PREPARATION AND CHARACTERIZATION ON CARRAGEENAN DERIVATIVES AS SOLID BIOPOLYMER ELECTROLYTE

RAFIQ IZZUDDIN BIN RADZALI

BACHELOR OF APPLIED SCIENCE (HONS)

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PREPARATION AND CHARACTERIZATION ON
CARRAGEENAN DERIVATIVES AS SOLID BIOPOLYMER
ELECTROLYTE

RAFIQ IZZUDDIN BIN RADZALI

Thesis submitted in fulfillment of the requirements
for the award of the degree of
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JANUARY 2017

SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Honor) Material Technology.

Signature

Name of Supervisor   :   DR. AHMAD SALIHIN BIN SAMSUDIN

Position   :   SENIOR LECTURER

Date   :   JANUARY 2017

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Name   :   RAFIQ IZZUDDIN BIN RADZALI

ID Number   :   SC13052

Date   :   JANUARY 2017

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Bio-polymer are the renewable resources which easily can degraded by natural processes. Since this material was abandoned in earth, this present research was conducted in order to produce solid form biopolymer electrolyte. The solid biopolymer electrolyte which produced by using kappa carrageenan doped with ammonium nitrate was successfully prepared. The objective of this research were to prepare the solid biopolymer electrolyte based on kappa carrageenan doped NH_4NO_3 complexes, to identify the transport properties and ionic conductivity of kappa carrageenan doped with NH_4NO_3. In this research content 3 phase which is preparation phase, characterization phase and lastly analysis phase. The prepared sample were characterized by using Electrical Impedance Spectroscopy (EIS), Fourier Transform Infrared Spectroscopy (FTIR) and Transference Measurement Number (TNM). From EIS result, the highest ionic conductivity was found to achieve for sample with 40 wt. % at 9.64×10^{-4} Scm^{-1}. The analysis of EIS including the dielectric study was carried out in order to investigate the behavior such as dielectric loss, and dielectric constant. Moreover, the result FTIR is show the shifted peak of functional group which indicate the complexation has occurred between kappa carrageenan and ammonium nitrate. The FTIR deconvolution study also need to study on FTIR analysis. The TNM shown that the ionic conducting species of solid biopolymer electrolytes due to the cation.

ABSTRAK

Bio-polimer adalah sumber-sumber yang boleh diperbaharui yang boleh diuraikan oleh proses semula jadi. Oleh kerana bahan ini telah ditinggalkan banyak di bumi, penyelidikan yang dijalankan ini dilaksanakan bagi menjadikan bentuk pepejal seperti biopolimer elektrolit. Elektrolit biopolimer pepejal yang dihasilkan dengan menggunakan kappa karrageenan didopkan dengan ammonium nitrat telah berjaya disediakan. Objektif kajian ini adalah untuk menyediakan biopolimer elektrolit pepejal berdasarkan kappa karrageenan didopkan dengan kompleks NH_4NO_3, untuk mengenal pasti sifat-sifat pengangkutan dan kekonduksian ionik kappa carrageenan didopkan NH_4NO_3. Dalam kajian ini mengandungi 3 fasa iaitu fasa persediaan, fasa pencirian dan fasa analisis akhir sekali. sampel yang disediakan dicirikan dengan menggunakan Impedans Elektrik Spektroskopi (EIS), Spektroskopi Inframerah Transformasi Fourier (FTIR) dan Pengukuran Pemindahan Nombor (TNM). Dari hasil EIS, kekonduksian ionik yang paling tinggi didapati mencapai untuk sampel dengan 40 wt. % pada $9.64 \times 10\text{-}4$ Scm^{-1}. Analisis EIS termasuk kajian dielektrik telah dijalankan untuk menyiasat tingkah laku seperti kehilangan dielektrik, dan pemalar dielektrik. Selain itu, hasilnya FTIR adalah menunjukkan puncak beralih daripada kumpulan berfungsi yang menunjukkan complexation telah berlaku antara kappa karrageenan dan ammonium nitrat. The FTIR kajian deconvolusi juga perlu mengkaji didalam analisis FTIR. TNM menunjukkan ionik yang menjalankan spesies elektrolit biopolimer pepejal kerana kation.

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LIST OF SYMBOLS

%	-	percent
λ	-	wavelength
g	-	grams
t	-	time
μ	-	ionic mobility of mobile ions
ε	-	dielectric
ε_r	-	dielectric constant
ε_i	-	dielectric loss
σ	-	electrical conductivity
η	-	number of mobile ion
A	-	area
Cm	-	centimetre
D	-	diffusion coefficient
D_-	-	diffusion coefficient of anion
D_+	-	diffusion coefficient of cation
E_a	-	activation energy
f	-	frequency
Hz	-	hertz
I	-	current
k	-	boltzmann constant
ml	-	millilitre
K	-	kelvin
tan δ	-	tangent Loss
R_b	-	bulk resistance
S	-	siemens
s	-	second
M_r	-	real modulus
M_i	-	imaginary modulus

LIST OF ABBREVIATIONS

XRD   -   X-Ray Diffraction

FESEM   -   Field Emission Scanning Electron Microscope

SEM   -   Scanning Electron Microscopy

EDS   -   Energy Disperse Spectroscopy

AFM   -   Atomic Force Microscopy

EIS   -   Electrical Impedance Spectroscopy

TNM   -   Transference Number Measurement

FTIR   -   Fourier Transform Infrared

CHAPTER 1

INTRODUCTION

1.1   BACKGROUND OF STUDY

The electrolyte is the part of battery component which is very important. It is because to give electrical power to device. Nowadays, every electronic device use battery to make it functioning. Its have variety shaped and sizes including rectangular, z-folded geometry and spiral wound. A battery is a gadget that can store electrical vitality as concoction vitality, and proselyte that vitality into power. There are three primary segments of a battery which is two terminals made of various chemicals (metal) known as the anode and the cathode; and the electrolyte, which isolates these terminals. There are three type of electrolyte such as liquid (aqueous), solid, and gel. Basically, the liquid electrolyte has low cycle of energy but very costly in production. The leakage in electrolyte is happen due to corrosion of metal terminal. It is very harmful and very toxicity especially for human because mostly use lithium and nickel as chemical in electrolyte which is the dangerous chemical. Moreover, the electrolyte may explode when expose to the high temperature. For that reason, solid electrolyte is identified to overcome this problem. Solid electrolyte which made from polymer materials is more flexible in shape, no leakage, more safe and no possibility of corrosion (Ahmad, 2009).

The study shown that the using of natural product which is polymer / biopolymer can be used as polymer electrolyte. The electrolyte which is based on biopolymer are made from waste material. So it is very low cost in production but useful to human being. It can manage the many problem happen on electrolyte. By applying the waste to wealth concept in this research show the used the waste material which is no value for human become something useful. Besides that, this is one way to save our nature. A class of

material that made up of a high number of particles is called polymer, which is formed from simple and small chemical units with repetition called monomer that linked by covalent bond.

In this research, polymer that had been choose is kappa carrageenan. The kappa carrageenan (k-carrageenan) is one of the carrageenan type. The carrageenan is a linear polysaccharide that extracted from Rhodophyceae which is red seaweed (Mobarak, et al., 2012). Moreover, it also can form cross-linking networks with electrolytes (Rudhziah, et al., 2015) and (Mobarak, et al., 2012). Carrageenan can be as host of polymer but its conductivity is low; thus the addition of dopant system was found to be a suitable way to enhance the performances of conductivity. Then, the ionic dopant used is ammonium nitrate (NH_4NO_3).

1.2 PROBLEM STATEMENT

Nowadays, the electrolyte are used widely in daily life and industry. But they have many disadvantage in long term such as non-environmental friendly, toxicity, and hazardous. The electrolyte are made from synthetic material such as fossil fuel which is will have depletion in future. In order to overcome this problem, the investigation and research on biopolymer. Biopolymer is the polymer that is biodegradable. Biodegradable is very important to save our nature. It resources for production of polymer may be renewable (natural polymer) which is based on plant or animal and synthetic. Regular which is natural polymers are especially fascinating because of their abundance in nature and biodegradable properties (Navaratnam, et al., 2015). Biopolymer is more convenient, environmental friendly, and easy to fabricate than polymer. Biopolymer also have structure more complex and advance than other polymer.

The dopant system also are important role give higher conductivity for electrolyte. Mostly, the dopants such as ammonium thiocyanate (NH_4SCN) which is not stable, very expensive, and highly toxic. To overcome in this research will use ammonium nitrate (NH_4NO_3) as dopant which is prepared by neutralizing nitric acid with ammonia, or by double decomposition between potassium nitrate and ammonium sulphate. The

ammonium ion is chosen cause of highly soluble in water. The ionic salt that chosen are cheaper than others and easily can be found. The ammonium nitrate also is the most stable among the other ammonium salt.

1.3   OBJECTIVES OF RESEARCH

In the present research, the objective based on:

1. To prepare the solid biopolymer electrolyte based on kappa carrageenan doped with NH_4NO_3 complexes.

2. To determine the structural properties between kappa carrageenan and NH_4NO_3 of solid biopolymer electrolyte system.

3. To identify the transport properties and ionic conductivity of kappa carrageenan doped with NH_4NO_3.

1.4   THESIS OUTLINE

The Chapter 2 is about the literature review based on other people work which is related to this research. Furthermore, the history and concept about the research which is the researcher discovered and also the implementation of the research. The study in the research which is conductivity study, and the structural study were also included in this chapter.

In the Chapter 3 were focus to the material and methodology. The kappa carrageenan was chosen and will act as biopolymer host by doping with ionic dopant namely ammonium nitrate (NH_4NO_3) in order to perform as solid biopolymer electrolyte (SBE) system. The solid biopolymer electrolyte (SBE) system will be characterized using Transference Number Measurement (TNM), Electrical Impedance Spectroscopy (EIS), and Fourier Transform Spectroscopy (FTIR). The TNM are used to analyse the ionic conducting species of solid biopolymer electrolyte. The function of EIS is to measure

ionic conductivity of samples over a wide range of frequencies, while FTIR used for the complexion between the polymer host and ionic dopant.

Result and discussion is the more important than others in this research which in the Chapter 4. In this chapter, the data are obtained from the analysis of sample in Chapter 3 were discussed. There are two type of analysis from characterization, structural and electrical. For the structural will be study about the FTIR deconvolution study. Besides that, the electrical analysis study about the ionic transport, dielectric constant, dielectric loss, modulus real, tangent loss and modulus imaginary.

Lastly, the conclusion which is overall result about this thesis are on the Chapter 5. Moreover, the implementation and recommendation also include in this chapter which can be used to improve for next research.

CHAPTER 2

LITERATURE REVIEW

2.1   POLYMER ELECTROLYTE (PES)

Polymer electrolyte may 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, 1991). Wright and co-worker first discovered polymer electrolyte in 1973 (Fenton and Wright, 1973). It was Armand who recognised their potential as novel electrolyte in 1978 (Armand et al, 1978). The second decade which is 1980 in the improvement of polymer electrolytes. This decade saw the advancement and the far reaching dispersion of smaller scale and compact gadgets. Thus, in this decade surprisingly humankind represented a solid interest for very light, cheap and highly performing secondary batteries and the interest in polymer electrolytes became crucial (Di Noto et al, 2011). The third decade, generally correspond to the 1990s, was the period that saw the widespread market dissemination of lithium-ion batteries and a slopes increase in a low-cost production of portable electronics devices. During this decade, the polymer electrolytes based on amorphous PEO were considered "classic" (Wright et al, 1998).

There have three type of polymer electrolyte such as liquid electrolyte, gel electrolyte, and solid electrolyte. The liquid electrolyte are variously called ionic liquids, liquid salts, ionic fluids, fused salts, ionic melts, or ionic glasses (Michael, 2009). Some of example of liquid electrolyte is 1-Ethyl-3-methylimidazolium dicyanamide (EMIMDCA), lithium, and sodium. Mostly the research are focus in lithium which making lithium batteries. It is because lithium has higher conductivity than others but

have disadvantage such as leaking. The chemical in lithium batteries are toxic and hazardous. That why the researcher found by changing using the gel electrolyte. The gel electrolyte is between liquid electrolyte and solid electrolyte. The example of gel electrolyte is poly (vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) (Li and Ardibili, 2016). But the gel electrolyte is not convenient even have higher conductivity because of very costly for production. Solid electrolyte is safety and good thermal and dimensional stability than other electrolyte (Zhang et al. 2016). The example of solid electrolyte is kappa carrageenan, and poly (ethylene oxide) (PEO).

2.2   SOLID POLYMER ELECTROLYTE (SPESs)

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Solid polymer electrolytes (SPEs) including a polymer an inorganic salt and as a matrix have been developed by many scientists to expand their application area. SPEs consist of a polypropylene oxide or polyethylene oxide matrix containing disintegrated salts that are characterized by other more recent innovations or low lattice energy, such as in LiBOB (Fergus, 2010). The main roles of SPEs for battery technology are enhancing safety and durability of the batteries, especially large batteries for electric vehicles and load levelling systems with wind or solar power plants, and simplifying the cell structure (Nakano et al, 2016). Other examples SPEs are polyvinyl acetate (PVA), polypropylene oxide (PPO), Polyvinyl chloride (PVC) Polyethersulfone (PES), and Polyvinylidene fluoride (PVDF) (Mohamed, 2009). Solid polymer electrolyte (SPE) is user friendly, no leakage, and very flexible in their shape.

2.3   THE ENHANCEMENT FOR SBES (SOLID BIOPOLYMER ELECTROLYTE)

Solid biopolymer electrolyte is one of way to enhancing of solid polymer electrolyte. The polymer dopant system is used in making structure of biopolymer electrolyte. A dopant which is ionic salt are added to biopolymer electrolyte to increase the ionic conductivity. Solid Biopolymer electrolyte have 2 type which is natural polymer and synthetic polymer. Solid biopolymer electrolyte uses the natural polymer which is

not harm to human being and biodegradable. Polyethylene oxide, polyvinyl alcohols and polyacrylic acid are synthetic polymers that used in the making of proton conducting electrolytes (Majid and Arof, 2005). The self-dopant itself is used as method to enhance the biopolymer electrolyte. Ammonium salt act as a dopant in this research which is doped with kappa carrageenan. The ammonium salt is a good proton donor in solid polymer electrolyte matrix. (Sohaimy& Isa, 2014). There have many prove that used of ammonium salt can increase conductivity such carboxymethyl cellulose doped with ammonium chloride solid biopolymer electrolyte (Ahmad and Isa, 2016).

Carrageenan is the biopolymer that been commercial used in many application such as thickening, gelling, and stabilizing agent especially in food product (Saha D & Bhattacharya S, 2010). Moreover, the carrageenan also used in medicine, cosmetic, and industrial applications (Popa G et al, 2011). The carrageenan are water soluble sulphated polysaccharides which is from red seaweed. These natural polysaccharides which exist in three main forms such as kappa (κ), iota (ι) or lambda (λ). The structures are shown in Figure 2.1. Ideally, carrageenan are composed of a repeating unit of disaccharide which consisting mainly of 3,6-anhydrogalactose polysaccharides and sulfate esters of galactose; these hexoses are alternately linked α-1,3 and β-1,4 in the copolymer (Prajapati et al., 2014).
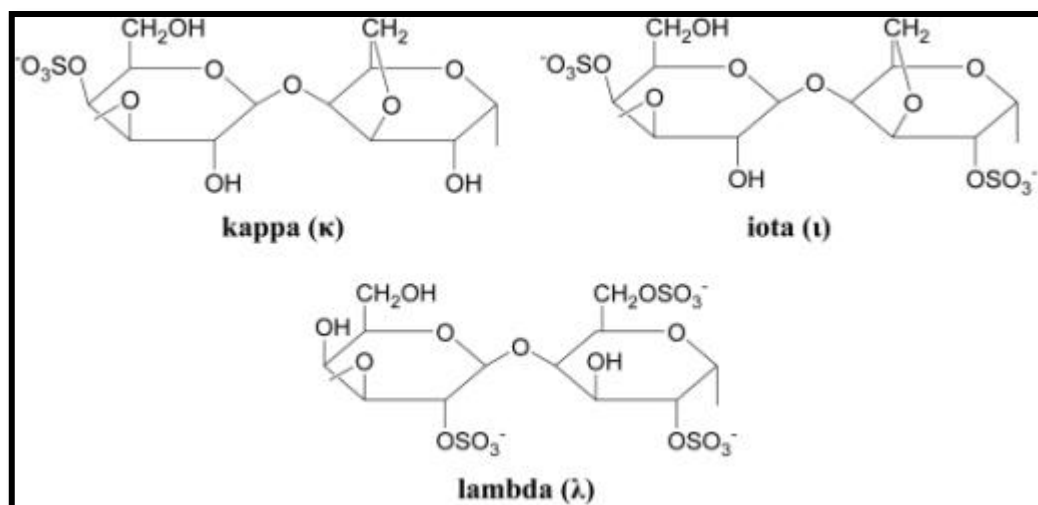
Figure 2.1. The type of carrageenan structures

7
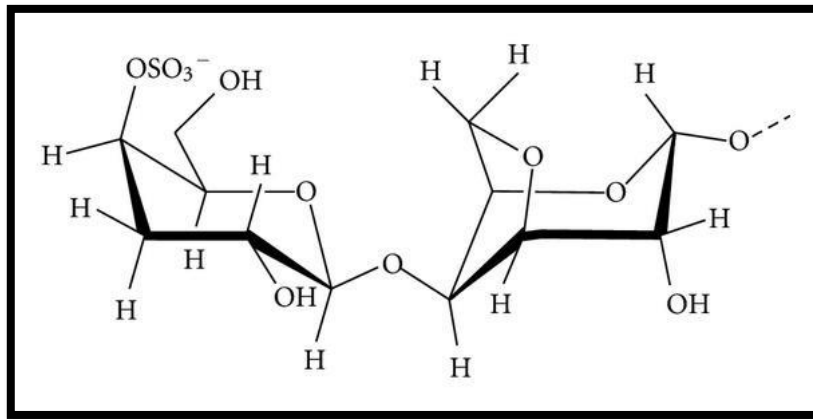
Figure 2.2. Molecular structure of *k*- Carrageenan

In this research, the chosen carrageenan is kappa. The *k*-carrageenan is a linear, sulphated polysaccharide which extracted from certain species of red seaweeds known as Rhodophyceae (McHugh, 2003). The molecular structure of the kappa carrageenan is shown in Figure 2.2. This is because kappa carrageenan has most hydroxyl group in chemical structure which in polymer chain (Andreas Leiter et al, 2017). Besides that, k-carrageenan will have higher number in oxygen and create more vacancy for the cations or proton to coordinate; it will have high ionic conductivity (Mobarak, et al., 2012). Based on the previous research, the stimulation of carrageenan are naturally by adding of plasticizer or dopants.

Table 2.1

Type of carrageenan biopolymer electrolyte and the conductivity of previous research

Carrageenan	Conductivity, σ (Scm^{-1})	References
Iota - orthophosphoric acid	6.29×10^{-3}	(Arof et al., 2010)
Carboxymethyl kappa carrageenan – imidazolium ionic liquid	5.76×10^{-3}	(Shamsudin et al, 2015)
k-carrageenan	5.3×10^{-7}	(Mobarak et al, 2012)

Table 2.1 show the type of carrageenan biopolymer electrolyte and the conductivity of previous research. It shown that the carrageenan give the higher conductivity based on other research.

The ionic conductivity increased when adding of the dopant or plasticizer. The research is to find highest conductivity, so the dopant in adding by weight percentage to know whether have higher conductivity. The ammonium salts is chosen in this research which act as dopant.

Table 2.2

The previous research of doped polymer with ammonium salt.

Polymer Host	Salt	Conductivity,σ (Scm^{-1})	References
carboxy methylcellulose (CMC)	dodecyltrimethyl ammonium bromide (DTAB)	$7\cdot72 \times 10^{-4}$	(Samsudin et al, 2012)
carboxymethyl kappa-carrageenan/carboxymethyl cellulose	Ammonium iodide (NH$_4$I)	2.41×10^{-3}	(Rudhziah et al., 2015)
carboxymethyl cellulose	Ammonium Acetate-BMATFSI	2.18×10^{-3}	(Rani et al., 2015)

The table 2.2 show the previous research of doped polymer with salt. Based on the table show that the conductivity are higher when added dopant into polymer host. Its enhance performance of the polymer host which is the electrolyte. The ammonium nitrate (NH$_4$NO$_3$) is chosen to be the dopant in this research. This is because of high soluble in water and good proton donor. This is due to their free ion (H$^+$) where easily can dissociate and interact with polymer host in polymer-salts system. The kappa carrageenan is doped with the ammonium nitrate, and also determine the weight percentage is needed that enhance the solid biopolymer electrolyte.

2.4   CONDUCTIVITY STUDY

In the conductivity study, the Electrical Impedance Spectroscopy (EIS) and Transference Number Measurement (TNM) are used. The conductivity can be calculated but need the value of Rb which is bulk resistance. The Rb plot as known as cole-cole plot which the value of Rb can be found in real parts, Zr against imaginary part $-Zi$ of the impedance.   Based on the previous work by Majid and Arof, the chitosan acetate complexed with ammonium nitrate (NH_4NO_3) have higher conductivity which is 2.53×10^{-5} Scm^{-1} for the film containing 45wt% of NH_4NO_3. The sample have been prepared by the solution-cast technique. The conductivity decrease when added more than 45wt% of NH_4NO_3. The conclusion can be made by the conductivity is depends on the concentration of the weight percentage.

The dielectric real and imaginary can be calculated by using the impedance data. For the dielectric which have 2 type, the dielectric constant, ε_r and the dielectric loss, ε_i. The dielectric loss is to measure the energy loss for the each cycle for applied electric field. Besides that, the dielectric constant is known as storage component. According to Hema et al., important insights into the ionic transport phenomenon can be gleaned from the dielectric behaviour of the system. The ionic conduction mechanism in carboxymethyl cellulose/chitosan biopolymer blend electrolyte impregnated with ammonium nitrate was studied by Rani et al, 2015. Based on their research, frequency range between 1 and 6 Hz which show there are no definitive relaxation peaks were observed. Shown that the increment of conductivity is affected by the increasing concentration of mobile ions in the system (Singh et al, 1992). The non-Debye dependence was confirm when ε_r and ε_i increase sharply towards the low frequencies which show indicates that electrode polarization effects have occurred.

Furthermore, the modulus were the real part of modulus, Mr and the imaginary part of modulus, M_i can be calculated using the equations. According to Majid and Arof, an indicator that the polymer electrolyte films are ionic conductors which is the presence of peaks in the modulus formalism at higher frequencies. The appearance of a long graph which at low frequencies shown there might be a large capacitance which collaborate

with the electrodes used in EIS measurement, which further confirms non-Debye behaviour in the samples (Ramesh et al, 2007).

For the study of conducting species of solid biopolymer electrolytes is by using Transference Number Measurement (TNM). The relationship between the conductivity and the diffusion of ion and suing the dc polarization (Chai & Isa, 2016). According to Linford, the electron conduction in solid biopolymer electrolyte can be neglected. When the polarization current become saturates, the cationic transference value are shown by measurement of the polarization current.

2.5   THE STRUCTURAL STUDY

The structural study is by using the Fourier Transform Infrared (FTIR) which is to determine the complexation between kappa carrageenan doped with ammonium salt of solid biopolymer electrolytes. Based on the previous work by Arof & Majid, the sample were finish by using casting technique. The spectra of CA-NH$_4$NO$_3$ complexes in region from 400 to 2000 cm^{-1} which the amine band of pure chitosan acetate film appears at the 1553 cm^{-1} and also the carbonyl band at 1636 cm^{-1}. When chitosan has been dissolved in acetic acid, a chitosan acetate or chitosan–acetic acid salt is formed. The reported that the cation of the acetic acid will be interact with the nitrogen atom of the amine group (Arof & Majid, 2005).

CHAPTER 3

MATERIALS AND METHODS

3.1   INTRODUCTION

This chapter details the research methodology employed in the present research. The Table 3.1 is list of apparatus and materials that was used in the research. The experimental research were divided into 3 phases which is phase 1 is preparation of kappa carrageenan with ammonium nitrate; phase 2 is characterization of kappa carrageenan with ammonium nitrate; and lastly phase 3 is analysis the kappa carrageenan with ammonium nitrate. The overview of all phase are on the Figure 3.1 were shown. The research was conducted in Faculty of Industrial Science and Technology.

Table 3.1
List of apparatus and materials that was used in the research.

No	Apparatus and Materials
1	Kappa Carrageenan
2	Ammonium Nitrate
3	Acetone
4	Distilled Water
5	Beaker, 250 ml
6	Beaker, 1000 ml
7	Measuring Cylinder, 250 ml
8	Glass Petri Dishes
9	Magnetic Bar
10	Aluminum Foil
11	Spatula
12	Tweezer

3.2   RESEARCH METHODOLOGY

Figure 3.1 shows that the flow chart of research.

```
                         ┌─────────────────┐
                          Start the Project
                         └─────────────────┘
                                  │
                                  ▼
Phase 1   ┌───────────────────────────────────────────────────────┐
          │ Preparation of solid biopolymer electrolytes Kappa     │
          │ Carrageenan doped with NH4 NO3 (0-50 wt. %)            │
          └───────────────────────────────────────────────────────┘
                                  │
                                  ▼
Phase 2              ┌──────────────────────────┐
                     │     Characterization      │
                     └──────────────────────────┘
              ┌───────────────┐          ┌──────────────────────────┐
              │ Electrical    │          │ Structural               │
              │ Characterization│        │ Characterization         │
              └───────────────┘          └──────────────────────────┘
               │          │                              │
             ┌────┐    ┌─────┐                        ┌──────┐
             │EIS │    │ TNM │                        │ FTIR │
             └────┘    └─────┘                        └──────┘
                              │
                              ▼
Phase 3              ┌──────────────────────────┐
                     │      Data Analysis        │
                     └──────────────────────────┘
                                  │
                                  ▼
                           ( Project End )
```

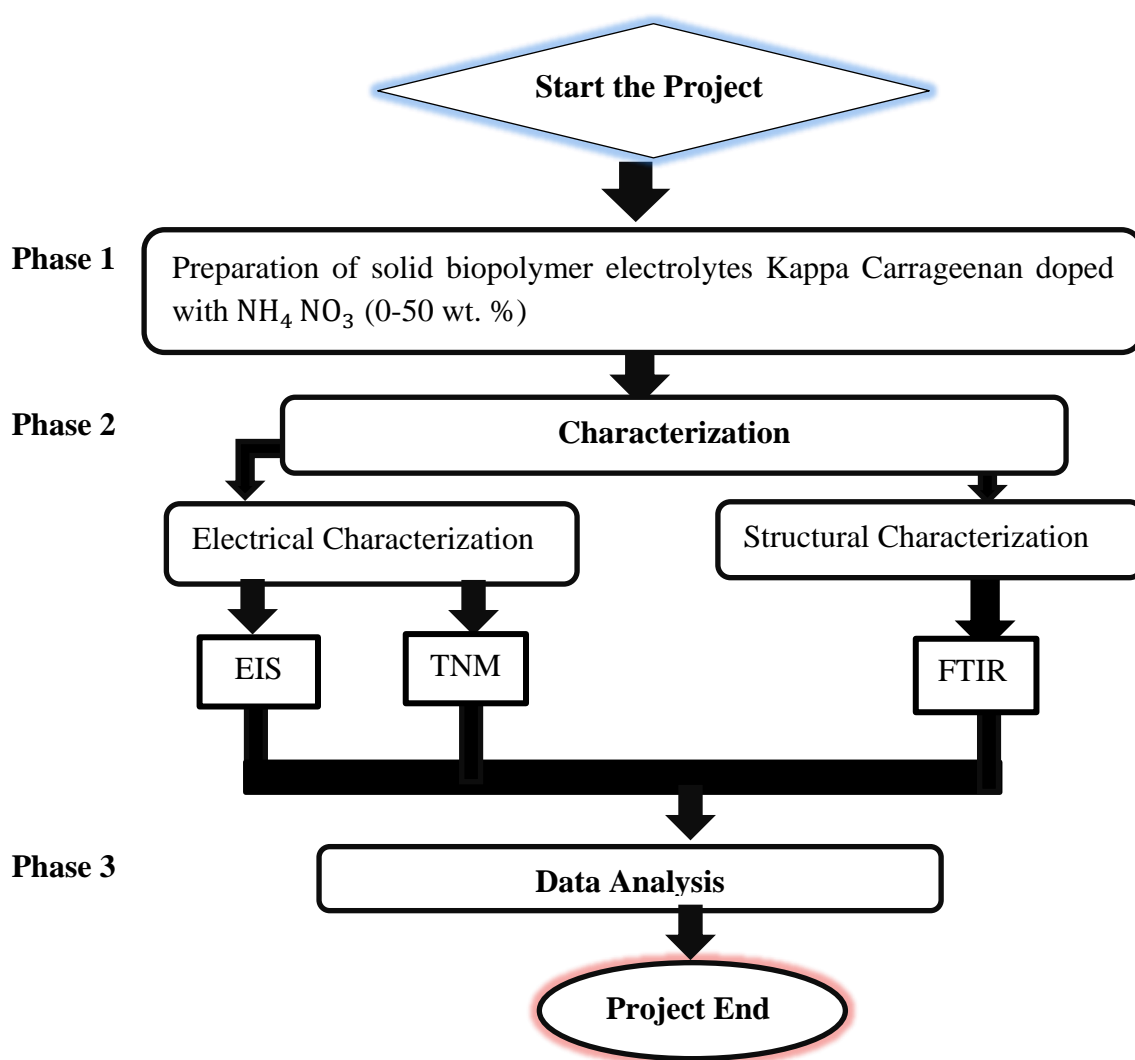Preparation of solid biopolymer electrolytes Kappa Carrageenan doped with $NH_4 NO_3$ (0-50 wt. %)

Figure 3.1. Flow chart of research

3.3   PREPARATION OF SAMPLE

In this research, the biopolymer electrolyte film was prepared by using casting technique. Kappa carrageenan which from Takara Sdn. Bhd. was dissolved with distilled water. Preparation of kappa carrageenan by using water bath technique which is the beaker of contain sample on the water bath. Next, varied amount of NH_4NO_3 in weight percentage (0 – 50 wt %) was added into kappa carrageenan solution and need to be stirred until the mixture become homogenous. The ammonium nitrate is from Merck & Co., Inc. The calculation to get the weight of ammonium nitrate: -

$$\frac{x}{x + y} \text{x } 100\% = z \text{ wt. \%} \tag{3.1}$$

$$100x = zx + zy \tag{3.2}$$

S

$$(100 - z) \, x = zy \tag{3.3}$$

$$x = \frac{zy}{100 - z} \tag{3.4}$$

Where;

x = weight of NH_4No_3 in gram

y = weight of k-carrageenan in gram

z = wt. % of NH_4No_3

After the sample become homogenous, then the samples was cast into petri dish. Next, the samples were dry into oven at 60ºC for 4 hours and then keep in the desiccator for further drying. The composition of NH_4NO_3 are tabulated in Table 3.2:-

Table 3.2

List of samples with their compositions respectively

Name	k-carrageenan (g)	NH_4NO_3 (wt. %)	NH_4NO_3 (g)
R1	2	0	0.0000
R2	2	5	0.1053
R3	2	10	0.2222
R4	2	15	0.3529
R5	2	20	0.5000
R6	2	25	0.6667
R7	2	30	0.8571
R8	2	35	1.0769
R9	2	40	1.3333
R10	2	45	1.6363
R11	2	50	2.0000

3.4   CHARACTERIZATION OF SAMPLE

There are 2 section to characterize the biopolymer electrolyte film:

1. Structural Characterization
2. Electrical Characterization

Table 3.3
The technique and characterization proposed in this research.

Section	Technique	Characterization
Structural Characterization	Fourier Transform Infrared (FTIR)	To determine the complexation between kappa carrageenan doped with NH_4NO_3 of solid biopolymer electrolytes
Electrical Characterization	Electrical Impedance Spectroscopy (EIS)	To study conductivity and the electrical properties of solid biopolymer electrolytes
	Transference Number Measurement (TNM)	To study the conducting species of solid biopolymer electrolytes

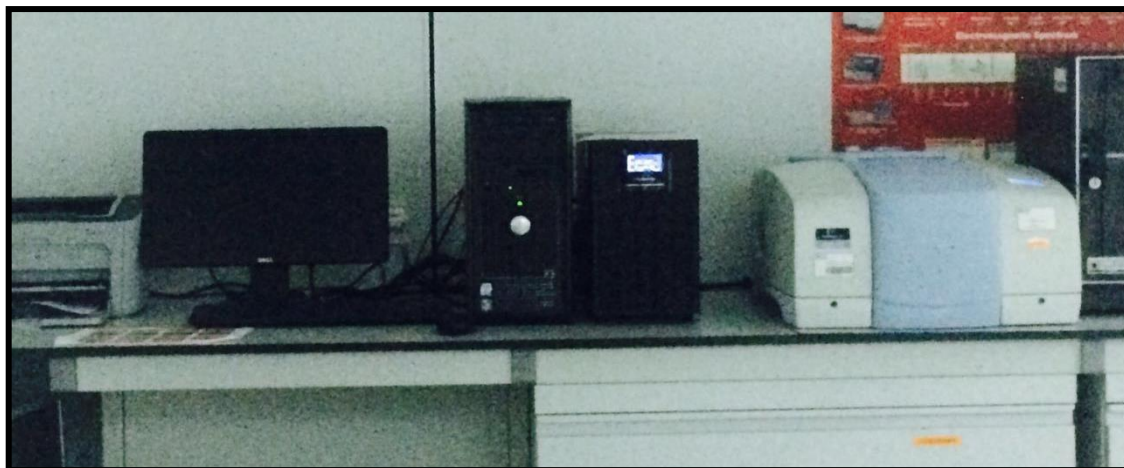### 3.4.1 FOURIER TRANSFORM INFRARED (FTIR)

Figure 3.2. The Fourier Transform Infrared Spectroscopy (FTIR)

The Figure 3.2 shown the Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) is a technique that used to acquire an infrared spectrum of absorption or emission of a solid, gas or liquid. Moreover, it is one of the techniques used to determine the complexation between kappa carrageenan doped with NH_4NO_3 of solid biopolymer electrolytes. The FTIR were converted the collected data from raw data to actual spectrum. FTIR spectroscopy measurement was carried out by using the PerkinElmer Spectrum 100. The Attenuated Total Reflection (ATR) which contain germanium crystal as the tips is equipped and used in FTIR. The tips is act as scanner which to scan the sample. The sample is put on germanium crystal which use infrared as ray to record data. It will pass through sample with frequency from 4000 to 675 cm^{-1} with the spectra resolution of 4 cm^{-1}. Using the transmittance mode were used to record the data FTIR (A.S. Samsudin et al., 2012).

3.4.1.1 FTIR DECONVOLUTION

The FTIR deconvolution is where Gaussian-Lorentz function is adapted to the Origin Lab software. This technique is done by Isa & Chai on their previous research. In this deconvolution technique, the sum of all intensity which is deconvulated peak was to be ensured to fit the original spectrum. Moreover, the dominant ionic movement were selected by FTIR peaks.

The area which under peaks was determined and then the percentage of free ions was calculated by using the equation:-

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

Where,

A_f = area under peak represent the free ion region

A_c = area under peak represent the contact ions region.

Moreover, the calculation of mobility (μ), number of density (η), and diffusion coefficient (D) of mobile ion by the following equation:-

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

$$\mu = \frac{\sigma}{ne} \tag{3.7}$$

$$D = \left[\frac{kT\mu}{e} \right] \tag{3.8}$$

Where,

M = the number of moles of dopant used

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

V_{Total} = total volume of the electrolyte

σ = Conductivity of the electrolyte

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

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

T = the temperature (K)

3.4.2   TRANSFERENCE NUMBER MEASUREMENT (TNM)

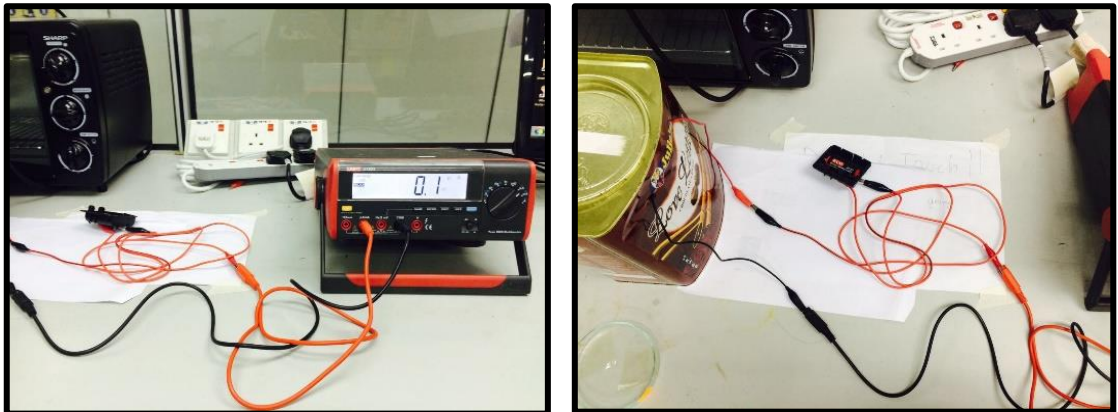*Figure 3.3.* Transference Number Measurement (TNM)

Figure 3.4. The circuit of TNM

Transference Number Measurement (TNM) is to study the ionic conductivity species of solid biopolymer electrolytes using dc polarization current technique. The sample was sandwiched between two stainless steel blocking electrodes and the current

through the circuit was monitored with the time until it homogenous. The Figure 3.3 and Figure 3.4 shows the circuit of TNM. The voltage used are fixed which is 1.5V. The anions and cations contribute to charge the transport in electrolytic processes in accordance with their different mobilities in an electric field. The proton (t_{H+}) or an electron (t_e) transport are shown by using TNM. Besides that, TNM are used dc for current supply with polarization method. The ionic proton transference number t_H+ can be found by calculation :-

$$t_{H^+} = \frac{I_{H+}}{I_o} \tag{3.9}$$

Where,

$I_H{}^+$ = the saturated proton current

Io = initial current

The transference number were calculated which is from the polarization current versus time plot using the equation (Selvasekarapandian et al, 2010):-

$$t_{ion=(I_i-I_f)/I_i} \tag{3.10}$$

$$t_{ele=I_f-I_i} \tag{3.11}$$

Where,

I_f = final current

I_i = initial current

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3.4.3. ELECTRICAL IMPEDANCE SPECTROSCOPY (EIS)

Figure 3.5. Electrical Impedance Spectroscopy (EIS)

Figure 3.6. The HIOKI 3532-50 LCR Hi-Tester and sample holder

Electrical Impedance Spectroscopy (EIS) is to study conductivity and the electrical properties of solid biopolymer electrolytes. The biopolymer kappa carrageenan doped $NH_4 NO_3$ film was sandwiched between the stainless steel electrodes of π cm^2 of surface area (Samsudin, and Isa, 2012). The impedance study was performed by using a HIOKI 3532-50 LCR Hi-Tester. The impedance data were collected for frequencies ranging from 50 Hz to 1 MHz over a temperature range from 30° to 100°C. The conductivity are calculate by using equation:-

$$\sigma = \frac{t}{R_b A} \qquad\qquad (3.12)$$

Where,

      t = thickness of sample

      A = area of sample

      R_b = bulk resistance

The data of this impedance spectroscopy are used to find dielectric constant, dielectric loss, modulus real, modulus imaginary and tangent loss.

CHAPTER 4

RESULT AND DISCUSSION

4.1   INTRODUCTION

In this chapter, explain about the result and was discuss about the research of kappa carrageenan doped with ammonium nitrate (NH_3NO_4) of solid biopolymer electrolyte. This electrolyte were produced by using casting technique which discussed in previous chapter. This electrical and structural properties of solid biopolymer electrolyte were characterized by using Electrical Impedance Spectroscopy (EIS), Fourier Transform Infrared Spectroscopy (FTIR), and Transference Measurement Number (TNM). Table 4.1 show the thickness of each composition of kappa carrageenan and ammonium nitrate specifically.

Table 4.1
List of compositions

Name	k-carrageenan (g)	NH_4NO_3 (wt. %)	NH_4NO_3 (g)	Thickness, t (cm)
R1	2	0	0.0000	0.0206
R2	2	5	0.1053	0.0116
R3	2	10	0.2222	0.0165
R4	2	15	0.3529	0.0145
R5	2	20	0.5000	0.0144
R6	2	25	0.6667	0.0150
R7	2	30	0.8571	0.0186
R8	2	35	1.0769	0.0235
R9	2	40	1.3333	0.0247
R10	2	45	1.6363	0.0269
R11	2	50	2.0000	0.0360

The colourless and transparent of solid biopolymer electrolyte which don't have phase separation were obtain which show in Figure 4.1.
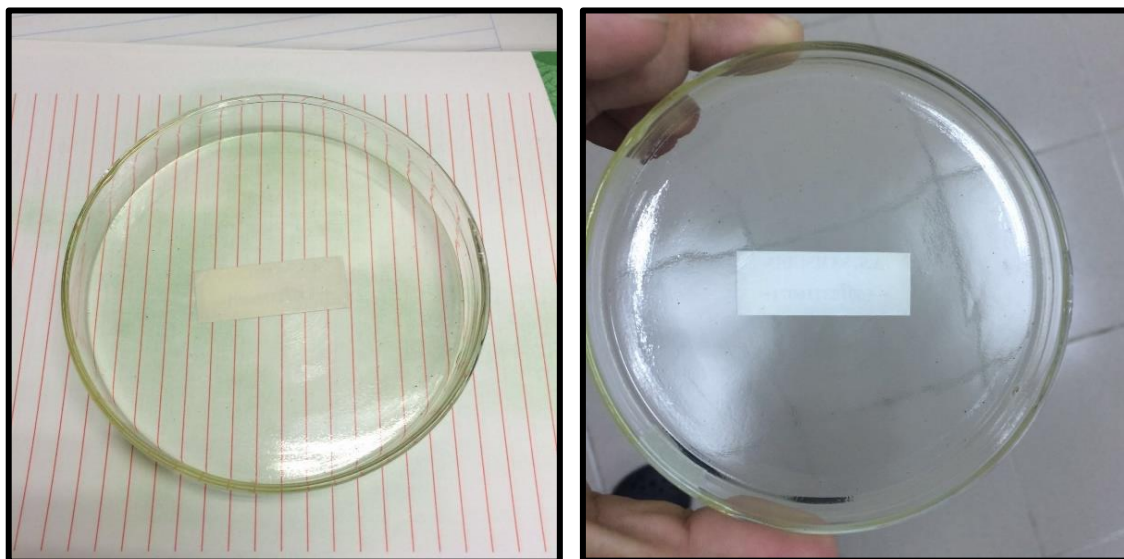

Figure 4.1. The solid biopolymer electrolyte

4.2   STRUCTURAL CHARACTERIZATION OF SOLID BIOPLOYMER ELECTROLYTE

There only have one structural characterization in this research which is Fourier Transform Infrared Spectroscopy (FTIR). Furthermore, the FTIR deconvolution are study since it under the FTIR analysis.

4.2.1   FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In this research, FTIR spectroscopy measurement was carried out by using the PerkinElmer Spectrum 100. The Attenuated Total Reflection (ATR) which contain germanium crystal as the tips is equipped and used in FTIR. The reason why used the ATR because of the sample are in solid phase. The data of FTIR are recorded in transmittance mode.

4.2.1.1   FTIR OF PURE KAPPA CARREGEENAN (KC) POWDERS

The functional group of kappa carrageenan based on others previous research are in Table 4.2. The molecular structure of pure kappa carrageenan is shown in Figure 4.2.

Table 4.2

Basics k-carrageenan bands by previous research

Functional group	Peak, cm^{-1}	Research
O=S=O, symmetric stretch	1210-1261	(Rudhziah, S., et al,2015; Silva, et al., 2010 and Tranquilan, et al., 2012)
C-O-SO$_3$, stretching vibration	846	(Rudhziah, S., et al,2015 and Tranquilan, et al., 2012)
C-O-SO$_3$, stretching vibration	851	(Rudhziah, S., et al,2015; Tranquilan, et al., 2012; and Silva, et al., 2010)
C–O-C of 3,6-anhydro-D-galactose	926	(Tranquilan, et al., 2012; Fan, et al., 2011 and Silva, et al., 2010)
-OH (stretch)bonding	3326	(N.H.Ahmad & M.I.N.Isa,2015)

The Figure 4.3 show the pure kappa carrageenan of FTIR spectrum. At the 1650 cm^{-1}, which is strong peak contain the H_2O element. Next, the O=S=O element which at strong peak 1226 cm^{-1}. At the 926 cm^{-1} that contain C–O-C element which is weak peak. The C-O-SO$_3$ element contain at two weak peaks which 846 cm^{-1} and 851 cm^{-1}.
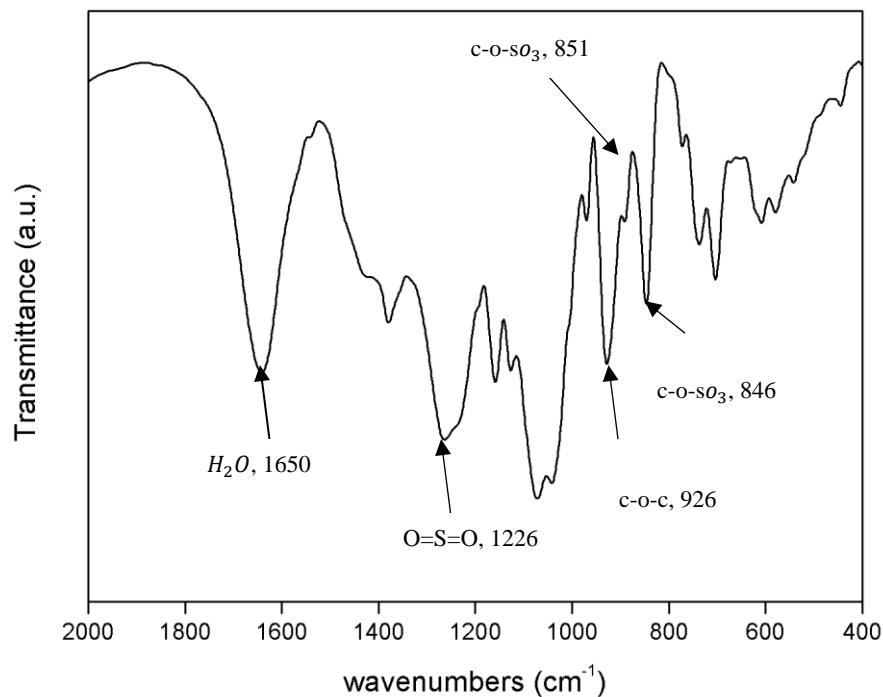
Figure 4.2. FTIR spectrum of pure kappa carrageenan

4.2.1.2 FTIR OF PURE AMMONIUM NITRATE (NH$_4$NO$_3$) POWDERS

The molecular structure of ammonium nitrate (NH$_4$NO$_3$)is shown in Figure 4.3. The FTIR spectrum of pure ammonium nitrate on Figure 4.4 with range wavelength 500 until 4000 cm^{-1}. Based on figure 4.4, there have strong peak of NH$_4^+$ at 3130 cm^{-1} and also strong peak of NH$_4^+$ at 1393 cm^{-1}. The bending band of NO$_3^-$ appear at 825 cm^{-1} (Zhang et al, 2005). The strong OH peak appear at 3131cm^{-1}.
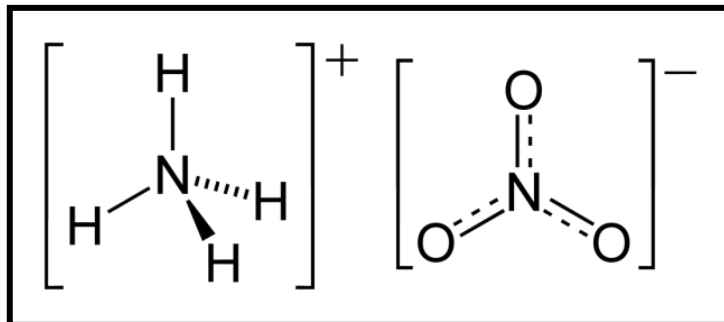
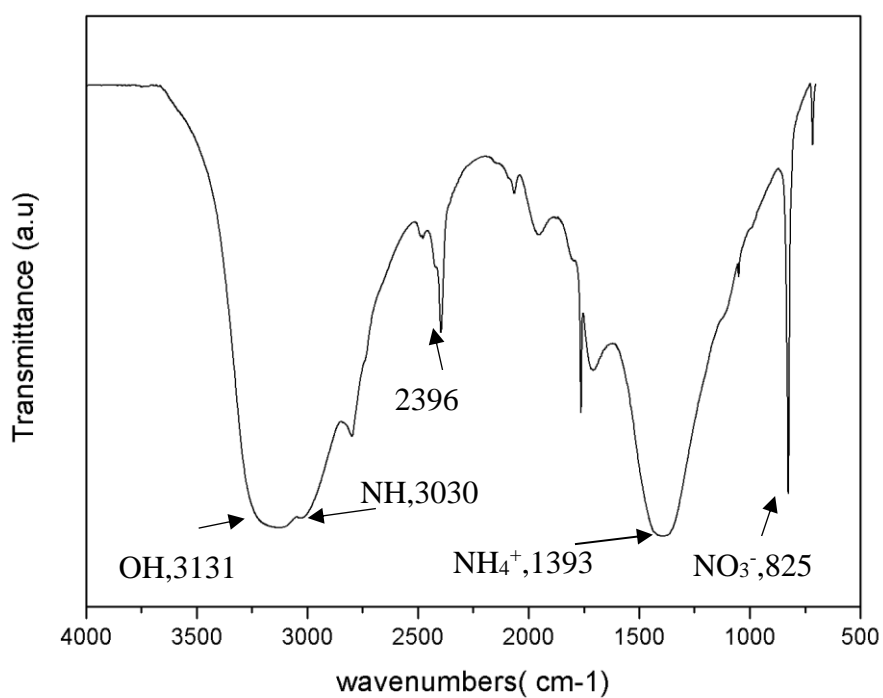*Figure 4.3*. Molecular Structure of Ammonium Nitrate

Figure 4.4. FTIR spectrum of pure ammonium nitrate

4.2.1.3 FTIR OF SOLID BIOPOLYMER ELECTROLYTE

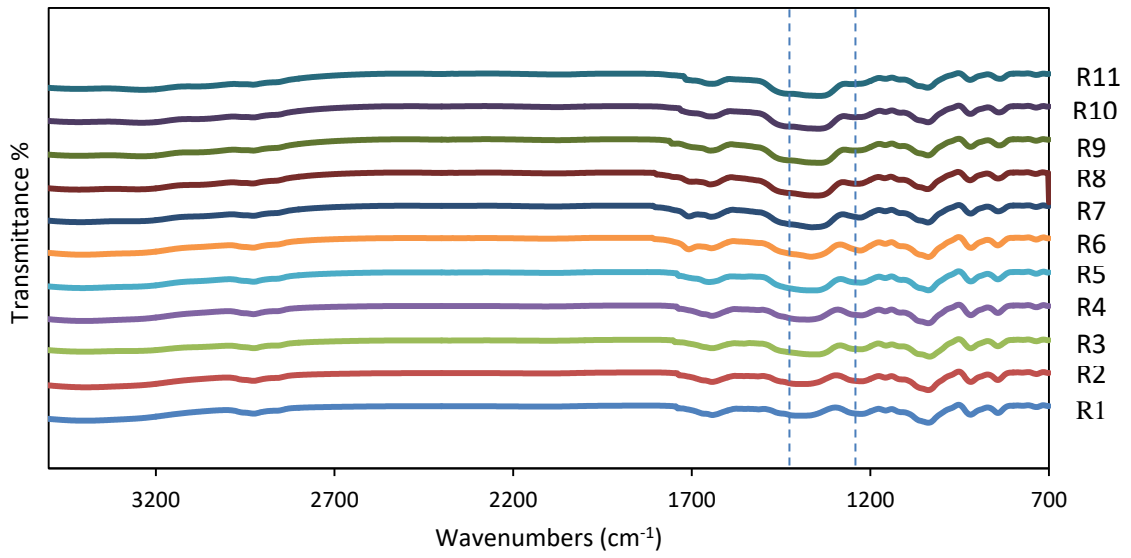The Figure 4.5 show the ATR-FTIR spectra of solid biopolymer electrolyte which from 700 cm^{-1} until 4000 cm^{-1}.

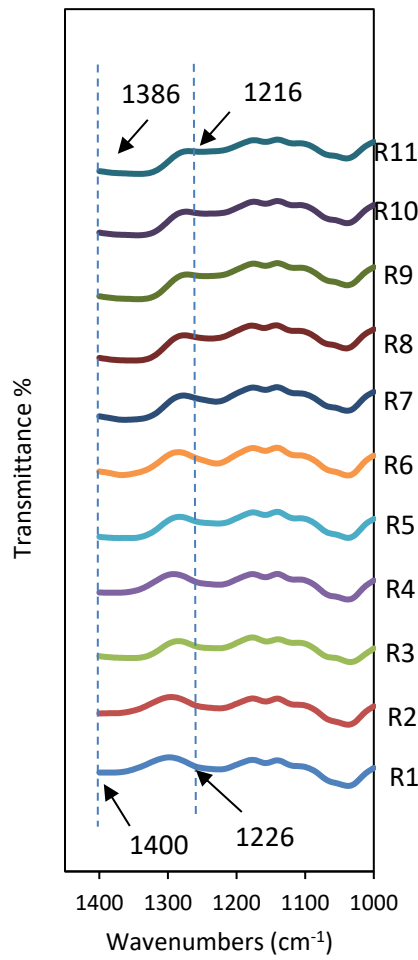*Figure 4.5.* ATR-FTIR spectra of solid biopolymer electrolyte

Figure 4.6. ATR-FTIR spectra of solid biopolymer electrolyte at 1000-1400 cm^{-1}

Based on Figure 4.6, which is the ATR-FTIR spectra of a samples in the specific region from 1000-1400 cm^{-1} that contain the kappa carrageenan doped with ammonium nitrate (NH$_4$NO$_3$). The O=S=O band of the kappa carrageenan has been found in wavelength of 1226 cm^{-1}. Then, the wavelength has been shifted to 1216 cm^{-1} as the increase weight percentage of ammonium nitrate. This could be happen due to the interaction of O=S=O the symmetry vibration moiety in kappa carrageenan with H$^+$ ion of NH$_4$NO$_3$ which show reflect the protonation of system cation, H$^+$ ion towards O=S=O (Hema et al, 2009). Moreover, the decreasing of peak which in the (O=S=O) band might because of the de-protonation of ions (H$^+$) and also turn to recombine with N$^+$ moieties of NH$_4$NO$_3$ to form neutral ion pair (Samsudin et al, 2012). The proton migration (H$^+$) which is possible due to the conduction occurs via Grotthus mechanism, i.e., the conduction occurs through the exchange of ions between complexed sites (Kadir et al, 2010).

In this research, with adding dopant of ammonium nitrate, there have the complexion which is kappa carrageenan and H$^+$ from the NH$_4$NO$_3$, which can be easily dissociated under the influence of electric field (Hema, Selvasekerapandian, & Hirankumar, 2007). This peak growth with increase of ammonium nitrate. The growth of the peak due to H$^+$ ion from the ammonium nitrate (Arof & Majid, 2005). At the 1400 cm^{-1}, existence of the NH$_4^+$ element which strong peak. The peak was shifted to 1386 cm^{-1}. Then, the weakly H$^+$ which easily dissociated to another site and bonded with oxygen of kappa carrageenan. The interaction between kappa carrageenan and ammonium nitrate were indicated by shifted of the band. The changes in the ATR-FTIR proved that the complexion between kappa carrageenan and ammonium nitrate were exists.

4.2.2 FTIR DECONVOLUTION STUDY

FTIR deconvolution was plotted and shown in Figure 4.7 which is FTIR deconvolution of (a) R9 (40 wt. % of NH$_4$NO$_3$), (b) R10 (45 wt. % of NH$_4$NO$_3$), (c) R2 (5 wt. % of NH$_4$NO$_3$). Figure 4.7 of (a) at the wavelength from 1180 cm^{-1} until 1280 cm^{-1}. The peak 1222 cm^{-1} shown the contact ions and free ion. The free ion is at the 1226 cm^{-1} and the contact ions shown at 1252 cm^{-1} and 1204 cm^{-1}. Figure 4.7 of (b) at the

wavelength from 1160 cm^{-1} until 1300 cm^{-1}. The peak 1220 cm^{-1} shown the contact ions and free ion. The free ion is at the 1202 cm^{-1} and the contact ions shown at 1250 cm^{-1} and 1223 cm^{-1}. Figure 4.7 of (c) at the wavelength from 1150 cm^{-1} until 1300 cm^{-1}. The peak 1231 cm^{-1} shown the contact ions and free ion. The free ion is at the 1226 cm^{-1} and the contact ions shown at 1259 cm^{-1} and 1211 cm^{-1}. The percentage of the contact ions and free ions can be calculated by ratio of area of contact ions or free ions to the total area of peak and multiply by 100%. The Table 4.3 show the table of percentage area of free and contact ions of the kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte.

The Figure 4.8 and Figure 4.9 show the transport parameter of the kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte. Based on Table 4.3, the percentage of free ions which is the highest on the sample R9 (40 wt. % of NH$_4$NO$_3$). This show that the sample R9 have more ion to dissociate, so will assisting more ion conduction. This result also can be proved from the highest conductivity that achieved from the Electrical Impedance Spectroscopy (EIS) result.

Based on Figure 4.13 which is graph of conductivity compared with Figure 4.8, it show that the shaped of graph are almost parallel and the conductivity is strongly influenced by diffusion coefficient (D) and ionic mobility (μ). The number of density of mobile ions (η) which show in Figure 4.9 have weak influencing of the kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte. The effect of diffusion coefficient and ionic mobility will further proved by Transference Measurement Number (TNM).
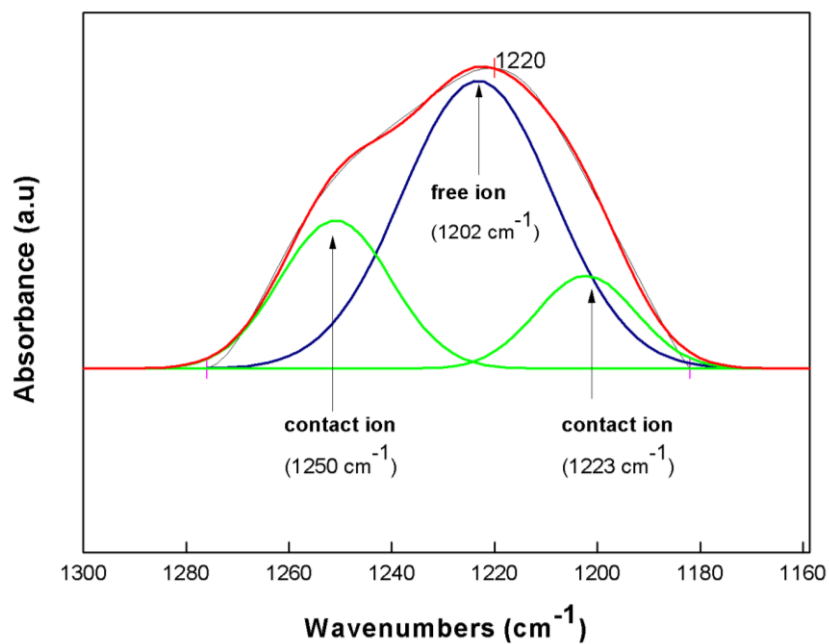
Table 4.3

Percentage area of free and contact ions of the kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte.
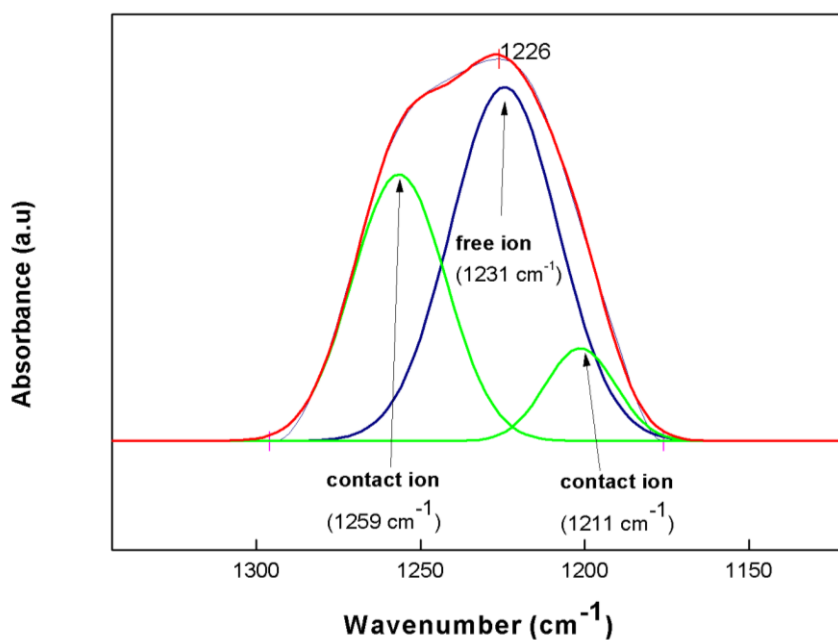
Name	Free ions (%)	Contact ions (%)
R1	26.24	73.76
R2	50.87	49.13
R3	56.45	43.55
R4	24.62	75.38
R5	26.00	74.00
R6	21.63	78.37
R7	28.12	71.88
R8	41.67	58.33
R9	64.53	35.47
R10	13.43	86.57
R11	17.40	82.60
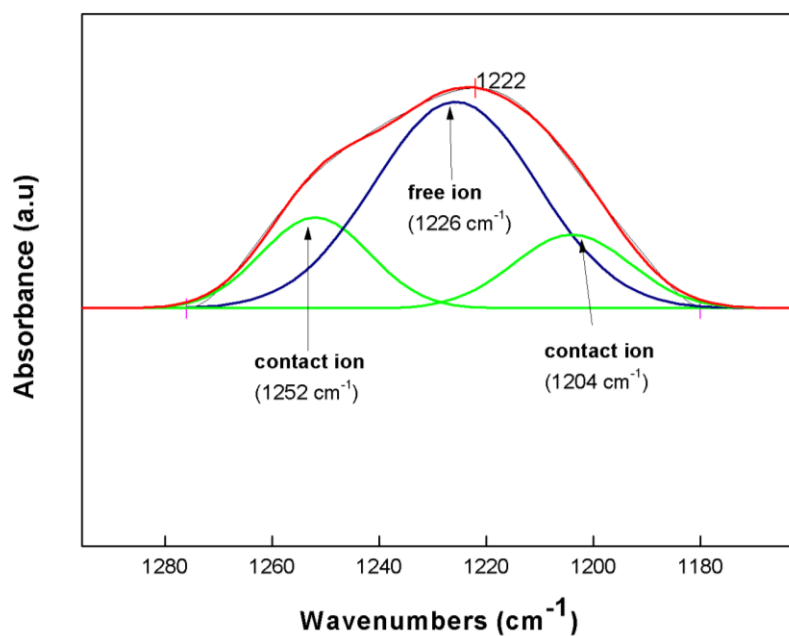
(a)

(b)

(c)

Figure 4.7. FTIR deconvolution of (a) R9 (40 wt. % of NH₄NO₃), (b) R10 (45 wt. % of NH₄NO₃), (c) R2 (5 wt. % of NH₄NO₃)
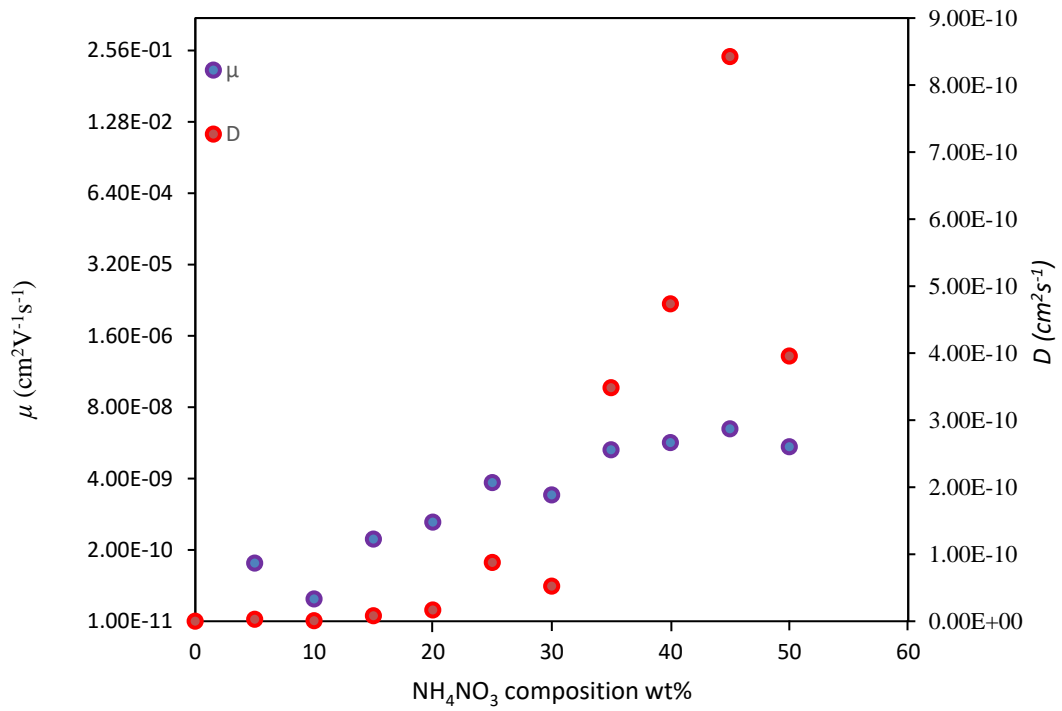
Figure 4.8. The diffusion coefficient and ionic mobility against weight percentage
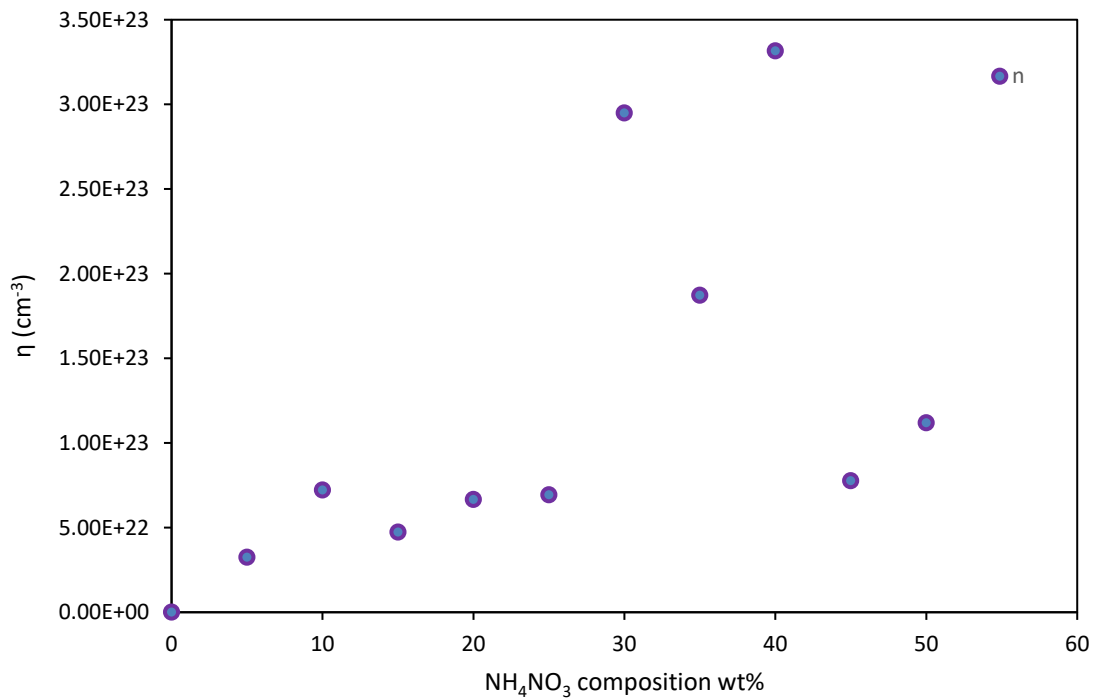

Figure 4.9. The density of mobile ion against weight percentage

4.3   ELECTRICAL   CHARACTERIZATION   OF   SOLID   BIOPLOYMER   ELECTROLYTE

There have two electrical characterization in this research which is Electrical Impedance Spectroscopy (EIS) and Transference Measurement Number (TNM). For the EIS, there also have to study about dielectric study and modulus study.

4.3.1 ELECTRICAL IMPEDANCE SPECTROSCOPY (EIS)

From the cole–cole plot, the conductivity can be obtained using the R_b plot by using calculation. The R_b is bulk resistance and obtained from the complex impedance plot at the intersection of the plot and the real impedance axis. Moreover, the A is the area of film and t is the thickness of film (M.H.Buraidah et al., 2009). The ionic conductivity behaviour was investigated by impedance spectroscopy. The Figure 4.11 show the cole-cole plot for pure kappa carrageenan at 303K. The Figure 4.12 show the cole-cole plot for 5 wt. % of ammonium nitrate at 303K which is the lowest conductivity and the Figure 4.13 show the cole-cole plot for 40 wt. % of ammonium nitrate at 303K which is the highest value of conductivity. Based on cole-cole plot show that have different type of region which is incomplete semi-circle in high frequency and a spur in low frequency. The ionic conduction which is in bulk of sample is related to the semi-circle part in high frequency region (Samsudin et al, 2012). The bulk resistance (R_b) value which get from the cole-cole plot are used to find the conductivity by using equation.

The conductivity versus NH_4NO_3 content by weight percentage at 303K is plotted in Figure 4.14. Based on the graph, the highest conductivity was 9.64×10^{-04} S cm^{-1} at 40 wt. % of ammonium nitrate dopant. . The oxygen atoms which have lone pair of electrons formed the coordinate bond with the H^+ which resulting in the formation of polymer complexes therefore affect the ionic conductivity. The higher the conductivity when added the dopant as the higher the weight percentage which show in Table 4.4. The decrease conductivity when reach 45 wt. % of ammonium nitrate. This is due to the

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number of charge carrier will be reduce and limitation in mobility of ion which is polymer complexes become crowded.

According to the Majid & Arof (2015), the ionic conductivity in biopolymer electrolyte were linked to the number and mobility of conducting ions. The decreasing the ionic conductivity at high weight percentage of ammonium salt that lead to rise the crystallinity. Moreover, based on discussion in FTIR analysis stated that the H^+ moiety of NH_4^+ which cannot accommodate with the kappa carrageenan when contain high composition of NH_4NO_3 and lead to recombination of ions (Sikkanthar et al., 2015).
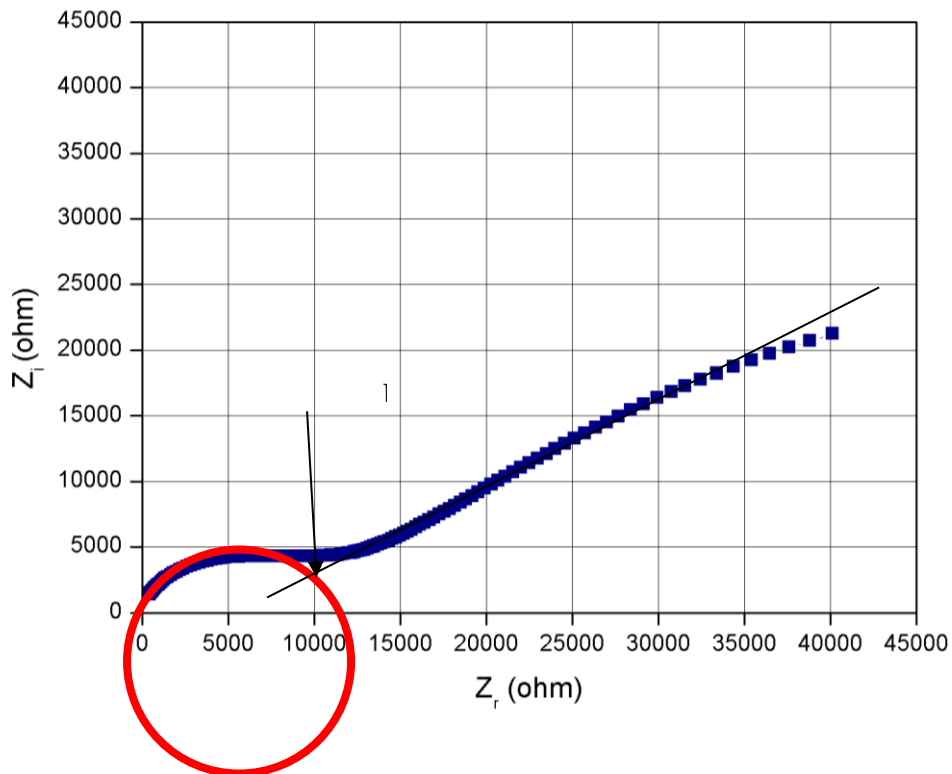

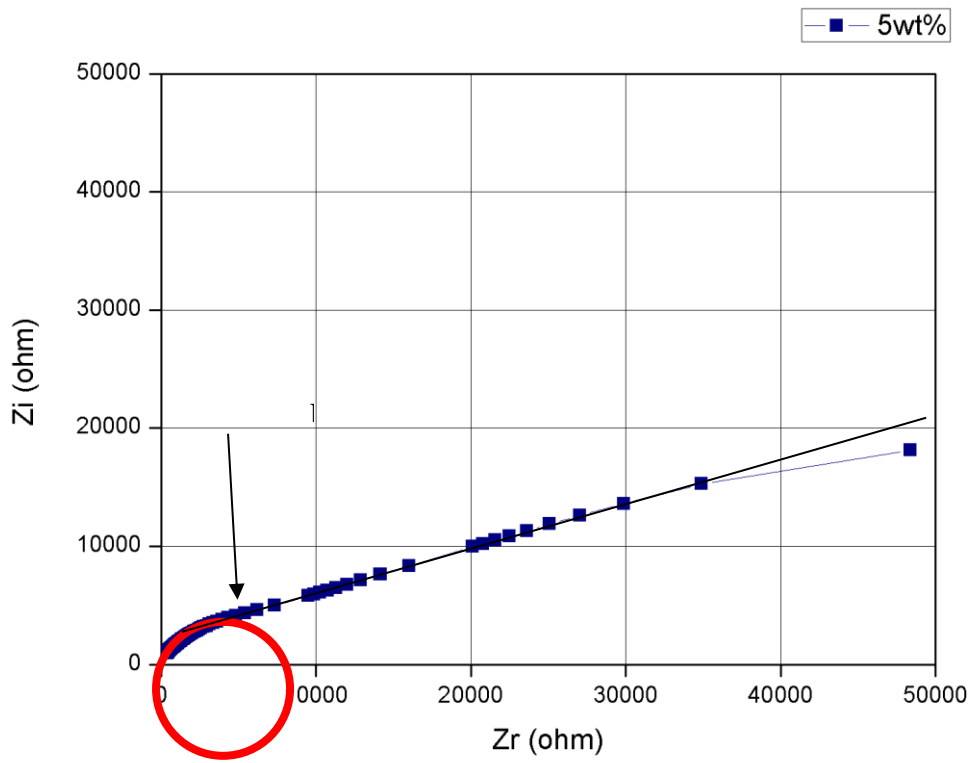*Figure 4.10.* The cole-cole plot of pure kappa carrageenan at 303K

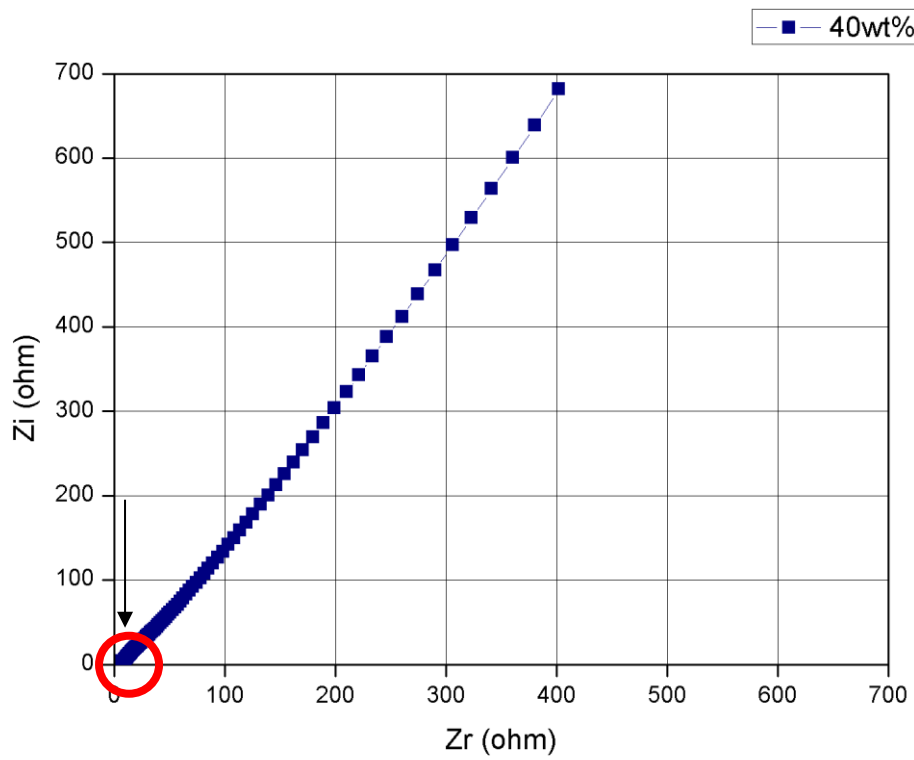*Figure 4.11.* The cole-cole plot of 5 wt. % at 303K

Figure 4.12. The cole-cole plot of 40 wt. % at 303K

Table 4.4

The thickness, and bulk resistance, of sample

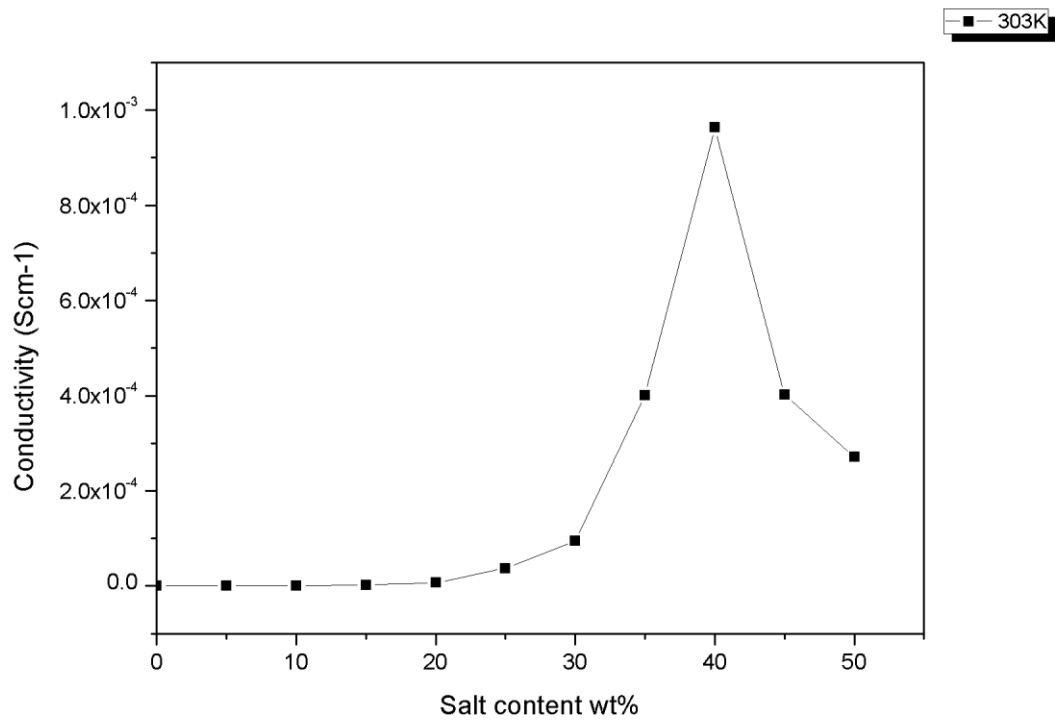| Name	Thickness, t (cm)	Bulk Resistance, R_b (Ohm)
R1	0.0206	9.8
R2	0.0116	6190
R3	0.0165	17800
R4	0.0145	1940
R5	0.0144	667
R6	0.0150	128
R7	0.0186	62.4
R8	0.0235	18.7
R9	0.0247	8.16
R10	0.0269	21.3
R11	0.0360	42.1

Figure 4.13. The graph of conductivity against NH_4NO_3 content wt. % at 303K

4.3.1.1 DIELECTRIC STUDY

The understanding about the conductive behaviour of solid biopolymer electrolyte system which can get from dielectric study (Hafiza, et al., 2014). To calculate the real and imaginary part of the complex permeability by using the measure impedance data. The dielectric constant, ε_r is representative of stored charge in a material. Besides that, the dielectric loss, ε_i is a measure of energy losses to move ion when polarity of electric field reverse rapidly. The calculation of dielectric constant and dielectric loss based on the equation below:-

$$\varepsilon_r = \frac{Z_i}{\omega C_o \left(Z_r{}^2 + Z_i{}^2\right)} \tag{4.1}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o \left(Z_r{}^2 + Z_i{}^2\right)} \tag{4.2}$$

Where,

Z_i = negative imaginary impedance

Z_r = real impedance

$C_o = \varepsilon_0 \frac{A}{t}$

t = thickness of samples

A = area electrode- electrolytes contact surface

$\omega = 2\pi f$

ε_0 = the permittivity of the free space

The plot of frequency dependent of dielectric constant, ε_r shown in Figure 4.14 and the graph of frequency dependent of dielectric loss, ε_i shown in Figure 4.15. The graph show the increase of dielectric constant at lower frequency. This could happen due to the enhancement of the charge carrier density which in the space charge of accumulation region which called as non- Debye type of behaviour (Azli et al, 2016). The number density of ion increase when more salt is added the stored charge which in the electrolyte

is increased (Shukur et al., 2014). That's mean the increase of dielectric constant, ε_r so the conductivity also be increase.

Besides that, the value of dielectric loss is increase as the frequency is decrease. It is because of the motion of free the charge carriers inside the material. According to Ramesh, the rise at low frequency which give result of electrode polarization effect by the biopolymer electrolyte. Furthermore, there is long tail for all samples at higher frequencies. This could happen because of the periodic reversal of electric fields which occurs faster. The interface of polymer electrolytes system cannot to build up which no time for charge. So, it will leads to decrease the value of dielectric due to the polarization of charge accumulation decreased. The decrease in dielectric with frequency implies on that systems is a non-Debye type (Shukur et al., 2014).
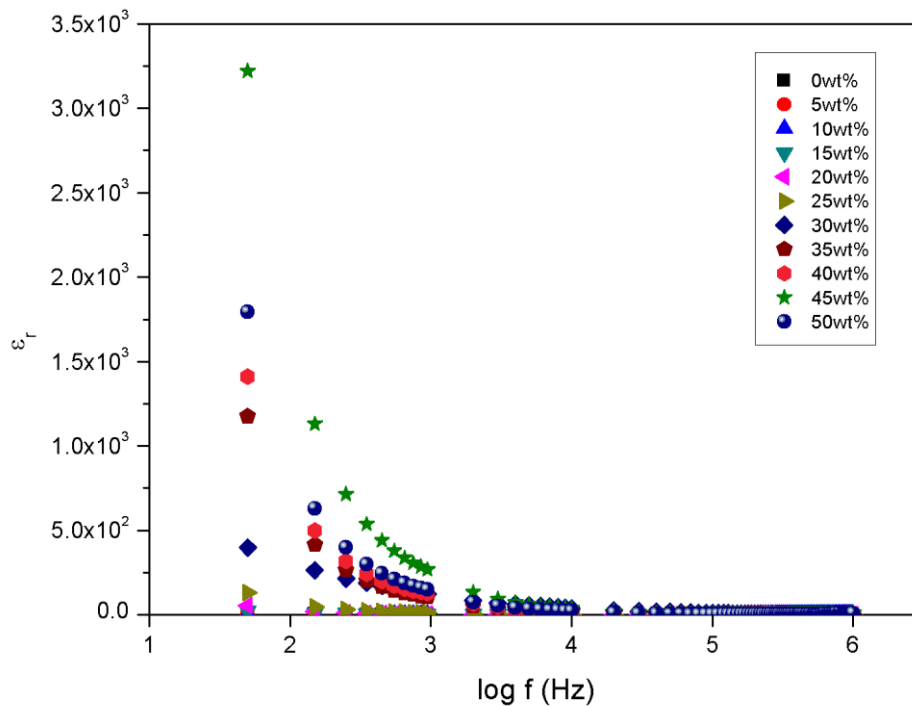

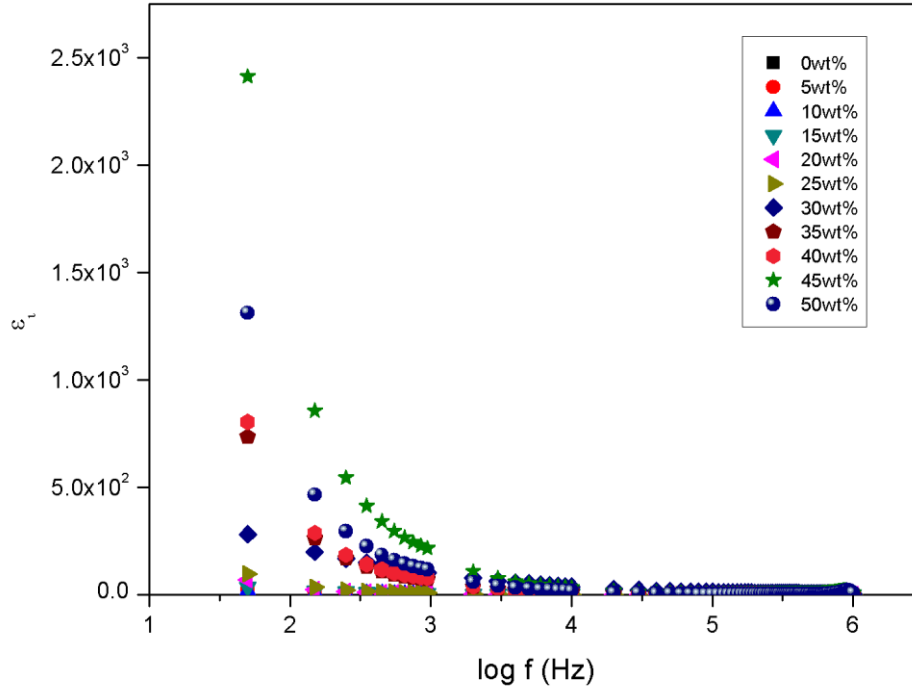*Figure 4.14.* The frequency dependent of dielectric constant, ε_r

Figure 4.15. The frequency dependent of dielectric loss, ε_i

4.3.1.2   MODULUS STUDY

According to Azli et al. (2016), the study of electrode polarization which is give effect in the electrolyte system was carried out which by plotting modulus spectra which is highlight the bulk of dielectric behaviour and also terminate the effect electrode polarization. In the modulus study, there have two which is real modulus, M_r and imaginary modulus, M_i. The calculation of this study based on the equation:-

$$M_r = \frac{\varepsilon_r}{(\varepsilon_i^2 + \varepsilon_r^2)} \tag{4.3}$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_i^2 + \varepsilon_r^2)} \tag{4.4}$$

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Where,

M_r = Real parts of modulus

M_i = Imaginary parts of modulus

The Figure 4.16 show the graph of the real modulus, M_r against frequency, f. Besides that, the Figure 4.17 show the graph of the imaginary modulus, M_i against frequency, f. Based on the graph of M_r against frequency, show that the trend the value of real modulus increase as the frequency increase. Its mean that the real modulus high at high frequency which the lower frequency almost zero. This also happen at imaginary modulus which is almost same the trend of graph. So, both of real modulus and imaginary modulus negligible about the contribution of electrode polarization. From both Figure 4.16 and 4.17, there shows the long tails at lower frequencies which was observed and also it is shows that large value of capacitance associated with the electrode. Then, this analysis confirmed again this solid biopolymer electrolyte system is a non-Debye type (Hafiza et al, 2014).
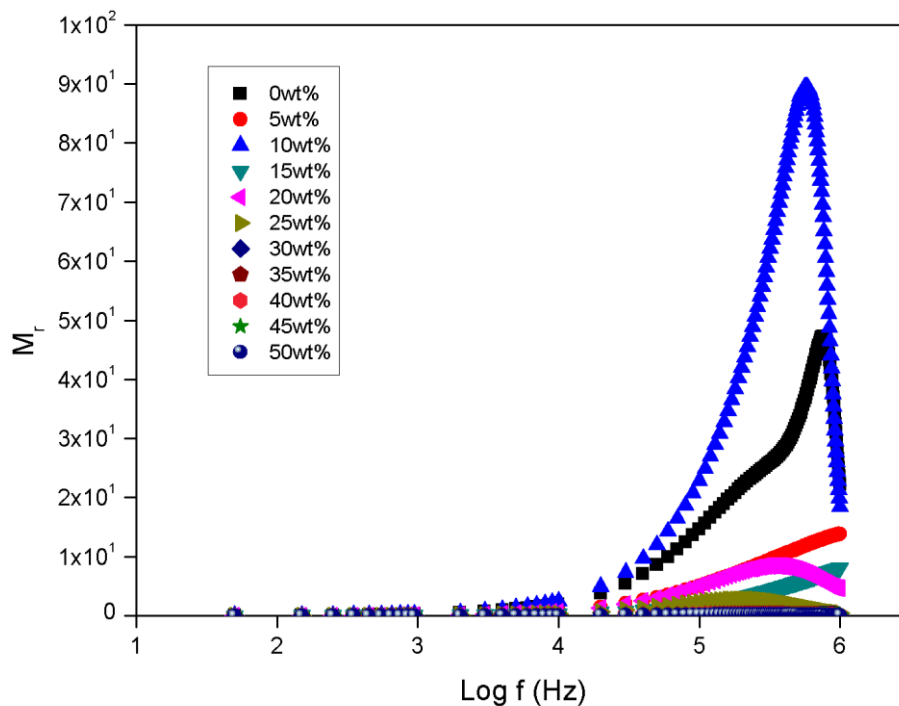

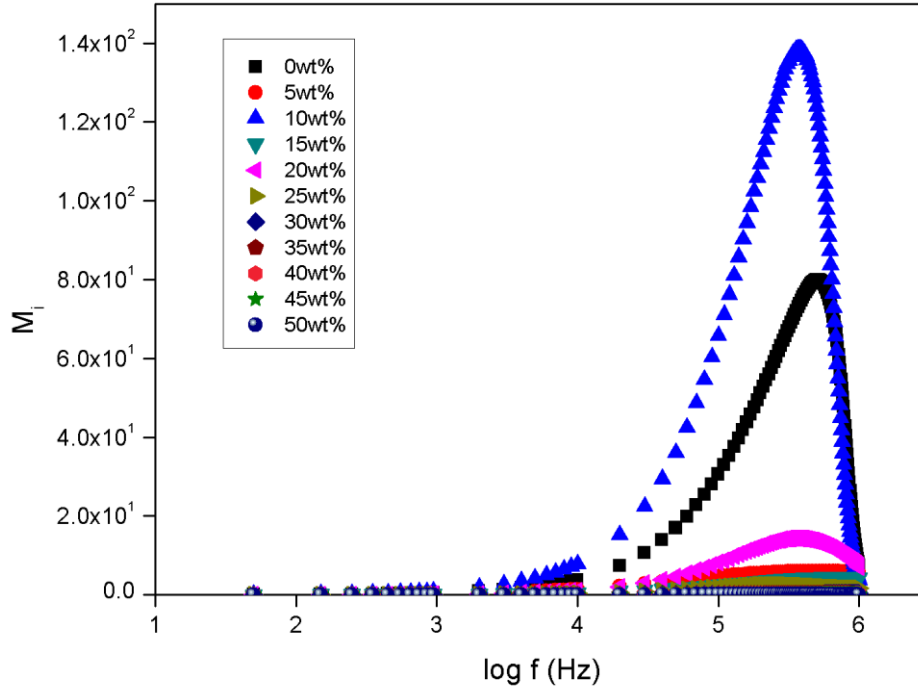*Figure 4.16.* The dependent of real modulus, M_r on frequency

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Figure 4.17. The dependent of imaginary modulus, M_i on frequency

4.3.2 TRANSFERENCE MEASUREMENT NUMBER (TNM)

Transference measurement number (TNM) were studied to show the relationship between the diffusion of ion to the conductivity behaviour of kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte. According to Linford, which in the solid biopolymer electrolyte the electron conduction can be neglected. So, the measurement of the polarization current supposedly give the cationic transference value when the polarization current which is become saturates (Chai & Isa, 2016). The diffusion coefficients of the anion and cation were calculated by using the values of cation transference number and conductivity according to the equation:-

$$t_+ = \frac{I_{cation}}{I_0} \qquad (4.5)$$

$$D = D_+ + D_- = \frac{kT\sigma}{ne^2} \qquad (4.6)$$

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$$t_+ = \frac{D_+}{D_+ + D_-} \tag{4.7}$$

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{nq} \tag{4.8}$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \tag{4.9}$$

Where,

μ_+ = ionic mobility of cation
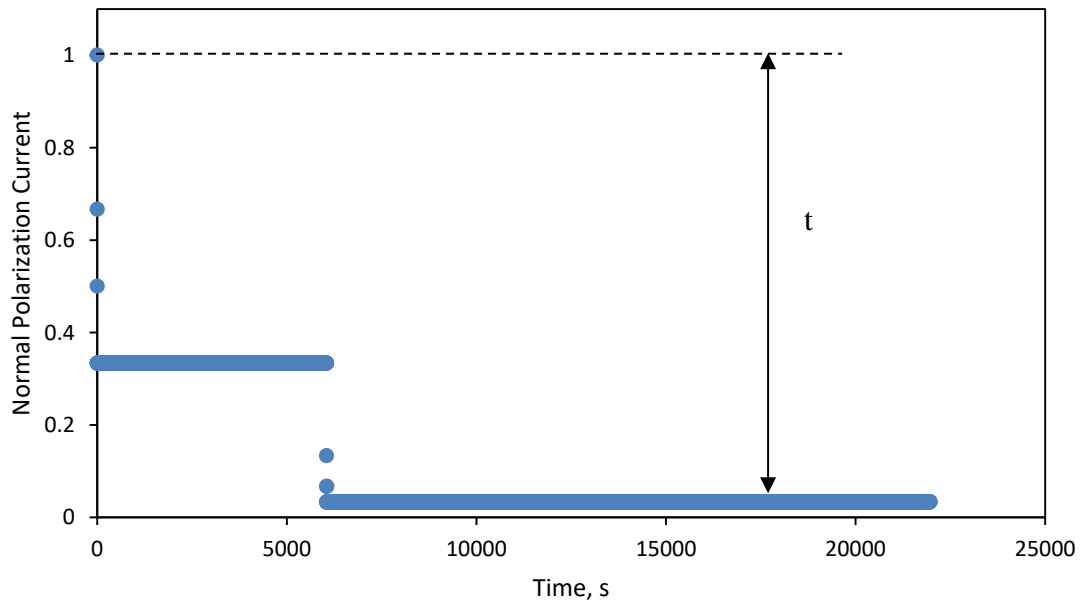
μ_- = ionic mobility of anion

Figure 4.18. Dc polarization current against time for R2 sample (5wt %)
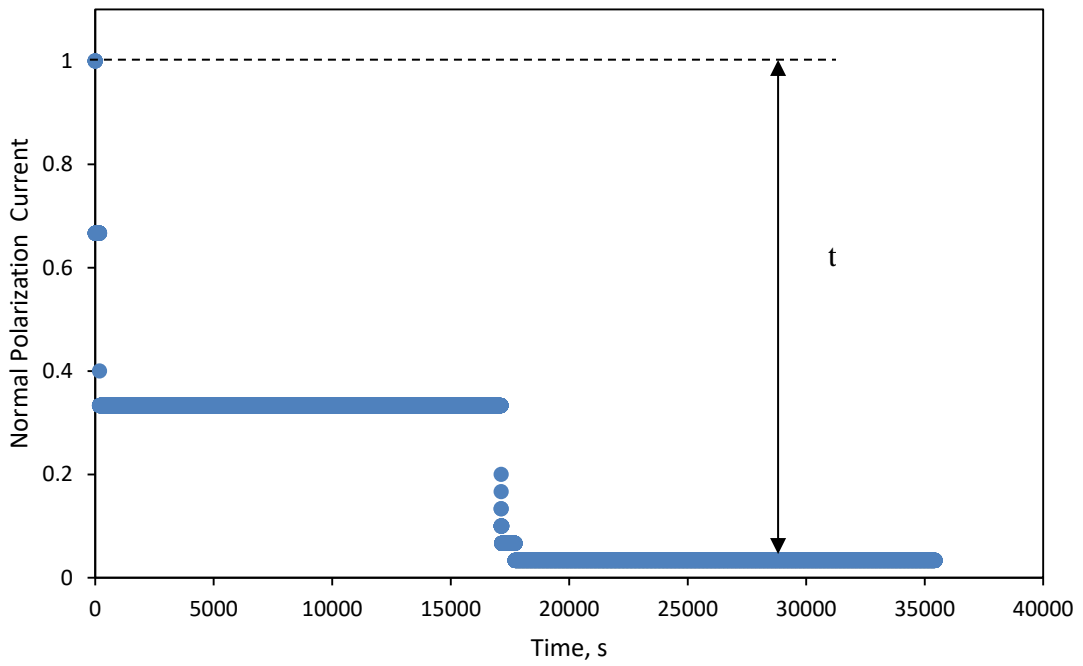
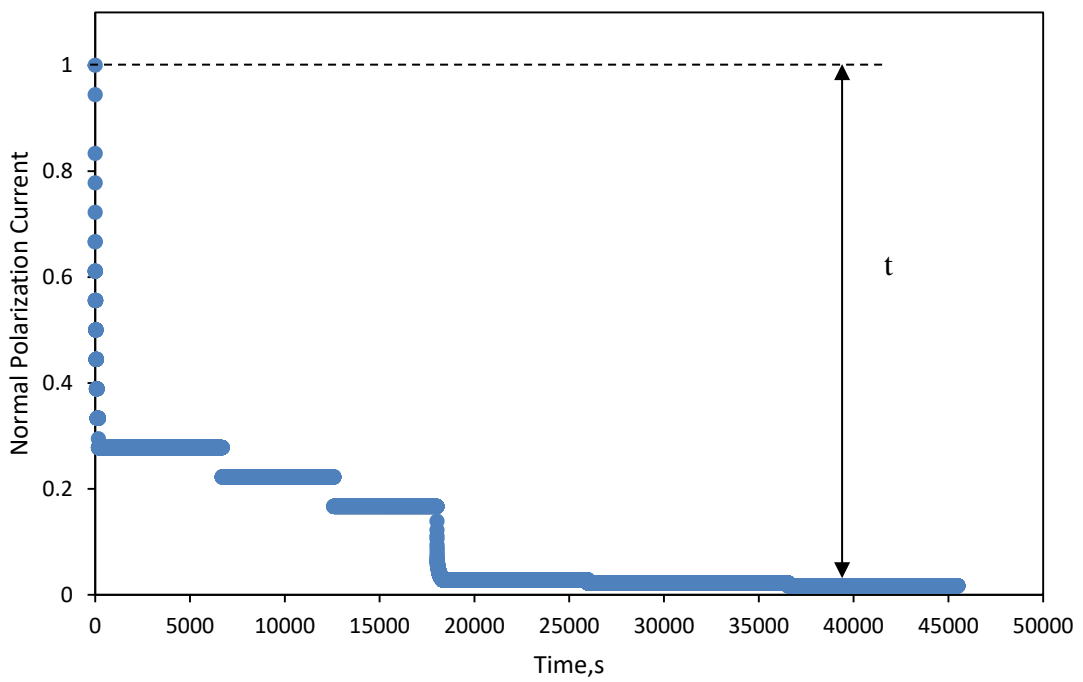*Figure 4.19.* Dc polarization current against time for R5 sample (20wt %)

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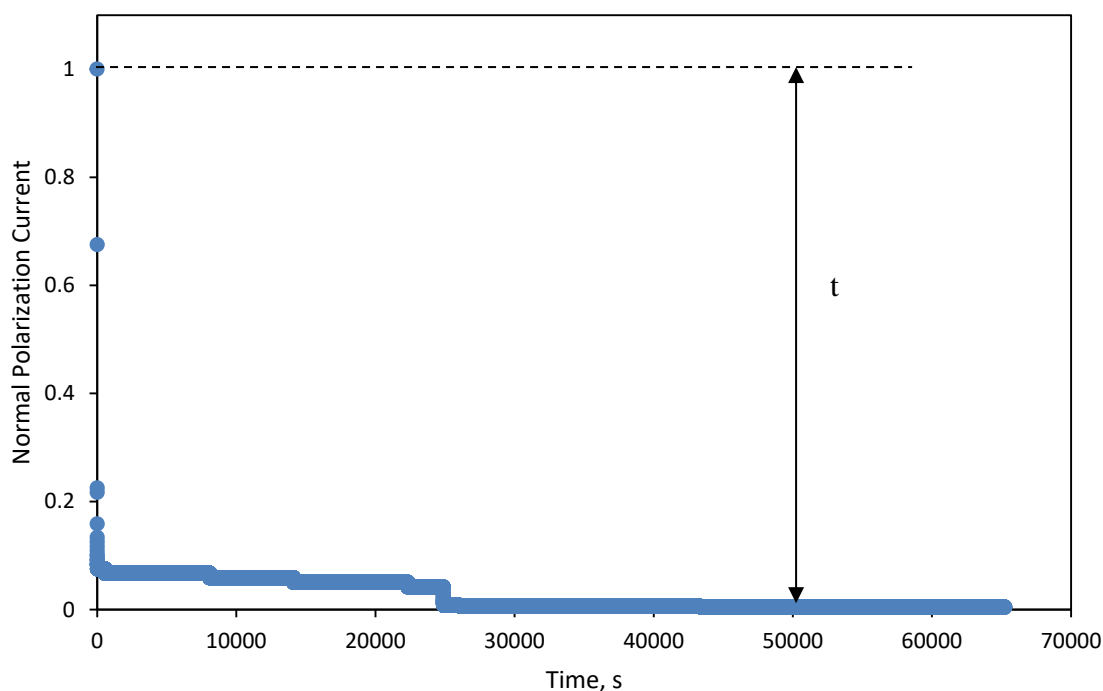*Figure 4.20.* Dc polarization current against time for R9 sample (40wt %)

Figure 4.21. Dc polarization current against time for R10 sample (45wt %)

Table 4.5
Ionic mobility and diffusion coefficient of anions and cations

Sample	t_{ion}	$\mu+$ $(cm^2V^{-1}s^{-1})$	$\mu-$ $(cm^2V^{-1}s^{-1})$	$D+$ (cm^2s^{-1})	$D-$ (cm^2s^{-1})
R2 (5wt%)	0.6667	7.67×10^{-11}	3.83×10^{-11}	1.99×10^{-12}	9.97×10^{-13}
R5 (20wt%)	0.6667	4.28×10^{-10}	2.14×10^{-10}	1.11×10^{-11}	5.57×10^{-12}
R9 (40wt%)	0.9833	1.78×10^{-08}	3.02×10^{-10}	3.42×10^{-10}	5.81×10^{-12}
R10 (45wt%)	0.9958	3.22×10^{-08}	1.36×10^{-10}	8.38×10^{-10}	3.58×10^{-12}

The Figure 4.18 show the graph of dc polarization current against time for R2 sample (5 wt. %). The Figure 4.19 show the graph of dc polarization current against time for R5 sample (20 wt. %). The Figure 4.20 show the graph of dc polarization current against time for R9 sample (40 wt. %). The Figure 4.21 show the graph of dc polarization current against time for R10 sample (45 wt. %). Based on the graph show that the decreasing of initial total current with the time due to the depletion of the ionic species in

the solid biopolymer electrolyte. Moreover, when fully depleted the current become constant. At the steady state, the current flow and the cell become polarized due to the electron migration across the biopolymer electrolyte and the interfaces. The Table 4.5 show the value of ionic mobility and diffusion coefficient of anions and cations which is the cation of ionic mobility and diffusion coefficient is higher than anion. This will give influenced of conductivity value of solid biopolymer electrolyte. Furthermore, the proton conducting electrolyte is proved as the cationic of ionic mobility and diffusion coefficient are higher than the anionic.

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CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this research, kappa carrageenan doped ammonium nitrate (NH_4NO_3) solid biopolymer electrolyte (SBEs) is produced by using the solution casting technique. The compositions of the NH_4NO_3 which were from 0 wt. % until 50 wt. %. The films that produced were transparent and no phase separation.

The conductivity studies of solid biopolymer electrolyte achieved the highest conductivity of 9.64×10^{-4} S cm^{-1} for system containing 40 wt. % of NH_4NO_3 at 303 K. Above the 40 wt. % shown the decreasing of conductivity. It is because when at high concentration of NH_4NO_3 solid biopolymer electrolyte cannot to accommodate which is leads to recombination of ions. So, the recrystallization of salt from the solid biopolymer electrolyte which caused the mobility and number of charge carrier decreased.

The complexion between kappa carrageenan and ammonium nitrate was proven by FTIR studies. It been observed that O=S=O band of kappa carrageenan at 1226 cm^{-1} was shifted to lower wavelength which is at 1216 cm^{-1}. This could be happen due to the interaction of O=S=O the symmetry vibration moiety in kappa carrageenan with H$^+$ ion of NH_4NO_3 which show reflect the protonation of system cation, H$^+$ ion towards O=S=O. When the NH_4NO_3 were added above 40wt% show the decreasing of peak intensity in the O=S=O which coordinated with cation, thus de-protonation of ions (H^+) been occurred. There have further study about the FTIR deconvolution. By the deconvolution can get value of the number density (η) the ionic mobility (μ), and the diffusion coefficient (D) of mobile ions. It show that the conductivity were strongly influence and almost parallel with the ionic mobility (μ), and the diffusion coefficient (D). Furthermore, the percentage of free ions which is the highest on the sample R9 (40 wt. % of NH_4NO_3). The highest percentage of free ions at 40 wt. % also same with the highest conductivity. This show

that the sample R9 have more ion to dissociate, so will assisting more ion conduction. This proved that the conductivity were related with FTIR deconvolution.

The studied relationship between the diffusion of ion to the conductivity behaviour of kappa carrageenan doped with ammonium nitrate of solid biopolymer electrolyte by using Transference measurement number (TNM). The chosen weight percentage of NH_4NO_3 which are 5, 20, 40 and 45 were discussed in this research. The decreasing of initial total current with the time due to the depletion of the ionic species in the solid biopolymer electrolyte. Moreover, when fully depleted the current become constant. At the steady state, the current flow and the cell become polarized due to the electron migration across the biopolymer electrolyte and the interfaces.

In the conclusion, the objective of the study are achieved. The solid biopolymer electrolyte which is kappa carrageenan doped with ammonium nitrate that produced are successfully characterised by using the Transference Number Measurement (TNM), Electrical Impedance Spectroscopy (EIS) and Fourier Transform Infrared (FTIR).

5.2   RECOMMANDATIONS

The structural properties of solid biopolymer electrolyte can be perform with other test such as Energy Disperse Spectroscopy (EDS), Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), tensile test and many more for further studies. Since the biopolymer are interesting and new, so a lot of testing that can be done.

Furthermore, the method of preparation can be improve by changing the way to prepare the sample. The surrounding also taking role while prepare the sample. This noted that the sample which is kappa carrageenan and ammonium nitrate are sensitive sample that can change the behaviour easily. It need extra careful while conducting the experiment.

The changing the polymer host which is use such as blend and etc. also the recommendation. Besides that, the dopant can be changed by using other ammonium salt and also adding the plasticizer which to increase the conductivity.

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