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A COMPARATIVE STUDY OF STRUCTURAL AND MORPHOLOGICAL CHARACTERISTICS OF POLYPYRROLE WITH CHEMICAL OXIDATION BY IRON(III) CHLORIDE, MICROEMULSION POLYMERISATION BY AMMONIUM PERSULFATE AND MICROEMULSION POLYMERISATION BY $FeCl_3$

(Satu Kajian Perbandingan Ciri-Ciri Struktur dan Morfologi Polipirol dengan Pengoksidaan Kimia oleh Besi (III) Klorida, Pempolimeran Mikroemulsi oleh Ammonium Persulfat dan Pempolimeran Mikroemulsi oleh $FeCl_3$)

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Abstract

Polypyrrole polymers are special polymers in which it has good conductivity of electricity for use in various fields due to its biocompatibility, thermal stability, easy to produce, etc. By use of various polymerisation methods like electro-chemical polymerisation, chemical polymerisation, microemulsion polymerisation, ultra-sonification polymerisation, vapour phase polymerisation, etc., pyrrole monomer is synthesised with various oxidants, dopants, surfactants, etc., to produce polypyrrole polymers. Two methods are widely used to produce polypyrrole one is chemical oxidation, and another is microemulsion polymerisation. There are few research papers on comparative studies of two methods and also between the two-oxidising agent used in the microemulsion method. The main objective is to compare both chemical oxidation by $FeCl_3$ polymerisation with microemulsion by iron(III) chloride and recompare the microemulsion by ammonium persulfate (APS) with microemulsion by iron(III) chloride. Therefore, three samples were first created: 0.1 M chemical oxidation, where iron(III) chloride was used as oxidising agent and sodium dodecyl sulfate as dopant. The second sample was 0.1 M microemulsion where ammonium persulfate was used as oxidant, sodium dodecyl sulfate as dopant, amyl alcohol as stabiliser. The three samples were 0.1 M microemulsion, where the oxidant was iron(III) chloride, sodium dodecyl sulfate acted as dopant, and amyl alcohol as the co-dopant. The three samples were characterised by Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS). The test result from EIS shows that the conductivity of 0.1 M chemical oxidation is 0.2211 S/cm, and that of

0.1 M microemulsion polymerisation is 0.9958 S/cm, and 0.1 M microemulsion by $FeCl_3$ is 1.1619 S/cm. The result from characterisation shows the successful development of polypyrrole, which can be used in fuel cell, supercapacitors, electrodes, biosensors, etc.

Keywords: polypyrrole, polymerisation, microemulsion

Abstrak

Polimer polipirol adalah polimer khas yang mempunyai kekonduksian elektrik yang baik untuk digunakan dalam pelbagai bidang kerana biokompatibilitinya, kestabilan haba, kemudahan penghasilan, dan sebagainya. Dengan menggunakan pelbagai kaedah pempolimeran seperti pempolimeran elektro-kimia, pempolimeran kimia, pempolimeran mikroemulsi, pempolimeran ultra-sonifikasi, pempolimeran fasa wap, dan lain-lain, monomer pirol disintesiskan dengan pelbagai oksidan, pendop, surfaktan, dan lain-lain untuk menghasilkan polimer polipirol. Dua kaedah yang digunakan secara meluas untuk menghasilkan polipirol ialah pengoksidaan kimia dan pempolimeran mikroemulsi. Terdapat beberapa kertas penyelidikan mengenai kajian perbandingan dua kaedah ini dan juga antara agen pengoksidaan yang digunakan dalam kaedah mikroemulsi. Objektif utama adalah untuk membandingkan kedua-dua pengoksidaan kimia oleh pempolimeran $FeCl_3$ dengan mikroemulsi oleh besi (III) klorida serta membandingkan mikroemulsi oleh APS dengan mikroemulsi oleh besi (III) klorida. Oleh itu, tiga sampel pertama kali dicipta: pengoksidaan kimia 0.1 M, di mana besi (III) klorida digunakan sebagai agen pengoksidaan dan natrium dodekil sulfat sebagai pendop. Sampel kedua ialah 0.1 M mikroemulsi di mana ammonium persulfat digunakan sebagai oksidan, natrium dodekil sulfat sebagai dopant, dan alkohol amil sebagai penstabil. Sampel ketiga ialah 0.1 M mikroemulsi, di mana oksidan adalah besi (III) klorida, natrium dodekil sulfat bertindak sebagai pendop, dan alkohol amil sebagai pendop bersama. Ketiga-tiga sampel itu dikaji menggunakan spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi elektron pengimbasan pancaran medan (FESEM), spesifikasi sinar-X penyebaran tenaga (XRD), dan spektroskopi impedans elektrokimia (EIS). Keputusan ujian daripada EIS menunjukkan bahawa kekonduksian pengoksidaan kimia 0.1 M ialah 0.2211 S/cm, pempolimeran mikroemulsi 0.1 M ialah 0.9958 S/cm, dan mikroemulsi 0.1 M oleh $FeCl_3$ ialah 1.1619 S/cm. Hasil daripada pencirian menunjukkan kejayaan pembangunan polipirol, yang boleh digunakan dalam sel bahan api, superkapasitor, elektrod, biosensor, dan lain-lain.

Kata kunci: polipirol, pempolimeran, mikroemulsi

Introduction

Polypyrrole is formed when the pyrrole monomer is synthesised with various oxidants and dopants in an aqueous or non-aqueous medium with proper time and temperature; this process is also known as polymerisation. The factors that affect conductive are oxidative agents, molar ratio, dopants, and temperature. In one of the research projects by Varga and co-workers, $FeCl_3.H_2O$, iron (III) sulfate hydrate and ammonium persulfate (APS) were used as oxidative in a nanotube polymerisation. Shows, $FeCl_3.H_2O$ oxidising agent had shown the maximum conductivity 66 S/cm as compare to other oxidising agent shows less than 10 S/cm of conductivity [1]. If oxidant concentration is high, the rate of polymerisation will increase but the conductivity will be decreased. Hence, a ratio of initial oxidation to pyrrole monomer is important, it requires high oxidising for electron removal at a particular degree so that over-oxidising is prevented [2,3]. Dopant plays an important role in increasing the conductivity of a polymer. The mechanism is to produce polarons or bi-polarons to carry the charge. To increase conductivity, various dopants are used, for instance, fumaric acid, BSna, itaconic acid, HCl, etc. For surfactant, SDS is mostly used as a dopant in polypyrrole [4]. Meanwhile, the solvent utilised in the process is also important for good conductivity. To achieve high conductivity, the donor number and nucleophilicity should be less in the solvent [5].

Temperature plays a vital role in polymerisation, where a liner polypyrrole that is produced due to polymerisation kinetic becomes low at low temperature because of charge carrier migration and due to conjugation regulation. Which shows that polypyrrole conductivity can be achieve in low temperature [6]. To produce polypyrrole, there are various methods, such as chemical oxidation, electrochemical polymerisation, microemulsion, ultra-sonication polymerisation, vapour-phase polymerisation, electro-spinning, photo-polymerisation, and mechanochemical polymerisation; however, chemical oxidation and microemulsion are more widely used. Chemical oxidative polymerisation

method is the oldest and simplest method for the bulk production of polypyrrole. This is done by preparing two solutions: a monomer solution and an oxidation solution. Then, they are combined to produce a polymer. This can be carried out in an aqueous or non-aqueous medium, where the powder is then produced [7]. Many researchers had changed dopant, oxidising agent and conducted the experiments in one of the research shown that, the use of iron(III) chloride in chemical oxidation increased the conductivity as compare to ammonium persulfate [8]. In microemulsion polymerisation method two components are used a surfactant and two immiscible liquids to stabilise the immiscible liquid surfactant is used. The use of right surfactant particles is crucial in this polymerisation, which results in polymeric particles [9].

Numerous studies have been conducted on APS and $FeCl_3$ as oxidising agent, SDS as dopant. In one of the study shown that the increase of dopant SDS concentration from 0.01 M to 0.2 M the conductivity resistance was decreased [10]. In another research $FeCl_3$ was used but instead of dopant, capping agent hexadecyltrimethylammonium bromide and moringa oleifera for production of Polypyrrole nanowires and nanofibers [11]. Meanwhile, potassium peroxydisulfate was used as oxidising agent, SDS and Cetrimonium bromide as surfactant and hydrochloric acid as dopant in microemulsion polymerisation of polypyrrole [12]. There are very limited research papers on comparation study of chemical oxidation and microemulsion, second microemulsion by SDS as dopant, amyl-alcohol as stabiliser and $FeCl_3$ as oxidising agent. Hence, to fulfil the research gap this research is conducted.

Materials and Methods

Sodium dodecyl-sulfate (molecular weight is 288.38%, reagent grade is 99%), pyrrole (molecular weight is 67.09 g/mol, reagent grade is 98%), amyl-alcohol (molecular weight is 88.15 g/mol, reagent grade is 98.5%), ammonium persulfate (APS) (molecular weight is 228.18 g/mol, reagent grade is 98%), methanol (molecular weight is 32.04 g/mol, reagent grade 99%), and $FeCl_3$ (molecular weight is 162.21 g/mol, reagent grade is 99%).

Preparation of polypyrrole

In the preparation of polypyrrole, two methods are used chemical oxidation and microemulsion polymerisation is used as in Table 1, where the pyrrole is treated with different dopant to material ratio, time, temperature, and molarity.

Table 1. Sample preparation by various polymerisation methods

SL No.	Method of Polymerisation	Molarity (M)	Dopant	Oxidising Agent	Time (hour)	Temperature (°C)
1	Chemical oxidation	0.1	Sodium dodecyl-sulfate	$FeCl_3$	4	25
2	Microemulsion polymerisation	0.1	Sodium dodecyl-sulfate	Ammonium persulfate	24	0–4
3	Microemulsion polymerisation	0.1	Sodium dodecyl-sulfate	$FeCl_3$	24	0–4

Preparation of polypyrrole by using a chemical oxidation

In 100 mL of distilled water, 0.1 M of SDS was added and stirred using a magnetic stirrer for 5 min prior to adding 0.1 M of $FeCl_3$ in the solution and stirring it for another 5 min at a temperature of 25°C. Then, 0.1 M of pyrrole was added dropwise in the solution of $FeCl_3$ and SDS solution. The solution was kept under continuous stirring around 500 rpm (revolution per minute) at a temperature of 25°C for 4 hours, since the polymerisation of pyrrole is an exothermic reaction. When the solution of oxidation and dopant react with pyrrole, the solution will slowly turn into black colour and during polymerisation a black ring is observed around the beaker which is formed just above the beaker. After 4 hours the solution is kept in storage for 12 hours, so that polymerisation takes place and precipitation is also observed. The solution is filtered and washed

thoroughly by use of ethanol and distilled water. Then remaining substance from the filter paper is transferred to clay container for drying at 60°C–70°C on a hot plate. Finally, the dried sample is transformed into powder form by use of mortar and pestle and stored in a tight container surrounded with silica gel to prevent moisture.

Preparation of polypyrrole by using a microemulsion polymerisation (APS)

In 100 mL of distilled water 0.1 M of SDS is added and stirred for 20 min at an RPM of 500 at temperature of 0°C to 4°C. Then 0.1 M of pyrrole monomer is added in SDS solution and stirred for 30 min. After 30 min 0.1 M of amyl alcohol is added to the solution and stirred for another 10 min before adding 0.1 M of ammonium persulfate (APS) and allowed the mixture to stirred for 24 hours at temperature of 0°C to 4°C. Black ring is observed around the beaker above the solution, where methanol is subsequently added to the solution to dismiss the polymerisation reaction. The solution is than centrifuged at 10000 rpm for 25 min to produce precipitation. Then, this precipitation is passed through filtration process along with washing thoroughly by methanol and distilled water. Dry the sample at 60°C–70°C at hot plate for 4 hours and by the help of mortar and pestle it is converted into powder form and stored in tight container surrounded with silica gel to prevent moisture.

Preparation of polypyrrole by use of microemulsion polymerisation ($FeCl_3$) process

In 100 mL of distilled water 0.1 M of SDS is added and stirred for 20 min at an rpm of 500 at temperature of 0°C to 4°C. Then 0.1 M of pyrrole monomer is added in SDS solution and stirred for 30 min. After 30 min 0.1 M of amyl alcohol is added to the solution and stirred for another 10 min before adding 0.1 M of iron (III) chloride and allowed the mixture to stirred for 24 hours at temperature of 0°C to 4°C. Black ring is observed around the beaker above the solution. The solution is then centrifuged at 10000 rpm for 25 min to produce precipitation. Next, this precipitation is passed through filtration process along with washing thoroughly by methanol and distilled water. The sample is dried at a temperature ranging from 60°C–70°C on a hot plate for 4 hours and by the help of mortar and pestle to convert it in into powder form and stored in a tight container surrounded with silica gel to prevent moisture.

Results and Discussion

The FTIR spectra found from polypyrrole samples as in Table 1 and by the help of Table 2. [13] radical, wavelength and bond formation were taken as references. The bands 3400, 3400, and 3394 are present in 0.1 M chem, 0.1 M emulsion, and 0.1 M emulsion $FeCl_3$, which show the presence of N-H bonds in the polypyrrole due to N-H stretching vibration. The presence of bands 1552, 1542, and 1542 in 0.1 M chem, 0.1 M emulsion, and 0.1 M emulsion $FeCl_3$ shows the presence of C=C bonds, C=C stretching vibration indicates the π bond, which is responsible for conductivity due to delocalised π that allows electron movement. The bands 1174 and 1038, 1174 and 1038, 1152 and 1038, in 0.1 M chem, 0.1 M emulsion and 0.1 M emulsion $FeCl_3$ show the presence of C-N bond due to C-N stretching shaking of oxidised. The bands 830 and 772, 848 and 786, 846 and 774 in 0.1 M chem, 0.1 M emulsion and 0.1 M emulsion $FeCl_3$ show the presence of C-H bond, where C-H is responsible for plan deformation. The observation of band in current study is justified and available in journal, thereby confirming the polymerisation of pyrrole [13–16].

Table 2. Reference for FTIR spectra for polypyrrole [13]

Radical	Wavelength Range (cm^{-1})	Bond Formation
C=C	1700–1500	C=C bond formation in the molecule
C-H	860–680	C-H bond in molecule
C-N	1200–1025	C-N bond in the molecule
N-H	3500–3300	N-H bond in the molecule

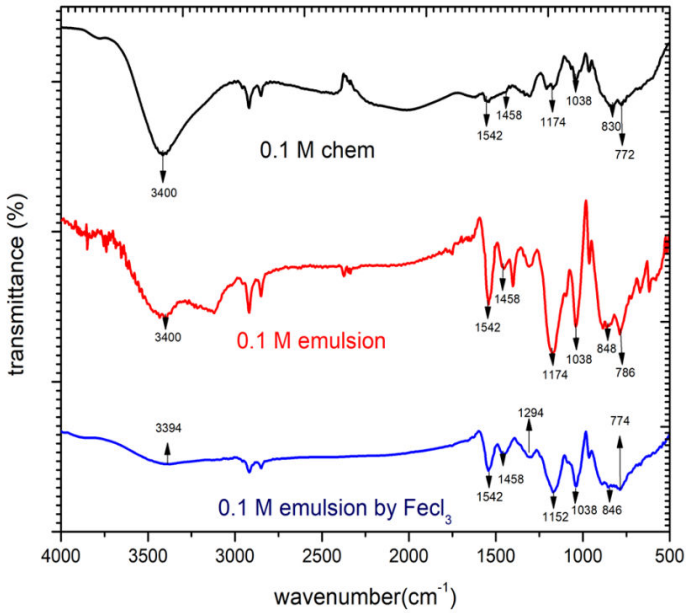

Figure 1. FTIR spectra of polypyrrole of different oxidation and same molarity (abbreviations: 0.1 M chem is 0.1 M chemical oxidation, 0.1 M emulsion is 0.1 M microemulsion by APS and 0.1 M emulsion by $FeCl_3$ is 0.1 M microemulsion by $FeCl_3$)

For surface characterisation of the three samples, Figure 2. shows the images of FE-SEM of (a) 0.1 M of chemical oxidation, (b) 0.1 M of microemulsion by APS and (c) 0.1 M of microemulsion by $FeCl_3$ of polypyrrole. The surface of three samples has rock like shape and distinctive rough surface and small granules [17,18]. By comparing Figure 2. FESEM images of samples (a) and (c), it is observed that polypyrrole produced from microemulsion by $FeCl_3$ has a rougher surface than chemical oxidation, since $FeCl_3$ used as oxidising agent, SDS as dopant in both methods with the same molarity.

To confirm that three samples have the necessary elements, mainly nitrogen and carbon, in polypyrrole, the EDX analysis was conducted. The tests results of EDX shows equivalent peaks as in Figure 3. (a), (b) and (c). Both carbon and nitrogen are observed in the three samples in sample (a) the atomic % of carbon and nitrogen are 80.16% and 19.84%, respectively. The details of the three samples values are measured in atomic and weight% are listed in Table 3. The following results are reported in previous work [19,20].

Table 3. EDX weight % and atomic % of polypyrrole of three samples

Number of samples	Carbon		Nitrogen	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Sample (a) 0.1 chemical oxidation	77.60	80.16	22.40	19.84
Sample (b) 0.1 microemulsion by APS	64.20	67.65	35.80	32.35
Sample (c) 0.1 microemulsion by $FeCl_3$	59.36	63.01	40.64	36.99

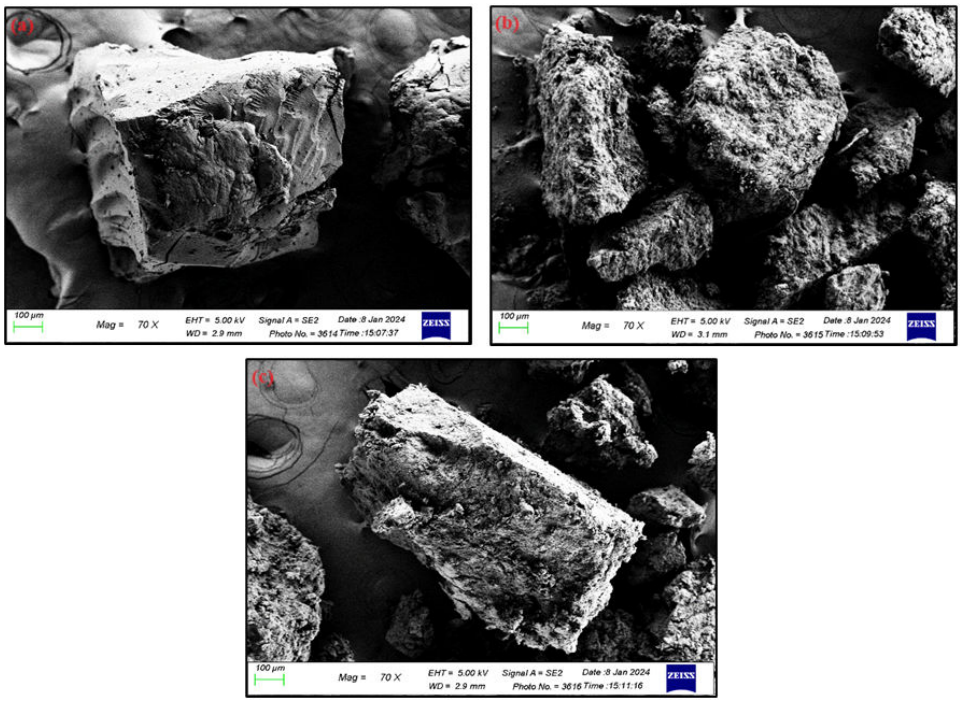

Figure 2. FESEM images of sample (a) chemical oxidation, (b) microemulsion (APS), and (c) microemulsion by $FeCl_3$

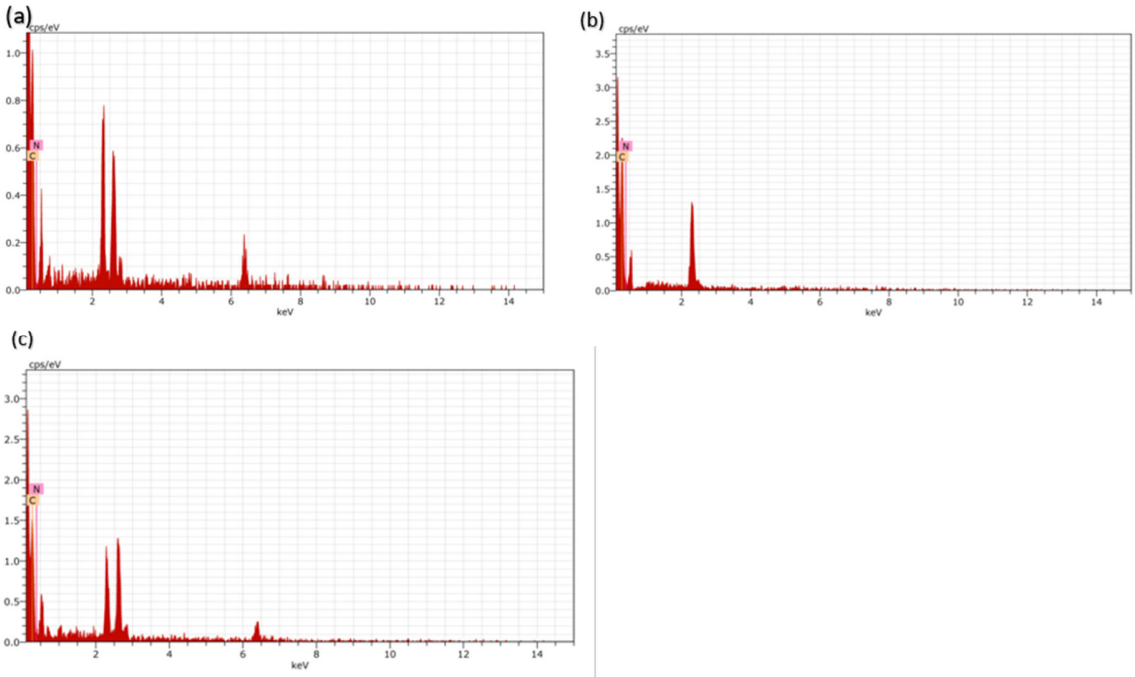

Figure 3. EDX result of sample (a) 0.1 M chemical oxidation, (b) 0.1 M microemulsion by APS (c) 0.1 M microemulsion by $FeCl_3$

The XRD patterns shows the broad peaks that are registered at 2θ equal to 20° and 21° of 0.1 M chemical oxidation, 0.1 M microemulsion APS as oxidant and 0.1 M microemulsion were $FeCl_3$ as oxidant as in Figure 4, the results detect amorphous region present in polypyrrole in three samples [21]. For the average crystallite size is taken from sharp peak at 20° and 21° by help of Scherrer's formula [22].

$$D = \frac{K \times \lambda}{\beta \times \cos\theta} \quad (1)$$

Where D is the crystallite size, K is the shape factor if the shape is unknown the value can be 0.89. θ is the maximum peck intensity at diffraction angle and β is full width at half maximum of diffraction angle in radian (FWHM). In the study sample 0.1 M microemulsion by $FeCl_3$ the cos θ value was 20.42875, β value was 0.03542 by converting FWHM radian value to degree from origin software. The K value was 0.89 and λ value is 1.5418 by putting all this values in (1) the average crystalline size was about 39 nm. The details values and results are mentioned in Table 4. The equation and calculation are taken from the research paper [23].

Table 4. Crystalline size by help of XRD analysis of sample 0.1 M chemical oxidation, Sample 0.1 M microemulsion by APS and Sample 0.1 M microemulsion by $FeCl_3$

	K	**Λ**	**β**	**θ**	**Crystalline size (nm)**
Sample 0.1 M chemical oxidation	0.89	1.5418	0.0673	20.95817	20.82
Sample 0.1 M microemulsion by APS	0.89	1.5418	0.05537	20.64522	25
Sample 0.1 M microemulsion by $FeCl_3$	0.89	1.5418	0.03542	20.42875	39

To determine the crystallinity and amorphous percentage of sample 0.1 M chemical oxidation, Sample 0.1 M microemulsion by APS and Sample 0.1 M microemulsion by $FeCl_3$. Crystallinity index in percentage [24] is used by the help of XRD data, the sharp peaks at 20° to 21° as in Figure 4.

$$Crystallinity\ index\ in\ \% = \frac{\text{area of crystalline peaks}}{\text{area of all peaks(crystalline+amorphous)}} \times 100 \quad (2)$$

In 0.1 M chemical oxidation the area of crystallinity peaks is 2060.739 and area of all peaks is 5888, then by putting the value in Equation (2) the crystallinity index percentage is 35% which means 65% of the material is amorphous. The details of all the three samples are in Table 5. The results of crystalline size from Table 4., crystallinity index % from Table 5. and broad peaks at 20° and 21° in Figure 4. it is seen that the samples are semi-crystalline in nature [25–27].

Table 5. Crystallinity index percentage of three samples

	Area of Crystalline Peaks	**Area of All Peaks**	**Crystallinity Index Percentage**	**Amorphous Percentage**
Sample 0.1 M chemical oxidation	2060.739	5888	≈35%	≈65%
Sample 0.1 M microemulsion by APS	839.5607	5744	≈15%	≈85%
Sample 0.1 M microemulsion by $FeCl_3$	396.8462	2736	≈15%	≈85%

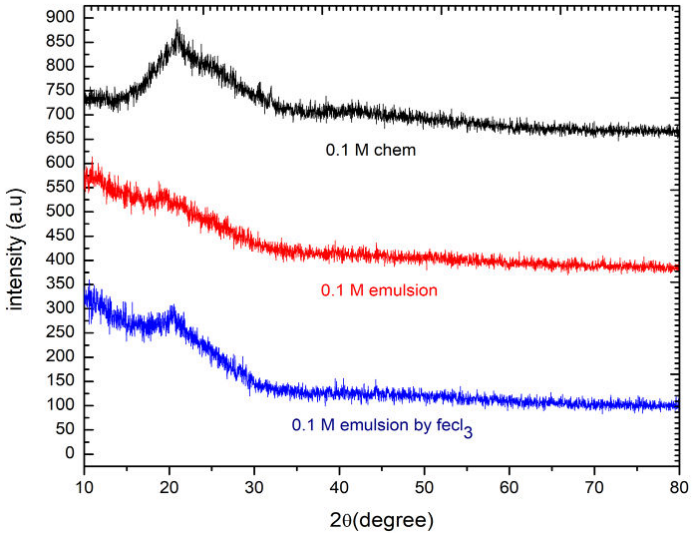

Figure 4. XRD of polypyrrole with different molarity and polymerisation method

For conductivity test Electrochemical Impedance Spectroscopy (EIS) is performed as in Figure 5 Cole-Cole plot of three samples (a), (b) and (c) the aim is to determine the conductivity of the samples. the values are obtained from Nyquist plot or Cole-Cole plot where ($Z^{/}$) is the real imaginary component and ($Z^{//}$) is the imaginary impedance component. The semi-circle formation in the plot denotes high frequency region and straight sloping line denotes low frequency region [28]

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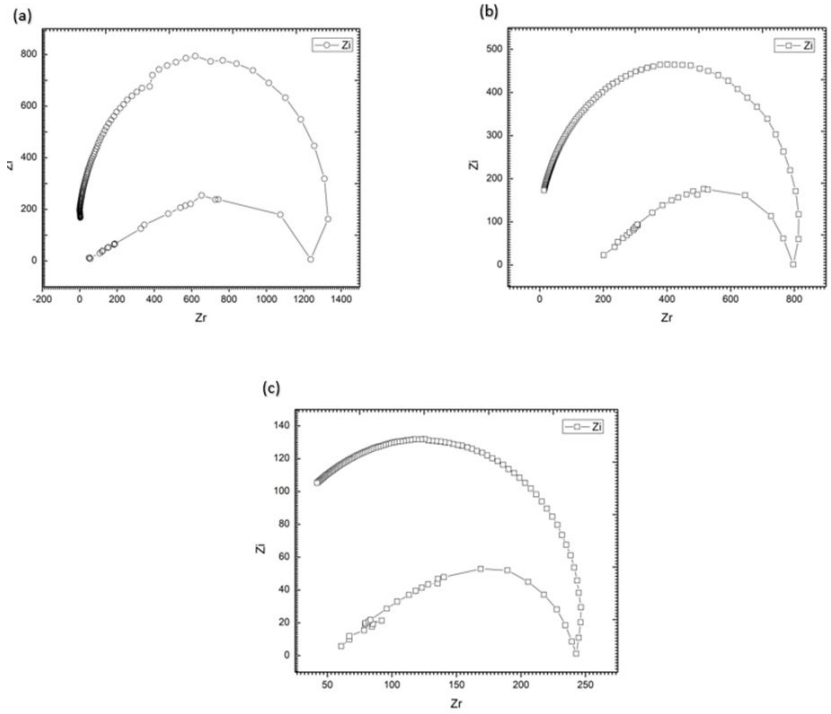

Figure 5. Cole-Cole plot of three samples (a) 0.1 M chemical oxidation, (b) 0.1 M microemulsion by APS and (c) 0.1 M microemulsion by $FeCl_3$

To confirm the conductivity of three samples as polypyrrole which is conductive in nature EIS test is executed. The conductivity is taken out by help of the conductivity formula:

$$\sigma = \frac{t}{R_b \times A} \quad (3)$$

where, σ is the ionic conductivity in $S.cm^{-1}$, t is the thickness of the sample in cm, R_b is the bulk resistance taken from the Cole-Cole plot, and A is the area of the contact between electrode and electrolyte in cm^2 [29]. In sample (a), t value is 0.272 cm, R_b value is 6.263017Ω and area is 0.1964 cm^2 putting the value in (3) gives $0.2211 \Omega^{-1} cm^{-1}$ of conductivity. The details of the three samples, namely, 0.1 M chemical oxidation, 0.1 M microemulsion by APS, and 0.1 M microemulsion by $FeCl_3$ are shown in Table 6.

Table 6. conductivity measurement by EIS of samples (a) 0.1 M chemical oxidation, (b) 0.1 M microemulsion by APS and (c) 0.1 M microemulsion by $FeCl_3$

Sample	Thickness (T) (cm)	Resistance Bulk (R_b) (Ω)	Area of the Electrode and Electrolyte (A) (cm^2)	Conductivity (Ω^{-1} cm^{-1})
Sample (a)	0.272	6.263017	0.1964	0.2211
Sample (b)	0.272	1.340834	0.1964	0.9958
Sample (c)	0.272	1.228653	0.1964	1.1619

Conclusion

By the test results and references it is concluded that by use of chemical oxidation and microemulsion the three samples are successfully polymerised from pyrrole monomer to polypyrrole. For the comparison study between chemical oxidation by $FeCl_3$ and microemulsion by $FeCl_3$, also comparison between microemulsion by APS and microemulsion by $FeCl_3$. Various characterisation tests were conducted, FE-SEM shows the rough, rocky surface in all three samples but by comparing Figure 2. FESEM images of sample (a) and (c) it is observed that polypyrrole produce from microemulsion by $FeCl_3$ has rougher surface than chemical oxidation since $FeCl_3$ used as oxidising agent, SDS as dopant in both method with same molarity. However, in case of microemulsion by APS and microemulsion by $FeCl_3$ same rough surface structure can be seen. Moreover, to confirm the chemical properties EDX and FTIR is performed where carbon and nitrogen are found in large number and by the FTIR the peaks show the bond formation in polypyrrole (i.e., C=C, C-H, C-N and N-H). Further to confirm XRD is performed to find the nature of the samples which are semi-crystalline in nature and the crystalline size are investigated. For conductivity measurement EIS test is performed where 0.1 M microemulsion by $FeCl_3$ have the highest conductivity of 1.1619 Ω^{-1} cm^{-1}. Thus, it illustrates that microemulsion by $FeCl_3$ is a much better option than the other two samples. Therefore, it is concluded that microemulsion by $FeCl_3$ is superior to APS oxidant for better conductivity, which can be used for future applications like in textile fields, medical fields, anti-corrosion, etc., by combining with other metals or non-metals.

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