diagrams- phase angle against log frequency indicates a maximum appropriate to a phase angle of about -70° which represents that in this occurrence the electrode has a strong capacitive behaviour, conformable with the Nyquist diagrams and in agreement with the data getting by electrochemical polarization.



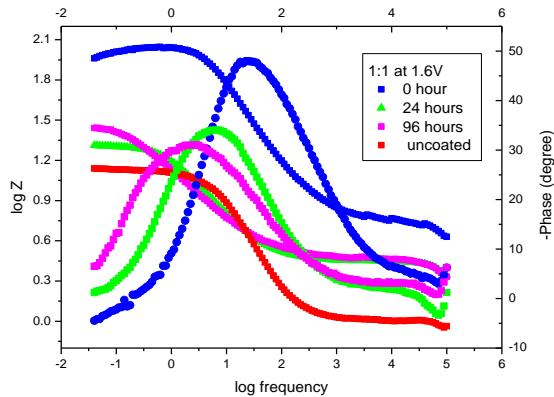


Fig. 10 Bode plots for uncoated and PPy-AOT/PNEA coated of OL 37 electrodes by potentiostatic technique for electrodeposition and at different immersion times

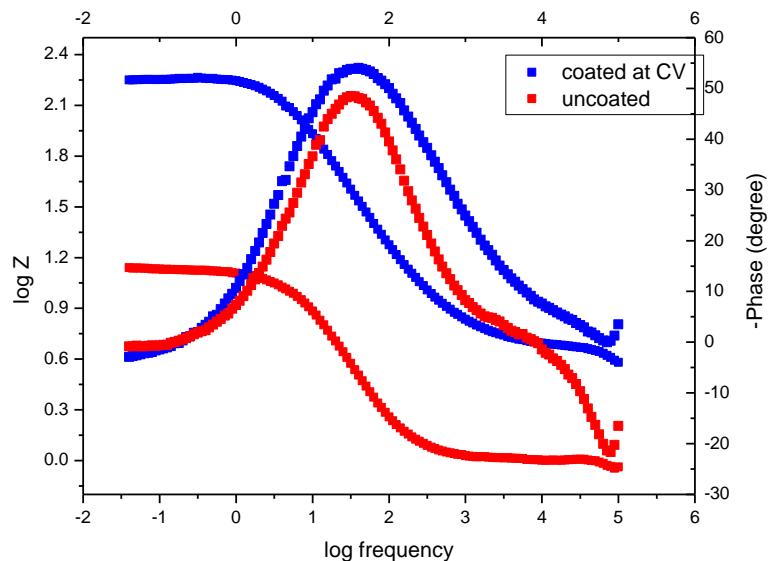


Fig. 11 Nyquist plots for uncoated and PPy-AOT/PNEA coated of OL 37 electrodes by cyclic voltammetry technique

The Bode plots for PPy-AOT/PNEA coating (see Figs. 10-11) revealed that the modules-Z decreases with increasing frequency, suggesting that the impedance of this coating increases with time. The Nyquist and Bode plots denote that the mechanism of corrosion hindering by electrodeposition of PPy-AOT/PNEA coating is performed like a diffusion blockade and by a charge transfer reaction.

6. Conclusions

PPY-AOT/PNEA composite coatings were successfully electrodeposited onto OL 37 substrate by potentiostatic and cyclic voltammetry technique.

Corrosion tests of OL 37 coated show a significant anticorrosion performance in H_2SO_4 , without peeling of these composite films. The corrosion rate of PPY-AOT/PNEA coated OL 37 has been indicated to be ~10 times lower than of uncoated electrode. The FT-IR analysis confirms presence of PPY-AOT/PNEA deposited over OL 37 electrode. The SEM micrographs of the PPY-AOT/PNEA coatings electrodeposited on OL37 are uniform, adherent, resistant and homogeneous and the quality of the coating is so excellent.

PPY-AOT/PNEA coating is promising and might lead to industrial applications in the protection of the carbon steel substrates against corrosion. The method used for obtaining of composite coating is simple enough and inexpensive. The best effectiveness is accomplished of PPY-AOT/PNEA obtained by electrodeposition at 1.6V applied potential in molar ratio 5:1 and very good efficiency by cyclic voltammetry in molar ratio 1:1. The corrosion protection effectiveness of the composite coating is more than 90%.

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