

COMPARISON OF HOMO AND COPOLYMER OF PYRROLE AND ANILINE
ELECTROSYNTHESIZED ON FERRIC ION REDUCTION

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Abstract

In this study, homo and copolymer of Aniline (Ani) and Pyrrole (Py) was electrosynthesized on composite graphite in acetic acid medium containing KCl as supporting electrolyte. The ability of electrosynthesized homo and copolymer on ferric ion reduction was compared and evaluated. The results show that the reduction properties of polyaniline (PAni) is greater than copolymer of aniline and pyrrole (Poly(Ani-co-Py)) and copolymer is more than polypyrrol (PPy). The FTIR and UV-visible spectra indicated that the increase of aniline monomer in the copolymer chain enhances the ferric ion reduction ability. Electrochemical Impedance Spectroscopy (EIS) was also used for further investigation. It was shown that the increase of aniline ring in the copolymer chain reduces the charge-transfer resistance and thus increases the reduction effect. The structure and morphology of homo and copolymer was confirmed by SEM, EDX and FTIR.

Keyword: Electrosynthesis, Ferric reduction, Poly(aniline-co-pyrrole), EIS

1. INTRODUCTION

Conductor polymers are a subset of larger and older group of organic and mineral electric conductors that have electrical, magnetic and optical properties of metals, while retaining the general properties (process ability, mechanical, etc.) of polymers [1]. In recent years, studies have been carried out on conducting polymers with conjugated dual bands. Polypyrrole (PPy) and polyaniline (PAni) are among the conductive polymers whose conductivities are due to the presence of a non-bonding electron pair of π in their heterocyclic ring [2]. Copolymers are polymers in which different monomers in the chain are randomly distributed and interconnected, and the structure of each copolymer depends on the method and conditions of synthesis. A large number of chemical and electrochemical methods have been proposed for the synthesis of copolymers; all are based on the oxidation of monomers, formation of radical cations, chain linking of these radical cations to each other and the formation of polymers. Among these, electrochemical methods have a special position due to their simplicity and repeatability. The process of forming a copolymer begins with its nucleation and growth and ends with the formation of film on the surface of the electrode [3]. Many applications have been proposed for these conductive polymers, among which are, sensors, electrochromic devices, corrosion inhibitors, super capacitors, electromagnetic coatings, polymer batteries and polymer stimulus. This wide range of applications is related to the electrochemical, optical, chemical and mechanical properties of the monomers forming these polymers [3, 4]. Fe plays an important role in catalyzing the physiological and biochemical processes in the body, although as a vital element for natural physiological functions, such as erythropoiesis, transportation, catabolism and storage, including DNA synthesis and RNA, oxygen transport, cellular respiration, multiple enzyme activity, immune function, and metabolism, it plays an important role among other ions. On the other hand, Fe overload in the

body causes many free radicals in the body, resulting in cell damage and death. The severity of cell damage depends on the amount of free radicals produced, and excess Fe can accumulate in vital organs, causing liver failure, heart failure, kidney failure, neurological and endocrine diseases [5, 6]. Fe is a ferromagnetic material that exhibits magnetic properties in the absence of a magnetic field. Fe^{+3} ions are very pale due to the unauthorized mutation of the electrons, and with the reduction and conversion to Fe^{+2} , there is a permissive electron mutation, which means that the chelates are rapidly attached to the authorized ligands and increase the color.

Fe (III), as an oxidant, tends towards the antioxidants found in the sample and makes contact with them, and turns electrons into Fe (II) [5, 7, 8]. Since electrochemistry relies on the fast transfer of electrons, and tripyridyltriazine (TPTZ) is an electron binder in which by the electron donor antioxidant, speeds up the conversion of [(Fe (III) -tripyridyltriazine (Fe (III) – TPTZ)] to [(Fe (II) -tripyridyltriazine (Fe (II) –TPTZ)] when the complex (Fe(III)-TPTZ) is reduced in proportion to the antioxidant strength of the sample to the complex formed (Fe (II) -TPTZ), the reduced amount of Fe is measured by absorbance at 593 nm [7, 9]. Thus, as the antioxidant power of the sample is reduced, the absorption is increased at 593 nm. One of the quantitative measurements of ionic ferric is its reduction in a complex, which is a measure of the strength and ability of the antioxidant of the reducing sample [10-12]. Examination of electrodes with conductive polymer coatings that have the ability to reduce ionic ferric is an interesting field for research. In this study, electrodes coated with homo and copolymer aniline and pyrrole were compared to study the reduction of Fe^{+3} in a complex, which implies the antioxidant ability of these polymeric coatings. Additionally, for quantitative and qualitative evaluation of electrochemical processes in conductive polymers film, cyclic voltammetry (CV) and EIS were used.

2. EXPERIMENTAL

2.1. Materials

Aniline (sigma chemicals, USA) was purified by distillation under a nitrogen atmosphere at reduced pressure. The resulting colorless liquid was kept in the dark at 5°C. Pyrrole (py) (Merk, Germany) was vacuum distilled before use. Potassium chloride (KCl), acetic acid (CH₃COOH) and 2, 4, 6- tripyridyl – s- triazine) (TPTZ) were of analytical grade and used as received. Potassium ferricyanide (K₃[Fe(CN)₆]) and ferrocyanide (K₄[Fe(CN)₆]) (Shanghahi No.1 Reagent Factory , China) were used as received . All aqueous solution were freshly prepared using ultra – pure water from Milli – Q plus (Millipore Corp., USA).

2.2. Equipment

The electrochemical system which consists of compactstat potentiostatic (Ivium Technologies, Netherlands) controlled by a personal computer equipped with the Ivium Soft, software package was used for the synthesis and characterization electrochemical impedance spectroscopy (EIS) measurements. A custom-made three-neck electrochemical cell was employed throughout. The three-electrode cell consists of 2B pencil composite graphite (1.8 mm diameter) (Staedtler Lumograph, Germany) as working electrode and a Pt electrode was used as the counter electrode against a pseudo Ag/AgCl reference electrode. The FTIR spectrophotometer System 2000 of Perkin Elmer USA and the UV/ visible spectrophotometer V-500 (JASCO Japan) were also used for structural analysis and characterization purposes. The scanning electron microscopy (SEM) equipped with an Oxford INCA 400 energy dispersive X-ray (EDX) using a Leo Supra 50 VP field emission microanalysis system (Bucks, UK) was used to elucidate the morphology of the homo and copolymer of Ani and Py.

2.3. Procedure

The electrosynthesis of homo and copolymer of Ani and Py on the surface of composite 2B pencil graphite was performed in 10 mL solution mixture of 50 mM Ani and Py, 1 M CH₃COOH (medium) and 1M KCl (supporting electrolyte) by sequentially sweeping the potential between - 0.4 and +1.2 V vs., scan rate 100 mV/s⁻¹, under OFN atmosphere and at 25 ± 2°C. The complex of 0.001 M Fe⁺³ was produced in 0.01 M TPTZ containing 1 M CH₃COOH and their maximum absorbance obtained at 593 nm after 30 min exposure to 0.1 g of PANi, Ppy and poly(Ani-co-py) electropolymerized. Cyclic voltammetry (CV) was carried out with use of a Potentiostat/Galvanostat (IviumTechnologies, Netherlands) by a computer equipped with the IviumSoft software package. Electrochemical impedance spectroscopy (EIS) was performed using (Versa STAT, USA). The EIS of homo and copolymer films in 1 M CH₃COOH containing 0.001 M K₄[Fe(CN)₆] and K₃[Fe(CN)₆] was performed using the following parameters: amplitude of 0.01 V; frequency range of 100 Hz to 100000 Hz, potential range : 0.5 V.

3. RESULTS AND DISCUSSION

3.1. Electrochemical synthesis of polyaniline

Figure 1 shows cyclic voltammograms of 50 mM aniline in 1 molar acetic acid containing 1 M potassium chloride on the composite graphite at a potential range of -0.4 to 1.2 V, with up to 20 cycles, and scan rate of 100 mV/s. In the acetic acid medium, the aniline radical cations produced at the beginning of oxidation are paired in the polymerization process, and the binding of aniline monomers creates different configurations that are effective in the properties of PANi. Three peak pairs were observed at a potential range of -0.2 to 1 V. The first peak pair is in the range of -0.2 to 0.3 V (O_aR_a), in relation to conversion of leucoemeraldine (LE) to

emeraldine salt (ES). The second pair above of the potential range of 0.6 V (O_b/R_b) is due to ES oxidation to PN (pernigraniline). Pair of peaks in the range of 0.3 to 0.6 V (O_c/R_c) is related to the degradation of hydroquinone products to quinone's [13-15].

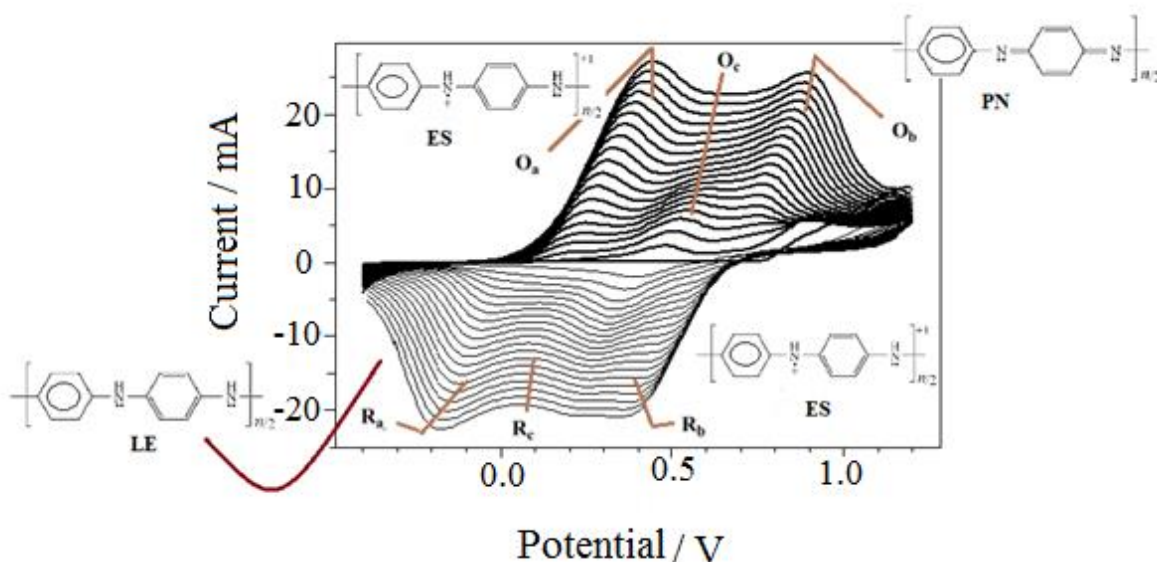


Fig. 1. The schematic of cyclic voltammograms obtained during electro-polymerization of aniline in 1 M CH_3COOH containing 1 M KCl. The potential is cycled between -0.4 to 1.2 V at a scan rate of 100mV/s for the 1st-20th cycle.

3.2. Electrochemical synthesis of polypyrrole

Figure 2 shows cyclic voltammograms of 50 mM Py in 1 M acetic acid containing 1 M Potassium chloride on the composite graphite, within the range of -0.4 to 1.2 V, with up to 20 cycles and scan rate of 100 mV/s. Generally, Py and Py family's cyclic voltammetry does not have a significant margin for configuration, and only peak synthesis can be used to interpret their electrochemical properties. The PPy synthesis peak shift is towards the more negative potentials due to the easier oxidation of pyrrole's monomer and easier formation of pyrrole cation radicals. Due to the reduced conductivity of the modified electrode as compared to graphite, the peak-synthesis current in subsequent surveys is reduced. In the PPy synthesis voltammogram, in the initial cycles, a configuration cycle was observed which disappeared in

subsequent cycles; it was reported that the peak is related to the impurities of the composite bed [16].

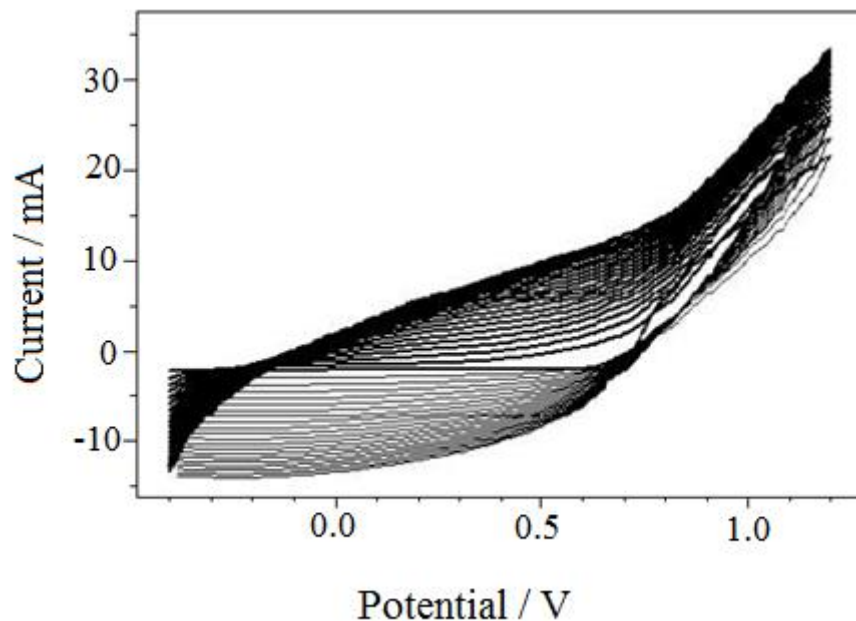


Fig. 2. The schematic of cyclic voltammograms obtained during electropolymerization of Py in 1 M CH_3COOH containing 1 M KCl .The potential is cycled between -0.4 to 1.2 V at a scan rate of 100 mV/s for the 1st-20th cycle.

3.3. Electrochemical synthesis of copolymer of aniline and pyrrole

Figure 3 shows cyclic voltammograms of 50 mM Py and Ani in 1 M acetic acid containing 1 M potassium chloride on composite graphite, within the potential range of -0.4 to 1.2 V, with up to 20 cycles and scan rate of 100 mV/s. The first stage of the copolymerization process starts with different anodic oxidation of the two monomers, which can either be adsorbed on an electrode or appear in a radical cationic solution. The relative velocity of oxidation of monomers depends on the nature of each monomer, copolymerization potential, material and apparent shape of the electrode. In the second step, the binding reaction of the radical cations to each other occurs in order to form copolymers [1, 14, 17].

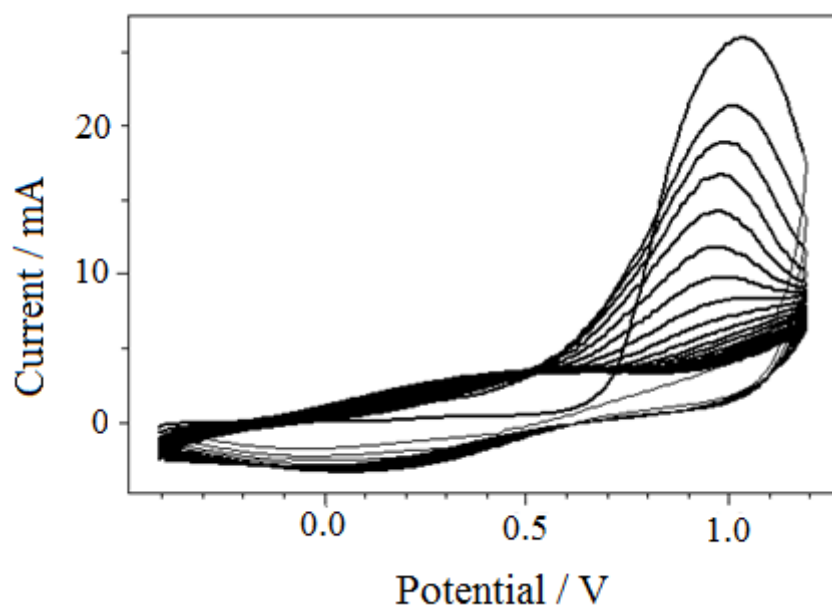


Fig.3. The schematic of cyclic voltammograms obtained during electrosynthesis of poly(Ani-co-Py) in 1 M CH_3COOH containing 1 M KCl. The potential is cycled between -0.4 to 1.2 V at a scan rate of 100 mV/s for the 1st-20th cycle.

3.4. Structural analysis

Figure. 4 shows the FT-IR spectrum of electrosynthesized PANi. The presence of a C-C stretching vibration band in the range of 1642 and 1567 cm^{-1} is related to the quinoid (Q) and benzenoid (B) rings, respectively, while the C-N stretching band in the range of 1494 and 1405 cm^{-1} belongs to the configurations (ES) of the PANi conductive form [18]. The absorption band at 1157 to 1039 cm^{-1} corresponds to in-plane and out-of-plane CH bending bond of the aromatic rings, respectively, and also the absorption band ranged from 704 to 472 cm^{-1} for the group $(\text{PO}_4)^{-3}$. Additionally, the integrals below the spectrum surface are evaluated to investigate the oxidation degree (Q/B ratio) of PANi and to prove the polymerization of polymer films. Ratio close to 1 indicates the electrosynthesized PANi conductive form; thus, the fully reduced PANi form is with a zero ratio (Q/B = 0), the protoemeraldine form is with a ratio between 0.5 and 1 (Q/B = 0.5-1), partially oxidized form is with a ratio of 1 (Q/B = 1) and completely oxidized form is with a ratio greater than 1 (Q/B>1). Electropolymerization of PANi in the presence of

KCl electrolyte support with an approximate ratio of (Q/B ~ 1) represents a semi-oxidized form of PANi, which indicates a more stable state of polymer due to the presence of B and Q rings [14, 17].

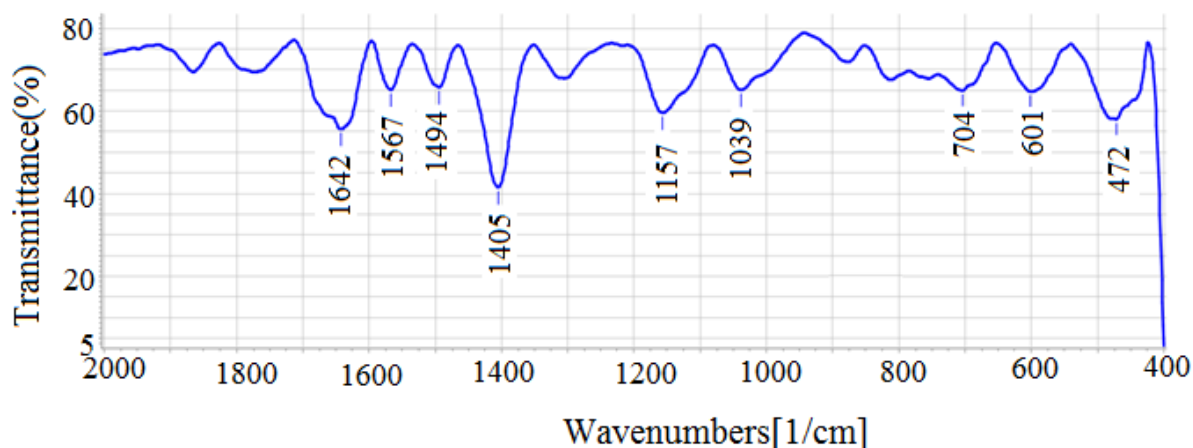


Fig. 4. Baseline corrected FTIR spectra (2000-400 cm^{-1}) of PANi electropolymerized in 1 M CH_3COOH containing 1 M KCl.

Figure 5 shows the FT-IR spectrum of electrosynthesized PPy. The absorption band observed in 1531 cm^{-1} is related to the C-C stretching vibration band in the PPy ring structure. Another absorbance band at 1406 cm^{-1} is the C-N stretching vibration bond in the Py ring structure. The absorbance band at 1203 cm^{-1} is attributed to in-plane C-H and N-H the vibration deformation. The absorption bands at about 1100 to 1250 cm^{-1} is related to the high vibration of the Py ring. A peak at 1038 cm^{-1} is assigned to out-of-plane C-H bending motions of the aromatic rings. Another peak was found in the absorption area of 820 cm^{-1} in relation to the out-of-plane deformation of the C-H ring [16, 19]. In areas of 666 and 601 cm^{-1} , it was observed that absorption bands are related to flexural C-C deformation and C-H out-of-plane vibrations of Py ring.

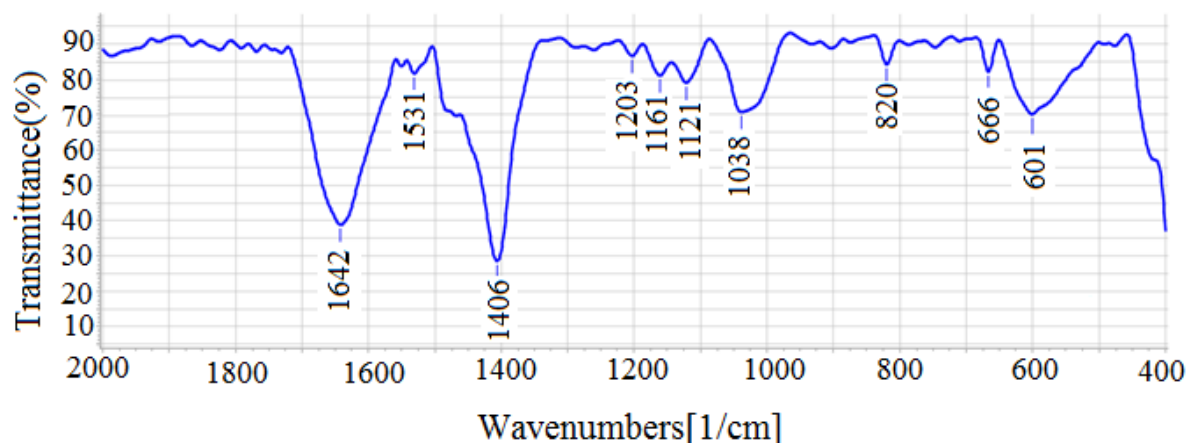


Fig. 5. Baseline corrected FTIR spectra (2000-400 cm^{-1}) of PPy electropolymerized in 1 M CH_3COOH containing 1 M KCl.

Fig 6 shows the FT-IR spectrum of electrosynthesized Poly(Ani-co-Py). The spectrum of copolymer indicates that presence of monomers of Ani and Py in its formation. The presence of two peaks at 1206 and 1290 cm^{-1} corresponds to the presence of PAni, and the stretching bands of C = C at 1541 cm^{-1} and the C-H vibrational band at 1033 cm^{-1} demonstrate the presence of PPy [17]. The band at 923 cm^{-1} can be attributed to out-of-plane C-H of the PPy aromatic ring. The C-N stretching bands are observed at 1250 cm^{-1} wavelength, although they are not observed in copolymers and are observed in a lower wavelength of 1206 cm^{-1} . Regarding the spectrum, it can be concluded that when two different monomers are in the form of a copolymer, although the spectrum is very close to the spectrum of homopolymers obtained from each of the monomers, it is not a simple combination of their spectra.

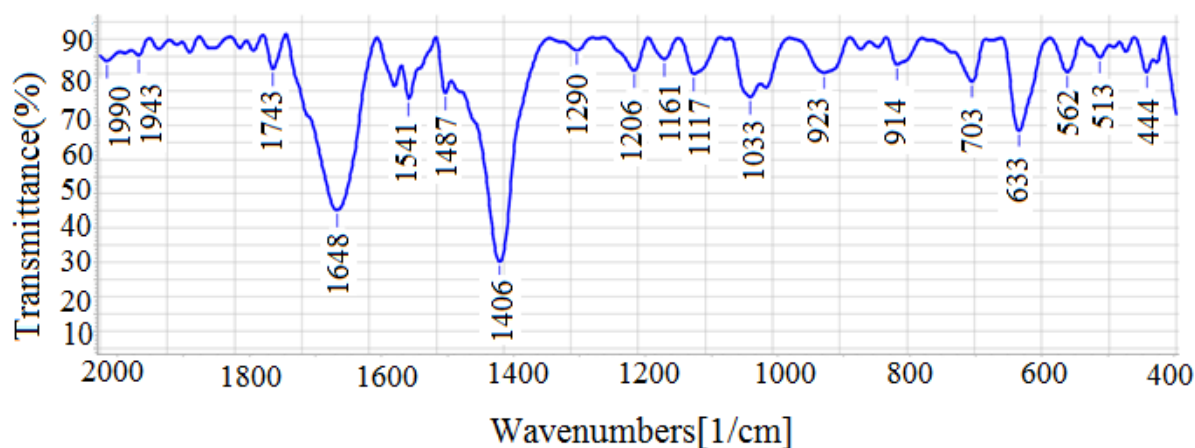


Fig. 6. Baseline corrected FTIR spectra ($2000\text{--}400\text{ cm}^{-1}$) of Poly(Ani-co-Py) electropolymerized in 1 M CH_3COOH containing 1 M KCl.

3.5. Morphology analysis

The experimental variables such as electrolyte support, solvent and the method used for polymer synthesis, have a great influence on the structure of the resulting polymer. Many researchers have studied the relationship between these variables and the polymer structure due to many impacts on the electrical and mechanical properties of the polymer film. The images obtained from the scanning electron microscope indicate the different morphologies of the electrosynthesized homo and copolymer Ani and Py films in the presence of potassium chloride support [16]. Figure 7 shows the SEM image of the PANi obtained from the 50 mM Ani electrosynthesis in 1 M acetic acid containing 1 M potassium chloride. The SEM image obtained from electrosynthesized PANi on the composite graphite shows a dense mass-shaped morphology.

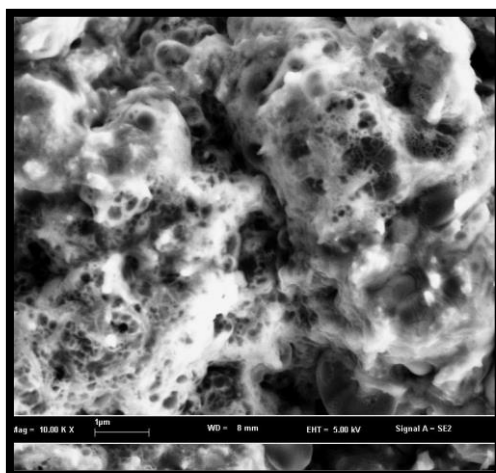


Fig. 7. The SEM image of electropolymerization of 50 mM Ani solution in 1 M CH_3COOH containing 1 M KCl on composite graphite.

Figure 8 shows the SEM image of the PPy obtained from 50 mM Py electro synthesized in 1 M acetic acid, including 1 M potassium chloride. The SEM image obtained from the electro synthesized PPy on the composite graphite shows cluster morphology. The EDX analysis results of PPy electro synthesized in the presence of KCl for carbon (C) and nitrogen (N) are 52.23 and 18.61%, respectively. These results are in good agreement with the calculated value in polymer, which is (C) 61.35% and (N) 15.90% [20].

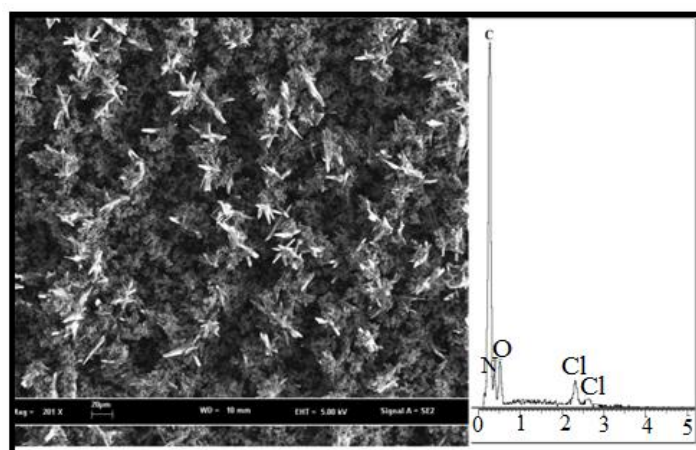


Fig. 8. The SEM image of electropolymerization of 50 mM PPy solution in 1 M CH_3COOH containing 1 M KCl on composite graphite.

Figure 9 shows the SEM image of Poly(Ani-co-Py) obtained from 50 mM Ani and 50 mM Py in 1 M acetic acid containing 1 M potassium chloride. The SEM image obtained from electrosynthesized Poly(Ani-co-Py) on the composite graphite shows a granular and rough morphology. The results of EDX analysis from Poly(Ani-co-Py) electrosynthesized in the presence of KCl for carbon (C) and nitrogen (N) are 88.28 and 1.60%, respectively. These results are in good agreement with the calculated value in polymer, which are 93.66% (C) and 1.76% (N), respectively. The obtained SEM and EDX show the morphology of electro-synthesized homo and copolymer aniline and pyrrole.

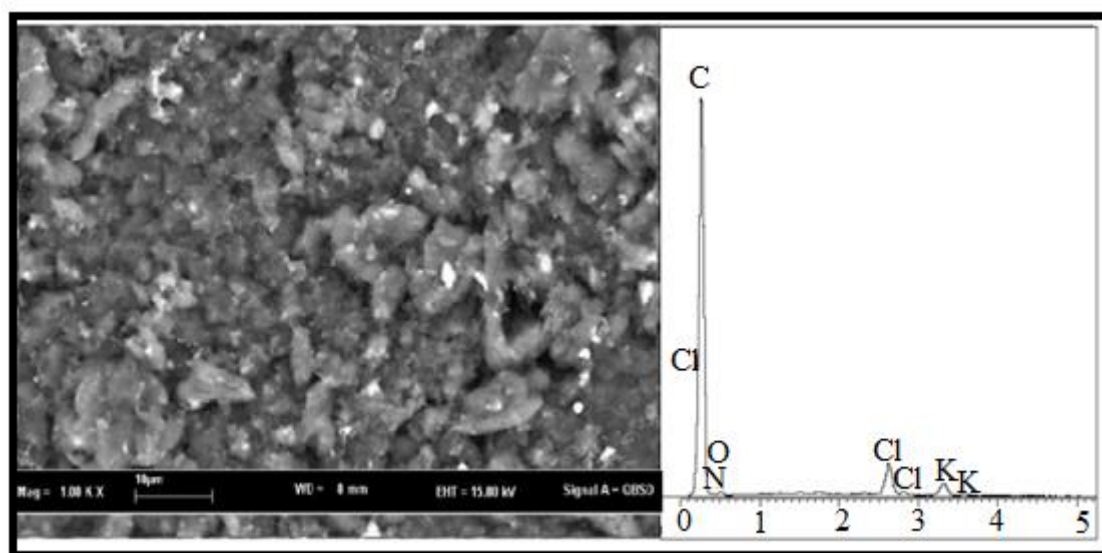


Fig. 9. The SEM images of copolymerization of 50 mM Ani solution and 50 mM Py solution in 1 M CH₃COOH containing 1 M KCl on composite graphite.

3.6. Ferric ion reduction

There are different methods for measuring Fe (III), these include a) Potentiometric b) amperometric c) Biamperometric d) Coulometric e) gravimetric and f) spectroscopy. In this research, spectrophotometry has been used to measure fast iron ions. Since Fe ion absorption is very small in spectroscopy, a colored complex is made of it that has a significant absorption

in the UV-visible range compared to Fe ion and has high sensitivity in measuring iron ions [7, 8, 21]. One of the most widely used ligands in spectroscopy is tripyridyltriazine 2, 4, 6(TPTZ) [9, 22]. Figure 10 shows the reaction of Fe (III) due to the complex with TPTZ. The Fe(III)-TPTZ complex is colorless and has a low absorption in the UV-visible range. Due to the ability of the polymer to transfer electrons, Fe (III) is reduced into Fe (II); thus, for the conversion or reduction of a very small amount of Fe (III) to Fe (II), the formation of Fe(II)-TPTZ shows an increase in color and a higher absorption in the UV-visible range. As a result, spectroscopy is a suitable method to evaluate the reduction of Fe (III) to Fe (II) in this complex [22-25].

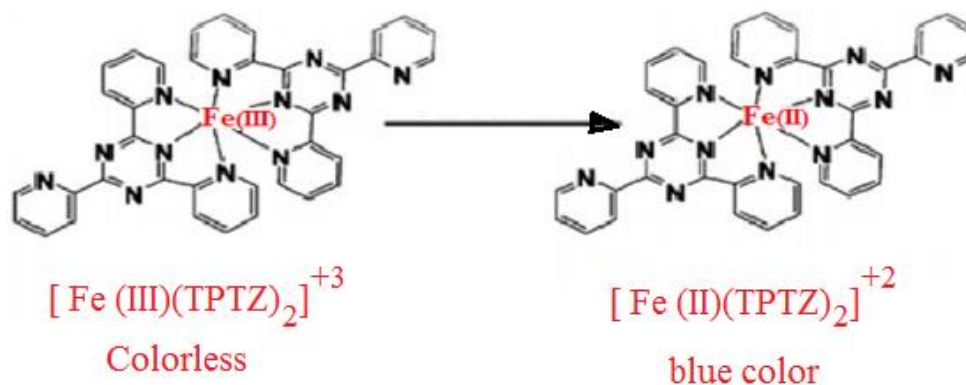


Fig. 10. Redox reaction for ferric complex in TPTZ

Figure 11 shows the UV-visible spectrum of 10 ml of the 0.001 molar Fe(III)-TPTZ, exposed to 0.1 g of (a) PANi, (b) PPy and (c) Poly(Ani-co-Py) for 30 min. In conductive polymers, the charge transfer is investigated through the intensity measurement of absorbing bands in polymer solutions using the UV-visible [23]. The difference in absorption intensity indicates the ability of the polymer to transfer electrons to the Fe⁺³-TPTZ complex, which indicates the greater ability of the polymer to transfer electrons and consequently the formation of a Fe⁺²-TPTZ blue complex with a higher absorption intensity [26]. Figure 11d shows the UV-visible spectrum of the Fe⁺³-TPTZ complex without being exposed to homo and copolymer. Due to

the transferring power of electron homo and copolymer Ani and Py electrosensitized by converting Fe (III) to Fe (II), the absorption intensity increases In other words, by liberating more electrons, the concentration of the Fe⁺²-TPTZ complex increases and as a result, the absorption intensity increases, and thus the concentration of the Fe⁺³-TPTZ complex decreases. Spectra: (a) The greater effect of PANi on electron release with the highest absorbance (0.5) and color (tint blue); (b) the less effective impact of Poly(Ani-co-Py) on release of electron as compared to PANi and the greater effect of copolymer on release of electron in comparison with PPy; and c) the lesser effect of a PPy on release of electrons with a minimum absorption intensity (0.3) and color (pale blue) in a 593 nm wavelength. These results indicate the ability of the polymer to reduce Fe (III) and the formation of a complex of Fe (II) with the TPTZ ligand.

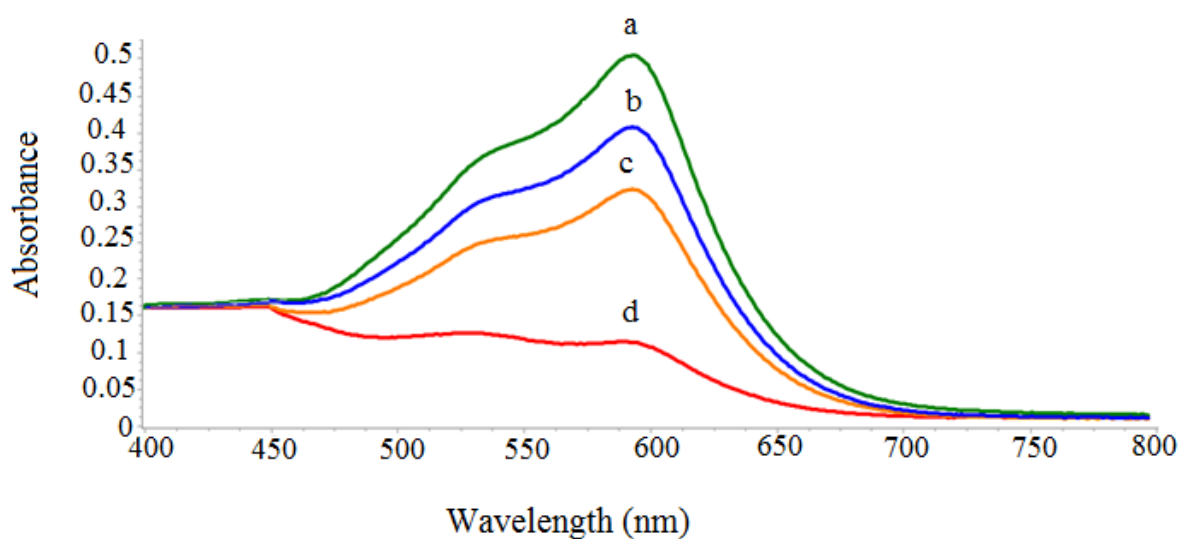


Fig. 11. UV-vis spectra of 0.001 M complex Fe⁺³ in 1 M CH₃COOH after 30 min exposure to 0.1 g from: a) PANi, b) Poly(Ani-co-Py), c) PPy electropolymerized. d) Absorbance of Fe⁺³ Ion in the absence of homo and copolymer is 0.11

3.7. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is used to evaluate conductivity polymers and composites. This method is based on application of the potential and receiving response in current form and can provide clear information on the processes that occur in the polymer matrix [18]. It is also a reliable method for extracting information on the electrochemical characteristics of electrochemical systems, including double layer capacity, charge transfer process, solvent resistance and Warburg impedance. The charge transfer and exchange of electrons occur at the surface of the pores and the areas where oxidation occurs at the electrode surface, and the impedance determines the common surface properties of the electrode/electrolyte as a set of real (Z') and imaginary (Z'') resistance [18]. Figure 12 shows a Nyquist spectroscopic impedance curve of modified electrode with: (a) PANi, (b) PPy; and c) Poly(Ani-co-Py) in 0.001 molar of potassium ferro and ferric cyanide at 0.5 V and frequency range used was from 100 to 100,000 Hz.

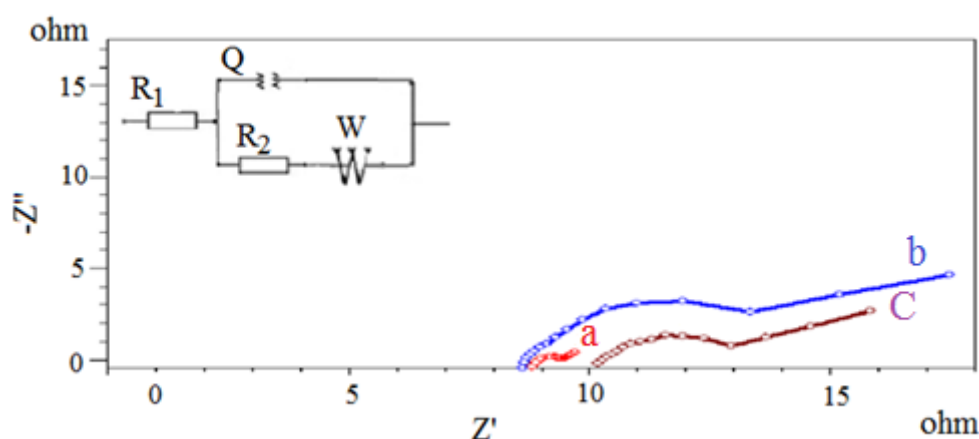


Fig. 12. Nyquist plots of modified electrode with: a) PANi, b) PPy, c) Poly(Ani-co-Py) in 0.001 M potassium ferric and Ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) solution at E_{app} 0.5 V. The ac potential amplitude was 10 mV and frequency range used was from 100 KHZ to 100Hz.

As shown in Figure 12a and b, the further increase of the observed current in the graphite electrode modified with PANi reduces the charge transfer resistance (10 ohms), and the decrease in the observed current in the graphite electrode modified with PPy increases the charge transfer resistance (21 ohms). This is due to the fact that the lesser the charge transfer resistance for the polymer, the higher the charge transfer, resulting in easier redox transfers for the conductive polymer. Another important parameter in EIS is the double layer capacity that is formed on the electrode/electrolyte surface and has an electron exchange feature. According to the calculations, the double layer (Q) capacity of graphite electrode modified with PANi is more electrically charged with more electron exchange and the double layer capacity of the graphite electrode modified with PPy is the least and has less electron exchange. On the other hand, Warburg's impedance shows the ion penetration process. As the Warburg impedance (Z_w) is low at the surface of the double layer, the penetration phenomenon is better at the electrode surface and there could be a better charge transfer [3, 18]. Thus, the Warburg impedance obtained in the test for a graphite electrode modified with PANi 42 [$1/\Omega \text{ sqrt (Hz)}$], PPy 89 [$1/\Omega \text{ sqrt (Hz)}$] and Poly(Ani-co-Py) 60 [$1/\Omega \text{ sqrt (Hz)}$], confirms the better penetration of Fe ions into the surface of the electrode modified with PANi, as compared to that modified with PPy. N represents the degree of surface roughness of the modified electrode, where the more porous and thicker it is, the lesser the electron transfer from the polymer surface. The numbers obtained in the table refer to the smoother surface of the PANi and hence the better electron transfer.

Table 1. The best fitted values of Randles' equivalent circulate elements simulated from impedance data for homo and copolymer of Ani and py films.

	$R_{(s)}$ (Ω)	$R_{(ct)}$ (Ω)	$W(1/\Omega \text{ sqrt (Hz)})$	Q (F)	N
PAni	8.6	1×10^1	4.2×10^1	1.5×10^{-3}	2.5×10^{-1}
Ppy	8.8	2.1×10^1	8.9×10^1	9.9×10^{-6}	5.1×10^{-1}
Poly Ani/py	9.8	1.5×10^1	6×10^1	9.2×10^{-6}	4.1×10^{-1}

4. CONCLUSIONS

The results show that the electrosynthesized homo and copolymer of aniline and pyrrole in acetic acid in the presence of KCl have electrical conductivity and their structural analysis by FT-IR and SEM is consistent with the homo and copolymer aniline and pyrrole formulas. Additionally, EIS studies show the polymer's ability to transfer the charge. The results showed a high sensitivity of electrosynthesized homo and copolymer of aniline and pyrrole proportional to Fe content. In addition, biologists have used Fe^{+3} -TPTZ complex as a measure of the antioxidant effect of compounds known as ferric reducing antioxidant power (FRAP). The more absorbance amount indicate that on the greater the antioxidant effect. Reduction of Fe (III) to Fe (II) using homo and copolymer aniline and pyrrole was not only investigated, but, according to biotechnology researchers, it can be concluded that homo and copolymer aniline and pyrrole have a good antioxidant effect.

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