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CHARACTERISTICS AND CORROSION PROTECTION OF POLYPYRROLE DOPED WITH SALICYLATE ANIONS ON CT3 STEEL PASSIVATED BY MOLYDATE

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Abstract. In recent years, the conducting polymers have attracted much attention in research and development because of their applications in medical and civil engineering. Here, the salicylate doped polypyrrole films were prepared on the carbon steel surface and their corrosion protection in 3 % NaCl solution were studied. Polypyrrole (Ppy) film was electrochemically synthesised with constant current techniques in a sodium salicylate solution (0.05M, 0.1M, 0.15M) and 0.1M pyrrole monomer on mild CT3 steel electrode passivated by molybdate. The morphological, structural, composition and thermal properties of salicylate doped Ppy films were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA) techniques. The anti-corrosion ability of these films was assessed by electrochemical measurements in 3 % NaCl solution. The obtained results suggested that salicylate anions contributed in corrosion protection ability of Ppy films for mild steel electrode. The concentration of sodium salicylate of 0.1M and pyrrole of 0.1M is most suitable for preparation of good protection coating. The self-healing mechanism has been also mentioned for salicylate doped Ppy films on CT3 steel substrate.

Keywords: Polypyrrole, corrosion protection, CT3 steel, sodium salicylate.

1. INTRODUCTION

In recent years, the conducting polymers have attracted much attention in research and development for various fields including anti-corrosion coating [1-4], drug delivery systems [5, 6], and biosensors [7]. In particular, polypyrrole (Ppy) is one of the promising conducting polymers thanks to its great advantages such as high biocompatibility, good mechanical properties, high electrical and thermal properties, and good stability in different environments [2, 8-11].

The Ppy films can be synthesized by using electrochemical or chemical methods in the presence of dopants to improve the physical and chemical properties of Ppy. For anti-corrosion application, Ppy films have usually been synthesized individually or combined with different inhibitors, for examples, salicylic acid [1], salicylate [2-4], oxalic acid [12], citric acid [13], succinic acid [14], molybdate [15], 10-camphorsulfonic acid and molybdate [16], etc. The presence of inhibitors plays an important role in enhancement of the anti-corrosion ability of Ppy films.

A. S. Liu *et al.* have synthesised Ppy film in presence of salicylic acid (SA) of various concentrations (50.0; 25.0; 12.5 and 6.25 mmol/L) directly at copper surface by *in situ* chemical deposition method using hydrogen peroxide as a catalyst and ethanol as a solvent [17]. The Ppy/salicylic films were homogeneous and could adhere well on copper surface. Ppy/salicylic films exhibited a good corrosion protection for copper surface. The higher concentration of SA in electrolyte was, the lower the order of corrosion resistance could be obtained.

Although there are many corrosion inhibitor anions for steel, there are only a few anions that could be used as dopant of Ppy film for corrosion protection [18-20]. Among all these inhibitor anions, salicylate has been found to be a good candidate [2-4, 17]. They can be prepared as a good conductivity electrolyte for the polymerisation of Ppy. Ppy doped with salicylate clearly shows the redox property. It is benefit for corrosion protection of substrate metal as anion-releasing mechanism. It has been demonstrated that the obtained Ppy coatings could provide corrosion protection of different metallic substrates.

In another report, we have studied the polymerization, electrical and corrosion properties of Ppy films in the presence of sodium salicylate by the electrochemical method [1]. In this study, Ppy films doped with salicylates were electrochemically deposited on the CT3 steel surface activated by molybdate and the corrosion protection mechanism of Ppy coating on iron has not been studied. In addition, the morphological, thermal and corrosion properties of the Ppy films which were synthesized electrochemically in sodium salicylate solution at different concentrations on CT3 steel substrate without any pre-treatment will be evaluated. Finally, the corrosion protection mechanism of Ppy films doped with salicylates for steel substrate will be suggested/proposed.

2. EXPERIMENTAL

2.1. Chemicals

Pyrrole monomer (was distilled under nitrogen before using), sodium salicylate ($C_7H_5NaO_3$, M = 160.11) were provided by Merck Co.

2.2. Preparation of salicylate doped Ppy films

In this study, the mild CT3 steel (TISCO company, Thai Nguyen) was used and treated following the processed reported in Ref. [15].

The salicylate doped Ppy films were prepared on the CT3 steel surface at a constant current of 1mA cm^{-2} for 60 minutes using Potentiostat/galvanostat model Zennium

(Germany). In this study, we paid more attention on the role of the anions as dopants so that all the film sample were synthesized with the same thickness, approximately 20 μm. The thickness of the film was calculated with the charge passed through the cell, assuming 0.4 $C.cm^{-2}.\ \mu m^{-1}$ [21].

The concentration of the pyrrole monomer was 0.1M and the concentration of the sodium salicylate solution was varied between the concentrations 0.05M; 0.1M and 0.15M. The obtained salicylate doped Ppy films were washed with distilled water and dried at 50°C in vacuum. The abbreviation of salicylate doped Ppy films is **M1**, **M2** and **M3** corresponding to the ratio of pyrrole monomer/sodium salicylate solution (M/M) of 0.1/0.05; 0.1/0.1 and 0.1/0.15 respectively.

2.3. Characterization of salicylate doped Ppy films

The FTIR spectra of salicylate doped Ppy films were recorded using Prestige - 21 (Shimadzu, Japan). TGA was carried out using Ghimashu - 50H (Shimadzu, Japan)) at the conditions of room temperature to 700 °C, the scan rate of 10 °C/min in air. SEM images and EDX spectra of films were taken on a FESEM 4800 (Hitachi, Japan).

2.4. Corrosion protection test

The open circuit potential (OCP), Tafel curves and electrochemical impedance spectroscopy (EIS) were tested in 3% NaCl solution using Zennium machine (Zaehner, Germany).

3. RESULTS AND DISCUSSION

3.1. Electrochemical synthesis of salicylate doped Ppy films

The potential curves of the electrosynthesis process of salicylate doped Ppy films with different salicylate concentrations are shown in Figure 1.

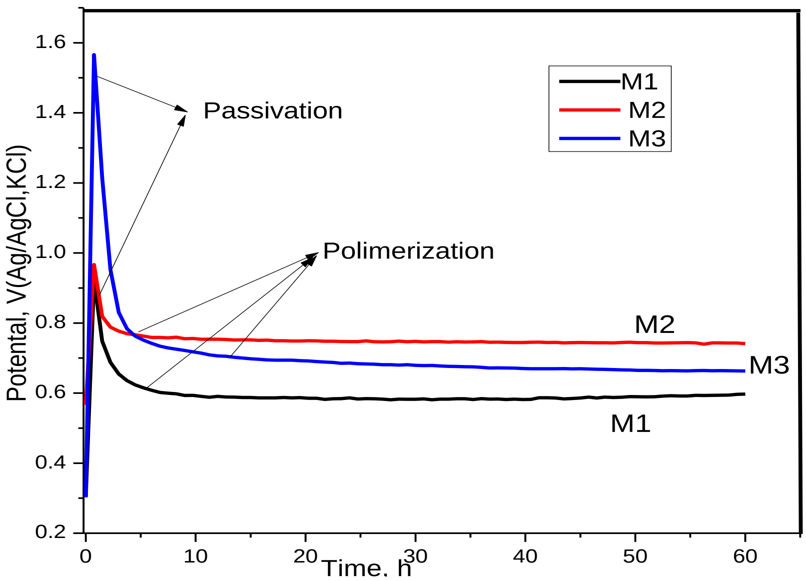


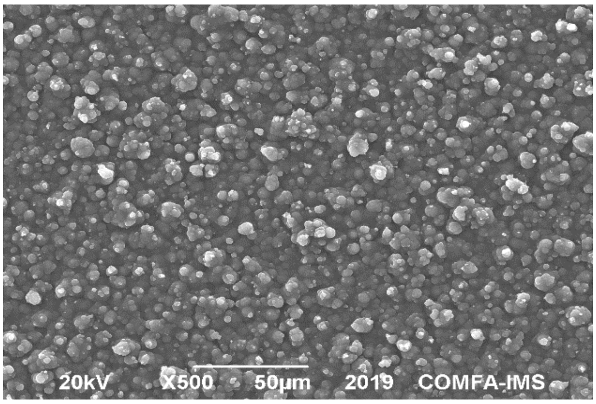
Figure 1. The current–time curves of electropolymerisation of Ppy indifferent solutions.

As observed in Fig. 1, steel samples were passivated before polymerization occurs. The obtained salicylate doped Ppy films were thin and homogenous with smooth and black colorand. The passive layer on steel was formed with molybdate as pretreatmentso that the polymerization of pyrrole monomer in the presence of salicylate anion could occur without any problem [3].

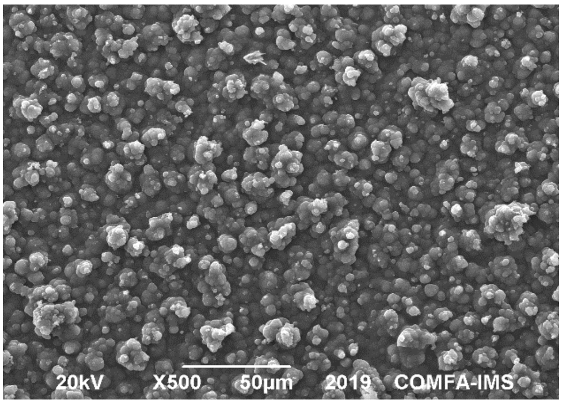
3.2. Morphology, structure and composition of salicylate doped Ppy films

3.2.1. SEM imagines of Ppy films

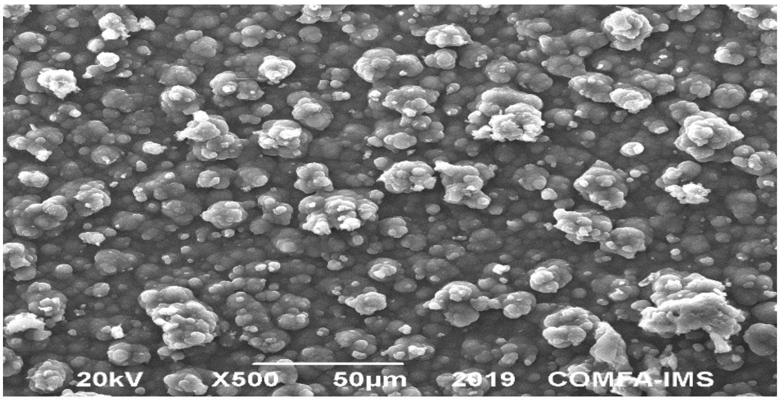
The SEM of salicylate doped Ppy films were shown in Figure 2. The salicylate doped Ppy films have homegenous morphology with the typical “cauliflower” structure [1]. As the concentration of sodium salicylate solution increased, the size of “cauliflower” was increased. This indicates that the PPy film doped with low concentration of sodium salicylate has a more compact structure.



M1



M2



M3

Figure 2. SEM images of salicylate doped PPy films on CT3 steel.

3.2.2. Infrared spectra of Ppy

The IR spectra of salicylate doped Ppy films were shown in Figure 3. It can be seen that the IR spectra of **M1**, **M2** and **M3** samples are similar suggesting that the concentration of sodium salicylate has a negligible effect on the functional groups of doped Ppy films.

Spectral patterns in the range of 2356 - 2359 cm^{-1} are typical for the valence bond C − H. The peaks at 1646 cm^{-1} (**M1**), 1667 cm^{-1} (**M2**), 1667 cm^{-1} (**M3**) were characterized for the vibrations of C = C bond in salicylate and Ppy structure. The bending vibration of N−H bond in Ppy and O–H bond in salicylate was appeared at 1449 – 1529 cm^{-1}. In addition, the stretching vibration of C–N and C–O bond was assigned at 1023–1136 cm^{-1} [17, 22]. The position of some main functional groups of doped Ppy films was presented in Table 1.

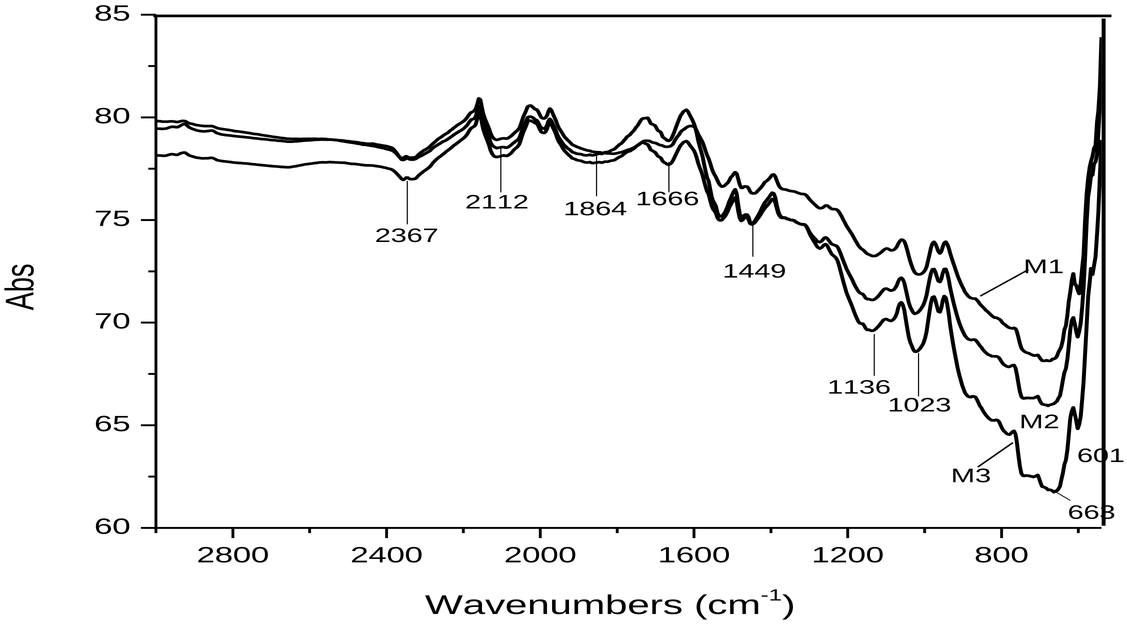


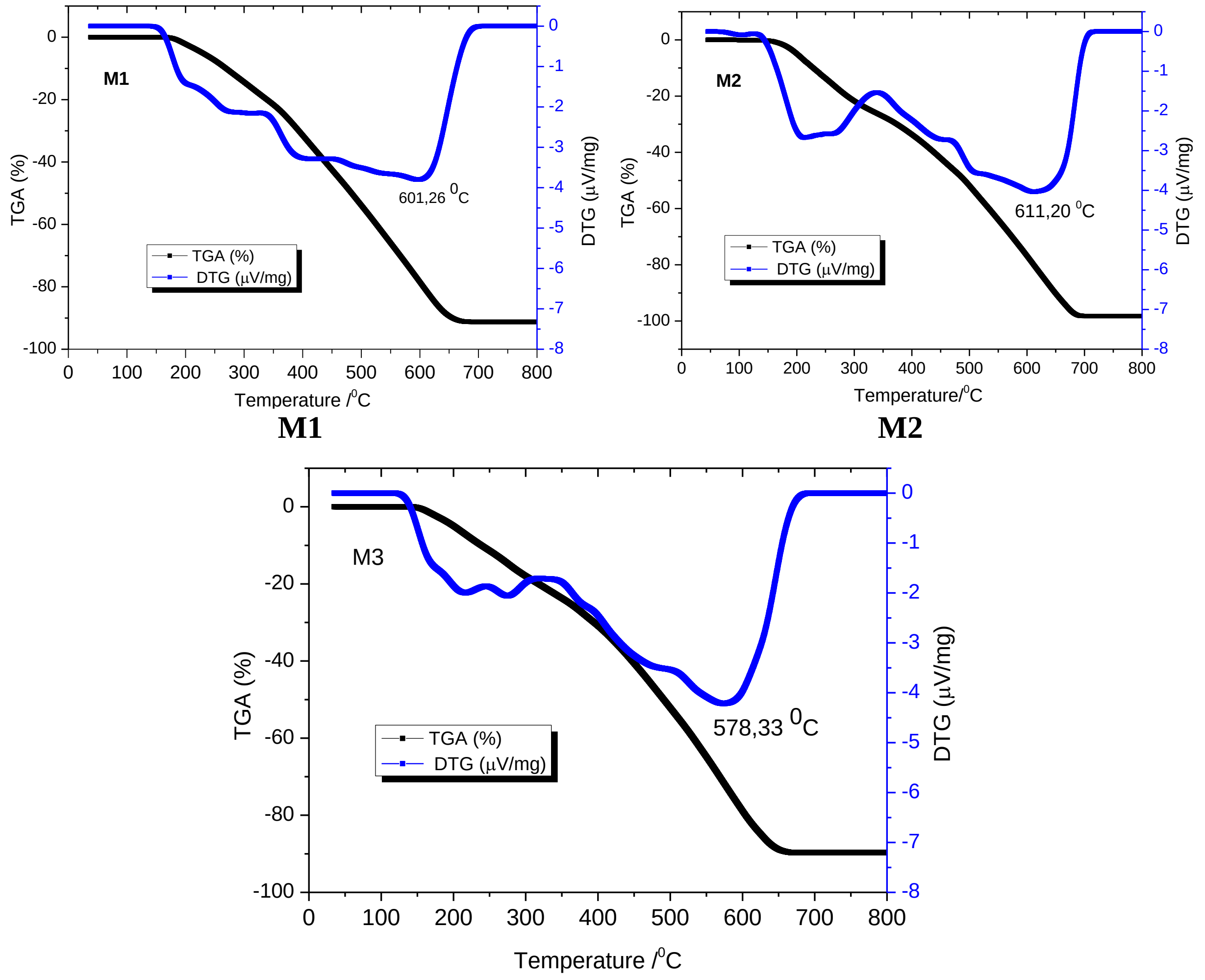
Figure 3. Infrared spectrum of **M1, M2, M3** samples.

Table 1. The position of some main functional groups of doped Ppy films.

Position (cm^{-1})			Shape	Intensity	Oscillate
M1	**M2**	**M3**			
2360	2357	2357	acute angle	medium	υ_{C-H}
1646	1667	1667	acute angle	medium	$\upsilon_{C=C}$
1524 1444	1531, 1450	1530, 1450	acute angle	medium	δ_{N-H}, δ_{O-H}
1016	1023	1136, 023	acute angle	medium	υ_{C-O}, $\upsilon_{C=N}$

3.3. Thermal stability of salicylate doped Ppy films

The TGA of coatings **M1**, **M2** and **M3** was investigated to evaluate its thermodynamic stability. Figure 4 shows the TGA and DTG diagrams of **M1**, **M2** and **M3** samples.



M1 **M2**

M3

Figure 4. TGA and DTG diagrams of **M1**, **M2**, **M3** samples.

The loss of weight under 200°C was attributed for the loss of water inside the samples. It related to the evaporation of water of samples. In the range 200 – 700°C, the decomposition of the Ppy molecule and salicylate produced the large weight loss as observed on TGA curves [16]. At 700°C, all samples were decomposed almost completely. Polymer chain could be decomposed. As seen from DTG curves, the maximum degradation temperatures of **M1**, **M2** and **M3** are 601°C, 611°C and 578°C, respectively. A broaden peak from 300°C to 700°C corresponds a large weight loss step showing that the decomposition of both Ppy molecule and salicylate. Table 2 listed the weight loss in range temperature and the remaining weight of samples at 700°C.

Table 2. Thermal analysis parameters of samples.

Temperature		**≤ 200°C**	**200 – 500°C**	**500 – 700°C**
Percentage change in mass (%)	**M1**	2.19	31.46	91.23
	M2	4.95	33.66	72.00
	M3	4.96	30.96	89.71

The above analysis shows that at 700°C **M2** is the most stable, 28% of the mass was remained, higher than that of the other two samples. Thereby the impact of the passive layer on the surface of steel has been seen or in other words, the effect of doped salicylate on the Ppy films. Dopant anions inhibited the fast degradation of the polymers under high temperature condition if there was enough in the film.

3.4 Corrosion protection test

Figure 5 shows the OCP curves of salicylate doped Ppy films with respect to immersion time in 3% NaCl solution. For comparison, OCP of bare CT3 steel is obtained in the same condition and presented.

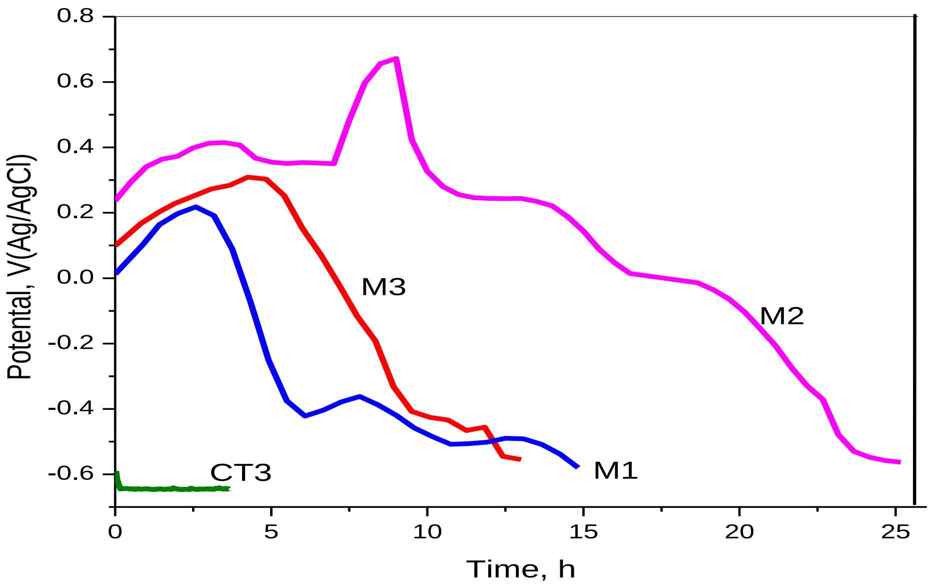


Figure 5. Open circuit potential of sample **M1**, **M2**, **M3**.

The OCP curves of the sample **M1**, **M2** and **M3** are nearly the same. They shifted to positive direction in about 2h at the beginning, kept in noble potential in certain time (potential plateau) and then felt down to the corrosion potential of bare CT3 steel.

This confirms the better performance of Ppy coating synthesized with salicylate dopant. All Ppy films could provide protection for steel in a certain time. However, the potential plateau of **M1**, **M3** was shorter than that of **M2**. It is noticeable that, OCP of **M2** could remain in the second period for a long time nearly 10 hours. The fluctuation of potential could be seen in this region. After nearly 26 h, **M2** could not protect steel any more. The self-healing property of Ppy could be used to explain the potential fluctuation. Active and passive action of Ppy could take place in the pin hole on the sample. The morphology of Ppy coating **M3** was less compact than that of **M2**. It could result the shorter protection time of **M3**. It can be concluded that electrolyte contained 0.1M sodium salicylate could be a optimizes solution to electrosynthesised of Ppy on steel in one step. The coating was compact enough to protect steel as a barrier layer.

The electrochemical polarization measurements of Ppy sample were obtained in 3 % NaCl solution (Fig.6 and Table 3).

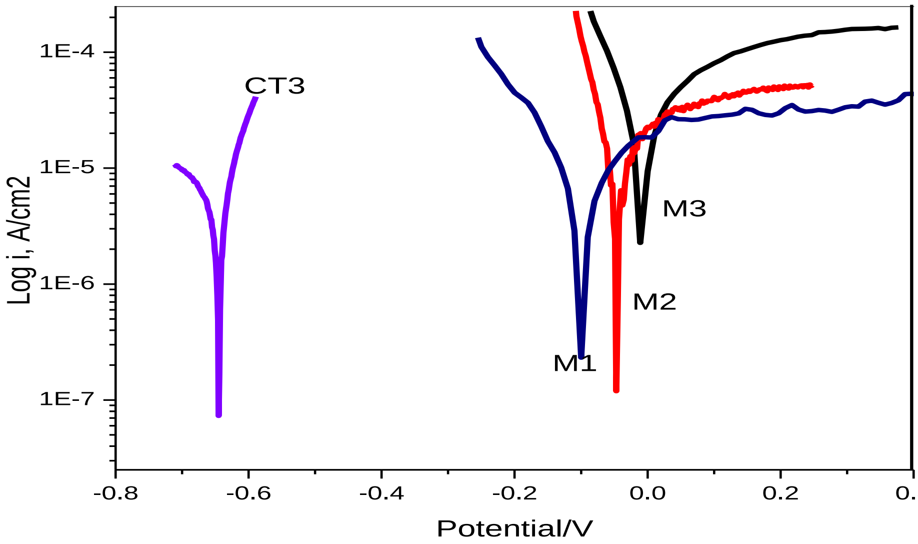


Figure 6. Polarization curves in 3 % NaCl solution of CT3 steel and samples.

It is clear to see that, all the samples **M1**, **M2**, **M3** have more positive corrosion potential than that of CT3 steel in 3 % NaCl solution. The corrosion current of **M2** was smaller at 10 order than that of CT3 steel. This proves that the Ppy coatings synthesized in salicylate solution could provide resistance to corrosion and protect CT3 steel substrate anodically.

Table 3. The corrosion potential and current of Ppy samples.

	CT3	**M1**	**M2**	**M3**
$\mathbf{I}_{corr}$ (A/cm^2)	1.0×10^{-4}	5.22×10^{-6}	9.84×10^{-6}	3.03×10^{-5}
$\mathbf{E}_{corr}$ (V/Ag/AgCl)	–0.57	–0.1	–0.05	–0.01

Figure 7 shows the EIS results of **M1**, **M2** and **M3** in 3 % NaCl solution measured at rest potential. The obtained impedance spectra of the polymer film can be divided in three regions: region 1 (high frequency > 1 kHz) characterizes the resistance of the electrolyte.

Phase angle is nearly zero. The resistance of the electrolyte is about 50 Ω. Region 2 (middle frequency) shows the properties of the polymer film. The Ppy film behaves as dielectricum with a capacitive impedance. The higher impedance of film in this region, the higher protection ability the film is. Region 3 (low frequency) represents the interface polymer/substrate. There are the capacitance of double layer and the charge transfer resistance of the interface.

It is clear to see in Figure 7, **M2** had the higher impedance than that of **M1**, **M3** in the region 2. The enough sodium salicylate as dopant could affect the corrosion protection of Ppy. The EIS results are similar with results of polarization and OCP tests.

4. CONCLUSION

The Ppy film were successfully electrosynthesised in the sodium salicylate solution on the molydate passivated CT3 steel substrate. The obtained film was homogeneous and compact with low salicylate concentration. The "cauliflower" structure of film could be observed. Film thermostability was improved with low salicylate concentration. The protection ability of Ppy film could be enhanced with sodium salicylate as dopant anions. The self-healing ability of Ppy film could be seen if the enough salicylate was used. All the electrochemical results such as OCP, EIS and polarization measurements were reliable to confirm the role of salicylate dopant in corrosion protection.

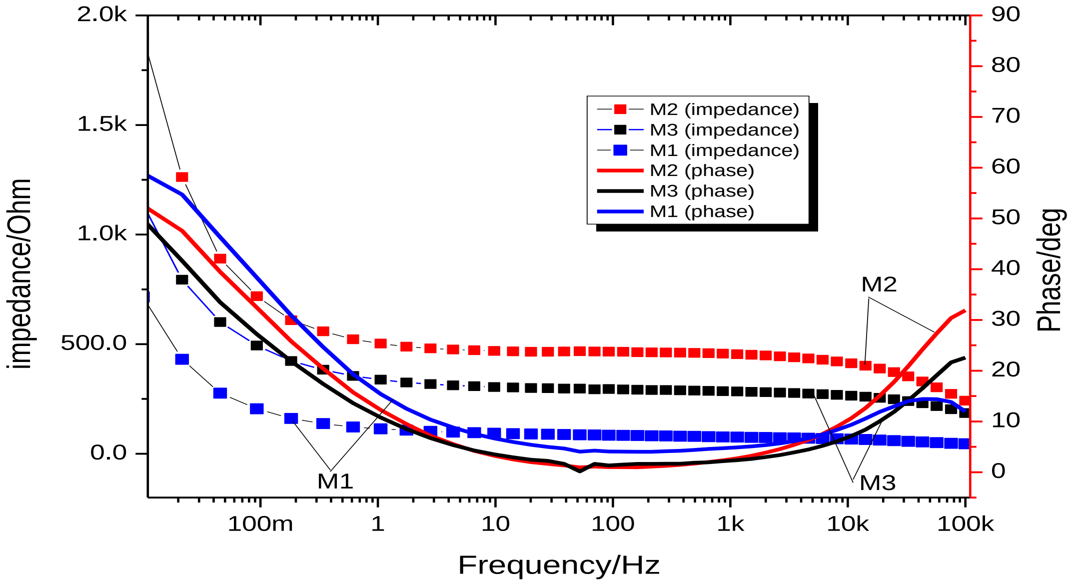


Figure 7. Bode plot of **M1**, **M2** and **M3** in 3% NaCl solution at rest potential.

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