

**AN ELECTROCHEMICAL STUDIES ON ALGINATE-
BASED SOLID BIOPOLYMER ELECTROLYTES**

**(PENGUJIAN ELEKTROKIMIA KE ATAS ALGINAT
BERDASARKAN BIOPOLIMER ELEKTROLIT
PEPEJAL)**



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**RESEARCH VOTE NO:
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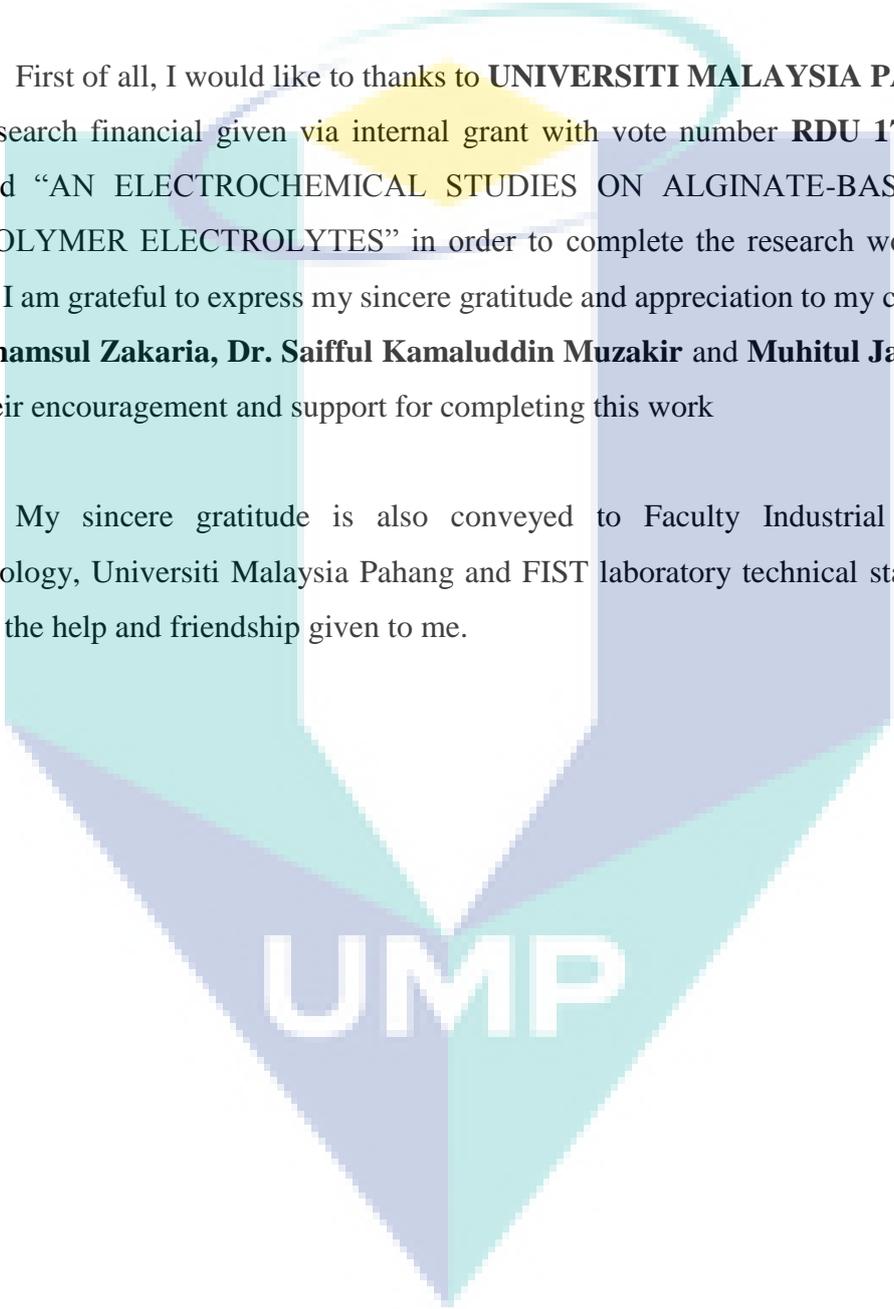
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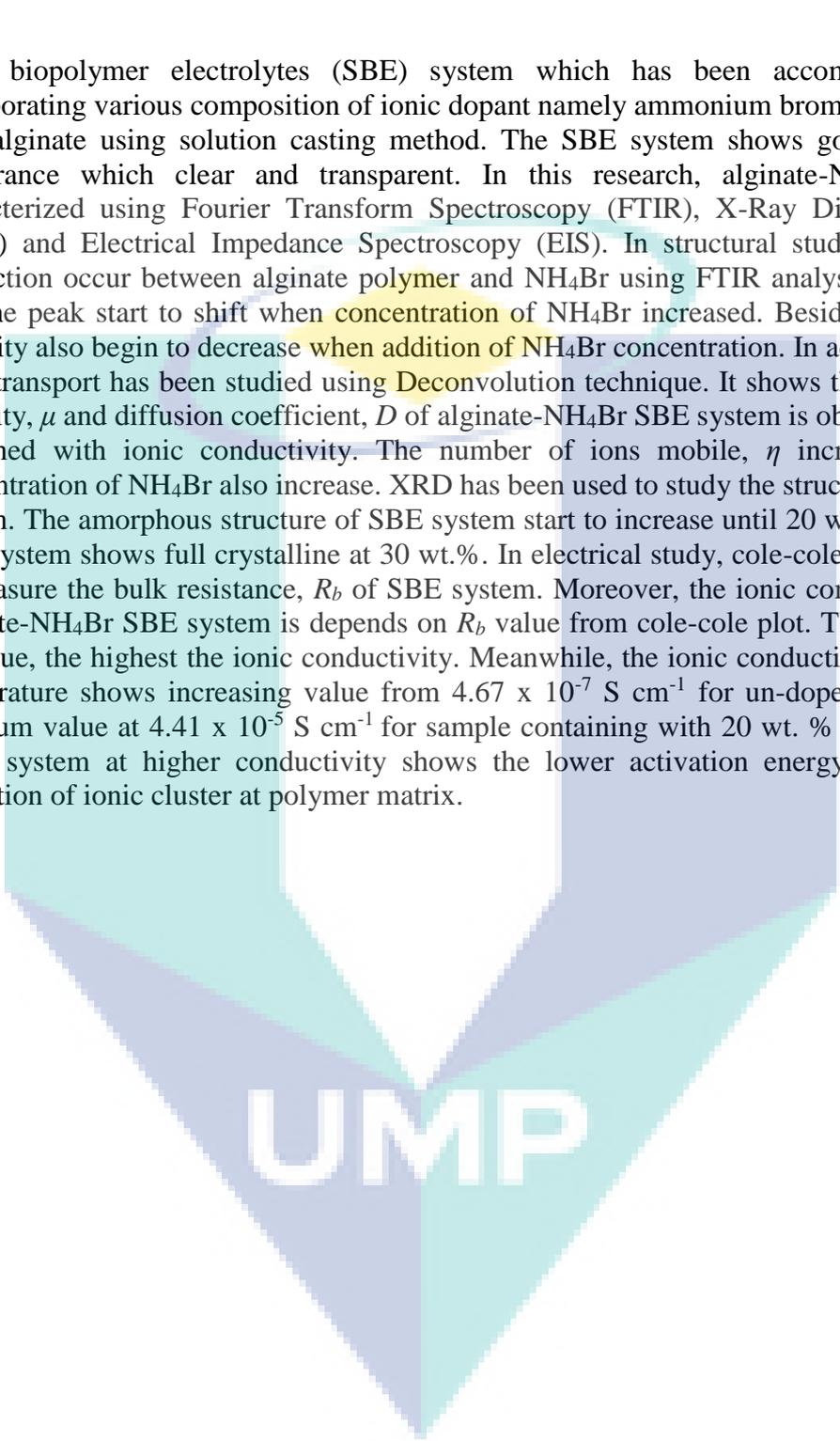
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ABSTRACT

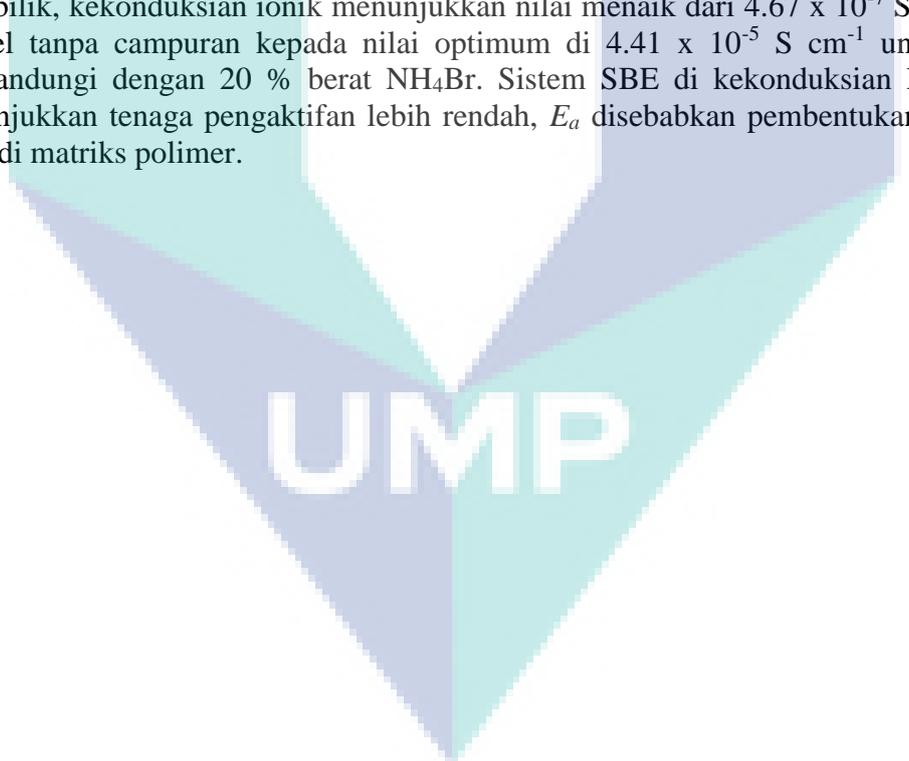
Solid biopolymer electrolytes (SBE) system which has been accomplished by incorporating various composition of ionic dopant namely ammonium bromide (NH_4Br) with alginate using solution casting method. The SBE system shows good physical appearance which clear and transparent. In this research, alginate- NH_4Br were characterized using Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS). In structural study, there are interaction occur between alginate polymer and NH_4Br using FTIR analysis. It shows that the peak start to shift when concentration of NH_4Br increased. Besides, the peak intensity also begin to decrease when addition of NH_4Br concentration. In advanced, the ionic transport has been studied using Deconvolution technique. It shows that the ionic mobility, μ and diffusion coefficient, D of alginate- NH_4Br SBE system is observed to be governed with ionic conductivity. The number of ions mobile, η increase as the concentration of NH_4Br also increase. XRD has been used to study the structural of SBE system. The amorphous structure of SBE system start to increase until 20 wt. % and the SBE system shows full crystalline at 30 wt.%. In electrical study, cole-cole plot is used to measure the bulk resistance, R_b of SBE system. Moreover, the ionic conductivity of alginate- NH_4Br SBE system is depends on R_b value from cole-cole plot. The lower the R_b value, the highest the ionic conductivity. Meanwhile, the ionic conductivity at room temperature shows increasing value from $4.67 \times 10^{-7} \text{ S cm}^{-1}$ for un-doped sample to optimum value at $4.41 \times 10^{-5} \text{ S cm}^{-1}$ for sample containing with 20 wt. % NH_4Br . The SBEs system at higher conductivity shows the lower activation energy, E_a due to formation of ionic cluster at polymer matrix.

The logo of UMPU (Universiti Malaysia Perlis) is a large, stylized letter 'U' composed of four overlapping triangles in shades of teal and light blue. The letters 'U', 'M', 'P', and 'U' are arranged within the shape of the 'U' and are rendered in a white, bold, sans-serif font.

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ABSTRAK

Sistem elektrolit biopolimer pepejal (SBE) yang mana telah dilaksanakan dengan menggabungkan pelbagai komposisi bahan dop ionik iaitu ammonium bromide (NH_4Br) dengan alginat menggunakan teknik penuangan larutan. Sistem menunjukkan keadaan fizikal SBE dalam keadaan baik di mana jelas dan telus. Dalam penyelidikan ini, alginat NH_4Br dikaji menggunakan Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer and Electrical Impedance Spectroscopy. Dalam kajian struktur, terdapat interaksi berlaku di antara polimer alginat dan NH_4Br menggunakan analisis FTIR. Ia menunjukkan bahawa puncak mula untuk berpaling apabila kepekatan NH_4Br menambah. Selain itu, puncak intensiti juga mula untuk berkurang apabila kepekatan NH_4Br bertambah. Di samping itu, pengangkutan ionik telah dikaji menggunakan teknik pengenyahkonvolutan. Ia menunjukkan bahawa mobiliti ion, μ dan pekali resapan, D sistem SBE alginat- NH_4Br diperhatikan untuk ditadbir dengan kekonduksian ionik. Jumlah kepergerakan ion-ion, η meningkat apabila kepekatan NH_4Br juga turut meningkat. XRD telah digunakan bagi mengkaji struktur daripada sistem SBE. Struktur amorfus sistem SBE mula untuk meningkatkan sehingga 20 % berat dan sistem menunjukkan SBE penuh berhablur di 30 % berat. Dalam kajian elektrik, plot “cole-cole” digunakan untuk mengukur rintangan pukal, R_b dalam sistem SBE. Tambahan pula, kekonduksian ionik sistem SBE alginat- NH_4Br bergantung pada nilai R_b dari plot “cole-cole”. Semakin rendah nilai R_b , semakin tinggi kekonduksian ionik. Sementara itu, pada suhu bilik, kekonduksian ionik menunjukkan nilai menaik dari $4.67 \times 10^{-7} \text{ S cm}^{-1}$ untuk sampel tanpa campuran kepada nilai optimum di $4.41 \times 10^{-5} \text{ S cm}^{-1}$ untuk sampel mengandungi dengan 20 % berat NH_4Br . Sistem SBE di kekonduksian lebih tinggi menunjukkan tenaga pengaktifan lebih rendah, E_a disebabkan pembentukan kelompok ionik di matriks polimer.



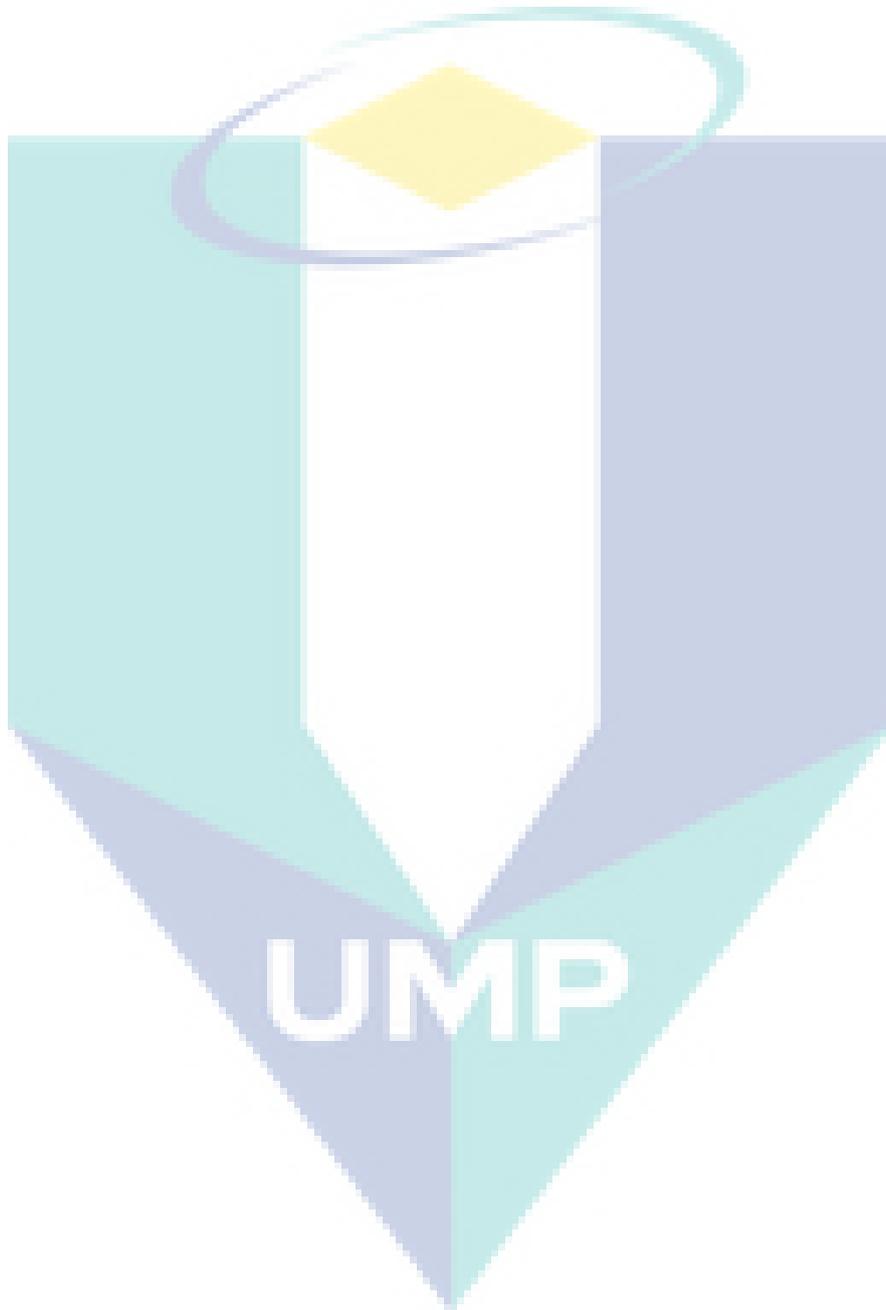
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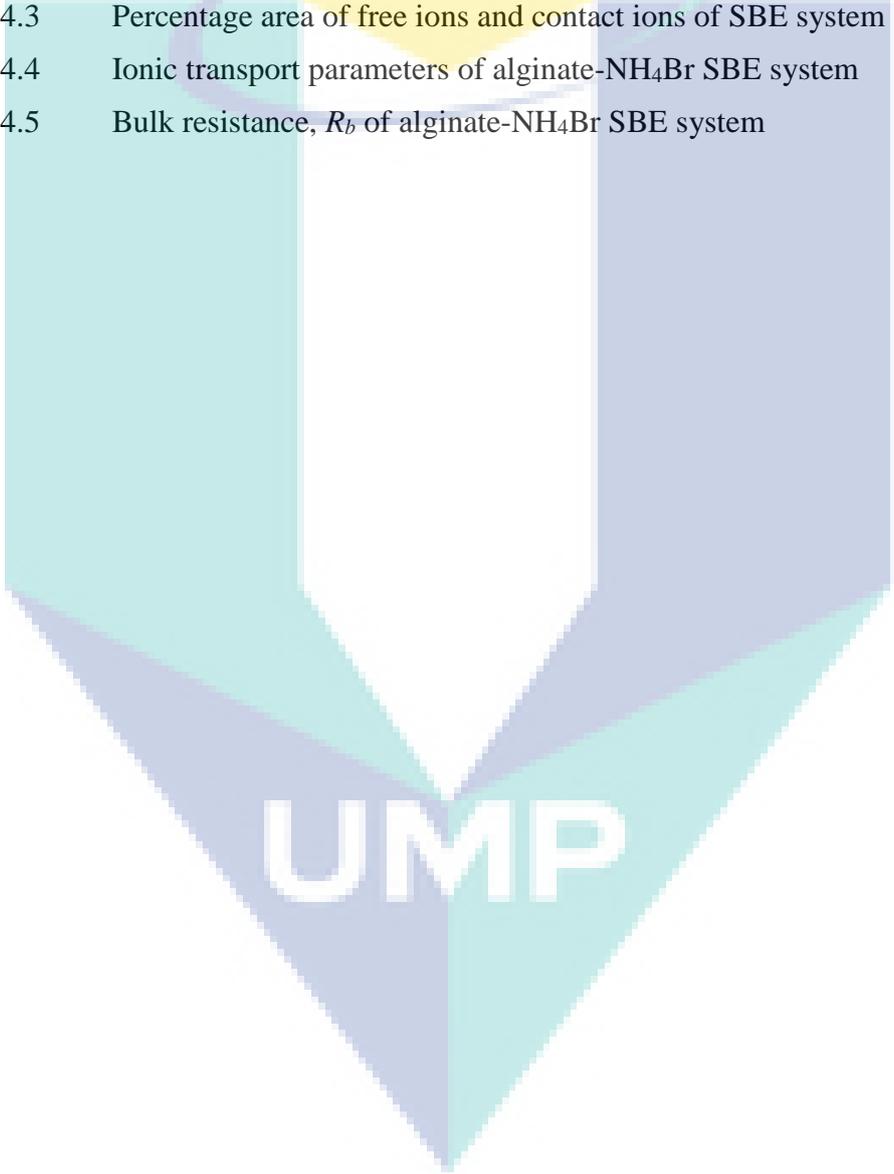
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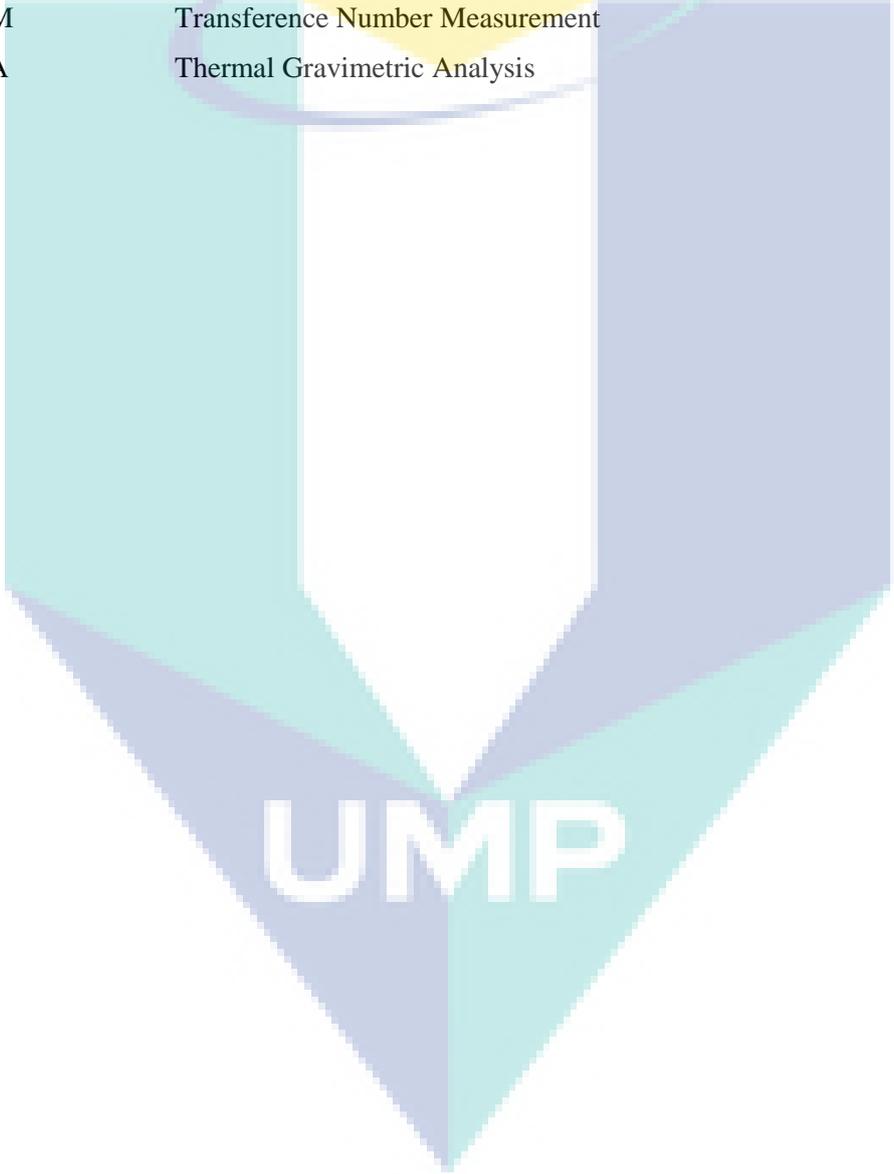
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LIST OF SYMBOLS

%	Percent
cm	Centimetre
cm ²	Square centimetre
cm ⁻¹	Per centimetre
cm ⁻³	Per cube centimetre
g	Grams
σ	Ionic conductivity
Hz	Hertz
K	Kelvin
R _b	Bulk resistance
S	Siemens
s	Second
wt. %	Weight percentage
E _a	Activation energy
k	Boltzmann constant
A	Area
D	Diffusion coefficient
μ	Ionic mobility
η	Density of mobile ions
A _f	Area under peak for free ion region
A _c	Area under peak for contact ion region
M	Number of moles
N _A	Avogadro's constant
V _{Total}	Total volume
e	Electric charge
K	Boltzmann constant
°	Degree
°C	Degree celcius
θ	Theta
π	Pi
t	Thicknes
V	Voltage

LIST OF ABBREVIATIONS

XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared
EIS	Electrical Impedance Spectroscopy
SBE	Solid biopolymer electrolyte
NH ₄ Br	Ammonium bromide
FESEM	Field Emission Scanning Electron Microscopy
TNM	Transference Number Measurement
TGA	Thermal Gravimetric Analysis



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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The electrolyte is the one of the part of battery component. It is functioning to supply electrical power to device. There are many applications of battery in this era of technology. For example, automotive, electronic device, military and aerospace, and etc. In battery, there are three main primary sections which is two terminals made of various chemicals (metal) as known as cathode and anode, and the electrolyte, which isolates these terminals. Liquid (aqueous), solid, and gel are the common electrolyte use in electrochemical devices.

Normally, the liquid electrolyte showed low cycle of energy and also costly in production (Q. Li & Ardebili, 2016). Corrosion of metal terminal is one of the main problem occur by the using of liquid form. Corrosion can bring damaging and toxicity directly to human due the materials used in electrolytes system such as lithium and nickel. Besides, the electrolyte will explode when expose to the high temperature which bring danger to the human and also environment. Therefore, the solid electrolyte is one of the solution to overcome this problem. Solid electrolyte which made from polymer materials is more flexible in shape, more safe which no leakage and no possibility of corrosion (Su'ait, Ahmad, & Rahman, 2009).

The research shown that using of renewable product which is polymer or biopolymer can be used as electrolyte. Biopolymer are made from natural material that widely been used system. So, the production is very low cost but useful and has good potential due to their good properties for electrolytes application. It will become one of the environmentally friendly product.

In this research, alginate has been chosen as biopolymer host for development of solid biopolymer electrolytes. Alginate is a polysaccharide that extracted from cell wall of brown seaweed. Generally biopolymer itself is low in ionic conductivity, therefore, the addition of dopant system namely NH_4Br was identified to be an appropriate way in order to enhance the ionic transports and conductivity of SBEs system.

1.2 STATEMENT OF THE PROBLEM

In this era of technology, electrolyte become the famous study in the battery production of electronic device. For example, lithium-ion battery function as rechargeable battery which mostly in electronic device. This liquid electrolyte already been used widely in industrial and also in our daily life. Somehow, the liquid electrolyte can bring many disadvantage for us and environment. The disadvantage that occur is high cost material for production of solid-state electrolyte. This may ensure us to use some renewable material for the future electrolyte production. Besides, the other disadvantage is non-environmental friendly and pollution which is hazardous. As we know, synthetic material such as fossil fuel is one of the material that been used for production of electrolyte which will reduce in the future.

In the meantime, there is many investigation and research on biopolymer in using for electrolyte. Biopolymer is chosen for this study because of the biodegradable behaviour. During the depletion of the number in the fossil fuel, biodegradable polymer become the most important thing to recreate and save our nature and environment. This biopolymer become one of the best production of electrolyte because it use renewable polymer. Renewable polymer is the natural polymer that currently came around us. For example, synthetic, animals and plants. The major advantages of using this biopolymer are low cost production and environmental-friendly which can been use renewable.

1.3 OBJECTIVES OF RESEARCH

The objective of research:

1. To formulate the solid biopolymer electrolyte (SBE) based on alginate doped varied amount of NH_4Br .

2. To determine the ionic conductivity of alginate-NH₄Br SBE system by using Impedance technique.
3. To identify the complexation and optical properties between the alginate and NH₄Br via deconvolution approach.

1.4 THESIS OUTLINE

Chapter 2 is the literature review where the explanation based on previous research. The concept of research can be elaborated further due to extensive work has been done in previous study. Furthermore, the used of Chapter 2 can improve our knowledge easily regard to the concept of our study. In this research, Chapter 2 cover the study of polymer electrolyte, solid polymer electrolyte and biopolymer electrolyte. Besides, it also shows the concept of dopant salt which is ammonium salt.

Then, the Chapter 3 were mainly focus on the methodology of the research. The alginate biopolymer act as a host polymer which doping with ammonium bromide (NH₄Br) to develop solid biopolymer electrolyte (SBE) system. The SBE was characterized and analysed by using Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS). The FTIR and XRD are used to analyze the ionic transport properties of SBE. The main function of EIS is to determine the ionic conductivity of SBE system over a wide range of frequencies.

Meanwhile Chapter 4, result and discussion is the main part of the research which consist of the calculation and analyse of the data. The data can be tabulated according to the procedure on previous Chapter 3. The structural and complexation between host polymer and salt dopant was investigated through FTIR and XRD analysis. In EIS, the cole-cole plot were used to study the electrical properties of the SBE system in terms of conductivity of material at various temperature, and also the activation energy.

CHAPTER 2

LITERATURE REVIEW

2.1 POLYMER ELECTROLYTES

Polymer electrolyte is the one of the low cost material which provide good conductivity in battery industry. By using casting technique to make the polymer electrolyte solution into thin film, it easy to flow the ionic conductivity through it. Polymer electrolyte also can be defined as the thin film which is consist of ionic salts disintegrated in an appropriate polymer, furthermore enable ionic conduction at room temperature (Linford, Radhakrishna, & Daud, 1991). In general, liquid electrolyte, gel electrolyte, and solid electrolyte are the main type of electrolyte.

The liquid electrolyte are variously called ionic liquids, liquid salts, ionic fluids, fused salts, ionic melts, or ionic glasses (Housaindokht et al., 2013). Some of example of liquid electrolyte is lithium, potassium chloride and sodium nitrate. In industry, lithium is the most material that been used in electrolyte. The liquid electrolytes in lithium batteries can easily cause harmful to the human and pollute to environment when explode (Daigle et al., 2015). Moreover, lithium is one of the hazardous, flammability and the leakage of the liquid electrolyte (Marc Brinkkötter et al., 2017). In general, liquid electrolyte is good for achieving high conductivity but somehow the lack of safety properties can reduce the production of electrochemical device.

To prevent the problem occur, the researcher used gel as electrolyte due to anti-oxidation, superior thermal porosities, mechanical properties and interfacial stability with lithium metal (W. Li et al., 2015). The main example of polymer gel electrolyte we can see is poly-ionic liquid poly(diallyldimethylammonium) bis(trifluoromethyl sulfonyl)imide (PDADMA-TFSI) (Brinkkötter, Gouverneur, Sebastião, Chávez, & Schönhoff, 2017). But the gel electrolyte is not suitable been used industry even have

higher conductivity. One of the disadvantage of gel electrolyte is costly material. So, we used solid electrolyte as main electrolyte in industry. Solid electrolyte is safely use in device due to thermal and dimensional stability among electrolytes (Quartarone & Mustarelli, 2011). The main example of solid electrolyte is polyethylene glycol copolymer (Si-PEG) which enhance ionic conductivity in electrochemical device (Meyer, 1998).

2.2 SOLID POLYMER ELECTROLYTES

Solid polymer electrolytes are solvent-free electrolytes based on polymers have potential for use in electrochemical device. Solid polymer electrolytes is non-harmful material compared to organic liquid electrolytes. Solid polymer electrolytes showed viable solutions to enhance the safety in high power rechargeable lithium batteries (Garcia-Calvo, Lago, Devaraj, & Armand, 2016). Besides, organic liquid electrolytes is not safety for daily use due to toxicity and hazardous which instability at high temperatures (Jung et al., 2015). Polymer electrolytes is an environmental friendly product which achieve good properties such as good ionic conductivity, low flammability high chemical stability and also easy to fabricate (Somsongkul, Jamikorn, Wongchaisuwat, Thang, & Arunchaiya, 2016). Nowadays, the enhancement of safety and also good in thermal and dimensional stability displayed that solid polymer electrolytes are good candidates for high temperature (Zhang et al., 2016). There are many type of polymer materials to enhance good solid polymer electrolytes. For example, polymethyl methacrylate (PMMA) (Achari, Reddy, Sharma, & Rao, 2007), poly(ethylene glycol) (PEG) (Polu et al., 2017), polyvinylidene fluoride (Jiang, Carroll, & Abraham, 1997), polypropylene, polyacrylonitrile (PAN) (Bandara et al., 2013) have been studied as polymer electrolyte matrix.

2.3 BIOPOLYMER ELECTROLYTES

Biopolymer is one of the biodegradable polymer (natural polymer) which bring environmental friendly because it doesn't bring hazardous and toxicity to human and environment. In industry, biopolymer electrolyte is one way to enhance the solid polymer

electrolyte due to biodegradable material. In industry, solid biopolymer electrolyte (SBE) system is low cost production. Two main type of SBE system are natural polymer and synthetic polymer. The examples of synthetic polymer are Polyethylene oxide, polyvinyl alcohols and polyacrylic acid (Majid & Arof, 2005). Alginate and carboxymethyl cellulose (CMC) are the example of natural polymer.

Nowadays, solid biopolymer electrolyte become widely famous study among researcher due to biodegradable properties. Various biopolymer (natural) material such as carboxy methylcellulose (CMC), corn starch, chitosan and carrageenan shows the good backbone of polymer matrix in SBE system (Kausar, 2016). This is because there have achieve good ionic conductivity in previous research. Table 2.1 shows the different type of SBE and the conductivity based on previous research.

Table 2.1 The various type of SBE system based on previous research

Biopolymer host	Dopant	Conductivity, σ (S cm^{-1})	Research
Carboxy methylcellulose (CMC)	Ammonium fluoride (NH_4F)	2.68×10^{-7}	(Ramlli & Isa, 2015)
Cornstarch	Ammonium bromide (NH_4Br)	5.57×10^{-5}	(Shukur & Kadir, 2015)
Chitosan	Ammonium bromide (NH_4Br)	4.38×10^{-5}	(Shukur et al., 2013)
kappa, κ -carrageenan	1-butyl-3-methylimidazolium chloride ([Bmim]Cl)	2.44×10^{-3}	(Shamsudin, Ahmad, Hassan, & Kaddami, 2016)
2-hydroxyethyl cellulose (2HEC)	dodecyltrimethyl ammonium bromide (DTAB)	2.80×10^{-5}	(N. Ahmad, Bakar, & Isa, 2017)

In this research, the host polymer chosen is alginate. Alginate is extracted from cell wall of brown seaweed. Alginate are water-soluble, strong, glossy, tasteless, odourless, flexible, low permeability to oxygen and oils (Xiao, Gu, & Tan, 2014). Moreover, alginate showed good biodegradability, non-immunogenicity, non-toxicity, biocompatibility, and can be easily gelled with divalent cations such as calcium ion and sodium ion (George & Abraham, 2006). By using the alginate, we can produce a complete host solid biopolymer electrolyte (SBE). Alginate shows same other biopolymer characteristics which low properties of water vapour barrier and bad flexibility (Huq et

al., 2012). Alginate can show ionic conductivity in electrolyte. Moreover, to improve the conductivity, biopolymer dopant with salt to achieve good conductivity of electrolyte.

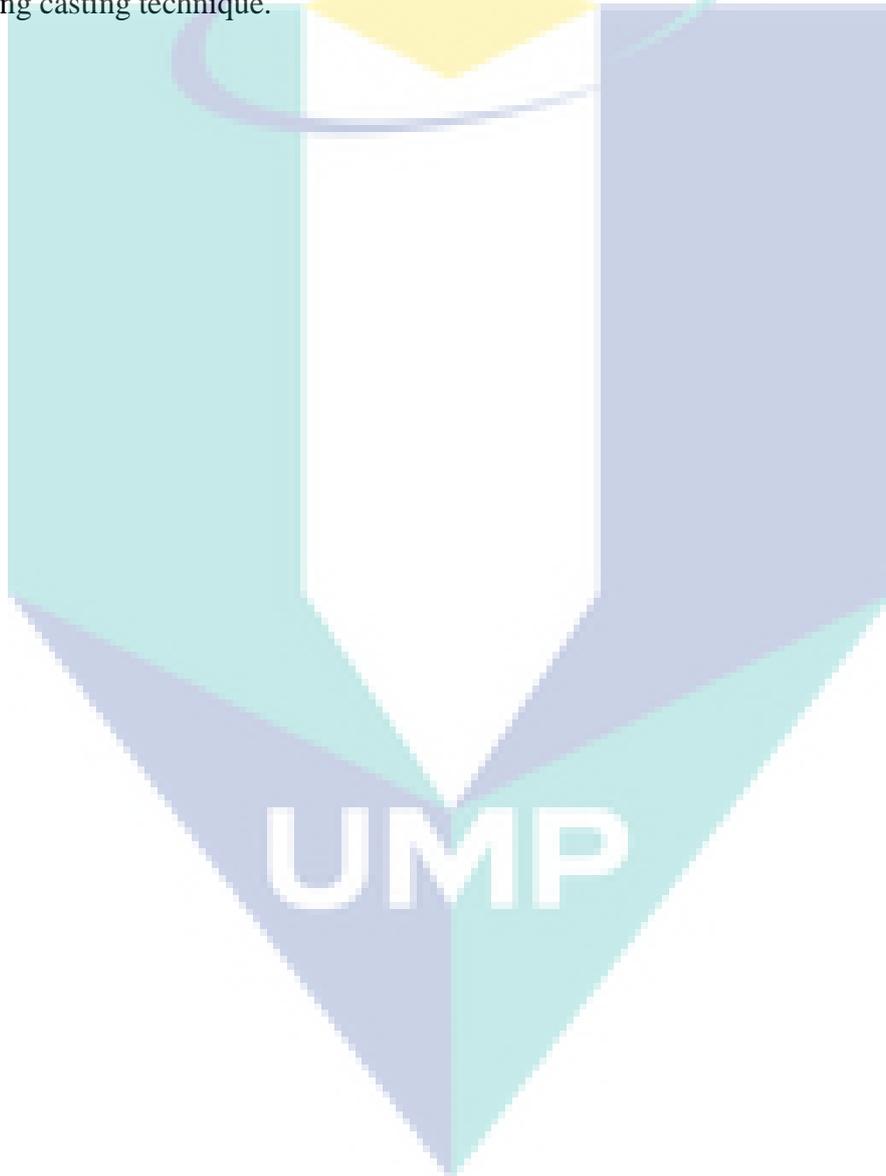
2.4 AMMONIUM SALT AS DOPANT SYSTEM

In Solid Biopolymer Electrolyte (SBE) system, the enhancement of ionic conductivity biopolymer will occur dramatically when added the dopant or plasticized. Ammonium salt is a dopant salt which have good proton donor in SBE matrix (Sohaimy & Isa, 2015). Table 2.2 shows the previous research about the ionic conductivity of different ammonium salt on same biopolymer which is carboxy methylcellulose (CMC). The increasing of ionic conductivity of the different CMC is due to decreasing order of ammonium halide in lattice energy (Parameswaran, Nallamuthu, Devendran, Nagarajan, & Manikandan, 2017).

Table 2.2 The various type of ammonium halide in SBE system based on previous research

Biopolymer host	Dopant (ammonium salt)	Conductivity, σ (S cm ⁻¹)	Research
Carboxy methylcellulose (CMC)	Ammonium fluoride (NH ₄ F)	2.68×10^{-7}	(Ramlli & Isa, 2015)
Carboxy methylcellulose (CMC)	Ammonium bromide (NH ₄ Br)	1.12×10^{-4}	(Samsudin, Lai, & Isa, 2014)
Carboxy methylcellulose (CMC)	Ammonium thiocyanate (NH ₄ SCN)	6.48×10^{-5}	(Noor & Isa, 2015)
Carboxy methylcellulose (CMC)	Ammonium chloride (NH ₄ Cl)	1.43×10^{-3}	(N. H. B. Ahmad & Isa, 2015)
Carboxy methylcellulose (CMC)	Ammonium acetate, (NH ₄ CH ₃ COO)	2.18×10^{-3}	(Rani, Dzulkurnain, Ahmad, & Mohamed, 2015)
Carboxy methylcellulose (CMC)	dodecyltrimethyl ammonium bromide (DTAB)	7.72×10^{-4}	(Samsudin & Isa, 2012a)

In this research, dopant salt is needed to enhance the ionic conductivity of alginate biopolymer in SBE system. Ammonium bromide (NH_4Br) is chosen as ammonium salt because of good proton donor (Hema, Selvasekerapandian, Sakunthala, Arunkumar, & Nithya, 2008). NH_4Br is ammonium halide which consists of NH_4^+ ion and Br^- ion. In this research, it can contribute to high efficiency of conducting proton during doping with alginate. NH_4Br has high melting points in range between $157\text{-}162^\circ\text{C}$. Doping the host biopolymer with NH_4Br (thin film) will bring excellent conductivity of electrolyte by using casting technique.

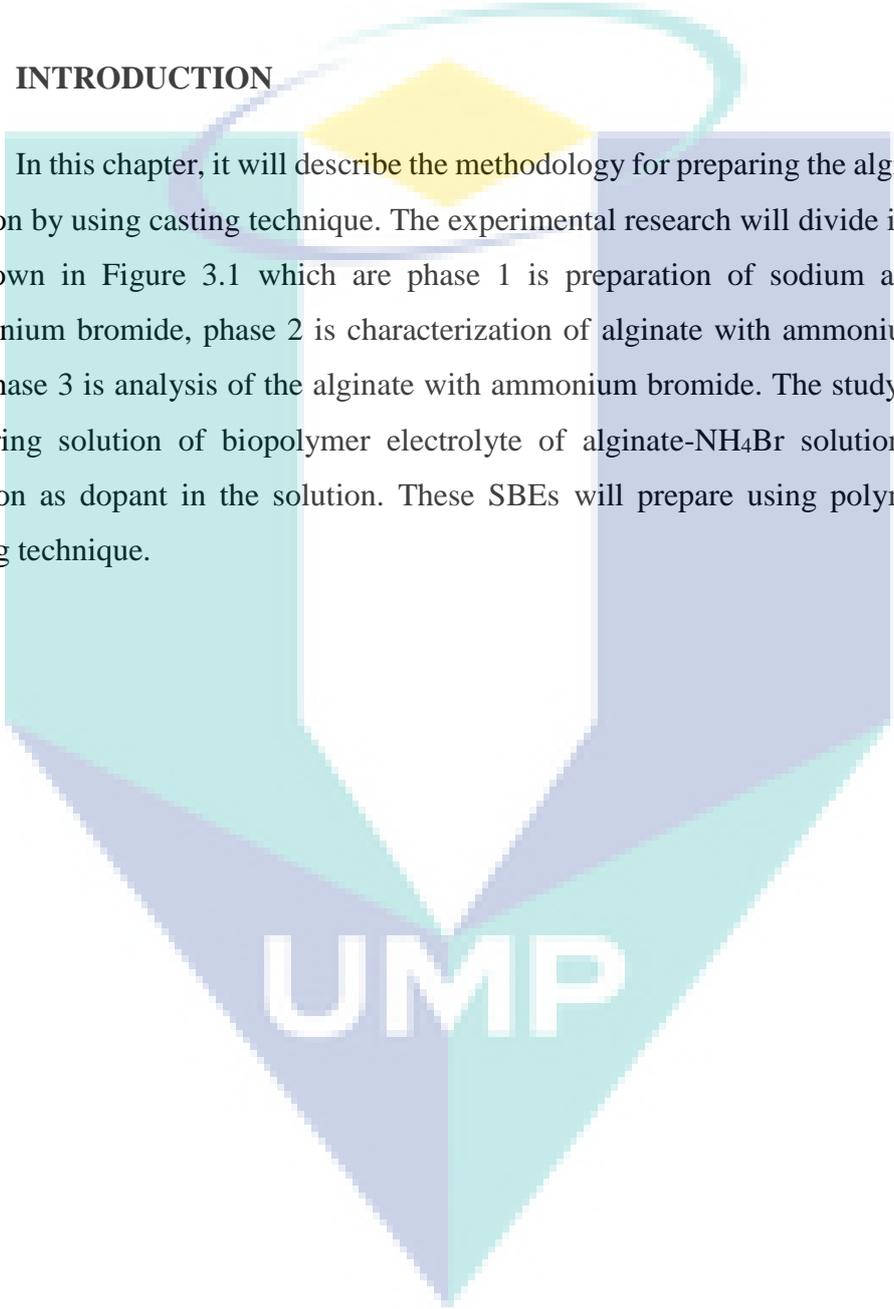


CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In this chapter, it will describe the methodology for preparing the alginate-NH₄Br solution by using casting technique. The experimental research will divide into 3 phases as shown in Figure 3.1 which are phase 1 is preparation of sodium alginate with ammonium bromide, phase 2 is characterization of alginate with ammonium bromide, and phase 3 is analysis of the alginate with ammonium bromide. The study is begin by preparing solution of biopolymer electrolyte of alginate-NH₄Br solution. NH₄Br is function as dopant in the solution. These SBEs will prepare using polymer solution casting technique.



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3.1.1 RESEARCH METHODOLOGY

Figure 3.1 shows the flow chart of research.

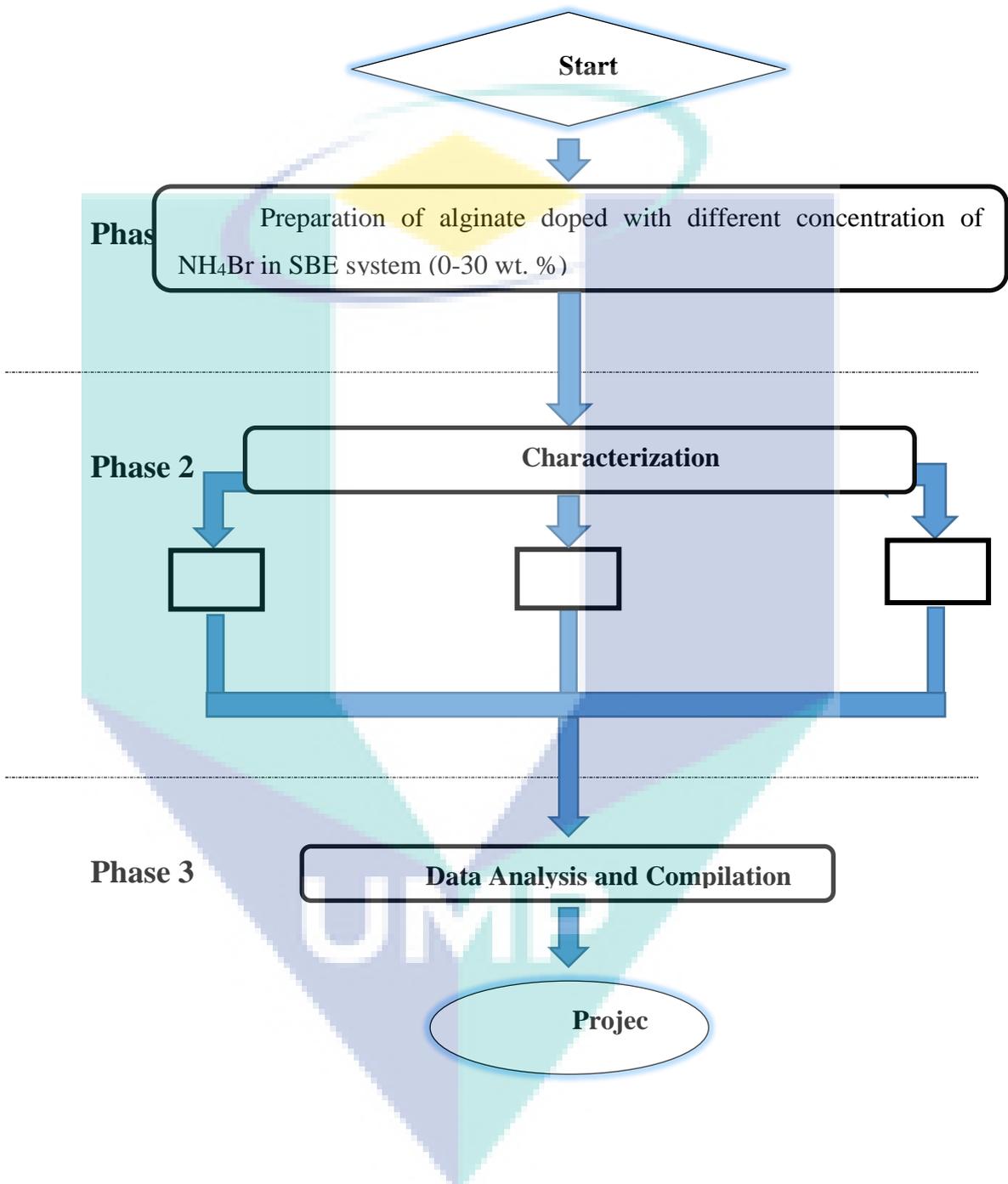


Figure 3.1 Flowchart of the experimental research for alginate-NH₄Br SBE system

3.2 SAMPLE PREPARATION

The preparation of the sample will be started by dissolving 2 g of alginate into 98 ml of distilled water. For precaution, the alginate powder must slowly put into distilled water in small amount for every dropping. Next, different (5 – 30 wt. %) of NH₄Br will be dissolved into the alginate solution. The alginate-NH₄Br solution is then stir slowly until a homogeneous solution will obtain. The calculation to get the weight of NH₄Br:-

$$\frac{x}{x+y} \times 100\% = zwt. \% \quad (3.1)$$

$$100x = zx + zy \quad (3.2)$$

$$(100 - z)x = zy \quad (3.3)$$

$$x = \frac{zy}{100 - z} \quad (3.4)$$

Where,

x = weight of NH₄Br in gram (g)

y = weight of alginate in gram (g)

z = wt. % of NH₄Br

The mixture of alginate-NH₄Br is then will be casted into different petri dishes and left to dry in the oven in order to produce flexible thin film. Polymer solution casting method is employing to obtain thin film samples. The film is then will be transfer to a desiccator filled with silica gel to further up drying. Table 3.1 shows the composition of the alginate-NH₄Br SBE system.

Table 3.1 Composition of alginate-NH₄Br SBE system

Alginate (g)	NH ₄ Br (wt. %)	NH ₄ Br (g)
2	0	0.0000
2	5	0.1053
2	10	0.2222
2	15	0.3529
2	20	0.5000
2	25	0.6667
2	30	0.8571

3.3 SAMPLE CHARACTERIZATION

In this research, there are three instruments used to study the characterization of the Alginate-NH₄Br SBE system. The sample has been characterized and analysed by using Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS).

3.3.1 FOURIER TRANSFORM INFRARED (FTIR)



Figure 3.2 The Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is the technique used to generate an infrared spectrum of absorption or emission of every matter. It is also one of the techniques used to identify the complexation between alginate-NH₄Br of SBE system. The infra-red spectra were obtained using Perkin Elmer Spectrum 100 with an attenuated total reflection (ATR) accessory with a germanium crystal. The infra-red light had passed through the sample with frequencies in the range between 700 cm⁻¹ until 4000 cm⁻¹ with a spectra resolution of 2 cm⁻¹.

3.3.1.1 FTIR DECONVOLUTION

The ionic transport properties of alginate-NH₄Br SBE system were determined using FTIR deconvolution. Deconvolution was analysed using Gaussian-Lorentz function which adapted to Origin Lab Pro 8.0 software. In this technique, the FTIR peaks due to complexation of alginate and NH₄Br were carefully chosen based on dominant ionic movement. Besides, the sum of the all intensity of the deconvoluted peaks was ensured to fit the original spectrum.

The absorbance peaks were fitted to a straight baseline and the area under the peaks was determined. The free ions percentage (%) were calculated using the equation:-

$$\text{Percentage of free ions} = \frac{A_f}{A_f + A_c} \times 100\% \quad (3.5)$$

Where,

A_f = Area under peak for free ion region

A_c = Area under peak for contact ion region

Moreover, the number of free mobile ions (μ), the number of density (η), and diffusion coefficient of ions (D) can be determined using following equation:-

$$\eta = \frac{M \times N_A}{V_{Total}} \times \text{free ions (\%)} \quad (3.6)$$

$$\mu = \frac{\sigma}{\eta \times e} \quad (3.7)$$

$$D = \left(\frac{k \times T \times \mu}{e} \right) \quad (3.8)$$

Where,

M = number of moles of NH₄Br used

N_A = Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$)

V_{Total} = total volume of SBE system

σ = Conductivity of SBE system

e = electric charge ($1.602 \times 10^{-19} \text{ C}$)

k = the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$)

T = temperature in kelvin

3.3.2 X-RAY DIFFRACTION (XRD)

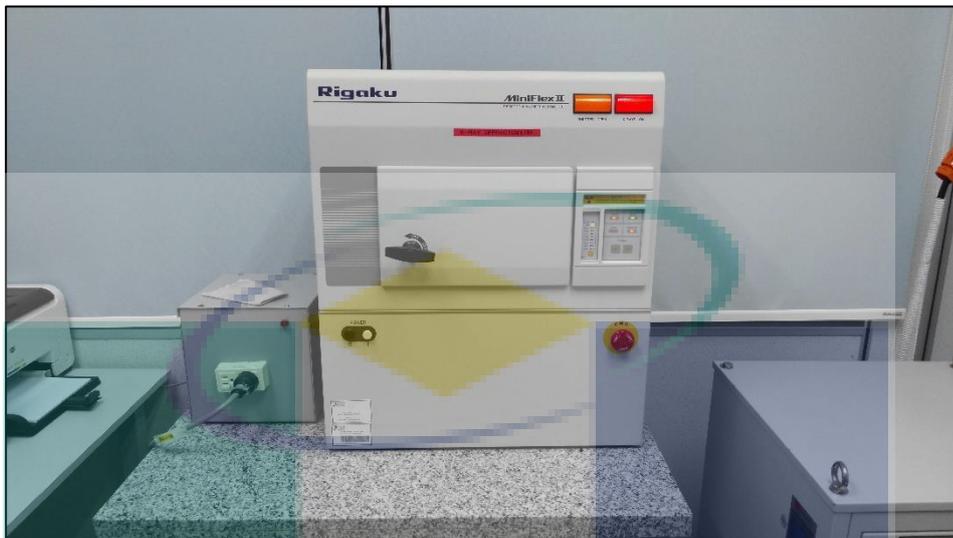


Figure 3.3 MiniFlex II from Rigaku X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is the technique to determine the phase of crystalline and amorphous of polymer-salt complexes. X-ray diffraction is depends on constructive interference of monochromatic x-rays and a sample by using Bragg's law. These x-rays are processed by using a cathode ray tube, then filtered to generate monochromatic radiation, and move towards the sample. MiniFlex II from Rigaku had performed to run out this XRD measurement. After scanning and analysing at 2θ angles between 5° and 80° , it will show the structure of the crystallization sample.

3.3.3 ELECTRICAL IMPEDANCE SPECTROSCOPY (EIS)



Figure 3.4 Electrical Impedance Spectroscopy (EIS) and Digital Thickness Gauge (DML3032)

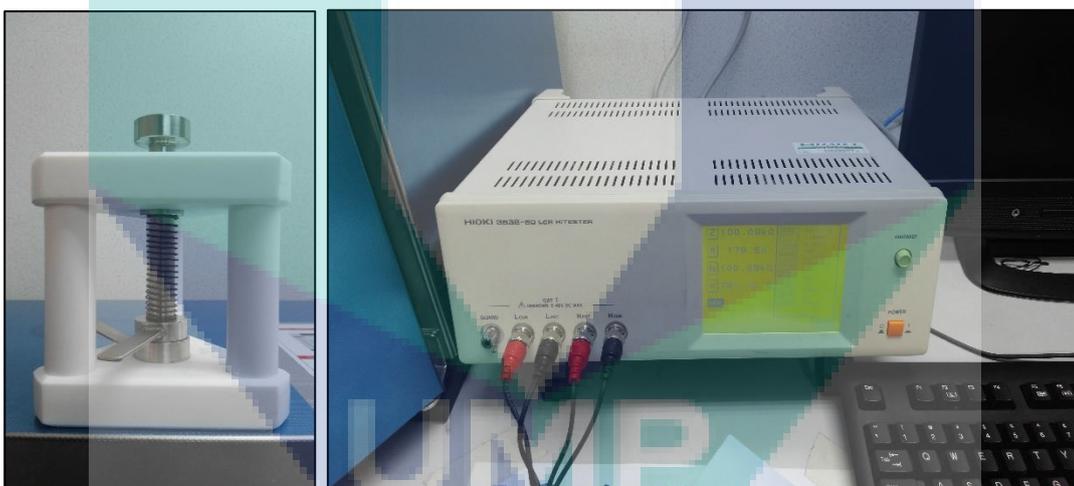


Figure 3.5 Sample holder and HIOKI 3532-50 LCR Hi-Tester

Electrical Impedance Spectroscopy (EIS) is to determine the ionic conductivity and electrical properties of SBE system. The alginate- NH_4Br film were cut into a suitable size and sandwiched between the stainless steel electrodes of surface area with $\pi \text{ cm}^2$ (Samsudin & Isa, 2012a). The ionic conductivity, σ was measured using a HIOKI 3532-50 LCR Hi-Tester from 303 K until 353 K with frequencies ranging from 50 Hz to 1 MHz. The thickness of SBE system, t was measured using a digital thickness gauge

(DML3032) which showed in Figure 3.4. The calculation for ionic conductivity of alginate-NH₄Br SBE system were calculated using equation:-

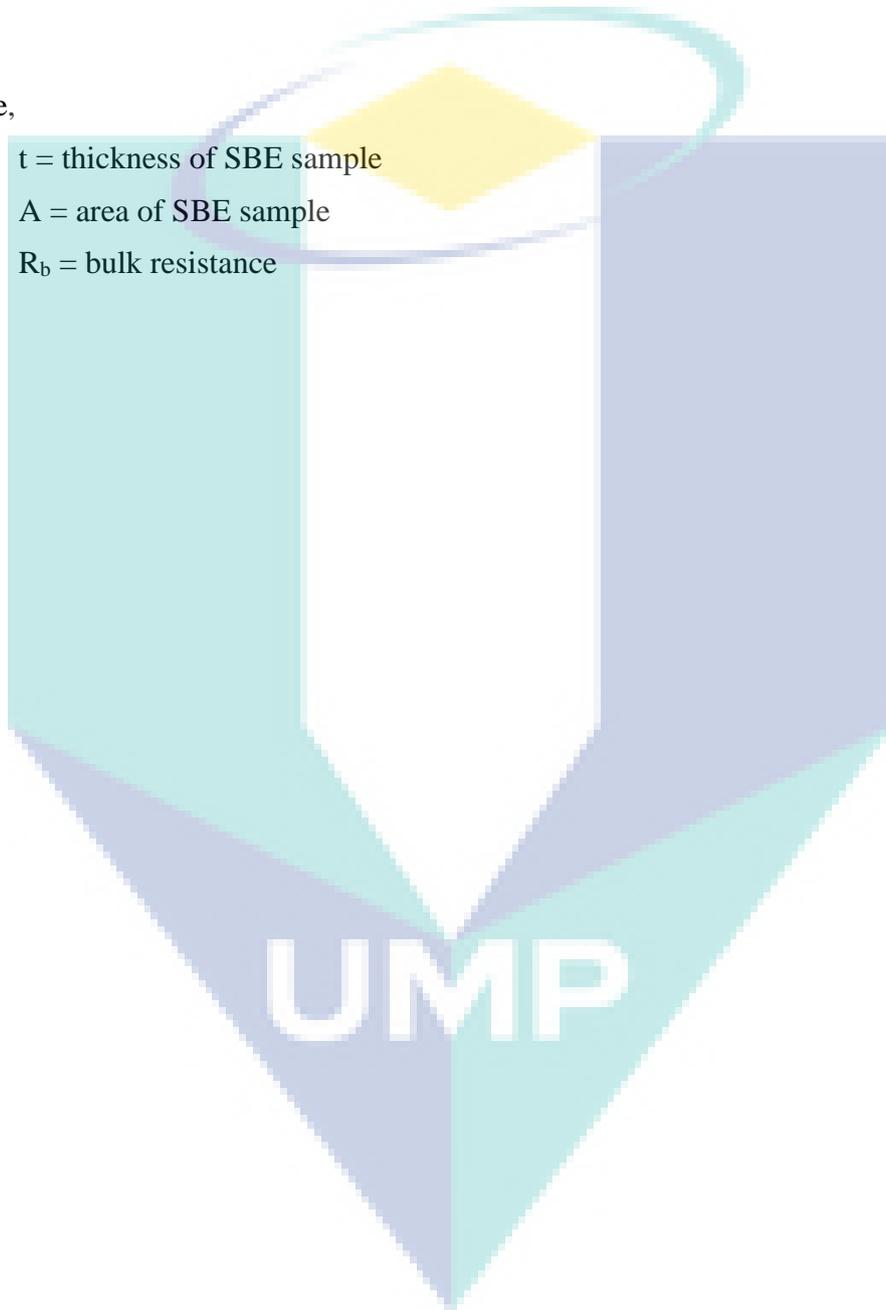
$$\sigma = \frac{t}{R_b A} \quad (3.9)$$

Where,

t = thickness of SBE sample

A = area of SBE sample

R_b = bulk resistance



CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

In this chapter, the SBE system of Alginate-NH₄Br has been analysed characterized by using Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS). This SBE were prepared and produced using casting technique. Table 4.1 below shows the mass for every composition of alginate-NH₄Br system. Figure 4.1 shows the image of alginate-NH₄Br SBE system which is transparent, clear and colourless.

Table 4.1 The mass of each composition SBE system

NH ₄ Br (wt. %)	Alginate (g)	NH ₄ Br (g)
0	2	0.0000
5	2	0.1053
10	2	0.2222
15	2	0.3529
20	2	0.5000
25	2	0.6667
30	2	0.8571

For optical studies, it indicated that solid biopolymer electrolyte of alginate- NH_4Br films were clear and transparent just after the preparation of which shows the dissolution completely of salt in the polymer matrix. According to Abdollahi et al., 2013 and Moon et al., 2011, alginate shows transparent appearance with good mechanical strength in solid thin films state.

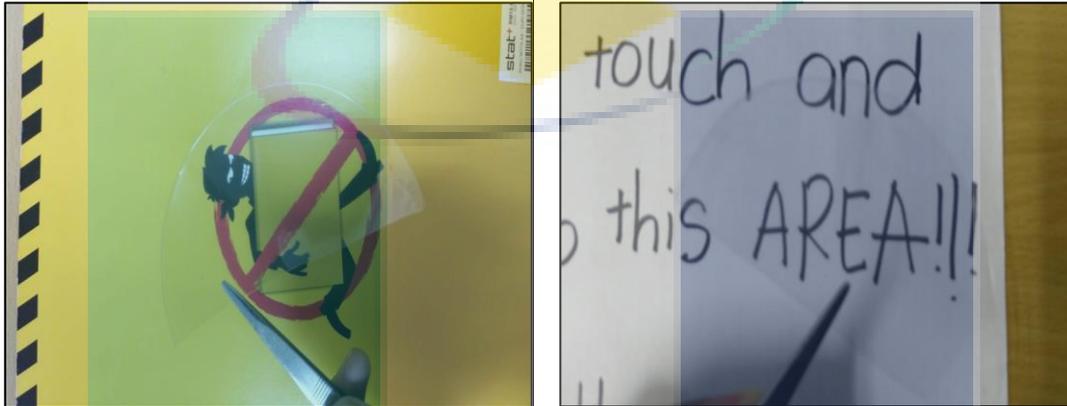


Figure 4.1 The physical appearance of solid biopolymer electrolyte (SBE)

4.2 FOURIER TRANSFORM INFRARED (FTIR)

FTIR spectroscopy had been used to analyse the complex formation and interactions between host polymer alginate and doped NH_4Br in SBE system. The Attenuated Reflection (ATR) which consist of germanium crystal is used because the sample are in solid phase. By using PerkinElmer Spectrum 100, the data are recorded in transmittance mode.

4.2.1 FTIR STUDY OF PURE ALGINATE

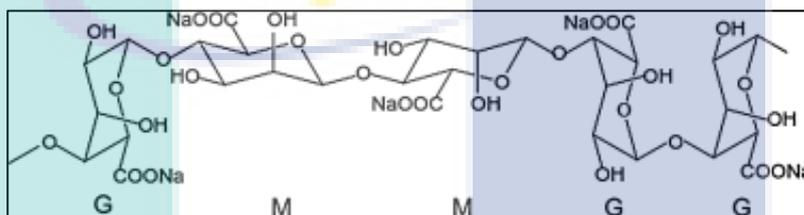


Figure 4.2 Molecule structure for pure alginate (Sellimi et al., 2015)

Pure alginate structure has been analysed using FTIR. Based on figure 4.2, the molecule structure of pure alginate shows the empirical formula of $\text{NaC}_6\text{H}_7\text{O}_7$. Based on previous research, the functional group of pure alginate are analysed in Table 4.1. Alginate is the host polymer of the SBE study. Therefore, the structure of alginate showed the backbone of SBE. Alginic acid, also called alginate, is a highly water-absorption biopolymer consisting of β -D-mannuronic acid and α -L-guluronic acid monomers (Kosik, Luchowska, & Świąszkowski, 2016).

The FTIR spectrum of pure alginate was observed in Figure 4.3. It shows two absorption peaks in the infrared spectrum which are carboxylate group of antisymmetric stretch at 1622 cm^{-1} and symmetric stretch at 1440 cm^{-1} . Therefore, the symmetrical structure show non-polar behaviour and the asymmetrical structure stated polar behaviour. At peak 3420 cm^{-1} , pure alginate displayed the strong peak of O-H functional group. The FTIR spectra of pure Ammonium bromide (NH_4Br) is displayed in Figure 4.4. There is strong absorption of N-H amine group in the NH_4Br at peaks 3105 cm^{-1} and 3200 cm^{-1} (Ramlli, Kamarudin, & Isa, 2015). Besides, there is one absorption peak intensity of ammonium ion (NH_4^+) at peak 1420 cm^{-1} (N. H. B. Ahmad & Isa, 2015).

Table 4.2 Basic alginate bands based on previous research

Functional group	Peak (cm ⁻¹)	Research
Stretching of hydroxate (OH-) group	3091-3728	(Helmiyati & Apprilliza, 2017 and Xiao et al., 2014)
Stretching of carbon-hydrogen (C-H) bond	2922-3046	(Sellimi et al., 2015 and Fawzy et al., 2017)
Asymmetric stretch of carboxylate (COO-) group	1625	(Pitchaya, et al., 2017; Mariana et al., 2013; and Gao et al., 2017)
Symmetric stretch of carboxylate (COO-) group	1440	(Treenate, et al., 2017; Mariana et al., 2013; and Gao et al., 2017)
Stretching vibration of glycoside bond (C-O-C) of polysaccharide	1043	(Kuzmanović et al., 2017 and Lopes et al., 2017)

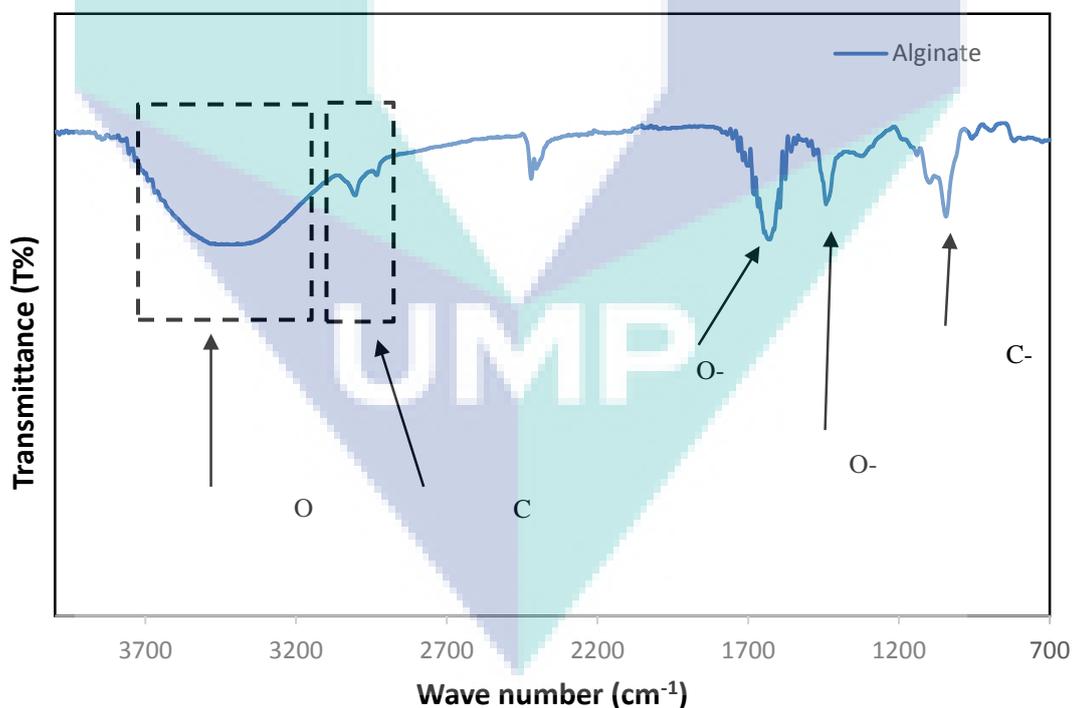


Figure 4.3 FTIR spectra for pure alginate

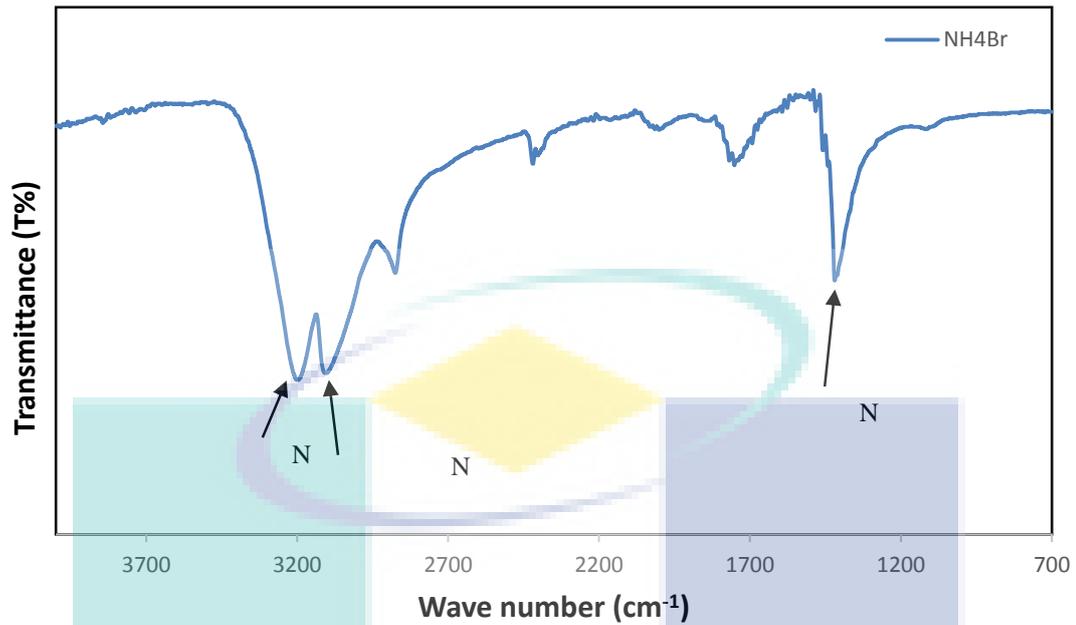


Figure 4.4 FTIR spectra for pure NH_4Br

4.2.2 FTIR STUDY OF SOLID BIOPOLYMER ELECTROLYTE

The molecule interaction of alginate- NH_4Br SBE system were studied using FTIR spectroscopy. It can be predicted that the biopolymer have molecule interaction with the ionic salt which result in significant changes either in terms of the change of the band shape or shift in the wavenumber. The complexation of SBE system affected by the cation of the salt which interact with the polar groups in the host biopolymer matrix (Sikkanthar et al., 2015). Figure 4.5 shows the study of FTIR spectra of alginate- NH_4Br SBE system.

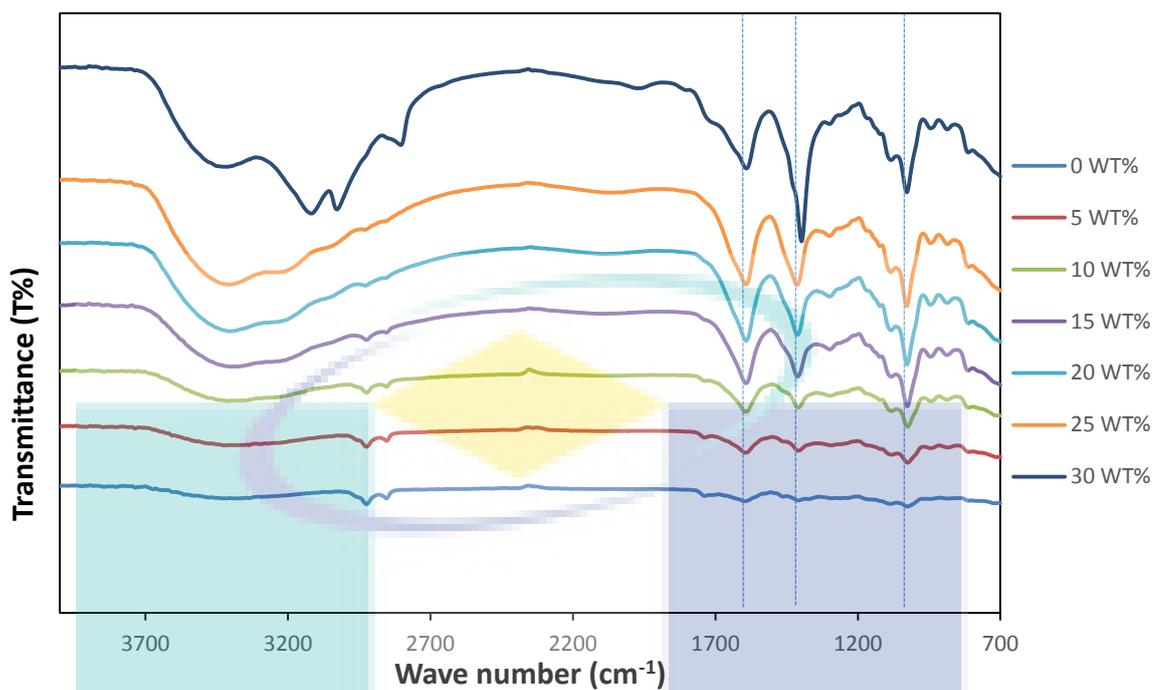


Figure 4.5 FTIR spectra for alginate-NH₄Br SBE system

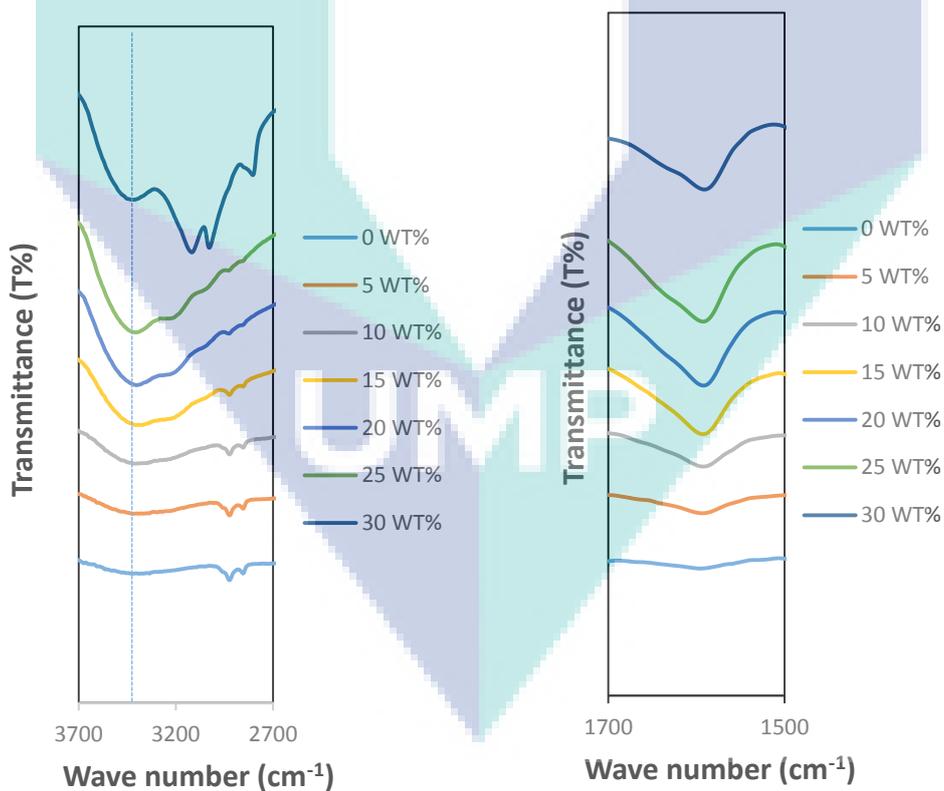


Figure 4.6 FTIR spectra for alginate-NH₄Br SBE system between range (a) 2700 cm⁻¹ to 3700 cm⁻¹ and (b) 1500 to 1700 cm⁻¹

Based on figure 4.5, there are interaction complexions occur in SBE system between range 900 cm^{-1} to 1100 cm^{-1} , 1300 cm^{-1} to 1500 cm^{-1} , 1500 cm^{-1} to 1700 cm^{-1} and 2700 cm^{-1} to 3700 cm^{-1} . In the presence work, the bands at 1595 cm^{-1} and 1409 cm^{-1} show stretching vibrations asymmetric and symmetric of carboxylate (COO^-) ions, respectively, of the polymeric backbone of alginate (Treenate & Monvisade, 2017). Besides, the peak 1026 cm^{-1} corresponds to the C–O–C stretching vibration in the spectrum of 5 wt. % of NH_4Br concentration in SBE system. The wavenumber peaks remain unchanged in addition of NH_4Br until 30 wt. % due to glycoside band of polysaccharide alginate molecule (Lopes, Bueno, AGUIAR JÚNIOR, & Finkler, 2017).

Figure 4.6 (a) shows the FTIR spectra of SBE system in range between 2700 cm^{-1} to 3700 cm^{-1} . The peak at 3391 cm^{-1} shows the functional group O–H (Xiao et al., 2014). The increasing of salt concentration shift to high wavenumber of spectra at peak 3415 cm^{-1} due to poor water barrier of alginate molecule (Wang, Shankar, & Rhim, 2017). Based on figure 4.6 (b), the peak intensity at 1595 cm^{-1} which correspond to carboxylate (COO^-) ions decrease with addition of NH_4Br until 20 wt. % due to movement of salt molecules to the lone pairs of carboxylate group at atom carbon (C) and exert optimum interaction (Samsudin & Isa, 2012). Upon addition of more salt, (more than 20 wt. %) the peak intensity become lower due to the increment of NH_4Br concentration. This can be explained by the phenomenon of decreasing in number density of ions that resulted in fewer available ionic species within the SBE system (Rasali & Samsudin, 2017). This phenomenon also referred as salt aggregation which can affect the conductivity of the polymer electrolyte.

4.2.3 FTIR DECONVOLUTION

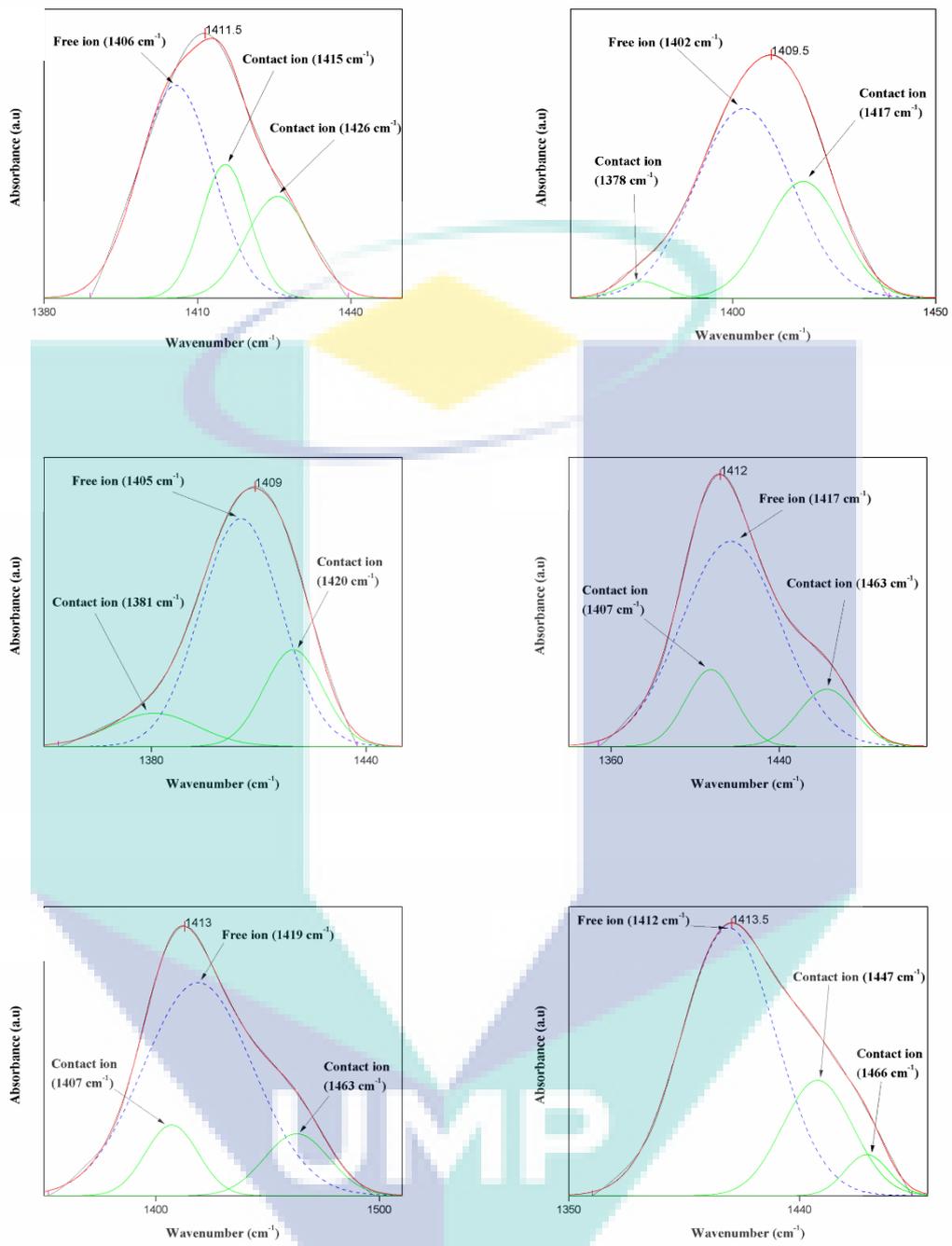
FTIR deconvolution for various sample of alginate- NH_4Br SBE system was shown in Figure 4.7. The area for deconvoluted peak was selected between 1300 cm^{-1} and 1500 cm^{-1} because the regions showed the free ions and the contact ions were within the region. Besides, it displayed the obvious changes of FTIR peak in the FTIR analysis. The peak observed at 1300 cm^{-1} to 1500 cm^{-1} correspond to symmetric carboxylate (COO^-) stretch (Treenate & Monvisade, 2017). Based on Figure 4.7 (e), the COO^- anions which represent free ions can be observed at 1419 cm^{-1} while contact ions appeared at 1407

cm^{-1} and 1463 cm^{-1} which represent to contact ions and also aggregate ions in SBE (Ramlli & Isa, 2016). By using equation (3.5), the percentage of free ions which correspond to movement of H^+ in the area of deconvoluted peak can be calculated. The result for the free ions and the contact ions was tabulated in Table 4.3.

From the table, it shows that the addition of NH_4Br until 20 wt. % increase the percentage of free ions. This is because increasing of ion dissociation between hydrogen ion (H^+) substructures of ammonium ion (NH_4^+), thus resulting more ion conduction occur which lead to the increment of ionic conductivity in SBE system (Rasali & Samsudin, 2017). Beyond the 20 wt. % of NH_4Br , the percentage of free ions started to decrease linearly due to the large amount of ion pairs and ion aggregates which accumulate in SBE system (Othman, Isa, Osman, & Yahya, 2017). Besides, the decrement of ionic conductivity is due to the re-associated of ions which supported the ionic conductivity reductions of alginate- NH_4Br SBE system (Chai & Isa, 2016).

Table 4.3 Percentage area of free ions and contact ions of SBE system

NH_4Br (wt. %)	Free ions (%)	Contact ions (%)
0	55.06	44.94
5	65.79	34.21
10	68.15	31.85
15	74.07	25.93
20	75.02	24.98
25	71.75	28.25
30	66.94	33.06



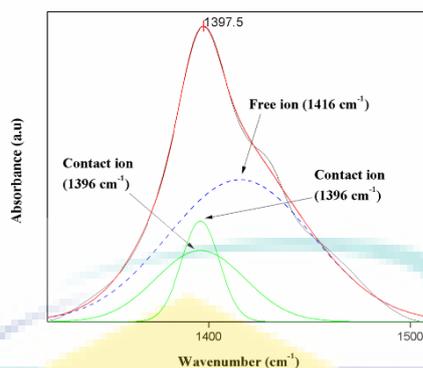


Figure 4.7 FTIR deconvolution for (a) 0 wt. % (b) 5 wt. % (c) 10 wt. % (d) 15 wt. % (e) 20 wt. % (f) 25 wt. % (g) 30 wt. % of alginate-NH₄Br SBE system

Based on the parameter on the Table 4.3, the number of ions mobility (μ), the number of density (η) and the diffusion coefficient number (D) were calculated using equation (3.6), (3.7), (3.8) and presented in Figure 4.8 and Figure 4.9.

Table 4.4 shows the conductivity of the sample were governed by the number of ions mobility (μ), the number of density (η) and the diffusion coefficient number (D). Based on Figure 4.8, the number of density (η) increase linearly to the concentration of NH₄Br. The higher value of η is $2.73 \times 10^{23} \text{ cm}^{-3}$ where contrast to the ionic conductivity due to the salt content of 30 wt. % NH₄Br higher than the optimum salt content of NH₄Br at 20 wt. %. The increment of η inferred that the salt content in the polymer matrix was too much, contributed to the decreasing of ion mobility (μ) and diffusion coefficient (D) which affected by formation of ion cluster and also overcrowding of mobile ions (H⁺) (Sohaimy & Isa, 2015).

Based on Figure 4.9, the number of ions mobility (μ) and the diffusion coefficient number (D) shows the similar trend where it rise sharply at 20 wt. % of NH₄Br and dropped rapidly at 25 wt. % of NH₄Br. The maximum ionic conductivity of alginate doped with NH₄Br at 20 wt. % exhibits maximum μ and D values of $1.00 \times 10^{-11} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.61 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ respectively. The diffusion ions of polymer matrix will contribute to the increment of ionic conductivity where the movement of the ions to the SBE system easily to interact (Salleh, Aziz, Aspanut, & Kadir, 2016). Besides, the decrement of ionic conductivity of alginate-NH₄Br SBE system was due to difficulty of

ionic movement in the polymer matrix at higher composition of ionic dopant (Rasali & Samsudin, 2017).

Table 4.4 Ionic transport parameters of alginate-NH₄Br SBE system

NH ₄ Br (wt. %)	Conductivity, σ (S cm ⁻¹)	Mobile ion, η (cm ⁻³)	Ionic mobility, μ (cm ² V ⁻¹ s ⁻¹)	Diffusion coefficient, D (cm ² s ⁻¹)
5	1.80×10^{-6}	4.31×10^{22}	2.61×10^{-10}	6.81×10^{-12}
10	2.17×10^{-6}	8.99×10^{22}	1.50×10^{-10}	3.93×10^{-12}
15	1.24×10^{-5}	1.48×10^{23}	5.26×10^{-10}	1.37×10^{-11}
20	4.41×10^{-5}	2.01×10^{23}	1.37×10^{-9}	3.58×10^{-11}
25	6.03×10^{-7}	2.42×10^{23}	1.56×10^{-11}	4.06×10^{-13}
30	4.38×10^{-7}	2.73×10^{23}	1.00×10^{-11}	2.61×10^{-13}

UMP

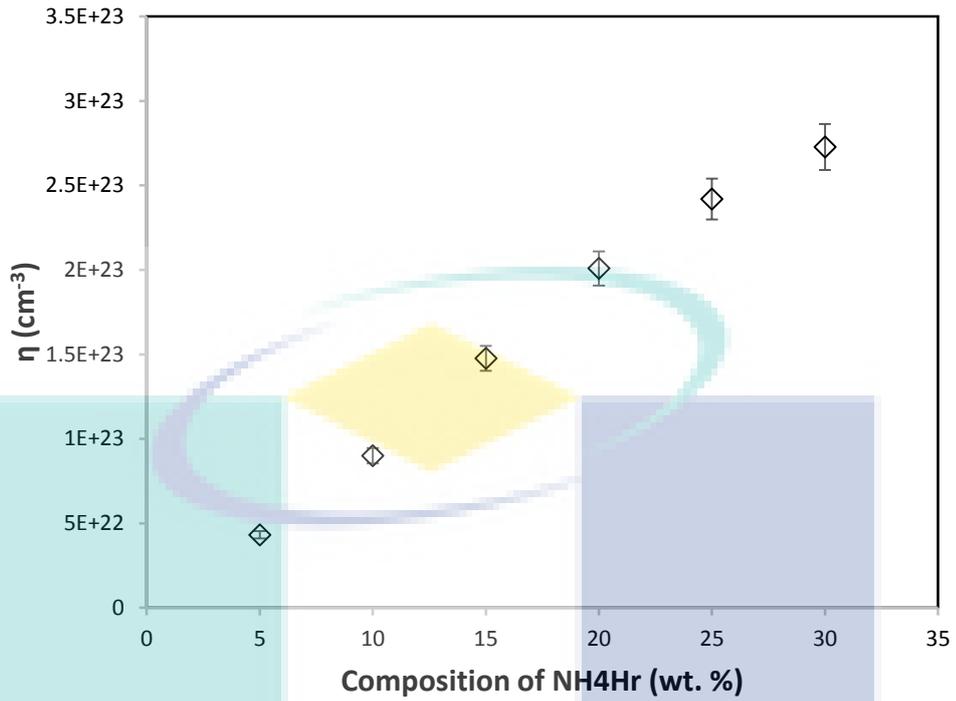


Figure 4.8 The density of mobile ions for alginate-NH₄Br SBE system

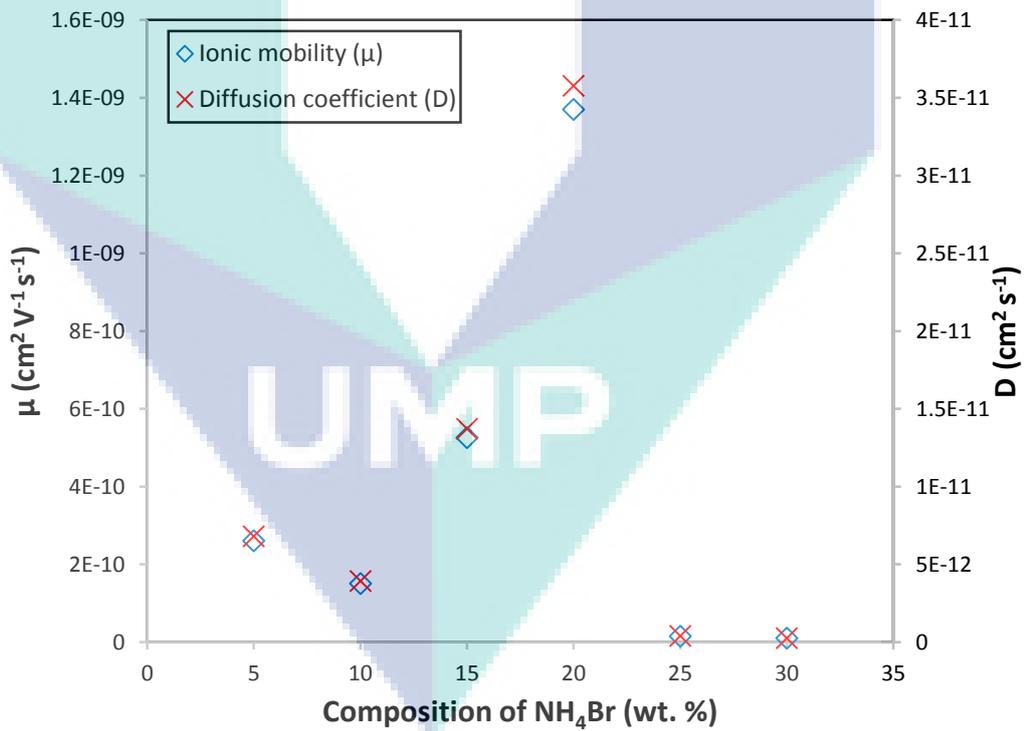


Figure 4.9 The ionic mobility and diffusion coefficient for alginate-NH₄Br SBE system

4.3 X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) function as structural characterization of membrane in SBE system. This non-destructive testing (NDT) can easily identify the variation of crystal structure and its orientation. In this study, two major phase that can be seen are amorphous and crystalline.

4.3.1 XRD OF PURE ALGINATE AND AMMONIUM BROMIDE (NH₄Br) POWDERS

Pure Alginate and NH₄Br has been analysed using XRD to determine the phase of membrane structure. Figure 4.1 shows typical x-ray diffractogram for pure alginate and NH₄Br. It can be seen that pure alginate has two broad peaks occur at central position with $2\theta = 13.38^\circ$ and 24.14° . This indicate that pure alginate has two different regions of amorphous (Gao, Pollet, & Avérous, 2017). Besides, there are ten crystalline peaks are observed at $2\theta = 22.36^\circ, 31.42^\circ, 38.62^\circ, 44.90^\circ, 50.46^\circ, 55.68^\circ, 65.24^\circ, 69.56^\circ, 73.90^\circ$ and 78.16° in the XRD pattern of pure NH₄Br as shown in Figure 4.1.

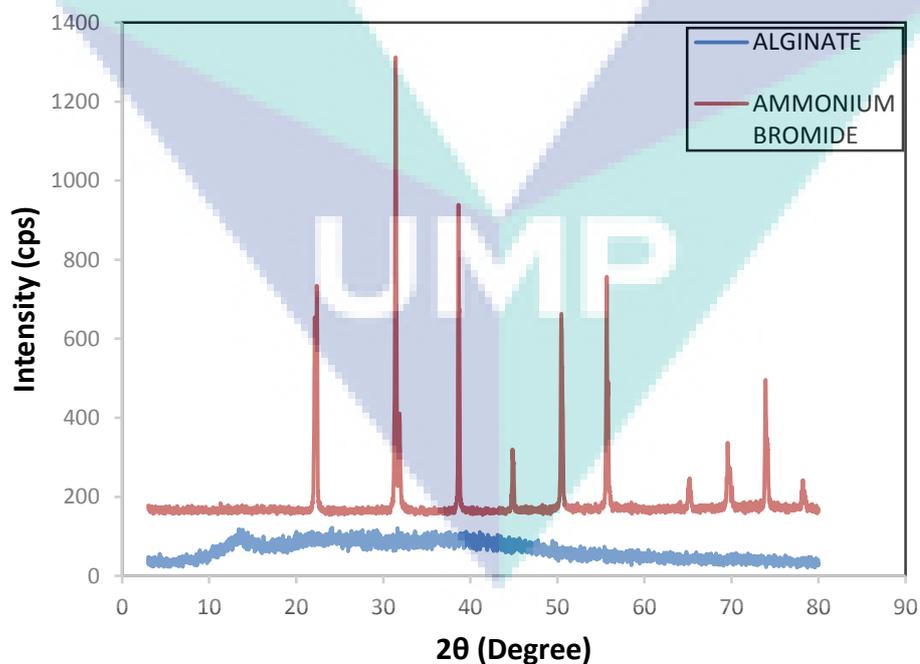


Figure 4.10 XRD pattern for pure alginate and NH₄Br

4.3.2 XRD OF SOLID BIOPOLYMER ELECTROLYTE

The effect of NH_4Br inclusion in the biopolymer alginate was investigated by XRD analysis. The X-ray diffractograms of alginate doped with various composition NH_4Br are depicted in Figure 4.2. The XRD pattern of SBE system show an increase in amorphous hump with the addition of 0–20 wt. % NH_4Br . The amorphous hump or broad peak is a typical characteristic of amorphous material (Sit, Samsudin, & Isa, 2012). According to Yusof, Illias, and Kadir (2014), polymer matrix will become complete dissociation of salt when there are no peaks found. Therefore, increases in ionic conductivity of the alginate- NH_4Br SBE system is because of the changes of amorphousness in the samples (Samsudin & Isa, 2012b). It can be predicted that the SBE of 20 wt. % NH_4Br shows the good conductivity at room temperature. The sample become highly amorphous until addition of NH_4Br over 20 wt. % in electrolyte. At 30 wt. % of NH_4Br , the structure become fully crystalline with peaks at $2\theta = 21.49^\circ, 30.74^\circ, 38.01^\circ, 44.32^\circ, 49.88^\circ, 55.05^\circ, 64.57^\circ, 69.09^\circ$ and 73.55° . Increasing of salt will enhance the crystalline structure of SBE system. Therefore, it will shows the decreasing number of mobile ions and the ionic conductivity will be reduce SBE system. According to Shuhaimi, the decrement of amorphous hump of SBE system will affect directly to the ionic conductivity. At 25 wt. %, the SBE shows the semi-crystalline structure which contribute to the decrement of ionic conductivity of the sample. Therefore, decreasing of conductivity shows the polymer host was incapable to accommodate the salt which bring to the recombination of the ions (Kadir, Majid, & Arof, 2010).

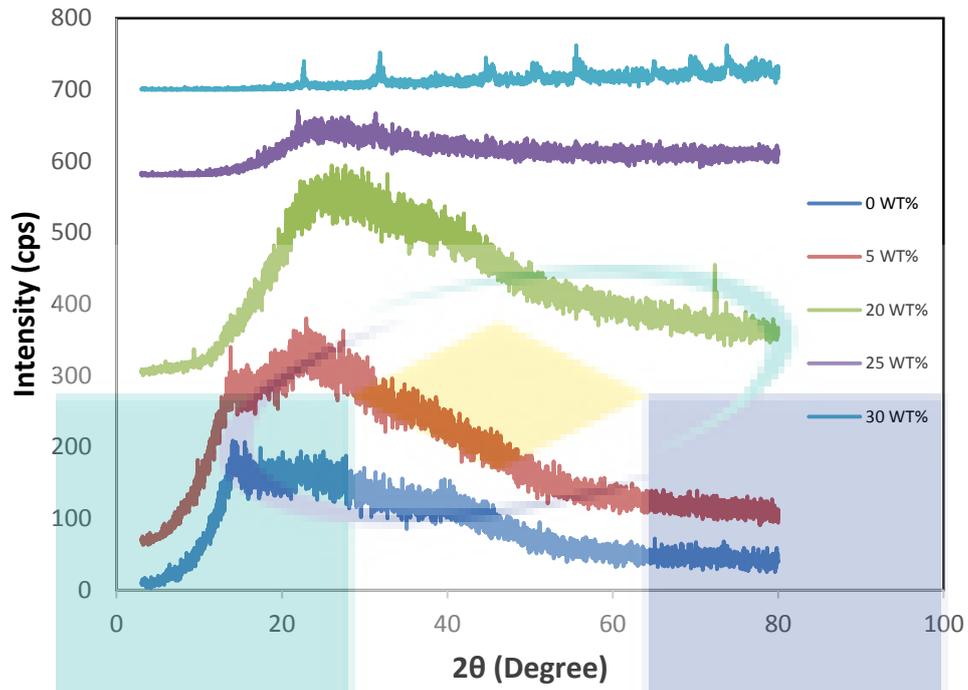


Figure 4.11 XRD pattern of alginate-NH₄Br SBE system

UMP

4.4 ELECTRICAL IMPEDANCE SPECTROSCOPY (EIS)

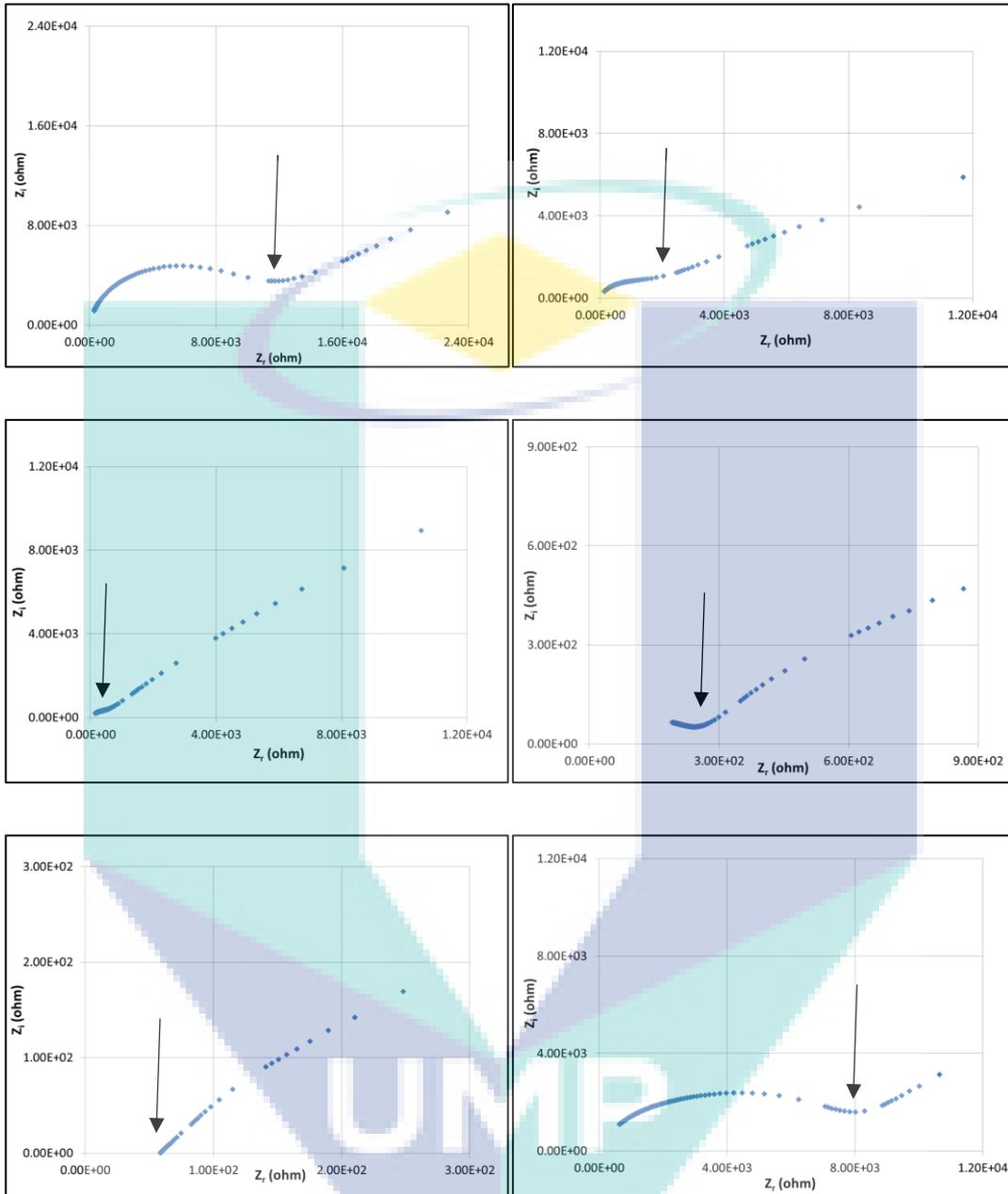
In this research, electrical impedance spectroscopy (EIS) are used to study electrical characterization of alginate-NH₄Br SBE system. It will be divided into three study which is cole-cole plot, ionic conductivity, temperature dependence study and activation energy, E_a .

4.4.1 COLE-COLE PLOT STUDY

Cole-cole plot or Nyquist plot is used to identify the bulk resistance, R_b from impedance measurement (Salleh et al., 2016). From equation (3.5), the ionic conductivity, σ of SBE system can be calculated. Figure 4.3 shows the cole-cole plot for alginate-NH₄Br SBE system at ambient temperature. Since the electrode had been used are stainless steel, the high frequency semicircle can be related to the ionic conduction process in the bulk of the SBE and the low frequency spike has been attributed to the effect of blocking electrodes (Zainuddin & Samsudin, 2017). Table 4.2 shows the bulk resistance, R_b value for each composition of alginate-NH₄Br SBE system. It shows that the R_b value for 20 wt% is the lowest among SBE system at ambient temperature. Lower R_b will give higher ionic conductivity for SBE system because of the increment of charge carrier mobility (Hamsan, Shukur, & Kadir, 2017).

Table 4.5 Bulk resistance, R_b of alginate-NH₄Br SBE system

NH ₄ Br (wt. %)	Bulk resistance, R_b (ohm)
0	12200.0
5	2030.0
10	881.0
15	266.0
20	59.9
25	8020.0
30	8000.0



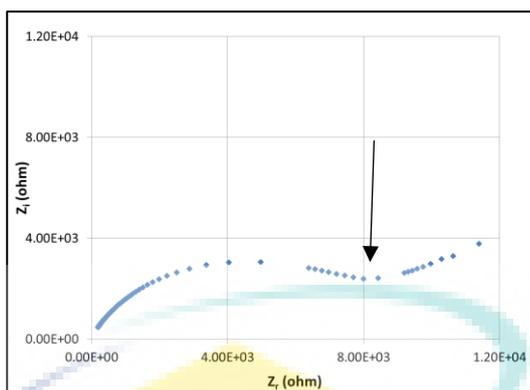


Figure 4.12 Cole-cole plot for (a) 0 wt. % (b) 5 wt. % (c) 10.wt% (d) 15 wt. % (e) 20 wt. % (f) 25 wt. % (g) 30 wt. % of alginate-NH₄Br SBE system

4.4.2 IONIC CONDUCTIVITY AT ROOM TEMPERATURE

Ionic conductivity, σ of SBE system can be measured from equation (3.5) which depends on the thickness of sample, t , area of the electrode, A and also the bulk resistance, R_b . For conductivity study, the SBE system will be analysed at room temperature which is 303 K. Figure 4.4 shows the ionic conductivity values of alginate samples containing with different amounts of NH₄Br at room temperature. The highest ionic conductivity at ambient temperature was found at $4.41 \times 10^{-5} \text{ S cm}^{-1}$ for sample containing with 20 wt. % of NH₄Br. The increment of ionic conductivity will increase of NH₄Br because of the complexation between alginate and NH₄Br gives to the high dispersion of H⁺, therefore will effect towards the increment of ionic conductivity (Aziz, Idris, & Isa, 2010). The ionic conductivity start to decrease when added NH₄Br above than 20 wt. %. According to Othman et al. (2017), the decrement of ionic conductivity after 20 wt. % because of neutral aggregation of the ions re-associated and also leading to formation of ion cluster.

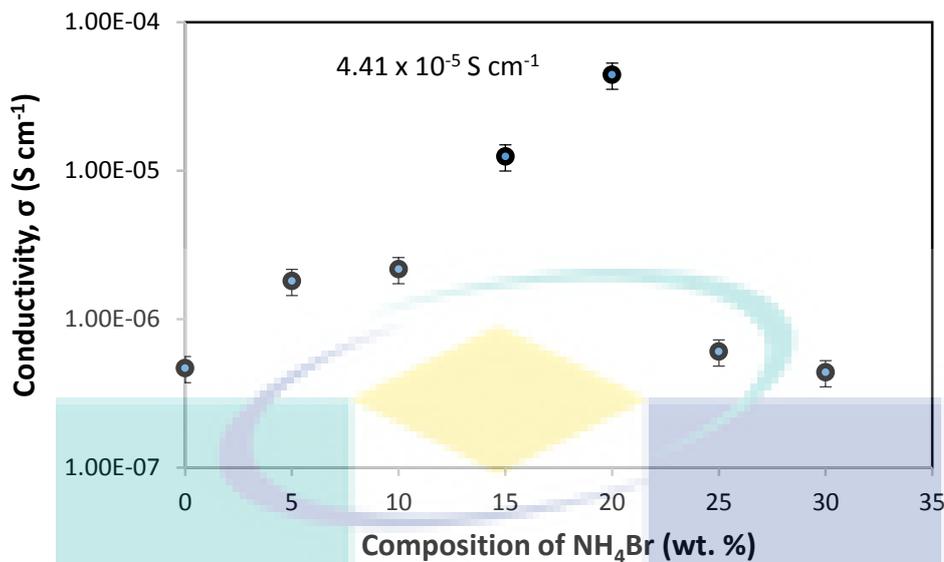


Figure 4.13 Ionic conductivity of alginate-NH₄Br SBE system at room temperature (303 K)

4.4.3 IONIC CONDUCTIVITY AT ELEVATED TEMPERATURE

The effect of temperature on the properties of the ionic conductivity in alginate-NH₄Br SBE system can be analysed using temperature dependence study of ionic conductivity. Figure 4.5 shows the log conductivity versus $1000/T$ for different composition at the temperature range from 303 K to 353 K. It shows that 20 wt. % of NH₄Br have higher conductivity among the other composition. The temperature dependent study of the SBE system obeys the Arrhenius characteristics, where the regression value, R^2 , is in the range of 0.95 to 0.99. (Salleh et al., 2016).

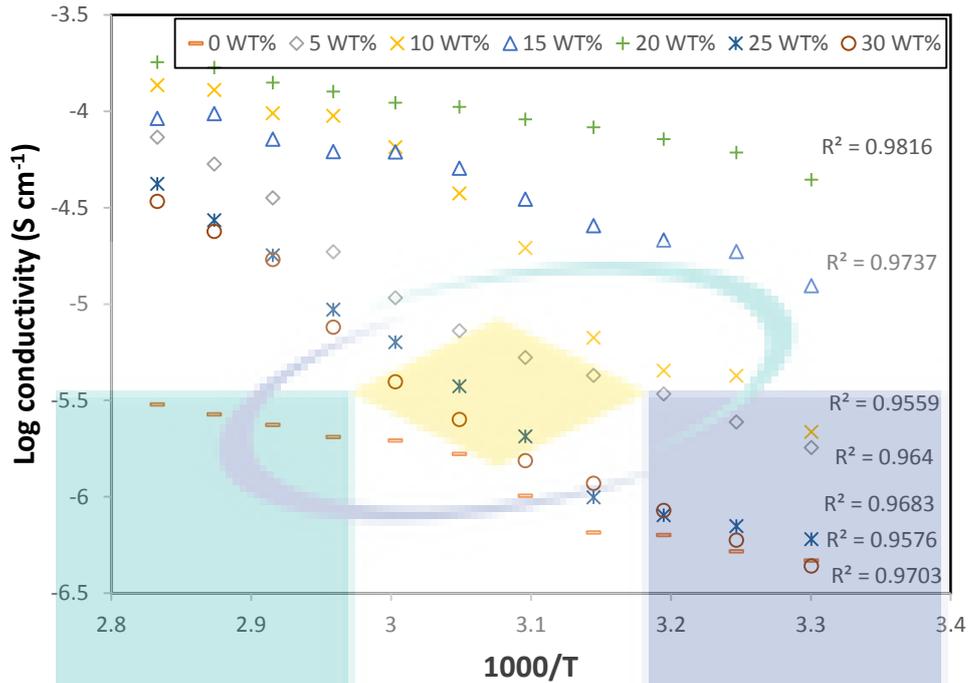


Figure 4.14 Ionic conductivity of alginate-NH₄Br SBE system at room temperature (303 K)

4.4.4 ACTIVATION ENERGY

The activation energy, E_a is the energy needed an ion to migrate from one site to another and can be due to the defect formation (Noor & Isa, 2015). The ions will be at same location if the energy good enough to overcome the binding energy, therefore the ions will be dislocated from its site (Zainuddin & Samsudin, 2017). From the relationship between conductivity and temperature, the activation energy, E_a can be measured using the following equation:-

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (4.1)$$

where E_a is the activation energy, σ is the conductivity of SBE system, σ_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the temperature in Kelvin. Figure 4.6 shows the value of E_a is inversely proportional to the conductivity shown in Figure 4.4. It can be observed that the increasing of ionic conductivity of SBE system will

decrease the E_a value and this showed that ions which correspond to H^+ only need lower energy to migrate to polymer backbone thus will enhanced the ionic mobility.

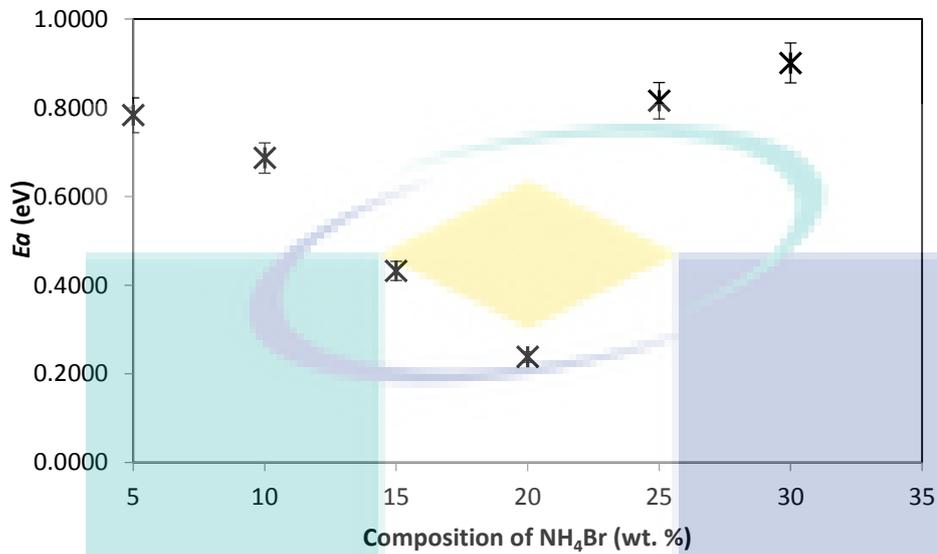


Figure 4.15 Activation energy for different composition of SBE system at room temperature (303 K)

UMP

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this research, solid biopolymer electrolyte (SBE) of alginate-NH₄Br was completely prepared by using solution casting technique. The concentration of NH₄Br that has been used in SBE system were 0 wt. %, 5 wt. %, 10 wt. %, 15 wt. %, 20 wt. %, 25 wt. % and 30 wt. % with the physical appearance of were no clear and transparent.

In structural study, The FTIR studies showed the presence of complexation between alginate biopolymer and dopant salt of NH₄Br. It been observed that asymmetrical of COO⁻ band start to decrease 1595 cm⁻¹ with addition of NH₄Br until 20 wt. %. This because the movement of salt molecules to the lone pairs of carboxylate group at atom carbon (C). At 30 wt. % of NH₄Br, the peak intensity become lower due to the increment of NH₄Br concentration. The ionic conductivity of SBE is observed to be governed with the ionic transport properties which are the number of ions mobility (μ), the number of density (η) and the diffusion coefficient number (D). Besides, the FTIR deconvolution showed that 20 wt. % of NH₄Br achieved high percentage of free ions among other composition. From XRD studies, two broad peaks of pure alginate occur at central position with $2\theta = 13.38^\circ$ and 24.14° . The addition concentration of NH₄Br displayed the increment of amorphous hump with the addition of 0–20 wt. % NH₄Br in SBE system. However, the fully crystalline structure can be seen at 30 wt. % due to incapable of biopolymer host to accommodate the salt which bring to the recombination of the ions.

In electrical study, the ionic conductivity of alginate-NH₄Br system start to increase rapidly from $4.67 \times 10^{-7} \text{ S cm}^{-1}$ of 0 wt. % NH₄Br until $4.41 \times 10^{-5} \text{ S cm}^{-1}$ of 20 wt. % NH₄Br. The addition of NH₄Br over 20 wt. % showed the decrement of ionic

conductivity due to the recombination of neutral aggregation ions start to form. The temperature dependence study of the SBE system obeys the Arrhenius characteristics, $R^2 \approx 1$, where the ionic conductivity of the samples generally affected by the increment of temperature. The activation energy of SBE system showed capsized of ionic conductivity.

In conclusion, the objective of the research were fully achieved. The solid biopolymer electrolyte system of alginate-NH₄Br were successfully prepared and characterized by using Fourier Transform Spectroscopy (FTIR), X-Ray Diffractometer (XRD) and Electrical Impedance Spectroscopy (EIS).

5.2 RECOMMENDATIONS

The solid biopolymer electrolyte system of alginate doped with NH₄Br can be analysed in differ characterization. The structural properties of SBE can be analysed using other testing for example Field Emmision Scanning Elcetron (FESEM), Tranference Measurement Number (TNM), Thermal Gravimetric Analysis (TGA), Energy Disperse Spectroscopy (EDS), Differential Scanning Calorimetry (DSC) and many more. Besides, SBE become the worldwide study because of its biodegradable properties.

The preparation of the sample is one of the important procedure need to be studied. This is because alginate biopolymer is a sensitive material which easily change the behaviour depends on surrounding. The precaution need to be taken seriously during preparation of the sample.

In electrical study, ionic conductivity of SBE system can be improve by adding blend and also plasticized. Besides, the various type of using ammonium halide as dopant also can be recommended to increase the conductivity.

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